622 (21(06) C 212 NX



Dept. Mines & Technical Surveys MINES ERANCH

NOV 22 1966.

LIBRARY

OTTAWA, CANADA.

EFFECT OF URANIUM ON THE TRANSVERSE DUCTILITY OF RESULPHURIZED CHROMIUM STAINLESS STEEL ROLLED PLATE

W. M. CRAWFORD

PHYSICAL METALLURGY DIVISION

MINES BRANCH

PEPARTMENT OF MINES AND

ECHNICAL SURVEYS, OTTAWA

RESEARCH REPORT

R 179

JULY 1966

(6) Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa, and at the following Canadian Government bookshops:

OFTAWA

Daly Building, Corner Mackenzie and Rideau

TORONTO

Mackenzie Building, 36 Adelaide St. East

MONTREAL

Acterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available for reference in public libraries across Canada

Price 75¢ Cat. No. M38-1/179

Price subject to change without notice

ONA BUING TO THEM AND Queen's Printer and Controller of Stationery: ATO SYSTEM IAO No

1966

PHYSICAL METALLUNGY DIVISION

社会联邦自被合体

建智斯 医囊性 医含化医素素 医多多数 医结节

MINES BRANCH

IESEARCH REPORT

R TYS

Mines Branch Research Report R 179

EFFECT OF URANIUM ON THE TRANSVERSE DUCTILITY OF RESULPHURIZED CHROMIUM STAINLESS STEEL ROLLED PLATE

by

W. M. Crawford*

= = = = =

ABSTRACT

Tensile ductility in the transverse and longitudinal direction was investigated for a group of experimental stainless steels, of AISI Types 416 and 430F, containing sulphur at levels of 0.15% and 0.30% and corresponding uranium contents to give U:S ratios of approximately 0, 1, 4, and 7.

The usual deleterious effect of sulphur on ductility was demonstrated in the uranium-free steels and, in particular, the poor transverse ductility due to the presence of the sulphides as stringers was noted.

Uranium was observed to have a pronounced effect on the morphology of the sulphides, suggesting a change in their chemical composition. At U:S ratios in the region of 4:1, globular sulphides replaced the stringers and the ratio of transverse/longitudinal ductility, as measured by per cent reduction of area, was of the order of unity. Also, in this condition, the 0.15% sulphur steels and the 0.30% sulphur steels showed similar ductilities. These beneficial effects were obtained for both grades of steel in the soft, annealed condition, and also for Type 416 quenched and tempered to a higher strength.

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

Direction des mines

Rapport de recherches R 179

EFFET DE L'URANIUM SUR LA DUCTILITÉ TRANSVERSALE D'UNE PLAQUE LAMINÉE D'ACIER INOXYDABLE AU CHROME RESULFURÉ

par

W. M. Crawford*

RÉSUMÉ

Une série de plaques d'essai en acier inoxydable, des types AISI 416 et 430F, contenant 0.15% et 0.30% de soufre et suffisamment d'uranium pour donner des rapports U/S d'environ 0, 1, 4 et 7, a été étudiée pour déterminer la ductilité à la traction en direction transversale et longitudinale.

L'effet nuisible habituel du soufre sur la ductilité a été démontré dans les aciers sans uranium et on a remarqué, en particulier, une faible ductilité transversale due à la présence de sulfures filiformes.

L'auteur a observé que l'uranium a un effet prononcé sur la morphologie des sulfures, ce qui semble indiquer une modification dans leur composition chimique. Pour des rapports U/S d'environ 4 à 1, des sulfures globulaires remplacent les sulfures filiformes et le rapport de la ductilité transversale/longitudinale, mesurée en pourcentage de la réduction de superficie, est de l'ordre de l'unité. Pour les mêmes rapports aussi, les aciers contenant 0.15% et 0.30% de soufre ont fait preuve de ductilités semblables. On a constaté ces effets utiles pour les deux qualités d'acier, à l'état doux et recuit, et aussi pour l'acier de type 416 trempé et revenu à une resistance à la traction plus elevée.

^{*}Agent scientifique, Section des métaux ferreux, Division de la métallurgie physique, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CONTENTS

	Page
Abstract	i
Résumé	ii
Introduction	1
Materials and Methods	2
Uranium Distribution	3
Results	4
Metallography	4
Sulphide Inclusions	4 5
Mechanical Tests	6
Types 416 and 430F, Annealed	6 7 7
Discussion of Results	8
Sulphide Morphology	8
Tensile Ductility	9
Conclusions	11
Acknowledgements	11
References	12
Tables 1 - 7	14 - 20
Figures 1 - 14	21 - 34

TABLES

No.		Page
1.	Chemical Composition of Heats	14
2.	Mechanical Properties of Uranium-bearing Type 416 Stainless Steel (Annealed)	15
3.	Mechanical Properties of Uranium-bearing Type 430F Stainless Steel (Annealed)	16
4.	Mechanical Properties of Uranium-bearing Type 416 Stainless Steel (Oil-quenched and Tempered)	17
5.	Notched Tensile Results of Uranium-bearing Type 416 Stainless Steel (Annealed)	13
6.	Notched Tensile Results of Uranium-bearing Type 416 Stainless Steel (Oil-quenched and Tempered)	19
7.	Notched Tensile Results of Uranium-bearing Type 430F Stainless Steel (Annealed)	20
	FIGURES	
1.	Photographic prints of autoradiographs from plates of uranium-bearing Type 416 stainless steel containing 0.15/0.16% sulphur	21
2.	Photographic prints of autoradiographs from plates of uranium-bearing Type 416 stainless steel containing 0.29/0.34% sulphur	22
3.	Photographic prints of (a) autoradiograph and (b) sulphur print of a plate of uranium-bearing stainless steel Type 416 containing 0.32% sulphur	23
4.	Photomicrographs (longitudinal sections) showing the effect of uranium on the sulphide inclusions of Type 416 stainless steel containing 0.13/0.16% sulphur	24

(Figures, cont'd) -

No.		Page
5.	Photomicrographs (longitudinal sections) showing the effect of uranium on the sulphide inclusions of Type 416 stainless steel containing 0.29/0.34% sulphur	25
6.	Photomicrographs (longitudinal sections) showing the effect of uranium on the sulphide inclusions of Type 430F stainless steel containing 0.11/0.14% sulphur	26
7.	Microstructure of uranium-bearing Type 416 stainless steel in the annealed condition	27
8.	Microstructure of uranium-bearing Type 430F stainless steel in the annealed condition	28
9.	Microstructure of uranium-bearing Type 416 stainless steel in the oil-quenched and tempered condition	29
10.	Effect of uranium on the strength of Type 416 stainless steel in the annealed condition	30
11.	Effect of uranium on the strength of Type 430F stainless steel in the annealed condition	31
12.	Effect of U/S ratio on the transverse and longitudinal tensile ductility of Type 416 s.s. containing 0.13/0.16% and 0.29/0.34% sulphur, and Type 430F s.s. containing 0.11/0.14% and 0.22/0.23% sulphur. (Annealed)	32
13.	Effect of uranium on the strength of Type 416 stainless steel in the quenched and tempered condition	33
14.	Effect of U/S ratio on the transverse and longitudinal tensile ductility of Type 416 s.s. containing 0.13/0.16% and 0.29/0.34% sulphur. (Quenched and tempered)	34

INTRODUCTION

In the development of steels to fulfill special engineering requirements, in some instances the alloy addition that produces the desired effect also produces deleterious side effects. With increasing amounts of this additive, these side effects can reach such a magnitude as to override the derived benefits and the full potential of the element's useful effect cannot be realised. Thus, the maximum beneficial effect that can be utilised is dependent on the maximum detrimental effects that can be safely tolerated.

Such is the case with resulphurized free-machining steels, where the sulphur added produces sulphide inclusions which act as chip-breakers during machining and thereby improve machinability and surface finish. The presence of these inclusions, however, has an adverse effect on certain other properties, such as corrosion resistance and forgeability, and their deformation into stringers during rolling is particularly deleterious to transverse ductility. Reduced transverse ductility is a common phenomenon even in steels of normally low sulphur content, especially high-strength steels, and can be shown to be related to the number of sulphide inclusions present (1). Recent German data on rolled mild steel plate demonstrated 40-60% reductions of this ductility on increasing the sulphur content from 0.010% to 0.10% (2). Many resulphurized grades, however, contain as much as 0.30% sulphur and it can be appreciated that such steels would be unsuitable for service conditions where low transverse ductility could not be tolerated. Increasing the tensile strength aggravates this detrimental effect of sulphur, and some high-strength stainless and low-alloy freemachining steels are restricted to a much lower sulphur content because of this.

It has been reported that anisotropy of ductility is due to the stress concentrations that arise at the edges of inclusions. Thus, when stringer inclusions are aligned perpendicular to the axis of the principal stress, as in a transverse test specimen, additional stresses are set up across the specimen that allow attainment of the fracture stress at a reduced strain (3)(4). The amount of reduction of the ductility is dependent on the magnitude of the stress concentration, which in turn is related to the inclusion shape. The effect of the latter can be explained using the analogy of holes in a plate. Calculations have shown that the stress concentration at the edge of a circular hole can be three times that of the uniform stress applied to the plate. At the edge of an elliptical hole, it will depend on the ratio of the major diameter to the minor diameter which, for a stringer inclusion, is conservatively estimated at five to one. This is reckoned to give a stress concentration of ten times the applied stress. The advantage of round

inclusions over stringer types is thus apparent, and since the stress concentration at a completely spherical inclusion would be the same in all directions, there is the possibility that the ratio of transverse/longitudinal ductility will approach unity.

Early work on uranium in steel, carried out at the Physical Metallurgy Division, Dept. of Mines and Technical Surveys, showed that globular sulphides could be achieved by the addition of uranium. These sulphides did not elongate on rolling, and preliminary Hounsfield tensile tests on two uranium-bearing resulphurized grades of stainless steel, AISI Type 303 and Type 416, gave some indications of an improvement in the transverse ductility as measured by the per cent elongation (5)(16).

As a result of this, and as part of an overall project on uranium-bearing resulphurized grades of AISI 400 series stainless steel, this investigation was undertaken to examine the effect more closely for Type 416 and Type 430F steel. A range of chemical compositions was chosen and a programme of testing laid down, such that the significance of the U/S ratio and sulphur content would be determined. Both types of steel were examined in the soft, annealed condition, while the martensitic Type 416 was also tested at a higher strength in the quenched and tempered condition.

MATERIALS AND METHODS

For each of the two types of stainless, eight compositions comprising uranium contents to give U/S ratios of approximately 0, 1/1, 4/1 and 7/1 at 0.15% and 0.30% sulphur, were prepared in a 50 lb airmelting induction furnace. The charge consisted of Armco iron with low-carbon ferro-alloy additions, and final deoxidation was carried out with about 2 pounds of aluminum per ton prior to the addition, in quick succession, of elemental sulphur and uranium.

The uranium was added as pure metal and was wrapped in a small piece of aluminum foil in an attempt to cut down oxidation loss. A recovery of the order of 70% was obtained. Each heat was poured at 1620°C (2950°F) into a preheated hand ladle and thence into a cast iron mould. Small test coupons were also poured and subsequently drilled for chemical analysis. The compositions of the experimental heats are given in Table 1.

After cropping of top and bottom ends, each ingot was forged and rolled to plate 3-1/2 in. wide x 3/4 in. thick -- Type 416 at 1150°C (2100°F), and Type 430F at 1065°C (1950°F). All heats forged and rolled successfully,

although those plates containing the highest uranium content did show some edge bursts.

Plates of both types were given an annealing treatment of 871°C (1600°F) for 1 hour, followed by a furnace cool, to produce material in the soft ferritic condition. To show the effect of higher strength, other plates of the martensitic Type 416 were oil-quenched from 982°C (1800°F) and tempered at 538°C (1000°F).

Charpy V-notch impact specimens and notched and unnotched tensile test specimens were cut from the plates in the transverse and longitudinal directions. The tensile specimens had a diameter of 0.25 in. and a gauge length of 1 in. and, for the notched specimens, a 60° circumferential notch at the centre with a small diameter of 0.177 in. and a root radius of 0.002 in.

Uranium Distribution

After heat treatment, each plate was surface-ground for autoradiography and sulphur-printing. Results of the autoradiography for the Type 416 heats are shown in Figures 1-3 and demonstrate the non-uniform distribution of some of the uranium in the form of areas of high uranium concentration. These areas have been termed 'uranium segregate', and show up white in the photographic prints of the autoradiographs. It will be observed that the occurrence of this segregate increases with uranium content and also appears more massive. The autoradiographs, however, give an exaggerated effect to the size of the segregate, which is actually made up of galaxies of small inclusions believed to be predominately UO2. The radiation from each particle, plus the scattering of the rays, gives the deceptive appearance on the film of a single large inclusion.

That uranium occurred elsewhere throughout the steel and not just in the segregate was evidenced not only by the metallographic examination, which will be discussed later, but by the fact that the ability of the steel to sulphur-print was significantly affected by the uranium. The failure of some uranium-bearing steels to sulphur-print has been mentioned, briefly, in earlier work on uranium in steel (6). This present investigation, however, with its variety of uranium and sulphur contents, afforded a more systematic examination of the phenomenon and it was subsequently found that the U/S ratio was the controlling factor. At the base uraniumfree compositions, vigorous sulphur-prints were obtained, as expected with sulphur contents of the order 0.15% and 0.30%. With increasing U/S ratio the prints became less distinct, until at the high ratios in the region of 7/1, no reaction was obtained. The segregate areas, however, always gave a reaction, which would suggest that the segregate contained some sulphur in combination with UO2. An example of this is shown in Figure 3(b) alongside the comparable autoradiograph Figure 3(a). The possibility

that all the sulphur had segregated to these uranium-rich areas was discounted, not only by the results of the metallographic examination of the general matrix, but by the consistent uniformity of the chemical analyses for sulphur. Any segregation of sulphur would have shown up in irregular chemical results. Also, surface drillings from an area which had not sulphur-printed gave a sulphur content which checked with that specified for the heat.

Thus the sulphur-printing phenomenon gave an indication that a constitutional change in the sulphide inclusions was effected by the addition of uranium. Metallographic examination gave visual evidence of this change.

RESULTS

Metallography

Sulphide Inclusions -

Samples were cut and polished in the plane longitudinal to the direction of rolling, and examination in the unetched condition showed that uranium produced a pronounced change in the morphology of the sulphide inclusions. At an optimum uranium content, the stringer sulphides, characteristic of resulphurized steel, were replaced by a random dispersion of globular sulphides. This change occurred in those heats with a U/S ratio in the region of 4/1. At the 7/1 U/S ratio the shape of the inclusions was noticeably mixed, many angular-shaped inclusions appearing along with globular types. For the lowest U/S ratios (approx 1/1), there were indications of a progression towards globular sulphides in that many inclusions exhibited an intermediate shape which suggested some resistance to deformation. Photomicrographs for three of the groups of heats are shown in Figures 4, 5, and 6, and readily demonstrate the change in inclusion shape with the addition of uranium. The difference between the (a) and (c) photomicrpgraphs in each figure is striking.

This and other metallographic work on uranium-bearing resulphurized steels have established that the morphological changes in the inclusions are controlled by the ratio of uranium to sulphur. A comparison of the types of inclusions found in heats of similar uranium but different sulphur contents is evidence of this fact. For instance, Heat 5134, containing 0.99% U and 0.29% S (U/S=3.5), showed completely spherical inclusions (Fig. 5c) and no sign of the angular inclusions found in Heat 5110 (Fig. 4d) or Heat 5183 (Fig. 6d). These latter heats had uranium contents (1.09%

and 1.05% respectively) similar to Heat 5134, but with their lower sulphur contents of the order of 0.15% this meant a higher U/S ratio of approximately 7/1 and hence a different morphology of inclusions. For heats of the 0.15% sulphur level, a similar inclusion type to that of Heat 5134 (and also Heat 5187) was attained at much lower uranium contents in the region of 0.60% (U/S=4/1); i.e., Heat 5109: U=0.68%, U/S=4.2, and Heat 5182: U=0.55%, U/S=4.2.

Careful scrutiny of the globular sulphides suggested that a constitutional change had accompanied globularization. They appeared to be of a different shade of grey than that of the stringer sulphides and, perhaps more significantly, many were duplex in character. These duplex sulphides were more noticeable in the higher sulphur heats (see Fig. 5c) and especially large complex ones were encountered in the combination of high sulphur and high uranium (see Fig. 5d).

One other noteworthy point in the metallographic study was the relative absence of the intermetallic constituent, UFe2. Occurrence of this phase, with resultant hot shortness in forging, is common in normal low-sulphur steels at uranium contents exceeding 0.35% (7). No hot shortness was experienced with the resulphurized heats of this investigation, even though they contained up to 1.48% uranium, and the UFe2 phase was observed only in very small amounts in those heats having a U/S ratio in the region of 7/1. Again, the dependence on the U/S ratio was most noticeable. The constituent, which is pale tan in colour, was discernible in Heat 5110 containing 1.09% U (U/S=7.3) but was absent in Heat 5135 containing 1.48% U (U/S=4.7). This and other accumulated data suggest that UFe2 begins to appear when the uranium is in excess of about 7 times the sulphur content.

Microstructure -

Specimens from the lower sulphur group of heats were etched in Vilella's reagent and examined for any effects of uranium on the general microstructure. The photomicrographs of Figures 7 and 8 show typical microstructures of chromiferrous ferrite plus carbides for the Type 416 and 430F groups, respectively, in the annealed condition. No notable effects of uranium were observed, apart perhaps for a tendency of the carbides of higher uranium heats to appear more massive. In the quenched and tempered condition the Type 416 group showed, in every heat, a normal structure of tempered martensite and ferrite (see Fig. 9). Using the Quantitative Television Microscope, a count of the amount of ferrite showed, however, about 10-15% more of this phase in the two highest uranium heats, and an intermediate increase at the lowest uranium, over the base uranium-free heat. This may have contributed to the significant drop in strength which was noted in the mechanical test results. Uranium is a very strong

carbide-former, however, and it is also possible that the hardness of the martensite was reduced as a result of the original austenite being depleted of carbon.

Mechanical Tests

Types 416 and 430F, Annealed -

Tensile and charpy results at room temperature are given in Tables 2 and 3. The effect of uranium on the strength of the two types of stainless steel is shown in Figures 10 and 11. In the case of Type 430F (Fig. 11) uranium had no effect, but for Type 416 (Fig. 10) there was a tendency for a slight drop and levelling off in strength with increasing uranium. Sulphur content had no significant effect on strength.

The effect on tensile ductility in the transverse and longitudinal directions is illustrated in Figure 12 (a) and (b), where reduction of area and elongation are plotted against U/S ratio. The results were more striking in the case of reduction of area. In the longitudinal direction uranium produced no change, but for the transverse direction a most significant improvement occurred in both types, at both levels of sulphur, at a U/S ratio maxima in the region of 4/1. At the base uranium-free compositions, the results demonstrated the characteristic division in ductility between the transverse and longitudinal test directions and between the higher and lower sulphur contents; e.g., the transverse and longitudinal reductions of area for the Type 416 Heat 5107 containing 0.13% sulphur were 61.4% and 73.1% respectively, and similarly 44.9% and 66.1% for Heat 5132 containing 0.33% sulphur. Note the greater disparity between transverse and longitudinal values at the higher sulphur level; and for similar test directions, compare the relatively small decrease in longitudinal ductility on increasing the sulphur content with the much larger decrease in transverse ductility. At the 4/1 U/S ratio, however, these differences due to test direction and sulphur content did not occur and the graphs clearly show an equalization of the test results. As stated above, the poorest combination for ductility was high sulphur content and a transverse test direction. Heat 5134, however, containing 0.29% sulphur but with a U/S ratio of 3.5, gave a transverse R.A. of 72.0% matching that of a much lower sulphur heat tested in the longitudinal direction, i.e., Heat 5107, 0.13% S; longitudinal R.A., 73.1%.

Elongation results for Type 430F were rather inconclusive (Fig. 12b), but for Type 416 (Fig. 12a) a similar maxima in the transverse values occurred in the region of the 4/1 U/S ratio.

Charpy V-notch impact test results, shown in Tables 2 and 3, were erratic and not very useful in equating test directions or uranium content.

It appeared that in the soft, annealed condition, for similar sulphur contents, the Type 430F was generally of a lower impact strength than the Type 416. In the lower sulphur group of the latter, a trend to lower impact strength with the addition of uranium was noticeable.

Type 416, Quenched and Tempered -

Test results for the Type 416 heats in this higher strength condition are given in Table 4. The strength levels plotted against uranium content appear in Figure 13 and show a significant decrease, and then a levelling off, with increasing uranium. Note that in the absence of uranium, or at a low content, the strength of the 0.30% sulphur group was lower than that of the 0.15% group, but that both became similar at higher uranium contents. In Figure 14, reduction of area and elongation are plotted against U/S ratio for the two levels of sulphur and both test directions. Improvement in the transverse ductility in the region of the 4/1 U/S ratio was again quite considerable, especially for reduction of area, and differences due to test direction and sulphur content were again practically eliminated. The addition of uranium to the 0.30% sulphur group in the ratio of 3.5/1 increased the transverse R.A. from 13.5% to 57.2% (longitudinal R.A.=57.6%), and for the 0.15% sulphur it was increased from 33.1% to 59.4% with a U/S ratio of 4.2 (longitudinal R.A.=65.2%).

It also appeared that longitudinal R.A. was improved by the addition of uranium and was particularly noticeable for the higher sulphur steels. This may have been connected with the corresponding decrease in strength which accompanied the increase in uranium content.

Elongation results showed improvements similar to the R.A. results, especially for the 0.30% sulphur group, where in the transverse direction an increase from 10% to 24% was obtained with the optimum uranium addition.

Notched Tensile Tests -

The notched tensile test is usually confined to studies of highstrength steels relating to toughness and brittle fracture susceptibility. It also provides an assessment of overall quality of the steel and can show up the 'fibre' effect in rolled plates by the differences between transverse and longitudinal tests (8)(9). It was this latter effect which prompted its use in this investigation. Although the material to be examined was of low strength it was felt that a directional notch sensitivity effect might show up, considering the large number of stress-raisers (i.e. inclusions) present.

The effective severity of a notch increases with the stress concentration factor, K_t , which is controlled by the geometry of the notch.

The following dimensions were calculated in accordance with the general recommendations for maximum sensitivity (9) applied to the 0.25 in. diameter tensile specimen previously used, and were such as to give a K_t value of about 6; notch angle, 60°; notch root radius, 0.002 in.; small diameter, 0.707 x 0.250 = 0.177 in.

Results of the notched and unnotched tensile tests are given in Tables 5, 6, and 7. For each heat the notch strength ratio (notched tensile stress/unnotched tensile stress) in both directions is listed, along with a ratio of transverse/longitudinal notched tensile stress. All NT/UNT strength ratios were greater than unity, indicating that, in the condition tested, the material was not sensitive to a notch embrittling effect. The test results, however, were of some value in terms of evaluating a degree of toughness, since these ratios were still less than 1.50. For the test piece dimensions used, this value is recognized as being the limit within which the test is sensitive to variations in toughness (9). Above 1.50, maximum toughness and ductility occur and the test is no longer sensitive to toughness variations.

From the results in Tables 5, 6, and 7, it will be seen that uranium improved the notch strength in the transverse direction. This was indicated by the equalization, at the 4/1 U/S ratio, of the NT/UNT ratios in the transverse and longitudinal directions and by the trend toward unity and over in the transverse notched tensile strength/longitudinal notched tensile strength ratios. These results were predicately more striking in the higher sulphur group of the Type 416 in the quenched-and-tempered condition (Table 6).

DISCUSSION OF RESULTS

Sulphide Morphology

Normally, sulphide inclusions in steel are essentially composed of manganese sulphide, and for steel in the as-cast condition prior to forging and rolling, these sulphides may exist in a globular or rounded shape. At forging and rolling temperatures, however, manganese sulphide is plastic, and during working the inclusions are readily deformed into long stringers parallel to the working direction. The persistence of globular sulphides after rolling, as observed in certain uranium-bearing steels of this investigation, indicated a lack of plasticity in the sulphide at rolling temperature and therefore suggested that this sulphide was very much different from that of manganese. In the metallographic examination, this

was also suggested by the different colour and structure noted in these sulphides as compared with those of the uranium-free steels. Results of a parallel investigation into the corrosion properties of the same group of experimental heats have contributed further evidence of a constitutional change in the sulphides on adding uranium (10). In this, the non-resulphurized Type 430 stainless steel was shown to be relatively inactive in nitric acid while the resulphurized Type 430F was readily corroded, thus demonstrating the deleterious effect of the presence of many inclusions of manganese sulphide. The addition of uranium to the resulphurized steel, however, increased its corrosion resistance in nitric acid to a level comparable with the non-resulphurized steel, thus suggesting that the sulphides in the uranium-bearing resulphurized steel must have been of a composition that was unreactive in nitric acid.

As yet, no definite chemical identification of these sulphides has been achieved. Uranium is known to form very stable sulphides, and thermodynamic data show that it is certainly a much stronger sulphide-former than manganese (11). This investigation has demonstrated the existence of a constant relationship between uranium and sulphur contents in steel, by revealing the influence of the U/S ratio in controlling not only the morphology of the sulphides but also the occurrence of the UFe2 constituent. This suppression of UFe2 formation in high-sulphur steel was highly significant. If, by the presence of an increased amount of sulphur, UFe2 formation was prevented in a steel of a uranium content that would normally produce UFe2, then it must be concluded that a uranium-sulphur reaction took place in preference to a uranium-iron reaction.

Recently, some X-ray diffraction studies were attempted on chemically extracted residues from a group of experimental ternary ironsulphur-uranium alloys (12). An identifiable uranium-sulphur compound showed up in only one instance, namely uranium oxysulphide (UOS). A crystalline compound was encountered in every sample but could not be identified, although in qualitative analyses of the residues the presence of uranium and sulphur was strongly indicated. In some recent Japanese work, however, Kawabata et al. have reported identifying US and UOS in high-sulphur austenitic steels containing uranium (13). Thus, while the results of the present investigation do not offer, in terms of definite chemical identification, any evidence of a sulphide of uranium in the steels studied, it is felt that consideration of the data presented offers alternative proof of the occurrence of such a sulphide.

Tensile Ductility

From an appraisal of the tensile test results, it appeared that reduction of area was much more sensitive to the effects of sulphide inclusions than was elongation. This is in agreement with the findings of

Vogels and Bruning (2). In discussing tensile ductility, therefore, reference will be to reduction of area.

In considering the tensile ductility results, attention should, first of all, be directed to the R.A. values of the resulphurized steels containing no uranium (see Figures 12 and 14). Here was demonstrated the predictable influence of test direction, sulphur content and strength level on tensile ductility. These results showed that test direction was more critical than sulphur content since, in every case, the transverse value for the 0.15% sulphur group was lower than the longitudinal value for the 0.30% sulphur group. The wider spread of results for the Type 416 stainless steel in the quenched and tempered condition showed how the effect of sulphide inclusions was more severe at higher strength.

It is clear that the change from stringer to globular sulphides brought about the improved transverse ductility of the steels having U/S ratios of 4/1. The magnitude of this improvement over straight resulphurized steel was such that the ratio of transverse/longitudinal ductility (R.A.) was in the order of unity, thus substantiating the predicted isotropy of the stress-concentration effect for globular inclusions. Also, at this optimum U/S ratio, the higher sulphur steels did not show a lower ductility over the lower sulphur steels as experienced, and expected, in the uranium-free steels. Thus, production of globular sulphides resulted in not only the elimination of the influence of test direction, but also the elimination of the influence of sulphur content in the range 0.13%-0.29%; i.e., shape of sulphides was the controlling factor, more so than total sulphur content. This equalization of ductilities, occurring for both the annealed and the quenched and tempered conditions, was perhaps the more striking in the latter case since the deleterious effect of sulphur is normally greater at higher strength (14).

For the levels of sulphur investigated, therefore, uranium appeared to produce a twofold beneficial effect when added in an amount approximately four times the sulphur content -- not only was the transverse ductility increased, thereby eliminating directionality in the plate, but higher sulphur content could be tolerated without the usual loss in ductility. Since machinability increases with increasing sulphur content, the implications of this are that better machinability could be attained without forfeiture of ductility; for example, a normal free-machining steel, in which the maximum allowable sulphur content is say 0.15% because of a limit on the minimum transverse ductility that could be tolerated, could be replaced by a uranium-bearing steel of much higher sulphur content, say 0.30%, which would have superior ductility and, presumably, increased machinability. No machining data are available on these steels, but some experimental machinability tests carried out on resulphurized carbon steels indicated that uranium was not detrimental (15).

The lower strength induced by uranium, as observed in the martensitic Type 416 in the quenched and tempered condition, could be regarded as a disadvantage. It is probable, however, that the effect of uranium could be offset and the desired strength obtained by a change in the tempering temperature, or by an adjustment in the carbon or alloy content of the steel.

CONCLUSIONS

The results of the investigation described lead to the following conclusions:

- (1) The addition of uranium to resulphurized 400 Series stainless steel effects a change in the chemical composition and morphology of the sulphide inclusions. The controlling factor in this change is the U/S ratio.
- (2) A U/S ratio in the region of 4/1 produces globular sulphides which are non-plastic at rolling temperatures and hence do not deform into stringers.
- (3) As a result of globularization of the sulphides, transverse tensile ductility, as measured by the reduction of area, is increased such that the transverse/longitudinal ratio is unity.
- (4) With a U/S ratio of 4/1, increasing the sulphur content from 0.13% to 0.29% does not result in a decrease in transverse tensile ductility, as is normally the case with uranium-free resulphurized steel. This effect is especially significant in higher strength material.
- (5) The intermetallic constituent UFe2 does not begin to appear until the U/S ratio approaches 7/1.

ACKNOWLEDGEMENTS

The author extends his thanks to the members of the technical staff of the Physical Metallurgy Division for their services rendered throughout the investigation, from production and processing of the material to mechanical testing and photomicrography, and, in particular, to Dr. G.P. Contractor, Head, Ferrous Metals Section, for his constructive comments and advice.

REFERENCES

- 1. D. E. Austin and D. D. Goehler, "How Inclusions Affect Ductility of Steel Forgings", Metal Progress, Sept. 1963, p. 94.
- 2. H.A. Vogels and F. Brüning, "Influence of the Form of Non-Metallic Inclusions on the Mechanical Properties of Steel Plates", Arch. Eisenhüttenwesen, Feb. 1964, Vol. 35, p. 115.
- 3. H.J. Wagner and J.W. Spretnak, "The Effect of Initial Increments of Hot Working on the Mechanical Properties of Certain Ferrous Materials", Trans. ASM, 1960, Vol. 52, p. 629.
- 4. A.T. English, "Influence of Mechanical Fibering on Anisotropy of Strength and Ductility", J. of Metals, April 1965, Vol. 17, No. 4, p. 395.
- 5. R.F. Knight and D.K. Faurschou (editors), "The Influence of Uranium Additions to Ferrous Alloys: An Interim Review", Mines Branch Research Report R-95, Chapter 6, Dept. of Mines and Technical Surveys, Ottawa, Canada, April 1962.
- 6. G.P. Contractor, "Autoradiographic and Analytical Surveys of Uranium-bearing Carbon Steel Ingots", Physical Metallurgy Division Internal Report PM-R-61-10, Dept. of Mines and Technical Surveys, Ottawa, July 1961.
- 7. G.P. Contractor, "Some Properties of Plain Carbon Steels Containing Uranium", Trans. CIMM, Vol. 66, 1963, p. 113.
- 8. J.J. Downs, C.G. Mickelson and H.W. McQuaid, "Properties of Pressure Poured Steels", Metal Progress, April 1963, p. 72.
- 9. Fourth Report of a Special ASTM Committee, "Screening Tests for High Strength Alloys Using Sharply Notched Cylindrical Specimens", Materials Research and Standards, March 1962, p. 196.
- 10. G. J. Biefer and W. M. Crawford, "Corrosion Behaviour of Uranium-bearing Resulphurized Chromium Stainless Steel", Mines Branch Research Report R-166, Dept. of Mines and Technical Surveys, Ottawa, July 1965.
- 11. V.D. Barth and G.W.P. Rengstorff, "Potential Metallurgical Uses of Depleted Uranium", Battelle Technical Review, Vol. 9, No. 7, July 1960, p. 3.

- 12. Communication with L.G. Ripley, Analytical Chemistry Subdivision, Mineral Sciences Division, Mines Branch, Dept. of Mines and Technical Surveys, Ottawa, 1965.
- 13. M. Kawabata et al., "On the Effect of Uranium Additions on the Behaviour of Carbon and Sulphur in Austenitic Stainless Steels", Tetsu-To-Hagane, Vol. 49, No. 10, 1963, p. 1543 (Henry Brutcher Translation No. 6107).
- 14. J.M. Hodge, R.H. Frazier and F.W. Boulger, "The Effects of Sulphur on the Notch Toughness of Heat-treated Steels", Trans. AIME, Vol. 215, Oct. 1959, p. 745.
- 15. Private communication with L.B. Schmitt, LaSalle Steel Company, June 1964.
- 16. Canadian Patent No. 690748, July 14, 1964.

= = =

TABLE 1
Chemical Composition of Heats

Гχ	rр	е	41	6	s,	s.

Type Tios,	ype 410 s, s.													
	Chemical Analysis - %													
Heat No.	U	Si	Mn	S	P	Cr	Total Al	Tota1 N	Tota1 U	Acid insol.	U/S			
5107	.08	. 26	1.06	.13	.008	13.6	.03	.024	, 0	0	0			
5108	.06	.26	1.06	.15	.012	13.8	.04	.025	.19	.047	1.3			
5109	. 08	.25	1.01	.16	.013	13.7	.04	.024	.68	, -	4.2			
5110	. 08	. 24	1.00	.15	.013	13.6	.04	.022	1.09	.41	7.3			
5264	. 05	.42	1.16	. 13	.019	13.7	.05	. 025	. 52	.005	4.0			
5132	. 09	. 31	. 96	.33	.008	14.2	.03	.022	0	0	0			
5133	.10	.32	1.00	.34	.008	14.1	. 04	.021	.24	.009	. 71			
5134	.12	.27	.96	. 29	.008	13.8	. 05	.019	.99	.006	3.5			
5135	.13	.28	.98	.32	.008	13.7	.04	.020	1.48	. 006	4.7			

Type 430 F s.s.

Type 430F	0.0.										
5180	. 08	. 32	1.02	. 14	.007	16.4	.02	.021	0	0	0
5181	. 08	.37	1.03	.14	.007	16.3	. 04	.019	.081	. 066	. 58
5182	. 08	. 36	1.06	.13	.008	16.5	.05	.020	.55	. 003	4.2
5183	. 07	.44	1.10	. 14	.011	16.1	.05	.021	1.05	. 003	7.5
5185	. 05	.25	67	. 11	.013	16.3	. 03	.019	0	0	0
5186	.06	.39	1.16	.23	.014	16.2	.05	.017	.19	. 023	.83
5187	.06	. 43	1.16	.22	.017	16.0	. 05	.019	.90	.022	4.1
5188	. 06	. 27	1.13	. 22	.018	16.5	. 07	.018	1.57	.077	7.1

TABLE 2

Mechanical Properties* of Uranium-Bearing
Type 416 Stainless Steel (Annealed)

Heat No.	U %	S %	U/S	Test Direction	0.2% P.S. kpsi	U.T.S. kpsi	EL. %	R.A. %	Charpy, ft-lb
5107	-	. 13	-	T L	38.5 35.5	69.2 65.7	25 34	61.4	15, 16, 16 15, 20, 24
5108	. 19	.15	1.3	T L	35.5 34.6	66.3 63.8	28 34	57.2 74.9	12,8,9 12,16,22
5264	.52	. 13	4.0	T L	34.5 33.1	62.3	29.5 35.5		6, 6, 4
5109	. 68	. 16	4.2	T L	34.0 32.9	60.8 60.1	31 36	73.5 69.9	4, 4, 6 2, 4, 8
5110	1.09	. 15	7.3	T L	34.8 33.0	59. 7 61.0	23	50.8 72.1	6, 10, 6 4, 6, 14

5 132	-	.33	-	T L	36.9 35.5	65.8 63.4	23 34	44.9	10, 12, 11 2, 12, 13
5133	.24	. 34	. 71	T L	34.1	61.1	27 38	56.3 68.9	8,6,6
5134	. 9 9	.29	3.5	T L	32.3 31.5	58.1 59.4	30 37	72.0 65.6	6,5,3
5135	1.48	. 32	4.7	T L	34.3 33.2	59.8 61.4	27 35	70.4	4,6,5 3,7,9

^{*} Tensile results - average of 5 tests.

TABLE 3

Mechanical Properties* of Uranium-Bearing
Type 430F Stainless Steel (Annealed)

Heat No.	U %	S %	U/S	Test Direction	0.2% P.S. kpsi	U.T.S. kpsi	EL.	R.A. %	Charpy, ft-lb
5185	-	. 11	-	T L	35.9 34.2	61.7	28 38	60.8	4, 2, 4
5180	-	. 14	_	T L	38.1 36.8	66.4	31 35	60.3 65.0	2, 3, 4
5181	. 08	.14	. 58	T L	38.8	63.8	24 35	58.3 69.7	4, 4, 4 6, 4, 2
5182	. 55	. 13	4.2	T L	36.9 36.9	64.9 63.4	32	64.4	2, 3, 3
5183	1.05	. 14	7.5	T L	38.6 37.5	65.2 63.3	30 36	67.1 66.5	3,2,4 2,2,3

5186	. 19	.23	.83	T L	36.6 36.8	62.7	28 36	54.7 66.2	4,5,8 6,10,9
5187	. 90	. 22	4.1	T L	38.1 36.6	60.6	26 34	66.0 63.2	3,3,3
5188	1.57	. 22	7.1	T L	38.0 36.3	62.7	26 37	45.7 66.2	6,4,4

^{*} Tensile results - average of 5 tests.

TABLE 4

Mechanical Properties* of Uranium-Bearing

Type 416 Stainless Steel (Oil-quenched and Tempered)

Heat No.	U %	S %	U/S	Test Direction	0.2% P.S. kpsi	U.T.S. kpsi	EL.	R.A. %
5107	-	. 13	_	T L	90.8 93.1	115.0 114.5	15 20	33.1 59.5
5108	. 19	. 15	1.3	T L	81.8 81.3	106.7 106.7	12 21	6.3** 57.2
5109	.68	. 16	4.2	<u>í</u> I.	66.5 66.3	91.0	20 25	59.4 65.2
5110	1.09	.15	7.3	T L	66.2	89.8 85.6	20 23	49.6 64.2
5132		.33	-	T	76.9 80.1	103.1 104.3	10 17	13.5 45.9
5133	. 24	.34	. 71	T	64.1 66.7	93.5 93.5	15 21	20 .9
5134	. 99	.29	3.5	T L	62.1 61.6	89.2 88.5	2 4 24	57.2 57.6
5135	1.48	. 32	4.7	T L	67.6 67.8	92.4 92.0	17 23	44.2 53.9

^{*}Tensile results - average of 3 tests.

^{**}Dirty fracture.

TABLE 5

Notched Tensile Results of
Uranium-Bearing Type 416 Stainless Steel (Annealed)

Heat No.	U %	S %	U/S	Test Direction		trength (kpsi) Unnotched**	NTS UNTS	NTS(T) NTS(L)
5107	0	. 13	0	T L	90.7 96.2	69.2 65.7	1.31	. 94
5108	. 19	.15	1.3	T L	88.6 93.0	66.3	1.34	. 95
5109	. 68	.16	4.2	T L	82.2 82.6	60.8 60.1	1.35	. 99
5110	1.09	. 15	7.3	T L	77.5 85.5	59.7 61.0	1.30	.91

5132	0	. 33	0	T L	79.0 85.5	65.8 63.4	1.20 1.35	. 92
5133	.24	. 34	.71	T L	76.7 82.5	61.1	1.26	.93
5134	. 99	.29	3.5	T L	80.0 82.5	58.1 59.4	1.38	.97
5135	1.45	.32	4.7	T L	82.9 87.3	59.8 61.4	1.39	. 95

^{*} Average of 3 tests.

^{**} Average of 5 tests.

TABLE 6

Notched Tensile Results of Uranium-Bearing
Type 416 Stainless Steel (Oil-quenched and Tempered)

Heat	υ	s		Test	Tensile St	rength (kpsi)	NTS	NTS(T)
No.	%	%	U/S	Direction	Notched*	Unnotched*	UNTS	NTS(L)
5107	0	. 13	0	T	15 4 .4	115.0	1.34	92
3107	U	.13	U	L	167.7	114.5	1.46	.92
5100	10		1.3	Т	144.0	106.7	1.36	. 94
5108	. 19	. 15		L	152.8	106.7	1.43	
5100	40	1.6	4.2	T	135.5	91.0	1.49	1.01
5109	. 68	. 16		L	133.7	90.8	1.47	
5110	1.09	. 15	7.3	Т	128.0	89.8	1.43	1.03
5110				L	124.3	85.6	1.45	
5132	0	.33	0	T	117.7	103.1	1.14	.82
1 3132	Ŭ			L	143.8	104.3	1.38	
5133	.24	.34	.71	Т	120.0	93.5	1.28	.93
2133				L	128.7	93.3	1.38	
5134	. 99	.29	3.5	T	122.7	89.2	1.38	.99
3134				L	123.3	88.5	1.39	
5135	1.45	. 32	4.7	Т	123.3	92.4	1.33	. 93
3133	1.45	5 .34	34 4.1	L .	132.2	92.0	1.44	. 73

^{*} Average of 3 tests.

Notched Tensile Results of Uranium-Bearing
Type 430F Stainless Steel (Annealed)

Heat No.	.U %	S %	ប/ន	Test Direction	Tensile S Notched*	trength (kpsi) Unnotched**	NTS UNTS	NTS(T) NTS(L)
5185	0	. 11	0	T L	64.7 63.2	61.7 61.4	1.05	1.02
5180	0	. 14	0	T L	68.9 70.6	66.4 65.6	1.04	. 98
5181	. 08	. 14	. 58	T L	77.0 73.9	63.8 63.4	1.21	1.04
5182	. 55	. 13	4.2	T L	74.5 64.6	64.9 63.4	1.15	1.15
5183	1.05	. 14	7.5	T L	79.8 68.4	65.2 63.3	1.22	1.17

5186	. 19	. 23	. 83	T L	71.4 80.2	62.7 62.1	1.14	. 89
5187	. 90	. 22	4.1	T L	82.5 72.3	60.6 62.2	1.36	1.14
5188	1.57	. 22	7.1	T L	78.5 71.3	62.7 61.8	1.25	1.10

^{*}Average of 3 tests.

^{**} Average of 5 tests.

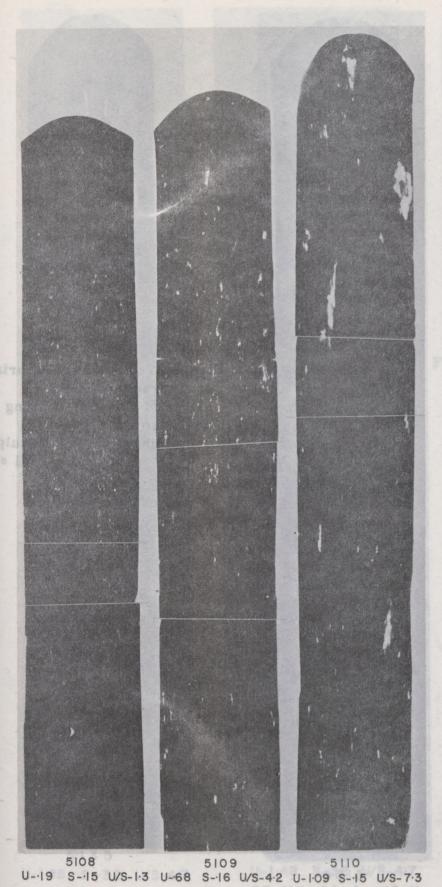


Figure 1. Photographic prints of autoradiographs from plates of uranium-bearing Type 416 stainless steel containing 0.15/0.16% sulphur (Approx 1/3 full size)

(a)

(b)

(c)

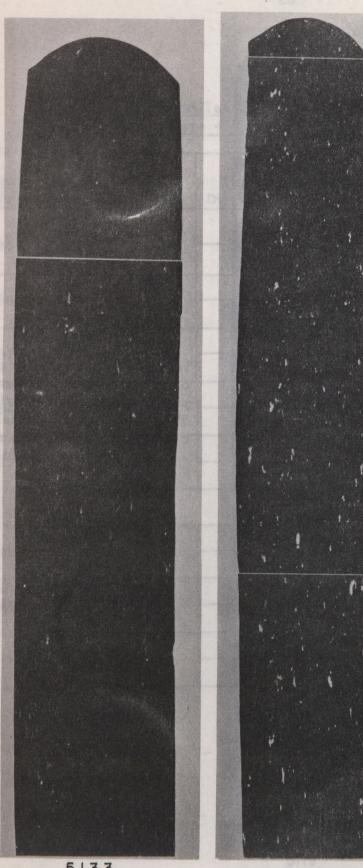
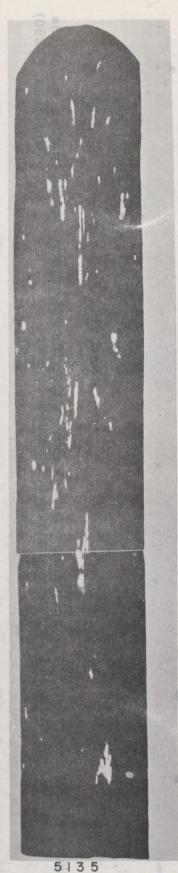


Figure 2. Photographic prints of autoradiographs from plates of uranium-bearing Type 416 stainless steel containing 0.29/0.34% sulphur (Approx 1/3 full size)

5133 U-·24 S-·34 U/S-·71

5134 U-99 S-29 U/S-35



U-1:48 S-:32 U/S-4:7



5135 U-1.48 S-32 U/S-4.7

Figure 3. Photographic prints of (a) autoradiograph and (b) sulphur-print of a plate of uranium-bearing stainless steel Type 416 containing 0.32% sulphur.

(Approx 1/3 size)



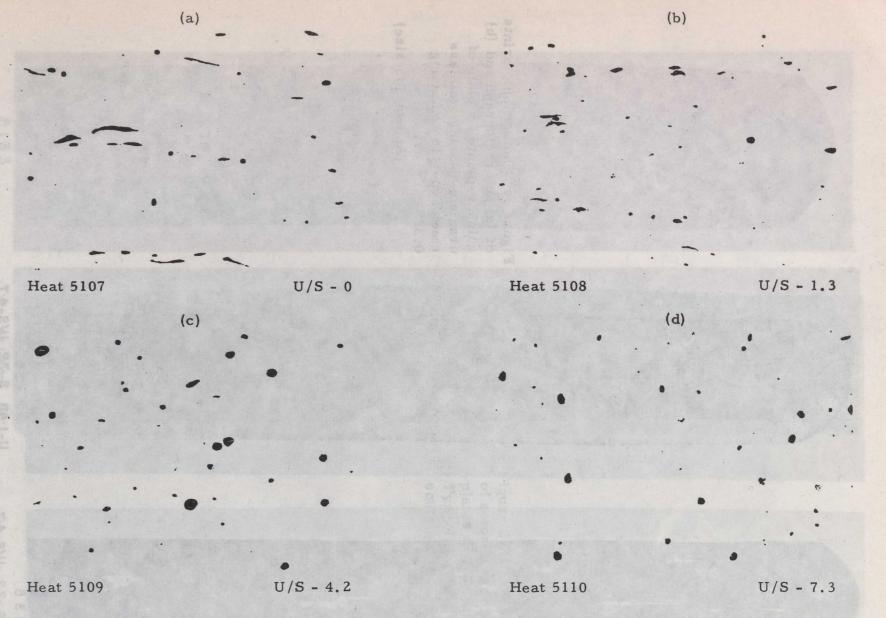


Figure 4. Photomicrographs (longitudinal sections) showing the effect of uranium on the sulphide inclusions of Type 416 stainless steel containing 0.13/0.16% sulphur. (Unetched. X250)

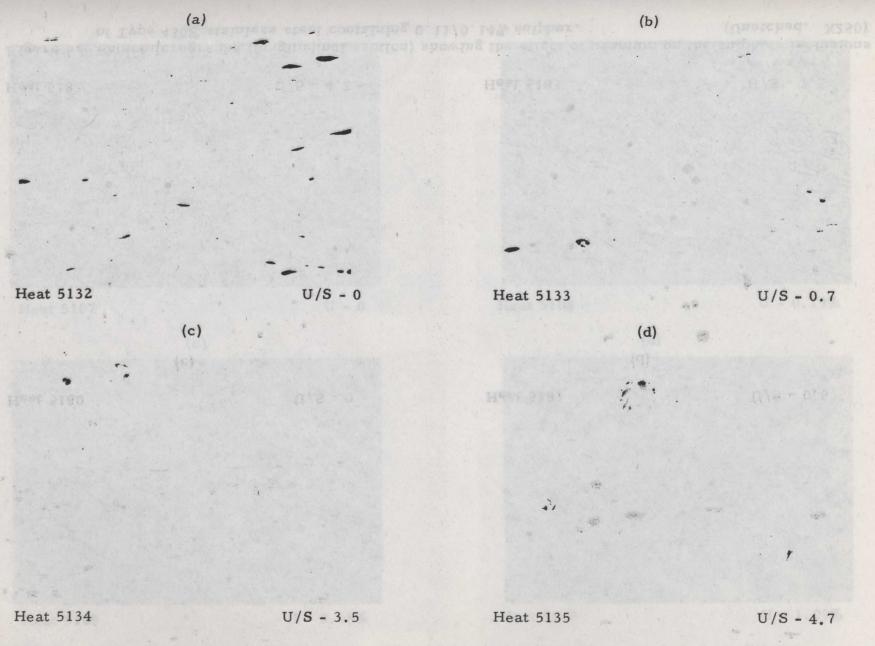


Figure 5. Photomicrographs (longitudinal sections) showing the effect of uranium on the sulphide inclusions of Type 416 stainless steel containing 0.29/0.34% sulphur. (Unetched. X250)

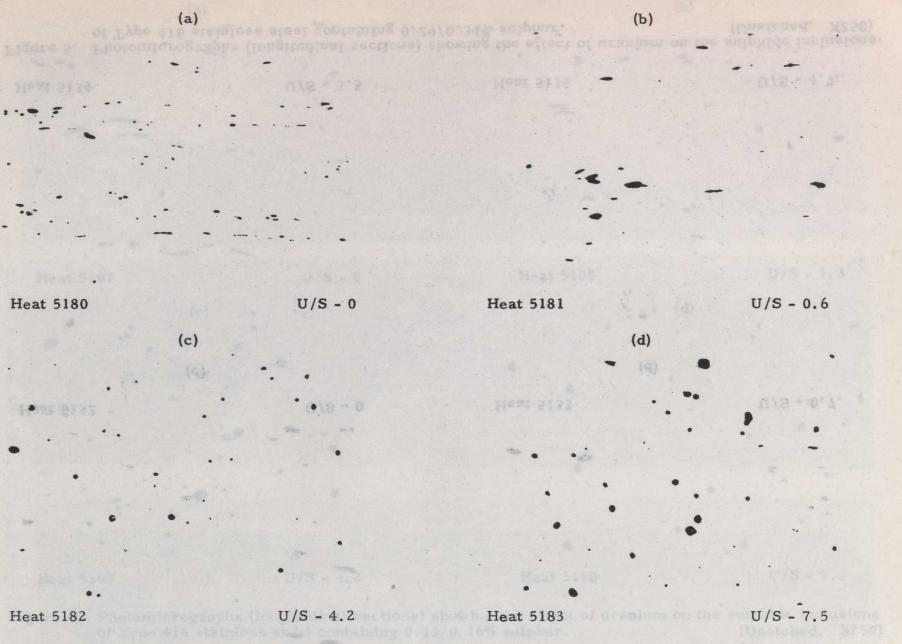


Figure 6. Photomicrographs (longitudinal section) showing the effect of uranium on the sulphide inclusions of Type 430F stainless steel containing 0.11/0.14% sulphur. (Unetched. X250)

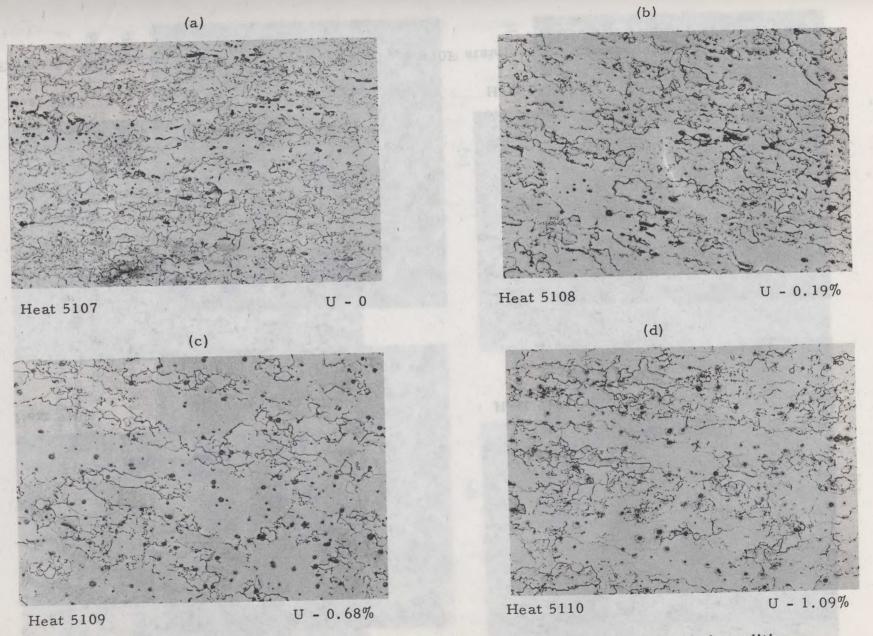


Figure 7. Microstructure of uranium-bearing Type 416 stainless steel in the annealed condition.

(Etched in Vilella's reagent. X100)

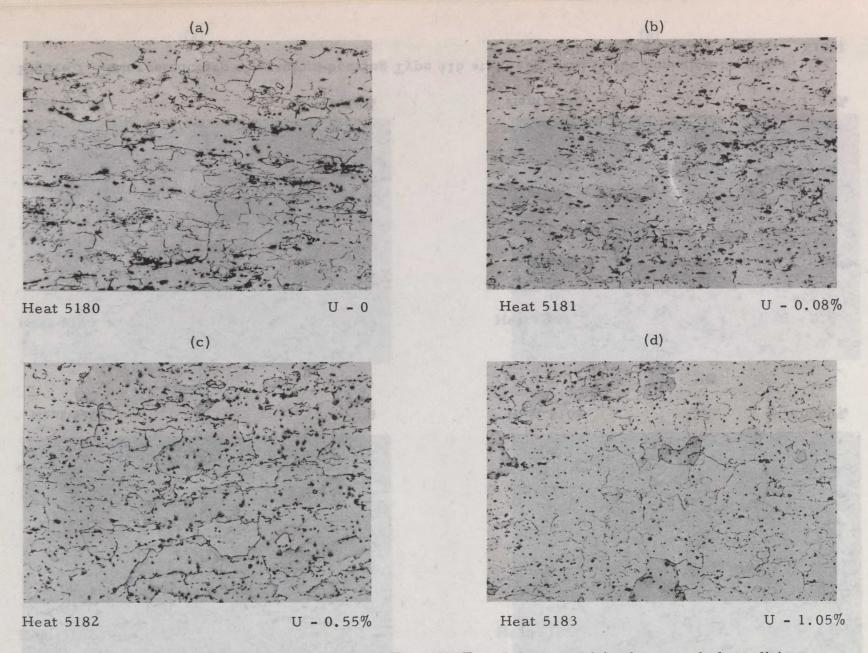


Figure 8. Microstructure of uranium-bearing Type 430F stainless steel in the annealed condition.

(Etched in Vilella's reagent. X100)



Figure 9. Microstructure of uranium-bearing Type 416 stainless steel in the oil-quenched and tempered condition.

(Etched in Vilella's reagent. X500)

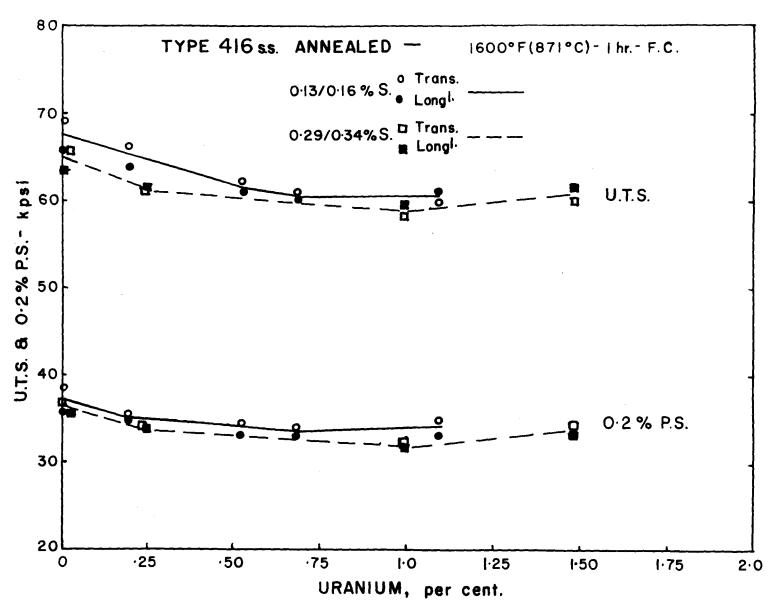


Figure 10. Effect of uranium on the strength of Type 416 stainless steel in the annealed condition.

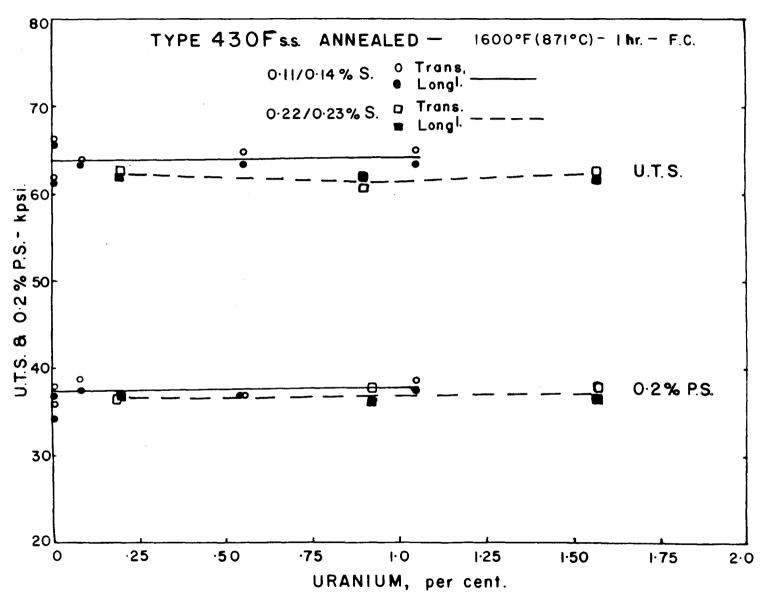


Figure 11. Effect of uranium on the strength of Type 430F stainless steel in the annealed condition.

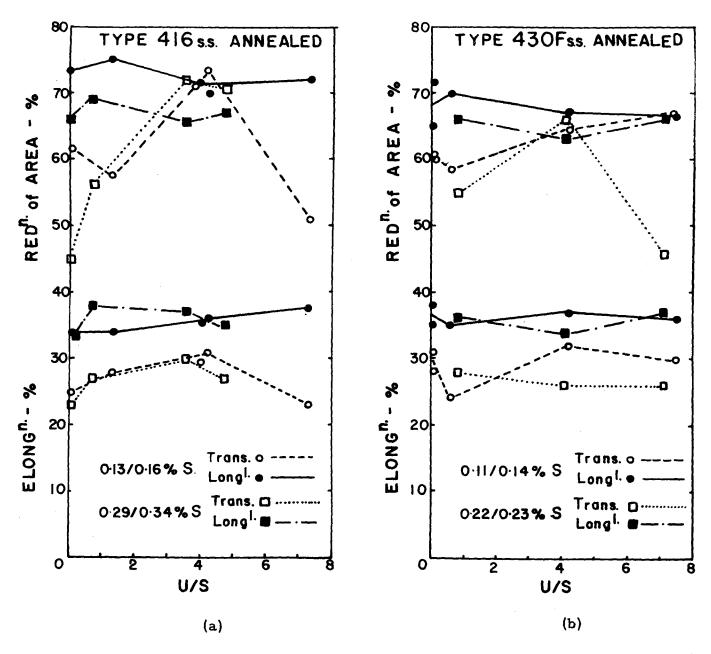


Figure 12. Effect of U/S ratio on the transverse and longitudinal tensile ductility of Type 416 s.s. containing 0.13/0.16% and 0.29/0.34% sulphur, and Type 430F s.s. containing 0.11/0.14% and 0.22/0.23% sulphur. (Annealed).

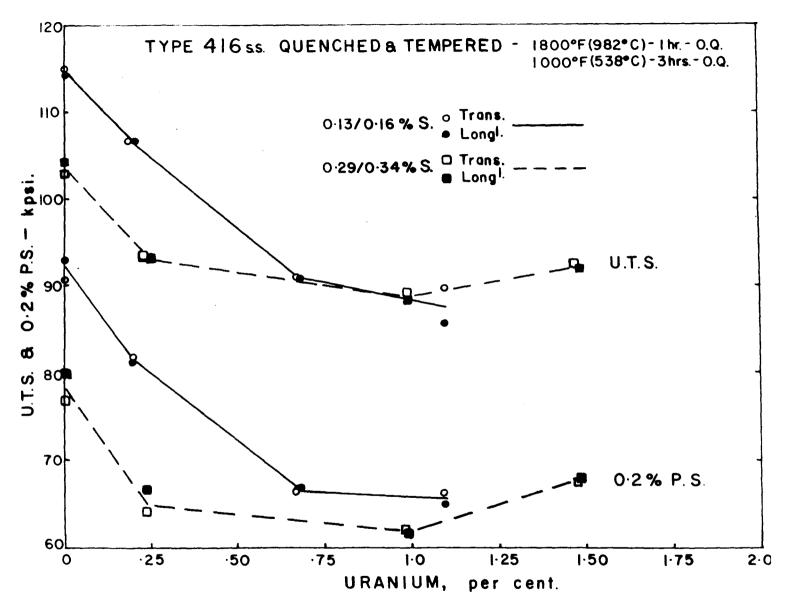


Figure 13. Effect of uranium on the strength of Type 416 stainless steel in the quenched and tempered condition.

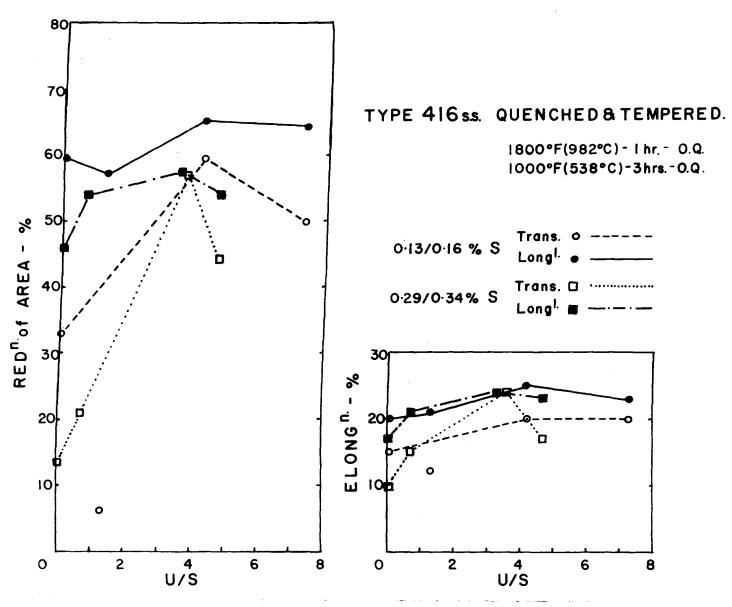


Figure 14. Effect of U/S ratio on the transverse and longitudinal tensile ductility for Type 416 s.s. containing 0.13/0.16% and 0.29/0.34% sulphur. (Quenched and tempered).