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THE INFLUENCE OF URANIUM ADDITIONS TO FERROUS ALLOYS:

AN INTERIM REVIEW

PREPARED BY

THE PHYSICAL METALLURGY DIVISION IN COLLABORATION WITH THE MINERAL SCIENCES DIVISION, THE EXTRACTION METALLURGY DIVISION, ELDORADO MINING AND REFINING LIMITED AND THE CANADIAN URANIUM RESEARCH FOUNDATION

EDITED BY

R. F. KNIGHT & D. K. FAURSCHOU

APRIL 1962

FOREWORD

In 1959 it was recognized that the Canadian Uranium industry was faced with a sharply reduced demand for its product. It was therefore decided to investigate the use of uranium in non-nuclear applications. One area considered was the use of uranium as an alloying element in ferrous materials. Since ferrous alloys, such as steel are produced in very large quantities, a relatively large new market for uranium would result if alloying additions were found to produce an economic technical improvement.

This research programme began in 1959 with the support of Eldorado Mining and Refining Limited. In January 1961 the producing uranium companies formed the Uranium Research Foundation, and since that time this group has contributed toward the programme being carried out at the Mines Branch. This report has been prepared to present, in general terms, the results of our work. A great deal of the research described is still under way, with new results being obtained daily from long time laboratory tests and plant trials. Detailed papers are being prepared on this work for publication in the technical societies. The importance of this programme may be summed up in a quotation from the recommendations of a special House of Commons Committee on research made early in 1961.

> "The finding and development of new uses for uranium is so vital to the future of the Canadian uranium industry that this Committee recommends that the full resources of the appropriate agencies of Government, and of the uranium industry itself, be marshalled in support of a co-ordinated and vigorous programme of research in this field".

John Convey,
Director,
Mines Branch.

AVANT-PROPOS

En 1959, il devint évident que l'industrie canadienne de l'uranium aurait à faire face à une baisse considérable de la demande, et cette perspective fut à l'origine du programme de recherches destiné à trouver pour ce produit des usages non-nucléaires. Une des possibilités envisagées fut l'emploi de l'uranium comme élément d'addition dans les alliages ferreux. Vu que la production de ces alliages, par exemple de l'acier, est très considérable, un débouché nouveau, mais relativement important, s'offrirait pour l'uranium si de telles additions s'avéraient avantageuses tant du point de vue économique que du point de vue technique.

Ce programme, inauguré en 1959, reçut l'appui de l'Eldorado Mining and Refining Limited. En janvier 1961, les compagnies productrices d'uranium créèrent l'Uranium Research Foundation et, depuis lors, ce groupement a apporté sa contribution au programme de recherches entrepris par la Direction des mines. Le but du présent rapport est donc de donner une idée générale des résultats de nos recherches. Toutefois nos travaux continuent et chaque jour apporte de nouveaux résultats des essais à long terme effectués en laboratoire ou à l'usine. Des études plus élaborées sont en voie de préparation et seront publiées par des sociétés techniques. L'importance de ce programme est soulignée par l'extrait suivant des recommandations faites au début de 1961 par un comité spécial de la Chambre des communes consacré à la recherche.

> "La découverte et la mise au point de nouveaux usages pour l'uranium sont à ce point essentielles à la survivance de l'industrie canadienne de l'uranium que le Comité recommande la mise en oeuvre de toutes les ressources des agences gouvernementales concernées et de l'industrie de l'uranium, afin de cristalliser tous les efforts en programme méthodique et ambitieux de recherches dans ce domaine." -

John Convey,
Directeur,
Direction des mines.

PREFACE

Some of the chapters of this report are a composite of contributions by several persons. However, only the principal contributors have been identified at the beginning of any chapter. Where possible, sources of information are referred to within the text.

An expression of gratitude and commendation is directed to the many anonymous associates who were involved from all sections of the Physical Metallurgy Division, from the Technical Services Division, from the Chemistry Laboratory and the Physics and Radiotracer Subdivision of the Mineral Sciences Division, from the Control Analysis Section of the Extraction Metallurgy Division, and from the Mines Branch library and administration staffs. The interest and cooperation of the steel industry is particularly gratifying and appreciated.

S.L. Gertsman,
Chief,
Physical Metallurgy Division.

PRÉFACE

Certains chapitres de ce rapport sont le fruit d'un effort collectif, mais seulement les noms des principaux collaborateurs sont mentionnés au début de chaque chapitre. A l'occasion nous présentons une courte bibliographie des ouvrages consultés.

Nous tenons à exprimer notre reconnaissance à tous ceux qui ont collaboré à cette étude et dont les noms ne sont pas mentionnés. Ces techniciens viennent d'un peu partout: Métallurgie physique, Services techniques, Laboratoire de chimie, section de physique et des radiotraceurs de la Division des sciences minérales, Section de l'analyse de contrôle de la Division de la métallurgie extractive, et enfin bibliothèque de la Direction des mines et du personnel administratif. Nous nous en voudrions de passer sous silence l'intérêt et la coopération sans prix de l'industrie sidérurgique.

S. L. Gertsman

S.L. Gertsman,
Chef,
Division de la Métallurgie physique.

CHAPITRE 1

LES PROPRIÉTÉS DE L'URANIUM ET DE SES COMPOSÉS

D. K. Faurschou* et C. E. Makepeace**

SOMMAIRE

Ce chapitre rassemble des données sur certaines propriétés physiques, chimiques, cristallographiques et thermodynamiques des oxydes, sulfures, nitrures, carbures d'uranium ainsi que du composé UFe_2. Le choix de ces propriétés repose sur la possibilité de leur application en sidérurgie. L'auteur décrit aussi le comportement possible dans l'acier des composés d'uranium. Ces notes pourront s'avérer utiles lors de la préparation et de l'interprétation de travaux de recherches sur l'emploi de l'uranium dans l'acier, soit comme élément d'alliage, soit comme simple agent métallurgique. Une note complémentaire décrit une technique spéciale d'extraction électrolytique des composés d'uranium de l'acier.

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* Chargé de recherches principal, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

** Ingénieur en métallurgie, Eldorado Mining and Refining Limited, détachés à la Division de la métallurgie physique

CHAPITRE 2

REVUE DES BREVETS ET DES TRAVAUX PARUS RELATIFS À L'UTILISATION DE L'URANIUM DANS LES ALLIAGES FERREUX

W. A. Morgan* et R. D. McDonald**

SOMMAIRE

Afin de faire le point des connaissances déjà acquises dans ce domaine, on a effectué un relevé de la littérature technique et des brevets qui concernent les aciers contenant de l'uranium et la production des ferro-alliages d'uranium. Les résultats de ce relevé indiquent que l'uranium améliore la résistance à la traction, accroît la trempabilité et favorise le durcissement structural. L'uranium forme des carbures plus stables que ceux du molybdène et du tungstène; comme l'uranium se combine à l'oxygène, l'azote et le soufre, il peut donc provoquer un décrassage.

Les projets de recherches de la Direction des mines ont été élaborés à partir des renseignements contenus dans ces deux premiers chapitres.

Respectivement *chef et** chargé de recherches principal, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CHAPITRE 3

RÉCUPÉRATION ET SÉGRÉGATION DE L'URANIUM DANS DES ACIERS ÉLABORÉS EN LABORATOIRE ET DANS L'INDUSTRIE

R. K. Buhr* et D. R. Bell*

SOMMAIRE

La récupération de l'uranium varie énormément lorsqu'on l'ajoute à l'acier en fusion car elle dépend de la teneur en oxygène de ce dernier. Dans le cas d'un acier fabriqué par le procédé L. D. basique, la récupération varie entre 7 et 29 p. 100 quand il s'agit d'une addition faite dans la poche de coulée. Des résultats d'analyses effectuées dans des régions exemptes de ségrégations révèlent une récupération moyenne de l'ordre de 45 p. 100 chez un acier au carbone désoxydé à l'aluminium et élaboré au laboratoire. Dans ces expériences, les quantités variables d'uranium ajouté à l'acier n'ont eu que peu d'effet sur les caractéristiques de la ségrégation ou de la récupération. Toutefois, pour des aciers commerciaux, la récupération de l'uranium varie entre 49 et 66 p. 100 si l'addition se fait après la désoxydation totale du métal, et quel que soit le procédé d'élaboration employé.

La marche en opération basique au four électrique permet d'éliminer l'uranium et prévient ainsi l'augmentation de la teneur en uranium résiduel lors de la remise en fusion des ferrailles.

La ségrégation de l'uranium a été détectée dans toutes les expériences; elle se présente sous la forme d'amas de fines particules de composés riches en uranium. L'autoradiographie a permis d'établir un lien entre la répartition des particules et la vitesse de solidification.

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*Chargés de recherches principal, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

Si le refroidissement est lent, comme c'est le cas pour les gros lingots industriels, les composés riches en uranium émigrent vers les régions inférieures des lingots ou des pièces coulées. A l'échelle des lingots de laboratoire, le refroidissement s'effectue à des vitesses supérieures et il en résulte des amas plus petits et plus dispersés.

Les zones ségrégées s'enrichissent considérablement en uranium, en oxygène et en aluminium insoluble dans l'acide, et elles ont parfois une teneur légèrement élevée en azote. Par ailleurs, les zones non ségrégées présentent une très faible teneur en oxygène total et en aluminium insoluble dans l'acide; l'azote peut aussi être présent en faible teneur. Il ne se produit pas de ségrégation de carbone, de manganèse, de silicium, de soufre, de phosphore, de chrome ou de cuivre dans les zones riches en uranium.

CHAPITRE 4

L'URANIUM DANS LES ACIERS AU CARBONE

G. P. Contractor*

SOMMAIRE

En variant la teneur en uranium jusqu'à 0.70 p. 100 dans les aciers au carbone des types doux et demi-durs, on a pu étudier ses effets sur la forgeabilité, le comportement aux traitements thermiques, les propriétés mécaniques et la microstructure.

Il se produit chez les aciers au carbone demi-durs une fragilité au rouge lorsque l'uranium excède une teneur de 0.35 p. 100, mais cette teneur peut être augmentée pour les aciers doux au carbone. Cette fragilité au rouge est associée à la présence du composé UFe_2 aux joints des grains.

La présence d'uranium n'affecte pas gravement les températures critiques de transformation, la trempabilité Jominy et la résistance au revenu.

L'uranium n'améliore guère, à la température ambiante, les propriétés de traction et d'endurance. Par contre, les valeurs de la résilience tombent à de très bas niveaux lorsque sa teneur dépasse 0.15 p. 100 car il apparaît alors une microstructure anormale caractéristique.

L'uranium améliore cependant les caractéristiques à chaud dans de courts essais de rupture à temps.

Il ressort des travaux réalisés sur des aciers de nuances diverses que la majeure partie du carbone d'uranium réagit pour former des inclusions cubiques complexes, U(O, C, N) ou U(C, N) pouvant contenir à la fois ou séparément de l'azote et de l'oxygène. Lorsque la teneur en uranium excède 0.35 p. 100, il est possible de retrouver le carbure UC sous la forme de particules sphéroidiques bien définies et qui demeurent stables aux températures employées dans la pratique des traitements thermiques.

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*Chargé de recherches principal, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CHAPITRE 5

L'URANIUM DANS LES FONTES

R. K. Buhr*

SOMMAIRE

Une augmentation marquée des propriétés mécaniques, à l'état brut de coulée, résulte de l'addition d'uranium à une fonte grise hypereutectique, à faible teneur en soufre, ainsi qu'à une fonte à 1 p. 100 de chrome. La charge de rupture est abaissée par la présence d'uranium dans une fonte grise hypoeutectique, à faible teneur en soufre. L'uranium abaisse dangereusement la charge de rupture des fontes à teneur normale en soufre.

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*Chargé de recherches principal, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CHAPITRE 6

L'URANIUM DANS LES ACIERS ALLIÉS

W. A. Morgan*, R. F. Knight**, C. E. Makepeace***
J. K. Pargeter**, D. E. C. King*** et R. J. McClure***

SOMMAIRE

Dans ce chapitre, les auteurs présentent les résultats d'essais sur l'influence de l'uranium dans les aciers alliés. Il reste encore beaucoup à faire pour étudier bien des aspects de ce vaste domaine métallurgique. On ne dispose parfois que de premiers résultats, qui sont forcément peu concluants, si bien qu'il est impossible de passer en revue autre chose que les grandes lignes des recherches en cours. Les auteurs se sont efforcés de présenter des généralités sur les sujets les plus intéressants touchant les diverses catégories d'aciers alliés.

L'uranium forme des carbures qui restent stables jusqu'à la température d'au moins 2250° F (1230° C). Ce phénomène se retrouve dans le cas des aciers qui, une fois trempés et revenus, perdent de la dureté s'ils contiennent assez d'uranium pour épuiser la carbone de la matrice. Dans l'acier austénitique inoxydable, l'uranium est un stabilisant efficace.

On a démontré que l'uranium n'influe guère sur la dureté secondaire et ne rend guère les aciers plus fragiles au revenu. On n'a pas encore évalué la résistance à l'usure des aciers à outils additionnés d'uranium.

Il ressort d'essais de fluage que de légères additions d'uranium ont un effet bienfaisant.

L'uranium des aciers inoxydables chauffés à des températures supérieures à 1850° F (1010° C) nuit à leur forgeabilité, sauf dans le cas des aciers resulfurés. Dans les aciers inoxydables resulfurés ordinaires et à outils, l'uranium améliore la morphologie des sulfures et, par là, la résistance à la traction transversale.

Respectivement *chef et ** chargés de recherches principal, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa.

***Ingénieurs en métallurgie, Eldorado Mining and Refining Limited, détachés à la Division de la métallurgie physique.

CHAPITRE 7

MICROSTRUCTURE ET DURETÉ DES ALLIAGES URANIUM-FER ET URANIUM-CARBONE-FER

W. J. Wrazej*

SOMMAIRE

L'auteur a fait des examens au microscope, des essais de la dureté et parfois des études de radiocristallographie par diffraction sur de petites masses fondues d'alliages de fer-uranium et de fer-carbone-uranium sous différents régimes de traitement thermique. Il a fait des comparaisons avec des substances libres d'uranium afin d'établir si l'uranium influe sur la microstructure et la dureté. Il a étudié l'influence de la composition et du traitement thermique sur la présence et l'apparition du monocarbure d'uranium UC et de sa phase epsilon UFe_2.

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*Chargé de recherches principal, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CHAPITRE 8

CORROSION DES ACIERS À L'URANIUM

G. J. Biefer*

SOMMAIRE

Bien des essais sur la corrosion dont l'auteur fait rapport ont été exécutés sur des échantillons d'aciers plongés dans des milieux fortement corrosifs, afin de pouvoir estimer rapidement l'effet de l'uranium et de savoir où diriger de nouvelles recherches. Différents milieux ont servi à éprouver des aciers au carbone, faiblement alliés et inoxydables. Dans les deux premiers cas, l'auteur a noté des indices d'effet favorable lorsqu'il y avait certaines concentrations d'acides chlorhydrique et sulfurique. Dans le cas de l'acier inoxydable, l'effet apparent a été une diminution de la perte de poids et de l'attaque du métal dans des solutions de chlorure ferrique acidifié. Les autres essais ont pour la plupart fourni des résultats peu concluants et il faudra poursuivre les expériences.

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*Chef, Section de la corrosion, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CHAPITRE 9

SOUDAGE D'ACIERS URANIFÈRES

K. Winterton* et W. P. Campbell**

SOMMAIRE

La récupération de l'uranium dans les dépôts de soudure de l'acier dépend du procédé de soudage. L'auteur a réussi à en récupérer environ 26 p. 100 par soudage à l'arc de tungstène en gaz inerte et de 1 à 2 p. 100 per soudage à l'arc métallique en gaz inerte.

Il a étudié la soudabilité d'aciers au carbone uranifères et surtout la question de savoir s'il y a fissuration dans la zone de transformation. Des essais cruciformes et de sévérité thermique contrôlée ont été faits sur divers aciers dont la teneur en carbone variait de 0.25 à 0.58 p. 100 et la teneur en uranium atteignait 0.23 p. 100. Sans faire une étude directe du sujet, l'auteur a formulé certaines observations sur l'effet possible de la présence de l'uranium sur la formation des fissures dans le métal déposé. Il a entrepris des essais de soudage en cordon longitudinal sur un acier uranifère ségrégé. Il a constaté que la présence de composés riches en uranium dans la zone de transformation n'y modifiait le degré de fissuration. Il semble que les aciers au carbone dont la teneur en uranium atteint 0.1 p. 100 se prêtent au soudage s'ils sont soumis à un régime convenant aux aciers semblables privés d'uranium.

Des essais de soudage par points ont été faits sur des tôles minces d'acier écroui, à faible teneur en carbone. La présence de petites quantités d'uranium (environ 0.05 p. 100) n'a pas créé de difficultés sérieuses. L'auteur déclare aussi qu'il a réussi à souder en bout par résistance, des aciers doux titrant jusqu'à 0.24 p. 100 d'uranium.

Respectivement * chef et ** chargé de recherches principal, Section de la soudure, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CHAPITRE 10

MÉTHODES TYPES D'ANALYSE POUR DOSER L'URANIUM DANS LES ALLIAGES DE FER ET D'ACIER

J. C. Ingles*, J. B. Zimmerman** et J. L. Horwood***

SOMMAIRE

Avant d'étudier et de produire des aciers et des alliages uranifères, il faut avoir des techniques exactes et appropriées d'analyse de l'uranium. Pour faciliter la tâche des chercheurs en ce domaine, les auteurs donnent des conseils sommaires sur les méthodes à appliquer en matière de fluorimétrie, de radiométrie, de radiospectrométrie, de volumétrie et de colorimétrie.

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*Chef, Section de l'analyse de contrôle, Division de la métallurgie extractive, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

**Chargé de recherches principal, Section de l'analyse de contrôle, Division de la métallurgie extractive.

***Chargé de recherches principal, Subdivision de la physique et des indicateurs radioactifs, Division des sciences minérales.

CHAPITRE 11

MANUTENTION SANS DANGER DE L'URANIUM ET ALLIAGES D'URANIUM

G. G. Eichholz*

SOMMAIRE

L'auteur résume les propriétés radioactives et toxiques de l'uranium. Il présente des conseils généraux sur le maniement sans danger de l'uranium et des substances uranifères. Il donne un aperçu de l'aspect juridique de l'emploi de l'uranium. Il offre un exposé sur les valeurs expérimentales ordinaires des niveaux de radiation auxquels on est exposé au cours de travaux à l'échelle industrielle ou de laboratoire: fusion, coulée, formage à chaud, découpage à sec ou meulage, écroûtage et soudage.

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*Chef, Subdivision de la physique et des indicateurs radioactifs, Division des sciences minérales, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

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CHAPTER 10

TYPICAL ANALYTICAL PROCEDURES FOR THE DETERMINATION OF URANIUM IN IRON AND STEEL ALLOYS

CHAPTER 1

THE PROPERTIES OF URANIUM AND ITS COMPOUNDS

D. K. Faurschou* and C. E. Makepeace**

SYNOPSIS

Selected physical, chemical, crystallographic and thermodynamic properties of uranium oxides, sulphides, nitrides, hydrides, and carbides and UFe_2 are presented. These properties were selected for their relevance to ferrous metallurgy. The possible behaviour of uranium compounds in steel is discussed. This information is regarded as being of value in the planning and interpretation of research into the utilization of uranium as an alloying element or as an otherwise useful metallurgical agent in steel. A refined technique for electrolytic extraction of uranium compounds from steel is also discussed.

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* Senior Scientific Officer, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

** Metallurgical Engineer, Eldorado Mining and Refining Limited.

INTRODUCTION

Solubility of uranium in most other metals is limited, because of its large atomic diameter, the unique crystal structure of its alpha phase and the complex structure of its beta phase. The chemical activity of uranium is so strong that it combines with most elements of the periodic table. Uranium oxides, sulphides, nitrides and carbides are very stable. These characteristics directly influence the alloying behaviour of uranium with the metallic elements, as summarized in Table 1.1

TABLE 1.1

Behaviour of Uranium With Metallic Elements(1)*

Behaviour	Metallic Element
Forms solid solutions but no intermetallic compounds	Mo, Nb, Ti, Zr
Forms intermetallic compounds	Al, Au, Be, Bi, Co, Cu, Fe, Ga, Ge, Hg, In, Ir, Mn, Ni, Pb, Pd, Pt, Sn, Tl, Zn.
Forms neither solid solutions nor intermetallic compounds	Ag, Ca, Ce, Cr, La, Mg, Na, Nd, Pr, Ta, Th, V, W

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*References are at the end of each chapter.

Rough and Bauer(2) have presented a comprehensive collection of information about the constitution and crystallography of many uranium alloys.

Although the physical, chemical and mechanical properties of uranium have been intensively studied, little information has been published on the properties of alloys containing uranium. Furthermore, knowledge of the properties of uranium compounds, other than those of importance in nuclear metallurgy, is scant, especially in the field of thermodynamics. The study of the partition of uranium in steels has been hampered by inadequate extraction techniques. The available information relevant to the utilization of uranium as an alloying element or as an otherwise beneficial metallurgical agent in steel is summarized and discussed in this chapter.

URANIUM METAL(1,3)*

General

In the periodic table uranium occupies a position in the actinide series analogous to neodymium in the lanthanide series(1). The actinides belong in Group IIIB. Until recently uranium was shown in Group VIB of the periodic table along with chromium, molybdenum and tungsten.

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*Basic references for this section.

Chemical Properties

Uranium is strongly electropositive, being intermediate between aluminum and beryllium in the electrochemical series. It forms stable compounds with non-metallic elements and intermetallic compounds with Group III and transition elements, and it can react with most of the other elements excluding the noble gases.

Uranium has six valence electrons, but the confirmed valency ranges from three to six. The stability of its compounds with a particular element decreases with increase of valence. The valence of uranium under alloying conditions is not known with certainty, but it is believed to be either four or six.(4)

Most of the semi-metallic compounds of the actinide elements and of the other transition elements deviate significantly from the Law of Definite Proportions. This behaviour is pronounced with uranium because of the multiplicity of stable oxidation states having relatively close energy levels. In general, transition elements may form semi-metallic compounds with anions such as oxygen, nitrogen, sulphur, selenium, phosphorus and carbon.

Crystal Structure

Metallic uranium exists in one of three allotropic phases depending on the temperature. The alpha phase, which is stable at room temperature and exists up to 668°C (1234°F), has a unique orthorhombic structure with $a_o = 2.8541$ A, $b_o = 5.8692$ A and $c_o = 4.9563$ A. The beta phase, stable from 668-774°C (1234-1426°F), has a complex tetragonal structure with $a_o = 10.759$ A and $c_o = 5.656$ A. The gamma phase, which is stable from 774°C (1426°F) to the melting point, has a body-centred cubic structure with $a_o = 3.525$ A.

Only gamma uranium has purely metallic bonding. The closest approach of atoms in this structure is 3.0 A for co-ordination number 8. The closest approach of atoms is a measure of the effective atomic diameter. Because alpha uranium is pseudo-metallic, its atomic diameter has less meaning than for metallic elements. However, for pseudo or non-metallic compounds it has been calculated that 3.14 A is the effective atomic diameter for co-ordination number 12.(5)

Physical and Thermodynamic Properties

Published values of selected physical and thermodynamic properties are collected in Table 1.2.

TABLE 1.2

Values of Selected Physical and Thermodynamic Properties of Uranium(1)

Property	Value
Melting point	1132 ± 1°C
Vapour pressure (1630-1970°K)	$\log p_{mm} = \frac{-2330}{T} + 8.583$
Boiling point	3818°C
Density (25°C)	19.04 g/cm^3
Heat of fusion	4.7 kcal/mole
Heat of vaporization	106.7 kcal/mole
Enthalpy (25°C)	1521.4 cal/mole
Heat Capacity	6.612 cal/°C mole
Entropy	11.99 ± 0.02 cal/°C mole
Enthalpy, $H_t - H_{298}$:	
alpha uranium	$3.15T + 4.22 \times 10^{-3}T^2 - 0.80 \times 10^5T^{-1} - 1046$; (298-935°K)
beta uranium	$10.38T - 3525$; (935-1045°K)
gamma uranium	$9.10T - 1026$; (1045-1300°K)
Specific heat, Cp:	
alpha uranium	$3.15 + 8.44 \times 10^{-3}T + 0.80 \times 10^5T^{-2}$
beta uranium	10.38
gamma uranium	9.10

URANIUM OXIDES(1,6)*

The uranium-oxygen system is exceedingly complex. A tentative phase diagram is available for the interval between UO_2 and U_3O_8 and enough is known of the complete binary system to understand the more important features.

A brief simplified description of salient equilibrium features of the uranium-oxygen system follows:

(1) In the region from pure uranium to UO_2 there is probably a heterogeneous mixture of uranium metal and UO_2 at room temperature. Occurrence of the monoxide has been reported at higher temperature.

(2) The composition ranging from $UO_{2.0}$ to $UO_{2.25}$ is a non-stoichiometric compound with a cubic fluorite-type structure.

(3) From $UO_{2.25}$ to U_3O_{8-x} a gradual conversion from cubic to tetragonal symmetry occurs. U_3O_{8-x} varies from $UO_{2.56}$ at elevated temperatures to $UO_{2.64}$ at room temperature.

(4) A homogeneous phase exists from U_3O_{8-x} to U_3O_8.

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*Basic references for this section.

A free surface is essential for the formation of UO and it has never been prepared in bulk. Complete conversion of UO_2 to UO in the presence of uranium has never been accomplished. U_3O_8 is the product of ignition in air of uranium, other uranium oxides, and most other uranium compounds. UO_2 is made by the reduction of U_3O_8 or UO_3 with hydrogen (700°C) (1290°F) or carbon monoxide (700-750°C) (1290-1380°F). Above 550-600°C (1020-1110°F) U_3O_8 loses oxygen continuously, reverting to UO_2 between 1150°C (2100°F) and 1400°C (2550°F). In ferrous metallurgy it would appear that non-stoichiometric UO_2 is the uranium oxide of interest.

Table 1.3 summarizes the pertinent information known about UO_2.

TABLE 1.3

Values of Crystallographic, Physical, and Thermodynamic Properties of UO_2

Property	Value
Crystallographic structure	Cubic, fluorite-type with $a = 5.4691 \pm 0.005$ A
Colour	Brown to black
Index of refraction	2.35
Density (X-ray)	10.96 g per cm^3
Heat of formation, ΔH°_{298}	-259.2 kcal/mole (7,8)
Entropy of formation, ΔS°_{298}	-42.2 cal/°C mole (7,8)
Enthalpy, $H_T - H_{298.16}$	$19.20T + 0.81 \times 10^{-3}T^2 + 3.957 \times 10^5T^{-1} - 7124$ (298-1500°K; 0.1%)
Specific heat, Cp	$19.20 + 1.62 \times 10^{-3}T - 3.957 \times 10^5T^{-2}$
Vapour pressure (effusion):	
1600°C	0.071×10^{-3} mm Hg
1750°C	1.7×10^{-3}
1800°C	4.0×10^{-3}
1900°C	18.0×10^{-3}
2000°C	72.0×10^{-3}

URANIUM CARBIDES(1,9)

Uranium and carbon form three semi-metallic compounds, UC, U_2C_3, and UC_2. Of these UC has the highest uranium content and is also the most stable. Therefore, it is considered to be the uranium carbide most likely to occur in steel. Pertinent information about UC is entered in Table 1.4

TABLE 1.4

Values of Crystallographic, Physical and Thermodynamic Properties of UC

Property	Value
Crystallographic structure	Face-centred cubic, NaCl type with $a_o = 4.961$ A
Density (X-ray)	13.63 g per cm^3
Vickers hardness	up to 800 kg per mm^2
Melting point	2350°C
Heat of formation, ΔH°_{298}	-20,000 cal/mole
Entropy of formation, ΔS°_{298}	-3.70 cal/mole (°K)
Free energy of formation, ΔF°_{298}	-18,900 cal/mole
Heat capacity	$7.6 + 2.85 \times 10^{-3}T$

U_2C_3 decomposes above 1800°C (3270°F) and has cubic symmetry with $1\bar{4}3d$ structure and $a_o = 8.088$ A.

UC and UC_2 are completely miscible at elevated temperatures. UC_2 melts at 2400°C (4350°F), and has tetragonal symmetry with a $CaCl_2$ structure having $a_o = 3.517$ A and $c_o = 5.987$ A.

URANIUM NITRIDES(1)

Three semi-metallic compounds, UN, U_2N_3 and UN_2, are considered. The higher of these nitrides dissociates above 700-800°C (1290-1470°F) to UN. The limited pertinent information available about the mononitride is given in Table 1.5.

TABLE 1.5

Values of Crystallographic, Physical and Thermodynamic Properties of UN

Property	Value
Crystallographic structure	Face-centred cubic, NaCl type with $a_o = 4.880 \pm 0.001$ A
Density (X-ray)	14.32 g/cm^3
Sintering point	2300°C
Melting point	2630 ± 50°C
Heat of formation, ΔH^o_{298}	-80,000 cal/mole
Entropy of formation, ΔS^o_{298}	-17 cal/mole °C
Free energy of formation, ΔF^o_{298}	-75,000 cal/mole

URANIUM HYDRIDE(3,6)

The stoichiometric compound, UH_3, is most readily formed in the temperature range of 225-250°C (440-480°F). At higher temperatures, decomposition becomes significant. The decomposition pressure has been represented by the equation.

$$\log P, \text{atm} = \frac{-4410}{T, {}^\circ K} + 6.26$$

based on data to 650°C (1202°F). This equation gives a decomposition pressure of 760 mm at 1031°C.

UH_3 has a cubic crystal structure with $a_0 = 6.634 \pm 0.002$ A and eight uranium atoms per unit cell. The X-ray density is 10.91 g/cc. The measured heat of formation is -30,400 cal/mole.

URANIUM SULPHIDE

The sulphides US, U_2S_3 and US_2 are known to exist. Compositions between U_2S_3 and US_2 give complex X-ray diffraction patterns and the phase relationships have not been unravelled.

Theoretically, US is more stable than the higher sulphides and therefore is probably the uranium sulphide of interest in ferrous metallurgy. The thermodynamic stability of uranium sulphides is considered to be almost the same as that of thorium sulphides.(10) US is therefore one of the most stable sulphides.

The limited information known about the uranium sulphides is entered in Table 1.6.

TABLE 1.6

Properties of Uranium Sulphides

Sulphide	M.P., °C	Density, g/cc	Crystal Symmetry	Crystal Structure	Lattice Parameters, A		
					a_o	b_o	c_o
US	>2000	10.87	Cubic	NaCl	5.484	-	-
U_2S_3	>2000	8.81	Orthorhombic	Sb_2S_3	10.64	10.41	3.89
US_2	1850	7.90	Orthorhombic	Pmnb	4.22	8.45	7.90

URANIUM SULPHOXIDE(11)

Uranium sulphoxide, UOS, has been synthesized. There is no direct evidence of the existence of other uranium oxide-sulphides.

UOS is a black material, soluble in concentrated nitric acid. The calculated density is 9.60 g/cc. The crystal structure is tetragonal with $a_1 = 3.843 \pm 0.001$ A and $a_2 = 6.694 \pm 0.001$ A.

IRON-URANIUM SYSTEM

Investigation of the iron-rich alloys of iron and uranium has not been extensive. The phase diagram in Figure 1.1 appears to be the best available.

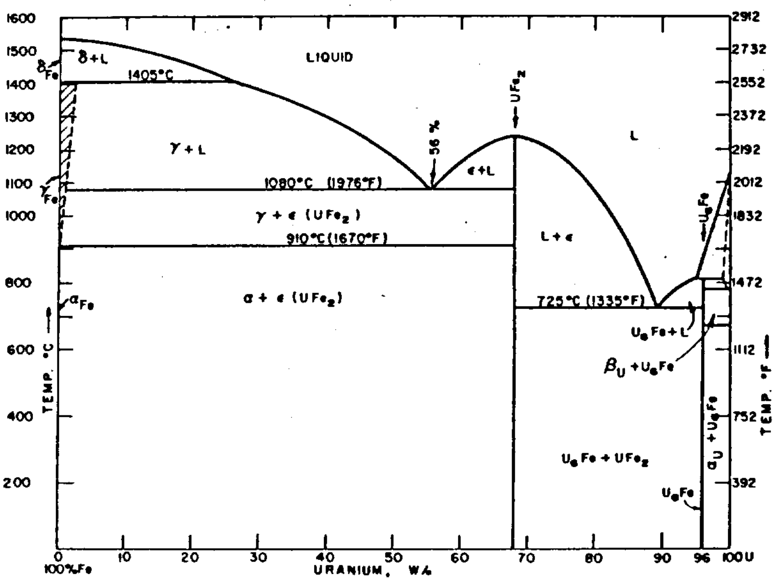

Figure 1.1 - Iron-Uranium Constitution Diagram(12)

There are two eutectic compositions, which may be suitable for ferroalloys. One at 56% uranium melts at 1080°C (1976°F). The other at 88.5% uranium melts at 725°C (1335°F).

Two intermetallic compounds, UFe_2 and U_6Fe, form but it is probable that only UFe_2 will occur in steel. The compound UFe_2, frequently referred to as the epsilon phase, has been identified by microscopical and X-ray techniques. It is stable up to its melting point of 1235°C (2255°F). It has a face-centred cubic structure with $a_0 = 7.061$ A, and an X-ray density of 13.19 g/cm^3 (13). UFe_2 has been reported to be isomorphous with UAl_2, UMn_2 and UCo_2.

The solubility of uranium in delta iron and in alpha iron appears to be zero. The solubility of uranium in gamma iron (austenite) is limited, reaching a maximum of about 2% at 1405°C (2561°F) and decreasing virtually to zero at 910°C (1670°F).

The phase diagram shows that iron with over 2% uranium and less than 68% uranium will solidify with a eutectic of UFe_2 and austenite between the primary grains of austenite. The minimum amount of this undesirable grain boundary eutectic will form under equilibrium conditions, which can only be approached with very slow rates of solidification.

Solidification of iron containing between about 1 to 2% uranium is complicated by the decreasing solubility of uranium in austenite as the temperature decreases, in a temperature interval within which austenite can coexist with uranium-rich liquid. At the monoperitectic temperature of 1405°C, delta iron and liquid with about 25% uranium completely transform, under equilibrium conditions, to austenite. However, it is considered qualitatively possible, under the non-equilibrium conditions prevailing in industry, that some uranium-rich liquid will be retained below 1405°C, perhaps even to the eutectic temperature of 1080°C, where it will solidify at grain boundaries. It may be important to note that even if this iron-uranium alloy solidifies completely at 1405°C, it will, providing the cooling rate is sufficiently slow, transform to a two-phase structure consisting of solid grains of austenite and uranium-rich liquid before the temperature drops to 1080°C. This occurrence is a theoretical possibility and not a prediction of what will necessarily happen in iron containing about 1 to 2% uranium. It is much less a prediction of what will happen in particular constructional steels modified with uranium. However, it is known (Chapter 4) that medium carbon steels containing over 0.35% uranium are hot short because UFe_2 forms at grain boundaries during solidification.

In the temperature range from 1080°C to 910°C, the UFe_2 precipitates from the austenite. Presumably this UFe_2 will occur as small particles that are well dispersed throughout the alpha iron and that may enhance yield strength and creep properties.

URANIUM COMPOUNDS IN STEEL

It has been concluded from known physical and thermo-chemical properties that UO_2, UN, US and UOS are compounds which may occur as indigenous inclusions in steel in preference to other oxides, nitrides and sulphides of uranium. Each of these compounds will not necessarily occur in its pure state, but may be in combination with other compounds. The occurrence of particular uranium-bearing inclusions and their form and amount will, of course, depend upon the composition and the metallurgical history of the steel. This all applies, also, to the intermetallic compound, UFe_2, and the carbide, UC, but these latter are not classified as inactive inclusions but as active metallurgical precipitants in steels alloyed with uranium. However, UC may contribute to the formation of complex U(CN) or U(O,C,N) inclusions because UN, UC and UO are isomorphous.

The comparison of free energies of formation offers a basis for estimating the relative stability of compounds. However, the free energy values available for uranium compounds and, in fact, for most other compounds, are for the formation of pure compounds from pure elements. These free energy values should be adjusted by values for the heats of solution of the reactants and of the products;

otherwise, the actual equilibrium constant for a particular reaction may be considerably less than the estimated equilibrium constant. For example, the actual equilibrium constant for deoxidation of iron by aluminum is one hundredth of the theoretical value. This disparity is due to uncertainty about the activity coefficient of aluminum in steel and to the false assumption that the deoxidation product was pure solid alumina(14).

When the limitations of their usefulness in steel are appreciated, it is informative to use the available data to compare the thermodynamic stability of uranium compounds with that of other compounds that form in steel. Such data are considered separately for oxides, sulphides, nitrides and carbides. Unfortunately, no thermodynamic data are available for UFe_2. In any event, it appears possible that the available uranium that does not combine with oxygen, sulphur, nitrogen or carbon will form UFe_2. The possibility of UFe_2 forming at grain boundaries has been discussed. The morphology of UFe_2 at other locations may be of significance.

At 1500°C (2732°F), the free energy of formation, per gram atom of oxygen, is so similar for pure crystalline ZrO_2, Al_2O_3 and UO_2 that it is not possible to predict which element, zirconium, aluminum, or uranium, will be the most effective deoxidizer in steel. The free energy of formation of elements which are good deoxidizers in steel may be compared in Table 1.7.

The stoichiometric ratio, by weight, of uranium to oxygen in UO_2 is 7.44 to 1.

Uranium has a very strong affinity for sulphur and it is known that uranium sulphide forms in steels. At 1500°C (2732°F) the free energy of formation of MnS is about -45,000 cal/g atom of sulphur. The corresponding free energy of formation of US has been estimated as about -90,000 cal/g atom of sulphur(17), which is approximately the same as for CeS. The high free energy of formation of US implies a small equilibrium constant, which is equivalent to saying that uranium lowers the solubility of sulphur in steel and therefore uranium may affect the morphology of sulphides in steel by increasing their temperature of formation.

The stoichiometric ratio of uranium to sulphur in US is 7.5 to 1, i.e., 0.025% sulphur can theoretically combine with 0.1875% uranium to form US. Therefore the actual amount of uranium combined with sulphur may be of importance.

TABLE 1.7

Free Energy of Formation of Selected Oxides, at 1500°C

Reaction	$\Delta F^\circ_{1500^\circ C}$, Calories per g atom of oxygen	Free Energy Equation	Reference
$\frac{1}{2}$ Mn + $\frac{1}{2}$ $O_2 \longrightarrow \frac{1}{2}$ MnO	-60,600	$\Delta F^\circ_{1500-2051^\circ K} = -95{,}400 + 19.62T$	15
$\frac{1}{2}$ Si + $\frac{1}{2}$ $O_2 \longrightarrow \frac{1}{2}$ SiO_2	-65,500	$\Delta F^\circ_{1770-1793^\circ K} = -108{,}785 + 24.40T$	15
2/3 V + $\frac{1}{2}$ $O_2 \longrightarrow$ 1/3 V_2O_3	-68,900	$\Delta F^\circ_{298-1995^\circ K} = -103{,}400 + 19.45T$	15
$\frac{1}{2}$ Ti + $\frac{1}{2}$ $O_2 \longrightarrow \frac{1}{2}$ TiO_2	-72,000	$\Delta F^\circ_{298-2080^\circ K} = -108{,}750 + 20.7T$	16
$\frac{1}{2}$ Zr + $\frac{1}{2}$ $O_2 \longrightarrow \frac{1}{2}$ ZrO_2	-89,000	$\Delta F = -128{,}000 + 22.0T$ (steelmaking temp)	
2/3 Al + $\frac{1}{2}$ $O_2 \longrightarrow$ 1/3 Al_2O_3	-89,500	$\Delta F^\circ_{930-2318^\circ K} = -128{,}750 + 22.15T$	15
$\frac{1}{2}$ U + $\frac{1}{2}$ $O_2 \longrightarrow \frac{1}{2}$ UO_2	-92,200	$\Delta F_{1500} = -129{,}600 + 21.1T$	7,8

The free energy of formation of refractory nitrides, as shown in Table 1.8, indicates that uranium mononitride is the most likely nitride to form in steel. The stoichiometric ratio of uranium to nitrogen is 17 to 1. Most steels contain at least 0.004% nitrogen. Half of this could fix 0.034% uranium as UN.

TABLE 1.8

Thermodynamic Properties of
Refractory Nitrides(18)

Nitride	ΔF°_{298}, cal/g atom N	ΔH°_{298}, cal/g atom N	ΔS°_{298}, cal/(g mole)(°K)	$\Delta F^\circ_{1773} = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$, cal/g atom N
VN	-34,500	-40,800	-21.0	- 3,600
AlN	-56,300	-64,000	-25.8	- 9,300
BN	-29,700	-33,500	-12.9	-10,600
TaN	-52,200	-58,100	-19.9	-22,800
NbN	-55,000	-59,000	(-20)	(-24,000)
LaN	-64,700	-72,100	-25.0	-27,800
TiN	-73,600	-80,400	-22.8	-40,000
ZrN	-75,300	-82,200	-23.2	-41,000
UN	-75,000	-80,000	-17	-50,000

Uranium may exercise its greatest influence in steel by the formation of uranium monocarbide, if sufficient uranium is present to deplete the austenite of soluble carbon. The stability of uranium carbides means that they probably form readily at elevated temperatures in steel. The stoichiometric ratio of uranium to carbon, to form UC, is 20 to 1, so that 0.01% carbon may combine with 0.2% uranium. In Table 1.9, the free energy of formation of certain carbides, calculated for or extrapolated to a value for 1500°C, is shown in the order of increasing energy.

Uranium monocarbide appears to be stable enough to form in steel at elevated temperatures when excess carbon and uranium are available. Goldschmidt(19) generalizes that iron does not form ternary carbides or solid solutions with metals that form close-packed cubic carbides having NaCl structure. These carbides, ZrC, NbC/Nb_4C_3, TaC, TiC, VC/V_4C_3, $Cr_{23}C_6$ and UC tie up the available carbon. Goldschmidt further generalizes that carbides having the same crystal structure are liable to show complete or partial intersolubility, depending largely on whether or not the atomic size factor of the metal atoms is favourable. Valency and other factors also influence intersolubility. Based on the size factor, however, it may be concluded that UC is soluble to some extent with ZrC, NbC, TaC and TiC and is insoluble with VC and $Cr_{23}C_6$.

TABLE 1.9

Free Energy of Formation of Certain Refractory Carbides

Reaction	$\Delta F°$, cal/g atom of oxygen, at 1500°C	Free Energy Equation	Reference
$3\ Fe + C \longrightarrow Fe_3C$	-1,830	$\Delta F°_{1115-1808°K} = 2475-2.43T$	19
$3\ Mn + C \longrightarrow Mn_3C$	-2,310	$\Delta F°_{1000-1193°K} = -5240 + 1.65T$	19
$2\ Mo + C \longrightarrow Mo_2C$	(-6,700)	$\Delta F°_{273-1273°K} = -6700 + 0.0T$	19
$Si + C \longrightarrow SiC$	-9,240	$\Delta F°_{1683-2000°K} = -24,100 + 8.33T$	19
$V + C \longrightarrow VC$	-9,670	$\Delta F°_{298-2000°K} = -12,500 + 1.6T$	19
$W + C \longrightarrow WC$	(-8,400)	$\Delta F°_{298} = -8400$	19
$U + C \longrightarrow UC$	(-13,440)	$\Delta F°_{T} = \Delta H°_{298} - T\Delta S°_{298} = -20,000 + 3.70T$	2
$U(l) + C \longrightarrow UC$	-15,610	$\Delta F°_{T} = -22,440 + 13.13T \log_{10}T - 2.46 \times 10^{-3}T^2 + 0.35 \times 10^5T^{-1} - 33.50T$	18
$Ta + C \longrightarrow TaC$	(-36,200)	$\Delta F°_{T} = \Delta H°_{298} - T\Delta S°_{298} = -38,500 + 1.3T$	20
$Zr + C \longrightarrow ZrC$	-36,500	$\Delta F°_{298-2273°K} = -36,500 + 0.0T$	19
$Ti + C \longrightarrow TiC$	-39,000	$\Delta F°_{1150-2000°K} = -44,600 + 3.16T$	19

None of the uranium carbides possess the required symmetry for coherence in iron. Also the uranium atom is considerably larger than the iron atom. Accordingly, it is improbable that coherent uranium carbides could form during the tempering of martensitic steels alloyed with uranium.

The carbide-forming elements, chromium, cobalt, manganese, molybdenum, titanium, tungsten, and vanadium, are soluble in varying quantities above 2.5% in alpha iron. By contrast uranium has virtually no solubility in alpha iron. This suggests that nucleation and growth of any uranium carbides during tempering will be difficult if not impossible.

ELECTROLYTIC EXTRACTION OF URANIUM COMPOUNDS(22)

Research in the field of uranium steels is hampered by the difficulty of interpreting metallurgical results in terms of the partition of uranium because of its ability to form oxides, nitrides, sulphides, carbides and intermetallic compounds.

Electrolytic extraction of particles from steel must be carried out in an environment that will permit them to remain physically and chemically unaltered during the process. This necessitates use of a non-aqueous electrolyte with very specific characteristics in place of the commonly used aqueous solutions.

Generally, the solvent must have sufficient chemical reactivity to form with the solute a co-ordination compound that is not too stable. This eliminates all non-reactive hydrocarbon liquids such as the saturated hydrocarbons, paraffins and halogen derivatives. However, a large variety of organic liquids form co-ordination compounds; among these are oxygen-containing compounds such as alcohols, ethers, ketones, and acids; nitrogen-containing compounds such as amines, amides, and nitrides; and unsaturated hydrocarbons such as benzene and toluene. Those metals which can be deposited from aqueous solutions can also be deposited from non-aqueous media. Hydrides have been used extensively in many non-aqueous electrolytes necessitating use of an inert atmosphere.

The newly developed Threshold Centrifuge may prove to be invaluable in sorting out extracted carbides and oxides in suspension so that they may be more readily identified by X-ray diffraction and electron microscopy.

Conventional electrolytic extraction cell equipment has been modified to provide for the use of non-aqueous electrolytes. A conductivity bridge and an amplifier are used to measure the conductivity of electrolytes being studied for the extraction process.

The amperometric method for measuring water concentrations in the range 1 ppm to 20,000 ppm is used to control water concentrations of non-aqueous electrolytes during the extraction cycle. This method employs a cell in one arm of a conductivity bridge and a stripper gas, in this case argon, to give a continuous determination of H_2O concentration in the electrolyte.

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CHAPTER 2

A REVIEW OF PUBLISHED WORK AND PATENTS ON URANIUM IN FERROUS ALLOYS

W. A. Morgan* and R. D. McDonald**

SYNOPSIS

The available technical literature and patent files were reviewed to assess the knowledge of uranium-bearing steels and of the production of uranium ferroalloys. The results suggest that uranium improves tensile properties, increases hardenability, induces precipitation hardening, forms carbides which are more stable than those of molybdenum and tungsten, and scavenges oxygen, nitrogen and sulphur. This information, together with that of Chapter 1, forms the basis for planning of most of the uranium projects at the Mines Branch.

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*Head and**Senior Scientific Officer, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

The technical literature and patents, prior to 1960, relating to the use of uranium in ferrous materials and to the production of uranium-bearing steels and ferroalloys, were surveyed. The findings have been the basis of, or have been an influence on, the planning of some of the investigations at the Mines Branch. This, in fact, appears to be the main justification for their inclusion in this research report. In any event, the information contained herein may also serve as useful background material to other investigators.

The literature revealed many contradictory and anomalous results. This is particularly so when they are viewed in the light of present theoretical considerations. Consequently, some of the research findings and patent claims of early investigators have been confirmed while others have been refuted by current studies. It is considered that one of the more serious handicaps of investigators, prior to the early 1930's, was the impurity of the available uranium metal and uranium master alloys(1). Reduction by thermite reaction was expensive and yielded a product containing a considerable amount of aluminum and oxides of aluminum and uranium. The ferroalloys prepared in electric arc furnaces contained variable amounts of carbon, silicon, oxides, and, usually, vanadium. Care in selection of uranium was required to keep the vanadium below 0.5%.

TECHNICAL LITERATURE

Ferroalloys

Polushkin(2) investigated complex alloys of uranium and iron which contained carbon, vanadium and silicon. Other elements were present only as impurities. This work was concerned with melting point determinations, decomposition in water, crystal structure, specific gravity, pyrophoric properties, radioactivity, and microstructures. Some typical compositions studied, together with their melting ranges, are given in Table 2.1.

TABLE 2.1

Typical Compositions of Iron-Uranium Alloys Studied by Polushkin (2,3)

Alloy No.	Percentage of Element					Melting Point Range	
	U	C	Fe	Si	V	°C	°F
10	28.7	0.34	66.81	1.44	0.53	1540-1660	2805-3020
35	41.6	4.57	46.88	3.55	1.76	1660-1785	3020-3245
21	47.5	2.29	47.40	2.59	1.66	1660-1710	3020-3110
3	55.2	0.98	41.90	1.11	0.71	1660-1785	3020-3245
*19	85.2	7.74	2.41	1.45	2.07	Disintegrated 1000	1830

*Also contains 0.08% aluminum.

Oxygen was excluded from the system for the determination of melting points in order to prevent the formation of an oxide crust with a high melting point. A technique was used in which several alloy samples, separated by finely powdered alumina, were heated and cooled in a boat under a hydrogen atmosphere. An examination of their structures revealed whether they had melted at the temperature used. By repeating the test at various temperatures it was possible to obtain melting ranges for the different alloys tested.

Specific gravity determinations were made in alcohol because of the water-decomposable nature of some of the alloys. Specific gravities were found to range from 7.34 to 12 as the percentage of uranium increased from 4.13% to 90.0%.

The proportion of uranium in an alloy was determined by the effect of the radioactivity on a Curie electroscope. The radioactivity also showed the distribution and location of the uranium-bearing constituents in the alloys.

Constructional Steels

Polushkin(2,3) also made small melts of uranium-bearing steel in an electric furnace. Ferro-uranium additions were made either in the furnace before tapping or in the ladle. Losses were high using furnace additions, but 50 to 75 per cent recoveries were obtained by ladle additions. It was reported that ferro-uranium alloys containing 30 to 40% uranium showed the best recovery, and that the carbon content of the ferroalloy appeared to have no influence on the recovery.

Microscopical examination of the steels revealed the presence of both uranium oxide and uranium carbide. The oxide was present even with a high proportion of silicon, manganese, chromium and nickel. This was attributed to the failure of the oxide to rise to the top of the ingot due to its high density.

Other work cited by Polushkin(3) covered a series of melts made in a small electric furnace using basic practice. Ferro-uranium and ferrocarbon were added either in the furnace or in the ladle. Forging, annealing, heat treating and mechanical testing were carried out. The determination of critical points was also included. From this work it was concluded that:

1. Uranium does not affect the Ac_1 temperature when the uranium content is less than 7%. The Ar_1 temperature is lowered when the uranium content exceeds 2%.
2. Uranium may be present in the steel as an oxide or carbide. Heat colouration was cited as a means of clearly identifying the oxide.

3. Uranium carbide does not enter into solid solution with iron even at a temperature of 1250°C (2280°F).

4. In carbon steels containing 0.25 to 0.45% carbon, uranium raises the elastic limit and the resistance to rupture without affecting the ductility. In carbon steel containing 0.60% or more carbon, uranium raises the elastic limit and resistance to rupture, but decreases the ductility.

5. Uranium increases the hardness of steel.

6. One heat of uranium-nickel steel gave good results, its ductility being superior to ordinary steel and chromium and vanadium steel; other melts showed no improvement.

7. The comparative value of the good effects mentioned in 4, 5, and 6 was not determined exactly, in view of the special conditions of manufacture and heat treatment of the steel. However, in all cases no remarkable results were obtained that could not have been developed with other special steels.

8. Uranium has no influence on either the resistance to impact or on the resistance to alternating stress.

Foote(4) carried out research on steels containing hypoeutectoid quantities of carbon and various levels of uranium. Included in his work were studies of the influence of uranium in structural and high speed steels.

Hypoeutectoid steels containing not more than 0.60% uranium are normally pearlitic, but any increase in the uranium content over this limit produces a characteristic carbidic component that heat-tints in a manner similar to uranium carbide. The steels under consideration contain from 0.25 to 0.54% carbon and from 0.22 to 4.14% uranium. Alloys containing chromium, nickel, molybdenum and vanadium are included in the materials tested.

It was stated that the most striking features of uranium as an alloying element are firstly, that it does not need to be augmented or intensified by the addition of other alloys, and secondly, that the uranium steels readily lend themselves to being water quenched. Uranium increases the hardness and hardenability of steels; the hardness imparted thereby is not accompanied by as great a degree of brittleness as that induced by other carbide-forming elements. Carbon-uranium steels are pre-eminently adapted for uses which necessitate a low drawing temperature, in that they possess under these conditions a remarkable combination of hardness, strength and ductility. The addition of a small amount of uranium imparts to steel a sufficient increase in elastic and tensile strengths to make it comparable to the more complex alloys.

A 1921 publication(5) contains some interesting summaries of the knowledge at that time on some possible uses of uranium in carbon, low alloy, and high speed steels. Analytical and etching techniques for uranium in steels are included.

Bennek and Holzscheiter(6) made reference in 1935 to the work carried out by Polushkin, Foote and others during the period 1918 to 1923. These authors believe that research during that period had not clearly determined the fundamental influences of uranium as an alloying element. Complete agreement prevailed neither on its influence on the microstructure and phase change points of iron-carbon steels, nor on its relationship to carbon. It was suggested that contradictions probably arose from unobserved irregularities in the castings and from liquation. In a programme endeavouring to clear up existing disagreements, close control was maintained on all procedures. Armco iron was used as a base material, and a ferroalloy containing 31.7% uranium and 0.84% carbon was used for the uranium addition. Castings were made which contained 0.1, 0.3 and 0.9% carbon, and up to 5% uranium. The castings were forged successfully from 1000° to 900°C

(1830° to 1650°F). This contradicted previous findings that showed uranium-bearing alloys to be unforgeable when the uranium content exceeded 2%.

Heat treatments and microstructural examinations showed the appearance of two new constituents which were considered to be carbides of uranium. Some evidence of a degree of solubility of uranium in the solid solution was observed. No increase in hardness was obtained when these steels were quenched from above 1100°C (2010°F). The improvement in the mechanical properties of structural steels due to uranium was believed to be only slight.

There was evidence of slight changes in the critical temperatures of uranium-bearing steels. In steels containing 0.1 to 0.25% carbon, it appeared that the A_1 temperatures were elevated slightly, but little or no change occurred in the location of the A_3 temperatures.

Tool Steels

Foote(4) states that in uranium-bearing high speed steels the uranium tends to promote the formation of complex carbides. Because these carbides apparently were more soluble in gamma iron than those complex carbides ordinarily found in high speed steels, he inferred that uranium should exert an important influence on the property of secondary hardness.

High-Temperature Alloys

In 1955 Harris and Child(7) compared the effects of uranium with those of niobium in cobalt-base heat resisting alloys. Increases in creep and stress-to-rupture strengths were attained by adding up to 2% uranium. Above this quantity forging became impossible. Creep properties were improved as much by 1% niobium as by 2% uranium.

PATENTS

General

Strong, specific patent claims were made utilizing the carbide-forming characteristic of uranium in high speed tool steels. However, in most of the patents relating to the use of uranium in steels, the claims were not specific for uranium but for groups of elements which form stable carbides, oxides, nitrides, or sulphides. The claims, on behalf of groups of elements, concern the use of uranium as a scavenging agent or as an element to improve tensile properties, induce precipitation hardening and to stabilize carbides.

The patent claims, prior to 1960, are grouped under the following sub-headings:

Production of Ferro-uranium
Tool Steels
Structural Steels
Precipitation Hardenable Steels
Stainless Steels
Magnetic Alloys
Cast Iron.

Production of Ferro-uranium

There are three patents relating to the production of ferro-uranium and the means of reducing uranium from a steelmaking slag into the molten steel.

Two U.S. Patents, No. 1,240,054 and No. 1,240,056 were dated September 11, 1917.. The first claims a process for producing ferro-uranium and the second claims improvements in the process.

The materials employed are uranium oxide, fluorspar a carbonaceous reducing agent, and iron or steel particles. Steel turnings may be employed with advantage. All of the materials should be as free as possible from impurities, especially silica or silicon. To obtain the best results the steel should not contain over 0.3% carbon, 0.15% silicon, 0.1% sulphur and 0.1% phosphorus. Sodium uranate may be used instead of uranium oxide. A typical charge was as follows:

Steel turnings - 10 lb
Uranium oxide - 7.5 lb
Coke - 6 lb
Fluorspar - 8 lb

The mixture is charged into an electric furnace at a rate depending on the size of furnace and the grade of alloy being made, but in no case should the mixture be charged fast enough to cool the furnace to any great degree.

The reactions involved are those of simple carbon reduction, the reduced uranium alloying with the steel turnings to form ferro-uranium. They may be represented as follows:

$$U_3O_8 + 8C = 3U + 8CO$$

Fluorspar was found to be the best, and probably the only slag-forming material that may be successfully used to obtain a reasonable proportion of uranium in the alloy. Of the uranium put in the charge, at least 76% will be contained in the alloy. By reprocessing the residue, approximately 85% of the uranium will be alloyed with the steel.

In the second patent, covering improvements to the process, a definite furnace practice is given. A Siemens electric furnace with a simple suspended electrode is used. If it is not necessary to keep the carbon of the alloy below 4%, the crucible may be made completely of carbon or graphite rammed into place with pitch as a binder.

To minimize the carbon content, the crucible may be lined entirely with ground, dead-burned magnesite rammed into place with pitch as a binder. There should be a roof of silica brick over the crucible. The furnace may be either the stationary or tilting type but must be capable of an intense concentration of heat because of the high reduction temperature of uranium oxide, approximately 1490°C (2715°F), with a carbon reducing agent.

In Dominion of Canada Patent No. 333671 dated February 1, 1932, an interesting invention is presented relating to a process for the production of metals and alloys low in carbon and also low in silicon or aluminum, or with a definitely controlled amount of silicon or aluminum. The process is particularly adapted to the treatment of the higher melting point metals such as chromium, vanadium, zirconium, titanium, tantalum and uranium. It is based on the facts that the fluorine compounds of these metals can be easily reduced and that, if the oxides are mixed with a substance adapted to generate fluorine at reducing temperatures, there appears to be some interaction of the fluorine with the oxide that permits the oxide to be readily reduced. The fluorine compound used may be one in which the resulting stable ingredients will be removed with the slag or will enter into the metal product; for example, a fluoride of the metal to be reduced or of some other high melting point metal, or a double fluoride of such a metal, or a somewhat different type of fluoride such as sodium fluoride may be used. The reducing agent can be silicon or aluminum. Lime is also added to take up excess fluorine thus forming fluorspar, which keeps the slag fluid; it also helps to prevent the escape of fluorine, which would tend to poison the atmosphere. The reaction is almost instantaneous and involves the generation of a large amount of heat.

Silicon is a more efficient reducing agent than aluminum due to the fact that silicon and fluorine combine to form a gas, which in turn reacts with the oxide.

Recommended refractories are a magnesite lining and a chromite furnace roof.

The latter patent is similar to the U.S. patents for the production of ferro-uranium except that it is of more general application to the reduction of other metals and also it uses silicon or aluminum as a reducing agent instead of carbon.

Tool Steels

The first specific claim for uranium as an alloying element in high speed tool steels was made in U.S. Patent No. 1,210,625 dated January 2, 1917. Uranium is the sole added toughening agent in quantities from 0.05 to 5.0%. No carbon content or other alloy content is mentioned. The inference is made that uranium will replace the tungsten normally present in high speed tool steels.

The objects of adding uranium are to:

(a) decrease the cost of manufacturing high speed steel,

(b) enhance the cutting efficiency of the steel,

(c) improve the hardness and toughness,

(d) act as a deoxidizing and denitrogenizing agent.

A second U.S. Patent No. 1,210,626 dated January 2, 1917, made out to the same inventor claims that uranium may be used to replace part of the tungsten in high speed steels. Three parts of tungsten were replaced by one part of uranium. A typical alloy containing 8% tungsten and 3% uranium was claimed to possess all of the qualities of an 18% tungsten steel plus greater toughness.

A third U.S. Patent No. 1,210,627 dated January 2, 1917, again made out to the same inventor, claims that uranium may replace a portion of the molybdenum used in high speed molybdenum steel. If uranium is added in the range 0.40% to 3.0%, the molybdenum content may be restricted to the range 3 - 10%. A reduction in the molybdenum content renders the steel less expensive. The addition of the uranium improves the cutting efficiency, hardness and toughness of the steel.

Under the above patents the uranium is incorporated into the steel in the form of ferro-uranium or uranium metal, the addition being made from five to ten minutes before pouring and after deslagging or in the ladle immediately after pouring.

In U.S. Patent No. 1,233,862 dated July 17, 1917, it was claimed that when both cobalt and uranium are added to steel containing tungsten, chromium and vanadium, a substantial increase in cutting efficiency is obtained. It was also found that uranium, when added with cobalt, improved the quality of the steel even though only a relatively small proportion of the uranium actually added is found to remain in the finished product.

The cobalt may range between 3 and 7% and the tungsten between 12 and 20%. If the cobalt is increased to 15 or 20% the tungsten may be reduced to 9%. The chromium should be between 3 and 4%, although it may range from 2 to 6%. If vanadium is added, it should be in the range 0.5 to 2%. The uranium, in all cases, may range from 0.1 to 2%.

In British Patent No. 422,167, uranium is claimed as an addition element in tool steels, presumably for its carbide forming characteristic.

In British Patent No. 510,617, 1939, the authors claim that the amount of tungsten in high speed tool steels can be decreased by the addition of one or more of a group of elements in a total quantity of 0.1 to 3.0 per cent. Since carbide formers are included in this group it appears that it was the intention to again use the carbide forming tendency of uranium.

British Patents No. 499,561 and 504,224, granted in 1939, basically refer to tool steels containing more than 10% chromium. They are claimed to be suitable for corrosion resistant tools with either a point or a cutting edge. Uranium is included with a group of elements including such carbide formers as titanium, niobium and tantalum. Again, it appears likely that the carbide forming property of uranium is being utilized. It should be noted that uranium is not a prerequisite in these patents.

Structural Steels

The only specific claims for structural steels containing uranium are given in U.S. Patent No. 1,366,254 dated January 18, 1921, and U.S. Patent No. 1,446,497 dated February 27, 1923, both assigned to the Standard Chemical Company of Pittsburgh.

In Patent No. 1,366,254 a claim is made for steel whose composition conforms to the following ranges:

Element	Composition Per Cent
Carbon	0.10 - 0.60
Uranium	0.20 - 1.00
Manganese	0.50 - 0.60
Nickel	2.00 - 3.50
Silicon	0.55 - 2.00
Phosphorus	0.03
Sulphur	trace

This steel is claimed to have high qualities of static and dynamic strength, ductility, and hardness "which render it eminently efficient and useful for the manufacture of such articles, for example, as automobile gears, light armour plate, rivet sets, etc."

In Patent No. 1,466,497 it is claimed that a steel alloy of the following composition range, preferable composition, and typical composition, possesses improved strength without brittleness.

Element	Composition Per Cent		
	Range of Invention	Preferable Range	Typical Composition
Carbon	0.10 - 1.00	0.60 - 0.70	0.62
Silicon	0.10 - 1.80	0.20 - 0.30	0.20
Manganese	0.20 - 1.00	0.40 - 0.60	0.63
Uranium	0.10 - 0.90	0.20 - 0.35	0.23
Vanadium	0.10 - 0.90	0.10 - 0.15	0.15

A steel of the above composition, when suitably heat treated, gives the following properties:

Elastic Limit, psi	Ultimate Strength, psi	% El, in 2 in.	% R A	Brinell Hardness
300,800	323,000	5.5	12.6	600
262,200	285,300	7.5	22.0	555

In both of the above patents it is stated that the ferro-uranium (38%) may be added in the ladle. Recoveries in 250 lb melts were about 80%.

In British Patents No. 540,601, No. 545,269, and No. 556,770 dated in 1941, 1942 and 1943, respectively, improvements in hardenability are attributed to such alloy additions as beryllium, boron, titanium, and thorium. In each of these patents uranium is included as one of a group of elements, one or more of which are also added to attain improved hardenability. Although no function is attributed to elements in the group containing uranium, it appears likely from present knowledge that some or all of these act as scavengers.

In French Patent 779,378, granted in 1935, uranium is used in welding rods for carbon and low alloy steels. The uranium functioned as a scavenging agent for sulphur, nitrogen and oxygen.

High-Temperature Steels

The use of uranium in heat-resisting steels for structural purposes is described in U.S. Patent No. 1,545,094 dated July 7, 1925. The object of the invention was to provide a readily forgeable and otherwise workable steel alloy which is suitable for the manufacture of components that must be resistant to thermal fatigue.

The steel alloy described "includes uranium or vanadium, or both, but preferably only the former. It also includes tungsten or molybdenum, preferably the former, and cobalt, chromium, silicon and carbon." The amounts of these elements present in the alloy are from about 0.2 to 5.0% uranium or vanadium, 0.2 to 7.0% tungsten or molybdenum, 0.2 to 5.0% cobalt, 2.0 to 8.0% chromium, 0.15 to 3.0% silicon and 0.2 to 1.5% carbon. The preferred alloy however, is of the following composition:

U	W	Co	Cr	Si	C
0.80%	6.00%	0.50%	6.00%	1.50%	0.45%

Valves, valve seats and valve sleeves for internal combustion engines manufactured from this alloy "were subjected to severe tests and found to be much superior to the same parts manufactured from the best known prior commercial alloy. Normally good valves withstood a standard test period of 100 hours. The new valves however, ran for 1,800 hours and were in excellent condition at the end of the test."

Austrian Patent No. 144,000 claims a new alloy containing 0.1 - 1.5% carbon, 0.5 - 3.5% silicon, 1 - 9% chromium, 2 - 8% molybdenum, up to 4% copper "and also nickel, manganese, tungsten, vanadium, titanium, aluminum, zirconium, uranium and cobalt up to a maximum of 3% each." This alloy was stated to have improved resistance to high pressures as in rifle barrels, improved high temperatures strength, and increased resistance to wear.

United States Patent No. 1,592,996 registers claims of a superior steel for hot work die-blocks and other applications subject to severe mechanical wear. The principal alloying elements are chromium and silicon. Uranium was added as a scavenging agent for elements such as sulphur, nitrogen and probably oxygen.

Precipitation Hardenable Steels

The effect of uranium on precipitation hardening in ferrous alloys is mentioned in Austrian Patent No. 137,301, dated 1934. It is claimed that the strength, hardness, and elastic limit of low carbon irons and steels are improved by additions of titanium, boron, zirconium, tantalum, columbium, cerium or uranium singly or mixed.

In British Patents No. 374,541, No. 419,680 and No. 495,562 claims are made relating to improvements in properties of iron and steel alloys by the addition of uranium, along with several other elements. In these patents uranium is considered to be a possible alternative to any element which will promote age or precipitation hardening. This application applies to alloys of iron and chromium or of iron, nickel, and chromium. The claims include improvements in hardness, tensile ductility, and in tensile and yield strengths of quenched and tempered alloys. For alloys which have been annealed, cold-worked, and hardened by heating in the temperature range 200° - 700°C (400° - 1300°F), it is claimed that benefits to elastic limits and elastic behaviour persist throughout the hardening temperature range.

Stainless Steels

One U.S. Patent No. 1,975,310 includes uranium in a group of stabilizing elements for stainless steels as follows:

..."this advantage is also inherent in chrome-nickel steel alloys having a stable surface which contain one or more of the elements, niobium, tantalum, zirconium, uranium, hafnium or rare earth metals such as cerium, thorium, lanthanum, yttrium, neodynium, samarium, etc. These elements also, as has been proven, form such a stable chemical combination with the carbon in solution in the austenitic base mass that the chemical and mechanical stability of the alloy is not affected for practical purposes after a heat treatment of above 500 to 900°C (930 to 1650°F).

Magnetic Alloys

A magnetic alloy containing uranium is described in U.S. Patent No. 2,073,455 dated March 9, 1937. In this patent uranium is used to deoxidize the alloy. The alloying effect is not considered to be important.

During the melting of iron base magnetic alloys, oxygen is dissolved in the alloy, forming on solidification inert materials poorly magnetic materials and generally deteriorating the steel by solutions of oxides therein and preventing the alloying of the desired constituents. The effect of this not only reduces the amount of magnetic material in a given volume but also decreases the interfacial contact areas of the alloy particles, tending to reduce the coercive force of the final product. In order, therefore, to remove the dissolved oxygen from the molten metal, uranium is added to the oxides. The uranium oxide thus formed, some of which remains in the steel, does not appear to be harmful to the magnetic properties of the steel. A large part of the uranium oxide appears to pass into the slag.

It was observed that, "the amount of uranium is not critical and considerable variations may be made in the amount added. When 2% of uranium is added it appears by chemical analyses that about 0.12% remains in the steel".

A point to note in this patent is that the claim for deoxidizing action is limited to removal of the effects of dissolved oxygen on magnetic properties. No reference is made to the deoxidizing effect of uranium on the modification of Type II sulphides in cast steel. No reference is made to the effect of uranium in reducing Al_2O_3.

Cast Iron

Only one Patent No. 1,247,252 dated November 20, 1917, refers to cast-iron or semi-steel. The patent makes claim for "an iron or semi-steel alloy consisting of cast iron or semi-steel from 0.05% to 1% of uranium alloyed therewith". The object of the alloying is to increase the strength and toughness of iron, increase the fluidity, enhance the machinability, increase the wear resistance and "increase the quality of shrinkage in the molding process". The uranium may be added to the molten iron either in the form of uranium metal or ferro-uranium. The addition should be made to the stream of the molten iron as it passes from the cupola into the ladle. When alloyed with cast iron or semi-steel the general statement is made that uranium acts as a deoxidizing and denitrogenizing agent and produces a finer grain casting.

CONCLUSIONS

In summary, the patents prior to 1960 and pertaining to the use of uranium in ferrous metals include the following claims:

1. Methods have been established for successfully producing ferro-uranium.

2. Uranium can be successfully substituted for tungsten and molybdenum in high speed tool steels.
3. Uranium has been shown to be useful in structural and heat resisting steels.
4. Uranium has been applied as a deoxidizer in magnetic alloys.
5. Mention has been made of uranium as a stabilizer of stainless steels, but no pertinent results have been quoted.
6. Uranium has been mentioned as a possible scavenger to enhance the effect of other alloying additions.

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CHAPTER 3

RECOVERY AND SEGREGATION IN LABORATORY AND COMMERCIAL STEELS

R.K. Buhr* and D.R. Bell*

SYNOPSIS

The recovery of uranium added to molten steel is extremely variable, and greatly dependent on the oxygen content of the steel. For ladle additions to basic oxygen steel the recovery varied from 7% to 29%. In plain carbon, aluminum-killed, laboratory heats uranium recoveries, based on analyses of the unsegregated areas averaged about 45%. Segregation characteristics or recoveries were not materially affected by the use of different uranium additives in the latter tests. In commercial heats, when the steel was fully deoxidized prior to the uranium addition, recoveries ranged from 49% to 66% regardless of the steelmaking process.

Normal basic electric steelmaking procedures removed uranium from the molten bath; hence recirculated scrap would not lead to uranium buildup.

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*Senior Scientific Officers, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Segregation of uranium occurred in all tests in the form of galaxies of small particles of uranium-rich compounds. The distribution of segregates has been shown by autoradiography to be related to the solidification rate. With slow cooling rates, equivalent to those of large commercial ingots, most of the uranium-rich compounds settled to the bottom portion of the ingot or casting. With the faster cooling rates of most of the laboratory ingots, the galaxies were small and more dispersed.

The segregated areas were high in uranium, oxygen, acid insoluble aluminum, and, in some cases, slightly high in nitrogen. The unsegregated areas were very low in total oxygen and acid insoluble aluminum, and occasionally lower in nitrogen. There was no segregation of carbon, manganese, silicon, sulphur, phosphorus, chromium, or copper to the uranium-rich areas.

INTRODUCTION

Uranium has a very high affinity for oxygen, and, when added to molten steel, will combine with this element in preference to others. Consequently, in order to obtain maximum recovery the amount of oxygen in the steel must be kept at the lowest value possible.

Uranium has a high density and most compounds formed with it will have a density greater than steel. Hence, segregation to the bottom could be anticipated.

An investigation was undertaken to determine the recovery and segregation characteristics of uranium in steel, and to determine whether or not benefits could be obtained with the use of uranium-base alloys instead of pure uranium as addition agents. The removal of uranium from scrap using normal steelmaking techniques was also examined.

Finally, the results obtained to date on the recovery and segregation of uranium in a few commercial heats made by the Oxygen Converter (L.D.), Open Hearth, and Electric furnace processes are included.

LABORATORY STEELS

Melting Equipment and Procedures

The laboratory steels were produced in a 500 lb basic electric arc furnace, or in induction furnaces of 50 lb or 450 lb capacity. The melts were adjusted to the desired compositions and thoroughly deoxidized with manganese, silicon and aluminum before the addition of uranium.

Uranium was usually added to the ladle after addition of aluminum to the tap stream. The uranium addition material, which was wrapped in aluminum foil and wired to a steel rod, was plunged and stirred in the ladle.

In split heats, the uranium was added in increments either to the ladle, or to the induction furnace, between pouring of ingots. In this way it was possible to investigate several uranium levels in steels of almost identical composition. Aluminum was added directly to the bath prior to addition of uranium in the induction furnace. With this latter procedure the stirring action resulting from the induced current was considered sufficient to give homogeneity in the molten bath.

Master Alloys

Aluminum with 13% uranium, prepared by dissolving uranium metal in molten aluminum, was made into shot (1,3). Uranium-titanium alloy, prepared by consumable-electrode arc melting of sponge titanium and uranium, was machined into chips(2,3). Consumable electrodes with $12\frac{1}{2}$% uranium, made by compacting electrolytic iron and uranium, and electrodes with 50% uranium, made by laminating alternate strips of steel and uranium metal, were melted in a vacuum arc furnace to make ferro-uranium(2,3). The larger quantities of 50% ferro-uranium required for commercial trials were prepared by vacuum induction melting(4).

It is of passing interest that production of uranium-aluminum-iron alloys, using a thermite reaction, is technologically feasible; provision of efficient equipment for collection and precipitation of uranium oxide dust(5,6,7) is necessary. This process is economically attractive for the production of a master alloy, because it uses U_3O_8, which is considerably less expensive per unit of uranium than refined uranium metal.

Uranium Recovery

Uranium recoveries were calculated for forty-seven carbon steel heats to which metallic uranium had been added. Recoveries were based on analyses of bar samples that were taken separately for each heat after the pouring of the ingots. Considerable variation in recovery was noted, as shown by Figure 3.1.

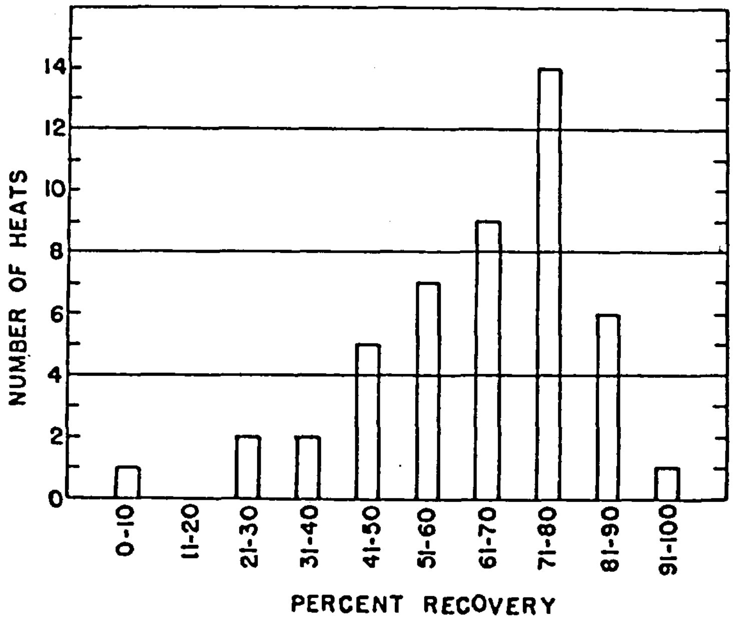


Figure 3.1 - Frequency Distribution of Uranium Recoveries in Forty-seven Carbon Steel Heats.

The uranium recovery tended to increase as the carbon content increased. The average recovery was 60% in ten heats with carbon below 0.20%; 64% in thirty heats with carbon between 0.20 and 0.40%; and, 69% for seven heats with carbon between 0.40 and 0.60%(8,9,10).

Bar sample recovery values were calculated for five additional series of heats as shown in Table 3.1.

TABLE 3.1

Bar Sample Recoveries for
Five Series of Steels

Type of Steel	Number of Heats	Uranium Addition Agent	Range of Recoveries, %	Average Recovery, %
carbon steel	7	50% Fe-U	23 to 91	50
low alloy	33	U metal	-	55
low alloy	14	50% Fe-U	-	50
low alloy	8	50% U-Fe-Si	-	61
AISI 300 stainless	19	U metal	-	73

These results do not permit concluding that recovery of uranium from master alloys is better than from metallic uranium.

Because of the variability in recovery values based on spoon sample analysis, recoveries were calculated from analyses of both spoon samples and unsegregated areas for a series consisting of nine aluminum-killed steels, one silicon-killed steel, (Heat No. 4802) and one AISI 52100 steel, (Heat No. 4818) reported later in Table 3.4. These recovery values are entered in Table 3.2.

TABLE 3.2

Uranium Recoveries Calculated on Spoon Sample and Unsegregated Area Analyses

Uranium Additive	Heat	Spoon Sample		Unsegregated Area	
		% U	% Recovery	% U	% Recovery
80% U-Al	4592	0.059	63	0.031	33
	4611	0.059	60	0.041	42
	4594	0.082	82	0.045	45
	4631	0.093	91	0.041	40
50% U-Al	4579	0.145	131	0.040	36
50% U-Fe	4567	0.080	84	0.057	60
	4580	0.060	60	0.048	48
Metallic uranium	4565	0.078	76	0.043	42
	4569	0.084	82	0.046	45
	4802	0.11	104	0.082	78
	4818	0.11	104	0.093	88

The uranium recovery based on spoon sample analysis, although always greater, has no constant relationship to the uranium recovery based on analysis of the unsegregated portions of the ingot. It is obvious that the recovery values greater than 100% must be due to segregation.

Elimination of Uranium During Steelmaking

A series of heats was made in the basic arc furnace to determine the extent to which uranium would be removed by normal steelmaking procedures(11). Heats were made to both single and double slag practice. In each heat 0.20% uranium was plunged into the bath after meltdown. The subsequent carbon boil was controlled either by iron ore additions or by oxygen injection. The bath and slag were well stirred before metal and slag samples were taken. Pertinent information from these heats is recorded in Table 3.3

TABLE 3.3

Elimination of Uranium From
Basic Electric Steel Melts

Period	Double Slag -Ore Boil		Single Slag -Ore Boil		Double Slag -Oxygen Injection		Single Slag -Oxygen Injection	
	%U in		%U in		%U in		%U in	
	Slag	Metal	Slag	Metal	Slag	Metal	Slag	Metal
Meltdown	0.077	0.059	0.99	0.006	1.34	0.009	1.98	0.054
End of Boil	1.58	0.009	1.20	0.0008	1.24	0.0035	1.81	0.00085
Tap	0.28	0.005	1.13	0.0012	0.22	0.0012	1.18	0.0068

As expected, uranium was reduced to very low levels by the usual steelmaking techniques, and most of the uranium was retained in the slag.

Segregation

An autoradiographic investigation of the segregation pattern of the various ingot types available in the laboratory was carried out.(12) The segregation in a forged uranium-bearing steel railroad axle and in a variable section sand casting was also studied. Some chemical analyses were also carried out to determine the composition of the segregated areas.

The steels tested with uranium metal were cast in ingot moulds, ranging widely in shape and size. Ingot weights were 15, 50, 150, 350, 375, 500 and 1000 lb. The 1000 lb ingots required the combined output of the induction furnace and the direct arc electric furnace.

Longitudinal slices, cut from the centre-line of each ingot, were milled and ground smooth. Segregation of uranium was then determined by autoradiography. In this technique, the steel surface to be examined is placed in direct contact with high-speed X-ray film. The beta radiation emitted by the uranium daughter elements in the steel reacts with the X-ray film. The amount of radiation emitted is directly related to the uranium content in a given area. Exposure times were usually 24 or 48 hours. In the developed film, uranium-rich areas are dark. On prints, of course, uranium-rich areas are white.

Autoradiographic prints of some of the ingots are shown in Figures 3.2 to 3.5. Figure 3.6 shows the segregation pattern in a sectioned railway axle forged from a 1000 lb ingot. This axle passed the routine tests specified by the American Association of Railroads. Figure 3.7 shows the macro-segregation in a slice from a casting having 1 in., 3 in. and 5 in. sections.

It should be understood that the autoradiographic technique, employed in this study of segregation effectively magnifies the sources of radiation, because it does not generally resolve individual sources of radiation. In fact the radiations from numerous small sources of radiation in proximity to one another are recorded as though they emanate from a single large source of radiation. The technique, therefore, makes the degree of segregation look worse than it is. The truth of this statement can be illustrated by a comparison of the typical areas of extreme segregation in Figures 3.3 and 3.8. In Figure 3.3, autoradiography indicates that the segregates are massive. However, no massive uranium-rich phases have been observed by microscopical examinations in segregated areas. The main sources of radiation in segregated areas are, in fact, believed to be small uranium-rich particles such as those shown in Figure 3.8.

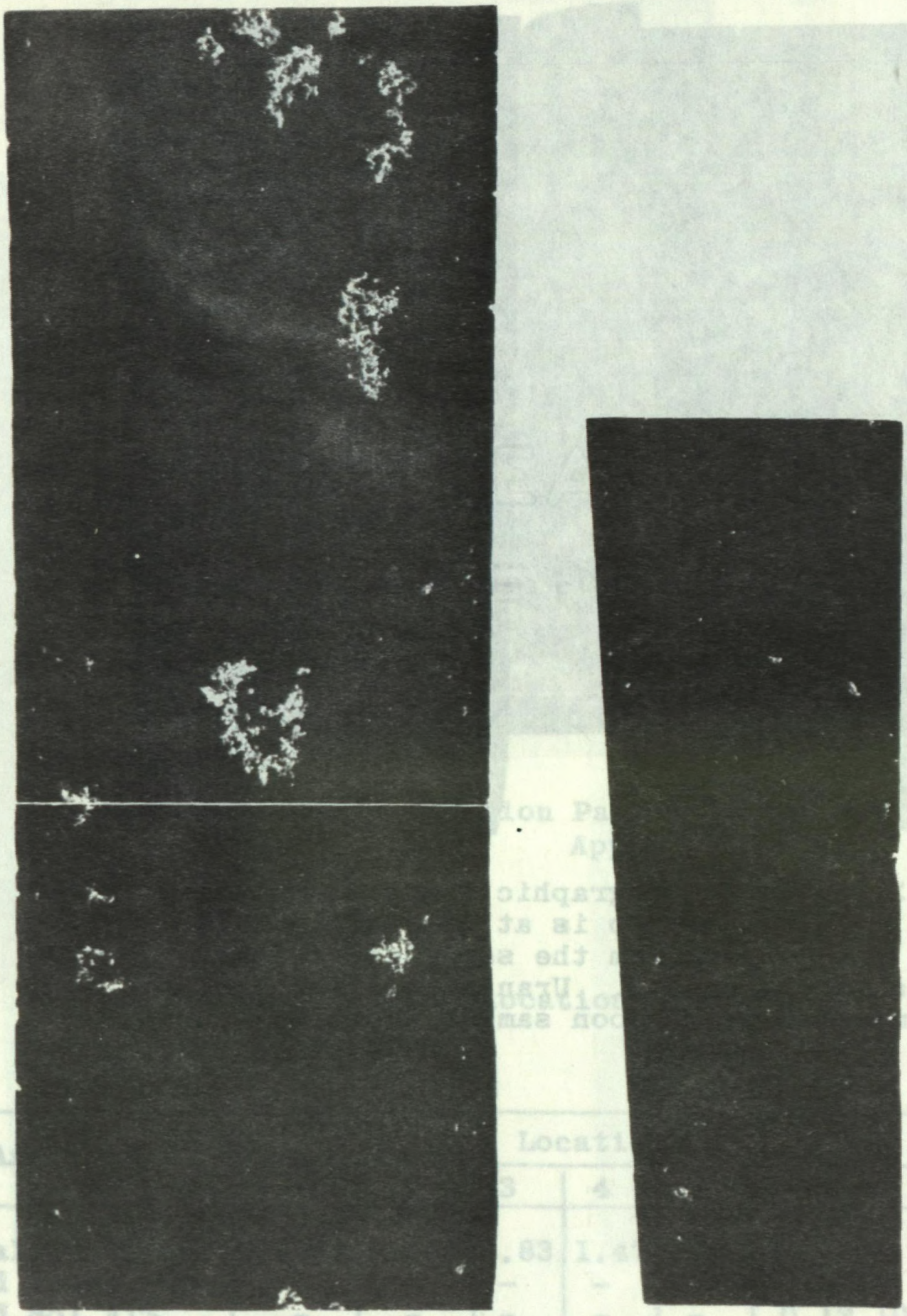


Figure 3.2 - Segregation Patterns in Ingots, shown by Autoradiography. Separate bar samples representing the 150 lb ingot on the left and the 50 lb ingot on the right analysed 0.055 and 0.056% Uranium, respectively. Both ingots were cast from the same heat.
Approx. X 1/2

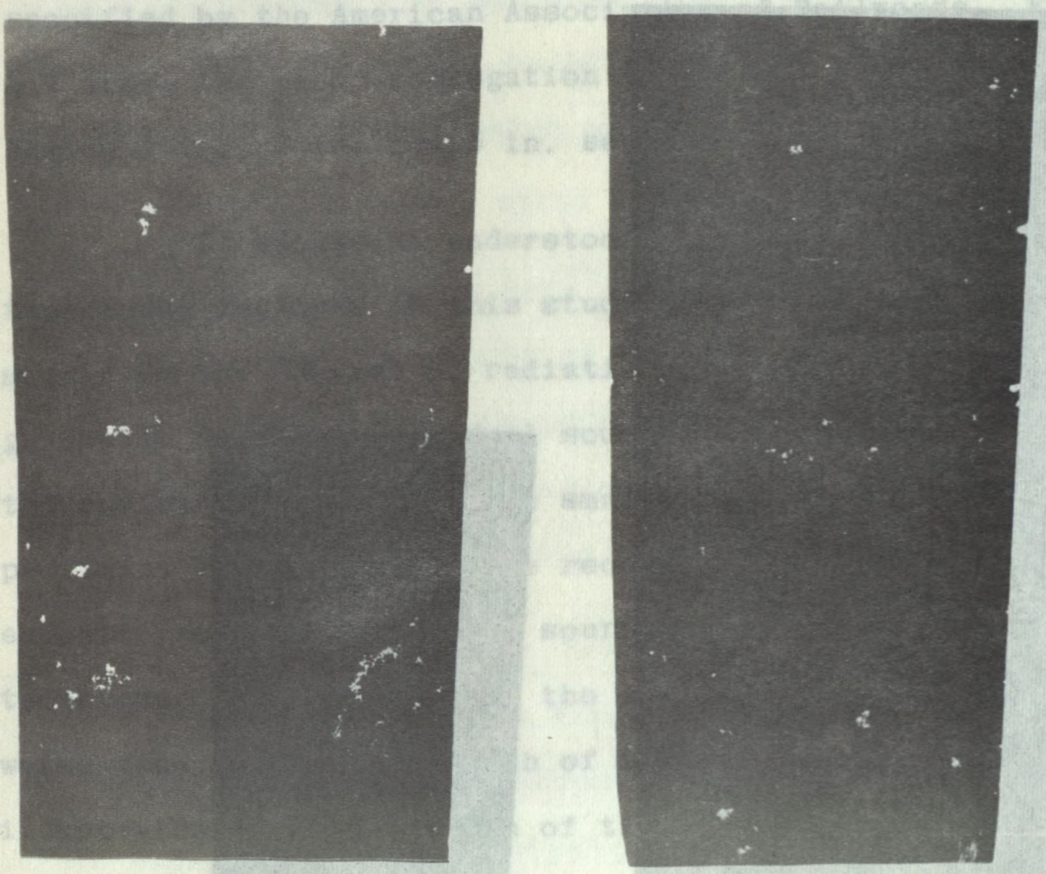


Figure 3.3 - Autoradiographic Print of 375 lb ingot. The ingot top is at the left. This ingot was poured from the same heat as the ingots in Figure 3.2. Uranium content, as determined from a spoon sample was 0.047%. Approx. X 1/2

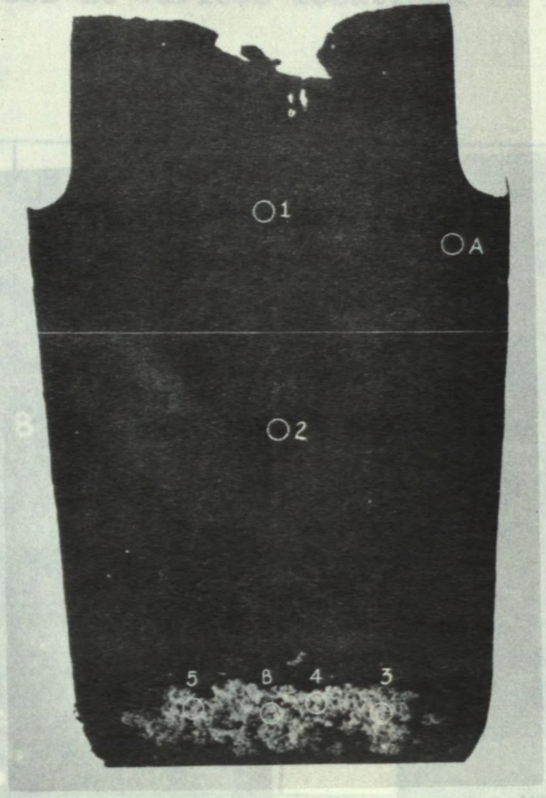


Figure 3.4 - Segregation Pattern in Squat 350 lb Ingot. Approx. X 1/5

Analyses at various locations were:

Analysis	Location						
	1	2	3	4	5	A	B
Total U%	0.043	0.035	1.83	1.47	2.01	-	-
Acid Insol. U%	-	-	-	-	1.16	-	-
Acid Sol Al%	-	-	-	-	-	0.12	0.12
Acid Insol. Al%	-	-	-	-	-	<0.001	0.03
O_2	-	-	-	-	-	0.002	0.195
N_2	-	-	-	-	-	0.003	0.006

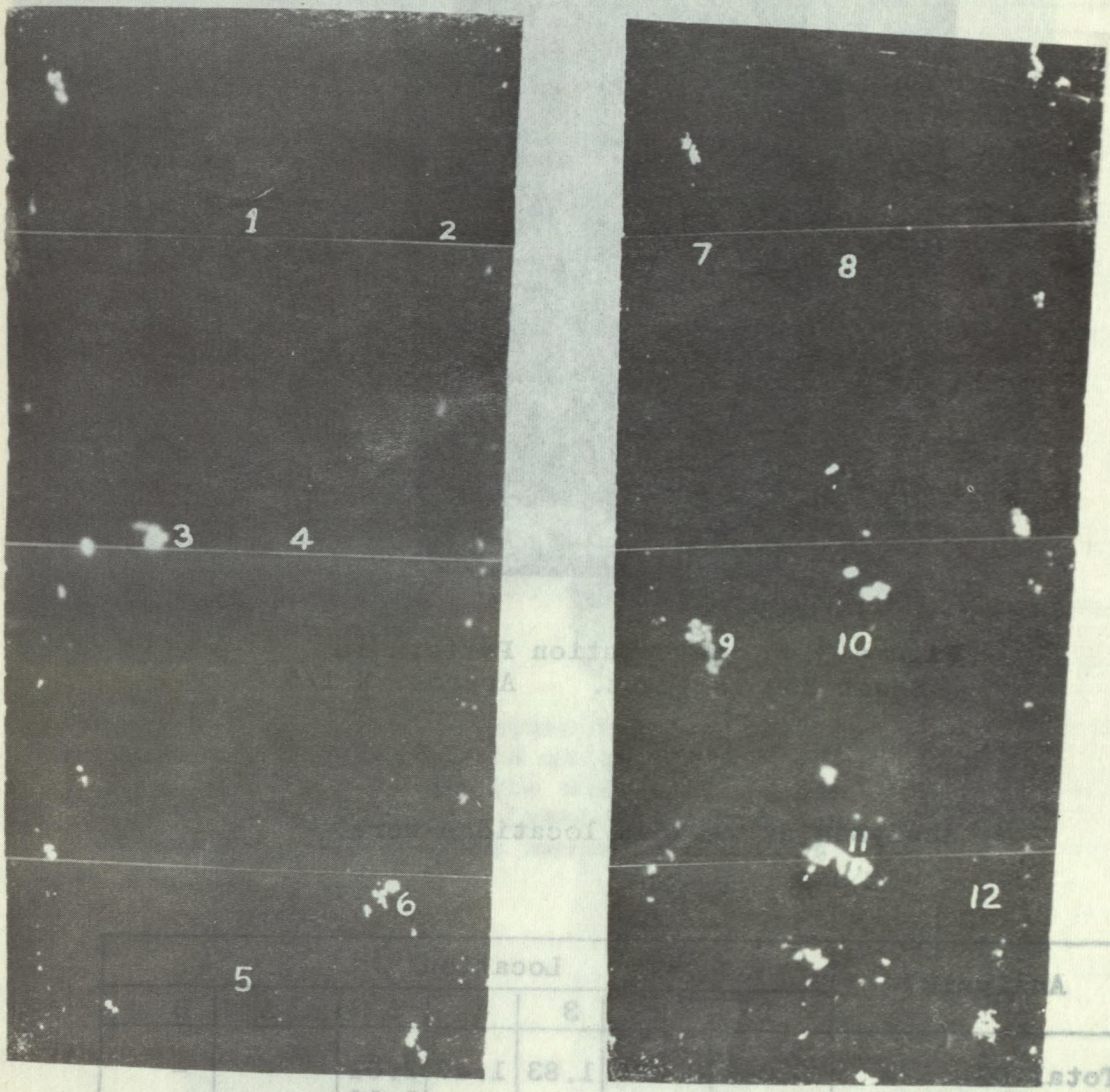


Figure 3.5 - Segregation Pattern in a 500 lb Ingot.
The ingot top is at the left. Approx. X 2/5

Analyses at various locations in Figure 3.5 were:

Location	C, %	S, %	P, %	Acid Insol U, %	Total U, %
1	0.49	0.027	-	0.016	0.062
2	-	0.027	-	0.0076	0.075
3	0.45	0.027	0.011	0.21	0.26
4	0.45	0.026	-	0.026	0.067
5	-	0.026	-	0.022	0.074
6	0.47	0.027	-	0.022	0.070
7	-	0.026	-	0.012	0.067
8	-	0.026	-	0.022	0.064
9	0.46	0.025	-	0.038	0.093
10	-	0.025	-	0.026	0.071
11	0.46	0.024	0.011	0.12	0.169
12	-	0.026	-	0.014	0.067
Spoon Sample	0.47	0.026	0.012	0.022	0.079
				-	0.087

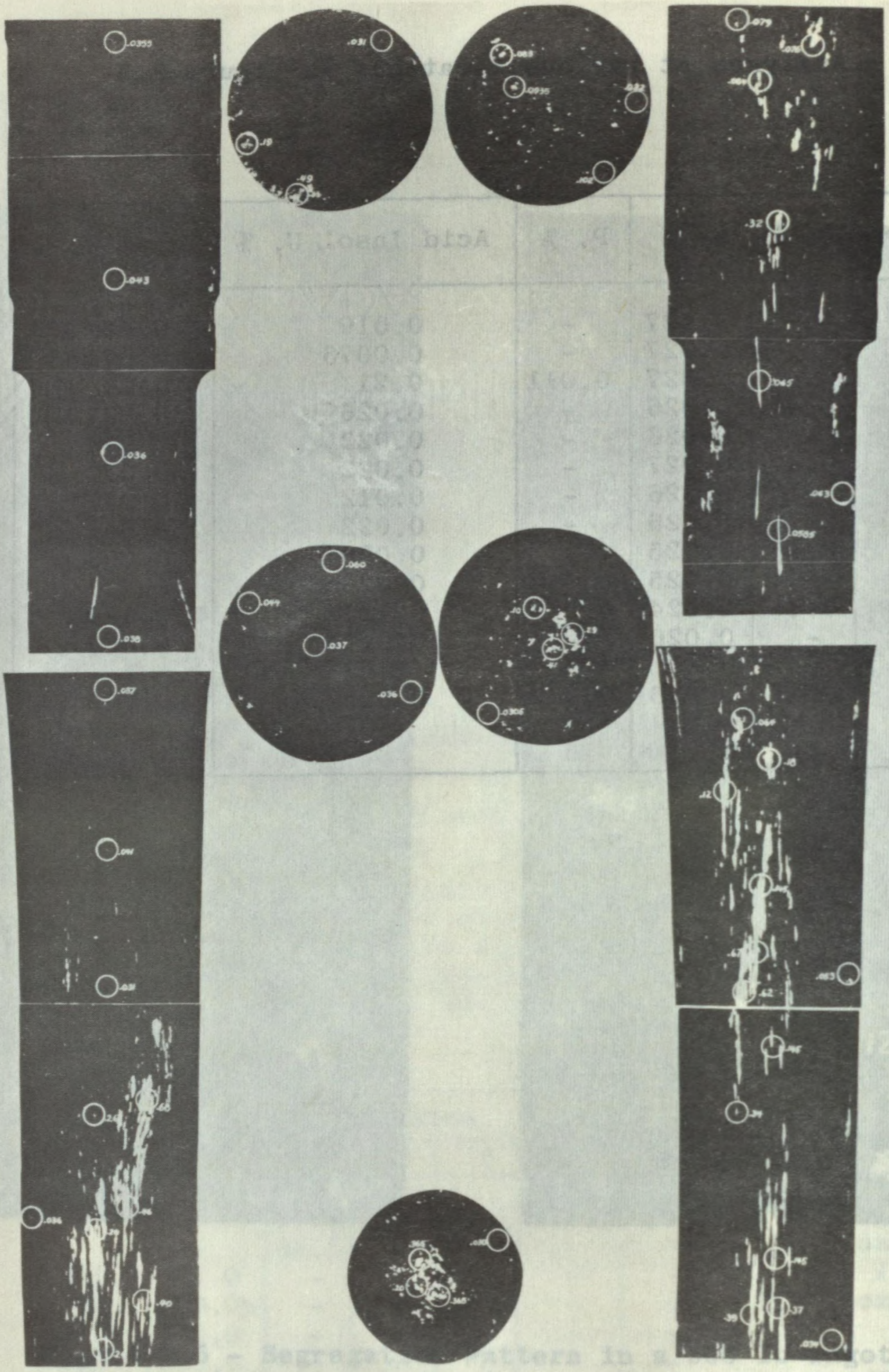


Figure 3.6 - Autoradiographic Print of a Slice from a Railway Axle Forged from a 1000 lb Ingot. The areas where drillings were taken and the uranium analyses are shown. The left part of the photograph corresponds to the original top of the ingot. Approx. X 1/5

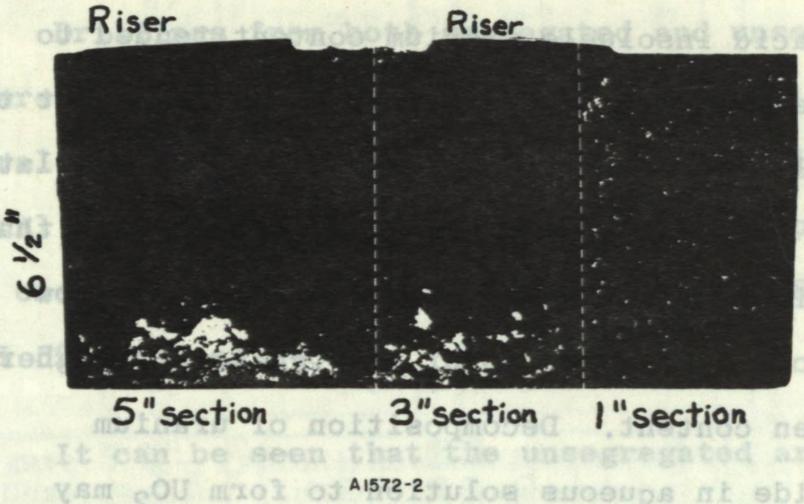


Figure 3.7 - Segregation Pattern in Longitudinal Mid-section From Sand-cast Step Block. Approx. X 1/4

These preliminary studies indicated the following:

(1) Segregation of uranium occurred in all ingots.

(2) Of all the laboratory ingots examined, only the squat 350 lb ingot had a sufficiently slow solidification rate to allow the segregate to settle to the bottom. Convincing evidence of the effect of solidification rate on uranium segregation is shown by the autoradiograph of the variable-section sand casting.

(3) Preliminary analyses indicated that the segregate was high in uranium, oxygen and acid insoluble aluminum. The unsegregated areas were low in total oxygen and acid insoluble aluminum.

(4) The acid insoluble uranium content tended to increase as the total uranium increased, but the results were erratic and could not be correlated with carbon content. It had been expected that the insoluble uranium would be higher in low carbon steels because of the inherently higher oxygen content. Decomposition of uranium carbide in aqueous solution to form UO_2 may account for some of the variability.

To confirm the initial findings and to evaluate the influence of various master alloys on the recovery of uranium and on the segregation characteristics, a series of carbon steel heats was made in the 450 lb induction furnace. A constant percentage of uranium was added to each heat. Tapping temperatures were maintained at 1620°C ± 10°C (2950°F ± 18°F) and each uranium addition was plunged into the ladle at 1585°C ± 10°C (2885°F ± 18°F). For each squat 350 lb ingot poured, a corresponding spoon sample bar was obtained for chemical analysis. Longitudinal slices along the centreline were autoradiographed, sulphur printed and deep-etched. Of the nine aluminum-killed carbon steels, seven showed a segregation pattern similar to that shown in Figure 3.4, one contained a small area of segregation in the middle of the ingot (4631) and one contained randomly-dispersed areas of segregation (4611).

Drillings from both segregated and unsegregated areas were analysed. The locations of the drillings were, in general, as shown in Figure 3.4. Table 3.4 lists the analytical results for the nine aluminum-killed plain carbon steels, one silicon-killed plain carbon steel (4802), and one AISI 52100 steel (4818).

It can be seen that the unsegregated areas are consistently low in total oxygen (average of 0.002%) and consequently in acid insoluble aluminum (less than or equal to 0.001%). The segregated areas are high in uranium, total oxygen, acid insoluble aluminum, and, in some cases, slightly higher in nitrogen. There was no indication of segregation of carbon, manganese, silicon, sulphur, phosphorus, chromium or copper.

As might be expected from the low oxygen content, the unsegregated areas contain fewer and smaller inclusions than would normally be found in uranium-free steel. The segregated areas are, however, extremely dirty. The inclusions in the segregated areas are predominantly oxides. Figure 3.8 shows typical fields in both unsegregated and segregated areas.

TABLE 3.4

Analytical Results of Segregated and Unsegregated Areas in Squat 350 lb Ingots

Uranium Additive	Heat No.	Percentage of Element*								
		Total U			Acid Insol. Aluminum		Total Oxygen		Total Nitrogen	
		Spoon	Unseg.	Seg.	Unseg.	Seg.	Unseg.	Seg.	Unseg.	Seg.
80% U-Al**	4592	0.059	0.031	2.14	<0.001	0.014	0.0012	0.154	0.003	0.003
	4611	0.059	0.041	0.44	0.001	0.014	-	-	-	-
	4594	0.082	0.045	1.44	0.001	0.03	-	-	-	-
	4631	0.093	0.041	1.36	<0.001	0.038	-	-	-	-
50% U-Al	4579	0.145	0.040	1.77	<0.001	0.03	0.002	0.195	0.003	0.006
50% U-Fe	4567	0.080	0.057	0.41	-	-	0.0016	0.077	0.004	0.005
	4580	0.060	0.048	1.51	<0.001	0.014	0.0012	0.154	0.003	0.003
Metallic uranium	4565	0.078	0.043	0.82	<0.001	0.015	0.002	0.045	0.0025	0.004
	4569	0.084	0.046	0.65	-	-	0.003	0.095	0.003	0.002
***	4802	0.11	0.082	1.24	<0.001	0.001	-	-	-	-
****	4818	0.11	0.093	0.26	-	-	-	-	-	-

* - Since there was no significant evidence of segregation of C, Mn, Si, S, P, Cr, Cu or acid soluble Al, the analytical results for these elements are not included.

** - 80% U-Al pellets were made by compacting a mixture of uranium and aluminum powders - Heats 4592 and 4611.

*** - Silicon-killed carbon steel - Si = 0.31%.

**** - AISI 52100 steel - Average composition - C = 1.00%, Cr = 1.72%.

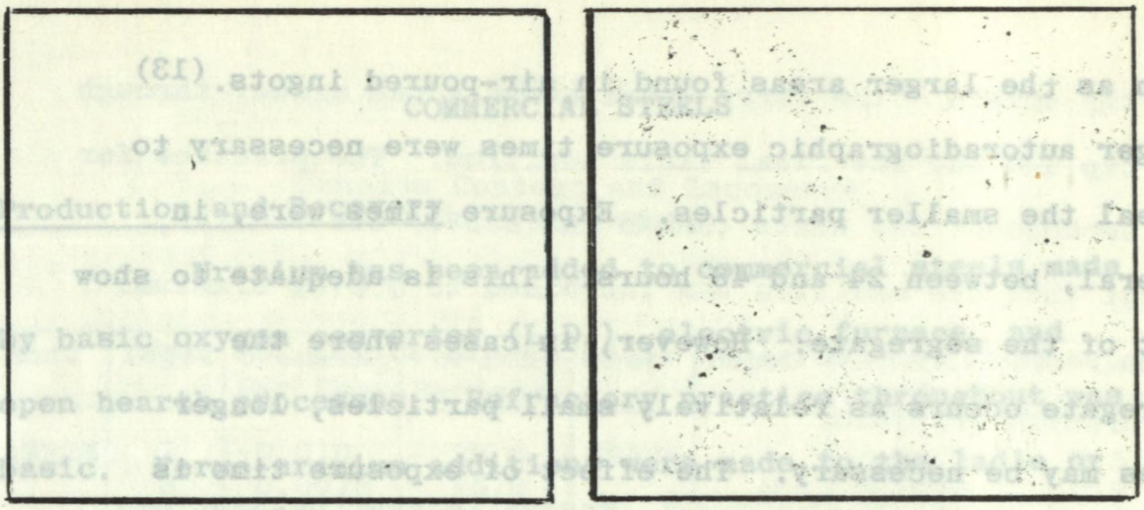


Figure 3.8 - Typical Unetched Microstructures in Unsegregated (left) and Segregated (right) areas in Ingot 4565. X100

In order to estimate the cooling rate of the 350 lb ingot, two induction heats were made, keeping melting and pouring conditions as similar as possible. After solidification intervals of 5 minutes for the first heat and 10 minutes for the second heat, the unsolidified metal was poured out by tipping the mould. The solidified portions were sectioned, and the wall and bottom thickness determined. The constant in the solidification formula $D = K\sqrt{t}$ was then calculated. The constants were almost identical for both heats and are in line with those found for larger industrial ingots, where K is reported to be between 0.90 and 1.30. The solidification rate for the 350 lb ingot can be approximated as follows:

$$\text{Edge solidification} = D = 0.96\sqrt{t}$$

$$\text{Bottom solidification} = D = 1.29\sqrt{t}$$

Vacuum degassing of uranium-bearing steel resulted in the segregate being dispersed through the 500 lb ingot as numerous small uranium-rich particles, rather than as the larger areas found in air-poured ingots.[13] Longer autoradiographic exposure times were necessary to reveal the smaller particles. Exposure times were, in general, between 24 and 48 hours. This is adequate to show most of the segregate. However, in cases where the segregate occurs as relatively small particles, longer times may be necessary. The effect of exposure time is shown in Figure 3.9.[13]

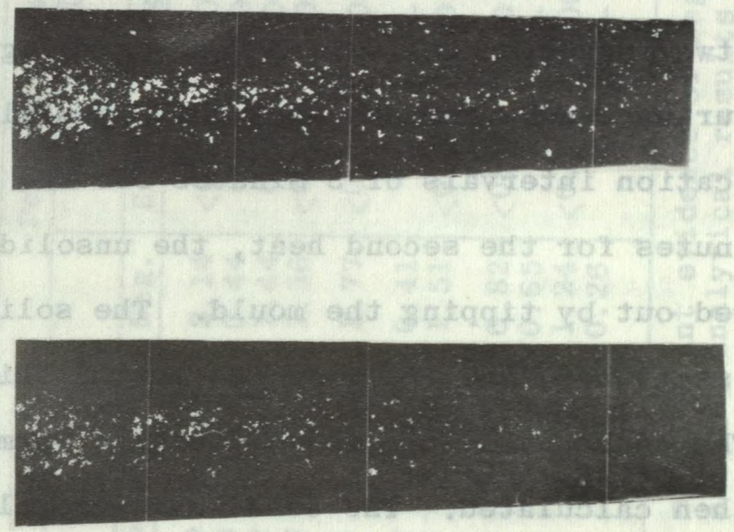


Figure 3.9 - Autoradiographic Prints of Vacuum Stream Degassed Ingot. A-1630, Exposed for 113 hours (upper) and 24 hours (lower). Spoon sample analysis showed 0.36% C, 0.025% S, and 0.11% U. Approx. X1/7

COMMERCIAL STEELS

Production and Recovery

Uranium has been added to commercial steels made by basic oxygen converter (L.D.), electric furnace, and open hearth processes. Refractory practice throughout was basic. Ferro-uranium additions were made to the ladle or to ingot moulds. Although both steelmaking practice and addition technique influence the recovery of uranium, the former is the more important factor. Hence, production details and information relating to recovery in various trials are grouped according to the steelmaking process.

(a) Basic Oxygen Converter (L.D.) Trials

Uranium was added to three 110 ton heats and to a single ingot of another heat.

In the first trial (A2928), 0.05% uranium, in the form of 50% ferro-uranium, was added to the steel. Three-quarters of the ferro-uranium had a carbon content of 1%, and the remainder had 0.10% carbon. In all other trials the carbon content of the ferroalloy was approximately 0.1%.

The ferroalloy, sized to -2 in. + 1 in., was canned in 20 lb lots. The cans were thrown into the tapping stream or into the ladle at the point of entry of the tap stream. The ferro-uranium was added midway through the tap and was the final ladle addition. The practice for the subsequent two heats (E3375 and E3378) was similar, except that the addition was increased to 0.075% uranium. Spoon samples were obtained at intervals during the pour for uranium analysis.

In the fourth trial (E3373), 0.075% uranium was added to a 10 ton ingot. The low-carbon 50% ferro-uranium, crushed to mostly 1/2 in., was added in twelve lots at equal intervals during teeming.

The base compositions (ladle analysis) of the trial heats are given in Table 3.5 and the uranium contents and recoveries in the various ingots are given in Table 3.6.

TABLE 3.5

Base Composition of L.D. Heats

Heat	C, %	Mn, %	Si, %	S, %	P, %
A2928	0.85	0.38	0.16	0.027	0.007
E3375	0.18	0.76	0.16	0.019	0.012
E3378	0.54	0.95	0.27	0.017	0.013
E3373	0.06	0.34	-	0.021	0.010

TABLE 3.6

Uranium Content and Recovery* in L.D. Ingots

Heat	Ingot	Uranium, Per Cent	Per Cent Recovery	Heat	Ingot	Uranium, Per Cent	Per Cent Recovery
A2928	2	0.010	20.0	E3375	1	0.0071	9.5
	8	0.0078	15.6		8	0.0058	7.8
	14	0.010	20.0		13	0.0048	6.4
	15	0.0082	16.4		14	0.0057	7.6
	16	0.0093	18.6		15	0.0052	7.0
E3378	2	0.022	29	E3373	Top	0.037	50
	5	0.022	29		Middle	0.039	52
	8	0.018	24		Bottom	0.042	56
	9	0.016	21				

*Based on spoon samples, except for E3373.

The reported uranium content of the single ingot, Heat E3373, was determined from drillings taken from the non-segregated portions of full transverse slices of the slab. Consequently, the total uranium reported is less than that actually present in the section, and the recovery shown is smaller than the full value.

The uranium recovery was much better from the ingot addition than from ladle additions. It would be anticipated that recoveries in the ladle would have been higher if the metal had been thoroughly deoxidized before the uranium was added. However, this was not feasible under current standard L.D. operating procedures.

(b) Electric Furnace Trial

Uranium was added to a 35 ton low-alloy heat made according to normal double slag practice. The heat was fully deoxidized in the furnace. Additions of calcium, silicon and aluminum were made to the stream early in the tap. The uranium was then added to the stream in 20 lb lots wrapped in aluminum foil. A total of 0.125% uranium in the form of 50% ferro-uranium was added. Each of the sixteen ingots teemed was 20-1/2 in. in diameter and 70 in. high. A spoon sample was obtained after the eighth ingot. Samples for uranium analysis were also obtained from 5 in. billets representing the top and bottom of this ingot. The nominal heat composition and the results of uranium analyses reported by the steelmaker are shown in Table 3.7.

TABLE 3.7

Nominal Heat Composition and Reported Uranium Analyses of Electric Furnace Heat

Per Cent of Element						Per Cent Recovery of Uranium
C	Mn	Si	Cr	Mo	Uranium	
0.95	0.30	0.25	1.00	0.25	0.063 (spoon) 0.071 (top)* 0.073 (bottom)*	49 55 57

*Heat D7447, Ingot No. 8

(c) Open Hearth Trials

Uranium was added to a single ingot from each of two heats of open hearth steel. In both cases, uranium was added as 1 lb lots of 50% ferro-uranium wrapped in aluminum foil, at equal intervals during the teeming of the ingots.

One heat, 84129, was a killed low-alloy grade, partially deoxidized with silico-manganese in the furnace, with additions to the ladle of manganese, silicon and aluminum. Ten pounds of ferro-uranium was added to the fifth of thirty ingots, i.e., 0.06% uranium.

The other heat, 123867, was a low-carbon rimming grade. Ingot No. 1, made to standard practice, rimmed more violently than desirable. It was capped 14 minutes after teeming, and rose and sealed quickly. Fourteen pounds of ferro-uranium was added to ingot No. 2, i.e., 0.06% uranium. This ingot had a good rimming action for the first three to five minutes, after which the boil increased with a drop of metal level in the mould. This ingot was capped at 19 minutes, but did not rise and seal until a further 13 minutes had elapsed.

The killed steel was rolled to 2-1/2 in. billets, the capped steel to 2 in. billets. Drillings for uranium analyses were obtained from the tops of billet samples representing the top, middle and bottom of both ingots. Due to obvious pipe in the top billet sample of the capped ingot, this material was not analysed. Results of the analyses are given in Table 3.8.

TABLE 3.8

Composition of Open Hearth Heats and Results of Uranium Analyses of Billet Samples

Heat	Sample	Per Cent of Element					Per Cent Recovery of Uranium
		C	Mn	Si	Cr	U	
84129	Ladle	0.59	0.89	0.25	0.785		
	Ingot top					0.0374	63
	Ingot middle					0.039	66
	Ingot bottom					0.1275	124
123867	Ladle	0.06	0.31	-	-		
	Ingot top					-	-
	Ingot middle					0.0068	11
	Ingot bottom					0.032	54

Recoveries in the top and middle of the killed ingot are better than the average recovery in laboratory heats. The recovery of uranium is very low in the mid-section of the rimmed ingot.

Segregation

Autoradiographs were made of sections from blooms, and/or billets from the commercial heats. Sulphur prints were made from the majority of the sections, and all were deep etched in hot 1:1 HCl and water.

Autoradiographs of blooms and billets from the first ingot of Heat A2928 did not show any appreciable segregation, as illustrated by Figure 3.10. However, segregation was found in other ingots from this heat, as illustrated in the autoradiograph of Figure 3.11.

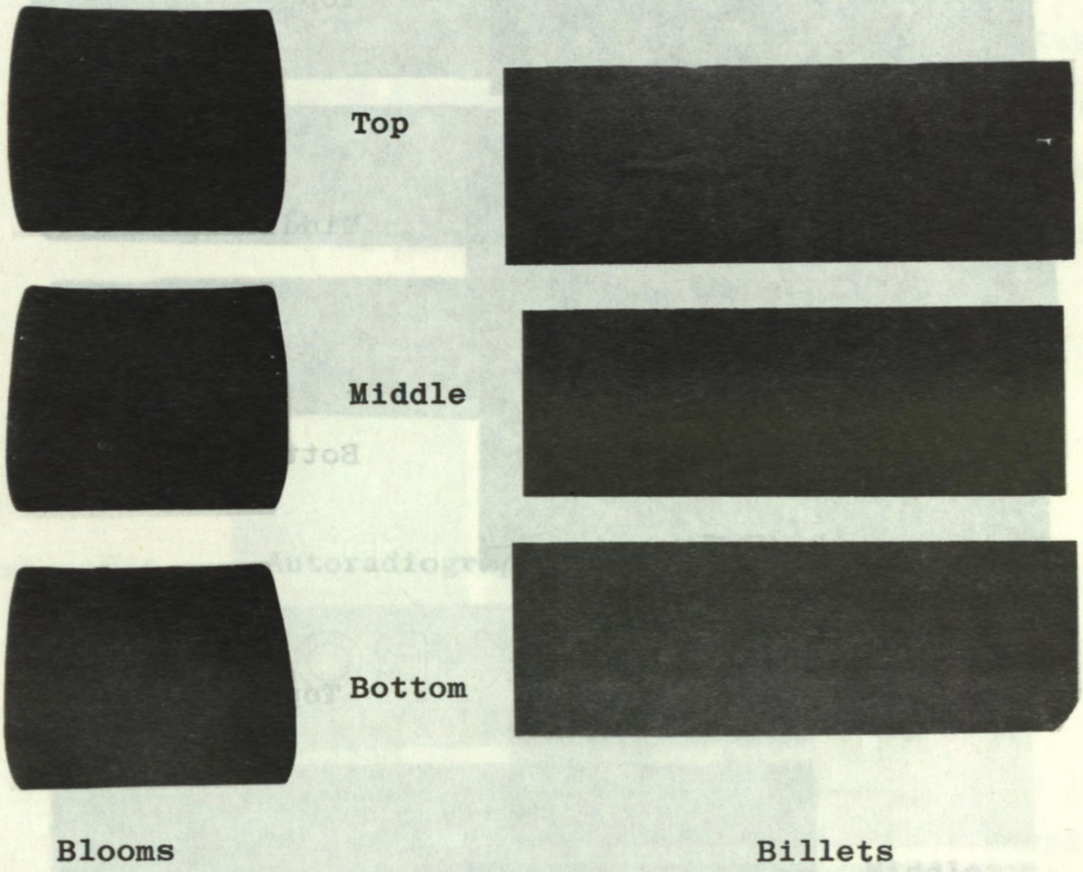
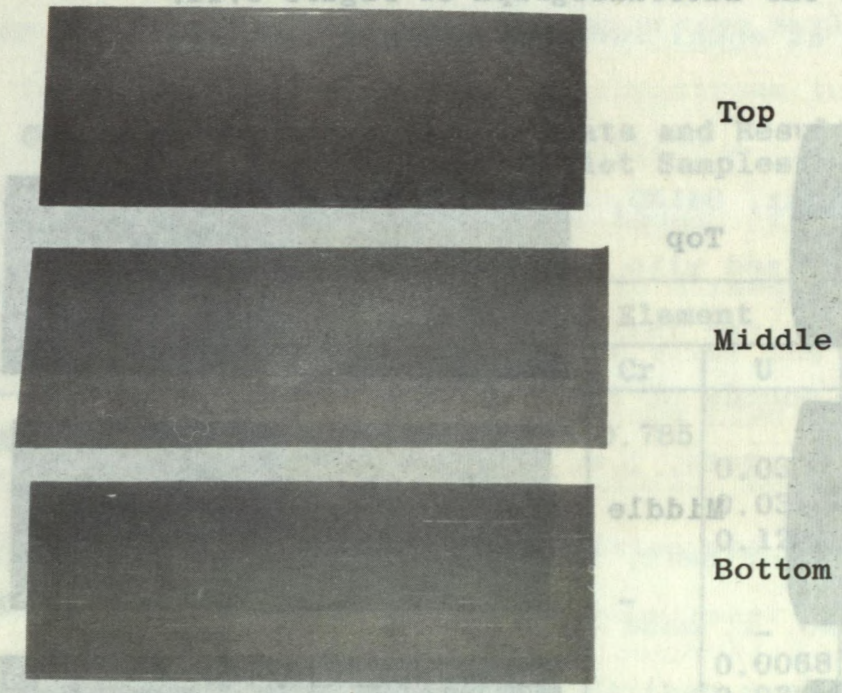
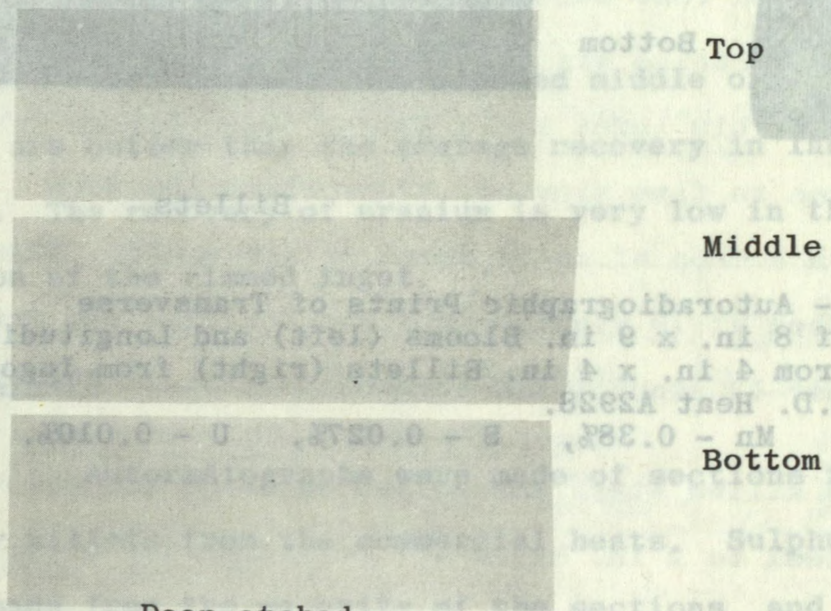


Figure 3.10 - Autoradiographic Prints of Transverse Sections of 8 in. x 9 in. Blooms (left) and Longitudinal Sections from 4 in. x 4 in. Billets (right) from Ingot No. 1 of L.D. Heat A2928.
C - 0.85%, Mn - 0.38%, S - 0.027%, U - 0.010%.

Autoradiography detects uranium macro-segregation with greater sensitivity and selectivity than does macroetching. For example, in Figure 3.11 segregation revealed by the autoradiography is not revealed by macroetching.



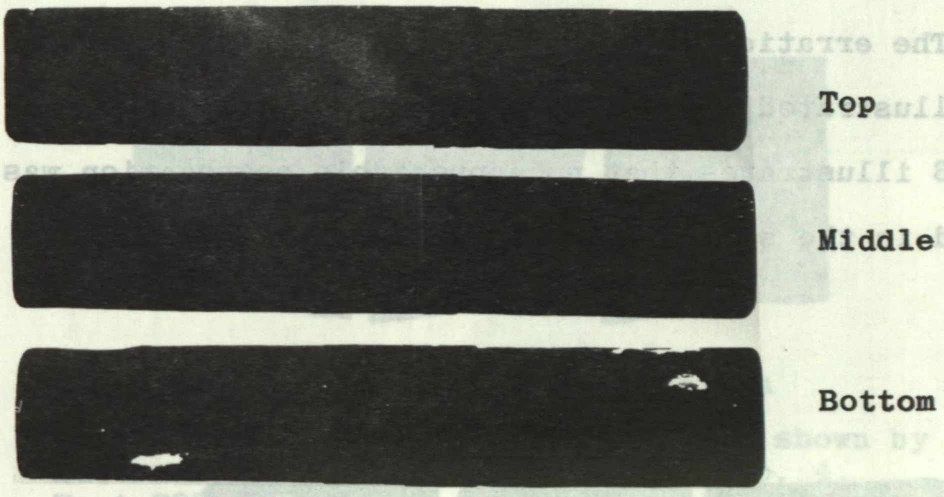
Autoradiograph Prints



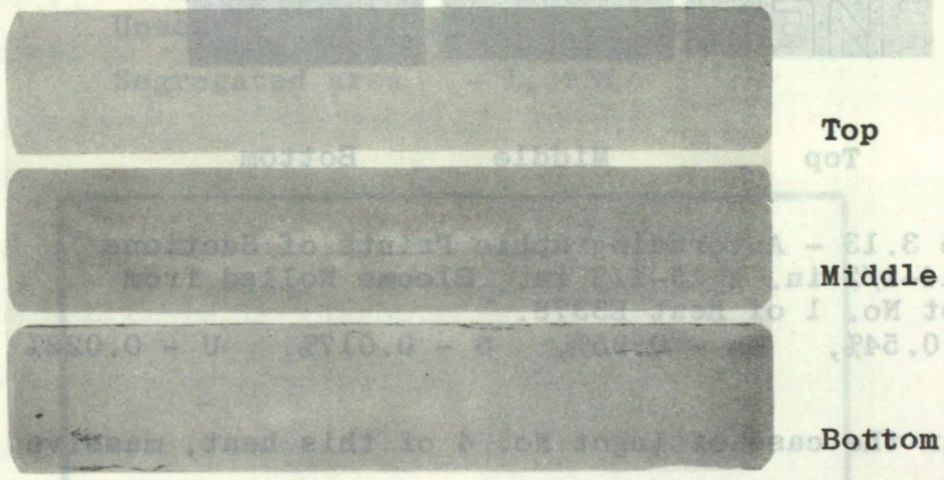
Deep-etched

Figure 3.11 - Longitudinal Sections of 4 in. x 4 in. Billets Rolled from Ingot No. 16 of Heat A2928.

In the case of the L.D. heat, E3373, in which an ingot addition was made, some areas of massive uranium segregation were found. Such segregation was revealed by both autoradiography and deep etching, as illustrated by Figure 3.12.



Autoradiographs



Deep-Etch

Figure 3.12 - Sections of 22 in. x 4 in. Slab from Heat E3373.

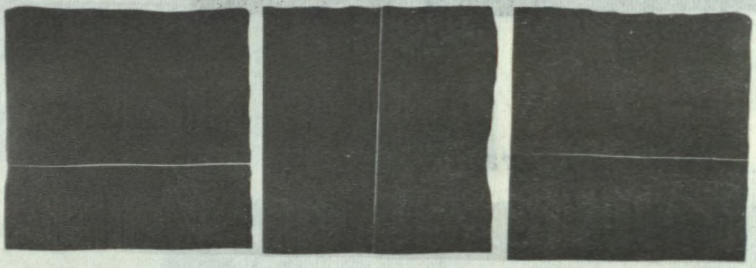
Uranium analyses were as follows:

Top section - 0.037%

Middle section - 0.039%

Bottom section - 0.042% (unsegregated area)
0.816% (segregated area)

The erratic occurrence of uranium-rich segregates is again illustrated in oxygen converter heat E3378. Figure 3.13 illustrates that no appreciable segregation was encountered in the sections examined in the case of Ingot No. 1.



Top Middle Bottom

Figure 3.13 - Autoradiographic Prints of Sections of 14-1/2 in. x 15-1/2 in. Blooms Rolled from Ingot No. 1 of Heat E3378.
C - 0.54%, Mn - 0.95%, S - 0.017%, U - 0.022%

However, in the case of Ingot No. 4 of this heat, massive segregation was shown by autoradiography, sulphur printing and deep etching, as illustrated by Figures 3.14, 3.15 and 3.16. This is the only ingot in which the segregation is apparently in the middle rather than in the bottom section. However, close examination of the deep-etched surfaces and of the sulphur prints suggests that there has been an error in sample identification, and that the sample showing heavy segregation is actually from the bottom.

Figure 3.14 - Uranium-rich Segregates, shown by Autoradiography of Blooms of Ingot No. 4, Heat E3378. About X 1/2

Uranium analysis results for the section designated as the middle were:

Unsegregated area - 0.022%
Segregated area - 1.495%

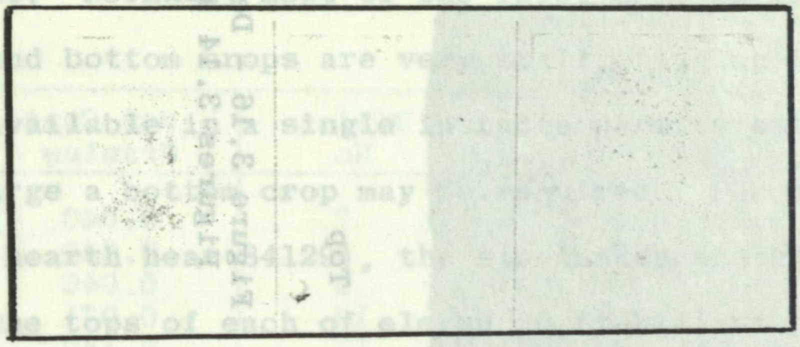
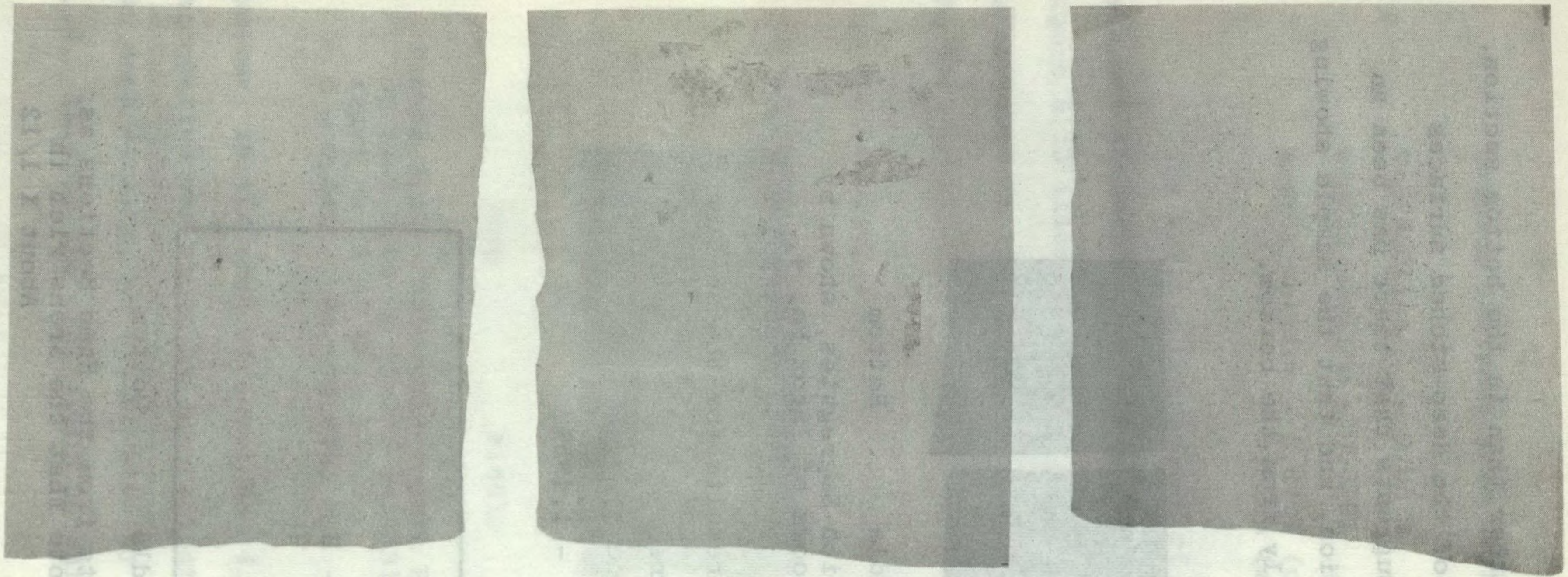


Figure 3.15 - Sulphur prints from the Same Sections as shown in Figure 3.14. Note that the areas rich in uranium appear white. About X 1/12



Top

Middle

Bottom

Figure 3.16 - Deep Etched Structure of the same Sections Shown in Figures 3.14 and 3.15. Approx. X 1/5

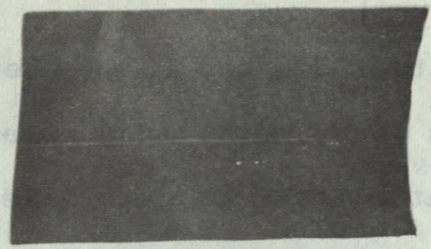
In the cases of heats E3378 and E3373 where massive uranium segregate was found, drillings were taken from segregated and unsegregated areas to determine the uranium contents. The results, shown in Table 3.9 indicate the severe segregation that can occur in commercial ingots.

TABLE 3.9

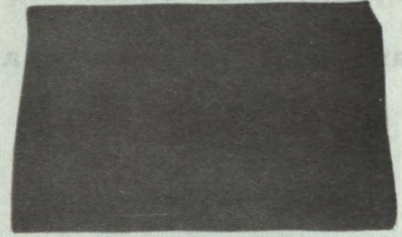
Uranium Content of Segregated and Unsegregated Areas

Sample	Designated Ingot Location	Per Cent Uranium	
		Segregated Area	Unsegregated Area
E3378-4	Middle	1.495	0.022
E3373-1	Bottom	0.816	0.042

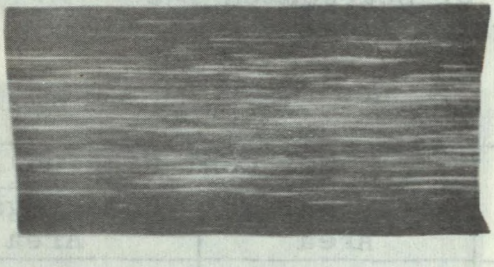
An unfortunate consequence of the segregation of uranium to the bottom of the ingot is that the bottom crop will have to be increased to achieve a uniform uranium content. Normally most of the ingot crop is taken at the top, and bottom crops are very small, ranging from 1 to 5%. Data available in a single instance permits estimation of how large a bottom crop may be required. For this heat (open hearth heat 84129), the steelmaker analysed drillings from the tops of each of eleven 30 ft billets produced from the one ingot. The results are given in Table 3.10. Autoradiographs of sections representative of top, middle and near bottom of this ingot are shown in Figure 3.17.



Top, Billet 1



Middle, Billet 6



Bottom, Billet 11

Figure 3.17 - Autoradiographic Prints of Longitudinal Sections. Uranium-bearing Ingot from Open Hearth Heat 84129. About X 1/2

C - 0.59%; Mn - 0.89%; Si - 0.25%;
Cr - 0.785%; S - 0.023%; P - 0.012%;
Cu - 0.063%; Ni - 0.04%; Mo - 0.008%.

TABLE 3.10

Results of Steelmaker's Analysis on Tops of Billets of Heat 84129

Billet No.	Per Cent Uranium	Billet No.	Per Cent Uranium
1	0.043	7	0.040
2	0.039	8	0.040
3	0.040	9	0.040
4	0.045	10	0.071
5	0.037 - 0.086	11	0.157
6	0.039		

These results show some localized segregation in the sample from billet 5 and, more important, give a quantitative value to the amount of bottom segregation. It is apparent that the bottom two billets, and most probably half of the next billet, would have to be discarded if only material of uniform composition could be used. This would mean increasing the bottom crop to 18% for this particular ingot. It is considered probable that redesign of the ingot would substantially improve yield. Furthermore, deoxidation with zirconium rather than aluminum promises to improve yield.

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CHAPTER 4

URANIUM IN PLAIN CARBON STEELS*

G. P. Contractor**

SYNOPSIS

Medium and low plain-carbon steels modified with uranium were studied to investigate the effect of uranium on forgeability, response to heat treatment, mechanical properties, and microstructure. Uranium contents ranged up to 0.70%.

The medium carbon steels are hot short if the uranium content exceeds 0.35%. More uranium can be tolerated in low carbon steels. The hot shortness is caused by intergranular UFe_2.

Critical transformation temperatures, Jominy hardenability, and resistance to tempering are not significantly affected by the presence of uranium.

Uranium does not significantly improve room temperature tensile or fatigue properties. When the uranium content exceeds 0.15%, abnormally low impact values are obtained and a characteristic abnormal microstructure is observed.

Uranium improves short-time stress-rupture properties.

In each experimental steel it appears that most of the uranium carbide combines to form complex cubic inclusions of U(O,C,N) or U(C,N) rich in oxygen or nitrogen or both. Above 0.35% uranium, UC is believed to occur as discrete, spheroidal or dot particles which are stable at heat treating temperatures.

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*This chapter is primarily based on reference (1).

**Senior Scientific Officer, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

A series of medium carbon steels and a series of low-carbon steels were prepared for preliminary investigation to determine the influence of uranium. The results form a basis for more intensive evaluation of the physical and mechanical properties of uranium-bearing steels.

The spoon sample analysis of each experimental steel is given in Table 4.1. The heats, using electrolytic iron as the melting stock, were melted in a 50 lb induction furnace. Each heat, except 4371, was deoxidized with 0.125% aluminum before the addition of uranium metal. The cropped ingots, about 13 in. long and 4-1/4 in. square, were upset forged and rolled to plate, about 8-1/2 in. square and 1-1/4 in. thick. The respective forging and rolling temperature ranges were 1060° to 1175°C (1950° to 2150°F) and 1150° to 1175°C (2100° to 2150°F).

HOT SHORTNESS

The remarks column of Table 4.1 records the heats which were hot short due to an intergranular eutectic phase that cannot be removed by heat treatment. This phase, believed to be UFe_2, was present in the as-cast structure, as shown in Figure 4.1.

TABLE 4.1

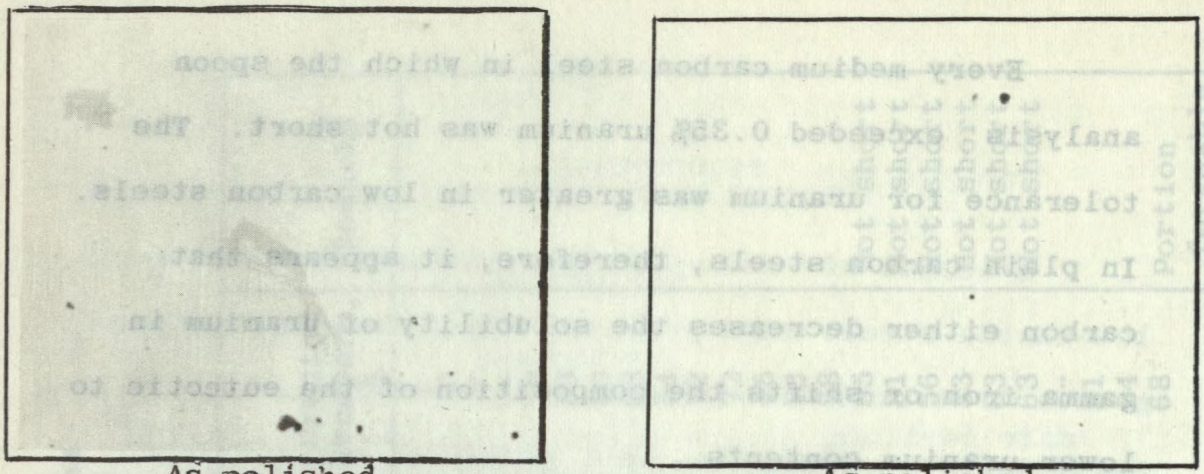
Chemical Compositions, Uranium Recoveries and Hot-Working Details of Experimental Steels

Heat No.	Percentage of Element										Uranium Recovery, %	Remarks
	C	Mn	Si	S	P	N_2*	O_2*	Acid Insol Al	Total Al	U		
4176	0.37	0.77	0.09	0.004	0.010	-	-	0.012	0.070	Nil	-	
4285	0.34	0.68	0.44	0.019	0.011	0.007	0.007	0.004	0.078	Nil	-	
4382	0.40	0.71	0.08	0.010	0.006	-	-	0.003	0.014	Nil	-	
4166	0.40	0.78	0.17	0.009	0.014	0.001	0.006	0.008	0.020	0.020	8	
4416	0.35	0.81	0.11	0.005	0.006	0.006	0.005	<0.001	0.016	0.060	83	
4383	0.37	0.84	0.18	0.013	0.007	-	-	0.003	0.077	0.10	80	
4415	0.38	0.78	0.21	0.004	0.006	0.005	0.006	-	-	0.11	88	
4345	0.33	0.68	0.17	0.005	0.007	0.003	0.006	0.003	0.053	0.15	54	
4370	0.34	0.68	0.10	0.006	0.007	0.003	0.010	0.003	0.074	0.20	72	
4265	0.31	0.64	0.17	0.018	0.018	-	-	0.004	0.076	0.20	72	
4167	0.38	0.77	0.13	0.007	0.006	0.005	0.006	0.001	0.045	0.25	45	
4346	0.27	0.81	0.20	0.005	0.005	0.005	0.003	0.003	0.081	0.30	73	
4371	0.38	0.67	0.17	0.007	0.007	0.003	0.007	0.001	0.002	0.32	78	
4360	0.34	0.82	0.31	0.021	0.008	0.004	0.008	-	-	0.38	85	Hot short
4266	0.34	0.62	0.17	0.018	0.017	-	-	<0.001	0.066	0.45	81	Hot short
4187	0.39	0.78	0.16	0.005	0.007	0.003	0.005	0.001	0.088	0.47	56	Hot short
4309	0.35	0.68	0.14	0.016	0.015	0.009	0.008	0.001	0.099	0.458	83	Hot short
4177	0.37	0.87	0.11	0.004	0.010	0.003	0.006	0.002	0.034	0.70	63	Hot short
4188	0.38	0.83	0.15	0.005	0.009	-	-	-	-	0.66	63	Hot short
4284	0.10	0.28	0.07	0.019	0.008	0.007	0.018	0.011	0.069	Nil	-	
4302	0.10	0.37	0.16	0.015	0.014	0.008	0.008	0.005	0.067	0.060	21	
4299	0.09	0.38	0.26	0.013	0.015	0.008	0.008	0.001	0.118	0.305	54	
4300	0.09	0.37	0.38	0.013	0.013	0.008	0.013	-	-	0.576	68	Portion forgeable
4303	0.11	0.37	0.15	0.015	0.013	0.011	0.010	0.001	0.063	0.686	62	Hot short

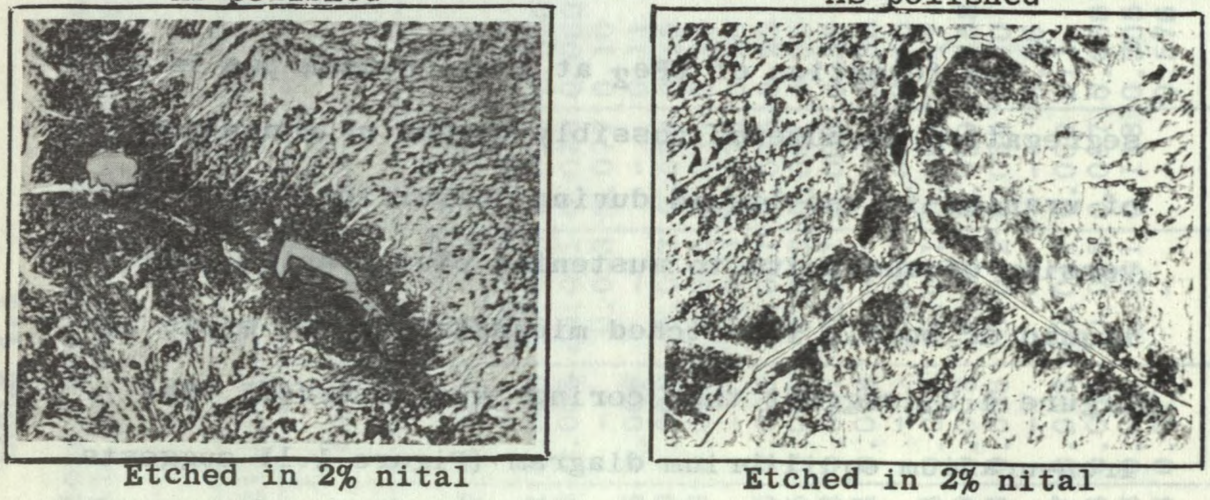
*Vacuum fusion.

Every medium carbon steel in which the spoon analysis exceeded 0.35% uranium was hot short. The tolerance for uranium was greater in low carbon steels. In plain carbon steels, therefore, it appears that carbon either decreases the solubility of uranium in gamma iron or shifts the composition of the eutectic to lower uranium contents.

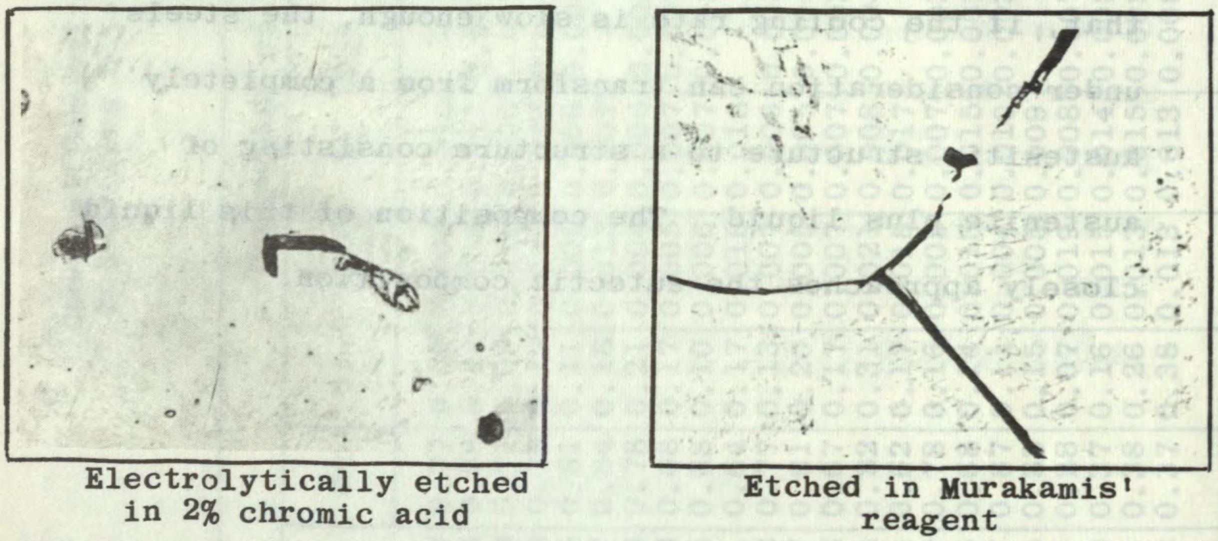
The formation of UFe_2 at grain boundaries is a segregation phenomenon possibly caused by concentration of uranium in the liquid during solidification or by reversion of austenite to austenite plus uranium-rich liquid or both. The etched microstructures, shown in Figure 4.2, suggest that coring has occurred. The iron-uranium equilibrium diagram (Figure 1.1) suggests that, if the cooling rate is slow enough, the steels under consideration can transform from a completely austenitic structure to a structure consisting of austenite plus liquid. The composition of this liquid closely approaches the eutectic composition.



As-polished As-polished



Etched in 2% nital Etched in 2% nital

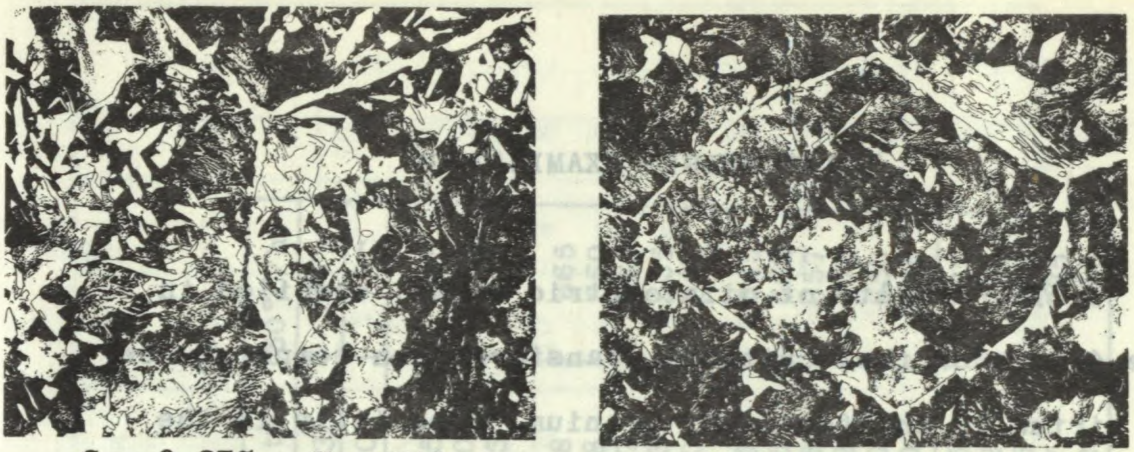


Electrolytically etched in 2% chromic acid

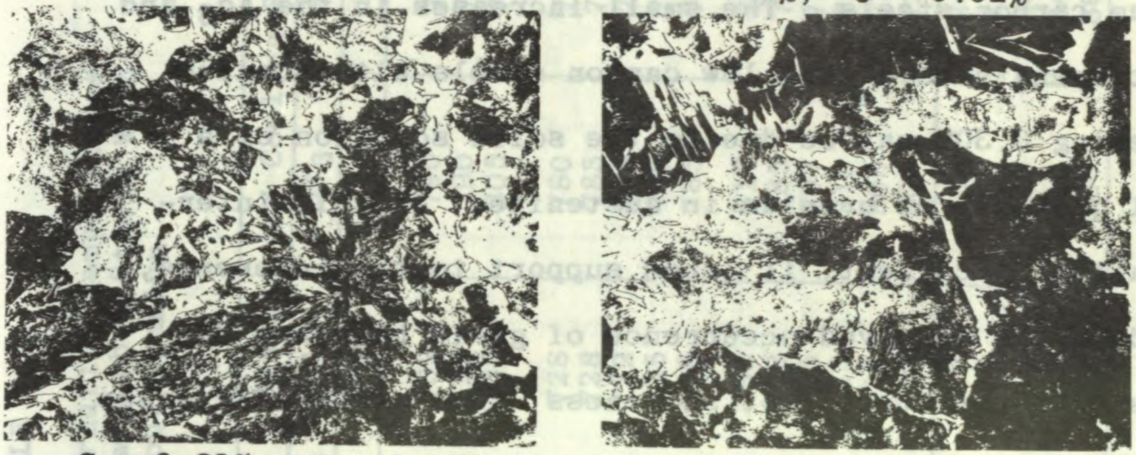
Etched in Murakamis' reagent

Figure 4.1 - Microstructures of Medium Carbon Uranium-bearing Steels in the As-cast Condition Showing the Distribution of the Grain Boundary Constituent UFe_2. X1000

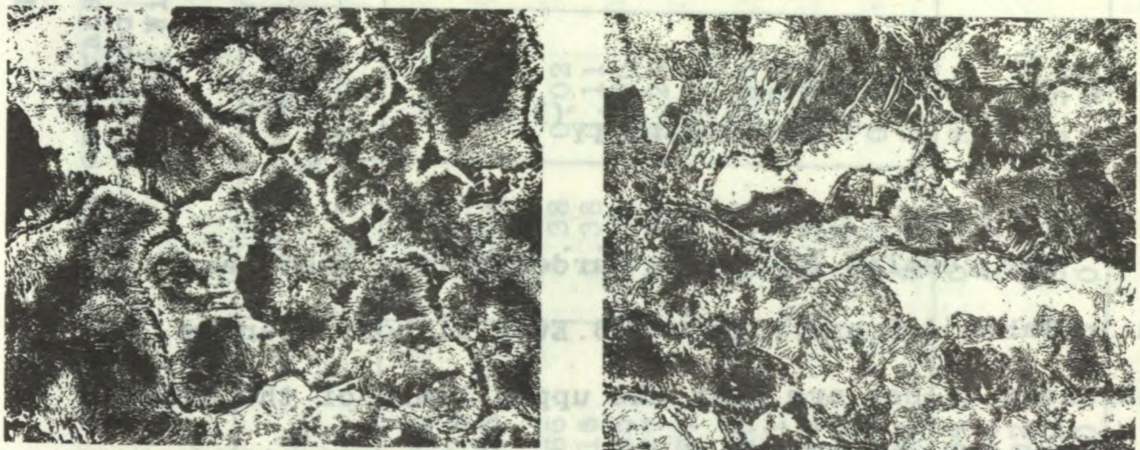
Left: C = 0.38%, U = 0.25%
Right: C = 0.37%, U = 0.70%



C = 0.37%, U = Nil   C = 0.40%, U = 0.02%



C = 0.38%, U = 0.11%   C = 0.34%, U = 0.20%



C = 0.38%, U = 0.25%   C = 0.37%, U = 0.70%

Figure 4.2 - Microstructures of As-cast Medium Carbon Steels With and Without Uranium. Note cored structure in the steels containing 0.25% and 0.70% U. Etched in 2% nital. X100

DILATOMETRIC EXAMINATION

The results of dilatometric tests, compiled in Table 4.2, show that critical transformation temperatures were virtually unaffected by uranium, especially in the medium carbon steels. The small increases in the Ac_3 and Ar_1 temperatures of the low carbon steels with uranium exceeding 0.30% may be due to the solid solution of a small quantity of uranium in austenite. If this interpretation is correct, it lends support to the inference, based on the observed occurrence of grain boundary UFe_2 and susceptibility to hot shortness, that carbon decreases the solubility of uranium in austenite.

HARDENABILITY(1,2)

The results of Jominy hardenability tests are shown in Table 4.3 and Figure 4.3. Even without uranium the hardness values are near the upper limit of the hardenability bands specified for corresponding SAE 1037 and 1040 steels(3). The results show that uranium does not significantly affect hardenability.

TABLE 4.2

Critical Transformation Temperatures of Medium and Low Carbon Steels With and Without Uranium

Heat No.	Composition, %		Heating and Cooling Rate: 150°C/hr			
			Ac_1	Ac_3	Ar_3	Ar_1
	C	U	°C	°C	°C	°C
4176	0.37	Nil	732	790	735	665
*4176	0.37	"	725	790	740	670
4285	0.34	"	738	805	755	675
4166	0.38	0.02	728	780	728	665
4415	0.38	0.11	728	785	728	660
4265	0.31	0.20	732	805	747	660
4167	0.38	0.25	735	785	723	655
*4167	0.38	0.25	728	785	730	665
4346	0.27	0.30	732	817	752	645
4371	0.38	0.32	732	785	725	662
4360	0.34	0.38	735	797	728	657
4309	0.35	0.46	735	810	752	670
4177	0.37	0.70	732	800	730	650
*4177	0.37	0.70	730	800	730	655
4284	0.10	Nil	740	880	845	785
*4284	0.10	Nil	740	880	852	785
4302	0.10	0.060	740	880	845	780
4299	0.09	0.30	745	910	847	785
4300	0.09	0.58	745	900	862	810

*These specimens were tested at the heating and cooling rate of 40°C/hr.

TABLE 4.3

Jominy End-quench Hardenability Results for Carbon Steels With and Without Uranium

Heat No.	Composition, %			Distance from quenched end of specimen - sixteenth in.											
				2	4	6	8	10	12	14	16	20	24	28	32
	C	Mn	U	Rockwell C Hardness											
4382	0.40	0.71	none	51	27	21.5	18.5	18	14	14.5	14	8.5	10.5	7	7
4285	0.34	0.68	none	47	22	18.5	15.5	14	13	11	10.5	9	7	7.5	7
4166	0.40	0.78	0.02	43	26	23	20.5	19.5	17	16	15	12	12	10	9
4416	0.35	0.81	0.06	45	24	20	18	17	15	15	14	11	10	9	7
4383	0.37	0.84	0.10	51	26	23	21	18	14	15	14	10	9	8	6
4415	0.38	0.78	0.11	45	24	22	20	18	17	16	15	12	10	8	8
4714	0.38	0.44	0.11	51.5	33	24	21	20	17	15	14	12	10	9.5	8
4370	0.34	0.68	0.21	50	32.5	20	18	16	14	13	11	7	6	4	
4371	0.38	0.67	0.32	53.5	28.5	26.5	25	22.5	21	19	18	15	13	11	10
SAE 1037	0.35 to 0.42	0.40 to 0.70	none	52 to 33	30 to 20	25 to 17	23 to 14	21 to 12	20 to 10	19 to 9	18 to 8	16 to 6			
SAE 1040	0.37 to 0.44	0.60 to 0.90	none	53 to 34	31 to 22	27 to 18	25 to 15	24 to 14	23 to 12	22 to 11	21 to 11	20 to 10			

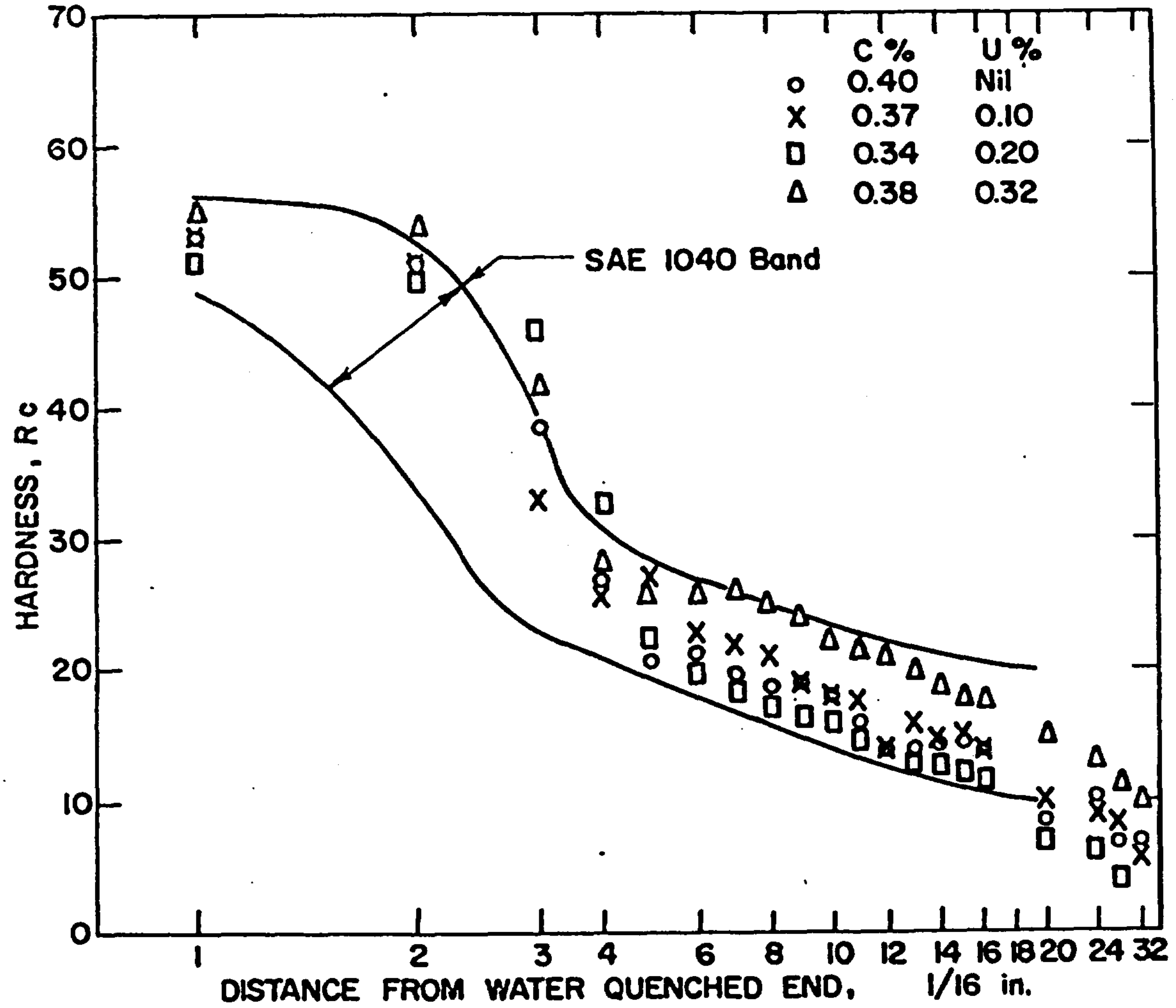


Figure 4.3 - Jominy End-quench Hardenability Test Results for Medium Carbon Steels With and Without Uranium. Note that the results fall in the corresponding SAE 1040 band. Test specimens were austenitized at 840°C (1550°F).

GRAIN SIZE

The effect of austenitizing temperature on Shepherd's fracture grain size of medium carbon experimental steels is summarized in Figure 4.4. Because Shepherd's fracture grain rating and ASTM grain size are nearly identical (4) it can be said that uranium has no grain refining effect for all practical purposes. In low carbon steels, however, there are indications that uranium has a tendency to coarsen the grain structure.

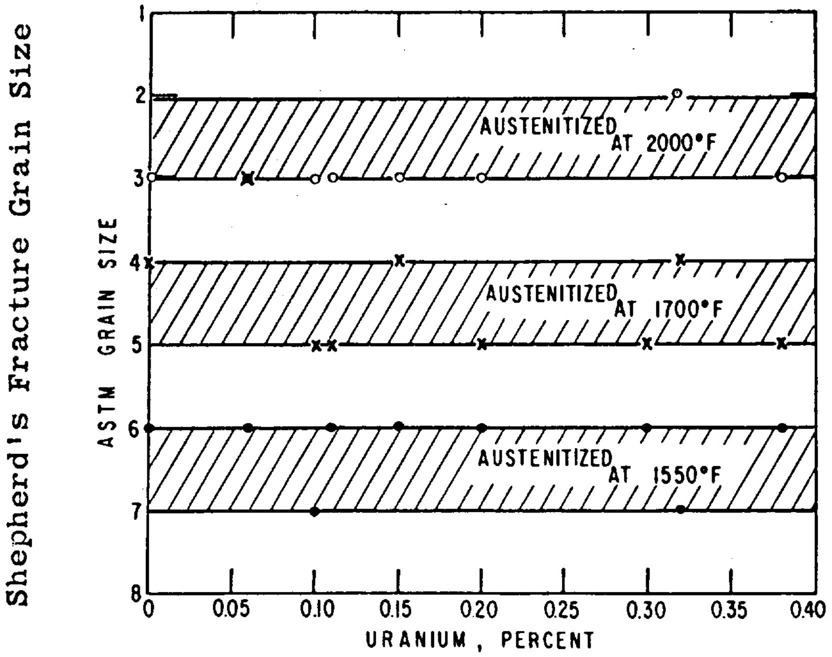


Figure 4.4. - Grain Size of Medium Carbon Steels, With and Without Uranium, Related to Austenitizing Temperature.

QUENCHED AND TEMPERED HARDNESS

Figure 4.5 shows that uranium does not significantly affect the as-quenched hardness or the response to tempering of medium carbon steels. Figure 4.6 demonstrates that the as-quenched and tempered hardness of uranium-bearing medium carbon steels is insensitive to variations of the austenitizing temperature from 840° to 1095°C (1550° to 2000°F).

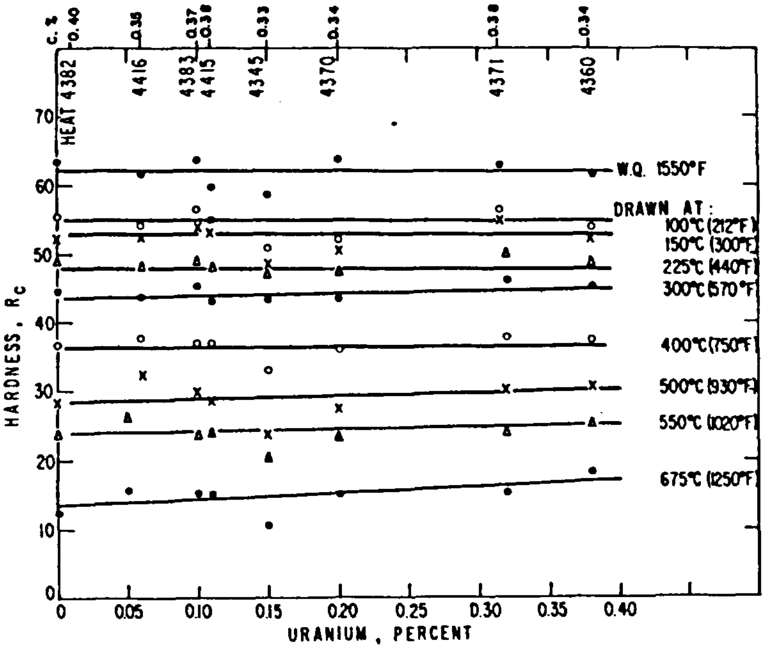


Figure 4.5 - Effect of Uranium on the Hardness of Water-Quenched and Tempered Medium Carbon Steels.

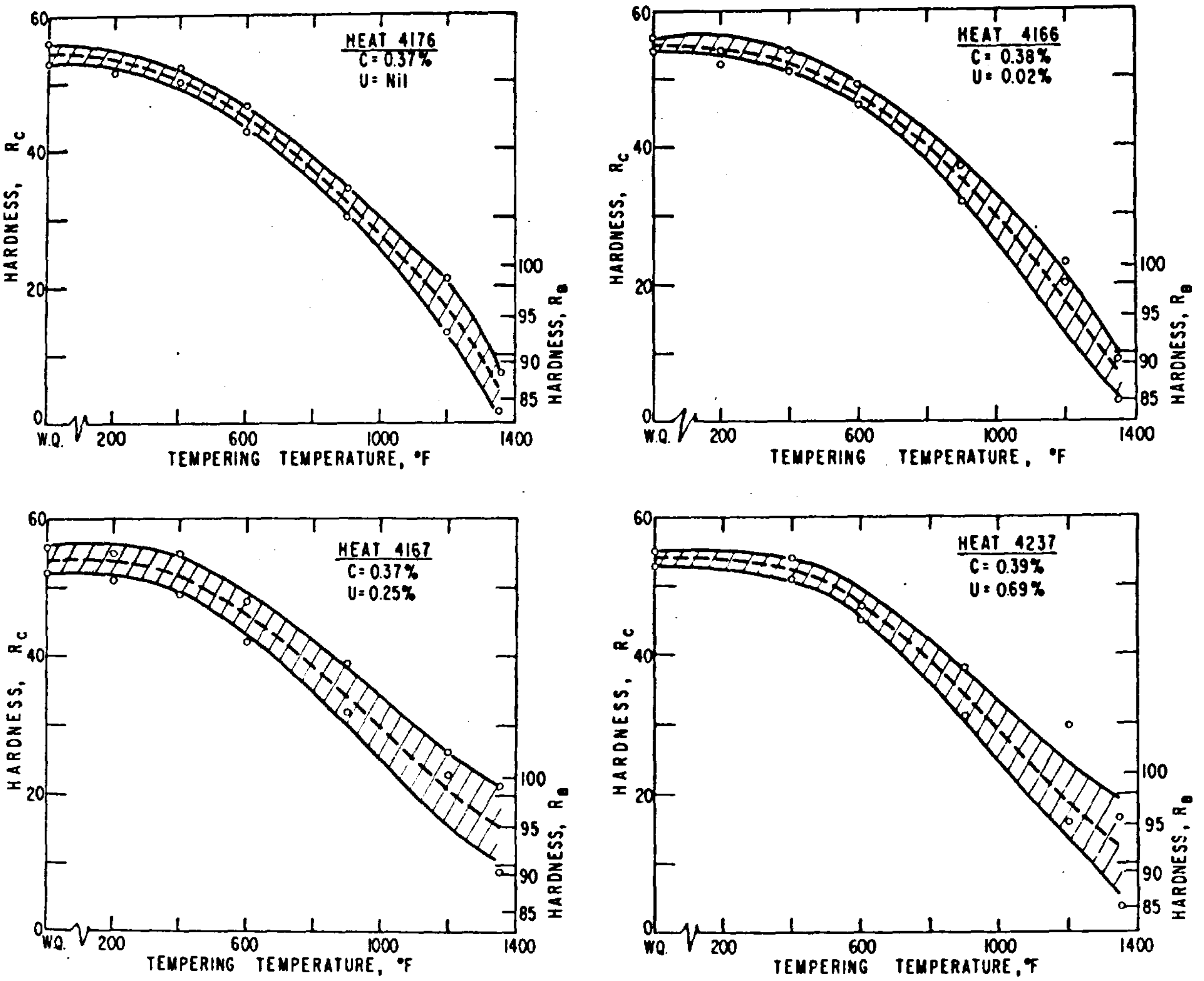


Figure 4.6 - Hardness Bands of Tempered Medium Carbon Uranium-bearing Steels Austenitized at 840°C (1550°F), 900°C (1650°F), 950°C (1750°F), 1010°C (1850°F) and 1095°C (2000°F). Each band shows the maximum and minimum hardness obtained in the austenitizing range mentioned above.

MECHANICAL PROPERTIES

Tensile and Impact Properties

The effect of uranium on tensile and impact properties, in the as-rolled and normalized conditions, is shown graphically for medium carbon steels in Figure 4.7 and for low carbon steels in Figure 4.8.

Superficially, uranium appears to improve slightly the ultimate tensile strength and the yield point. Tensile ductility is not decreased until uranium exceeds about 0.30%. Because uranium has virtually no solubility in alpha iron or ferrite and no apparent influence on the mechanism or rate of transformation of austenite, it is not surprising that uranium has little influence on tensile properties.

Uranium does not appear to adversely affect tensile ductility of medium carbon steels in the quenched and tempered condition. The relationships existing between tensile properties of these steels, as shown graphically in Figure 4.9 and as recorded in Table 4.4, are consistent with those of commercial constructional steels. These results show that uranium has not affected resistance to tempering.

Figures 4.7 and 4.8 show that, beyond about 0.15% uranium, the impact strength is drastically reduced. The occurrence of low impact values is associated with isolated areas having the characteristic microstructure shown in Figure 4.10. This structure has a bainitic appearance at low magnification. At high magnification, numerous inclusions, believed to be uranium oxides or uranium oxysulphides, are observed throughout the unique structure. Tukon hardness testing did not reveal any hardness variation between the isolated areas and the normal matrix.

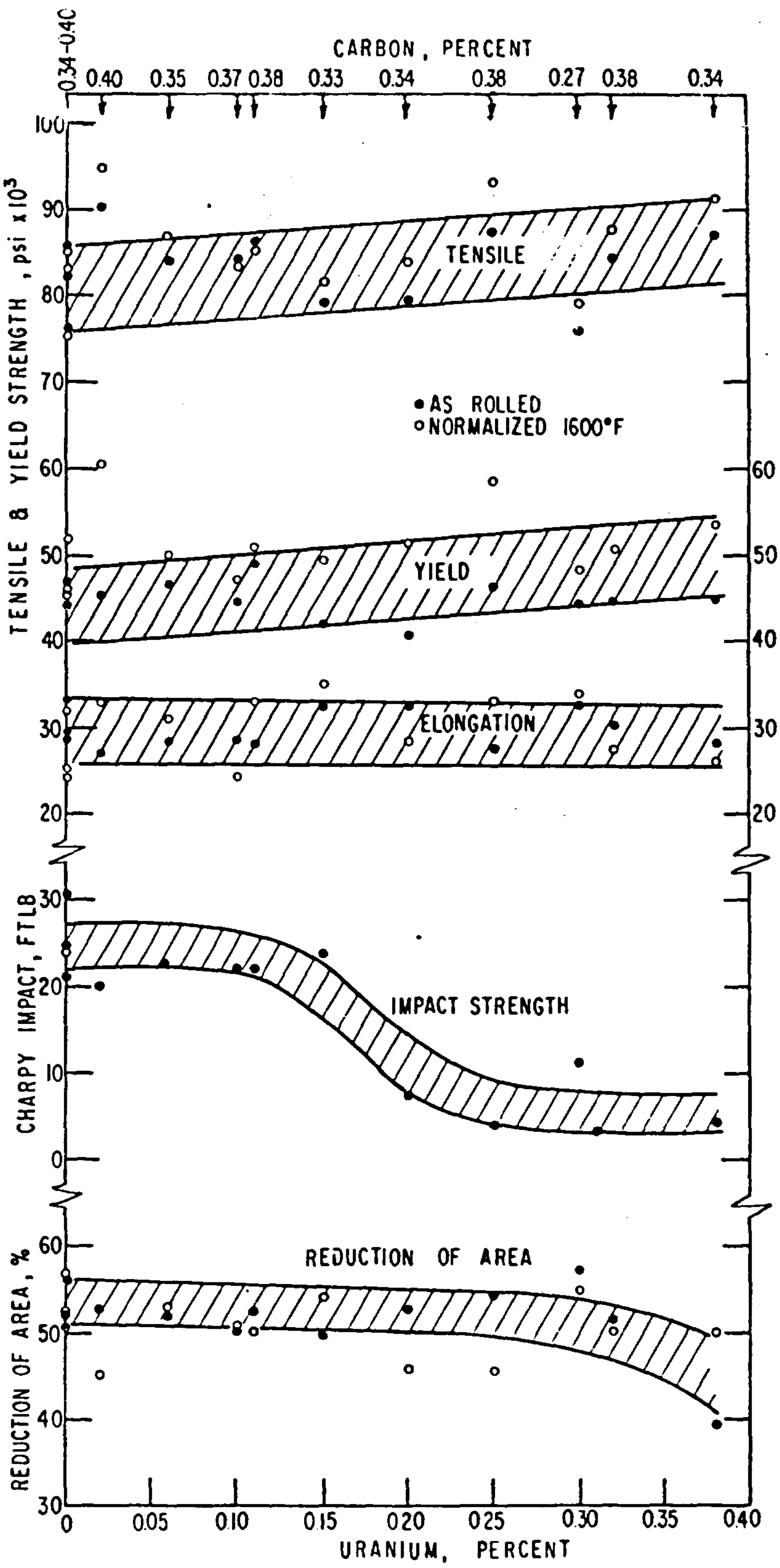


Figure 4.7. - Effect of Uranium on the Tensile and V-notch Impact Properties of Medium Carbon Steels.

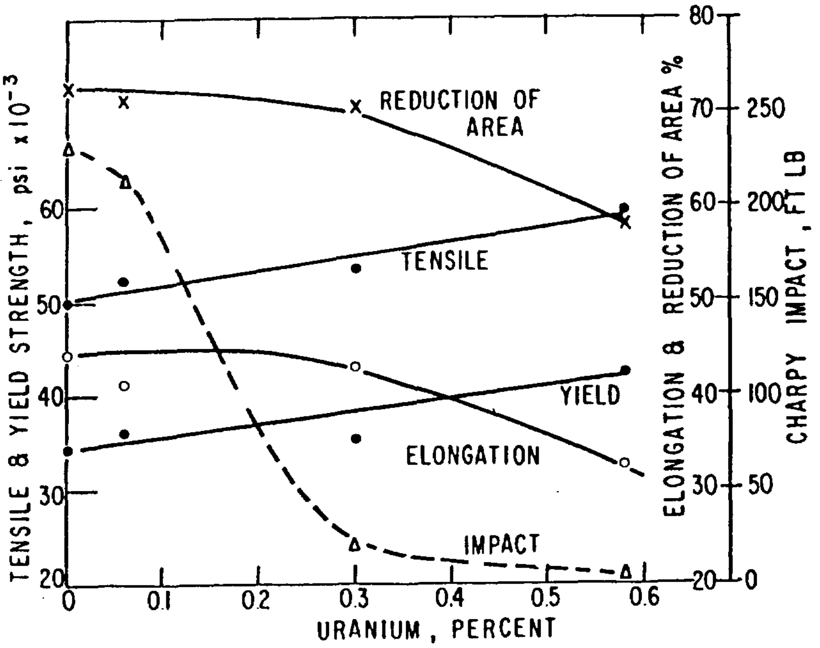


Figure 4.8. - Effect of Uranium on Tensile and V-notch Impact Properties of As-rolled Low Carbon (0.1% C) Steels.

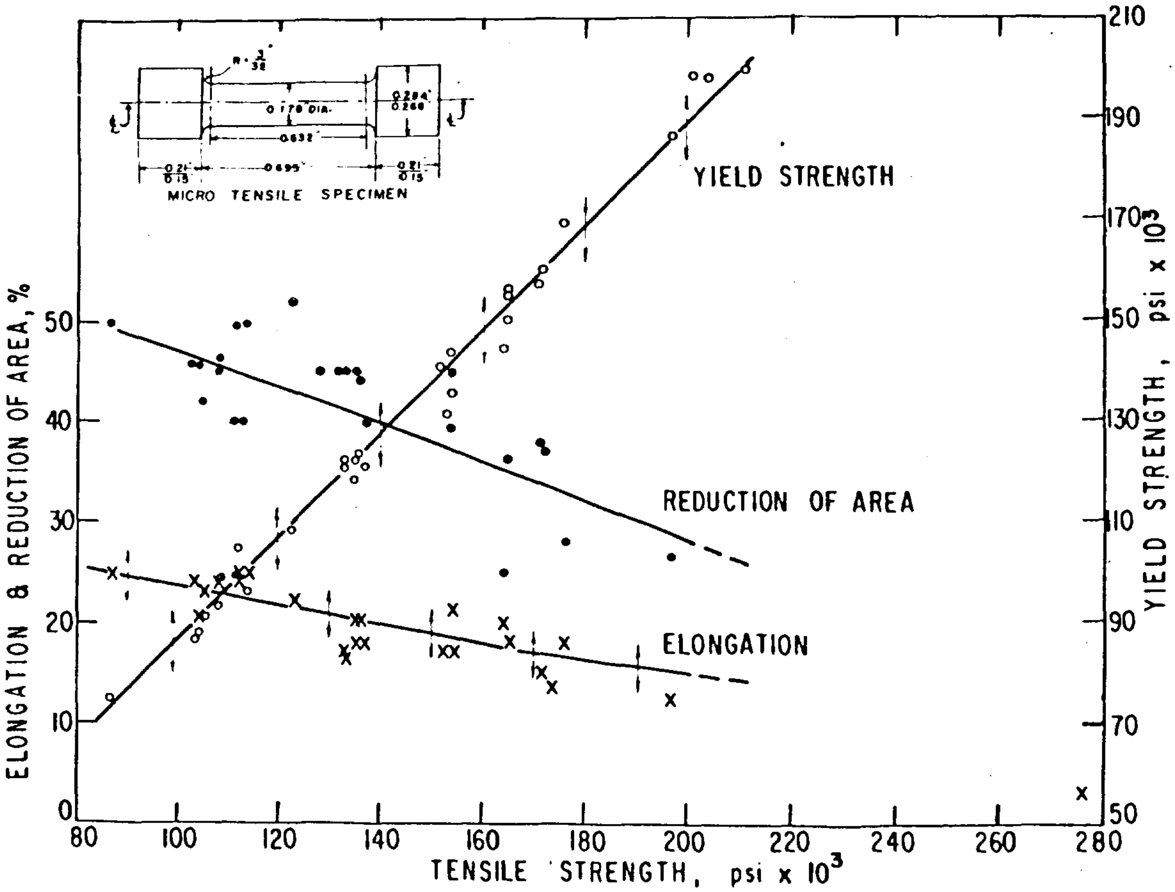


Figure 4.9. - Relationship Between Tensile Properties of Tempered Martensite of Medium Carbon Uranium-bearing Steels.

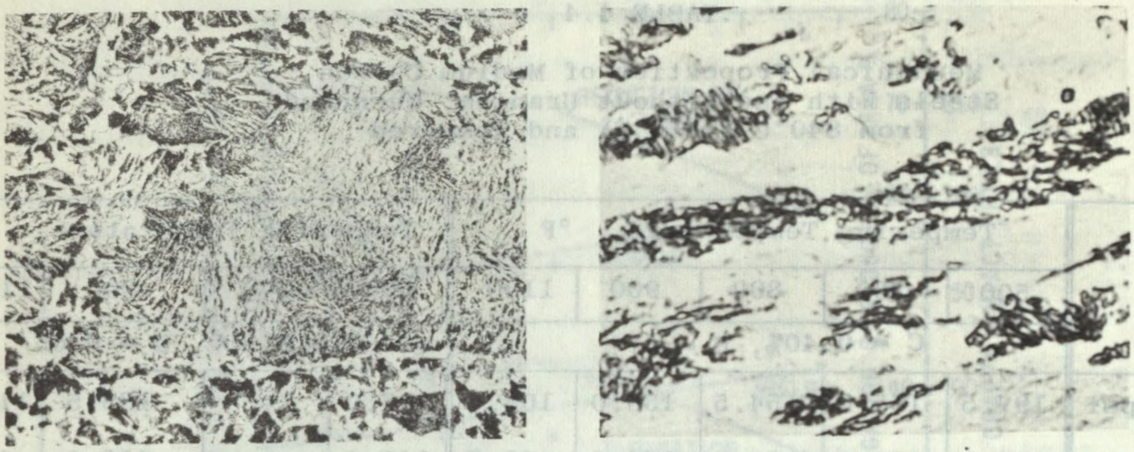
TABLE 4.4

Mechanical Properties of Medium Carbon Steels With and Without Uranium, Quenched from 840°C (1550°F) and Tempered

	Tempering Temperature, °F					Tempering Temperature, °F			
	500	700	800	900	1100	500	700	900	1100
	C = 0.40%, U = Nil					C = 0.35%, U = 0.06			
U.T.S., kpsi	197.5	165.0	154.5	136.0	108.0	207.0	-	135.5	114.0
Yield, kpsi	186.0	150.0	135.0	123.5	98.5	199.5	-	122.0	96.0
Elong., %	12.0	18.0	21.0	20.0	24.0	6.5	-	20.0	25.0
R.A., %	26.0	36.0	39.0	44.0	46.0	4.0	-	45.0	50.0
	C = 0.38%, U = 0.11%					C = 0.33%, U = 0.15%			
U.T.S., kpsi	-	173.0	153.0	137.5	108.5	230.0	152.2**	123.0	103.5
Yield, kpsi	-	154.5	131.0	121.0	93.4	222.0	141.0	108.5	87.2
Elong., %	-	18.5	14.0	18.6	24.0	15.0	17.0	22.0	24.0
R.A., %	-	28.5	12.0	40.0	45.0	25.0	45.0	52.0	45.0
	C = 0.34%, U = 0.20%					C = 0.27%, U = 0.30%			
U.T.S., kpsi	-	164.0	154.0	133.0	112.0	204.0	154.5	112.5	87.2
Yield, kpsi	-	-	140.5	121.0	105.0	198.5	144.5	99.2	75.0
Elong., %	-	15.0	20.0	17.0	25.0	5.0	17.0	24.0	25.0
R.A., %	-	35.0	40.0	45.0	50.0	4.0	45.0	40.0	50.0
	C = 0.38%, U = 0.32%					C = 0.34%, U = 0.38%			
U.T.S., kpsi	-	172.7	157.0	135.0	105.5	-	171.0	133.5	104.1
Yield, kpsi	-	160.5	142.5	118.5	91.2	-	157.0	121.5	88.3
Elong., %	-	13.5	16.0	17.5	23.0	-	15.0	17.0	20.5
R.A., %	-	37.5	15.0	45.0	42.0	-	38.0	45.0	46.0

*The results reported here were obtained on Hounsfield micro tensile specimens, as shown in Figure 4.9.

**This specimen was tempered at 400°C (750°F).



X100 X2000

Figure 4.10. - Abnormal Microstructure Observed in Wrought Uranium-bearing Steels Exhibiting Low Room Temperature Impact Strength. Etched in 2% nital.

Stress-Rupture Properties

The influence of uranium on the stress-rupture strength of carbon steels is shown in Figures 4.11 and 4.12. These preliminary results indicate that uranium has a favourable effect on the stress-rupture properties. The improvement may possibly be ascribed to the precipitation of finely dispersed particles of UFe_2 phase (Figure 4.13), and possibly to the stable dot-carbides (Figure 4.19) of uranium in the matrix. Since uranium carbide resists growth even after a long sub-critical anneal it is possible that spherical UC particles together with the fine precipitates of UFe_2 would hinder the movement of dislocations, thus creating one of the conditions conducive to good creep properties. It is also likely that the grain-coarsening effect of uranium in low carbon steels may contribute to the improvement of stress-rupture properties.

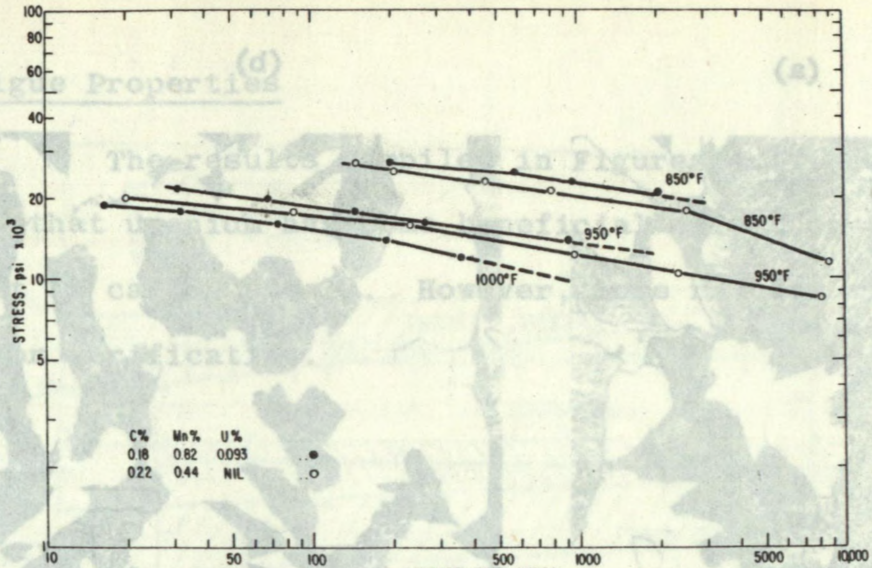


Figure 4.11. - Stress-rupture Properties of 0.2% Carbon Steels, With and Without Uranium, at 455°C (850°F) and 510°C (950°F). The curves for steel without uranium are reproduced from the publication, Ref. 5.

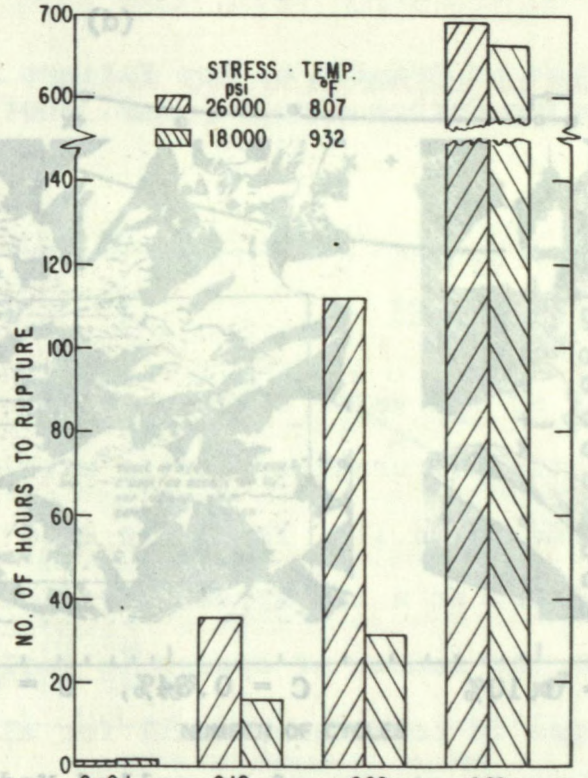
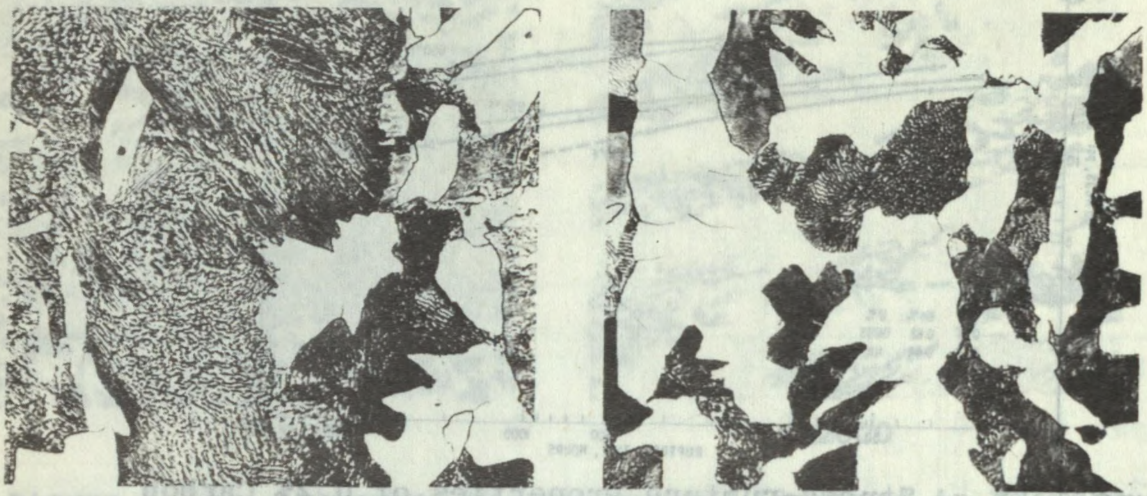


Figure 4.12. - Effect of Uranium on Stress-rupture Characteristics of 0.1% Carbon Steels. The uranium-free steel was tested at 37,000 psi at 430°C (806°F) and 23,000 psi at 500°C (932°F). The difference in stress levels invalidates comparison of uranium-bearing steels with uranium-free steel.

(a) (b)



C = 0.40%, U = Nil C = 0.35%, U = 0.06%

(c) (d)

C = 0.37%, U = 0.10% C = 0.34%, U = 0.20%

Figure 4.13. - Microstructures of As-rolled Medium Carbon Uranium-bearing Steels. Note the presence of large "cubic" inclusions of U(O,C,N) or uranium oxide in photomicrograph (c), and plate-like precipitates of possibly UFe_2 phase in ferrite grains in the photomicrographs (c) and (d). Etched in 2% nital. X500

Fatigue Properties

The results compiled in Figures 4.14 and 4.15 show that uranium has some beneficial effect on the fatigue limit of carbon steels. However, more results are required for verification.

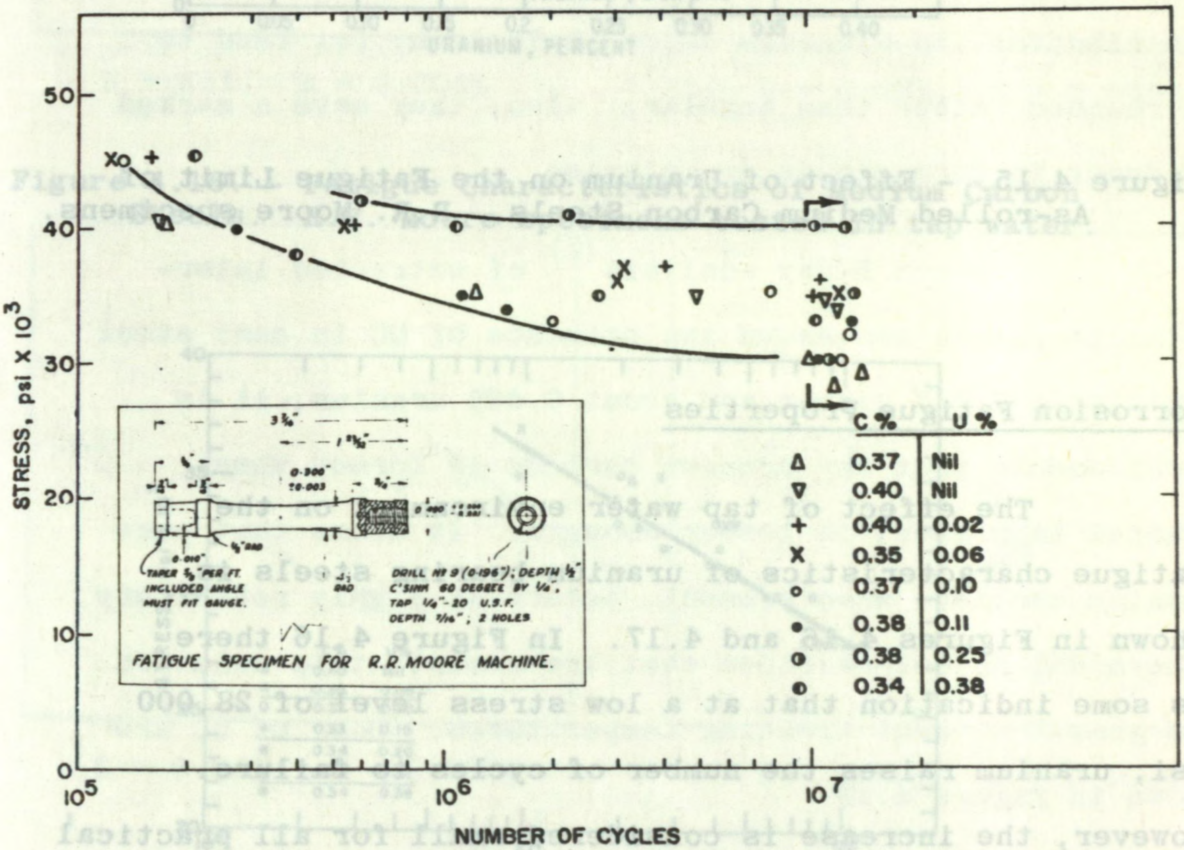


Figure 4.14. - Rotating-beam Fatigue Characteristics of As-rolled Medium Carbon Steels With and Without Uranium.

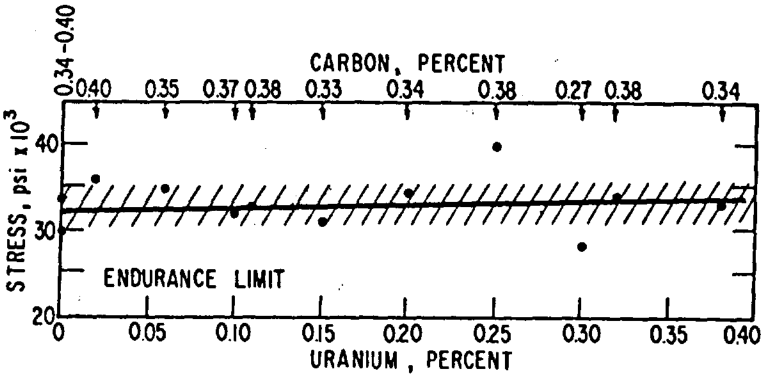


Figure 4.15. - Effect of Uranium on the Fatigue Limit of As-rolled Medium Carbon Steels. R.R. Moore specimens.

Corrosion Fatigue Properties

The effect of tap water environment on the fatigue characteristics of uranium-bearing steels is shown in Figures 4.16 and 4.17. In Figure 4.16 there is some indication that at a low stress level of 28,000 psi, uranium raises the number of cycles to failure. However, the increase is considered small for all practical purposes.

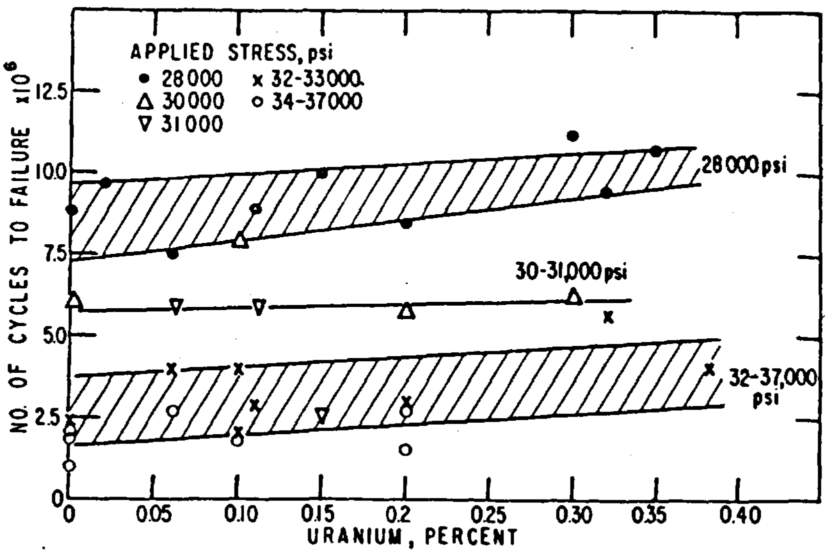


Figure 4.16. - Fatigue Characteristics of Medium Carbon Steels. R.R. Moore specimens tested in tap water.

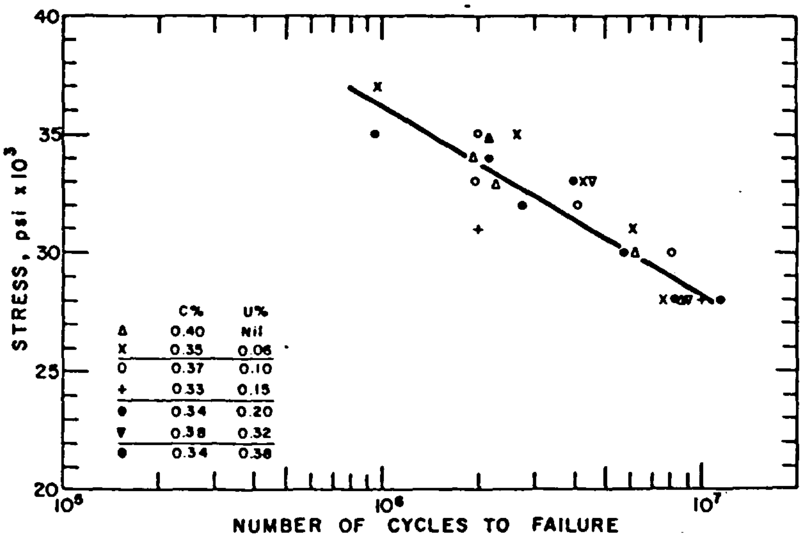
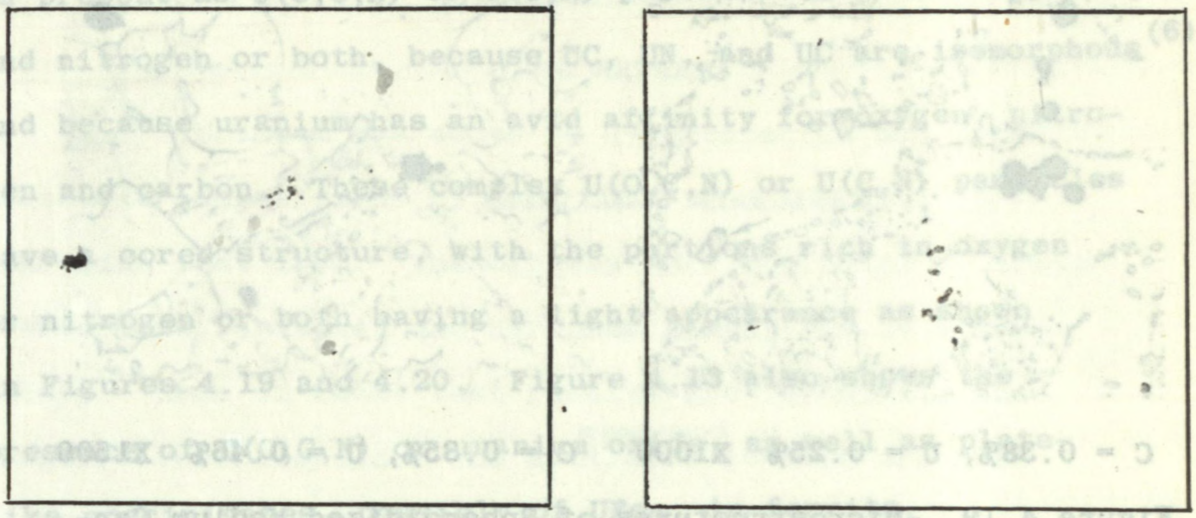


Figure 4.17. - Effect of Uranium on the Fatigue Limit of Medium Carbon Steels. R.R. Moore specimens tested in tap water.

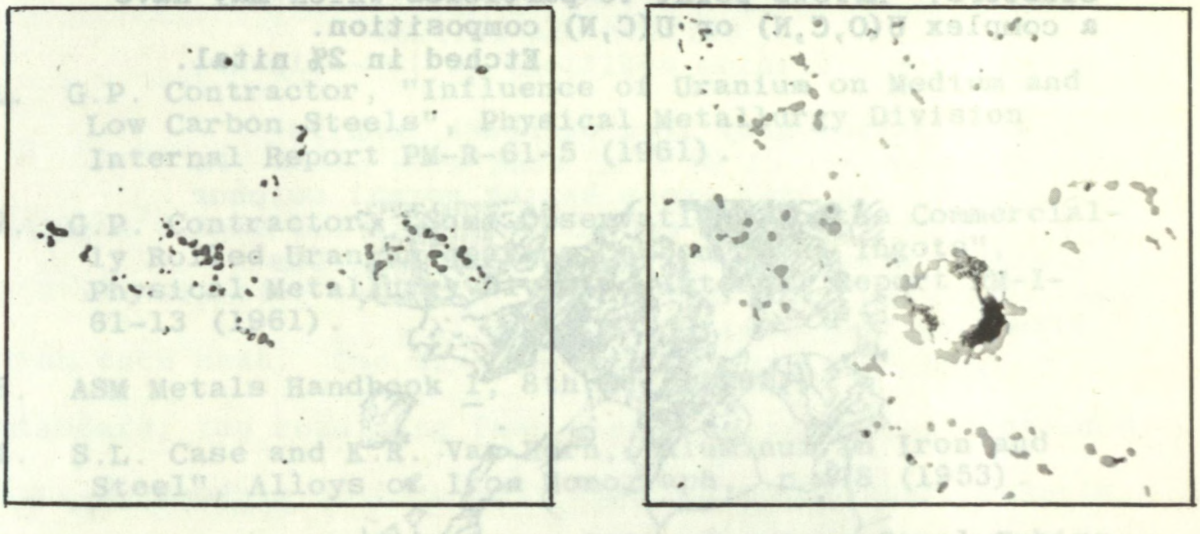
URANIUM-BEARING INCLUSIONS

In steel, uranium forms characteristic refractory inclusions believed to be uranium oxides or uranium oxysulphides. The as-cast appearance of these inclusions at various uranium levels in low sulphur steel is shown in Figure 4.18. The inclusions are similar in size and distribution to aluminum oxide inclusions, but tend to be rounded rather than angular; also, they have a marked tendency to form clouds or galaxies.

Although X-ray analysis(1) of extracted intermetallic phases has shown the presence of UC in cast steel containing 0.35% carbon and about 0.46% uranium, it is questionable that any uranium carbide is formed when uranium is present in lesser amounts. It seems that pure uranium carbide, when present, occurs as highly refractory, spheroidal or dot carbides that are resistant to solution and growth at heat treating temperatures. Dots of UC are shown in Figure 4.19.

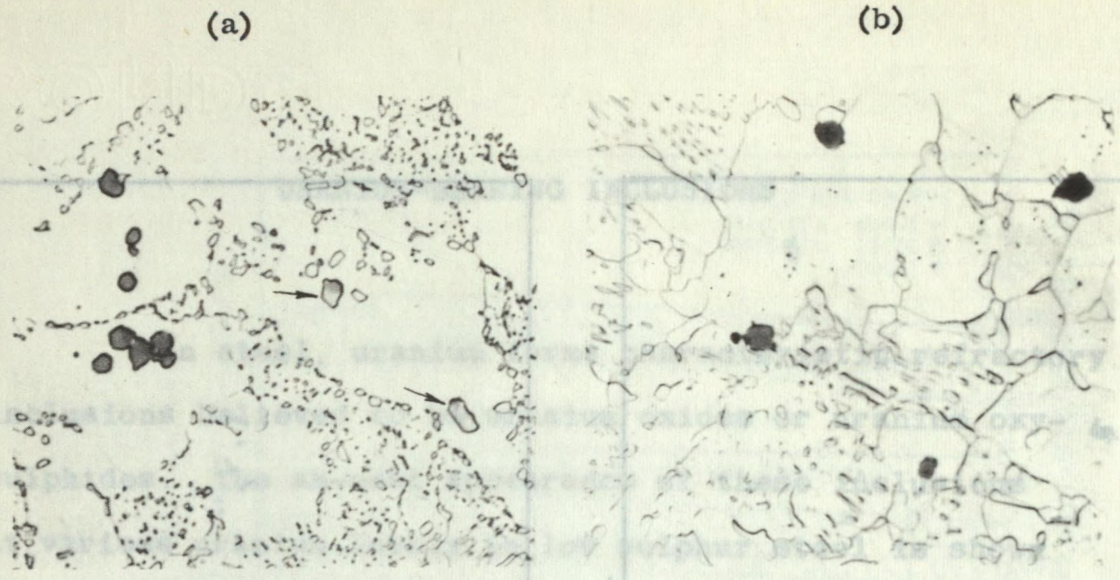


U = Nil, S = 0.004%   U = 0.02%, S = 0.009%



U = 0.25%, S = 0.007%   U = 0.70%, S = 0.004%

Figure 4.18. - Photomicrographs of Inclusions in As-cast Medium Carbon Steels With and Without Uranium. Note the formation of galaxy-type inclusions as the uranium content increases. As-polished. X500



C = 0.38%, U = 0.25% X1000 C = 0.35%, U = 0.46% X1500

Figure 4.19. -Microstructures of Spheroidized Medium Carbon Uranium-bearing Steels. Dot carbides, believed to be UC, are present in the 0.46% uranium steel, but not in the 0.25% uranium steel. Dark UO_2-type inclusions showing cubic habit occur singly or in clusters. Arrows point to particles which may have a complex U(O,C,N) or U(C,N) composition. Etched in 2% nital.

C = 0.35%, U = 0.46%

Figure 4.20. - Photomicrograph of Normalized Medium Carbon Uranium-bearing Steel Showing Cored Particles (arrows) of U(O,C,N) or U(C,N). Etched in 2% nital. X1500

It is believed that most of the uranium carbide is present as U(O,C,N) or U(C,N) particles rich in oxygen and nitrogen or both, because UC, UN, and UC are isomorphous$^{(6)}$, and because uranium has an avid affinity for oxygen, nitrogen and carbon. These complex U(O,C,N) or U(C,N) particles have a cored structure, with the portions rich in oxygen or nitrogen or both having a light appearance as shown in Figures 4.19 and 4.20. Figure 4.13 also shows the presence of U(O,C,N) or uranium oxide, as well as plate-like precipitates, possibly of UFe_2, in ferrite.

REFERENCES

1. G.P. Contractor, "Influence of Uranium on Medium and Low Carbon Steels", Physical Metallurgy Division Internal Report PM-R-61-5 (1961).

2. G.P. Contractor, "Some Observations on the Commercially Rolled Uranium-bearing Carbon Steel Ingots", Physical Metallurgy Division Internal Report PM-I-61-13 (1961).

3. ASM Metals Handbook 1, 8th Ed. (1961).

4. S.L. Case and K.R. Van Horn, "Aluminum in Iron and Steel", Alloys of Iron Monograph, p. 478 (1953).

5. "Properties of Carbon and Alloy Seamless Steel Tubing for High-Temperature and High-Pressure Service", Tech. Bull. No. C-G, Babcock and Wilcox Company, Tubular Products Division (1955).

6. K.E.G. Meredith and M.H. Waldron, "Inclusions in Uranium Metal", J. Inst. Metals (London) 87, (1958-59).

CHAPTER 5

URANIUM IN CAST IRONS(1)

R. K. Buhr*

SYNOPSIS

Uranium additions to low-sulphur, hypereutectic, grey cast iron and to 1% chromium cast iron markedly increase the as-cast tensile properties. Uranium additions to low-sulphur, hypereutectic, grey iron decrease tensile strength. In cast irons having normal sulphur contents uranium addition has a disastrous effect on the tensile strength.

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* Senior Scientific Officer, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

Uranium was added to hypereutectic and hypoeutectic compositions of grey cast iron and to a 1% chromium cast iron. The effects were evaluated by transverse bend, tensile, and hardness tests, and by microscopy. Some of these test results are incomplete and require verification. The available results are presented to indicate progress to date and to illustrate the effects noted.

MELTING AND TESTING

All heats were made in a 50 lb induction furnace using a common melting stock of low sulphur content. Five 1.2 in. diameter by 21 in. long arbitration bars were cast from each heat. One uranium-free bar was cast as a standard; the remaining four bars from each heat contained varying amounts of uranium. When higher sulphur contents were required, pure elemental sulphur was added directly to the bath.

The arbitration bars were broken to obtain transverse load and deflection values. Tensile bars were machined from one broken half and the second half was used for chemical analyses, Brinell hardness determinations, microscopy, corrosion tests and high-temperature oxidation tests. All test materials were in the as-cast condition.

CHEMICAL COMPOSITIONS

The chemical compositions of the various bars are listed in Table 5.1. Values shown for HrO are the averages of four results. Those shown for Hr1, Hr2, Hr3, Hr5 and HcO are the averages of two results. The remainder are individual results. The analyses showed little variation from bar to bar and heat to heat. The uranium values are the average of analytical results from two laboratories. In all cases, the agreement was good between the two laboratories.

MECHANICAL PROPERTIES

The results of transverse bend tests and Brinell hardness tests are listed in Table 5.2. The sample identification, and the number of tests relating to the values shown, are the same as for Table 5.1.

The effect of increasing uranium content on the ultimate tensile strength is shown by Figure 5.1. It should be noted that the curves for low- and high-sulphur hypoeutectic cast irons are not directly comparable because the latter have low manganese and silicon contents. The curves for low- and high-sulphur hypereutectic cast irons are comparable because base composition variation is negligible.

Figure 5.1 shows that additions of uranium to low-sulphur hypereutectic cast iron result in a marked increase in the ultimate tensile strength. At 0.345% uranium there has been a threefold increase in the tensile strength, from 18,900 psi to 59,700 psi, with only a minor decrease in transverse deflection, from 0.288 in. to 0.245 in. Two-thirds of this threefold increase occurred between the reported uranium contents of 0.30% and 0.345%. The range of combined carbon content for the three irons referred to was only 0.52 to 0.56%, which would have little bearing on the tensile results. It should be noted that none of the bars have been checked for uranium segregation. If segregation has occurred, some of the reported uranium analyses may be in error.

TABLE 5.1

Composition of Bars Tested

Sample *	Total C,%	Comb. C,%	Mn, %	Si, %	S, %	Cr, %	Total U,%
Hr0	3.68	0.52	0.78	2.19	0.010	-	-
Hr1	3.67	0.53	0.75	2.20	0.010	-	0.064
Hr2	3.67	0.45	0.75	2.20	0.010	-	0.110
Hr3	3.66	0.54	0.75	2.20	0.010	-	0.226
Hr4	3.72	0.56	0.82	2.20	0.009	-	0.30
Hr5	3.66	0.54	0.82	2.20	0.009	-	0.345
Hr6	3.65	0.55	0.82	2.17	0.009	-	0.40
Hr7	3.62	0.92	0.78	2.16	0.009	-	0.48
Hr8	3.58	1.04	0.78	2.16	0.009	-	0.71
Hr9	3.64	0.65	0.75	2.24	0.009	-	0.95
Hr10	3.64	0.74	0.75	2.16	0.008	-	1.15
Hr11	3.62	0.84	0.78	2.16	0.009	-	1.26
Hr12	3.59	0.85	0.78	2.16	0.009	-	1.57
HrS0	3.61	0.56	0.69	2.21	0.091	-	-
HrS1	3.66	0.47	0.69	2.21	0.091	-	0.047
HrS2	3.64	0.44	0.69	2.21	0.091	-	0.115
HrS3	3.64	0.40	0.69	2.21	0.091	-	0.18
HrS4	3.67	0.44	0.69	2.20	0.082	-	0.275
HrS5	3.66	0.51	0.69	2.20	0.082	-	0.415
HrS6	3.68	0.51	0.69	2.20	0.108	-	0.55
HrS7	3.58	0.44	0.69	2.20	0.108	-	0.78
HrS8	3.59	0.46	0.69	2.19	0.091	-	0.91
HrS9	3.58	0.46	0.69	2.18	0.091	-	1.20
Ho0	2.98	0.78	0.70	1.87	0.011	-	-
Ho1	2.94	0.54	0.70	1.87	0.011	-	0.049
Ho2	2.97	0.59	0.70	1.87	0.011	-	0.098
Ho3	2.95	0.65	0.70	1.87	0.012	-	0.19
Ho4	2.95	0.72	0.70	1.87	0.012	-	1.05
HoS0	2.88	1.87	0.20	1.33	0.069	-	-
HoS1	2.86	1.88	0.20	1.33	0.069	-	0.044
HoS2	2.86	1.27	0.20	1.33	0.069	-	0.093
HoS3	2.85	1.63	0.19	1.32	0.074	-	0.22
HoS4	2.80	0.82	0.19	1.32	0.074	-	0.93
Hc0	3.64	0.93	0.74	2.18	0.010	1.08	-
Hc1	3.64	0.80	0.73	2.17	0.010	1.08	0.056
Hc2	3.62	0.86	0.73	2.19	0.009	1.08	0.098
Hc3	3.63	0.97	0.74	2.18	0.009	1.07	0.245
Hc4	3.63	0.86	0.75	2.20	0.010	1.06	0.39
Hc5	3.64	1.36	0.75	2.20	0.010	1.04	0.50
Hc6	3.64	1.49	0.75	2.20	0.010	1.04	0.58
Hc7	3.63	1.15	0.75	2.21	0.009	1.04	0.61
Hc8	3.60	0.95	0.74	2.16	0.009	1.06	1.25

* - Hr - Hypereutectic compositions
Ho - Hypoeutectic compositions
Hc - 1% chromium compositions
HrS and HoS - high-sulphur compositions

Note: 1 - Range of phosphorus in all irons was 0.025 to 0.030%.

TABLE 5.2

Results of Transverse Bend Tests and Brinell Hardness Tests

Sample	Transverse Break Load, lb	Maximum Deflection, in.	BHN	Sample	Transverse Break Load, lb	Maximum Deflection in.	BHN
Hr0	1645	0.288	152	Ho0	2600	0.294	221
Hr1	1375	0.314	137	Ho1	2800	0.333	223
Hr2	1085	0.286	143	Ho2	2460	0.294	219
Hr3	1470	0.264	165	Ho3	1490	0.228	189
Hr4	1585	0.215	170	Ho4	1700	0.150	229
Hr5	3170	0.245	240				
Hr6	3045	0.222	235	HoS0	2350	0.172	309
Hr7	2860	0.299	280	HoS1	2500	0.187	302
Hr8	2225	0.147	372	HoS2	1900	0.162	268
Hr9	3005	0.238	267	HoS3	2650	0.203	303
Hr10	3180	0.213	262	HoS4	1240	0.137	193
Hr11	3110	0.205	273				
Hr12	2910	0.194	272				
HrS0	1545	0.299	246	Hc0	2165	0.254	230
HrS1	1430	0.239	244	Hc1	2125	0.286	205
HrS2	1445	0.257	244	Hc2	2020	0.271	203
HrS3	1465	0.249	250	Hc3	2175	0.262	231
HrS4	1595	0.303	202	Hc4	1670	0.168	248
HrS5	1350	0.275	251	Hc5	1810	0.121	302
HrS6	1165	0.325	207	Hc6	2440	0.160	249
HrS7	1055	0.335	212	Hc7	2890	0.190	352
HrS8	855	0.284	165	Hc8	3295	0.169	325
HrS9	780	0.261	214				

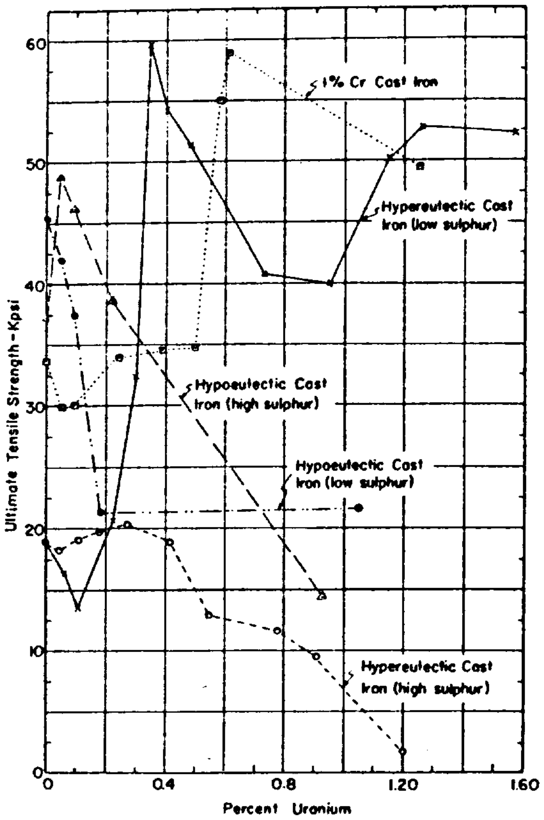


Figure 5.1. - Graph Showing the Effect of Increasing Uranium Content on the Ultimate Tensile Strength of Various Cast Irons.

Unfortunately, these marked increases in tensile strength are extremely sensitive to the sulphur content. Adding uranium to iron of the same base composition, but with sulphur increased to approximately 0.10% was found to be disastrous to the tensile strength. At 1.20% uranium, and 0.091% sulphur, the tensile strength is only 1,800 psi, whereas at 0.009% sulphur, the ultimate tensile strength is over 50,000 psi.

The addition of 1% chromium to the same hypereutectic composition results in similar, but not so marked, increases in tensile strength with increasing uranium contents. The per cent combined carbon in the 1% chromium series varies in much the same manner as with the low-sulphur hypereutectic series, but is, of course, at generally higher levels. No tests have as yet been performed with higher sulphur contents in the 1% chromium series.

In the hypoeutectic series, even at the low sulphur levels, uranium has a detrimental effect on the tensile properties. The uranium-free bar had a tensile strength of 45,000 psi, whereas at 0.19% uranium the tensile strength was only 21,300 psi. An increase in the uranium to the 1.50% level resulted in little further change. The range between 0.19% and 1.05% uranium has not as yet been investigated.

As previously mentioned, the high-sulphur hypoeutectic cast iron curve should not be compared directly with the low-sulphur hypoeutectic curve because of composition differences. However, the tensile properties, after a slight initial increase, drop rapidly with increasing uranium when higher sulphur contents are present.

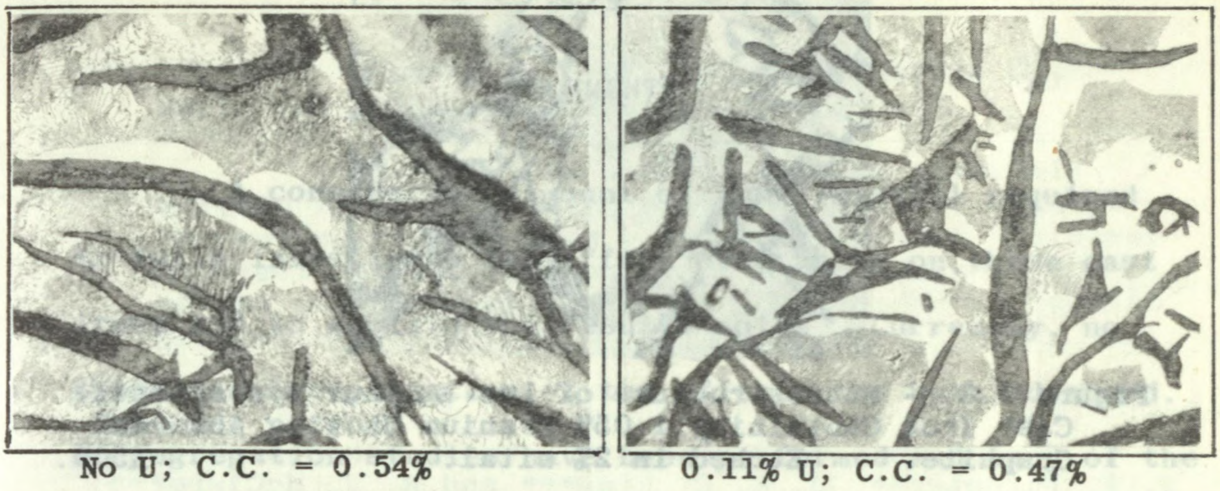
MICROSTRUCTURE

Increasing the uranium content of hypereutectic and 1% chromium cast irons results in the graphite flakes being broken into small, irregularly shaped pieces. This effect becomes noticeable around 0.35% uranium. In the hypereutectic series, uranium alternates in its effect as a graphitizer and as a carbide former or stabilizer. The effect of increasing uranium appears to change as follows:

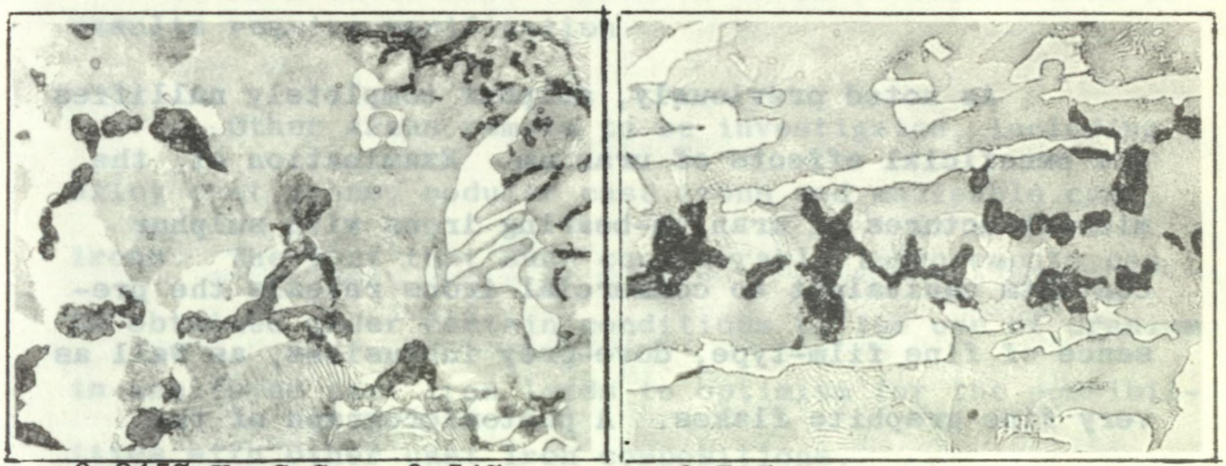
Range of Uranium, %	Effect
0 to 0.10	Graphitizer
0.10 to 0.70	Carbide former (strong)
0.70 to 1.00	Graphitizer
1.00 to 1.60	Carbide former (weak)

Figure 5.2 is a series of photomicrographs which show how increasing uranium affects the as-cast microstructure. The microstructures of the 1% chromium cast iron series are similar to those shown in Figure 5.2, the main difference being a larger amount of carbide.

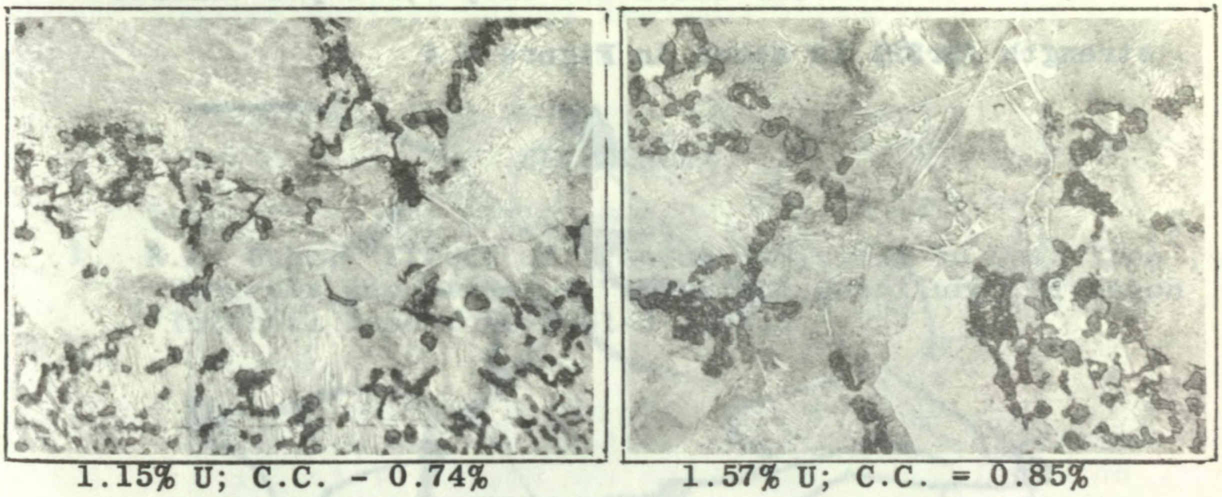
When uranium is added to hypoeutectic cast iron, it appears to have a poisoning effect on the flake graphite, i.e., the graphite flakes tend to form fine offshoots, which have a deleterious effect on the properties. This effect is illustrated by Figure 5.3.



No U; C.C. = 0.54%   0.11% U; C.C. = 0.47%



0.345% U; C.C. = 0.54%   0.71% U; C.C.- 1.04%



1.15% U; C.C. - 0.74%   1.57% U; C.C. = 0.85%

Figure 5.2 - Change in As-cast Microstructure of Hypereutectic Cast Iron With Increasing Uranium up to 1.57%. (3.65% C, 2.15% Si, 0.75% Mn, 0.010% S and 0.026% P). Etched in 2% nital. X500

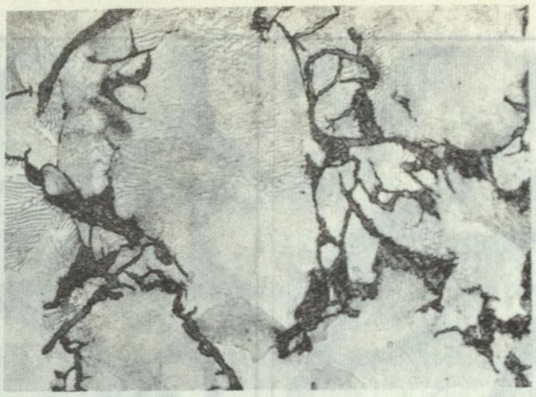


Figure 5.3. - Microstructure of Low-sulphur Hypoeutectic Cast Iron Containing 1.05% Uranium Showing Abnormal Graphite. Etched in 2% nital. X500.

As noted previously, sulphur completely nullifies the beneficial effects of uranium. Examination of the microstructures of uranium-bearing irons with sulphur contents equivalent to commercial irons reveals the presence of fine film-type, dove-grey inclusions, as well as very fine graphite flakes. A photomicrograph of the structure of the bar which had only 1,800 psi tensile strength (HrS9) is shown in Figure 5.4

Figure 5.4. - Photomicrograph of High-sulphur Hypereutectic Cast Iron Containing 1.20% Uranium, Showing Fine, Film-type Inclusion and Very Fine Graphite Flakes. As-polished. X500

COMMENTS

A considerable amount of work is still required to fully investigate the effect of uranium on these cast irons and to explain the results noted. Currently, no theoretical explanation of the effects has been advanced. No segregation studies have been performed and many of the results require verification.

Other areas remain to be investigated, including alloy cast irons, nodular cast irons and malleable cast irons. The fact that such considerable improvements can be obtained under certain conditions by the use of uranium in unalloyed cast iron leads to optimism for the possibilities with other cast iron compositions.

REFERENCE

1. R.K. Buhr, "Effect of Uranium Additions to Cast Iron , Progress Report No. 1," Physical Metallurgy Division Internal Report PM-R-61-3 (1961).

CHAPTER 6

URANIUM IN ALLOY STEELS

W. A. Morgan*, R. F. Knight**, C. E. Makepeace***
J. K. Pargeter**, D. E. C. King*** and R. J. McClure***

SYNOPSIS

The results of a number of investigations of the influence of uranium in alloy steels are presented in this chapter. Many facets of this broad field remain to be investigated, and in some cases only initial and, therefore, inconclusive results are available, making it impractical to review more than the direction of current research. An attempt has been made to give general coverage to topics of major interest in the various categories of alloy steels.

Uranium forms carbides that are stable up to at least 1230°C (2250°F).

This is reflected in lowered as-quenched and tempered hardness when sufficient uranium is present to deplete the matrix of carbon. In austenitic stainless steel, uranium is an effective stabilizing element.

Uranium has been shown to have no statistically significant influence on secondary hardness and to aggravate the degree of temper embrittlement. The wear resistance of tool steels modified with uranium awaits evaluation.

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* Chief and **Scientific Officers, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

** Metallurgical Engineers, Eldorado Mining and Refining Limited, attached to the Physical Metallurgy Division.

Results of creep testing indicate that small additions of uranium are beneficial.

In stainless steels, uranium adversely affects forgeability above 1010°C (1850°F), except in resulphurized grades. In resulphurized stainless and tool steels, uranium improves the morphology of the sulphides so as to benefit transverse tensile properties.

GENERAL INTRODUCTION

The characteristics of alloy steels are so diverse that comprehensive investigation of the influence of uranium has not been possible. The limited amount of research has been reported according to the type of steel involved.

In low alloy steels, temper embrittlement was investigated using AISI 3310 steels; secondary hardening characteristics, creep properties and microstructure were investigated using a steam turbine alloy containing 1% chromium, 1% molybdenum, and 1% vanadium.

High speed tool steels of the AISI T-1 and M-2 types were modified for evaluation of as-quenched and tempered hardness, wear resistance, machinability and transverse mechanical properties.

A variety of AISI 300 and 400 series stainless steels were modified with uranium and evaluated on the basis of recovery of uranium, distribution of uranium-bearing phases, and hot workability. Particular attention was focussed on the forgeability, unetched microstructure, transverse properties, and machinability of Types 303 and 416, which are resulphurized steels. Steels of the 300 series were subjected to a form of Huey test to determine their relative susceptibility to sensitization. Other corrosion tests were also carried out, but they are reported in Chapter 8.

LOW ALLOY STEELS

Temper Embrittlement of AISI 3310 Steel(1)

The impact properties of most alloy steels are impaired by tempering within or cooling too slowly through a certain temperature range below the Ac_1 transformation temperature. This phenomenon is known as temper embrittlement. Molybdenum is the only element known to inhibit susceptibility to temper embrittlement. The mechanism by which molybdenum operates is not known. The possibility that uranium might also be effective was investigated.

After examination of the literature, it was decided that AISI 3310 would be an ideal base analysis for investigation. Six 50 lb heats, representing the base composition, molybdenum-modified, and uranium-modified at four levels of uranium, were prepared in an induction furnace. All heats were killed with aluminum before addition of uranium. Uranium was added as uranium metal at the highest level and as 12 wt % ferro-uranium at the other levels. The uranium addition material, wrapped in aluminum foil, was plunged and stirred in just prior to tapping.

The heats were tapped between 1600°C (2910°F) and 1620°C (2950°F) directly into 50 lb cast iron ingot moulds.

The chemical analyses results for the experimental heats are given in Table 6.1.

TABLE 6.1

Chemical Analyses of Experimental Heats (Weight %)

Element	Specification Range for AISI 3310	Heat Designation					
		A	B	C	D	E	F
Carbon	0.08 to 0.13	0.13	0.14	0.15	0.15	0.14	0.14
Manganese	0.45 to 0.60	0.42	0.41	0.43	0.44	0.40	0.48
Silicon	0.20 to 0.35	0.26	0.23	0.31	0.28	0.21	0.31
Sulphur	0.025 max.	0.022	0.022	0.021	0.021	0.023	0.023
Phosphorus	0.025 max.	0.019	0.020	0.020	0.019	0.017	0.018
Chromium	1.40 - 1.75	1.43	1.48	1.48	1.46	1.59	1.62
Nickel	3.25 - 3.75	3.38	3.62	3.52	3.44	3.49	3.53
Uranium:							
(Total)	-	nil	0.014	0.033	0.056	0.110	nil
Acid Insol	-	nil	0.002	0.009	0.018	0.047	nil
Acid Sol*	-	nil	0.012	0.024	0.038	0.063	nil
Molybdenum	-	0.02	0.04	0.02	0.02	0.01	0.26

*By difference

The tapered ingots were heated to 1260°C (2300°F), then forged to 2 in. square billets and rolled to 1-1/8 in. bar. The average reduction ratio was 7 to 1. At this point, suitable lengths were cut for heat treatment and testing.

The bars to be tested in the embrittled condition were heat treated as follows:

(a) Austenitize at 920°C (1700°F) for 1 hour and oil-quench.

(b) Temper at 700°C (1300°F) for 1 hour and water-cool.

(c) Temper at 490°C (915°F) for 24 hours and air-cool.

The bars to be tested in the tough condition were given the following retempering:

(d) Temper at 700°C (1300°F) for 30 minutes and water-cool.

Duplicate tensile bars from each of the heats were tested in the embrittled and retoughened conditions. The average hardness and tensile results are presented in Table 6.2.

All samples subjected to the toughening treatment exhibited cup-cone fractures, and all samples in the embrittled condition had star-type (longitudinally split) fractures.

Charpy V-notch specimens were broken at a number of testing temperatures to determine the impact energy curves, and hence the transition temperatures, for each of the materials in both conditions of heat treatment. The curves are reproduced in Figure 6.1, and transition temperature data in Table 6.3.

TABLE 6.2

Average Results of Hardness and Tensile Tests

Heat	Condition	Hardness, R_B	UTS, psi	Upper Yield Point, psi	Yield Strength at 0.2% Offset, psi	Estimated Proportionality Limit, psi	% R.A.	% El in 2 in.
A	Tough	95	95,000	-	63,650	30,350	69.6	27.8
	Emb.	94.5	93,100	75,550	74,200	65,000	72.1	27.0
B	Tough	96	98,450	-	67,700	32,800	69.6	28.5
	Emb.	95.5	95,300	75,600	75,200	63,100	70.3	28.8
C	Tough	97	100,000	-	66,300	36,000	67.3	28.0
	Emb.	96	96,700	81,450	79,400	66,300	70.2	29.0
D	Tough	97	99,000	-	64,950	35,400	69.8	28.5
	Emb.	96	95,750	77,850	76,750	70,000	71.3	30.0
E	Tough	99	104,750	-	70,300	41,000	67.6	28.5
	Emb.	97.5	97,200	79,600	79,800	66,500	72.9	28.0
F	Tough	100	112,650	-	71,250	45,000	66.9	26.3
	Emb.	100	109,100	-	87,650	73,000	69.4	26.8

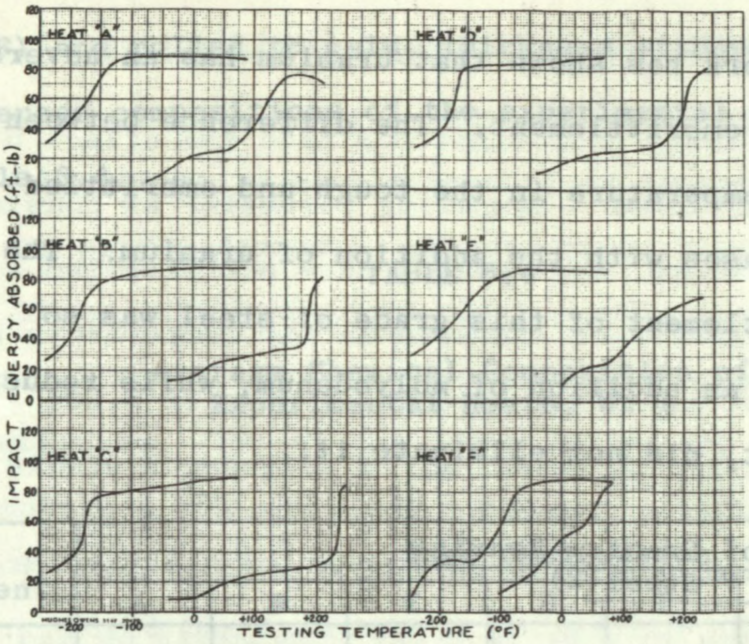


Figure 6.1 - Impact energy curves for test materials. The curve at the left of each graph is for the tough condition, and the curve at the right is for the embrittled condition.

TABLE 6.3

Transition Temperature Data

Heat Designation	30 ft-lb level TT$_T$ (°F) *	TT$_E$ (°F) **	Δ TT (°F) ***	40 ft-lb level TT$_T$ (°F)	TT$_E$ (°F)	Δ TT (°F)	50 ft-lb level TT$_T$ (°F)	TT$_E$ (°F)	Δ TT (°F)
A	-240	+73	313	-213	+97	310	-188	+110	298
B	-228	+95	323	-204	+180	384	-188	+185	373
C	-221	+181	402	-189	+229	418	-178	+235	413
D	-228	+153	381	-193	+186	379	-180	+201	381
E	-245	+90	335	-212	+112	324	-181	+140	321
F	-214	-32	182	-128	-19	109	-109	+2	111

* TT$_T$ - transition temperature of material in tough condition.

** TT$_E$ - transition temperature of material in embrittled condition.

*** Δ TT - change in transition temperature.

This work has shown that uranium has an adverse effect on temper embrittlement. The difference between the transition temperature in the tough and embrittled conditions increases with the addition of uranium. The degree of embrittlement of this grade of steel was so severe that even an addition of molybdenum, while reducing the embrittlement, did not eliminate it.

Some Properties of Uranium-Bearing 1% Cr, 1% Mo, 1% V Steel(2)

a - Introduction

When alloy steels such as those of the chromium-molybdenum-vanadium type are austenitized, quenched, and tempered at various temperatures for varying periods of time, they exhibit a characteristic peak hardness in the temperature range 480° to 590°C (900° to 1100°F). High secondary hardness and high secondary hardening temperature are necessary attributes of a high temperature structural steel.

The influence of uranium on the secondary hardening characteristics, creep properties and microstructure of a steel intended for steam turbine rotors was investigated on a statistical basis. The 50 lb induction heats were split and cast into three 12 lb ingots with varying uranium contents. The 2 in. square ingots were heated to 1040°C

(1900°F) and rolled to $\frac{1}{2}$-in. thickness without difficulty. The average compositions of the experimental steels are in Table 6.4.

TABLE 6.4

Average Chemical Composition of
Experimental Heats, Wt %

Element	Heat Designation						
	A	B	C	D	E	F	G
Carbon	0.253	0.243	0.220	0.217	0.303	0.283	0.250
Manganese	0.93	0.96	0.82	1.02	0.90	0.90	0.75
Silicon	0.11	0.08	0.20	0.13	0.23	0.10	0.09
Sulphur	0.023	0.025	0.025	0.023	0.028	0.021	0.025
Phosphorus	0.008	0.007	0.007	0.010	0.002	0.002	0.005
Chromium	1.00	0.92	0.87	1.05	0.98	1.04	1.39
Molybdenum	1.14	1.04	0.95	0.96	0.84	1.07	0.98
Vanadium	1.25	1.07	1.03	1.06	0.97	1.40	1.07
Aluminum *	0.067	0.069	0.003	0.09	0.057	0.064	0.03
**	0.067	0.064	n.d.	0.10	0.265	0.060	0.03
***	0.063	0.199	0.284	1.17	0.157	0.136	0.03
Uranium *	0.0003	0.0005	0.0002	0.024	0.0003	0.001	0.0008
**	0.063	0.039	0.087	0.045	0.114	0.060	0.110
***	2.110	0.360	0.270	1.10	0.60	2.12	0.509
Titanium *			0.03				
**			0.46				
***			0.39				

* - first ingot
** - second ingot
*** - third ingot

b - Tempered Hardness and As-quenched Hardness

Preliminary investigations into the effect of uranium on the hardness - tempering parameter at constant time (2 + 2 + 2 hours, air-cooled) have not revealed a statistically significant increase in the temperature at which the maximum secondary hardness occurs in 0.25% carbon, 1% chromium, 1% vanadium, 1% molybdenum steels.

This has since been confirmed on a larger scale for similar steels containing 5% chromium and 0.45% carbon(3).

Investigations into the effect of tempering time and temperature are in progress.

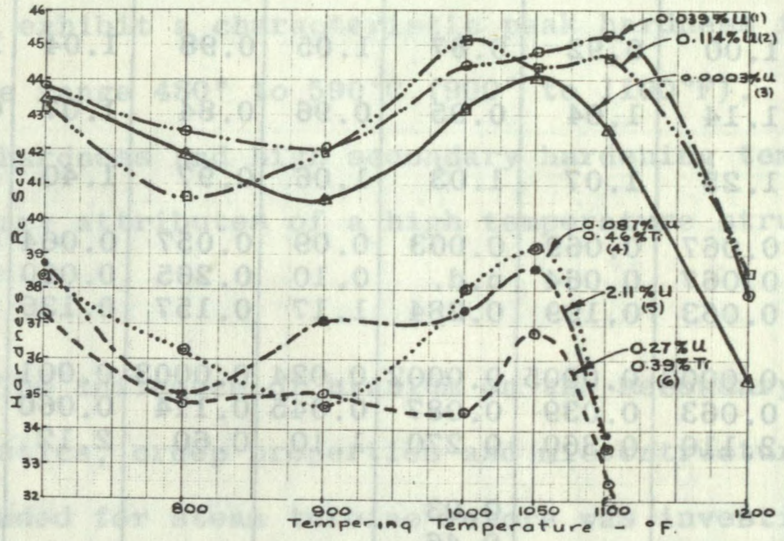


Figure 6.2 - Tempering curves showing the effect of carbon depletion of the matrix.

The hardness curves, Figure 6.2, show some evidence that carbon fixation by uranium and titanium has lowered the effective carbon content of the austenite. All of the curves represent uranium-bearing steels, as shown. Three of these curves are an average of 10 Rc below the others although they all have similar total carbon contents. Two of the lower curves are for steels which contain 0.39% and 0.46% titanium, a very strong carbide former, and the other is for steel with 2.11% uranium but no titanium. The 2.11 wt % of uranium is equivalent to 0.44 wt % titanium on an atomic basis.

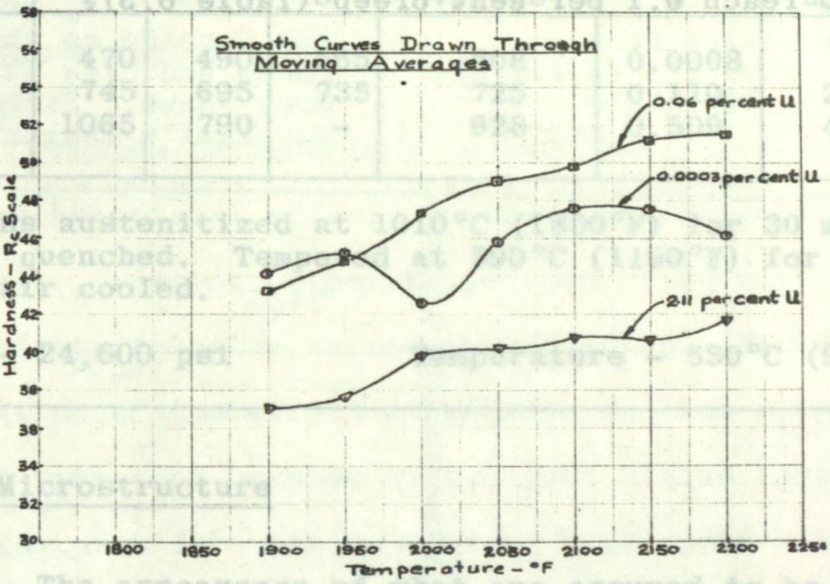


Figure 6.3 - Hardness Versus Temperature Curves for Specimens Quenched in Water from Various Austenitizing Temperatures.

Reference to Figure 6.3 shows that austenitizing temperatures in the range 1010° to 1230°C (1850° to 2250°F) do not dissolve the uranium carbide formed at the 2.11% uranium level. This conclusion has statistical significance. No statistically sound inferences may be made about the slope of the curves using the available data.

c - Creep Properties

There is an indication from the results of 1000 hour creep tests that the 0.11% uranium addition produces a significant improvement in the per cent creep at 1000 hours and a corresponding increase in the time required to reach 0.1 per cent creep (Table 6.5).

TABLE 6.5

Creep Properties of Experimental Steel

Specimen Number	Creep in 1000 hours, Per Cent (Heat 4491)				Uranium, %	Decrease in Creep %
	Replicates			Arithmetic Average		
	1	2	3			
U-1	0.142	0.140	0.148	0.143	0.0008	-
U-2	0.116	0.132	0.121	0.123	0.110	20
U-3	0.097	0.114	-	0.106	0.509	37

Specimen Number	Hours to Reach 0.1 Per Cent Creep				Uranium, %	Increase in time, hours
	Replicates			Arithmetic Average		
	1	2	3			
U-1	470	490	565	508	0.0008	-
U-2	745	695	735	725	0.110	217
U-3	1065	790	-	928	0.509	420

Specimens austenitized at 1010°C (1850°F) for 30 minutes and oil quenched. Tempered at 590°C (1100°F) for 2 hr + 2 hr air cooled.

Stress - 24,600 psi Temperature - 530°C (984°F)

d - Microstructure

The appearance of what are assumed to be the monocarbide, UC, and the epsilon phase, UFe_2, in the as-cast steel is shown in Figures 6.4 and 6.5. The appearance of UC and/or UFe_2, after hot rolling is shown in Figures 6.6 and 6.7.

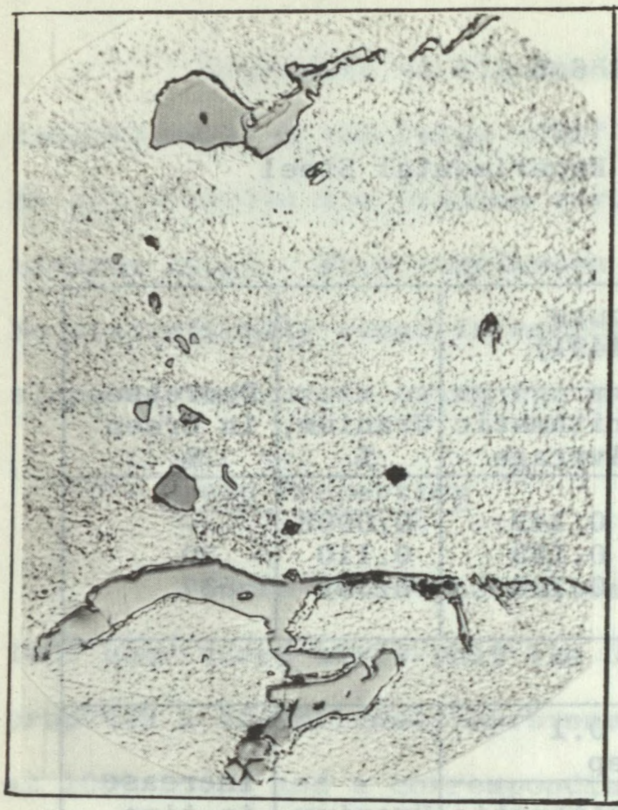


Figure 6.4 - Heat 4358, Specimen IC, As-Cast, Furnace-Cooled From 1040°C (1900°F). (2.11% U). Etched in Villela's Reagent. X750

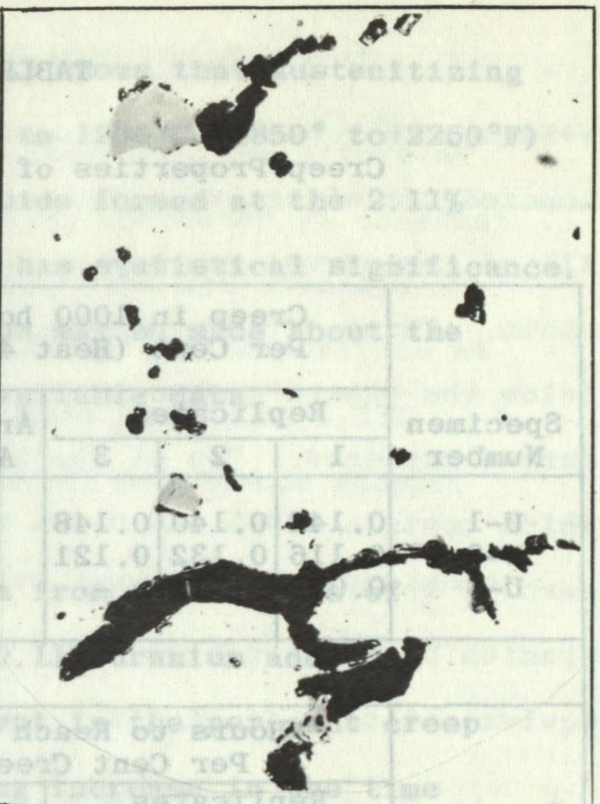


Figure 6.5 - Same Field As In Figure 6.4, Showing the Carbide as the Dark Phase and UFe_2 as the Grey Phase. Etched in Murakami's Reagent. X750

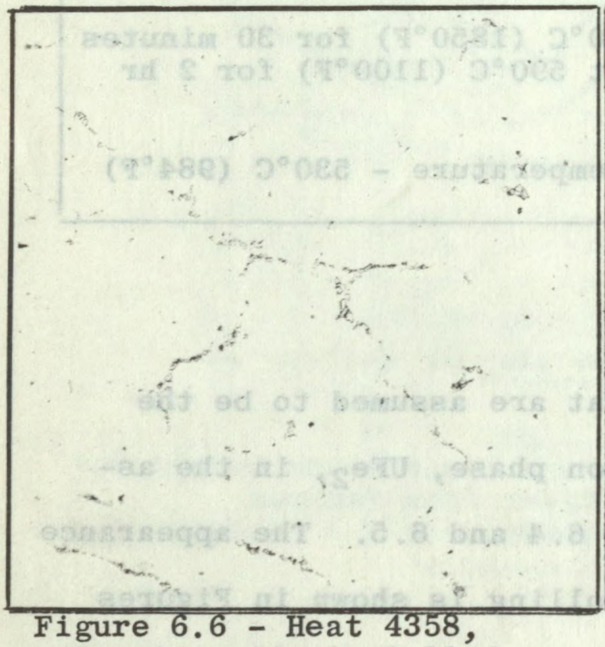


Figure 6.6 - Heat 4358, Specimen IC, As-Rolled. (2.11% U). Etched in Nital. X100

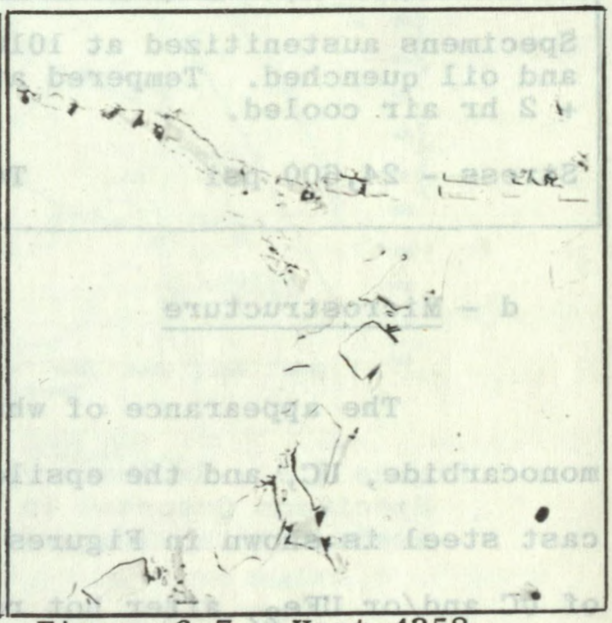


Figure 6.7 - Heat 4358, Specimen IC, As-Rolled. (2.11% U). Etched in Nital X750

HIGH SPEED TOOL STEELS(4)

General

The service performance of high speed tool steel depends on the maintenance of high hardness and wear resistance at the temperatures developed at cutting edges. Present day commercial high speed tool steels contain one or more of the elements, vanadium, molybdenum, tungsten and chromium. All these elements form hard, stable carbides, and together or singly form complex carbides with iron. Steels containing these elements display secondary hardening when tempered in the range 600 to 700°C (1110 to 1290°F). This is an age hardening process involving precipitation of coherent alloy carbides.

Uranium carbide (UC) is hard and stable and thus might have beneficial effects on the wear resistance of tool steels. However, other properties of UC cast doubt on its ability to cause secondary hardening. Nevertheless, investigation of the effect of uranium on high speed tool steels is warranted because extravagant claims have been made in the past for uranium-bearing high speed steels. Several trial heats were, therefore, prepared in order to assess the effects of uranium additions.

Compositions

So as to include both molybdenum and tungsten types, the steel compositions were based on the AISI Types T-1 and M-2, with uranium replacing part of the normal alloy content. The analyses are reported in Table 6.6.

TABLE 6.6

Compositions of Steels Tested

Material	Percentage of Element								
	C	Mn	Si	W	Cr	V	Mo	U	S
AISI T-1	0.70	0.30	0.30	18.00	4.00	1.00	-	-	-
AISI M-2	0.85	0.30	0.30	6.00	4.00	2.00	5.00	-	-
Heat 1	0.89	0.54	0.63	8.84	4.36	1.95		4.70	-
Heat 2	0.90	0.43	0.59	6.93	4.78	1.92	-	7.24	-
Heat 3	1.09	0.48	0.39	7.04	4.72	1.79	-	1.07	-
Heat 4	0.96	0.40	0.44	3.91	3.56	2.80	4.45	4.44	-
Heat 5	0.78	0.27	0.21	1.93	3.51	2.24	5.47	5.3	0.1

Results

a - Hardness

The material from Heat 1, containing 4.7% uranium, had an annealed hardness of 16 Rc, which is satisfactory for machining, and could be air-hardened from 1205°C (2200°F) to 65 Rc. High hardness was maintained even after tempering at high temperatures. Hardnesses of 63, 62, 57 and 52 Rc were obtained at 540°C (1000°F), 595°C (1100°F), 650°C (1200°F) and 705°C (1300°F) respectively. These results compare favourably with standard high speed steels.

Heat 2, containing 7.2% uranium, was cast into a 50 lb ingot and forged without difficulty to a 2 in. by 1 in. flat. The maximum as-quenched hardness obtainable with this alloy was only 63 Rc. It is probable that at this higher uranium level the uranium depleted the matrix of sufficient carbon to prevent the development of full hardness.

Heat 3, with 7% tungsten and 1% uranium, and Heat 4, with 4% tungsten, 4½% molybdenum and 4½% uranium, both exhibited satisfactory hardening, as shown in Table 6.7. Figure 6.8 shows the tempering behaviour of these steels compared with published values for commercial Types M-2 and T-1.

TABLE 6.7

Hardness Produced by at Various Austenitizing Temperatures

Heat	Hardness, Rc, After Austenitizing at Various Temperatures, °F					
	1800	1900	2000	2100	2200	2300
1	45	52*	58	63	65	65
2	36	41	47½	53½	57½	63
3	-	59	63	65	65	65
4	-	47	53	59*	64	66

* - Interpolated values

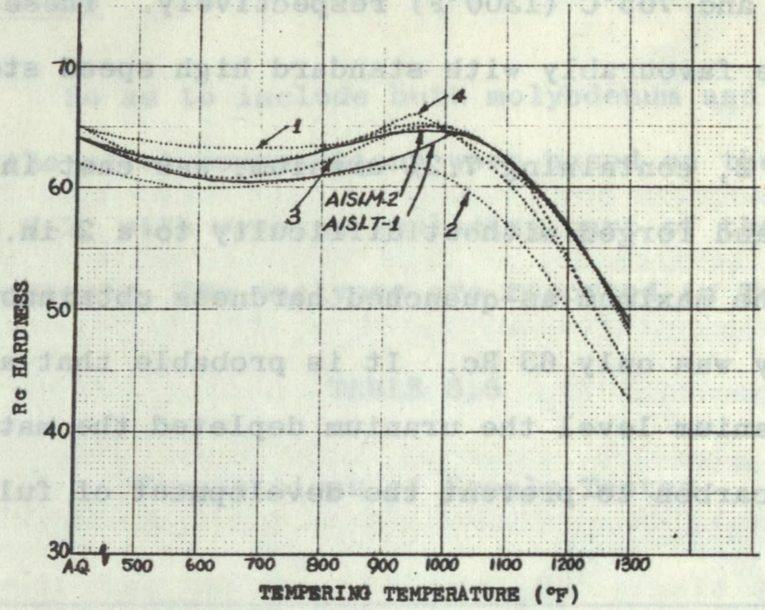


Figure 6.8 - Hardness Versus Tempering Temperature Curves for Experimental and Commercial Steels.

An additional heat, containing 0.1% sulphur, was made based on the M-2 composition, to investigate the effect of uranium on the free-machining type of high speed steel. When forged, this material did not show the usual sulphide stringers, but rather, exhibited small evenly distributed sulphides. This effect should produce noticeable improvements in transverse properties and possibly in machinability, but these properties have not been assessed to date.

b - Accelerated Service Tests

Tool bits have been prepared from these experimental materials and accelerated service tests are being carried out to assess the wear properties. No results are available for presentation.

THE "300" SERIES STAINLESS STEEL (5)

Introduction

Uranium was added to the 300 series stainless steels to assess its effect on stabilization, mechanical properties, machinability, and resistance to corrosion.

Austenitic stainless steels may be stabilized by elements that form carbides that are more stable and that form at higher temperatures than chromium carbides. Uranium has strong carbide forming tendencies, and thus was used to stabilize Type 304 stainless steel.

The effect of uranium on corrosion resistance was studied, since other work had shown uranium to have some effect in this field.

The mechanical properties and machinability of resulphurized Type 303 stainless steel containing uranium were investigated when it was noted that uranium had a high affinity for sulphur.

Uranium Addition and Yield

The addition of uranium to the laboratory melts was carried out as described in Chapter 3. No advantage was found for the use of ferro-uranium (50% U) rather than uranium metal. The average yield of uranium for the 300 series stainless steels was 77%, with a range of 45 to 86%.

Both total uranium and acid insoluble uranium analyses were carried out. The average content of acid insoluble uranium for Types 304, 309, and 316 laboratory steels was approximately 0.25%. However, when sulphur was present as in Type 303 (resulphurized), the acid insoluble uranium content averaged only 0.10%.

A 1500 lb ingot (13 in. square, 42 in. high) of Type 304 steel was teemed at a commercial site with 20 lb of uranium per ton of metal added during pouring. The chemical composition was as follows:

C	Mn	Si	Cr	Ni
0.07	1.41	0.61	18.39	10.21

Metallic uranium in aluminum foil packages was added during the teeming of the ingot. The ingot was forged to 4 in. by 6 in. billet (giving a total length of approximately 175 in.) and sectioned. Table 6.8 indicates the uranium analyses obtained at various locations along the length. No significant differences were found for drillings taken at the centre or edge of the billet sections, and the results reported are the averages of these determinations.

TABLE 6.8

Average Uranium Contents Along the Billet Length of the Commercial Steel

Sample No.	Distance From Top, inches	Total Uranium %	Acid Insoluble U, %
1	6	0.25	0.06
2	21	0.35	0.06
3	62	0.36	0.06
C1	81	0.38	0.06
C2	97	0.36	0.06
4	116	0.39	0.07
5	128	0.38	0.07
6	140	0.40	0.09
7	152	0.41	0.06
8	164	0.46	0.14

The bulk of the metal was reasonably uniform with respect to uranium, the exceptions being the low content in the hot top and the high content near the bottom. In all cases the acid insoluble uranium contents were low. Some of the uranium was added too quickly, and it is apparent that it did not go into the melt. This would account for the relatively low uranium yield of approximately 40%. The ingot was forged from 1205°C (2200°F) and some difficulty was encountered with the bottom end where the uranium content was higher.

Hot Working

The 300 series stainless steels were capable of being forged and rolled, although in some instances special considerations were necessary. Significantly, no difficulties were encountered with resulphurized grades modified with uranium.

Uranium may adversely affect the forgeability of Types 304, 309 and 316 by promoting the formation of ferrite or of eutectic UFe_2. Uranium may indirectly be considered as a ferritizer because it may deplete the matrix of carbon. A duplex structure of austenite and ferrite is less forgeable than a completely austenitic structure. UFe_2 impairs forgeability because the melting point of the UFe_2 - Fe eutectic is about 1080°C (1975°F), which is within the normal hot working temperature range. The amount of UFe_2 which may be tolerated has not been determined.

Type 303 is a resulphurized grade and generally is difficult to forge. However, with uranium levels up to 1.4% no difficulties were encountered. Two 360 lb ingots with 0.3 and 0.5% uranium were forged at a commercial site at 1205°C (2200°F) with better than average results.

Stabilization

Stabilization with titanium or niobium requires an addition of at least the stoichiometric amount required to combine with carbon, i.e., % titanium = at least 5 times % carbon, and % niobium = at least 10 times % carbon. On an analogous basis a uranium addition of 20 times % carbon was used.

The degree of stabilization or, conversely, the degree of sensitization was qualitatively evaluated using a modified Huey test(4). This test involves exposing the specimens to boiling 70% nitric acid for extended periods of time.

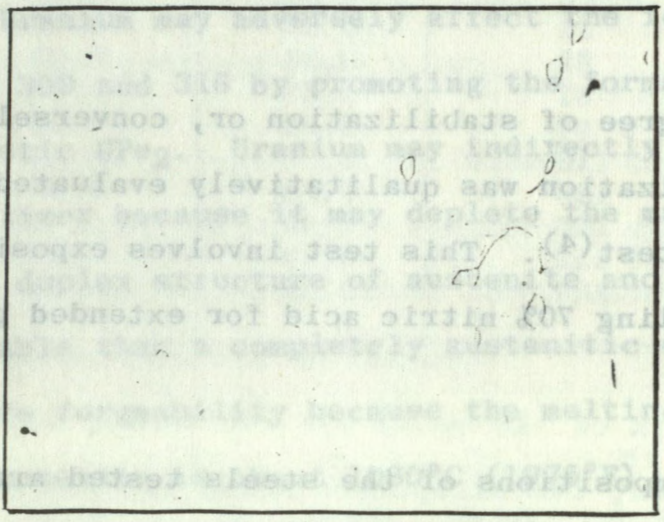
The compositions of the steels tested are given in Table 6.9.

TABLE 6.9

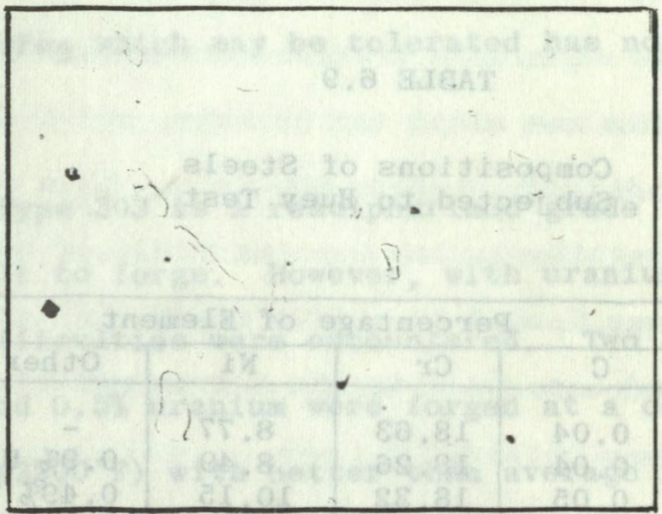
Compositions of Steels
Subjected to Huey Test

Type	Percentage of Element			
	C	Cr	Ni	Other
304	0.04	18.63	8.77	-
304	0.04	18.26	8.49	0.9% U
321	0.05	18.32	10.15	0.49% Ti
347	0.05	18.10	9.45	0.70% Nb

The Type 304 steels, produced in the laboratory, were forged, quench annealed, and held at 650°C (1200°F) for 1 hour (See Figure 6.9). The stabilized Types 321 and 347, commercially produced, were also given the latter heat treatment to precipitate chromium carbides (See Figure 6.10).

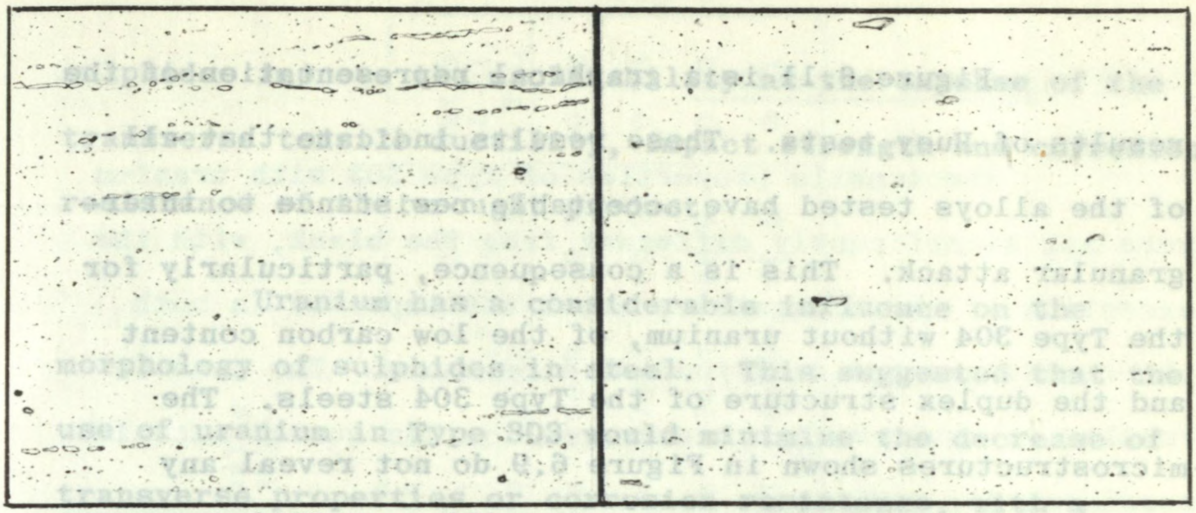


No Uranium



0.9% Uranium

Figure 6.9 - Type 303, With and Without Uranium, Quench Annealed and Held at 650°C (1200°F) for 1 Hour to Precipitate Chromium Carbides. Electrolytically etched in 10% NaCN. X500



AISI Type 321 AISI Type 347

Figure 6.10 - Commercially Produced Stabilized Stainless Steels in As-received Condition Plus 1 Hour at 650°C (1200°F). Electrolytically etched in 10% NaCN. X500

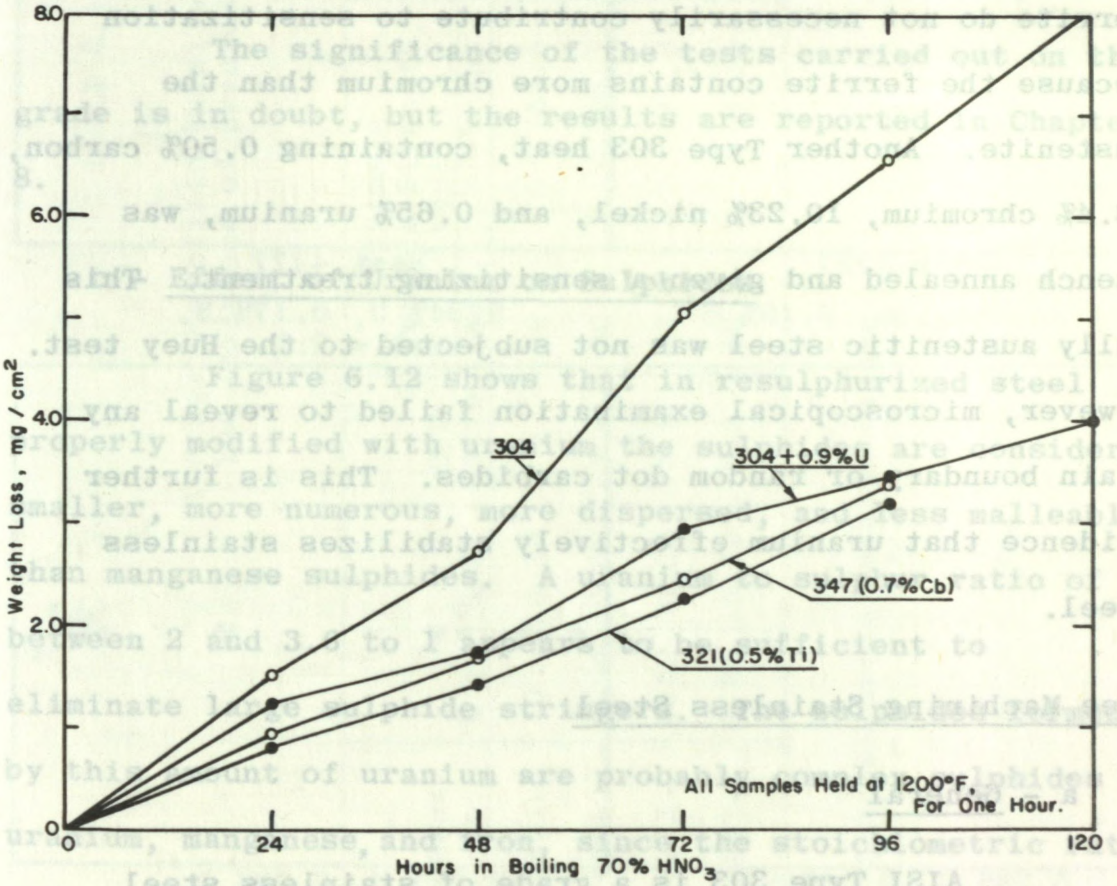


Figure 6.11 - Results of Huey Tests

Figure 6.11 is a graphical representation of the results of Huey tests. These results indicate that all of the alloys tested have acceptable resistance to intergranular attack. This is a consequence, particularly for the Type 304 without uranium, of the low carbon content and the duplex structure of the Type 304 steels. The microstructures shown in Figure 6.9 do not reveal any chromium carbides in the austenitic grain boundaries of the Type 304 with uranium, and only a minor amount in the austenitic grain boundaries of the Type 304 without uranium. The chromium carbides at the periphery of the ferrite do not necessarily contribute to sensitization because the ferrite contains more chromium than the austenite. Another Type 303 heat, containing 0.50% carbon, 18.4% chromium, 10.23% nickel, and 0.65% uranium, was quench annealed and given a sensitizing treatment. This fully austenitic steel was not subjected to the Huey test. However, microscopical examination failed to reveal any grain boundary or random dot carbides. This is further evidence that uranium effectively stabilizes stainless steel.

Free Machining Stainless Steel

a - General

AISI Type 303 is a grade of stainless steel containing a minimum of 0.15% sulphur. The manganese sulphides improve the machinability at the expense of the transverse tensile ductility, impact strength and corrosion resistance of the wrought product.

Uranium has a considerable influence on the morphology of sulphides in steel. This suggested that the use of uranium in Type 303 would minimize the decrease of transverse properties or corrosion resistance, with a favourable, or at least not unfavourable effect on the improved machinability of this grade.

b - Corrosion

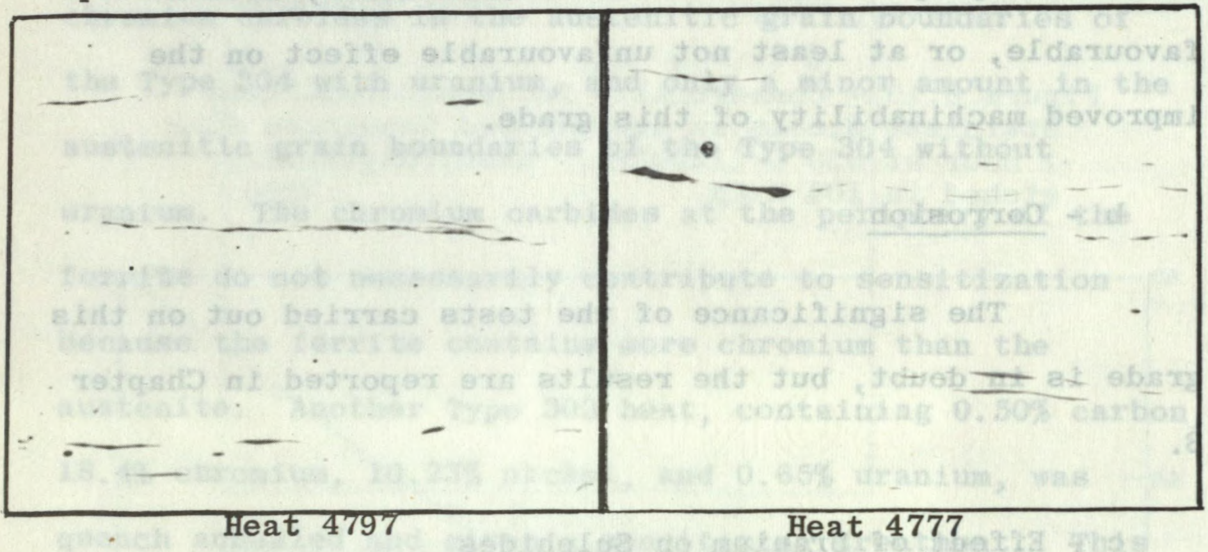
The significance of the tests carried out on this grade is in doubt, but the results are reported in Chapter 8.

c - Effect of Uranium on Sulphides

Figure 6.12 shows that in resulphurized steel properly modified with uranium the sulphides are considerably smaller, more numerous, more dispersed, and less malleable than manganese sulphides. A uranium to sulphur ratio of between 2 and 3.6 to 1 appears to be sufficient to eliminate large sulphide stringers. The sulphides formed by this amount of uranium are probably complex sulphides of uranium, manganese, and iron, since the stoichiometric ratio of uranium to sulphur for the formation of uranium monosulphide is 7.5 to 1.

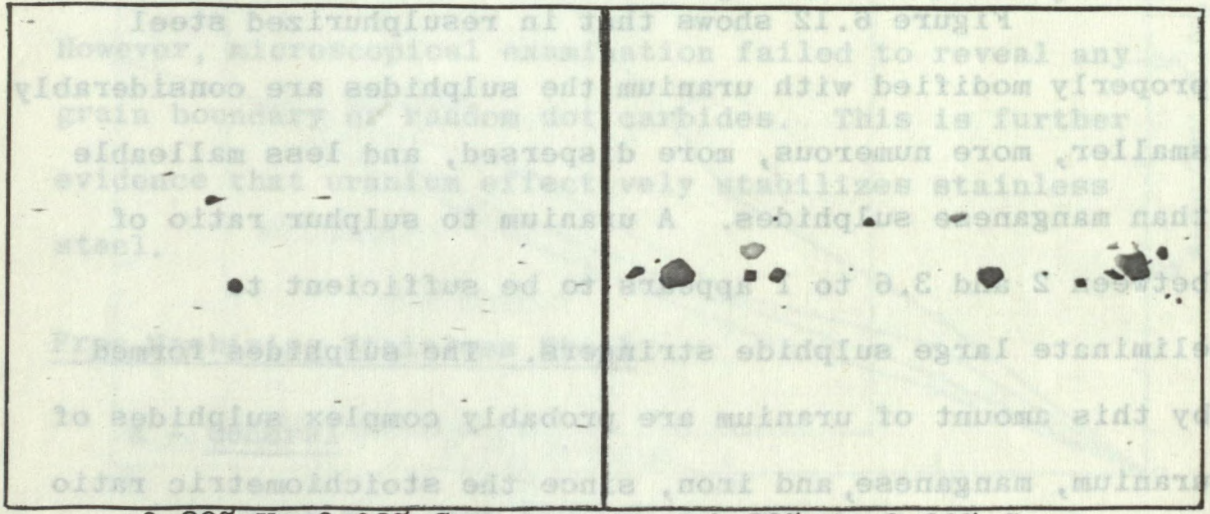
d - Tensile Properties

The tensile properties of Type 303 with uranium were not significantly different from the blank, with the exception of the elongation, which was improved in both the transverse and longitudinal directions. The tensile results in Table 6.10 are averages for ten quench annealed specimens for each heat.



Heat 4797
No Uranium, 0.19% S

Heat 4777
0.34% U, 0.17% S,
U:S = 2:1



0.29% U, 0.08% S,
U:S = 3.6:1

0.52% U, 0.09% S,
U:S = 5.3:1

Figure 6.12 - Longitudinal Microstructure of Type 303 Steels, Showing the Influence of Uranium on Sulphides, Unetched. X1000

TABLE 6.10

Average Hounsfield Tensile Properties Showing The Influence of Uranium in AISI Type 303

Heat No.	% U	% S	U/S Ratio	Ultimate Tensile Strength, kpsi		Yield Strength, 0.2% Offset, kpsi		% El. in 0.4 in.		Ratio of El. T/L
				Long.	Trans.	Long.	Trans.	Long.	Trans.	
4691-1	0	0.19	0	89.2	85.5	31.8	31.5	59.8	49.3	0.82
4786	0.29	0.08	3.6	90.4	89.7	32.5	35.8	76.5	65.2	0.86
4763	0.52	0.09	5.8	93.7	91.8	30.8	32.4	74.0	68.0	0.92
4691-2	1.38	0.19	7.3	96.7	97.5	40.4	43.0	62.8	31.8*	0.51

*Samples broke outside gauge.

e - Machinability

Machinability is being evaluated on the following grades:

Type 303 (standard resulphurized grade)
Type 303 Se (selenium added)
Type 303 + 0.29% U (heat 4786)
Type 303 + 0.52% U (heat 4763)

No results are available to date.

THE "400" SERIES STAINLESS STEELS (6)

Introduction

An examination of the effects of uranium on the AISI 400 series stainless steels has been undertaken. The wide scope of the investigation has necessarily resulted in some facets of the programme receiving superficial attention. Some of the results, while meagre, are nevertheless reported in order to illustrate problems which exist and to indicate direction for further study. Other aspects of the programme, such as-quenched hardness, temper hardness, corrosion resistance, and the transverse properties of resulphurized free-machining grades, have been studied in more detail.

Production of Steels

The steels used for this work were prepared in either a 50 lb or a 400 lb induction furnace. In general, Armco iron was used as melting stock, with low-carbon ferrochromium the principal additive. Melting and pouring were carried out under stmospheric conditions. The uranium was added to the furnace for the 50 lb heats, and to the pouring ladle for the 400 lb heats. The uranium additive was metallic uranium in most cases, and ferro-uranium in a few cases. No advantage in yield was observed when uranium was added as ferro-uranium rather than as uranium metal. In all cases aluminum was used as a deoxidizer, some of it being added as foil wrapped around the uranium additive to minimize oxidation of the uranium. Except in the case of special forging tests, all materials were forged and rolled to break up the as-cast crystal structure prior to heat treatment and preparation of test pieces.

Composition of Heats

Analyses of all the heats which are discussed in this section are given in Table 6.11.

TABLE 6.11

Analyses of Steels

AISI Type	Structure	Element, %										Sample
		Total U	Cr	Ni	C	N	Mn	Si	S	P	Al	
403	Martensitic	Nil	13.7	-	0.1[illegible]		0.63	0.69	-	-	-	4456 A
		0.27	13.7	-	0.16	-	-	-	-	-	-	B
		0.67	13.6	-	0.16	-	-	-	-	-	-	C
		Nil	13.7	-	0.11	-	0.59	0.53	0.024	0.006	-	4469 A
		1.21	13.5	-	0.10	-	0.58	0.49	0.024	0.006	-	B
		Nil	12.5	-	0.11	0.022	0.34	0.20	0.024	0.016	0.0034	4598 A
		0.46	12.5	-	0.10	0.026	0.34	0.23	0.026	0.016	0.0041	B
		1.06	12.4	-	0.11	0.026	0.37	0.24	0.027	0.015	0.001	C
		2.71	12.1	-	0.09	0.036	0.37	0.29	0.027	0.014	0.0075	D
403 (Mod.)	Martensitic	Nil	11.8	1.96	0.10	0.018	1.83	1.62	0.020	0.019	0.100	4546 A
		0.48	11.7	1.89	0.09	0.020	1.78	1.59	0.020	0.018	0.031	B
		1.29	11.6	1.90	0.09	0.027	1.82	1.62	0.020	0.015	0.039	C
		1.87	11.5	1.82	0.11	0.041	1.81	1.59	0.017	0.014	0.058	D
		Nil	11.8	1.86	0.10	0.013	0.45	0.30	0.024	0.016	0.008	4639 A
		0.003	11.8	0.90	0.08	-	0.45	0.30	0.031	0.016	0.007	B
		0.0028	11.9	0.68	0.10	0.015	0.46	0.28	0.038	0.016	0.005	C
		0.24	11.8	1.94	0.09	0.016	0.45	0.29	0.024	0.016	0.005	D
		Nil	11.7	1.94	0.10	0.015	0.48	0.40	0.015	0.011	0.0032	4593 A
		0.96	11.2	1.96	0.11	0.014	0.48	0.43	0.017	0.011	0.0050	B
		0.75	11.4	1.87	0.10	0.012	0.52	0.45	0.018	0.011	0.0097	C
		1.30	11.4	1.88	0.11	0.015	0.52	0.54	0.018	0.011	0.0095	D
403 (Mod.)	Ferritic*	Nil	13.5	-	0.03	-	0.43	0.51	0.025	0.010	-	4473 A
		0.22	13.6	-	0.03	-	0.46	0.54	0.025	0.010	-	B
416	Martensitic	Nil	12.12	-	0.11	-	0.12	0.09	0.32	0.011		4746 A
		0.008	12.00	-	0.11	-	0.12	0.07	0.33	0.011	-	B
		0.014	12.12	-	0.11	-	0.12	0.07	0.27	0.011	-	C
		0.043	11.76	-	0.11	-	0.12	0.07	0.28	0.011	-	D
		0.051	12.78	-	0.10	-	0.08	0.07	0.33	0.012	-	E
		0.120	12.48	-	0.12	-	0.12	0.08	0.32	0.011	-	F
		0.33	12.04	-	0.10	-	0.15	0.08	0.29	0.011	-	G
		0.83	12.04	-	0.10	-	0.15	0.09	0.24	0.012	-	H
		1.39	11.68	-	0.10	-	0.15	0.11	0.23	0.011	-	I
		1.43	12.04	-	0.11	-	0.20	0.11	0.20	0.011	-	J
		1.19	11.88	-	0.12	-	0.20	0.14	0.27	0.011	-	K
		0.80	12.6	-	0.09	-	0.09	0.08	0.20	0.015	-	4779
		0.28	13.1	-	0.08	-	0.07	0.09	0.25	0.015	-	4787
430	Ferritic	Nil	14.0	-	0.04	-	0.65	-	0.024	0.008	0.04	4489 A
		0.35	14.1	-	0.04	-	0.75	0.51	0.025	0.008	-	B
		0.89	14.0	-	0.04	-	0.74	0.52	0.026	0.008	-	C
		1.43	13.8	-	0.04	-	0.70	-	0.024	0.008	0.08	D
		Nil	17.2	-	0.10	0.02	0.91	0.88	0.024	0.015	0.005	4669 A
		0.0036	17.5	-	0.10	0.02	0.91	0.89	0.024	0.015	0.003	B
		0.046	17.4	-	0.10	0.026	0.91	0.89	0.024	0.015	0.006	C
		0.27	17.2	-	0.10	0.033	0.88	0.89	0.024	0.015	0.006	D
440A	Martensitic	Nil	16.5	-	0.65	-	0.56	0.47	0.017	0.004	0.0075	4497 A
		0.244	16.5	-	0.65	-	0.52	0.46	0.019	0.004	0.023	B
446	Ferritic	Nil	24.6	-	0.20	0.06	0.76	0.76	0.021	0.020	0.001	4725 A
		0.042	24.7	-	0.20	0.06	0.86	0.76	0.020	0.020	0.001	B
		Nil	26.0	-	0.29	0.028	1.25	0.90	0.019	0.011	0.001	4683 A
		0.0037	25.4	-	0.28	0.017	1.43	0.95	0.020	0.011	0.004	B
		0.024	25.4	-	0.31	0.012	1.30	0.95	0.021	0.012	0.010	C
		0.19	25.2	-	0.29	0.007	1.44	0.96	0.021	0.011	0.004	D

* - 403, Modified, Ferritic steels had 0.63% and 0.64% Mo respectively.

Uranium Distribution

Most of the heats were poured into 12 lb sand-cast ingots. In order to establish whether or not uranium was dispersed uniformly, autoradiographs were prepared for forged billets and also, in the case of Heat 4683, for sectioned ingots. Figure 6.13 is an autoradiographic print of the ingots from the latter heat. The radioactive segregates are uniformly dispersed throughout ingots B, C, and D which contain different uranium levels. The base metal A, of course, gives a blank picture. The reservation should be made that the highest uranium level of this heat is only 0.2%. Higher uranium contents may or may not lead to greater segregation in ingots of this size.

Ingot A No U | Ingot B 0.0037% U | Ingot C 0.024% U | Ingot D 0.19% U

Figure 6.13 - Autoradiographic prints of Ingots From Heat 4683. X 1/2

Forging

All ingots, with the exception of those of the Type 446 (Heat 4725), were hot forged and rolled to suitable dimensions before machining and heat treatment of test specimens.

Some difficulties with hot shortness were encountered in the initial forging work at a temperature of 1095°C (2000°F). This led to a brief investigation of upset forging characteristics to establish a suitable forging temperature. The required number of $1\frac{1}{2}$ in. diameter, $1\frac{1}{2}$ in. long samples were machined from two as-cast ingots of Type 403 stainless steel, one with no uranium, and the other with 1.2% uranium (Heat 4469). Samples were upset forged over a range of temperatures from 980° to 1230°C (1800° to 2250°F), to progressively thinner sections or to failure, using 1, $\frac{1}{2}$, and $\frac{1}{4}$ in. steel spacers. The results showed that 1010°C (1850°F) was the maximum temperature at which the uranium-bearing steel could be reduced to $\frac{1}{2}$ in. thickness. The uranium-free control could be forged to $\frac{1}{4}$ in. without difficulty.

Figure 6.14, illustrating the unetched microstructure of uranium-bearing Type 410 stainless steel, shows the grain boundary eutectic that was responsible for the hot shortness. Subsequent to the upset tests, a forging temperature of 1010°C (1850°F), which is just below the eutectic temperature, was found to be satisfactory for all the steels provided they were not allowed to cool too much during working.

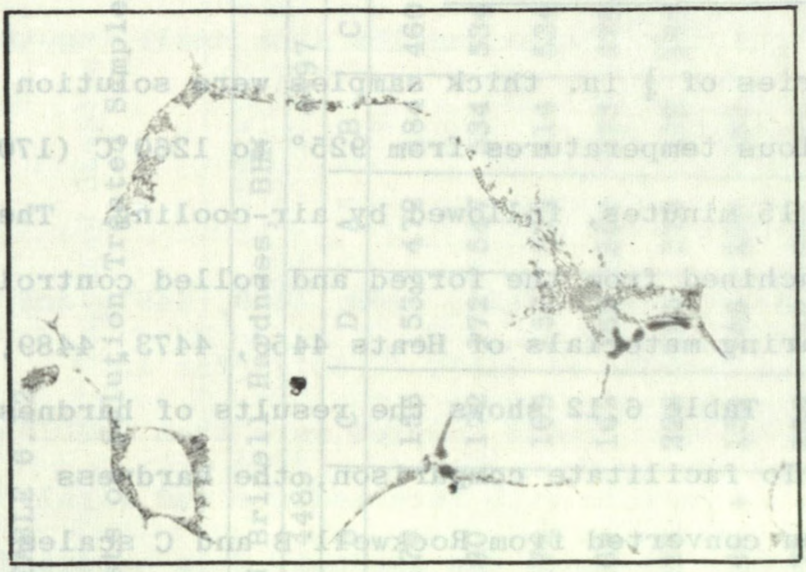


Figure 6.14 - Unetched Microstructure of Ingot 4469 B (1.21% uranium) Showing UFe_2/Fe Eutectic Which Caused Hot Shortness. X1000

Resulphurized Type 416 and 430F free machining grades have consistently forged and rolled well at 1175°C (2150°F). It is apparent that sufficient uranium is combined with sulphur and sometimes carbon in these steels to prevent the formation of UFe_2.

In view of the importance of forgeability to commercial acceptability, a study will be made of forging characteristics of martensitic, ferritic, and duplex steels as well as the resulphurized grades of the "400" series. For this purpose both drop weight and hot twist tests will be conducted.

Air-quenched Hardness After Solution Treatment at Various Temperatures

A series of ¼ in. thick samples were solution treated at various temperatures from 925° to 1260°C (1700° to 2300°F) for 15 minutes, followed by air-cooling. The samples were machined from the forged and rolled control and uranium-bearing materials of Heats 4456, 4473, 4489, 4497, and 4546. Table 6.12 shows the results of hardness measurements. To facilitate comparison, the hardness values have been converted from Rockwell B and C scales to the Brinell scale.

There appears to be a general trend toward a lower peak hardness, as well as lower hardnesses for each particular solution temperature when uranium is present. This supports the supposition that uranium carbides are so stable at elevated temperatures that uranium depletes the carbon content of the matrix. Furthermore, microscopical examination revealed massive uranium carbides which had not dissolved at the soaking temperatures used.

TABLE 6.12

Results of Hardness Tests on Solution Treated Samples

Solution Temp., °F	Converted Brinell Hardness, BHN													
	4456		4473		4489				4497				4546	
	A	B	A	B	A	B	C	D	A	B	C	D	A	B
1700	352	332	216	172	172	176	156	153	472	484	460	415	404	415
1800	352	437	216	190	195	190	172	172	547	534	534	534	-	426
1900	372	437	195	185	190	172	169	159	573	614	534	534	342	352
2000	415	352	195	169	185	169	162	165	560	573	573	372	372	352
2100	534	534	228	205	240 +	228	228	195	372	372	393	352	496	472
2200	554	448	219	190	240 +	240 +	159	188	290	283	-	297	460	431
2300	437	472	-	180	237	171	156	169	255	360	-	258	460	-

The validity of any conclusions based on these preliminary hardness results is in doubt for two reasons. Firstly, the differences in hardness between each steel, with and without uranium, were generally relatively small, possibly within the limits of experimental error. Secondly, the results are based on single samples from small ingots only.

Tempered Hardness

Samples from heats 4456, 4473, 4489, 4497, and 4546 were solution treated at 955°C (1750°F) for 15 minutes, and air-cooled. These samples were then double-tempered for 1 hour periods with intermediate and final air-cooling. Table 6.13 shows the hardness data obtained for various tempering temperatures.

Slight secondary hardening is evident over the range 315° to 480°C (600° to 900°F) in all the materials tested. The degree of secondary hardening was estimated as the difference between the lowest tempered hardness, before secondary hardening, and the maximum secondary hardness. Uranium additions apparently made no significant difference in the degree of secondary hardening. In general, uranium appears to lower the hardness over the whole tempering range.

TABLE 6.13

Hardness Data For Quenched and Tempered Samples

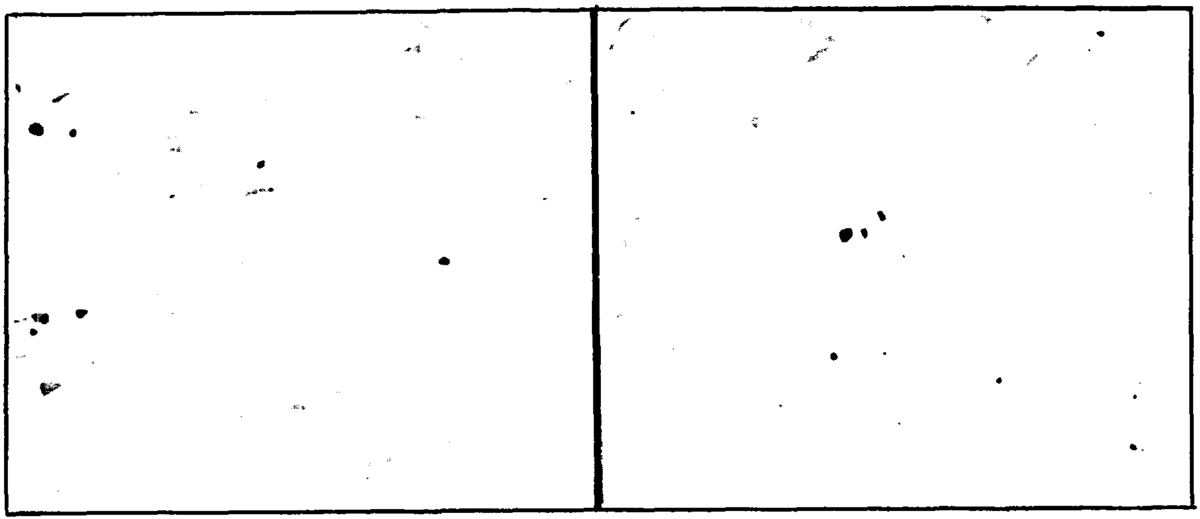
Heat	% U	Scale	Hardness After Tempering at Temperature Shown, °F											
			As-quenched	500	600	700	800	900	1000	1100	1200	1300	1400	1500
4456	Nil	Rc	42.5	40.5			39.5	39.5	25.5	23.5	20.5			
	0.27	Rc	39.5	38			39.5	37.5	26.5	24	17.5			
4497	Nil	Rc	52	50	48	49	51.5	51	36	33		23		
	0.244	Rc	48.5	47.5	46.5	51.5	49	51.5	36	32		23		
	0.77	Rc	51	48	46	50	46	50	33.5	25		13		
	0.97	Rc	48.5	46	47.5	47	47	47	35	29		18		
4546	Nil	Rc	43	40	38.5	41	40	39.5	30.5	27.5				
	0.48	Rc	40.5	41	40	41	41.5	39	29	28	27	22.5		
	1.29	Rc	39.5	40	41	42	42.5	41	32	30	27.5	24		
	1.87	Rc	40	40	41	41.5	42	39	33.5	31	28	27		
4473	Nil	Rb	92	90.5			94	91	88.5	85	84	81.5	81.5	86.5
	0.22	Rb	87	86			88	85.5	84	81	80.5	78	77.5	84.5
4489	Nil	Rb	86	87	86	88	88.5	88	84	83		80.5	74	71.5
	0.35	Rb	87	87	87	88.5	87	89	82.5	82.5		80.5	71	71
	0.89	Rb	82	80	80	81	84	86	79	78		77	73	71
	1.43	Rb	89	85.5	83	86	89.5	86	82	81		80	74.5	72.5

Tempering these steels in the range where secondary hardening occurs results in 475°C (885°F) embrittlement and impairment of corrosion resistance. Addition of uranium did not result in any significant change in the temperature of maximum secondary hardening, and hence there would be no change in the temperature range that is to be avoided in these steels.

Transverse Properties of Resulphurized AISI 400 Series Steel

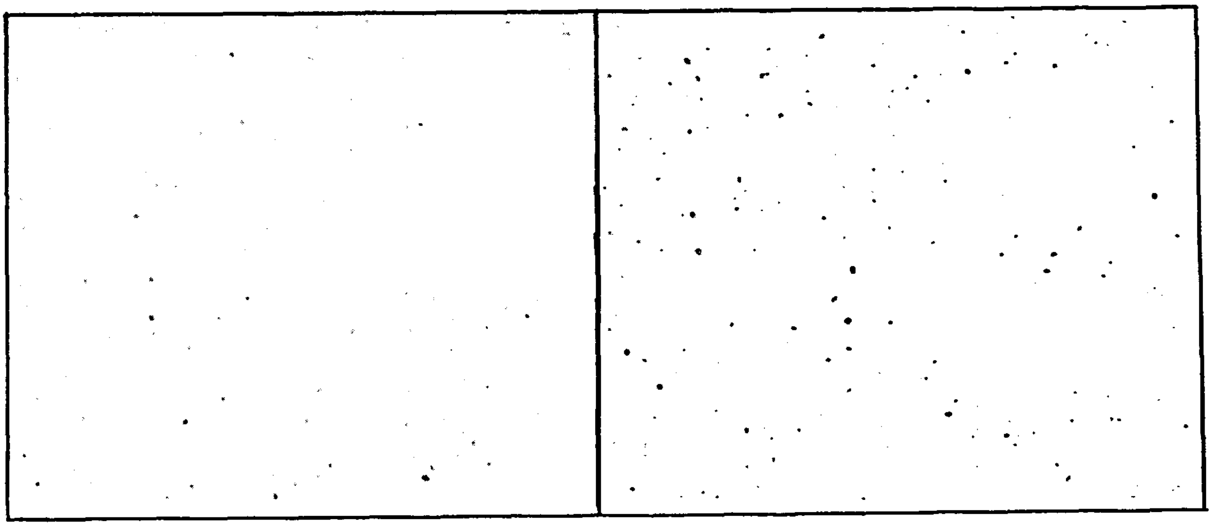
For a preliminary investigation of the effect of uranium on the transverse properties of wrought resulphurized AISI 400 series steel, a 50 lb induction heat (No. 4746) of Type 416 stainless steel was prepared. Ten ingots were cast, the first a uranium-free control, and the others containing nine different levels of uranium. The 1 in. diameter ingots were hot rolled to 1/16 in. strip. Hounsfield tensile specimens were cut from a number of locations with both transverse and longitudinal orientations. All specimens were solution treated at 1095°C (2000°F), oil quenched, then double tempered for 1 hour periods at 650°C (1200°F) with intermediate and final oil quenches.

From the effect of the uranium on the appearance of the sulphides, as illustrated by Figure 6.15, it was expected that considerable improvements in transverse tensile properties would be evident. The average results of the tensile tests are presented in Table 6.14. It is apparent that the addition of uranium consistently increased the transverse ductility and that there was a slight trend towards higher ratios of transverse to longitudinal ductility at the higher uranium levels tested, i.e., at the higher per cent uranium/per cent sulphur ratios. However the validity of any conclusions drawn from these preliminary results is in doubt, due to the small quantity of materials available, and to the variations inherent with testing the small Hounsfield specimens.



U - Nil
S - 0.32%
U/S - 0

U - 0.33%
S - 0.29%
U/S - 1.1



U - 0.83%
S - 0.24%
U/S - 3.5

U - 1.43%
S - 0.20%
U/S - 7.2

Figure 6.15 - Effect of Uranium Content on Sulphides in Heat 4746. The sample were polished in the plane of rolling. Sufficient uranium results in the sulphide inclusions being present as many fine inclusions, rather than as stringers. X150

TABLE 6.14

Tensile Properties of Samples From Heat 4746 (Type 416)

Sample	% S	% U	Ultimate Tensile Strength		0.2% Offset Yield Strength		% Elongation		
			Trans., kpsi	Long., kpsi	Trans., kpsi	Long., kpsi	Trans. kpsi	Long.	$\frac{\text{Trans.}}{\text{Long}}$
A	0.32	Nil	90.6	92.4	71.5	70.6	11.4	19.2	0.59
B	0.33	0.008	88.6	-	70.3	-	17.5	-	-
C	0.27	0.014	85.6	91.2	65.6	68.4	13.2	19.2	0.69
D	0.28	0.043	89.4	91.2	70.6	69.6	12.5	19.6	0.64
E	0.33	0.051	88.2	93.8	70.1	69.9	13.9	19.6	0.71
F	0.32	0.120	92.9	93.6	73.9	68.5	12.1	22.1	0.55
G	0.29	0.33	91.4	-	71.2	-	15.7	-	-
H	0.24	0.83	93.7	93.2	75.7	72.0	20.4	20.0	1.02
I	0.23	1.39	96.0	97.5	79.9	74.9	13.2	20.0	0.66
J	0.20	1.43	95.6	98.6	79.7	79.3	14.0	20.0	0.70

In order to further investigate the apparent improvement at the higher uranium levels, two 350 lb heats (No. 4779 and No. 4787) were prepared. The lower halves of the two ingots were forged to 1 in. thick by 8 in. wide slabs, and then rolled to 1/8 in. thick strip.

In order to determine whether the results would be affected by segregation, the strips were autoradiographed on both sides and the superimposed films were used to select three sampling zones, two free of segregation, and the third containing the heaviest segregation. Flat tensile and Charpy V-notch impact specimens were prepared. In the case of the segregated sampling zone the samples were cut so that the gauge lengths and notches were centred in the segregated areas.

The samples were solution treated at 925°C (1700°F) for 30 minutes, air-cooled, then tempered at 650°C (1200°F) for 1 hour and air-cooled.

The results of the tensile and impact testing are shown in Table 6.15.

TABLE 6.15

Average Results of Tensile and Impact Tests on Heats 4779 and 4787

Heat	% S	% U	Sampling Zone	Sample Orientation	Room Temperature Charpy-V Impact		No. of Tensile Samples	Average UTS, kpsi	Average YS, kpsi	Average % El.	Elong. T/L
					No. of Samples	ft-lb					
4479	0.20	0.80	A	T	6	4	8	96.8	74.0	13.8	0.90
				L	6	15	8	95.5	76.5	15.3	
			B	T	5	4	8	96.0	76.2	14.8	0.98
				L	6	14	8	95.4	74.1	15.1	
			C*	T	6	4	7	81.6	73.7	13.9	0.91
				L	6	14	8	92.8	65.4	15.3	
4787	0.25	0.28	A	T	6	8	8	90.9	69.9	15.8	0.88
				L	5	13	8	87.4	65.4	17.9	
			B	T	6	8	8	89.1	65.1	14.5	0.96
				L	6	14	8	86.9	64.1	15.1	
			C*	T	4	8	3	90.0	68.4	9.7	0.56
				L	4	14	4	88.6	67.8	17.3	

*Segregated zone.

The ratios of transverse elongation to longitudinal elongation in the unsegregated materials are considered excellent at both uranium levels, i.e., at per cent uranium/ per cent sulphur ratios of 4.0 and 1.1. The degree of uranium segregation in heat 4779 was much more severe than in heat 4787, commensurate with the higher uranium level. In the segregated material the ultimate and yield strengths were lower at the lower uranium level, and the average elongation of the transverse samples (based on only three samples) appeared to be considerably lower at the higher uranium level.

Machinability of Resulphurized Steel

The top half of the ingots from heats 4779 and 4787 have been forged to 4 in. rounds for evaluation of machinability and determination of the effect of the changed character of the sulphides. The testing is in progress, but no results are available to date.

Cold Heading of Resulphurized Steel

The directionality of wrought resulphurized steels is undesirable for cold heading operations, causing failure by splitting. Therefore removal of directionality by the use of uranium as an alloying element might be expected to improve the adaptability of resulphurized grades to this type of operation.

Swaged rods of Types 416 and 430F stainless steels containing various levels of uranium are being prepared for cold heading tests, but no results are available.

REFERENCES

1. R.F. Knight, "The Effect of Uranium on Temper Embrittlement", Physical Metallurgy Division Internal Report PM-R-61-11 (1961).
2. C.E. Makepeace, "An Investigation of Uranium-Bearing Cr-Mo-V Steels for Elevated Temperature Service, Part 1, Project F-37", Physical Metallurgy Division Internal Report Pm-R-61-6 (1961).
3. C.E. Makepeace, Unpublished Research.
4. J.K. Pargeter, Unpublished Research.
5. R.J. McClure, Unpublished Research.
6. D.E.C. King, Unpublished Research.

CHAPTER 7

MICROSTRUCTURE AND HARDNESS OF IRON-URANIUM AND IRON-CARBON-URANIUM ALLOYS(1)

W. J. Wrazej*

SYNOPSIS

Microscopical and hardness examinations and, in some cases, X-ray diffraction studies have been carried out on small melts of iron-uranium and iron-carbon-uranium alloys in different conditions of heat treatment. Comparisons have been made with uranium-free materials to determine the influence of uranium on microstructure and hardness. The influence of composition and heat treatment on the occurrence and appearance of uranium monocarbide, UC, and epsilon phase, UFe_2, have been studied.

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* Senior Scientific Officer, Ferrous Metals Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

Comprehensive studies of hydrogen-purified electrolytic iron alloyed with uranium and carbon have proceeded in four sequential stages. Microscopical observations have been correlated with hardness determinations and some X-ray diffraction data. The intent of this work has been to identify uranium phases, other than inclusions, which may occur in steels modified with uranium, and to study the influence of uranium on the microstructure and hardness of ferrous alloys in various conditions of heat treatment. The results should prove useful for the identification of uranium monocarbide (UC) and the epsilon phase (UFe_2) in experimental steels, thus furthering our understanding of the behaviour of uranium in ferrous materials.

Stage one is concerned with binary iron-uranium alloys, containing up to 10.0% uranium.

Stage two compares iron-carbon-uranium alloys with commercial plain carbon steels. The experimental alloys contain up to 10.0% uranium and 1.2% carbon.

Stage three is a study of iron containing 12.4% uranium and 0.03% carbon.

Stage four, which is unpublished and not reported here, is a study of the uranium carbide and epsilon phases, in a uranium,7.15% carbon binary melt, in carburized uranium; in carburized iron-uranium-carbon alloys containing 50, 46, 76 and 12.5% uranium and 0.03, 1.02 and 0.03% carbon, respectively; and in iron-uranium-carbon alloys containing 5 and 10% uranium plus 0.4, 0.8 and 1.2% carbon, respectively; and in iron-uranium-carbon alloys containing up to 50% uranium and 2.75% carbon.

MATERIALS AND HEAT TREATMENT

The melting stock for the binary and ternary alloys, except for the iron 12.4% uranium alloy, was electrolytic iron purified in dry hydrogen for 2 and 5 hour periods, followed by wet hydrogen treatment for the same times at 1200°C (2190°F). These alloys were melted under an argon atmosphere in a tungsten-arc furnace. They solidified in the water-cooled crucible of the furnace in the form of 50 to 100 g bar-shaped ingots. These alloys were examined in three conditions, specifically, as-cast, subcritically annealed in argon or air for 2 hours at 700°C (1290°F) followed by air cooling, and brine-quenched after being held for 15 minutes at 1050°C (1920°F). The specimens for heat treatment were about 1/4 in. thick.

The reference commercial steel bars were examined in three conditions of heat treatment: normalized, subcritically annealed at 700°C (1290°F), and as-quenched. Normalizing and quenching followed heating in argon for 30 minutes at 1200°C (2190°F). The specimens of SAE steels were also about 1/4 in. thick.

Uranium was present in the charges as purified metal. Carbon was in the form of a white cast iron master alloy analysing:

Mn	Si	P	S	Cu
none	<0.01%	0.003%	0.016%	0.01%

Check analyses of selected melts indicated that recovery of uranium and carbon was virtually complete.

MICROSTRUCTURES

Hydrogen-Purified Iron

Electrolytic iron, which had not been purified by hydrogen, was observed to contain oxide after being remelted in vacuum. The quantity of oxide decreased after the melting stock was purified. Treatment in hydrogen also removed virtually all of the carbon, as evidenced by complete lack of grain boundary serration in quenched specimens. A subgrain structure usually observed in carbon-free irons was not detected.

Iron-Uranium Alloys

Figures 7.1 to 7.21 represent the microstructures observed in hydrogen-purified electrolytic iron to which additions of 0.01, 0.1, 0.5, 1.0, 5.0 and 10.0% uranium were made.

Fewer oxides were observed microscopically with, than without, the addition of 0.01% (0.002 at. %) uranium. The structure in Figures 7.1 and 7.2, 7.8 and 7.9, and 7.15 and 7.16 is pure ferrite marred by etch pits and distortion of the surface.

The addition of 0.1% (0.023 at. %) uranium causes the epsilon phase, UFe_2, to appear in the form of minute dots at the grain boundaries and within the grains of ferrite. (Figures 7.3, 7.10 and 7.17). The particles are scarce. As they also appear in the quenched specimen (Figure 7.17), it is evident that quenching does not retain 0.1% uranium in solution.

Occasional globules and many small discrete particles of UFe_2, formed by 0.5% (0.118 at. %) uranium are shown in Figures 7.4, 7.11 and 7.18. The globules are larger and more numerous in the specimens with 1.0% (0.236 at. %) uranium (Figures 7.5, 7.12 and 7.19).

With the addition of 5% (1.2 at. %) uranium the epsilon phase appears at the grain boundaries as a eutectic of iron in UFe_2 as shown in Figures 7.6, 7.13 and 7.20. The amount of this eutectic is proportionately greater in the specimens with 10.0% (2.5 at. %) uranium (Figures 7.7, 7.14 and 7.21).

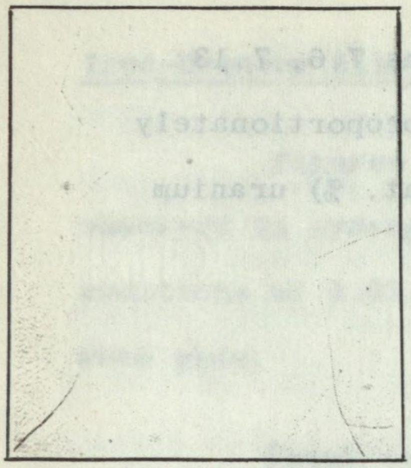

Fig. 7.1 - Nil % U
DPH 65

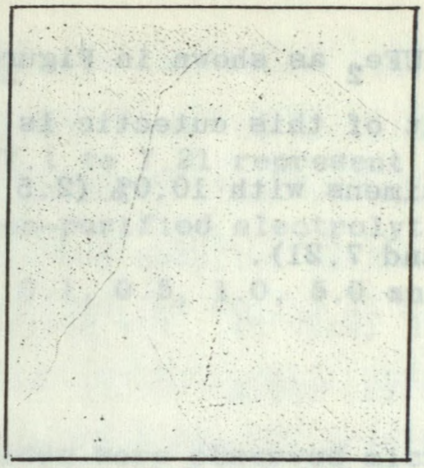

Fig. 7.2 - 0.01% U
DPH 76

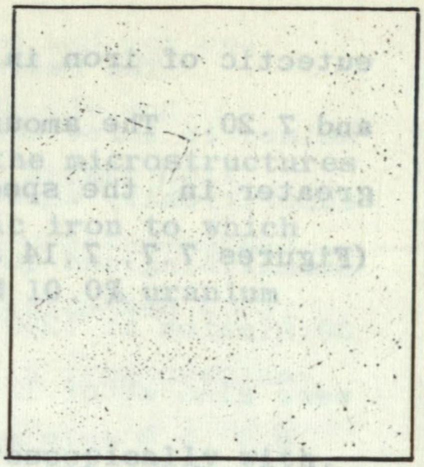

Fig. 7.3 - 0.1% U
DPH 89

Fig. 7.4 - 0.5% U
DPH 125

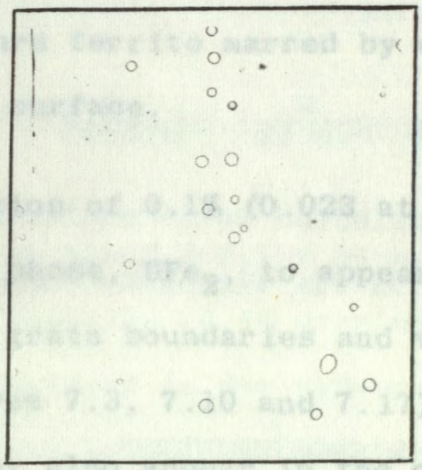

Fig. 7.5 - 1.0% U
DPH 119

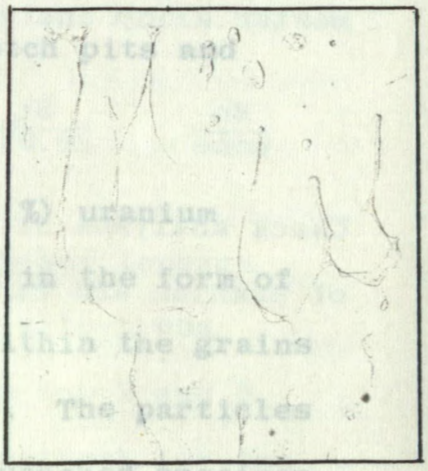

Fig. 7.6 - 5.0% U
DPH 128

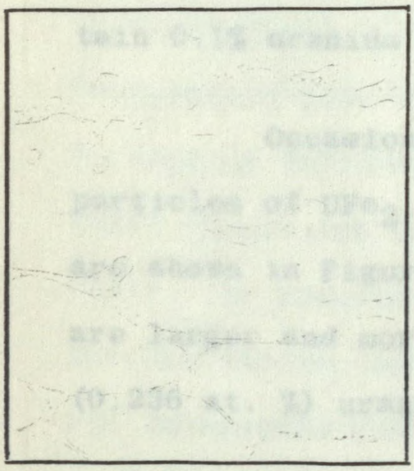

Fig. 7.7 - 10.0% U
DPH 156

Figures 7.1 to 7.7 - Influence of Uranium on the Microstructure and Hardness of As-cast Hydrogen-purified Electrolytic Iron. Etched in 2% nital. X500

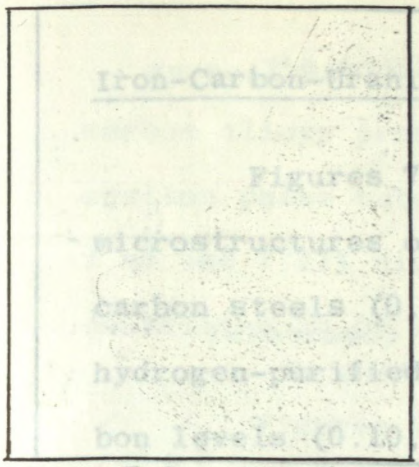

Fig. 7.8 - Nil % U
DPH 59

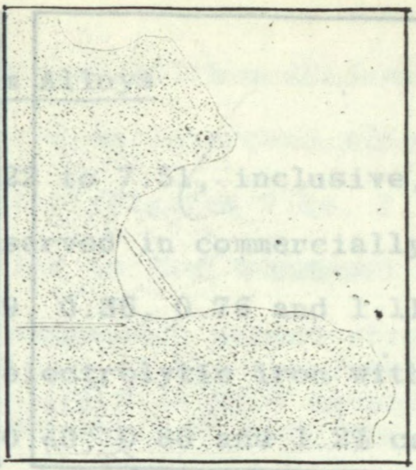

Fig. 7.9 - 0.01% U
DPH 77

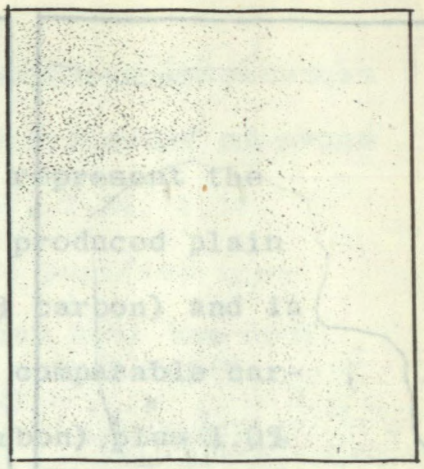

Fig. 7.10 - 0.1% U
DPH 95

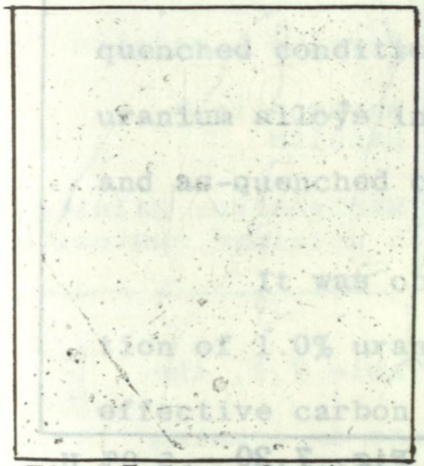

Fig. 7.11 - 0.5% U
DPH 104

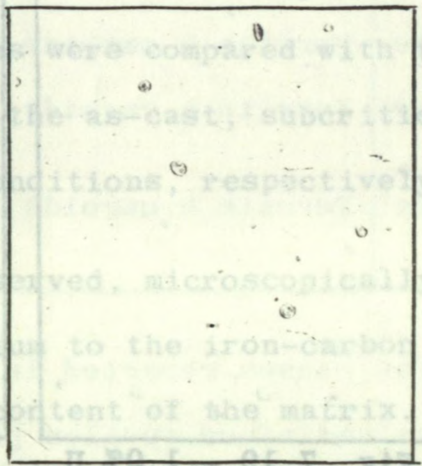

Fig. 7.12 - 1.0% U
DPH 103

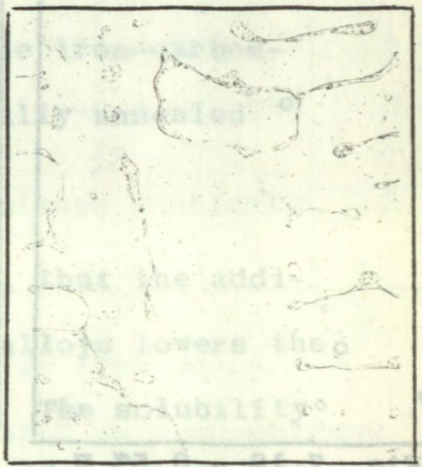

Fig. 7.13 - 5.0% U
DPH 121

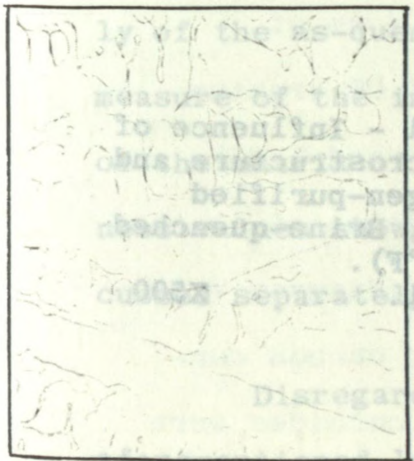

Fig. 7.14 - 10.0% U
DPH 141

Figures 7.8 to 7.14 - Influence of Uranium on the Microstructure and Hardness of Hydrogen-purified Electrolytic Iron. Subcritically Annealed at 700°C (1290°F) for 2 hours. Etched in 2% nital. X500

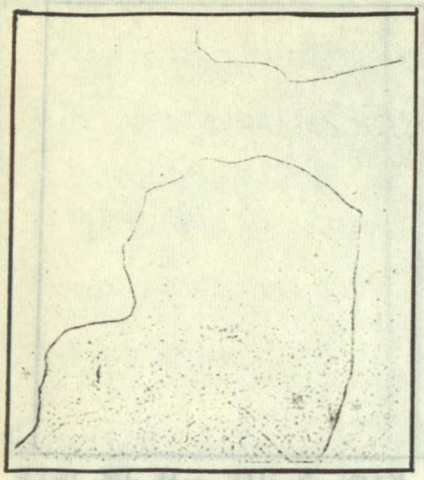

Fig. 7.15 - Nil % U
DPH 66

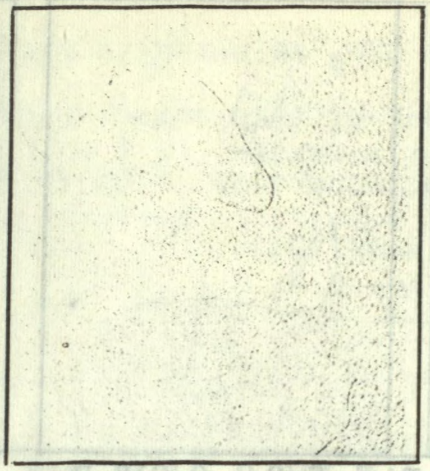

Fig. 7.16 - 0.01% U
DPH 92

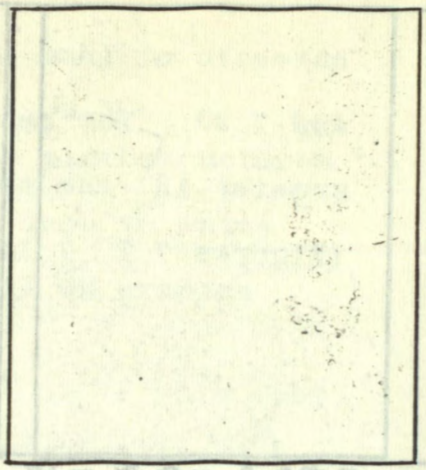

Fig. 7.17 - 0.1% U
DPH 118

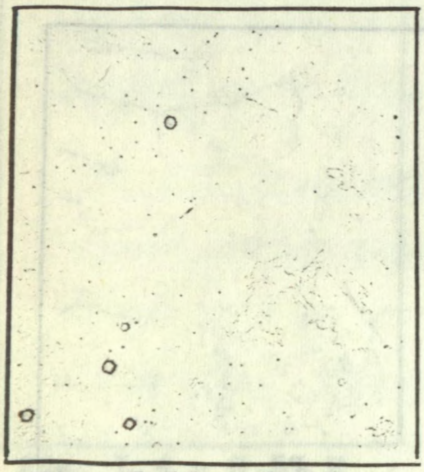

Fig. 7.18 - 0.5% U
DPH 148

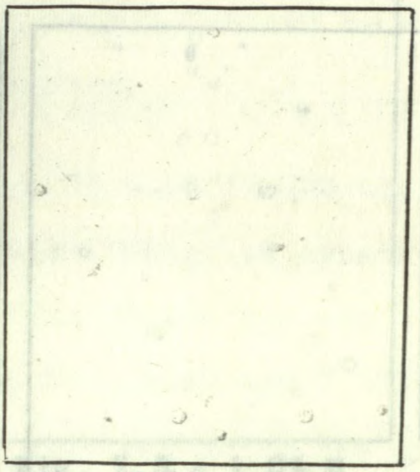

Fig. 7.19 - 1.0% U
DPH 174

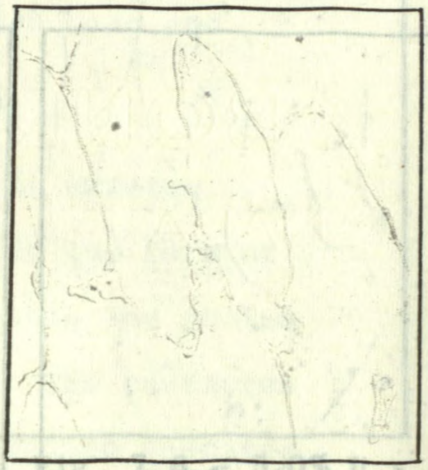

Fig. 7.20 - 5.0% U
DPH 189

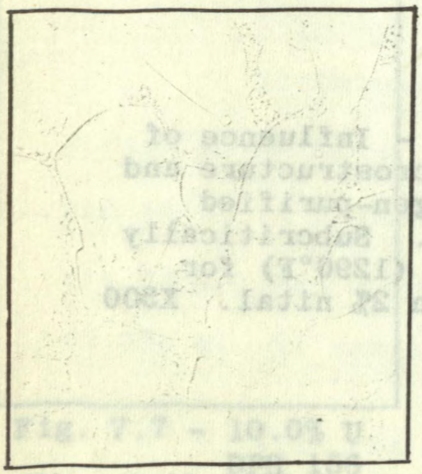

Fig. 7.21 - 10.0% U
DPH 197

Figures 7.15 to 7.21 - Influence of Uranium on the Microstructure and Hardness of Hydrogen-purified Electrolytic Iron, Brine-quenched from 1050°C (1920°F). Etched in 2% nital. X500

Iron-Carbon-Uranium Alloys

Figures 7.22 to 7.51, inclusive, represent the microstructures observed in commercially produced plain carbon steels (0.09, 0.36, 0.76 and 1.11% carbon) and in hydrogen-purified electrolytic iron with comparable carbon levels (0.10, 0.40, 0.80 and 1.2% carbon) plus 1.0% uranium and in some cases 10.0% uranium (0.10 and 0.40% carbon levels). The plain carbon steels in the normalized, as-received plus subcritically annealed, and as-quenched conditions were compared with the iron-carbon-uranium alloys in the as-cast, subcritically annealed and as-quenched conditions, respectively.

It was observed, microscopically, that the addition of 1.0% uranium to the iron-carbon alloys lowers the effective carbon content of the matrix. The solubility of carbon in austenite is further decreased by the addition of 10.0% uranium. However, the hardness values, particularly of the as-quenched specimens, offer a more quantitative measure of the influence of uranium on the microstructure of the matrix of iron-carbon alloys. The average hardness values shown under the photomicrographs are discussed separately.

Disregarding uranium phases and allowing for the aforementioned lowered solubility of carbon in the austenite of the uranium-bearing alloys, the structures represented by Figures 7.22 and 7.51 may be classified as shown in Table 7.1 below.

TABLE 7.1

Iron and Iron Carbide Phases Observed in Commercial Plain Carbon Specimens and Fe-C-U Specimens (Figures 7.22 to 7.51)

Carbon Level,%	Condition		
	Normalized or As-cast	Subcritically Annealed	As-quenched
0.1	Ferrite & pearlite	Ferrite & carbide	Ferrite & bainite
0.4	Ferrite & pearlite	Ferrite & carbide	Ferrite & bainite
0.8	Ferrite & pearlite	Ferrite & carbide	Martensite & bainite
1.2	Carbide & pearlite	Ferrite & carbide	Martensite, bainite & retained austenite

As well as the phases reported in Table 7.1, the uranium-bearing alloys contained epsilon phase or uranium carbide.

Epsilon phase was observed in the form of globules and grain boundary network at the 1.0% uranium level in the 0.1% carbon alloy (Figures 7.23 and 7.33). The presence of epsilon phase could not be detected at the 1.0% uranium level in the 0.4% carbon alloy (Figures 7.26, 7.36 and 7.46) or in the alloys with greater carbon content. However, minute particles of uranium carbides were reported in these alloys.

The addition of 10.0% uranium to the iron-carbon alloys produced an interdendritic network of iron-epsilon phase eutectic (Figures 7.24, 7.27, 7.34, 7.37, 7.44 and 7.47) similar to that observed in purified iron containing 10.0% uranium.

Figures 7.34 and 7.37 show the iron-epsilon phase eutectic partially decomposed or transformed due to surface oxidation.

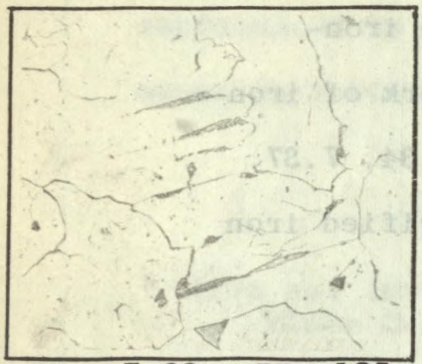

Fig. 7.22 - DPH 135
SAE 1010 (0.09% C)

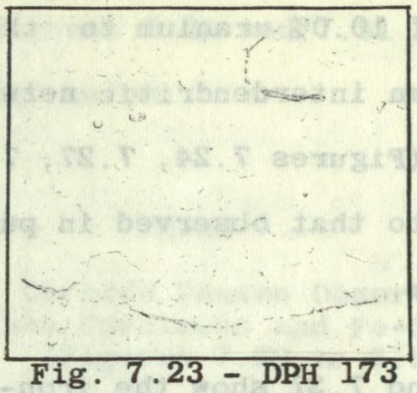

Fig. 7.23 - DPH 173
0.1% C + 1.0% U

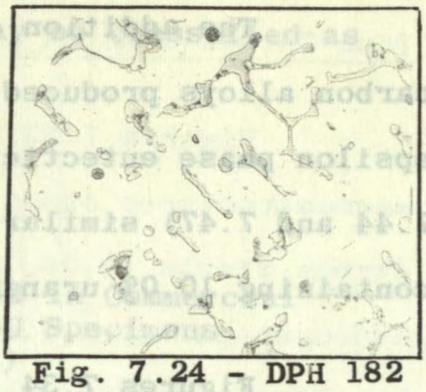

Fig. 7.24 - DPH 182
0.1% C + 10% U

Fig. 7.25 - DPH 245
SAE 1035 (0.36% C)

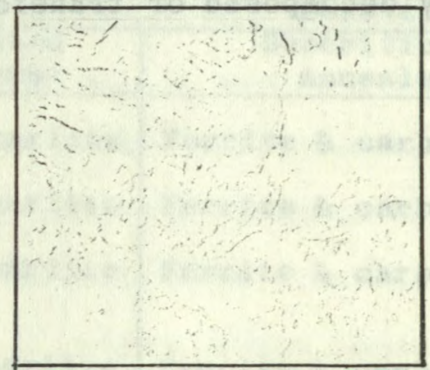

Fig. 7.26 - DPH 178
0.4% C + 1.0% U

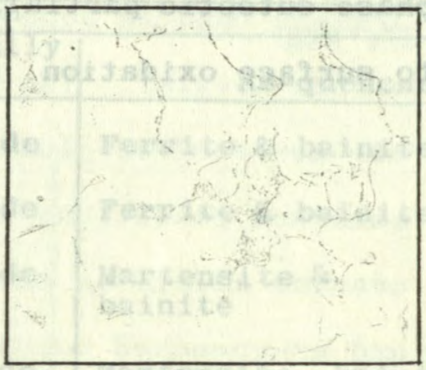

Fig. 7.27 - DPH 198
0.4% C + 10% U

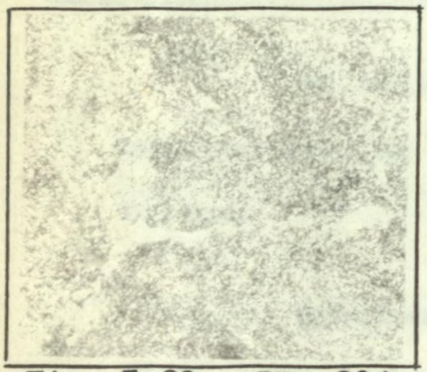

Fig. 7.28 - DPH 304
SAE 1075 (0.76% C)

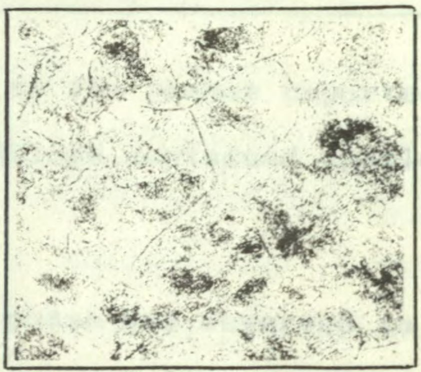

Fig. 7.29 - DPH 278
0.8% C + 1.0% U

Figures 7.22 to 7.31 - Microstructure and Hardness of Some Commercial Carbon Steels, Normalized from 1200°C (2190°F), and of As-cast Hydrogen-purified Electrolytic Iron, at Comparable Carbon Levels, with 1.0% or 1.0% and 10.0% Uranium. Etched in 2% nital. X500

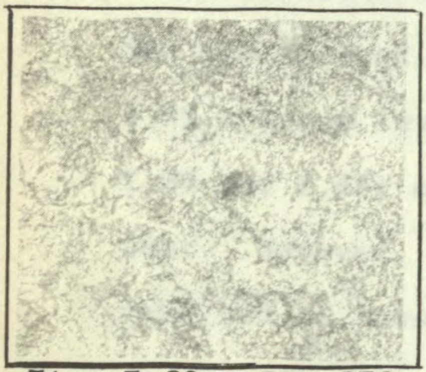

Fig. 7.30 - DPH 373
1.11% C (analysed)

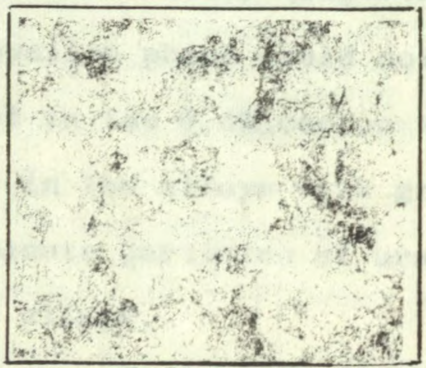

Fig. 7.31 - DPH 313
1.2% C + 1.0% U

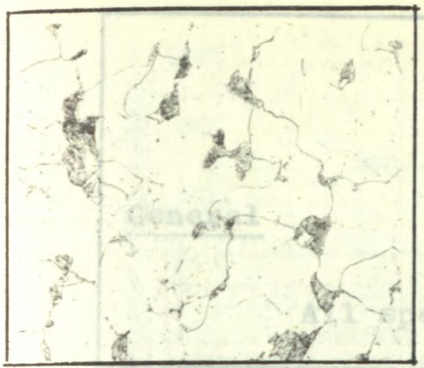
Fig. 7.32 - DPH 120
SAE 1010 (0.09% C)

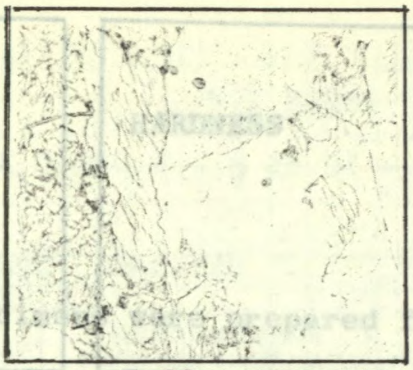
Fig. 7.33 - DPH 143
0.1% C + 1.0% U


Fig. 7.34 - DPH 136
0.1% C + 10.0% U

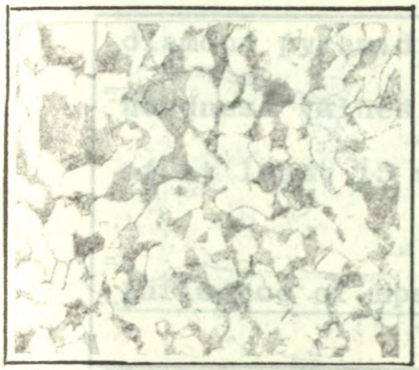
Fig. 7.35 - DPH 200
SAE 1035 (0.36% C)


Fig. 7.36 - DPH 146
0.4% C + 1.0% U

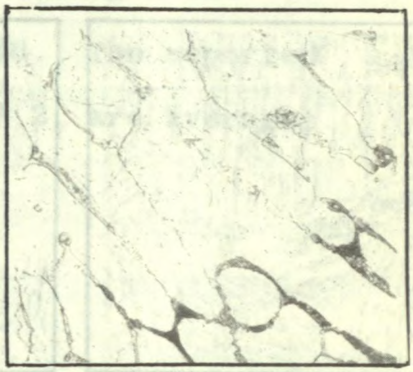
Fig. 7.37 - DPH 128
0.4% C + 10.0% U

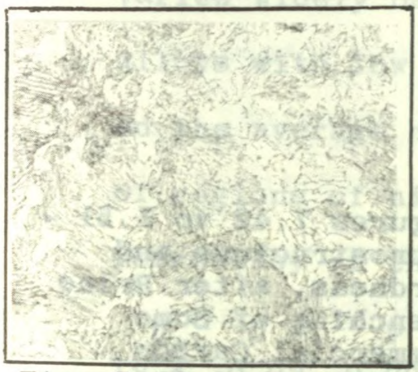
Fig. 7.38 - DPH 234
SAE 1075 (0.70% C)


Fig. 7.39 - DPH 190
0.8% C + 1.0% U

Figures 7.32 to 7.41 - Microstructure and Hardness after Subcritical Annealing for 2 hours, at 700°C (1290°F), of Some As-received Commercial Carbon Steels and of Hydrogen-purified Electrolytic Iron, at Comparable Carbon Levels, with 1.0%, or 1.0% and 10.0% Uranium. Etched in 2% nital. X500

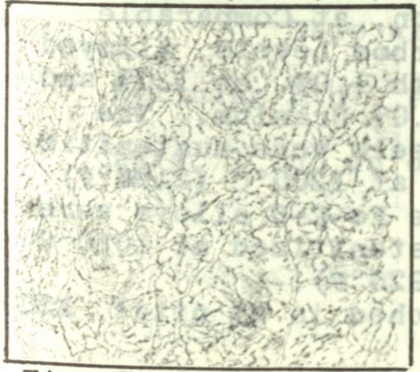
Fig. 7.40 - DPH 253
1.11% C (analysed)


Fig. 7.41 - DPH 198
1.2% C + 1.0% U

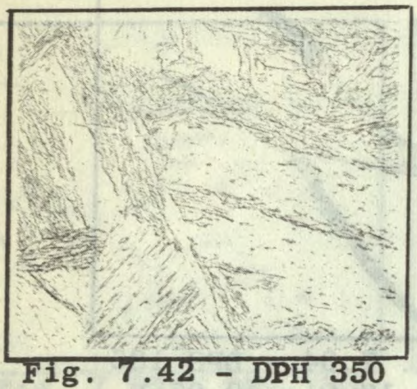

Fig. 7.42 - DPH 350
SAE 1010 (0.09% C)

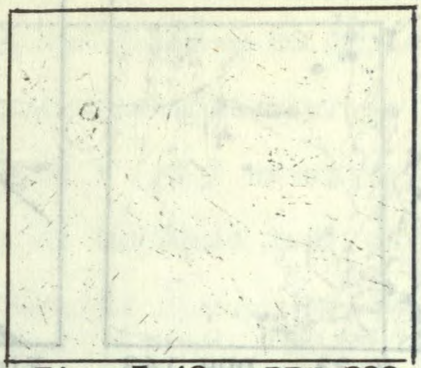

Fig. 7.43 - DPH 288
0.1% C + 1.0% U

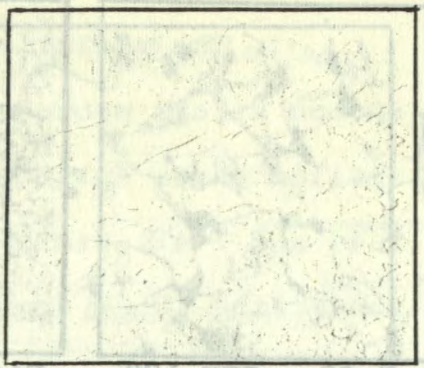

Fig. 7.44 - DPH 277
0.1% C + 10% U

Fig. 7.45 - DPH 690
SAE 1035 (0.36% C)

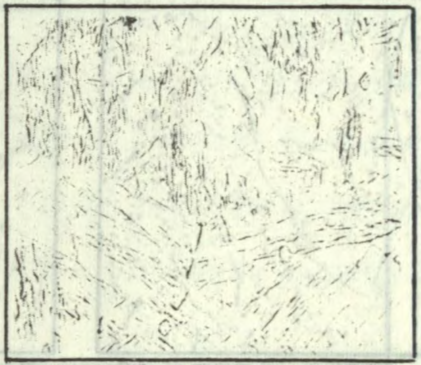

Fig. 7.46 - DPH 389
0.4% C + 1.0% U

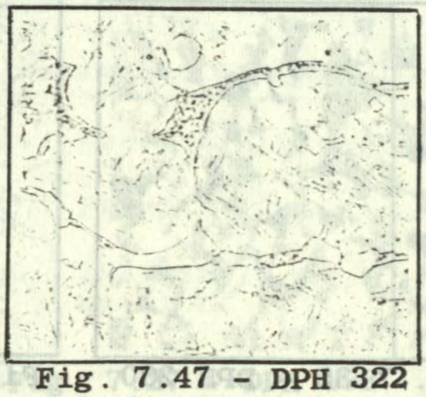

Fig. 7.47 - DPH 322
0.4% C + 10% U

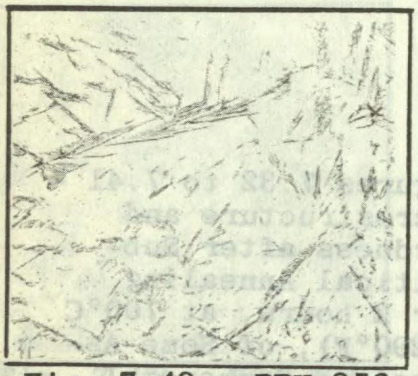

Fig. 7.48 - DPH 856
SAE 1075 (0.76% C)

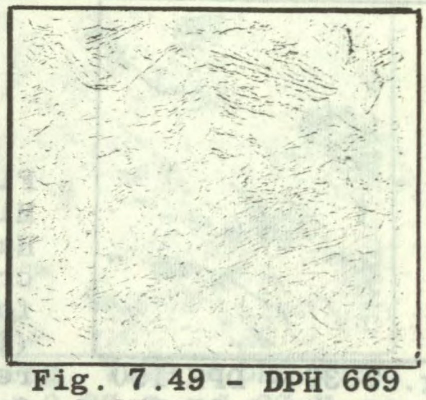

Fig. 7.49 - DPH 669
0.8% C + 1.0% U

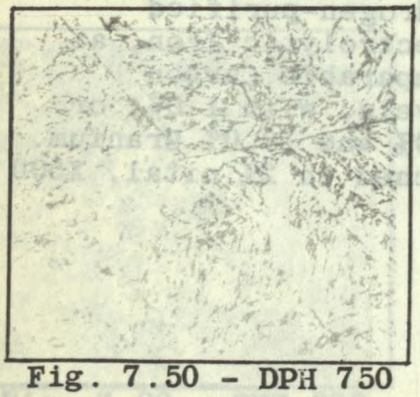

Fig. 7.50 - DPH 750
1.11% C (analysed)

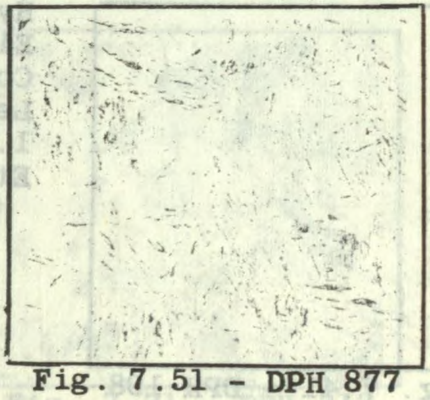

Fig. 7.51 - DPH 877
1.2% C + 1.0% U

Figures 7.42 to 7.51 - Microstructure and Hardness, after Brine Quenching of Some Commercial Carbon Steels and of Hydrogen-purified Electrolytic Iron, at Comparable Carbon Levels, Alloyed with 1.0%, or 1.0% and 10.0% Uranium. The steels were austenitized at 1200°C (2190°F). The Fe-C-U alloys were austenitized at 1050°C (1920°F).
Etched in 2% nital. X500

HARDNESS

General

All specimens were prepared for hardness determinations in the same manner as for microscopical examination. Hardness determinations were made using a 136° diamond pyramid indentor and a 500 g load. The reported hardness values, except those in Table 7.2, are averages of at least 15 values.

Influence of Epsilon Phase

In the high uranium alloys, the hardness values varied widely because of the eutectic epsilon phase. In alloys with low carbon content the epsilon phase increased the average hardness. Table 7.2 shows hardness values of regions of high, medium, and low epsilon content in a ferroalloy of the following analysis:

U	C	P	Si	Ni	Cr	V	Mo	Al
12.4	0.03	0.004	0.001	0.027	0.005	0.005	0.0008	0.006

This alloy was obtained from Eldorado Mining and Refining Ltd., Port Hope, Ontario, in the form of as-cast bars, 1 in. in diameter.

TABLE 7.2

Hardness of Fe - 12.4% U - 0.03% C Alloy

	Hardness, DPH		
Location	As-cast	As-Quenched 1100°C (2010°F), 15 min, brine	Subcritically Annealed 700°C (1290°F), 6 hr, air
Low UFe_2 content	62	85,139	-
Medium UFe_2 content	97,103,100	151,192	121,126,108
High UFe_2 content	117,118	212,212	-

Iron-Uranium Alloys

Average hardness values obtained on hydrogen-purified iron containing up to 10.0% uranium are presented in Figure 7.52 for the as-cast, subcritically annealed, and as-quenched conditions. In each of these conditions the increase of hardness with increase of uranium approaches linearity on the semi-logarithmic graph. Some or all of this increase of hardness must be associated with the amount of epsilon phase. In spite of the metallographic evidence that, after quenching, only a minute amount (below 0.1%) of uranium remains in solution, the hardness of the quenched specimens becomes increasingly greater than that of the as-cast or subcritically annealed specimens, as the uranium content increases.

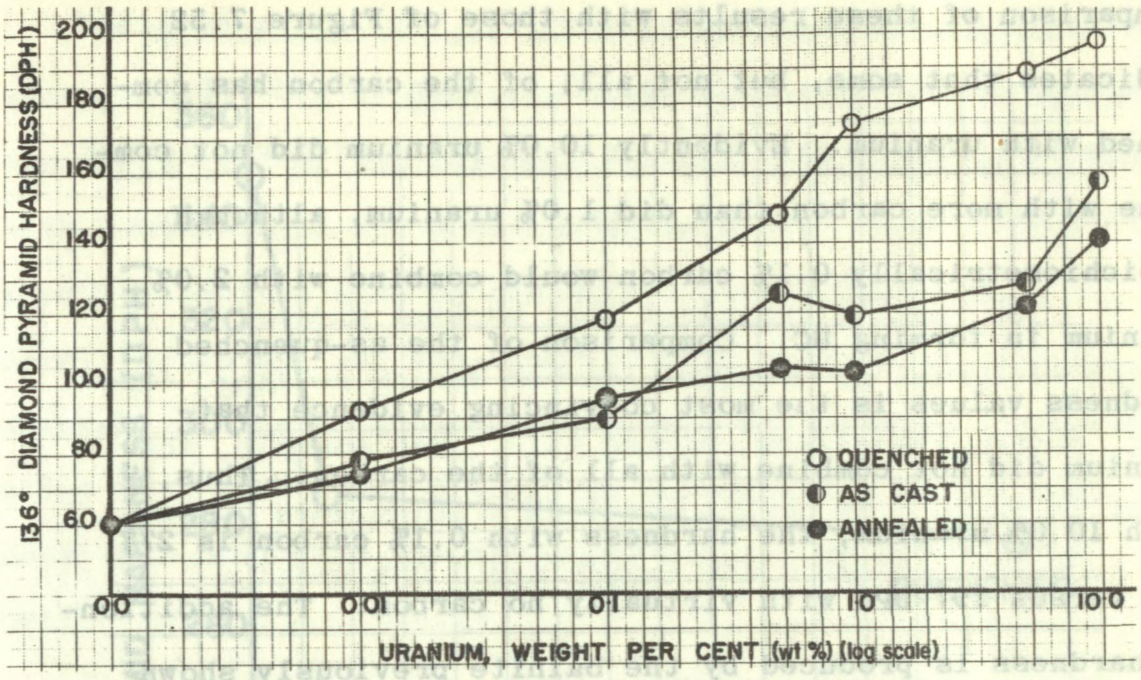

Figure 7.52 - Average Hardness of Hydrogen-purified Electrolytic Iron Containing up to 10% U.

Iron-Carbon-Uranium Alloys

Figures 7.53 and 7.54 show the influence of up to 10.0% uranium on the hardness of hydrogen-purified iron at the 0.1 and 0.4% carbon levels, respectively.

Figure 7.53 indicates that 1.0% uranium in 0.1% carbon steel has increased the as-cast (versus normalized SAE 1010) and the subcritically annealed hardness, possibly by the formation of the epsilon phase, UFe_2, and has decreased the as-quenched hardness, possibly by the formation of uranium carbide. The average hardness values obtained on the alloy with 10.0% uranium were almost the same as on the alloy with 1.0% uranium.

Comparison of these results with those of Figure 7.52 indicates that some, but not all, of the carbon has combined with uranium. Evidently 10.0% uranium did not combine with more carbon than did 1.0% uranium, although stoichiometrically 0.1% carbon would combine with 2.0% uranium in forming UC. Comparison of the as-quenched hardness values is the most convincing evidence that uranium did not combine with all of the carbon. Thus, with 10.0% uranium, the hardness with 0.1% carbon is 277 DPH versus 197 DPH with virtually no carbon. The additional hardness is produced by the bainite previously shown in Figure 7.44.

Figure 7.54 indicates that the average hardness values, of as-cast and subcritically annealed hydrogen-purified iron to which 0.4% carbon and 0.1, 1.0 and 10.0% uranium were added, are lower than those of SAE 1035 (0.36% carbon) in the normalized and in the subcritically annealed conditions. This suggests that some of the carbon may be combined with uranium as a carbide that does not increase hardness as effectively as cementite. The as-quenched hardness of the uranium-bearing alloy decreases linearly with increase of uranium on the semi-logarithmic graph of Figure 7.54. Again the as-quenched hardness values especially of the 10.0% uranium alloy and its microstructure (Figure 7.47) show that all of the carbon did not combine with uranium. There is

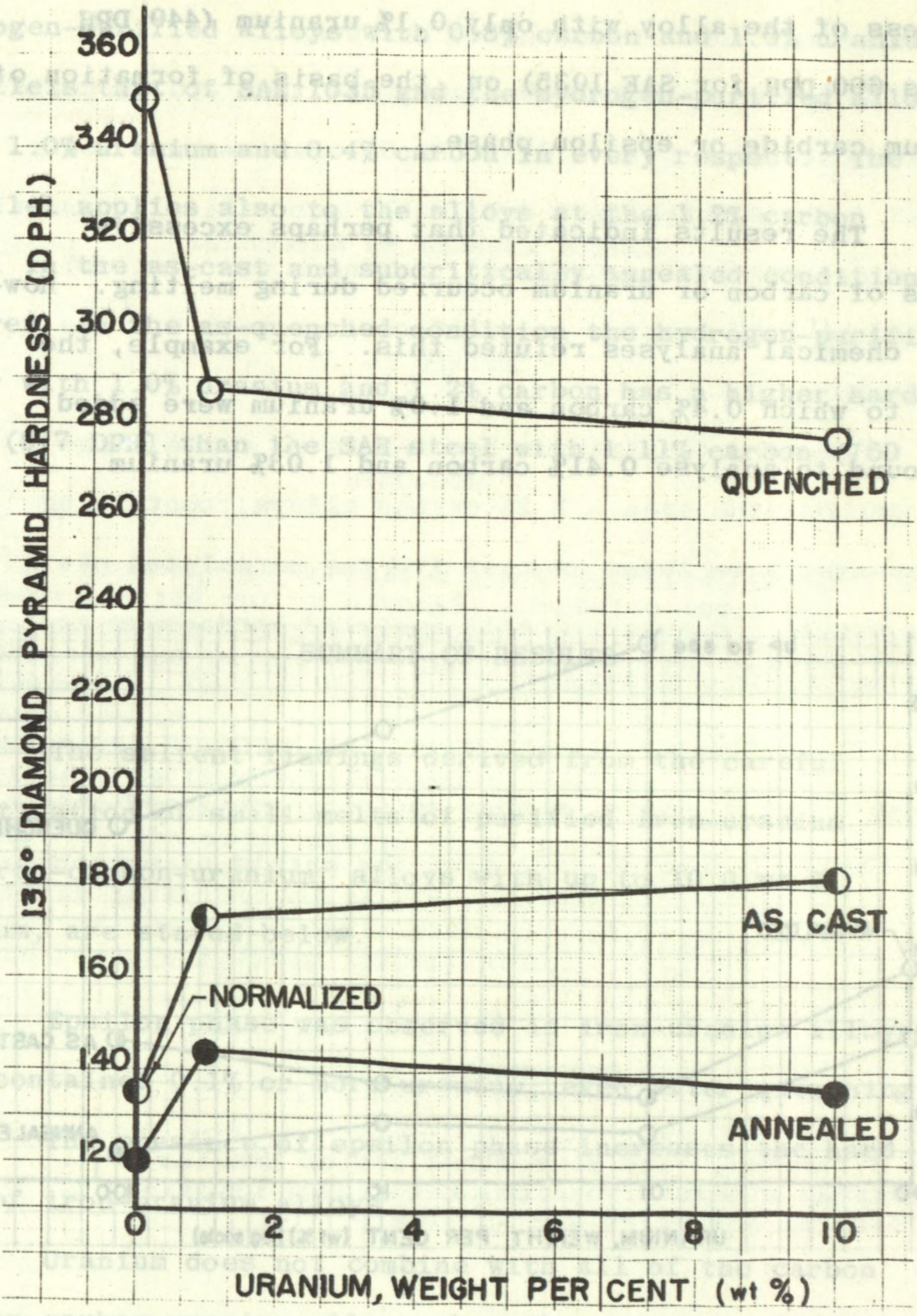

Figure 7.53 - Hardness of SAE 1010, 0.09% Carbon Steel and of Hydrogen-purified Electrolytic Iron to Which 0.10% Carbon Plus 1.0 and 10.0% Uranium were Added.

therefore, no apparent explanation for the low as-quenched hardness of the alloy with only 0.1% uranium (440 DPH versus 690 DPH for SAE 1035) on the basis of formation of uranium carbide or epsilon phase.

The results indicated that perhaps excessive losses of carbon or uranium occurred during melting. However, chemical analyses refuted this. For example, the alloy to which 0.4% carbon and 1.0% uranium were added was found to analyse 0.41% carbon and 1.03% uranium.

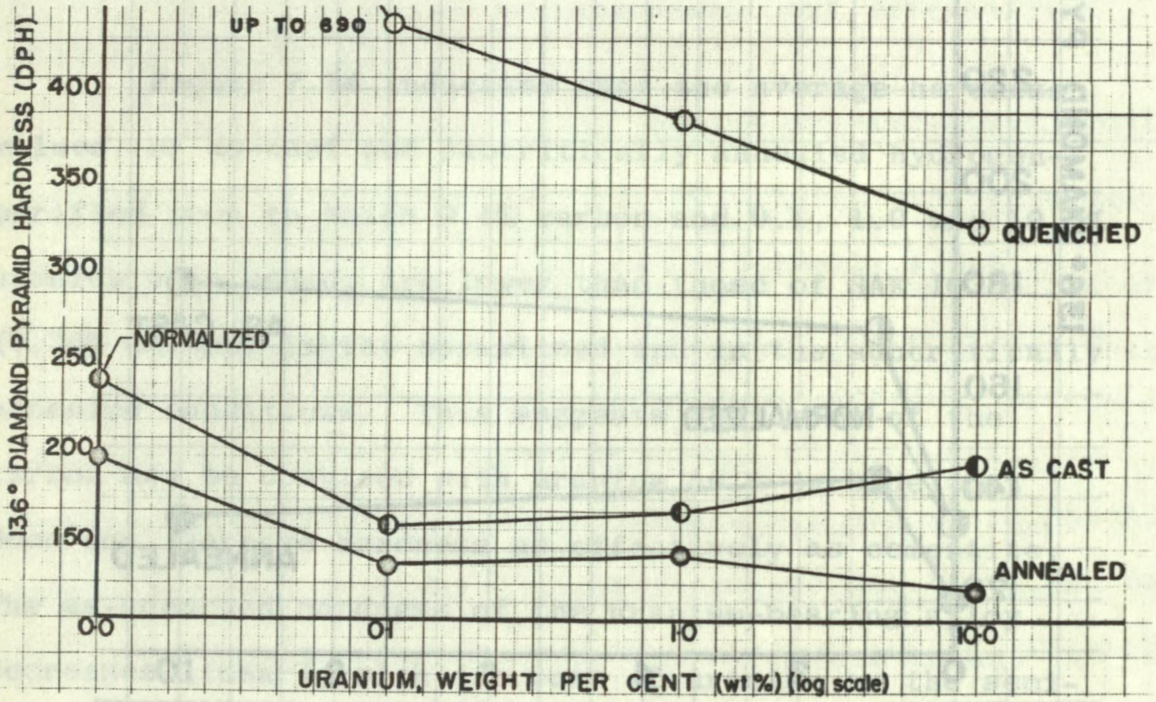

Figure 7.54 - Hardness of SAE 1035 0.36% Carbon Steel and of Hydrogen-purified Electrolytic Iron to Which 0.40% Carbon Plus 0.10, 1.0 and 10.0% Uranium were Added.

Discussion of the hardness of SAE 1075 and the hydrogen-purified alloys with 0.8% carbon and 1.0% uranium parallels that of SAE 1035 and the hydrogen-purified alloys with 1.0% uranium and 0.4% carbon in every respect. The parallel applies also to the alloys at the 1.2% carbon level in the as-cast and subcritically annealed conditions. However, in the as-quenched condition the hydrogen-purified alloy with 1.0% uranium and 1.2% carbon has a higher hardness (877 DPH) than the SAE steel with 1.11% carbon (750 DPH).

SUMMARY OF RESULTS

The salient findings derived from the careful investigation of small melts of purified iron-uranium and iron-carbon-uranium, alloys with up to 10.0 wt % uranium, are stated below.

1. Epsilon phase was observed in iron-uranium alloys that contained 0.1% or more uranium, even after quenching.

2. The presence of epsilon phase increases the hardness of iron-uranium alloys.

3. Uranium does not combine with all of the carbon in iron-carbon-uranium alloys when there is a stoichiometric excess of uranium.

4. Compared to SAE 1010 steel, the iron - 0.1% carbon alloys, containing 1.0 and 10.0% uranium have higher as-cast

(versus normalized SAE 1010) and subcritically annealed hardnesses and lower as-quenched hardness.

5. Compared to SAE 1040 steel, the iron - 0.4% carbon alloys, containing 0.1, 1.0 and 10.0% uranium have lower as-cast (versus normalized S E 1040), subcritically annealed, and as-quenched hardnesses. Hardness was similarly affected by 1.0% uranium in purified iron with 0.8 and 1.2% carbon.

6. Compared to plain carbon SAE steel containing 1.11% carbon, the iron - 1.2% carbon alloys, containing 1.0% uranium have lower as-cast (versus normalized plain carbon steel) and subcritically annealed hardnesses and, higher as-quenched hardness.

7. The influence of uranium on the hardness, as cited in items 5 and 6, above, cannot be fully explained only on the basis of uranium depleting the matrix of carbon.

REFERENCE

1. W. J. Wrazej, "The Microstructure of Uranium-Bearing Steels", Physical Metallurgy Division Internal Report PM-R-61-8 (1961).

CHAPTER 8

CORROSION OF URANIUM STEELS

G. J. Biefer*

SYNOPSIS

Many of the corrosion tests reported herein were carried out in strongly corrosive media so as to obtain a rapid assessment of the effect of uranium and to indicate the direction for further research. Carbon, low alloy and stainless steels were tested in a variety of media. In the case of carbon and low alloy steels there were indications of a favourable trend in certain concentrations of hydrochloric and sulphuric acids, and for the stainless steels there appeared to be a tendency to lower weight loss and reduced pitting attack in acidified ferric chloride solutions. Many of the other tests gave inconclusive results and require further investigation.

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* Head, Corrosion Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

Some uranium-bearing, plain-carbon, low-alloy, and high-alloy steels were subjected to exploratory laboratory tests for resistance to aqueous corrosion, high-temperature oxidation and stress corrosion. A limited number of field tests of aqueous and atmospheric corrosion resistance were also conducted. The results, summarized herein according to alloy type, are generally not conclusive. However, they do form a basis for planning a more intensive evaluation and study. Some of the anomalous results may have been related to macro-segregation.

The possibility that uranium may improve the corrosion behaviour of steel was first suggested by the observation that the surfaces of steel anodes, bearing 0.02 to 0.25% uranium, remained relatively smooth and bright during electrolytic dissolution in aqueous 3% hydrochloric acid. By contrast, the surfaces of steels, either without uranium or with over 0.25% uranium,were severely pitted and blackened by the same carbide extraction treatment(1). Subsequently it was found that some uranium-bearing steels did not respond to the conventional sulphur printing technique(2), which entails exposure to 2% sulphuric acid.

CARBON STEELS

Preliminary Tests

Initial scouting tests on some medium carbon steels indicated that uranium reduced pitting and general corrosion in 70% nitric acid, 14% hydrochloric acid, and 10% sulphuric acid. Uranium-free steel was equal or superior to the uranium-bearing alloys in concentrated sulphuric acid.

These results stimulated further testing under more controlled conditions. Care was taken to obtain comparable surface finish on all specimens, to eliminate galvanic effects, and to restrict contamination of the solution by corrosion products.

Medium Carbon Steels

A number of exploratory tests were carried out on two as-rolled carbon steels. One of the steels was free from uranium, and contained 0.33% carbon and 0.023% sulphur. The other steel contained 0.12% uranium, 0.35% carbon and 0.036% sulphur. These steels were received as 1 in. diameter bars, and the corrosion specimens were discs cut from the bars so that their major surfaces were transverse to the rolling direction, i.e., in the plane most sensitive to corrosion attack along inclusion stringers.

Table 8.1 shows the results obtained when these two steels were tested in 50°C (122°F) sulphuric acid over the concentration range 1 to 96.5% in a series of relatively short tests on single specimens. The uranium-bearing alloy showed consistently lower weight losses over the concentration range 1 to 60%, but the effect was minor. No significant differences were observed in the pitting behaviour of the two alloys.

TABLE 8.1

Corrosion Behaviour of As-Rolled Medium Carbon Steels at 50°C (122°F) in Sulphuric Acid of Various Concentrations

H_2SO_4 Concentration, Wt %	Duration of Tests, hr	Weight Loss, mg/cm^2	
		Heat 1369 No uranium 0.33 % C 0.023% S	Heat 1373 0.12 % U 0.35 % C 0.036% S
1	1/6	1.0	0.8
10	1/4	2.7	2.2
20	1/4	4.2	3.2
30	1/4	5.8	3.8
40	1/4	8.3	6.7
50	1	58.1	43.6
60	16	16.8	16.3
70	16	3.3	4.3
80	16	3.7	3.7
90	16	8.8	9.7
96.5	24	3.3	3.0

The differences between the alloys shown in Table 8.1 were considerably less than in the scouting tests, which were carried out in 10% sulphuric acid. It was therefore decided to carry out a series of longer tests (45 to 90 minutes) in a number of acid environments. (The tests were interrupted at 5 or 10 minute intervals for weighing of the specimens). Table 8.2 shows the results of this series of tests, each result being for a single specimen.

TABLE 8.2

Corrosion Behaviour of As-Rolled 0.33-0.35% Carbon and 0.023-0.036% Sulphur Steels in Acid Solutions at 50°C (122°F)

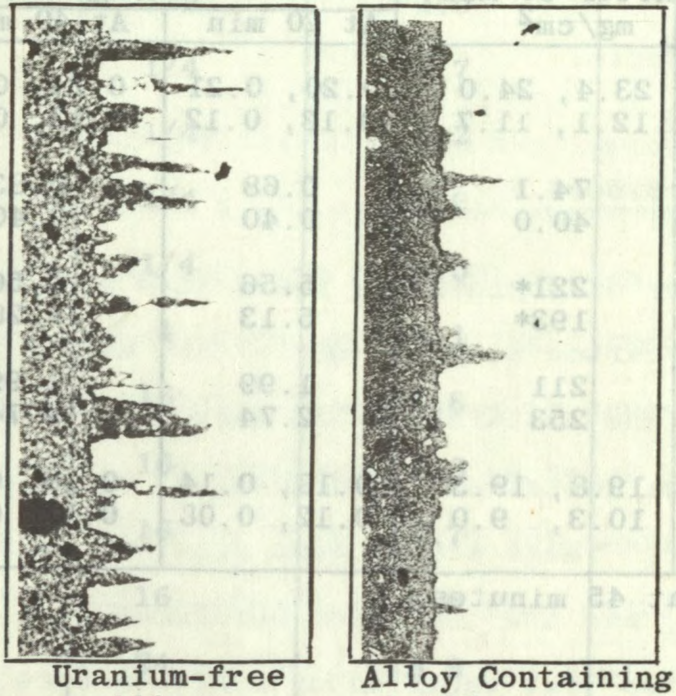
Solution	Alloy	Weight Loss After 90 min, mg/cm^2	Rate of Weight Loss During Tests mg/cm^2/min		
			At 20 min	At 40 min	At 80 min
10% HCl	U-free 0.12% U	23.4, 24.0 12.1, 11.7	0.20, 0.21 0.13, 0.12	0.24, 0.25 0.13, 0.12	0.32, 0.33 0.13, 0.14
20% HCl	U-free 0.12% U	74.1 40.0	0.68 0.40	0.83 0.40	1.03 0.53
37% HCl	U-free 0.12% U	221* 193*	5.56 5.13	5.56 4.28	- -
10% HNO_3	U-free 0.12% U	211 253	1.99 2.74	1.99 2.74	2.07 2.20
10% H_2SO_4	U-free 0.12% U	19.8, 19.3 10.3, 9.0	0.18, 0.14 0.12, 0.08	0.18, 0.19 0.12, 0.09	0.26, 0.27 0.12, 0.10

* Weight loss at 45 minutes.

Considering the 10% sulphuric acid solution, the differences in weight loss between the alloy containing 0.12% uranium and the alloy free of uranium were disproportionately greater after 90 minutes than after 10 minutes (Table 8.1). This was due to the greater increase of corrosion rate with time shown by the uranium-free alloy.

From the results in Table 8.2, the following general observations were made:

1. The uranium-bearing alloy showed lower weight losses in 10% and 20% hydrochloric acid and in 10% sulphuric acid.
2. In these three media, the uranium-bearing alloy showed significantly fewer and shallower end-grain pits than the uranium-free control. (Figure 8.1).



Uranium-free Alloy

Alloy Containing 0.12% Uranium

Figure 8.1 - Photomicrographs of Cross-Sections of 0.33-0.35% Carbon As-rolled Steels After Immersion for 90 Minutes in 20% HCl Solution at 50°C (122°F). About X50. Rolling direction is in the horizontal plane.

Weight losses were as follows:

U-free alloy - 74.1 mc/cm^2

0.12% U alloy - 40.0 mg/cm^2

3. In these three media, the uranium-bearing specimens showed weight-loss rates which were constant or increased to a relatively slight extent with time. The uranium-free specimens showed definite increases in rate of weight loss with time. It is probable that the development of pits, increasing the effective area of the specimens, brought about these increases in rate.

4. In 37% hydrochloric acid, total weight losses over the 90 minute test were not very different, but the uranium-bearing alloy showed a lower rate at the end of the test.

5. In 10% nitric acid, the 0.12% uranium alloy showed a greater total weight loss over the 90 minutes. However, at the end of the run its rate had decreased to a value very nearly equal to that shown by the uranium-free alloy.

These results are not considered to be conclusive, but will be helpful in planning a testing programme for uranium-bearing steel sheet, expected to be available soon, which will be essentially free from uranium microsegregation.

Effect of Manganese and Uranium in 0.15% Carbon Steel

It has been observed that the corrosion of carbon steels in citric and sulphuric acids increases with increasing sulphur content. When copper, which is a strong sulphide former, is alloyed with the steels, the effect is counteracted(3,4). Sulphur-bearing high-purity iron shows similar behaviour when copper alloying additions are present (5).

In order to compare the effects of uranium and manganese upon corrosion behaviour, two split heats were prepared to yield steels with varying manganese-sulphur and uranium-sulphur ratios. The as-cast alloys were tested in 10% hydrochloric acid and 10% sulphuric acid at 50°C (122°F) in 90 minute exposures. The results, in terms of weight loss, appear in Table 8.3.

TABLE 8.3

Corrosion Behaviour of As-Cast 0.15% Carbon Steels in Acid Solutions at 50°C (122°F)

Alloy No.	Composition, %			Weight Loss After 90 min on Test, mg/cm^2	
	Mn	S	U	In 10% HCl	In 10% H_2SO_4
1A	0.001	0.009	0.034	6.4, 6.0	13.6, 11.2
1B	0.001	0.031	0.031	10.3, 12.0	22.5, 21.9
1C	0.001	0.031	0.24	9.4, 7.7	17.7, 16.4
2A	0.007	0.009	nil	6.0, 5.5	12.0, 8.8
2B	0.008	0.031	nil	9.4, 9.1	21.8, 20.2
2C	0.19	0.029	nil	11.2, 10.9	22.8, 21.4

In both split heats an increase in sulphur content caused an increase in corrosion. Addition of sufficient uranium to combine with the higher level of sulphur reduced the corrosion, though the resistance was not equal to that of the low sulphur steel. On the other hand, the addition of sufficient manganese to combine with the sulphur generally led to a further increase in the corrosion rate.

While it appears from these results that uranium additions might decrease corrosion rates for carbon steels by combining strongly with sulphur, these results cannot be considered conclusive. It should be noted that these steels showed areas of intense localized attack, possibly resulting from the presence of macrosegregates.

Tests in Neutral Salt Solutions

Corrosion tests were carried out on as-rolled 0.37 to 0.39% carbon and 0.004 to 0.009% sulphur steels containing 0.02 to 0.25% uranium and on an as-cast alloy containing 0.69% uranium(1). A number of different calcium chloride and sodium chloride solutions were used, and the samples were either continuously or intermittently immersed. No significant differences were observed in the corrosion resistance of uranium-bearing and uranium-free alloys (Figure 8.2). These negative findings were confirmed by tests carried out on as-rolled steels containing 0.33 to 0.35% carbon and 0.023 to 0.036% sulphur (Table 8.4).

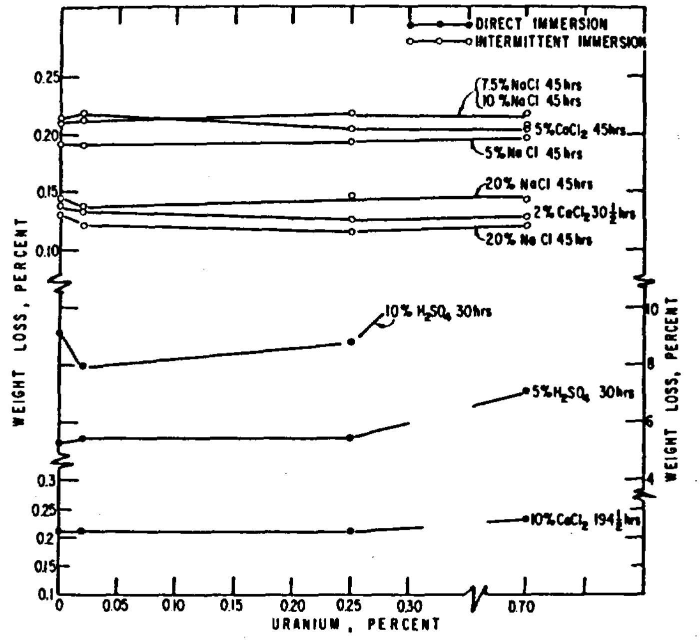


Figure 8.2 - Effect of Uranium on the Corrosion Behaviour of Medium Carbon Steels in Aqueous Sulphuric and Neutral Chloride Solutions(1).

TABLE 8.4

Corrosion Behaviour of Specimens of As-Rolled 0.33 to 0.35% Carbon and 0.023 to 0.036% Sulphur Steels Immersed in Neutral Salt Solutions at Room Temperature

Solution	Duration of Immersion, days	Weight Loss, mg/cm^2	
		Heat 1369 No uranium	Heat 1373 0.12% U
3% NaCl	29	6.0, 6.1	6.3, 6.8
	55	14.2, 13.2	13.3, 13.9
	82	20.5, 19.4	20.2, 19.9
5% $CaCl_2$	17	3.5	3.4

Stress-Corrosion Tests (6)

The comparative behaviour of plain carbon steels, with and without uranium, was evaluated in the laboratory under the combined influence of tensile stress and corrosion. Three corrosive media were employed, specifically, a 4% sodium chloride solution, a 1% sodium chloride solution equilibrated with hydrogen sulphide, and a solution of calcium nitrate and ammonium nitrate. Further testing is indicated to reconcile anomalous results. Therefore the test procedures and results are not presented in detail.

A stress-rupture testing machine was used to hold notched specimens of 0.38 to 0.42% carbon steel at a stress slightly less than the unnotched ultimate tensile strength. The specimens were sprayed intermittently with 4% sodium chloride solution. The initial results, indicating that uranium was decidedly beneficial, have not been substantiated by subsequent tests.

A range of carbon steels (0.17 to 0.58% C) was tested at 66°C (150°F) in 1% sodium chloride solution into which hydrogen sulphide was bubbled. This test was used to simulate sulphide cracking encountered in sour gas and crude oil fields. The steels were heat treated to hardness levels of Rockwell B-80 and C-33. The specimens were bent uniformly and held under restraint in a fixture. At the lower hardness level none of the specimens cracked, although a progressive thinning was apparent, and it was observed that pitting appeared less severe on the uranium-bearing materials than on the uranium-free materials. At the higher hardness level, where many of the specimens cracked, the uranium-free steel was superior to those which contained uranium.

Similar tests on the same steels were performed in a boiling solution of calcium nitrate and ammonium nitrate designed to produce nitrate cracking. The uranium-free steel appeared to be slightly superior to the corresponding steel containing 0.12% uranium. Two steels which contained 0.07% uranium plus both higher and lower carbon contents than the control appeared to equal it under the test conditions. At the Rockwell C-33 hardness level, the control material and the 0.12% uranium steel appeared equally susceptible to cracking. However, two materials which contained 0.073% uranium, 0.17% carbon, and 0.09% uranium and 0.51% carbon respectively appeared to be superior to the available control.

Passing mention may be warranted of the observation that while ordinary steels were embrittled after acting as cathodes in 4% sulphuric acid, similar uranium-bearing steels remained ductile. Further investigation of this interesting and potentially important phenomenon is planned.

Field Tests

Three field tests were initiated, exposing uranium-bearing carbon steels to atmospheric conditions, acid leaching solutions and sea water.

As-rolled 0.35% carbon steel sheet, with and without 0.12% uranium, is being exposed to atmospheric attack in central Ottawa. After one year of exposure, no significant difference in type of attack was observed, and it was found that weight losses of the uranium-bearing steels were inconsistent (7). More controlled testing has been initiated.

As-rolled 0.20% carbon steel bar stock, without uranium and with 0.056 and 0.097% uranium, is being exposed in several locations in an acid leaching plant. After six months, no significant differences in type or extent of attack were evident. This test is continuing.

Chain links made from 0.2% carbon steels containing 0.06 and 0.24% uranium were attached to a buoy and submerged in sea water(8). After ten months the tests were terminated because of excessive wear.

High-Temperature Oxidation Tests

In oxidation tests at temperatures up to 860°C (1580°F) uranium alloying additions did not affect the behaviour of 0.33 to 0.39% carbon steels to a marked degree(1). Similarly, high-purity iron alloyed with uranium showed only minor differences in behaviour from uranium-free high-purity iron at temperatures up to 900°C (1650°F).

LOW ALLOY STEELS

Tests in Acid Solution

In the single series of tests carried out on as-cast low alloy steels (1% Cr, 1% Mo, 1% V) uranium additions had a striking effect. In 14% HCl at 50°C (122°F) alloys containing 0.063 and 2.11% uranium showed much more uniform attack than a similar uranium-free alloy (Figure 8.3). The uranium additions appeared to cause a sharp decrease in the severity of pitting. Further investigations are planned on this type of alloy.

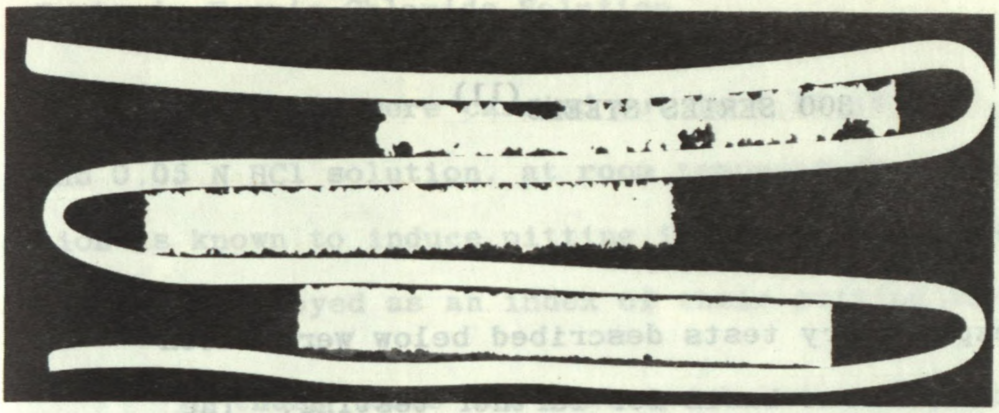


Figure 8.3 - Cross Sectional View of As-Cast Low Alloy Steels (based on heat 4358; 0.25% C, 0.024% S, approx. 1% Cr, 1% Mo, 1% V). After 23 hr in 14% HCl at 50°C (122°F). About X8.

High-Temperature Oxidation Tests

The alloys described above were subjected to exploratory high-temperature oxidation tests. At temperatures of 570°C (1060°F) and 890°C (1635°F), there was a tendency for the uranium-bearing alloys to oxidize at a higher rate, particularly the alloy containing 2.11% uranium(9).

Field Tests of Corrosion Resistance

Buoy chain links made from AISI 4617, modified with 0.02 and 0.12% uranium, and from AISI 8620 steels were put in marine service for ten months(8). The test was terminated because of wear losses. The uranium-bearing alloys had slightly lower weight losses, but exhibited the same type of attack as the uranium-free alloy.

300 SERIES STEELS(11)

General

The exploratory tests described below were inconclusive, but form some basis for further testing. The corrosive media used were acidified ferric chloride, hydrochloric acid and sulphuric acid solutions. Other tests carried out in nitric acid solution are described separately in Chapter 6. The steels used in the tests are listed according to grade and composition in the Table 8.5 below.

TABLE 8.5

Chemical Analyses of Corrosion Samples, %

Type	Heat No.	C	Cr	Ni	U	Other
303	4797	0.12	18.24	12.17	0	S 0.17
	4786	0.05	18.60	9.17	0.29	S 0.08
	4763	0.08	18.44	9.03	0.52	S 0.09
304	4585-1	0.04	18.63	8.77	-	
	4585-2	0.04	18.26	8.49	0.90	
	4814	0.06	19.00	9.58	-	
	4815	0.06	19.88	9.43	0.46	
	4819	0.06	18.68	9.34	1.07	
309	4806	0.12	24.08	11.87	-	
	4820	0.07	24.64	12.64	0.98	
316	4793	0.10	17.60	13.72	-	Mo 2.23
	4761	0.11	17.56	11.93	0.34	Mo 2.25

Tests in Ferric Chloride Solution

The tests were carried out in a 10.8% $FeCl_3$, $6H_2O$ and 0.05 N HCl solution, at room temperature. This solution is known to induce pitting in 300 series alloys, and has been employed as an index of their pitting susceptibility(10).

In these tests the flat specimens were polished on a surface parallel to the forging direction. The other surfaces of the specimens were shielded with a resistant paint. The specimens, with the polished surface upwards, were immersed in the corrosive medium, which was agitated by a magnetically controlled stirrer.

Strong attack sometimes occurred in the crevice between paint and metal, or at weak spots or blisters remote from the crevice. However, the errors from this source did not appear to be sufficient to affect the main trends in the observations.

Table 8.6 lists the results of corrosion tests in which the specimens were weighed at 4 hour intervals, with a total exposure of 20 or 24 hours. Corrosion rates were determined from the final slope of each curve.

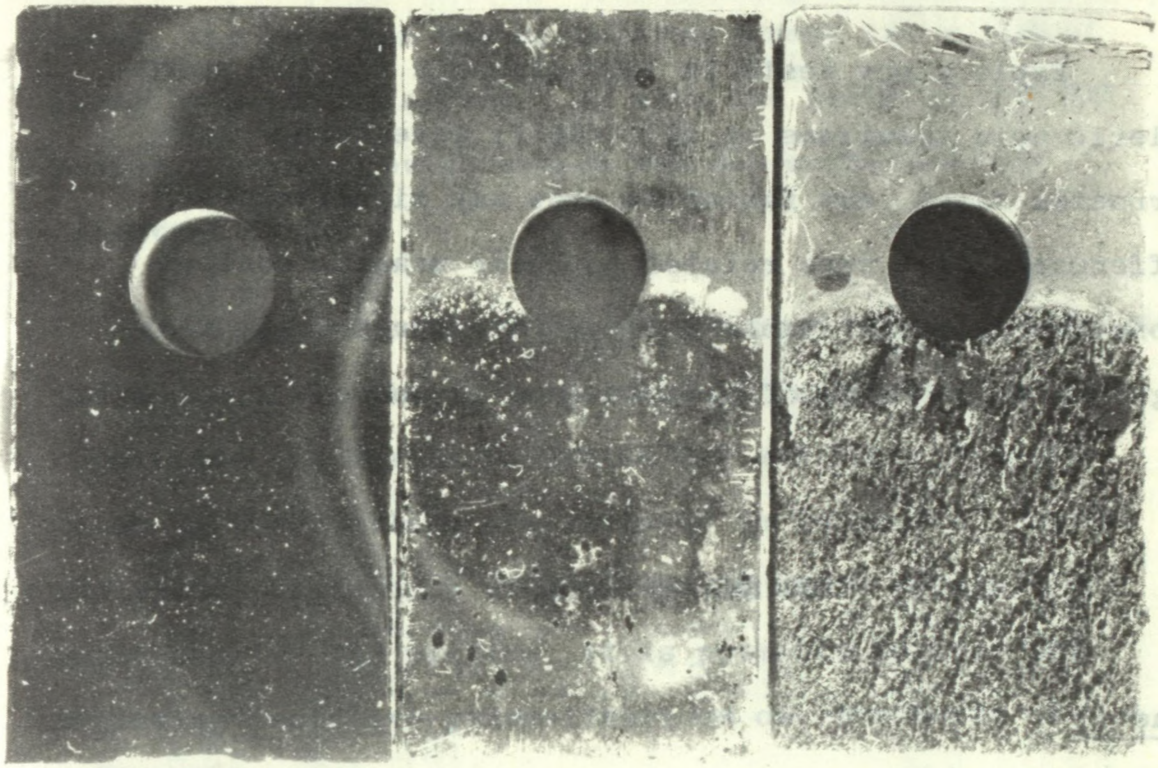
TABLE 8.6

Corrosion of AISI 300 Stainless Steels in Aqueous 10.8% $FeCl_3.6H_2O$ + 0.05 N HCl(11)

AISI Type	Heat No.	U %	C %	S %	Corrosion Rate, mg/sq cm^2/hr Condition*			Time, hr
					"A"	"B"	"C"	
303	4797	0.0	0.12	0.17	23.	10.8	9.4	24
	4786	0.29	0.05	0.08	8.0	7.3	11.1	24
	4763	0.52	0.08	0.09	5.7	3.9	5.7	24
304	4585-1	0.0	0.04	-	-	-	11.	20
	4585-2	0.9	0.04	-	-	-	20.	20
	4814	0.0	0.06	-	4.9	-	-	24
	4815	0.46	0.06	-	3.8	-	-	24
	4819	1.07	0.06	-	4.8	-	-	24
309	4806	0.0	0.12	-	5.5	-	-	24
	4820	0.98	0.07	-	5.9	-	-	24
316	4793	0.0	0.10	-	3.9	1.4	4.9	24
	4761	0.34	0.11	-	3.7	0.5	1.4	24

* Condition: "A" - as-forged and rolled
"B" - "A" plus quench anneal
"C" - "A" plus "B" plus 1 hr at 650°C (1200°F).

The as-forged uranium-bearing Type 303 steels showed considerable improvement in corrosion resistance as compared to the uranium-free control (Figure 8.4). This improvement is considered to be related mainly to the uranium content, despite the lower sulphur and carbon contents of the uranium-bearing steels.



Alloy 4763 A
0.52% U
0.09% S
0.08% C

Alloy 4786 A
0.29% U
0.08% S
0.05% C

Alloy 4797 A
No U
0.17% S
0.12% C

Figure 8.4 - As-forged Type 303 Alloys of Different Uranium Content After 24 hr in 10.8 $FeCl_3.6H_2O$ 0.05 N HCl Solution at Room Temperature(11). X4

There was no indication that uranium alloying additions were beneficial in Types 304 or 309 stainless steels. In Type 316, uranium lowered the corrosion rates in the B and C conditions.

Tests in H_2SO_4 and HCl Solutions

Exploratory tests in 10% sulphuric and 10% hydrochloric acid solutions at 30°C (86°F) gave rather low corrosion rates, and failed to show any significant differences that were related to their uranium content among the alloys of Table 8.5. More comprehensive testing on a wider range of compositions is needed.

400 SERIES STEELS

General

Exploratory corrosion tests on 400 Series steels, described below, indicated that uranium alloying additions imparted increased resistance to attack by non-oxidizing acids and neutral salt solutions. However, it should be emphasized that these results are preliminary in character and will require confirmation and extension in a wider range of alloy compositions and corrosive media.

Tests in Acid Solutions

Most of the tests(12) were carried out in acidified ferric chloride solution(10). The flat metal specimens were polished on one surface transverse to the direction of rolling. The other surfaces were shielded with acid resistant paint. The specimens were immersed, polished face up, on the flat bottom of a plastic tank. During tests, the solution was circulated across the polished faces by means of a pump. As with the tests on the 300 Series steels, crevice attack was not considered an important factor.

Weight losses in standard 4 hour tests on ferritic and martensitic alloys in several different metallurgical conditions are listed in Tables 8.7 and 8.8. Compositions of these alloys are included in Table 6.1. Though additional tests on a wider range of alloy compositions would clarify the picture, it is possible to make the following tentative generalizations on the basis of available results.

1. Uranium improved corrosion resistance most effectively in as-forged alloys. To a lesser extent, improvements were observed for annealed ferritic and the quenched martensitic alloys. Uranium alloying additions were least effective in tempered alloys.

2. Improvements in corrosion resistance were produced by smaller amounts of uranium in the alloys containing higher chromium (except where carbon was also high) than in the alloys with lower chromium. Thus, in general, uranium additions were more beneficial for the ferritic than the martensitic alloys.

TABLE 8.7

Results of 4 hr Corrosion Tests in 10.8% $FeCl_3.6H_2O$ 0.05 N HCl Solutions at Room Temperature for Ferritic 400 Stainless Steel Alloys Alloyed with Uranium, in Different Metallurgical Conditions(12)

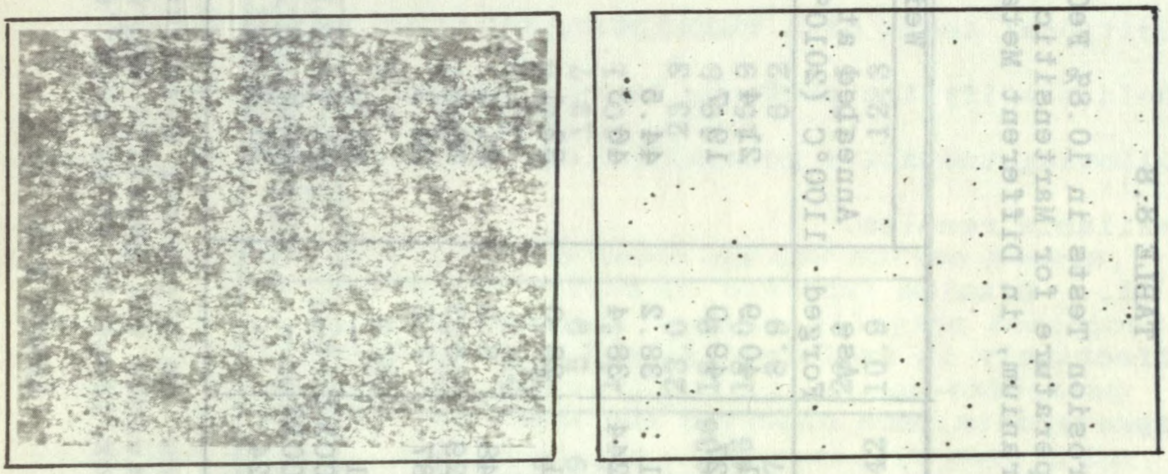
Heat No.	Alloy Type	Composition, %			As-Forged	Weight Loss, mg/cm^2	
		Cr	C	U		Annealed 760-790°C (1400-1450°F)	Oil Quenched 1100°C (2010°F) Tempered at 650°C (1200°F)
4473	403 (modified) 0.64% Mo	13.6	0.03	nil	32.3	9.5	19.1
				0.27	31.8	21.7	19.4
4489	430	14.0	0.04	nil	31.7	23.3	92.4
				0.35	30.5	15.9	30.4
				0.89	5.9	12.7	31.1
				1.43	11.1	10.1	27.3
4669	430	17.4	0.10	nil	23.0	23.3	15.9
				0.0036	18.2	19.8	19.7
				0.046	18.0	15.9	18.9
				0.27	8.9	6.2	15.3
4725	446	24.7	0.20	nil	20.8	10.6	11.7
				0.042	10.9	12.3	12.2

TABLE 8.8

Results of 4 hr Corrosion Tests in 10.8% $FeCl_3.6H_2O$ 0.05 N HCl Solutions at Room Temperature for Martensitic 400 Series Stainless Steels Alloyed with Uranium, in Different Metallurgical Conditions(12)

Heat No.	Alloy Type	Composition, % Cr	C	U	As-Forged	Weight Loss, mg/cm^2 Annealed at 1100°C (2010°F)	Oil Quenched 1100°C (2010°F) Tempered at 650°C (1200°F)	300°C (570°F)
4456	403	13.7	0.16	nil	40.9	21.4	25.2	28.0
				0.27	49.0	19.7	28.6	18.4
4497	440A	16.5	0.65	nil	38.2	44.5	24.1	53.1
				0.244	38.4	46.3	23.5	55.5
4546	403 (modified)	11.6	0.10	nil	28.0	32.1	23.5	22.5
	1.9% Ni			0.48	8.2	21.4	25.7	20.6
	1.8% Mn			1.29	5.3	26.5	21.3	32.8
	1.6% Si			1.87	7.5	24.2	23.4	30.2
4639	403	11.9	0.09	nil	-	22.0	23.4	-
	(modified)			0.003	-	11.4	17.5	-
	1.9% Ni			0.0028	-	14.8	20.7	-
				0.24	-	20.2	23.1	-

It was difficult to generalize concerning the appearance of the specimens after the tests. However, the uranium-free alloys generally showed intergranular attack, sometimes accompanied by end-grain pitting. Addition of sufficient uranium resulted in specimens that maintained a shinier surface with reduced end-grain pitting. An example of the corrosion resistance of the as-forged uranium-bearing alloys appears below (Figure 8.5).



No uranium 0.27% uranium

Figure 8.5 - Surfaces of As-forged Type 430 Stainless Steel Specimens (Heat 4669) After Testing in Acidified Ferric Chloride Solution(12). X6

As-forged Type 430 stainless with and without uranium was also tested in three acid media as reported in Table 8.9. The results indicated reduced corrosion and end-grain pitting for the alloy containing 0.27% uranium in 4% hydrochloric and 10% sulphuric acid solutions at 30°C (86°F). No significant improvement was observed in boiling 65% nitric acid solution.

TABLE 8.9

Corrosion Behaviour of As-Forged Alloys of 430 Stainless Steel (Heat 4669) Immersed in Acid Solutions

Test No.	% U	Solution	Temperature	Test Duration, hr	Weight Loss, mg/cm^2	Surface Appearance
1	nil 0.0036 0.046 0.27	4% HCl	30°C (86°F)	21	76.8 77.0 62.4 31.3	The alloy with 0.27% U appeared smooth and had only a few small shallow pits. The other alloys had rough surfaces with many end-grain pits.
2	nil 0.0036 0.046 0.27	10% H_2SO_4	30°C (86°F)	10	102.8 85.7 81.8 48.3	The 0.27% U alloy appeared smoother and had considerably fewer end-grain pits than the others.
3	nil 0.27	65% HNO_3	boiling	96	25.4 22.1	Both alloys showed equal pitting and intergranular attack. No significant differences were observed in either pitting or intergranular attack.

Tests in Neutral Salt Solution

Specimens of as-forged 430 stainless steel (Heat 4669) were tested in 3% sodium chloride solution. Behaviour in these tests may be indicative of behaviour in sea water.

In two experiments (Table 8.10) the alloys were tested for crevice corrosion by clamping one side of the flat specimens to a glass sheet. It was observed that the alloy containing 0.27% uranium remained pit-free in the crevice, while the other three alloys were heavily pitted on the crevice side.

In a third experiment, bare specimens were suspended in 3% sodium chloride solution at 85°C (185°F). This solution is known to induce pitting(13). All four alloys showed pits, but the weight loss was significantly lower for the alloy containing 0.27% uranium.

TABLE 8.10

Corrosion Behaviour of As-Forged Alloys of Type 430 Stainless Steel (Heat 4669) in 3% NaCl Solution

Test No.	% U	Type of Test	Temperature	Test Duration, hr	Weight* Loss mg/cm^2	Remarks
1	0 0.004 0.05 0.27	One side of specimen clamped to sheet of glass (crevice attack)	30°C (86°F)	51	2.1 1.7 1.9 0.1	The specimen with 0.27% uranium was unpitted. The others were heavily pitted in the crevice.
2	0 0.004 0.05 0.27	One side of specimen clamped to sheet of glass (crevice attack)	30°C (86°F)	114	3.5 3.0 2.5 0.6	The specimen with 0.27% uranium was unpitted. The others were heavily pitted in the crevice.
3	0 0.004 0.05 0.27	All sides of specimens were exposed to oxygenated solution.	85°C (185°F)	96	4.3 4.6 4.3 2.4	All four alloys pitted.

*Calculated from crevice area in Tests 1 and 2, assuming negligible weight loss on the other surfaces.

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CHAPTER 9

WELDING OF URANIUM-BEARING STEELS

K. Winterton* and W.P. Campbell**

SYNOPSIS

Recovery of uranium in steel weld deposits depends on the joining process. Recoveries of about 26% were obtained with inert-gas tungsten-arc welding. Recoveries of 1 to 2% were obtained with metal-arc welding.

The weldability of uranium-bearing carbon steels has been assessed with principal emphasis on the possibility of heat affected zone cracking. Cruciform and controlled-thermal severity tests have been made on various steels with carbon content in the range 0.25 to 0.58%, and with uranium content up to 0.23%. Some comments have also been made on the possible effect of uranium content on weld-metal cracking, but this has not been directly investigated. Longitudinal bead weld tests were undertaken on segregated uranium-bearing steel, and it was found that the presence of uranium-rich segregates in the heat-affected zone does not affect the extent of cracking in that region. The indications are that carbon steels, with uranium up to 0.1%, are weldable under conditions appropriate for similar steels without uranium.

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*Head and **Senior Scientific Officer, Welding Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys.

Spot welding tests have been carried out on steels with lower carbon content in the form of cold-finished sheet. No special difficulties were introduced when small amounts of uranium (about 0.05%) were present. Mention is also made of the satisfactory joining, by resistance butt welding, of low carbon steels contains up to 0.24% uranium.

INTRODUCTION

The metallurgical investigations of uranium-bearing steels(1) have not so far revealed many effects that would find direct, beneficial applications in welding technology. High-temperature strength, resistance to corrosion and improved corrosion-fatigue life are all important properties ascribed to uranium-bearing steels(1), but these do not bear directly on the joining process.

The primary aim of the work described in this section was to determine the influence of uranium on steel weldability, since this would be important for industrial application of new alloys. A fuller account of the work is available in an internal report(2).

ADDITION OF URANIUM TO WELD METAL

Metal-arc Welding

Some 12% ferro-uranium alloy was pulverized and mixed with a solution of sodium silicate to make a slurry for coating conventional electrodes. Commercial E6012 electrodes were coated, with the ferro-uranium constituting 3% and 1% of the total electrode weight. Also, control electrodes were coated with sodium silicate only. Comparative welding trials were made with these three types of electrode, as well as with untreated electrodes.

There was no apparent variation in the arc characteristics of the different electrodes. Bead contour was good and spatter losses were minor. Penetration into the base plate was uniform, and the resultant beads had similar microstructure. Complete cracking occurred in all double-fillet hot-cracking tests at the highest level of severity. Lehigh restraint tests at the highest level of severity, despite some variation in the crack length, showed no significant tendency for uranium to promote cracking in the weld metal.

Unfortunately, most of the uranium was lost in passage across the arc. The uranium contents of the deposited metal were 0.003 and 0.002%, respectively, thus showing that only 1 to 2% of the uranium was recovered in the deposit. It is considered that, even under optimum conditions, metal-arc welding would provide inadequate shielding for the successful transfer of uranium.

Inert-gas Tungsten-arc Welding

Using uranium-bearing carbon steel wire (0.44% C, 0.16% U) as filler, tests were made using tungsten-arc welding with argon shielding. Weld deposits were made in grooved uranium-free steel plates of about the same carbon content as the wire.

The uranium steel wire melted in quietly, producing a smooth deposit. There were no obvious defects associated with the deposit or the base plate metal. The weld surface was clean, showing no signs of an oxide film.

The uranium content of the deposited metal was 0.041%, representing a recovery of about 26%. This is less than the recovery of titanium in stainless steels welded under argon shielding, but similar to the recovery of titanium under carbon dioxide shielding. Due to the low recovery of uranium from the welding wire, it may be more practicable to use alloying elements other than uranium, when it is necessary to produce weldments with properties matching those of uranium steels.

Autoradiographic studies revealed no obvious segregation of uranium within the weld metal.

HEAT-AFFECTED ZONE CRACKING IN METAL-ARC WELDS

General Considerations

By analogy with titanium and other similar metals, uranium would be expected to have a beneficial effect on heat-affected zone cracking, if it fulfilled the role of withholding some carbon from solution, while the metal adjacent to the weld was heated to high temperatures. However, results of other investigations have cast doubt on the formation of any iron-rich carbide when uranium is below about 0.35%.

Metallurgical investigations have also shown that, although uranium has negligible influence on the critical points or peak austenitization temperatures, there may be a slight increase in hardenability. Considering this latter effect, uranium might be expected to cause a slight, perhaps imperceptible, increase in heat-affected zone cracking.

There is, therefore, the possibility that uranium might have two slight but opposed effects on heat-affected zone cracking. Similar, though much stronger, opposed effects occur with molybdenum and vanadium, and this explains why these elements have a variable effect on heat-affected zone cracking; for molybdenum and vanadium the net effect is usually beneficial.

Varying Carbon and Uranium Contents

Steels with the spoon sample compositions shown in Table 9.1 were tested for weldability in the cruciform test (Figure 9.1).

TABLE 9.1

Compositions of Steels Tested

Designation	C, %	Mn, %	U, %	Carbon Equivalent*
1403	0.58	0.75	0.08	0.70
1395	0.51	0.57	0.09	0.61
4345	0.33	0.68	0.14	0.44
1369	0.34	0.50	Nil	0.42
1373	0.35	0.34	0.11	0.41
1398	0.25	0.48	0.23	0.33

* - Determined from the formula C.E. = % C + % Mn/6, ignoring the effect, if any, of uranium.

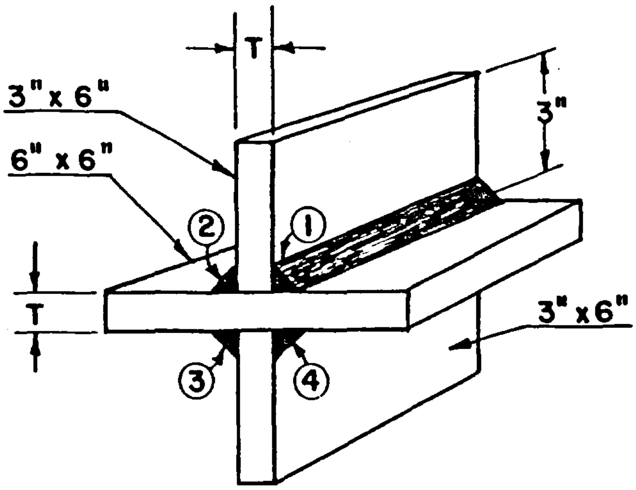


Figure 9.1 - Cruciform Weldability Test Assembly. Four welds are laid successively as indicated, with a 2-hour interval between welds. After a 48-hour delay the welds are sectioned transversely, and examined, most attention being given to the area adjacent to weld No. 3.

Normally, low-hydrogen electrodes would be recommended for these steels, with the exception of steel 1398, which has the lowest carbon equivalent. Accordingly, a number of tests were carried out using low-hydrogen E7016 electrodes on the three steels with the highest carbon equivalents, i.e., steels 1403, 1395 and 4345. To obtain comparative data on the tendency to produce heat-affected zone cracking, steels 1398, 1373, 1369 and 1403 were subsequently tested with E6010 and E6012 electrodes. Cracks, adjacent to weld No. 3, were detected and evaluated by magnetic powder inspection and, where necessary, by microscopy, on four transverse sections taken from the cruciform assembly. The occurrence of cracking is significantly influenced by energy input. The energy input values are included with the test results in Table 9.2.

Severe cracking was obtained on one of the higher carbon steels (1395), even with low-hydrogen electrodes, when the energy input was low. No cracking was obtained with any of the steels tested using low-hydrogen electrodes when the energy input was in the range 51,000 to 57,400 joules per in.

No cracking was obtained with the steels tested using conventional high-hydrogen electrodes when the energy input was in excess of about 50,000 joules per in.;

the steels tested included that with the highest carbon equivalent, steel 1403. This latter steel cracked when the energy input was reduced to 41,700 joules per in., whereas a low carbon steel, 1398, resisted cracking even when the energy input was as low as 36,100 joules per in.

TABLE 9.2

Results of Cruciform Testing of Uranium-Bearing Carbon Steels

Designation	Electrode	Energy Input, (joules/in.)	Cracking
1403	7016	55,000	Nil
1403	7016	57,400	Nil
1403	6010	59,600	Nil
1403	6012	41,700	Complete fracture
1395	7016	51,000	Nil
1395	7016	39,000	Complete fracture
4345	7016	53,500	Nil
1369	6010	56,000	Nil
1369	6012	50,000	Nil
1369	6012	40,000	Severe cracking* in all sections
1373	6010	57,000	Nil*
1373	6012	35,000	Nil*
1398	6010	57,400	Nil**
1398	6010	55,000	Nil**
1398	6012	36,100	Nil*

* - Magnetic powder examination only
** - Some weld metal cracks were observed

Steel 1369, with a carbon equivalent of 0.42 and no uranium, cracked extensively at an energy input of 40,000 joules per in., whereas steel 1373, with a carbon equivalent of 0.41 and a uranium content of 0.11%, resisted cracking even when the energy input was as low as 35,000 joules per in. While this might be considered to indicate that uranium inhibits the occurrence of heat-affected zone cracking, more extensive testing would be required to establish the significance of the results. In general, the steels tested behaved as might be expected of similar steels without uranium. Indications from this work are that uranium does not have a major influence on the occurrence of heat-affected zone cracking. Welding conditions can be chosen, in terms of electrode type and energy input, for the production of sound joints.

Subsequent examination of the test plates showed that considerable segregation was present, and the results must be viewed in this light.

Fixed Carbon (0.4%) and Varying Uranium Content

Steel, with and without uranium, was produced for welding tests from a split heat to minimize compositional variation. The chemical compositions of these steels are shown in Table 9.3.

TABLE 9.3

Composition* of Medium-Carbon Steels Tested

Designation	C, %	Mn, %	Si, %	S, %	P, %	Acid Insol. U, %	Total U, %
1551-1	0.40	0.52	0.07	0.017	0.005	Nil	Nil
1551-2	0.38	0.54	0.07	0.017	0.005	0.0068	0.027**

* - Values obtained from separate spoon samples.
** - Separate samples from two parts of the plate analysed 0.023% total uranium.

Cruciform tests and controlled thermal severity (CTS) tests (Figure 9.2) were made on these steels using two kinds of electrodes. Low-hydrogen electrodes (E7016) were baked until the moisture content was 0.41 to 0.47%. Rutile electrodes (E6012) were also used, taken directly from open storage shelves. The results of the tests are shown in Table 9.4.

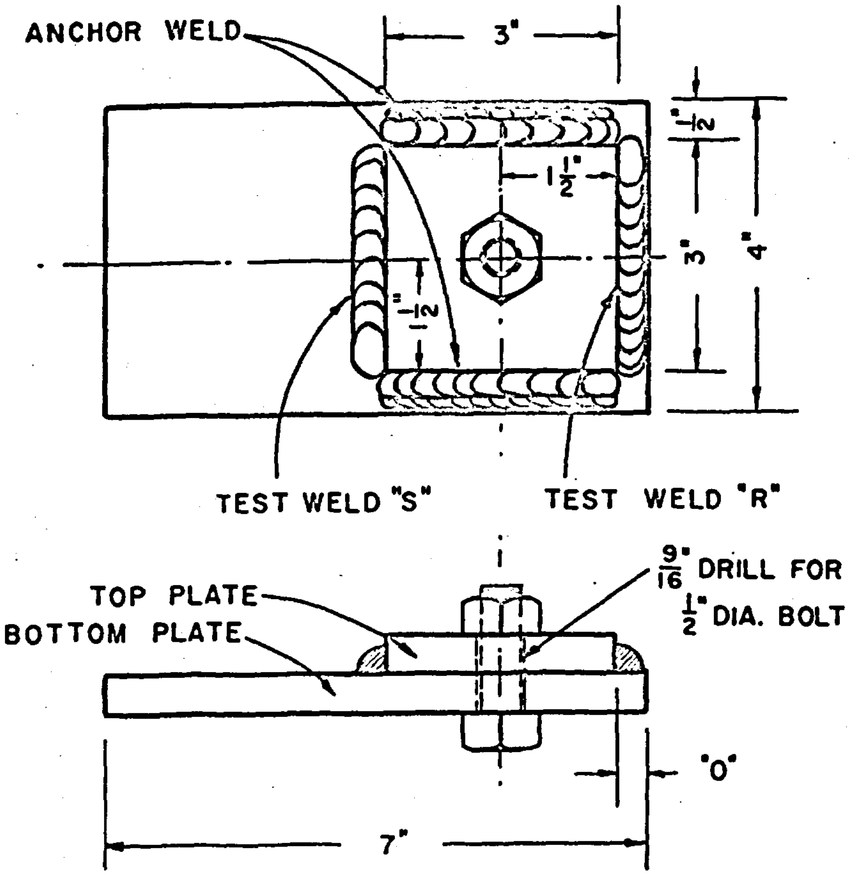


Figure 9.2 - CTS Weldability Test Assembly (t = ½ in., b = 1-1/4 in.). Inspection of the assembly is delayed for 48 hours after preparation. The left-hand test weld, as shown, is laid last and is the most prone to crack. Three sections of this weld were studied.

TABLE 9.4

Effect of Uranium on the Extent of Heat-Affected Zone Cracking in Medium-Carbon Steel

		CTS Test		Cruciform Test	
Electrode	Uranium Content, %	Energy Input, j/in.	Crack Rating (three sections)	Energy Input, j/in.	Crack Rating (four sections)
7016	Nil	21,000	0 0 0	17,800	0 0 0 0
		23,600	0 0 0	20,200	0 0 0 0
		36,200	0 0 0	40,000	0 0 0 0
		39,200	0 0 0	42,000	0 0 S S
7016	0.027	25,100	0 S S	18,000	0 0 0 0
		34,300	0 0 0	39,800	0 0 0 0
		38,500	0 0 0		
6012	Nil	35,700	0 0 M	36,500	0 0 0 0
		37,200	S S M	38,800	0 0 0 0*
6012	0.027	36,800	0 0 S	39,200	0 0 0 0

* - Slight cracking in the weld metal.

Notes: 0 - no cracking

S - slight cracking, not in excess of 25% of the length of the weld fusion line

M - cracking with extent in the range of 25 to 50% of the length of the weld fusion line.

In metal-arc welding of steel with about 0.4% carbon content, low-hydrogen electrodes would normally be specified. As expected, negligible cracking occurred in those tests using E7016 electrodes.

Tests with the high-hydrogen electrode gave tentative indications that uranium has a slight beneficial effect in reducing heat-affected zone cracking. More testing would certainly be required to establish its influence more definitely.

Tests on Segregated Steel

A second heat was split. The two resulting steels had the composition shown in Table 9.5.

TABLE 9.5

Composition* of Steels Tested for Effect of Segregation

Designation	C, %	Mn, %	Si, %	S, %	P, %	Acid Insol. U, %	Total U, %
1569-2	0.43	0.53	0.14	0.016	0.010	Nil	Nil
1569-4	0.43	0.53	0.13	0.016	0.010	0.039	0.124

* - Spoon sample analyses

Autoradiographs of steel 1569-4 showed severe segregation. Sample drillings from two locations with relatively minor segregation analysed 0.073% and 0.093% uranium, respectively. A third sample from a heavily segregated location analysed 0.41% uranium.

Because it is difficult to avoid all traces of segregation in uranium steels, the influence of the segregation on heat-affected zone cracking assumes considerable importance. It was decided that longitudinal weld bead tests, with an attempt made to lay the test welds in regions of high segregation, would be the most revealing. Low-hydrogen electrodes (E7016) and conventional high-hydrogen electrodes (E6010) were used. Longitudinal weld bead tests were also made on steel 1569-2 for comparison. The welds were sectioned longitudinally, and examined for heat-affected zone cracking using a magnetic method, and in some instances, microscopy. The results of the tests are shown in Table 9.6.

TABLE 9.6

Extent of Cracking in Longitudinal Bead Tests

Test No.	Designation	Uranium Content, %	Electrode Type	Cracking, % of Bead Length
1	1569-2	Nil	E7016	Nil
2	1569-2	Nil	E7016	Nil
3	1569-4	0.124	E7016	Nil
4	1569-4	0.124	E7016	Nil
5	1569-2	Nil	E6010	95
6	1569-2	Nil	E6010	75
7	1569-2	Nil	E6010	Nil
8	1569-2	Nil	E6010	Nil
9	1569-4	0.124	E6010	75
10	1569-4	0.124	E6010	70
11	1569-4	0.124	E6010	10
12	1569-4	0.124	E6010	Nil

The variable extent of cracking under apparently constant test conditions is characteristic of this test. The similar cracking behaviour of the two steels indicates that uranium at the level used has little effect on the tendency of this grade of steel to crack in the heat-affected zone.

Particular care was taken in the microscopical examination to detect any effect of segregates in and near the heat-affected zone. In some isolated areas, cracking was associated with uranium-rich segregates, but most of the cracking was remote from segregated areas. It may be concluded that the presence of such segregates has very little, if any, significance in determining the tendency for heat-affected zone cracking.

Tests on Uranium-bearing Steel With Minimum Segregation

Two heats of steel were cast to the composition shown in Table 9.7. Autoradiographs of the machined test plates revealed only minor segregation.

TABLE 9.7

Chemical Compositions of Test Materials

Designation	C, %	Mn, %	Si, %	U, %	Carbon Equivalent
4594	0.42	0.85	0.19	0.045*	0.56
4764	0.42	0.81	0.16	Nil	0.55

* - Plate analysis (others are spoon analyses)

The results of cruciform and CTS tests on the uranium steel are shown in Table 9.8.

TABLE 9.8

Results of Welding Tests

Electrode	CTS Tests		Cruciform Tests	
	Energy Input, j/in.	Cracking	Energy Input, j/in.	Cracking
E7016	48,300	Nil	38,800	Severe cracking in two sections
E6012	35,700	Severe cracking in all sections	34,000 34,600 21,000	Complete fracture adjacent welds 3 and 4

It is evident that this steel is prone to heat-affected zone cracking, as would be expected from the relatively high carbon equivalent. No conclusion concerning the effect of uranium can be drawn until the companion uranium-free steel is tested.

WELD-METAL CRACKS IN METAL-ARC WELDS

Except for steels and weld metal of very high strength, one of the most common forms of weld-metal cracking is hot cracking, associated with the formation of low melting-point compounds at the grain boundaries.

It might be thought that uranium, because it interferes with the sulphur balance and the formation of the sulphides, might have some influence on hot cracking. It is, however, difficult to theorize about this.

Another, and perhaps more important, effect of uranium in connection with susceptibility to hot cracking is the possible formation of the epsilon phase, UFe_2, which is associated with thermal cracking, poor forgeability and other indications of hot shortness. From the metallurgical investigations, it appears unlikely that troubles from this source would normally be encountered with uranium contents less than 0.15%.

Slight cracking of the weld metal occurred in two cruciform tests on steel 1398, which contained 0.23% uranium with about 0.25% carbon. The cracks tended to be remote from the uranium-bearing parent metal, but even so they may have been associated with pick-up of uranium in the weld metal from the steel. No such cracking was found in the welds of cruciform tests made on other steels containing up to 0.11% uranium, or in deposited weld metal containing 0.041% uranium deposited from uranium-bearing steel wire using the tungsten-arc process. It is of interest that no weld-metal cracking was found in a third cruciform test on steel 1398, in which the test conditions differed somewhat from the two tests where cracking occurred.

With a lower energy input, 36,100 joules per in. instead of 55,000 to 57,400 joules per in., and using an E6012 electrode instead of an E6010 electrode, no weld-metal cracking occurred. These changes would reduce dilution of the weld metal with base plate metal and therefore reduce pick-up of uranium in the weld metal.

No evidence of hot shortness was encountered in the spot welding of low carbon uranium-bearing steel sheet (0.11% carbon, 0.05% uranium), but it is intended to undertake Houldcroft tests on this material to investigate further any tendency for hot cracking.

RESISTANCE WELDING

Spot Welding

Spot welding tests were carried out on cold finished steel sheet having a thickness of 0.063 to 0.069 in. and of the following reported composition:

C, %	Mn, %	Si, %	S, %	P, %	Total U* %
0.11	0.79	0.13	0.027	0.029	0.048

*Sheet analysed (others are spoon analyses)

Autoradiographic studies of the material revealed only minor segregation.

The chosen conditions resulted in spot welds with a diameter of about $\frac{1}{4}$ in. Tension-shear tests on twenty-six consecutive welds gave values from 4200 to 5350 lb with an average of 4780 lb. These values are considerably in excess of the minimum values normally suggested for low-carbon steels of the same thickness used. All failures were by nugget shear, with no sign of pulling of metal from the sheet. Further observations regarding the influence of uranium on quality of spot welds must await testing of a uranium-free steel produced and welded under the same conditions.

Upset Resistance Butt Welding

Two grades of steel, modified with uranium, were resistance butt welded at the plant of a co-operating chain manufacturer into chain intended for corrosion tests. The composition of each steel is given in Table 9.9.

No special difficulties were encountered during fabrication of the test chains from these steels. Some minor adjustments were made to the settings for the resistance welding of individual steels, but the heating cycle employed was quite similar to that used in the fabrication of conventional chain steels.

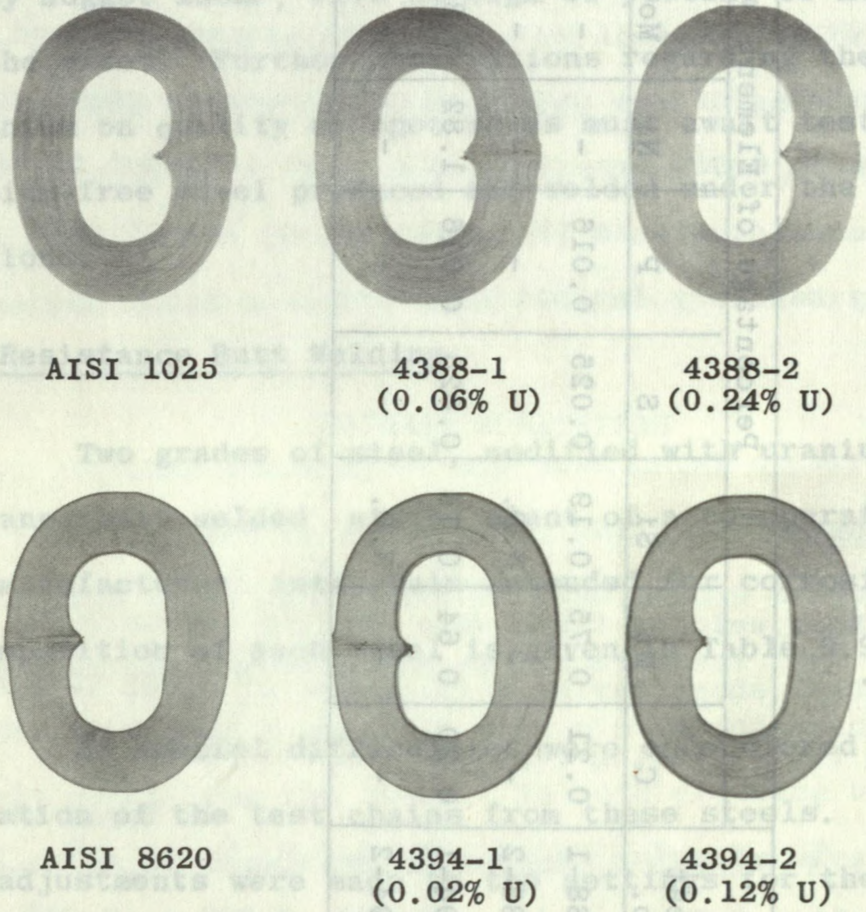
For comparison, chains were also made from commercial uranium-free AISI 1025 and AISI 8620 steels.

TABLE 9.9

Analysis of Steels for Resistance Welding

AISI Grade	Heat No.	Percentage of Element								
		C	Mn	Si	S	P	Ni	Mo	Acid Insol. U	Total U
1020	4388-1	0.21	0.75	0.19	0.025	0.016	-	-	0.0625	0.0633
	4388-2	-	-	N.D.	-	-	-	-	0.0845	0.236
4620	4394-1	0.20	0.64	0.14	0.026	0.016	1.82	0.25	0.011	0.022
	4394-2	-	-	N.D.	-	-	-	-	0.080	0.119

Sample links from each experimental chain length were removed for examination of the longitudinal mid-section. These samples were deep-etched in 1:1 hydrochloric acid solution at 74°C (165°F). Photographs of these deep-etched samples are shown in Figure 9.3.



AISI 1025

4388-1
(0.06% U)

4388-2
(0.24% U)

AISI 8620

4394-1
(0.02% U)

4394-2
(0.12% U)

Figure 9.3 - Structure of Mild and Low Alloy Steel Chain Links after Deep-etching. Approx. X 1/2

No abnormalities were revealed by an examination of the microstructures of welds from the two commercial steels and from the experimental steels with the higher uranium levels. These welds were clean and sound.

It may be concluded that AISI 1020 steel containing up to 0.24% uranium and AISI 4620 steel containing up to 0.12% uranium may be satisfactorily joined by upset resistance butt welding, though it should be borne in mind that possible segregation effects were not studied in this investigation.

CONCLUSIONS

1. Carbon steels, with uranium up to 0.1%, appear to be weldable under conditions appropriate for similar steels without uranium.

2. The presence of uranium-rich segregates in the heat-affected zone does not seem to affect the extent of cracking in this region.

3. In larger quantities, uranium may induce weld-metal cracking, since such cracks in weld deposits have been noted under some conditions in the welding of steels containing approximately 0.23% uranium.

4. Attempts to introduce uranium into weld metal have shown that losses occur by oxidation, and the best recovery so far achieved is about 26%. It may be necessary, for the welding of uranium-bearing steels, to secure any special properties required of the weld metal by means other than by the addition of uranium.

5. Preliminary results indicate no special difficulties in spot welding low-carbon steels containing about 0.05% uranium, or in resistance butt welding low-carbon steels containing up to 0.24% uranium.

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1. G.P. Contractor, "Influence of Uranium on Medium and Low Carbon Steels". Progress Report No. 1, Physical Metallurgy Division Internal Report PM-R-61-5 (May 1961).

2. K. Winterton, "Welding of Uranium-Bearing Plain Carbon Steels", Physical Metallurgy Division Internal Report PM-I-61-23 (1961).

CHAPTER 10

TYPICAL ANALYTICAL PROCEDURES FOR THE DETERMINATION OF URANIUM IN IRON AND STEEL ALLOYS

J.C. Ingles*, J.B. Zimmerman*, and
J.L. Horwood**

SYNOPSIS

The investigation and production of uranium-bearing steels and alloys presupposes accurate and convenient techniques for the analysis of uranium. Recommended procedures for fluorimetric, radiometric, X-ray emission spectrometric, volumetric and colorimetric techniques are presented in this chapter in summary form as an aid for researchers in this field.

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*Head and Senior Scientific Officer, respectively, Control Analysis Section, Extraction Metallurgy Division,
**Senior Scientific Officer, Physics and Radiotracer Subdivision, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

The analytical chemistry of uranium has been investigated extensively during the last decade, and as a result many excellent procedures are available for its determination. The literature on the subject has been summarized, with particular reference to the analysis of iron and steel alloys, in a companion publication(1), and this chapter is confined to actual working descriptions of methods used at the Mines Branch for the analytical control of the experimental production of uranium-bearing steel. Of the methods given, the fluorimetric method is the most widely applicable, but where a restricted range of alloys is involved, the radiometric and X-ray fluorimetric methods offer advantages in speed and simplicity of operation. Volumetric and colorimetric methods are also described and will be of interest to those laboratories that are not equipped to carry out the determinations by the other methods.

It should be pointed out that the chemical methods presented for the separation and determination of uranium are those that are believed to be most generally applicable in steel analysis. In the case of a particular mixture of alloying constituents, different combinations of the steps, made possible by the absence of a particular group of interfering elements, may provide a simpler method. Alternatively, a study of the more complete discussion in the Information Circular(1) may suggest a combination of methods which is simpler than any of those described here.

FLUORIMETRIC METHOD

Outline

This method is based on the measurement of the fluorescence produced when uranium, fused into beads of sodium fluoride, is illuminated with ultra-violet light. Large amounts of certain elements, such as iron, tend to decrease the fluorescent output, and in the following procedure, ethyl acetate extraction of uranyl nitrate from an aluminum nitrate medium is used to effect a separation of uranium from iron. This extraction separation procedure eliminates virtually all other elements, although a small fraction of any zirconium, titanium or thorium present will probably accompany the uranium.

Range

The method as written will permit the determination of as little as 0.001% uranium. It can be used to analyse almost any uranium-bearing alloy, but for precise results in the higher ranges a colorimetric or volumetric method is preferable.

Preparation of Equipment

a - Platinum Dishes

The platinum dishes used in this technique are prepared by pressing them from 3/4 in. x 0.015 in. platinum-rhodium alloy discs. A tray capable of holding twenty-four of the dishes is also required.

Care must be taken in cleaning the platinum dishes. Wash them in running hot water for ½ hour. Keep all the dishes of one set together and place them in 100 ml beakers, stacking them carefully so that one dish is not fitted into another one. Cover the dishes with concentrated hydrochloric acid and boil them for ½ hour. Repeat the acid treatment and rinsing. Finally, decant off the tap water, replace with distilled water and store for use. Do not touch the platinum with the fingers again until the beads have been read on the fluorimeter.

Occasional hand buffing with a household silica detergent cleanser helps to reduce quenching from contaminants absorbed into the dishes. From time to time the dishes may be cleaned with molten potassium bisulphate. Eventually the dishes absorb so much iron and other quenchers that erratic results are obtained. About once a year, depending on use, the used platinum dishes should be exchanged for new platinum.

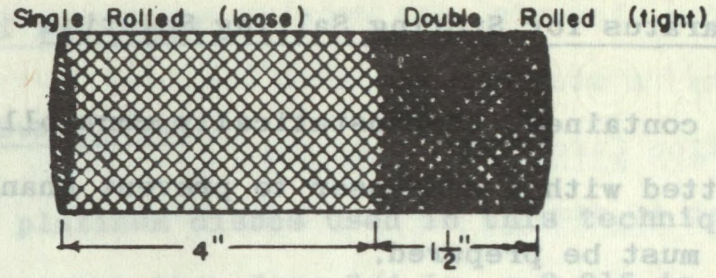
b - Apparatus for Storing Salting Solution

A container, thermostatically controlled at 80°C and fitted with a condenser to prevent change in concentration, must be prepared.

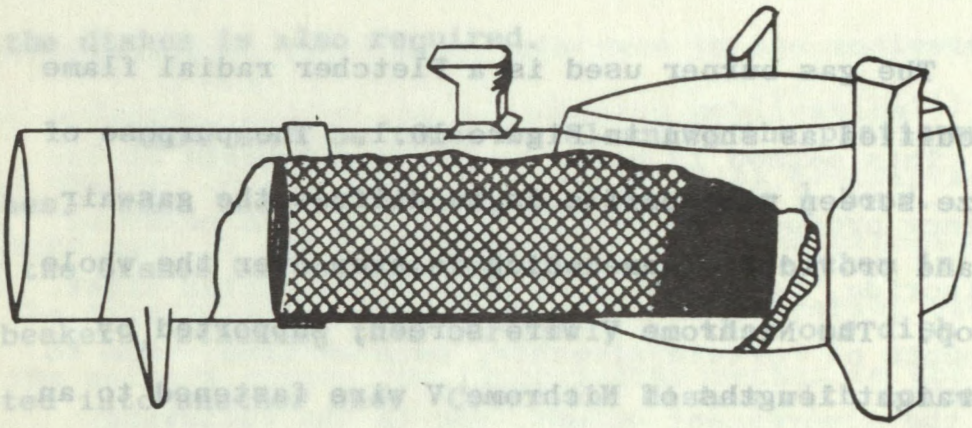
c - Gas Burner

The gas burner used is a Fletcher radial flame burner modified as shown in Figure 10.1. The purpose of the bronze screen wire baffle is to diffuse the gas-air mixture and provide a flame which is even over the whole burner top. The Nichrome V wire screen, supported by short straight lengths of Nichrome V wire fastened to an 8 in. cast iron tripod ring, is mounted ½ in. to 3/4 in. above the surface of the burner cap and serves to hold the dishes over the flame. A household vacuum cleaner provides a large volume of low-pressure air to support combustion of the gas.

After the gas has been ignited, the gas and air controls are adjusted to give a flame in which the bright blue gas cones are 1/4 in. to 3/8 in. high and of even height over the whole burner. (If the flame is not even, shut off the burner, take it apart and adjust the screen wire baffle). Then increase the air flow, by means of an adjustable air escape port, until the burner "howls". Cut the air back just sufficiently to prevent the howling, and leave the air setting in this position. Note the gas flow setting and then shut off the burner.



SCREEN WIRE BAFFLE



CUTAWAY VIEW OF BURNER SHOWING POSITION OF SCREEN WIRE BAFFLE

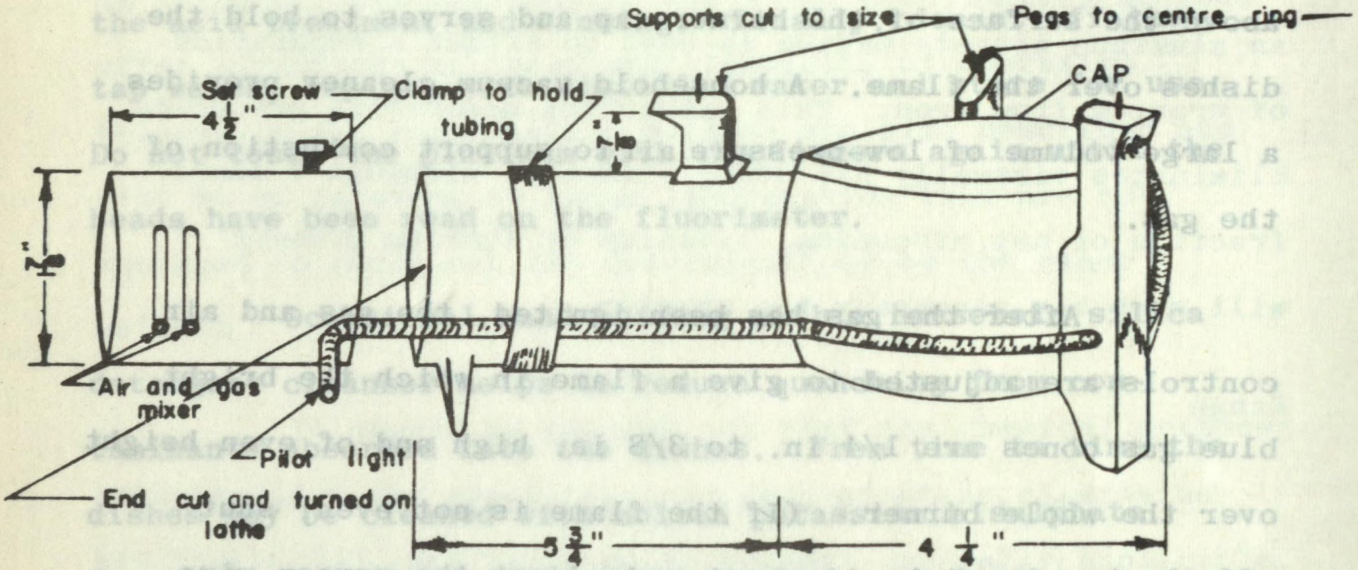


Figure 10.1 - Details of Modified Fletcher Radial Flame Burner (Compressed Air Supply)

Measure a flux pellet into each of twenty-two dishes, using the same technique as in preparing samples. Place them on the Nichrome screen support over the burner. Turn on the gas and ignite it. Leaving the air control as previously set, quickly adjust the gas to approximately the same gauge reading as before, and start the stop watch. By means of further small adjustments of the gas control, adjust the flame so it just stops "howling". Note the time it takes for the pellets to melt. If they take longer than 1-1/2 minutes, repeat the burner adjustment using a larger gas flow. If they melt too quickly, adjust the burner using a smaller gas flow. Once the proper adjustment is obtained, leave the air control as set and control the flame with the gas. It appears desirable to use a flame which is just hot enough to melt the pellet in the 1-1/2 minute period. Too rapid melting leads to quenching. On the other hand, too slow a fusion wastes gas and may result in quenching.

d - Fume Hood

A standard commercial 4 ft hood, lined with fire-brick (and fitted with a suitable flame baffle consisting of two sheets of heavy 1/4 in. mesh wire screening in the upper portion to protect the exhaust fan) is required to house the gas burner. This hood should have a face velocity of 150 to 200 linear feet per minute with a

1 ft sash opening. In operation, the sash is removed and a sliding panel of 1/4 in. asbestos board with an 8 in. x 8 in. mica window for observation of the flame, is used.

e - Galvanek-Morrison Fluorimeter

This is the most commonly used commercial fluorimeter. Details of its operation will be found in the literature supplied by the manufacturer.

Preparation of Reagents

a - Aluminum Nitrate Salting Solution

A 1 lb batch of C.P. aluminum nitrate should be tested for blank before being stocked. This reagent is used at the rate of ten determinations per pound.

Place approximately 1800 g (4 lb) of aluminum nitrate ($Al(NO_3)_3 . 9 H_2O$) in a 4 litre beaker and add 100 to 200 ml of distilled water. Cover the beaker and heat the mixture on a hot plate. If a clear solution does not result after 5 to 10 minutes boiling, add 50 ml of water and continue boiling for 5 more minutes. Repeat this step until a clear solution is obtained after boiling. Remove the cover glass and concentrate the solution by boiling until a boiling point of 130°C is reached. This will give about 1000 ml of salting solution. Cover the beaker with a watch glass and either transfer the solution to a constant temperature apparatus or keep the solution warm, finally heating to 110°C before use. If the reagent is to be stored, transfer to a 1000 ml three-neck reaction flask set in a heating mantle controlled by a Variac. Adjust the Variac so that the solution is kept at about 80°C. In one of the necks place a water condenser, in another neck a thermometer, and in the third neck a removable glass stopper. This third neck is used for pipetting the salting agent. Bring the salting agent to 110°C before pipetting it into the separatory funnel. At lower temperatures crystallization may occur at the stopcock of the separatory funnel.

b - Aluminum Nitrate Wash Solution

Add 100 ml of aluminum nitrate salting solution (B.P. 130°C) to 73 ml of distilled water and 4 ml of concentrated nitric acid.

c - Standard Uranium Solution

Dissolve 0.118 g of U_3O_8 in 100 ml of 5% nitric acid. Dilute 1 ml to 1000 ml with 5% nitric acid. 0.1 ml = 100 mγ U.

d - Sodium Fluoride-Lithium Fluoride Pellets

These pellets are obtainable commercially. They should be tested for fluorescence under normal fusing conditions with or without standard uranium addition. With the 100 milligamma U_3O_8 standard aliquot, the pellet will give a meter reading of 500 units with the Galvanek Morrison instrument, and the blank a reading of 10 to 20 units.

Procedure

a - Sample Dissolution

i - Plain Carbon Steel

Weigh a 2 g sample into a 250 ml beaker. Add 25 ml concentrated nitric acid, 15 to 20 ml of water, and slowly add concentrated hydrochloric acid dropwise until the steel begins to react (only a few drops are needed). When the initial reaction subsides, cover the beaker with a watch glass, transfer to a hot plate and boil until the sample is completely dissolved. Usually there is no residue, but if any is found, treat it by the fusion procedure described under "Stainless Steel", to follow. Combine the solution from the fusion with the main solution; transfer to a 250 ml volumetric flask, and dilute to the mark with 5% nitric acid. Proceed to "Ethyl Acetate Extraction".

ii - Stainless Steels

Weigh a 2 g sample into a 250 ml beaker. Add 25 ml concentrated nitric acid, 15 to 20 ml water, and stir. Slowly add concentrated hydrochloric acid until the sample starts to dissolve (about 10 to 40 ml will be required). Cover with a watch glass and, when the initial reaction subsides, transfer to a hot plate and boil until decomposition is complete. Filter the hot solution with suction, using a No. 2 Buchner funnel and a 7 cm No. 42 Whatman filter paper. Wash the residue on the paper thoroughly with hot water. Transfer the filtrate in the suction flask to a 250 ml volumetric flask, completing the transfer with water. Reserve this solution. Place the paper in a 40 ml platinum crucible, dry, and ignite at low heat. Add 2 to 3 g of potassium pyrosulphate and fuse at 700° to 800°C. Cool and dissolve the melt in 5% (v/v) nitric acid, adding the solution to the volumetric flask containing the main solution. Dilute to the mark with 5% (v/v) nitric acid. Proceed to "Ethyl Acetate Extraction".

iii - High Speed Steel

Weigh a 1 or 2 g sample into a 250 ml beaker, and add 25 ml of aqua regia. Cover with a watch glass, transfer to a hot plate and bring to a boil. When the sample is completely decomposed, filter as before and wash with hot water. Transfer the filtrate and washings to a volumetric flask of suitable size and dilute to the mark with 5% nitric acid. In general, uranium is not occluded by any hydrolytic precipitate that deposits out, but may be contained in any undissolved residues. Proceed to "Ethyl Acetate Extraction".

iv - "Acid Insoluble" Uranium: (Uranium Insoluble in 16% (v/v) Hydrochloric Acid)

Weigh a 2 g sample into a 250 ml beaker. Add 50 ml water and 8 ml concentrated hydrochloric acid. Place the beaker on an asbestos-padded hot plate and warm. Do not boil or agitate. Let the sample digest on the warm hot plate until it is completely disintegrated*.

Filter the sample, wash the residue with warm water, and discard the filtrate and washings. Place the filter paper containing the undissolved residue in the original beaker. Return the beaker to the hot plate, let it dry well, and ignite it so as to burn off the paper as completely as possible. Treat any residual carbon in the beaker with concentrated sulphuric and nitric acids until completely destroyed, and fume to dryness. Transfer the

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* - Note - Plain carbon steels will dissolve in about 1/2 hour. High alloy steels often require several days treatment, with additions of 16% (v/v) acid as make-up.

contents of the beaker to a volumetric flask of suitable size and make to volume with 5% (v/v) nitric acid. Filter a portion of the solution from the volumetric flask. If the quantity of residue is small the ethyl acetate separation can be omitted. After a second dilution (if necessary) proceed to "Aliquotting the Samples into the Platinum Dishes".

TABLE 10.1

Sample Size and Dilution Table

Range % U	Solution		Extraction	
	Sample size, grams	Dilute to, ml	Take, ml	Dilute to, ml
<0.01	2	50	10	25
0.01 to 0.10	2	100	10	50
0.10 to 0.50	2	250	5	100
0.50 to 1.00	2	500	5	250
>1.00	dilute proportionately			

b - Ethyl Acetate Extraction

Pipette a suitable aliquot of the sample solution (see Table 10.1) into a 60 ml separatory funnel. Add by means of a graduated pipette, 6.5 ml of aluminum nitrate solution (at 110°C) for every 5 ml of sample solution taken.

Cool the solution to room temperature and add 20 ml of ethyl acetate. Stopper the funnel with a polyethylene stopper and shake the funnel for 45 to 60 seconds. If crystallization takes place near the stopcock, place the lower part of the funnel in a beaker of hot water until the solidified material redissolves.

After the layers have separated, drain off and discard the salted aqueous (lower) layer. Do not drain off any cloudiness that appears at the interface in the funnel. Rinse the inside of the stem of the separatory funnel with a stream of water from a wash bottle and discard the rinsing.

Add 15 ml of water to the separatory funnel containing the ethyl acetate, stopper the funnel and shake the mixture for about 1 minute. After washing off the stopper (into the funnel) with a jet from a wash bottle, drain the aqueous layer into a volumetric flask of suitable size (Table 10.1). Wash the separatory funnel and the ethyl acetate layer four or five times with 5 ml portions of water and add the washings to the volumetric flask. Make the solution in the flask to volume with 5% nitric acid.

c - Aliquotting the Samples into the Platinum Dishes

Lay out the set of clean dishes (twenty-two in all) on the tray in a predetermined order, using platinum-tipped forceps. Place the tray in the infra-red drier for several minutes. Pipette the samples into the dry dishes with a 100 λ micropipette held in a rubber bulb, using one set of dishes for every two samples. In preparing the dishes, rinse the pipette with the first sample, and pipette an aliquot into each of five dishes. Rinse the pipette with the second sample, and pipette an aliquot into each of the next five dishes. Finally, rinse the pipette with the standard uranium solution (100 λ = 100m γ U) and pipette an aliquot into the next ten dishes. Leave two dishes empty as blanks.

Return the tray of dishes containing the aliquots of standard and sample solutions to the infra-red drying oven and let them dry slowly without spattering.

Remove the tray of dry dishes and place a pellet of flux in each dish. Using the platinum-tipped forceps remove the dishes from the tray and arrange them on the burner in a predetermined order.

d - The Fusion

Turn on the gas supply to the Fletcher burner and ignite it. Adjust the gas flow to a value that has been found to give satisfactory fusing conditions. Turn on the air supply and adjust the gas control until the burner begins to "howl", then increase the gas flow just enough to prevent the howling.

If the conditions are correct, the pellet will melt in about 1-1/2 minutes. When the fusion is complete shut off the gas and air and play a stream of steam over the burner and beads till they no longer glow red. Remove the dishes from the burner with the platinum-tipped forceps and replace them in the tray in their proper order. Let the beads cool to room temperature and read them on the fluorimeter.

e - Fluorimeter Operation - GM fluorimeter

The following revised procedure simplifies the reading of the fluorescence.

Remove the 100 m γ (white) standard from the standard position by lifting out the front stop, drawing out the sample slide, removing the standard and replacing the slide as before. The former standard position (slide fully out) is now used for dark current adjustment.

Turn the instrument on and allow it to warm up for 15 minutes. Pull the slide out and insert one of the 100 mγ standard beads. With the slide out, zero the instrument by depressing the zero switch and adjusting the microammeter. (Alternatively, a quicker adjustment can be made by pushing the slide in and adjusting the microammeter without depressing the zero switch). With the slide in (i.e., with the sample position, containing the standard bead, under the photocell) close the 0.01 multiplier switch and adjust the coarse and fine voltages until the microammeter reads about 50 microamperes. Rezero the instrument and repeat the adjustment. Now pull the slide out and adjust the dark current control so as to rezero the instrument.

With the sample slide out, remove the standard bead and insert the sample bead (removed from its dish). Move the slide in, and close successive multiplier switches from right to left until the maximum reading that is still on scale is obtained. Note and record the reading. Release the multiplier switch (with the slide in) and note the zero reading.

Pull the slide out to remove the sample bead and replace it with the next one. Continue reading the beads and checking the zero until all the beads are read.

Calculations

$$\% \text{ U} = \frac{\text{1st dilution (ml)}}{\text{sample wt}} \times \frac{\text{2nd dilution}}{\text{1st dilution aliquot}}$$

$$\times \frac{\text{m}\,\gamma\text{ U in bead}^*}{\text{2nd dilution aliquot (ml)}} \times \frac{100}{109}$$

*"m γ U in bead" is found from

$$\frac{\text{R sample} - \text{R blank}}{\text{R (100 m}\gamma\text{ standard)} - \text{R blank}} \times 100$$

where R is the galvanometer reading.

RADIOMETRIC METHODS

Outline

Although the refining process eliminates the highly radioactive daughter elements which are present in uranium ores, it is nevertheless possible to determine the uranium content of steel and alloys at moderately low levels using the weak radioactivity of the uranium itself and of its immediate short-lived decay elements. Both beta and gamma counting methods are applicable, but since the beta-ray emission is a surface effect while the gamma-ray emission originates throughout the sample (for thin specimens), gamma counting will give more reproducible results.

Beta counting uses a beta-sensitive Geiger tube with a 1 sq. in. (or larger) window, and a ratemeter or scaler. In view of the fact that beta emission is from the surface only, sample preparation is highly critical.

Gamma counting uses a scintillation detector. A preamplifier, which is an integral part of the counting apparatus, amplifies the pulses, which are then directed to a single-channel pulse analyser. This analyser passes only those pulses in the energy range 60 to 200 keV, thus rejecting most of the energy arising from background radiation.

Since the gamma-radiation being counted is relatively soft, internal absorption within the sample is a factor, and the thickness of the sample pellets should therefore be limited to about 0.25 in. The chemical composition of the alloy plays a minor part, but use of chemically analysed standards of composition similar to the samples may be advantageous.

Range

The lower limit of counting methods is determined largely by the level of the background and its variability. This is partly dependent on the instrumentation and partly on location. Under the conditions described here, uranium could be determined down to about 0.01% by both beta and gamma methods. With longer counting times, the background and sample count-rates can be established with greater precision, so that smaller differences can be made statistically significant, thus lowering the limit of determination.

Pellet Preparation

Prepare the sample in the form of very fine chips, using a drill bit specially ground for this purpose. Weigh out a standard amount, i.e., 20 g of sample, and spread out on an aluminum-foil pie plate. Spray the sample with an even, thin coating of acrylic resin in a fume hood and dry under an infra-red lamp. Let the sample cool, and then pour it into a 1.25 in. diameter mould and press at 24,000 psi on an hydraulic press at room temperature.

Beta-ray Method

a - Counting Equipment

This method requires beta radiation counting equipment consisting of:

1 - A lead shield or castle with a 2 in. wall thickness, an inner cavity measuring 3 in. x 3 in. x 2 in., and fitted with a sliding tray or hinged lead brick door.

2 - A Geiger tube, such as that produced by Anton Laboratories, 1001-H.

3 - A scaling circuit with high-voltage power supply and timer, e.g., Nuclear-Chicago, Baird-Atomic Instruments Co., Electronic Associates Ltd., or others.

b - Calibration

Determine the background count (counts per minute) by counting a sample containing no uranium for 10 minutes in the castle. Count a group of samples containing several different uranium concentrations whose values are known by chemical analysis. Count each face of a pellet for 5 minutes and record the count (for particularly good accuracy the period might be as long as 30 minutes if the sample is weak, <0.03% U). Subtract the background count, and plot a graph of the resulting net count-rate per minute versus the known per cent uranium concentration. Draw a straight line which passes through the origin and determine from it the sensitivity (measured in counts per minute per 1% uranium). This value will be about 2400 with a background of 20 counts per minute. Use the value for the sensitivity to determine the counting interval which results in a direct reading in the counter dial of the per cent uranium. A scale-of-64 counter produces one "register-pulse" for every 64 pulses from the Geiger tube. Consider count register to read 1/100ths of a per cent. Then count for $\frac{64 \times 100}{2400}$ or 2.67 minutes - each face of the pellet. Pellets of low uranium content might be counted longer for better accuracy, i.e., 10.67 minutes with a scale-of-256, or 26.7 minutes with a scale-of-64 considering the count register to read 1/1000 of a per cent uranium.

The background counted for the same interval will have to be subtracted to leave the net per cent uranium from the sample. This background reading is expressed as "equivalent per cent uranium".

c - Procedure

Prepare a compressed pellet of the sample in the manner described. Insert the pellet in the castle and set the counter-interval scaler for the interval which has been found, from the above calibration procedure, to give a direct reading in per cent uranium. Start the counter, and at the end of the automatically-timed interval, read the uranium content directly off the dial, subtracting the background correction. Turn the pellet over, and read the other face in the same manner. Report the average of the two values.

Gamma-ray Method

a - Counting Equipment

This method requires counting equipment consisting of:

1 - A lead shield or castle with a 2 in. wall thickness, an inner cavity measuring 4 in. x 4 in. x 12 in. high, or large enough to contain the detector and sample. It should be provided with a removable top.

2 - A mounted sodium iodide crystal, $2\frac{1}{2}$ in. x $\frac{1}{2}$ in. diameter, e.g., Harshaw Chemical Co., Cleveland, Ohio.

3. A photomultiplier tube type RCA 6655.

4 - A preamplifier, such as that manufactured by Nuclear-Chicago Corp.

5 - A single channel pulse separator, e.g., Nuclear-Chicago Corp., Model 132-B.

b - Calibration

An energy calibration standard (Cs-137 at 662 keV) is supplied by the manufacturer of the analyser. Following the detailed instructions in the manual, the high voltage is adjusted until the base scale of the analyser reads directly in kilo-electron-volts. The base is then set to "060" and the window width to "10". The detector will now detect and count gamma rays in the approximate range of 60 to 160 keV. The analyser is placed in a temporary lead castle of 2 in. thick bricks.

When the background count rate has been established, a range of standard size (20 g) compressed samples (previously assayed chemically) is counted to find a factor stated as "net counts per minute per one per cent uranium". This factor may also require a correction curve where a range of sample weights will be encountered; it is determined empirically for a range of weights, say 10 to 50 g, with 20 g as the value 1.000.

The factor c/min/%U, is now used to calculate a suitable counting time to have the register dial directly.

c - Procedure

Prepare a compressed pellet of the sample, in the manner described above. Having calibrated the instrument to read directly in per cent uranium, place the sample pellet on the detector in the castle. Start the counter, and at the end of the automatically timed period, read the uranium content directly off the counter dial, subtracting the background. Turn the pellet over and count the other face in the same manner. Report the average of the two values.

X-RAY EMISSION SPECTROMETRIC METHOD

Outline

Uranium, suitably excited by high-energy X-rays, emits discrete secondary X-radiation which can be measured to give an indication of its concentration in a variety of materials. In the procedure given here, the uranium L α line is used. A dilution technique using alumina powder is employed as an aid in overcoming matrix effects. It is not possible to completely eliminate the effect of other elements, however, so that it is necessary to use standards, either chemically analysed samples or synthetic mixtures, which closely approximate the composition of the samples being analysed.

Range

The X-ray emission method permits the determination of uranium down to about 0.05% in carbon steel. Sensitivity will vary slightly in alloy steels due to the matrix effect, and standards used for comparison should have approximately the same composition as the alloy being analysed.

Apparatus

The following equipment is required for this technique:

1 - Blender-mill:	Pitchford Pica, Cat. No. 3800
2 - Vial, hardened tool steel:	Pitchford, Cat. No. 202
3 - Balls, 5/8 in. dia. tungsten carbide:	Pitchford, Cat. No. 306
4 - X-ray spectrometer, consisting of:	
a - Basic X-ray generator unit, 60 kV-50mA:	Philips Electronics Ltd., Cat. No. 12045/3B
b - Molybdenum target X-ray tube:	

c - Universal All-vacuum X-ray Spectrograph attachment: Philips Electronics Ltd., Cat. No. 52360

d - Lithium fluoride analysing crystal: Philips Electronics Ltd., Cat. No. 52130

e - Electronic Circuit Panel including linear amplifier power supplies, scaler ratemeter assembly, timer and recorder: Philips Electronics Ltd., Cat. No. 12096

5 - Sample containers with Mylar film bottoms: To fit spectrograph

6 - Mylar film: To cover bottom of sample container

Reagents

Alumina powder: Finely ground (-200 mesh)

Plain carbon steel drillings or chips: Uranium-free, for preparation of standards (use other types of uranium-free steel to provide the same base alloy as the samples)

Uranium dioxide powder: Pure

Preparation of Standard Curve

Weigh a 5 g sample of uranium-free steel drillings or chips into a hardened tool steel vial, and add a carefully weighed 5.6 mg portion of the UO_2 powder.* Add 3 g

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*Uranium dioxide diluted with alumina can be used for the standard addition provided it is well mixed. Alternatively, standard uranium-bearing steels can be used.

of alumina powder and two tungsten carbide balls. Close the vial and mix on the blender-mill, until the sample is reduced to a homogeneous powder, corresponding to 5 g of a steel sample containing 0.1% uranium. Transfer to the spectrometer sample holder, tap lightly to pack, and level off the sample. Place the container in the spectrometer and rotate it into the counting position. Set the goniometer at the peak of the uranium L_α line ($2\theta = 26.14^\circ$ for the lithium fluoride analysing crystal). Use the following power settings on the X-ray tube: voltage, 55 kV; current, 45 mA. Set the scintillation counter high voltage to the previously determined optimum setting. Record the time required to accumulate 64,000 counts. Move the goniometer off the uranium peak to a nearby background region and count the background. Calculate the net counts per second due to uranium and record the value. Repeat for other standards similarly prepared and plot a graph of uranium concentration versus net counts per second.

Procedure

Weigh out a 5 g sample. Transfer to a clean tool steel vial. Add 3 g of alumina powder and two tungsten carbide balls. Carry out the balance of the procedure described under "Preparation of Standard Curve". From the net counts per second (corrected for background) read the uranium content from the standard curve.

VOLUMETRIC METHOD

Outline

This method employs a cupferron separation from sulphuric acid solution to effect the separation of iron and uranium. Following the separation, the uranium is reduced by titanous sulphate solution and the uranous ion is titrated with a standard solution of potassium dichromate.

Since, in addition to the iron, the cupferron extraction removes vanadium, titanium, molybdenum and tin, the procedure will be useful for master alloys containing these elements. Zirconium, niobium, and tungsten are also precipitated by cupferron (somewhat higher acidity than is recommended here is necessary to effect complete separation of the tungsten precipitate), but the precipitates in this case have limited solubility in chloroform. Hence if these elements are present in quantity, it will be necessary to filter off the cupferron precipitate rather than to extract it. The filtration should be carried out rapidly using very cold solution to avoid decomposition of the reagent.

The method described for dissolving the sample is satisfactory for use with the ferroalloy, but it would have to be modified for master alloys containing large amounts of refractory metals. For example, uranium-titanium alloys are attacked only slowly by this procedure, but respond well to the treatments usually employed to dissolve titanium metal. With unusual master alloys, it is necessary to use caution in establishing a suitable dissolution procedure. Zirconium alloys in particular are said to react vigorously under oxidizing conditions, and the use of nitric acid must be avoided in dissolving zirconium-uranium mixtures. Many finely divided metals tend to react rather violently with acids and oxidants, so that samples in the form of powders will also require cautious treatment.

Range

The method as written is designed for alloys containing more than 25% uranium. If the uranium content is lower, a larger sample should be taken and the bulk of the iron eliminated by a mercury cathode separation, details of which are included in the description of the colorimetric procedure. (Page 294)

Preparation of Required Reagents

a - Cupferron Solution, 8%

Dissolve 40 g of cupferron in water, dilute to 500 ml and filter if necessary. Store in a dark bottle in a refrigerator and cool to 5°C before use. Prepare fresh weekly.

b - Titanous Sulphate Solution, 10%

Measure 200 ml of 15% (v/v) sulphuric acid into a 400 ml beaker. Bring to a boil and add 5 g of titanium hydride in 0.5 g portions over a period of ½ hour. Once every 10 minutes remove the beaker from the hot plate, and add boiling water to bring the volume back to 200 ml. When the titanium hydride is completely dissolved, let the solution cool and decant into a clear bottle. Close with a vented stopper. The solution may be used as long as not more than 5 ml are required to reduced 150 mg of uranium.

c - Mercuric Perchlorate Solution, 8%

Dissolve in water, adding a few drops of perchloric acid to ensure complete solution.

d - Ferric Sulphate Solution, 20%

Dissolve 200 g of ferric sulphate with 20 ml of 1:1 (v/v) sulphuric acid and sufficient water to ensure complete solution. Dilute to 1000 ml.

e - Sulphuric-Phosphoric Solution

Mix 74 ml of orthophosphoric acid (85%) with 26 ml of concentrated sulphuric acid solution.

Procedure

a - Sample Dissolution

Weigh a 1 g sample into a 250 ml beaker. Add 25 ml of aqua regia, (cautiously), cover the beaker and let stand till the reaction subsides. Remove the cover, add 15-20 ml of dilute (1:1, v/v) sulphuric acid and evaporate just to strong fumes. Cool, cautiously add 50 ml water and warm to dissolve. If necessary, add a few drops of 30% hydrogen peroxide. Transfer to a 100 ml volumetric flask, and dilute to the mark with water.

b - Cupferron Extraction

Pipette a 25 ml aliquot into a 300 ml Squibb pear-shaped separatory funnel. Add sufficient dilute (1:1, v/v) sulphuric acid so that the total content is equivalent to 10 ml of concentrated acid. Dilute to 100 ml, add dilute potassium permanganate solution (about 7% in water) until a faint pink colour persists, and cool to 5°C.

Add 30 ml of 8% cupferron solution (cooled to 5°C) and shake. Extract with one 40 ml and two 30 ml portions of cold chloroform (5°C) or until the chloroform layer is clear after shaking. Add another 30 ml cupferron solution, shake, and again extract with chloroform. If the precipitate that appears upon addition of the cupferron is white, the separation is complete. Otherwise the extraction step must be repeated.

After completion of the final chloroform extraction, wash the sample solution into a 300 ml Erlenmeyer flask. Add glass beads and evaporate to about 35 ml. Add 35 ml of nitric acid and evaporate to fumes of sulphuric acid. Cool, wash down the sides of the flask with distilled water and add 15 drops of saturated potassium permanganate solution. Take to fumes again, finally fuming over a Meker burner until heavy fumes are apparent only at the neck of the flask. Repeat the steps of this paragraph until all organic matter is removed.

c - Reduction and Titration

Carry a reagent blank through this part of the procedure.

After the solution has cooled, adjust the acidity so that about 20 ml of 1:1 sulphuric acid is present. Dilute the solution to 40 ml with distilled water and add a drop or two of hydrogen peroxide. Boil to dissolve. Cool and add 2 ml of 5% copper sulphate solution. Add titanous sulphate solution by means of a 10 ml burette until a faint permanent darkening of the solution takes place due to precipitation of metallic copper. Add an excess of the titanous sulphate solution of about 20% of the initial volume added (e.g., if 2 ml were required, add 0.4 ml excess). Swirl the solution continuously during this step. (If more than 5 ml of the titanous solution is required, the solution is exhausted and should be discarded).

In successive steps, and without undue loss of time, add 10 ml of 8% mercuric perchlorate solution, 15 ml of 20% ferric sulphate solution, and 15 ml of sulphuric-phosphoric solution. After the addition of each reagent, rinse down the sides of the flask and mix thoroughly. Dilute the solution to about 250 ml and add 5 drops of diphenylamine sulphonate indicator. Titrate with the standard dichromate solution (0.025N), taking as the end point the point where the addition of one drop of dichromate solution causes no further deepening of the violet colour. The titration of a reagent blank, carried through the reduction and titration steps, is subtracted from the titrations of samples and standards. The net titration is recorded.

Calculations

1 ml 0.025N potassium dichromate solution = 0.002975 g U.

COLORIMETRIC METHOD

Outline

This procedure employs for the final determination step the yellow colour of the complex formed between uranyl and thiocyanate ions in acid solutions. Some iron can be tolerated provided it is reduced with stannous chloride during the colour development, but the bulk of it must be removed by means of a mercury cathode. The subsequent cupferron extraction step is necessary to remove molybdenum, titanium, and vanadium, which also interfere. The cupferron treatment is also capable of removing iron, but in the case of a steel sample, a rather large number of extractions is required, and a quick preliminary mercury cathode treatment will substantially shorten the overall time for the procedure.

Range

This procedure covers the range 0.05% uranium and up. It is suggested for use in analysing the occasional sample when fluorimetric facilities are not available. It is also suited for determining uranium in the higher ranges and is faster than the volumetric method. The coefficient of variation is better than 1%, determined at the 2 mg level.

Apparatus

The following equipment is necessary for this technique:

1 - Mercury Cathode, High current type:	Eberbach Dyna-Cath, or equivalent
2 - Separatory funnels:	125 ml size with Teflon stopcocks
3 - Flasks, volumetric:	100 ml size
4 - Spectrophotometer:	Beckman Model B or equivalent
5 - Spectrophotometer cells, Corex:	1 cm and 5 cm path length

Procedure

a - Preliminary

Weigh 2 g of sample into a 400 ml beaker. Add 25 ml of 10% v/v sulphuric acid, cover with a watch glass and heat to dissolve. If necessary, add hydrochloric or nitric acid to complete solution of the sample. When solution is complete, evaporate to strong fumes. If nitric or hydrochloric acids were used, wash down the sides of the beaker and fume again. Cool, take up in 50 ml of water and warm to dissolve the salts. Filter if necessary and wash the paper with a little 2% v/v sulphuric acid. If the residue may contain uranium, transfer the paper to a platinum crucible, dry and burn off at a low temperature.

Fuse with 2 or 3 g of potassium pyrosulphate. Cool and dissolve the melt, and combine with the main portion of the solution.

b - Mercury Cathode Separation

To the combined solution add ammonia dropwise till the solution becomes slightly turbid. Add dilute sulphuric acid (1:1, v/v) dropwise till the solution clears, then add 3 to 4 drops in excess. Dilute the solution to about 100 ml with water and transfer to the cell of a high-current mercury cathode electrolysis apparatus. Electrolyze at 15 to 20 amperes until the bulk of the iron is removed. Drain off the solution into a 400 ml beaker and wash out the cell with a little 1% sulphuric acid from a wash-bottle.

Evaporate the solution from the above treatment to dryness, fuming off as much of the sulphuric acid as possible. Cool, wash down the sides with a little hydrochloric acid and fume again.

Cool, add 100 ml water and warm to dissolve. Add 10 ml of a solution of aluminum chloride carrier solution (1 ml = 1 mg Al), and add hydrochloric acid dropwise to clear any turbidity. Add 5 g of ammonium chloride, bring the solution to a boil and precipitate the aluminum by the cautious addition of carbonate-free ammonium hydroxide (from a freshly opened bottle) to the hot solution. Digest for 1/2 hour and filter the solution on a fast paper. Wash with a hot 2% solution of ammonium chloride, discarding the filtrate and washings.

Place a clean 250 ml beaker under the funnel and dissolve the precipitate on the paper with 25 ml of hot 10% (v/v) hydrochloric acid. Transfer this solution to a 125 ml separatory funnel. Wash the paper and beaker with further portions of 10% hydrochloric acid and transfer the washings to the funnel as well, to give a final volume of about 50 ml.

c - Cupferron Separation

To the solution in the separatory funnel add sufficient saturated potassium permanganate solution (dropwise with shaking) to impart a permanent pink colour. Cool the funnel to 5°C, and add 15 ml of cold, 8% cupferron solution. Mix well, add 15 ml of chloroform and shake for 10 seconds. Let the layers separate, drain and discard the organic layer. Repeat the addition of chloroform and the extraction step three more times, discarding the chloroform each time (traces of cupferron interfere in the colorimetric finish). Pour the aqueous layer from the top of the separatory funnel (not through the stem) into a 100 ml volumetric flask. Rinse the funnel with water (5 to 10 ml) and add the rinsings to the flask.

d - Colour Development

To the volumetric flask add 2 ml of 10% stannous chloride. Stopper and shake well. Add 25 ml of 50% ammonium thiocyanate solution, and mix. Make to volume with distilled water and mix again. Determine the optical density of the solution on the spectrophotometer at 370 mμ using 1 cm or 5 cm Corex cells. Record the optical density and determine the uranium content of the final solution by means of a graph of uranium concentration versus optical density for the particular cell path used.

Calculations

$$\% \text{ U} = \frac{\text{mg U (from graph)}}{1000} \times \frac{100}{\text{Sample Wt}}$$

REFERENCES

1. J.C. Ingles, J.B. Zimmerman and J.L. Horwood, "The Analytical Determination of Uranium in Iron and Steel Alloys", Mines Branch Information Circular IC-134, (December 1961).

2. J.L. Horwood, "The Radiometric Analysis of Uranium-Bearing Steels", Mines Branch Technical Bulletin TB 25, Department of Mines and Technical Surveys, Ottawa, (November 1961).

CHAPTER 11

SAFE HANDLING OF URANIUM AND URANIUM ALLOYS

G. G. Eichholz*

SYNOPSIS

The radiation and toxicity characteristics of uranium are summarized, and recommendations for the safe handling of uranium and uranium-bearing materials are outlined. The legal aspects involved in the use of uranium are reviewed. Typical experimental values of the radiation levels involved during commercial and laboratory operations such as melting, pouring, hot forming, dry cutting or grinding, scarfing and welding are presented and discussed.

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*Head, Physics and Radiotracer Subdivision, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

The pertinent facts concerning the safe handling of uranium and its alloys have been compiled in this chapter for convenient reference. The information presented is relevant to the range of compositions contemplated in the current research development programme; further details are published elsewhere(1). It will be assumed throughout that the uranium involved is either natural uranium or uranium depleted in its normal content of the isotope U-235.

In the production of uranium alloys there are three distinct stages of materials handling: 1) transportation, storage, and handling of pure uranium metal; 2) melting and casting; and 3) further treatment and handling of the finished alloys.

Because of its reactive nature, uranium is highly pyrophoric when in finely divided form (2). This property seems to be associated with the formation of hydrides on exposure to moisture and is a factor of importance in the storage and handling of uranium metal in the form of powder, chips or turnings (3). Massive pieces, where the ratio of bulk volume to surface area is high, are not pyrophoric.

RADIATION CHARACTERISTICS OF URANIUM

Uranium is a radioactive element which decays spontaneously, changing its physical and chemical nature in the process. The probability of decay taking place is usually expressed in terms of the half-life of the material, which is the average time in which half the atoms involved will have decayed. In the case of uranium the decay products themselves are radioactive and a whole chain of radioactive elements is produced. On purification and refining, the uranium is freed from all the decay products, notably radium and its daughter products, which have accumulated in the source mineral over the years.

Pure uranium metal is made up essentially of three isotopes: U-238, U-235, and U-234. Table 11.1 lists the main properties of these isotopes and their immediate decay products(4,5). Only the more important radiations, contributing at least 10% of the total radiation for any nuclide, are listed.

TABLE 11.1

Properties of Principal Uranium Isotopes and Important Daughter Products

Nuclide	Abundance %	Half-life	Type of decay	Decay product	Energy of α or β particles, MeV	Energy of γ-rays, keV
U-234	0.0058	2.48×10^5 yr	α	Th-230	4.76, 4.71	-
U-235	0.71	7.13×10^8 yr	α, γ	Th-231	4.39, 4.56	180, 140
U-238	99.28	4.51×10^9 yr	α	Th-234	4.18	-
Th-230		8×10^4 yr	α, γ	Ra-226	4.68, 4.61	190, 68
Th-231		25.6 hr	β, γ	Pa-231	0.09, 0.30	22, 80
Th-234		24.1 days	β, γ	Pa-234	0.19, 0.10	93
Pa-231		3.4×10^4 yr	α, γ	Ac-227	5.00, 4.94	95, 320
Pa-234		1.18 min	β, γ	U-234	2.32	800

As can be seen from Table 11.1, highly-purified uranium will emit mainly alpha particles when freshly prepared. After a few weeks, however, the beta- and gamma-ray emitters Th-234 and its short-lived daughter Pa-234, and to a lesser extent Th-231, will build up to equilibrium concentrations and emit feeble, but measurable, beta and gamma radiations. Because of their low energy these radiations are emitted essentially from the surface of the metal only, the rest being absorbed internally, and an increase in bulk of the material will not greatly increase the total amount of radiation detected. The longer-lived decay products of uranium, listed in Table 11.1, will not build up again in measurable quantities once they have been separated out. This applies particularly to Ra-226, which, through its decay products, is the principal source of the gamma radiations detected in natural uranium ores. As alpha particles are readily absorbed by a few inches of air, a thin film of moisture or any thin layer of paper, the beta rays of Pa-234 constitute virtually the only radiations readily detected from uranium alloys and these have been utilized as a convenient means of checking the uniformity of composition of such metal samples.

The nuclide U-235 is fissionable and represents the most common and convenient source material for nuclear energy development at this time. However, in the concentrations in which it is found in natural uranium, it is impossible to start a nuclear chain reaction in air, no matter how great the quantity of uranium involved. In other words, natural uranium, without any enrichment in U-235 content, cannot by itself reach critical conditions(6,7). In a reactor such critical conditions can be created by immersion in heavy water or other moderating material. In any industrial plant, however, solid natural uranium metal can be piled readily without any worry on this score, (so long as the total tonnage is kept low and no lattice is formed with a moderator such as graphite).

TOXICITY CONSIDERATIONS

From the foregoing, it is evident that the radiation emitted from uranium metal is neither penetrating or intense. It does not, therefore, constitute a serious external radiation hazard. Nevertheless, gloves should be used when handling bare uranium metal to reduce the surface dose to the hands. However, when uranium is ingested into the body, its long half-life and the high energy of the alpha particles may constitute a hazard. It is important, therefore, to avoid ingestion by handling the metal with gloves at all times, by not eating or smoking while handling pure uranium metal, and by reducing the possibility of inhaling dust-borne uranium particles.

The chemical toxicity of uranium is a much more serious health factor than its radioactivity(8). Uranium in soluble form is concentrated in the kidney and some cases of acute uranium poisoning have been reported in the literature. The toxicity of uranium is comparable to that of lead or mercury, though the detailed physiological effects are different.

In the nuclear energy industry it is customary to express maximum permissible concentrations in microcuries per cubic centimetre ($\mu c/cc$) of air for any radioactive isotope. Table 11.2 lists the 1959 recommendations of the International Commission on Radiological Protection (I.C.R.P)(9), which have been used as a guide by the Government of Canada(10). In columns 2 and 4, the microcurie per cubic centimetre values have been converted to corresponding microgram per cubic metre ($\mu g/m^3$) values.

TABLE 11.2

I.C.R.P. Tolerances for Uranium

	Maximum Permissible Concentrations in Air			
	Occupational Exposure		General Public	
	μc/cc	μg/m³	μc/cc	μg/m³
Uranium-natural (soluble)	7×10^{-11}	200	3×10^{-12}	8.6
Uranium-natural (insoluble)	6×10^{-11}	170	2×10^{-12}	5.7

Under controlled operating conditions, such as must prevail at all licensed experimental and industrial operations for the production and manufacture of uranium-bearing steels and alloys in Canada, the maximum permissible concentration for occupational exposure (200 μg U/m^3 = 5.6 μg U/cu ft) has been adopted as satisfactory*.

Experience has shown that with proper ventilation no difficulties should be encountered during uranium-alloy preparation in maintaining uranium concentrations in air well below tolerance level. This also applies to uranium storage areas, which should be kept dry and well-ventilated.

Shipping and handling of uranium steel material should present no hazards. Transportation is subject to

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*Atomic Energy Control Board Permit 92/25/61, dated February 28, 1961.

the Board of Transport Commissioners' Regulations(11), but these concern primarily the rules for labelling and for maximum external radiation levels that have to be maintained. Bulk uranium steel should have less external radiation than bulk uranium ore which may be shipped in open cars at present.

The possible health hazards arising from a wide-spread use of uranium-bearing steels, e.g., in the manufacture of automobiles, have been discussed in detail in a report of the Radiation Protection Division of the Department of National Health and Welfare(12). The main conclusion reached in this report is that under most foreseeable conditions the wide-spread use of steel, containing around 0.25% uranium, would probably be acceptable from a health point of view.

LEGAL ASPECTS

In Canada uranium is a "prescribed substance" under the Atomic Energy Control Act. The Atomic Energy Control Regulations(10) lay down that an authorization from the Atomic Energy Control Board is required to authorize dealings within Canada as regards uranium contained in any substance that contains not less than 0.05 per cent by weight of the element uranium, or for dealings which involve, during any calendar year, a total of at least 10 kg of contained uranium element.

In the Appendix to the Regulations the "scheduled quantity" of natural uranium is listed as 500 microcuries*. This is equivalent to 1420 g of natural uranium. The Regulations also lay down the maximum permissible dose of ionizing radiation for whole-body exposure as 3 rem for any period of 13 consecutive weeks, and 5 rem for any period of 52 consecutive weeks. For exposures restricted to the extremities of the limbs, higher permissible doses are allowed.

Any large-scale use of uranium in industry requires, therefore, the authorization and approval of the Atomic Energy Control Board. In addition most provinces require concurrently the approval of the provincial health department, which should be consulted to ensure conformance with local regulations.

TEST PROCEDURES

In discussing the above rules and considerations as they apply to the production of uranium steels, three stages must be clearly distinguished for hazards evaluation. The first is the actual steelmaking operation, involving molten metal at a temperature well above the

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*Dealings in smaller amounts are not subject to regulation.

melting point of uranium. This operation is relatively brief and any liberation of uranium to the air will cause only short-time exposure of the operator. The second is one of cleaning, scarfing or grinding, where relatively heavy, uranium-bearing particles may be showered into the air. The third stage concerns the cold handling, forming and fabricating of the finished alloy, where the concentration of uranium is quite low, but long-term exposures are possible.

Tests on various uranium steels have been conducted at the Mines Branch laboratories of the Department of Mines and Technical Surveys over the past year. During several of these tests air samples have been collected to establish representative levels of uranium concentration in the plant air before, during, and after typical casting and rolling operations(13,14,15). In addition, air samples have been collected at all the Canadian plants where pilot plant work on the production of uranium-bearing steels has been started(16-20).

Concurrently, radiation measurements have been carried out to measure the dosage received by operating personnel and, as a subsidiary measurement, to check for segregation in billets and to locate any appreciable amounts of uranium in slag and scrap. Film badges have also been issued to staff and workers closely concerned with the handling of the raw materials or the finished alloy. In no case has any reportable exposure been found in the film badges, all of which have been processed by the Radiation Protection Division of the Department of National Health and Welfare. In all plant tests close contact has been maintained with the provincial department of health concerned, which has always willingly co-operated in this work.

Air samples were collected in all cases by means of a "Staplex" air sampler with 4 in. diameter felt filters, type BM-2133. The sampler was placed as near to the operating area as was feasible and was mounted on a stand or other support to avoid collection of dust from the floor. In some tests, a sampler was carried and held manually as close to the operator as possible while the actual work was in progress. In general, samples were collected in the same positions both before and after the actual test work to establish normal background conditions in the locality. The sampling time was governed by the duration of the critical operation; for background runs enough time was allowed to collect a representative sample of ambient airborne dust. These checks of background concentrations showed that in several instances enough uranium-bearing dust had settled out on the floor to affect subsequent tests if the dust was disturbed during or between tests.

After collection, all samples were taken to the Radiometric Laboratory of the Mineral Sciences Division for counting. In most cases the beta-ray activity only was determined using a large, end-window Geiger counter. Since most of the initial radioactivity of the samples was due to normal atmospheric radon, it was usually necessary to count after a delay of 2 to 3 days to permit the radon daughters to decay away.

In those cases where particularly high levels of activity were encountered, chemical determinations were obtained. The chemical results were then used to calculate the approximate uranium concentrations for the remaining samples. In all tests the maximum permissible uranium concentration in air has been accepted as 5.6 μg U per cubic foot of air (Table 11.2).

TEST RESULTS

Radiation Measurements

Radiation measurements have been conducted on a variety of uranium metal samples and uranium-bearing steels. The maximum range of the beta particles of energy 2.3 MeV in steel is of the order of 1/16 in. so that only the surface area contributes to the measured beta radiation. Also, the higher the uranium content the greater is the self-shielding character of the metal for gamma radiation. For these reasons, although some radiation from alloy samples and billets is readily detected by means of a thin-walled Geiger counter, the actual dose levels for all radiations recorded with a radiation survey meter have usually been less than 0.1 mr/hr, compared with a maximum permissible value of 2.5 mr/hr for continuous exposure for a 40 hour week.

Dosage readings in close contact with drums containing 60 to 200 lb of ferro-uranium master alloys, as measured at several plants(16,17), gave readings of the order of 1.3 mr/hr. As this material is required to be stored in a locked enclosure, no hazard would arise in storage or during necessary brief handling periods. No problem is expected to arise from this aspect in the handling of finished steel billets.

Measurements were taken in a few cases on massive slag samples. Fairly high radiation readings were obtained with a Geiger counter close to slag samples from tests where the uranium recovery in metal had been poor and the slag contained appreciable amounts of uranium(16). However, even in these cases, the radiation dosage levels were below 0.1 mr/hr.

Air Sampling Tests at the Mines Branch

1 - Steelmaking Tests

Attempts have been made to obtain representative air samples during all critical operations in all phases of the Mines Branch uranium-steel programme(13,14,15,21). The results of this work have shown, that, for the quantities of uranium employed, all foundry operations can be conducted with uranium concentrations in air well below the maximum permissible value. Even if the level rises momentarily during tapping, existing ventilation is sufficient to maintain air concentrations at a safe level. Good housekeeping is still a necessity. It is recommended that the foundry floor should be swept regularly and frequently, using a sweeping compound to avoid stirring up hazardous dust unnecessarily.

Table 11.3 contains a summary of critical data and maximum concentrations obtained during several of the steelmaking tests surveyed. In most cases the uranium concentration returned to background after the periods quoted. Further details on the heats involved and on sampling conditions may be obtained from previous chapters and from the detailed reports(15).

TABLE 11.3

Summary of Mines Branch Metal Shop Air Samples

Heat No.	Total Charge, lb	Total U Involved, g	Pouring Temp., °C	Sampling Period, min	Sampler Distance, ft	Max. U conc,, µg/cu ft
A1597	500	250	1630	11	6	0.01
A1598	500	450	1600	135	6	0.03
4565	405	181	1585	10	4	-
4566	405	182	1590	10	4	0.018
4567	405	182	1590	10	4	-
4568	405	182	1580	10	4	-
4569	405	184	1585	10	4	0.005
4570	405	184	1585	10	4	0.015
A1603	500	450	1600	3	1.5	2.23
4578	405	182	1585	15	4	0.10
4579	405	182	1585	30	4	0.34
4580	405	182	1590	10	4	-
4631	405	176	1585	10	4	0.06
A1642	500	169	1580	3	5	-

Maximum permissible concentration: 5.6µg U/cu ft

Similar tests are under way in connection with work on higher grade alloys and tool steels. To some extent the figures in Table 11.3 may be extrapolated for such cases. It is evident that for alloy steels containing over 1% uranium extra ventilation and the wearing of face masks may be required, except for very small heats.

2. Metal Forming Tests

Air sampling tests on various metal forming operations have also been conducted. In most of these cases the metal involved was either pure uranium or uranium metal containing minor alloying constituents. For this reason the momentary uranium concentrations in air sometimes reached relatively high levels, though only for very short times, and the wearing of face masks was required. Table 11.4 summarizes some of these operations and the measured maximum uranium concentrations in air(15,22).

TABLE 11.4

Summary of Metal Forming Tests

Date	Operation	Quantity of Uranium Involved	Sampling Period, min	Sampler Distance, ft	Max. U conc. µg/cu ft
5/4/60	Extrusion (hot)	50 lb pure U metal	3	2	24.2
5/4/60	Extrusion (hot)	70 lb pure U metal	8	1	161
26/5/60	Extrusion (hot)		3	2	0.40
26/5/60	Extrusion (hot)		3	2	3.06
26/5/60	Extrusion (hot)		2	2	1.78
26/5/60	Extrusion (hot)		4	2	0.42
21/6/60	Extrusion (hot)		120	2	0.03
21/6/60	Extrusion (hot)	2 tests	11	2	-
15/5/61	Arc welding	Electrodes, containing 0.16% U	25	1	0.0005
4/7/61	Hand sawing	Pure U metal	1	0.75	2690
4/7/61	Abrasive wheel cutting	Pure U metal	1	0.75	860
4/7/61	Hand polishing	7% U-steel	0.7	0.75	160
20/1/61	Forging at 2150°F	340 lb, Heat A-1597	55	6	0.052
20/1/61	Rolling at 1850°F	340 lb, Heat A-1597	8	3.5	0.011
16/2/61	Extrusion	25.75 lb U-Ti alloy, 98% U	17	3	9.4
13/4/61	Heating only, to 1150°F	50 lb U billet	17	2	2.6
17/4/61	Heating only, to 1850°F	50 lb U billet	17	2	113

Maximum permissible concentration: 5.6µg U/cu ft

Air Sampling Tests at Commercial Plants

Only preliminary work has been done by industry so far; however, as the acceptance of uranium steel by industry is greatly influenced by health and safety considerations, care has been taken to obtain as much information on these aspects of the operations as possible. Details of sampling conditions are contained in previous chapters and in the relevant reports (16-20). Table 11.5 summarizes the maximum uranium concentrations measured, firstly for furnace operations and secondly for scarfing and grinding operations. It will be seen that the latter raise considerably more uranium-bearing dust, as would be expected, and face masks must be worn for this work.

TABLE 11.5

Summary of Air Sampling Results, Commercial Tests

Date	Type of Operation	Amount of Metal Involved	Sampling Period, min	Sampler Distance, ft	Max. U conc., µg/cu ft
2/5/61	Oxygen converter	104 tons of steel, 107 lb U	27	12	1.98
2/5/61	Ingot pouring	16 ingots, 87 lb U total	33	10 - 30	1.62
17/5/61	Induction furnace	500 lb "Vibresist", 0.06% U	77	4	0.014
18/5/61	Induction furnace	500 lb Stainless 430, 0.39% U	12	4	0.65
18/5/61	Induction furnace	500 lb Stainless 430, 0.07% U	10	4	0.17
6/6/61	Oxygen converter	105 tons steel, 14 lb U	10	12	-
6/6/61	Ingot pouring	105 tons steel, 300 lb U	20	10 - 20	0.21
6/6/61	Ingot pouring	105 tons steel, 300 lb U	14	10 - 20	0.57
16/6/61	Induction furnace	35 tons "Vibresist", 0.09% U	5	6	0.11
18/7/61	Ingot addition	4.2 tons carbon steel, 5 lb U	2	5	-
19/7/61	Ingot addition	5.5 tons rimming steel, 7 lb U	1.5	5	2.54
3/5/61	Rolling (hot)	U steel billets, 0.015% U	67	14	0.04
3/5/61	De-seaming	U steel billets, 0.015% U	15	18	0.06
3/5/61	Hand scarfing	U steel billets, 0.015% U	10	3	0.09
19/5/61	Grinding	Stainless 430 billet, 0.07% U	5	2	11.2
19/7/61	Hand scarfing	Rimming steel, 0.06% U	10.1	2	0.42

Maximum permissible concentration: 5.6 µg U/cu ft.

DISCUSSION OF RESULTS

All the survey results obtained so far may be summarized as follows:

1. Steels containing up to 0.5% uranium appear to represent no radiation hazard in production, storage, and handling, although the wearing of gloves is recommended.
2. From the radiation standpoint the handling and storing procedures generally used appear to be satisfactory(1).
3. Provided good ventilation exists in the pouring area, the handling, tapping, and pouring of uranium-bearing steels does not appear to lead to excessive uranium concentrations in air. However, it is important to avoid cumulative contamination of the floor by uranium dust.
4. In operations involving the hot rolling or extrusion of metal containing a high proportion of uranium, face masks or respirators should be worn by the workmen close to the hot metal. Regular clean-up of the work area is essential.
5. Any operation involving the dry cutting, grinding, sawing or scarfing of uranium-bearing metal must be considered potentially hazardous and should be conducted in an enclosed, well-ventilated area. The operator should wear a face mask and gloves.

It can be said that wide use of uranium-bearing steel does not involve any unusual handling or ventilation requirements for industry.

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APPENDIX

Definition of Units (10)

1. Microcurie (μc) - means that quantity of a radioactive substance that is disintegrating at the rate of 37,000 disintegrations per second*.

   (1 curie = 10^6 microcuries)

2. Roentgen (r) - means that quantity of X- or γ-radiation such that the associated corpuscular emission produces in 1 cc of air, at normal temperature and pressure, ions carrying one electrostatic unit of quantity of electricity of either sign (16).

   (1 milliroentgen (mr) = 10^{-3} roentgens)

3. Rem (rem) - means, in relation to the body or any organ of the body, the dose of any ionizing radiation that has the same biological effectiveness as a dose of 200 to 250 thousand volt X-rays whose energy is absorbed by the body or such organ in the amount of 100 ergs per gram.

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* By long-established usage in internal dose calculations, one curie of recently extracted uranium is considered to correspond to the sum of one curie from U-238, one curie from U-234 and 0.048 curie from U-235.