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URANIUM IN NON-FERROUS METALS

R. THOMSON & J. O. EDWARDS

PHYSICAL METALLURGY DIVISION

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Mines Branch Research Report R 97

URANIUM IN NON-FERROUS METALS

by

R. Thomson* and J.O. Edwards**

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SUMMARY

The use of uranium metal in non-ferrous metallurgical practice is discussed with reference to its alloying behaviour and chemical activity, and it is suggested that the more promising applications are in the treatment of molten metals to combine with impurities. Mines Branch work along these lines is described for copper, zinc, magnesium, aluminum and nickel alloys. It is shown that a copper - uranium master alloy (25% U) successfully deoxidizes molten copper without detriment to the electrical or mechanical properties of the product at residual.uranium levels of up to 0.8 wt %. Additions of uranium to α brass in amounts greater than the lead impurity content were found to remove the deleterious effect of lead on hot-workability. Similar deoxidizing and malleableizing effects were found with uranium additions to nickel. It is thought that uranium forms stable intermetallic compounds with many impurity elements, thus a significant malleableizing effect can be expected in the presence of other elements besides lead.

The effects of uranium on hot dip galvanizing and on grain refinement in magnesium and aluminum alloys have been evaluated briefly, but no beneficial effects were noted.

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Direction des mines

Rapport de recherches R 97

L'URANIUM DANS LES MÉTAUX NON FERREUX

par

R. Thomson* et J.O. Edwards**

RÉSUMÉ

Les auteurs traitent de l'emploi de l'uranium métal, à deux points de vue: d'abord, son comportement comme élément d'alliage courant en métallurgie des métaux non ferreux, ensuite, son activité chimique. A leur avis, c'est dans le traitement de métaux en fusion visant à les combiner avec leurs corps étrangers que résident les meilleures chances d'appliquer l'uranium à certains usages. Les résultats des travaux entrepris dans ce domaine à la Direction des mines et portant sur les alliages de cuivre, zinc, magnésium, aluminium et nickel apparaissent dans les pages suivantes. On y montre qu'un alliage principal de cuivre-uranium (contenant 25% d'uranium) désoxyde le cuivre fondu de façon efficace sans nuire aux propriétés électriques ou mécaniques du produit, même s'il y reste jusqu'à 0.8% d'uranium. On a constaté que l'addition d'uranium à un laiton alpha en quantités supérieures à la teneur en plomb sous forme d'impureté élimine l'influence néfaste de ce dernier sur la forgeabilité. On a constaté de même que le nickel est désoxydé et rendu plus malléable par l'addition d'uranium. Il semble que l'uranium forme des composés intermétalliques stables avec un grand nombre de corps étrangers. On peut donc s'attendre à une augmentation sensible de la malléabilité des alliages contenant d'autres éléments sous forme d'impuretés, en plus du plomb.

Quelques essais visant à déterminer l'influence de l'uranium sur la galvanisation à chaud et sur l'affinage du grain dans les alliages de magnésium et d'aluminium ont indiqué que cette influence n'était pas avantageuse.

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1. INTRODUCTION

The potential metallurgical uses of depleted uranium in non-ferrous metals and alloys have been considered in some detail in theory(1) (2) from three basic aspects related to characteristics of the metal. Firstly, the density of uranium has suggested its incorporation in high-density alloys for ballast and radiation-screening applications. Manufactured by powder techniques, tungsten-base alloys (specific gravity, 17.0) have been developed experimentally to a specific gravity of 19.0 by incorporating about 10% U, and uranium counterweights have been used instead of lead in aircraft. A second use of uranium is concerned with its scavenging effect on impurities, and its 'gettering' action has been utilized in certain electronic applications. Uranium metal is, in fact, used as an essential part of certain gas purification trains at the Mines Branch. Though the concept is not new, there is no known published work on its application in molten metals. Established refining practices for the removal of oxygen, carbon, sulphur and nitrogen from metals are by no means perfect, and it is conceivable that the combination of high chemical affinity for all these elements, high density and high melting-point may strongly favour the use of uranium as a bath-refining addition. Finally, it has been noted that uranium shows marked solid solubility in certain metals, and conjectures have been made regarding the strengthening and other effects of such soluble additions.

In this work, only the chemical and alloying behaviour of uranium is discussed, compositions and alloy additions, etc., being reported as weight per cent unless otherwise stated. To give some perspective to the reported and projected work on these topics, a brief account of alloying and thermo-chemical data is given below.

2. THEORY

2.1 Alloy Systems

The phase diagram may be used in alloy development work to forecast strengthening effects such as solid solution hardening, precipitation and dispersion hardening, and martensitic transformations, and to indicate low-melting-point alloys. These criteria may be applied to the U-X binary systems(3), conveniently grouped here into four types of varying metallurgical interest. Table 1 enumerates this arbitrary classification and the maximum solid solubility of uranium, or a uranium compound phase, in the parent metal. It should be appreciated that these classifications are based on the whole equilibrium diagram in order to give a complete picture of possible reactions.

Type I: The largest group is characterized by extensive intermetallic compound formation between U and X. Liquids are miscible, and solids show limited or complete lack of solid solubility. An example of this system is given by the Ni-U phase diagram in Figure 1a, in which eutectics form between the parent elements and the series of high-melting-point compound phases.

Type II: These systems all exhibit a wide (~ 30 atomic per cent) range of liquid immiscibility and complete lack of solid solubility. The Cu-U diagram illustrates these features (Figure 1b).

Type III: All liquid compositions are miscible, and solids show an allotropic dependence on solid solution formation. Face-centred gamma uranium forms a complete range of solid solutions with the high-temperature form of the elements in this group. At lower temperatures, the single-phase region breaks down to partially miscible eutectoid and intermetallic structures, due to change in crystal habit in one or both parent metals with change in temperature. This pattern is exemplified by the U-Zr phase diagram in Figure 1c.

Type IV: The remaining systems to be considered form simple eutectic or peritectic phase relationships, with some considerable solid solubility of uranium in X. No congruent-melting-point intermetallics are formed. An example of this type is the Mo-U system.

It may be noted that the non-ferrous metals used in large tonnages (aluminum, copper, magnesium, nickel, lead, and zinc) appear in Types I and II in the above classification and would be expected to exhibit none of the strengthening criteria mentioned above, whereas the refractory metals in Types III and IV show promise of direct structural improvement by alloying with uranium. Work on these high-temperature materials has been neglected in favour of the pressing economic considerations involved in developing large-scale metallurgical uses of uranium.

The problem is therefore resolved to an attempt to utilize commercially the metallurgically unpromising properties of insolubility in, and compound formation with, Type I and II metals. From general considerations, the addition of uranium to these metals and their alloys might be expected to improve such structure-sensitive properties as galling and wear resistance, bearing performance, etc. Any increase in mechanical properties resulting from the introduction of a compound phase is more likely to occur in as-cast conditions, since the process of fabrication (forging, rolling, etc.) will tend to align uranium-bearing constituents in the direction of working, i.e., parallel to the axis of greatest structural importance.

2.2 Thermodynamic Aspects

The above considerations do not reveal many promising leads to the "physical" application of uranium to the common non-ferrous metals, and, in fact, it will be shown that research has been chiefly directed at the chemical treatment of these metals with uranium. To see the reasons for this approach, reference may be made to the 'free energy of formation' data summarized schematically in Table 2. It will be noted that while the uranium compounds do not have the greatest stabilities, their relative stabilities are very high. Thus, uranium should be a most useful scavenger of oxygen, carbon, nitrogen, and sulphur.

The programs of work described below are therefore chiefly concerned with the treatment of molten metals and alloys by uranium to scavenge or fix oxygen, sulphur, nitrogen, carbon and other impurities which impair founding and fabrication characteristics. Concurrently, the effects of residual alloyed uranium on the properties of the treated product are being investigated.

3. URANIUM ADDITIONS TO COPPER AND COPPER-BASE ALLOYS

3.1 Pure Copper

The interdependent high solubilities of hydrogen and oxygen in molten copper(4,5,6) incur the possibility of porosity resulting from the "steam reaction" during the freezing of the metal. This phenomenon is generally avoided by the use of an oxidation melting technique(7), followed by deoxidation with the cheap and efficient phosphorus-copper deoxidant. Excess phosphorus, however, remains in solution in the metal and markedly decreases electrical conductivity; hence, for electrical applications, other deoxidants must be used. In addition, under some circumstances, excess phosphorus in solution makes copper susceptible to stress-corrosion cracking.

The efficiency of uranium-deoxidation of molten copper has been examined by making bath additions of a copper-uranium eutectic master alloy (see Figure 1b)(8). It was found that, assuming oxygen to be removed according to the simple equation

$$\underline{U} + \underline{2O} \longrightarrow UO_2,$$

the deoxidation was approximately 100% efficient. From the data obtained in these experiments, and assuming arbitrary prices of ten dollars and four dollars per pound for natural and depleted uranium respectively, a comparison of the minimum costs of deoxidation of pure copper by uranium and standard deoxidants was made, and is reproduced in Figure 2. The revealed possibility of economic competition of uranium with lithium and calcium boride is enhanced by the practical advantages of ease of storage and simplicity of use of the heavier deoxidant. The only difficulties likely to be met with in using uranium in this field are concerned with the removal of the deoxidation product (uranium dioxide) from the melt. Although UO_2 (specific gravity, 10.9; melting point. 2176°C) does agglomerate on the surface of molten copper to form a sticky suspension that can be removed by skimming, the oxidation of excess (alloyed) uranium in the pouring stream gives rise to finely dispersed cubic inclusions of oxide in the cast metal. Dross from this source, and possible slag entrapment, can be avoided by careful teeming practice and high gating ratios in sand castings.

It is necessary that residual deoxidant should have no adverse effects on the properties of the metal. The lack of solid solubility of the intermetallic compound UCu5 (Figure 1b) would lead one to expect dilute copper-uranium alloys to have a performance closely akin to that of pure copper. Testing a series of deoxidized copper heats containing from nil to 0.8% U has shown this to be the case for the following properties:

A. Fabricability. All compositions were hot extruded to 3/4 in. diameter rod, cold swaged to 1/4 in. rod, and cold drawn, without difficulty, to 0.020 in. diameter wire.

B. Conductivity. The electrical resistance of 1/4 in. diameter swaged-and-annealed rod was measured on a Kelvin Bridge device, and the results, plotted as % International Annealed Copper Standard, related to uranium content (Figure 3). It is apparent that small amounts of soluble iron, aluminum and phosphorus far outweigh the effect of residual uranium deoxidant.

C. Softening Characteristics. Dilute copper-uranium alloy rods, swaged to 1/2 in. diameter to induce 50% cold working, were tensile-tested at room temperature after annealing for thirty minutes at various temperatures between 20°C and 650°C. Typical results are plotted in Figure 4, in which a slight strengthening effect at higher uranium contents is evident. There is, however, no useful decrease in softening kinetics with increase in uranium content. Hardness and grain size measurements were identical for all alloys at equivalent stages of annealing.

Those properties of copper that might be altered by the presence of a second phase include:-

D. "As-cast" Mechanical Properties. Uranium induces a moderate grain refinement in cast copper, probably due to the nucleating effect of minute amounts of small suspended particles of cubic UO_2. The intergranular $Cu-Cu_5U$ eutectic phase gives a strengthening effect particularly noticeable at higher temperatures (see Figure 5).

E. Machinability. Figure 6 illustrates the dispersion of the copper-uranium eutectic in an extruded rod. This type of duplex structure is often associated with good machinability; as in the case of copper-tellurium alloys, for example.

F. Oxidation and Corrosion Resistance. It is to be expected that the oxidation and corrosion resistance of pure copper will be considerably affected by the presence of the $Cu-Cu_5U$ eutectic phase. The only information available at present indicates that the oxide film is very adherent in uranium-bearing copper. This compares favourably with the exfoliation behaviour of oxygen-free and phosphorus-deoxidized grades of copper(9) for applications such as electrical machinery operating at higher temperatures.

G. Wear and Abrasion Resistance. A duplex structure of relatively hard eutectic islands in a pure copper matrix is, in theory, an attractive combination for applications, such as electrical contacts, where hardness, high conductivities and anti-galling characteristics are simultaneously required. Wear tests on uranium-bearing copper wire have been initiated to examine this possibility. Copper alloys containing substantial amounts of uranium have been mentioned in the literature for electrical applications(1).

3.2 Copper-Base Alloys

The effect of uranium additions to brasses, bronzes and cupro-nickels is being examined from the criteria of deoxidation, foundry characteristics, strength, fabricability, corrosion, and oxidation resistance. Deoxidation work on four widely used sand-casting alloys was postponed shortly after its inception, because of the unfavourable tendency of uranium oxide to be trapped in the mould cavity, forming dross inclusions that reduced the mechanical properties of the casting. This difficulty is thought to be accentuated by the pasty mode of freezing of these alloys, and has not presented any problem in alloys with short freezing ranges.

Attention was subsequently directed toward the high-zinc alloys whose low oxidation potential in the molten state renders them less susceptible to contamination by uranium deoxidation products. These alloys are susceptible to a type of stress-corrosion, known as "season cracking", in which various specific environments (particularly ammonia vapour) bring about severe intercrystalline disintegration of the material under stress. While the mechanism of this phenomenon is not fully understood, and no trace elements are known to produce any marked beneficial effect, it is known that certain solutes in the metal, e.g. excess phosphorus deoxidant, increase the susceptibility of copper alloys to this type of failure. The effect of uranium on this phenomenon is being investigated by exposing stressed strips of uranium-bearing and uranium-free alpha brasses to a controlled atmosphere of ammonia vapour(10,11).

It has been reported that trace additions to brasses of certain elements with a high affinity for oxygen (e.g. cerium, calcium) have been successful in neutralizing the harmful effects of lead on the workability of these alloys(12). This effect may be of potential industrial importance, since it permits the diversification of mill practice and may allow lead-contaminated copper and copper-base alloys (brasses, bronzes, cupro-nickels) to be fabricated by hot working. During the process of fabricating brasses for the stress-corrosion investigation mentioned above, it was decided to investigate the effect of uranium with respect to lead hot-shortness. Consequently, one batch of 70:30 (cartridge) brass containing 0.07% Pb was tested with and without uranium additions. Cast samples of the uranium-free alloy exhibited hot-shortness at rolling temperatures of 600°C, 725°C, and, less extensively, 800°C. The same alloy with a uranium content of 0.40% was successfully given a 50% reduction in thickness at all three temperatures (items 1-6 in Figure 7). The 0.07% Pb present in the alloy is considerably in excess of 0.02%, recognized as the upper limit for hot working cartridge brass(13).

Further rolling tests on this brass with 0.07% Pb and uranium nil, and 0.10% and 0.19% Pb with 0.42% U (items 7, 8 and 9 in Figure 7), made it apparent that the presence of uranium in brass renders innocuous the deleterious effect of lead on hot fabricability.

To examine the mechanism of this inhibiting effect, a series of melts of 65-35 copper-zinc (yellow brass) was made with various amounts of lead and uranium.

The results of hot-rolling tests on cast slabs of these alloys are presented in Figures 8 and 9, and yield the following conclusions:

(1) Uranium additions, made in amounts approximately equal to the lead content of alpha brass, negate the deleterious effect of this element on the hot workability of the alloy.

(2) To ensure that the beneficial effect of uranium was not due to a side-effect of deoxidation, three melts were deoxidized with phosphorus copper. This showed that complete deoxidation by phosphorus does not alleviate the hot-shortness problem, although this addition is claimed in the literature to be beneficial at residual phosphorus levels of around 0.1%.

(3) Where U:Pb ratios are greater than unity and the lead concentration is greater than 0.4%, as in sample 5B, Figure 8, the alloy may exhibit reduced ductility due to the large volume of secondary phases at grain boundaries. In practice, brasses with more than 0.4% Pb are included in the specifications for machining brasses, in which the lead is now an alloying addition and not an impurity.

Microscopic examination of the cast structures of the series of alloys has revealed that the appearance and mode of dispersion of lead are altered by the additions of uranium, the nature of the change being dependent on the U:Pb ratio. The grey globular constituent (lead) found in uranium-free leaded brasses (Figure 10a) darkens in colour, tends to angularity, and associates with the uranium-bearing eutectic phase, when the uranium content exceeds the lead content. In alloys where there is more lead than uranium (Figure 10b), the distinctive uranium-bearing eutectic phase has been replaced by groups of dark, discrete particles whose distribution suggests the intimate mixing of eutectic structures.

Although a micro-analysis of the phases illustrated will be required in order to discuss fully the mechanism by which hot-shortness is removed, it is felt that the addition of uranium to brass renders lead innocuous by forming with it high-melting-point alloy phases whose notch-forming capacities under stress at hot-working temperatures are insignificant as compared with the effect of molten lead at grain boundaries at these temperatures.

The use of uranium as a malleableizer in lead-contaminated brasses shows promise of potentially wide applications from two standpoints, namely:

(1) The hot working of (leaded) secondary brass becomes feasible, allowing mills greater freedom and diversity of operation in scrap usage and in fabrication procedures.

(2) If the presence of uranium-bearing phases is not deleterious to machinability, low- and medium-leaded brasses could be developed as hot-rolled products. These materials are, at present, limited to batch extrusion production or must be fabricated by cold rolling.

3.3 Conclusions and Future Research

It has been indicated that the chemical activity of uranium, and its lack of solid solubility in copper and copper alloys, can be turned to advantage in producing high-conductivity copper which at the same time might be strengthened, and made more resistant to oxidation and more machinable, by the presence of the copper-uranium eutectic phase. It will be of interest to obtain engineering data on this behaviour, and to study the application of uranium as a deoxidant in special alloys such as tellurium, zirconium and chromium coppers.

A potentially more important aspect of the work described the malleableizing effect of uranium on lead-contaminated brasses. It is believed that the lack of solubility of uranium in copper and all its alloys, and its strong compound-forming tendency with those elements held to be subversive from a fabrication point of view (lead, sulphur, bismuth, arsenic, antimony, etc.), suggest that uranium may be an extremely useful scavenger, not only in brasses but also in pure copper, cupro-nickels, nickel bronzes, and nickel-silver. These alloys all require expensive, stringent precautions to avoid pick-up of embrittling elements, or to fabricate such materials where contamination cannot be avoided. The elimination of these difficulties by bath additions of uranium as a malleableizer could become economically feasible. These proposals will be examined by preparing contaminated alloys and investigating the effect of uranium on working properties.

4. URANIUM IN ZINC(14)

Major industrial uses of zinc are in die casting alloys, as a constituent of brass, and for corrosion protection in the form of sacrificial anodes and galvanized coatings. A previous investigation, in which a number of elements were added to die-casting alloys, had shown little promise, and it was considered, therefore, that the possibility of uranium additions to the many thousands of tons of zinc used annually to protect steel against corrosion was the most promising field of investigation. It was suggested that the scavenging action of uranium might provide a change in the mechanism of the galvanizing process, or that a uranium phase deposited in the zinc coating might improve corrosion performance of the galvanized surface by cathodic protection.

Laboratory experimentation has involved the preparation of suitable master alloys to facilitate additions, galvanizing of test panels, and the evaluation of the structure and various properties of the coatings produced.

The galvanizing operation follows established pretreatment and dipping procedures to provide coatings on a single grade of steel sheet, at a constant bath temperature and at two immersion times. The two basic bath compositions (Zinc + 0.03% Fe and Zinc + 0.03% Fe + 0.15% Al + 0.30% Pb) were treated with additions of 0.01%, 0.05% and 0.1% U in the form of a 1% U-Zn master alloy.

The presence of even 0.01% U in the galvanizing bath was sufficient to cause rapid oxide formation on the bath surface, giving a bluish cast to the withdrawn coated test panel. This effect was suppressed by the usual brightening addition of around 0.005% Al. Despite this suppression of oxidation by aluminum, uranium oxidation losses of as much as 40% of the amount added were experienced. Skimming of the bath to remove oxidation and flux reaction products was probably the major factor responsible for this.

Only minor coating surface effects were observed in the uranium-treated galvanized panels. With the essentially aluminum-free coatings containing 0.05% U and 0.1% U, the normally smooth zinc surface was replaced by a fine pebbled texture. This was less pronounced at the longer immersion time. Microscopic examination of sections of these coatings revealed depressions of the surface in the vicinity of the grain boundaries; this suggests some modification in the solidification characteristics of the outer zinc layer. Segregation phenomena were not detected metallographically. In the high-aluminum bath (0.15% Al), the only evidence of any effect of uranium was a slight improvement in the definition and contrast of the spangle crystals in the coating.

Evaluation tests on the coatings produced from uranium-bearing baths have indicated no effect, desirable or otherwise, on the iron-zinc reaction or on the coating structure. Thus, the layer formation of iron-zinc phases produced from the aluminum-free zinc bath was not affected by the presence of 0.01-0.1% U. The continuity and the uniformity of the outer zinc layers were unaffected despite the modification of the surface appearance mentioned above. Similar remarks apply to the results obtained for the high-aluminum zinc bath.

To summarize, it appears that uranium offers little promise as a useful bath alloying agent in the galvanizing process. There is no modification of the iron-zinc reaction nor any improvement in galvanized coating formation or properties. Any effect on the corrosion resistance will be determined when outdoor exposure tests are complete.

5. EFFECT OF URANIUM ADDITIONS TO MAGNESIUM AND ITS ALLOYS (15)

Although the extremely low solubility of uranium in molten and solid magnesium would appear to preclude any alloying effects, the possibility of scavenging and grain-refining mechanisms operating in pure magnesium and the magnesium casting alloys Z6, AZ80 and ZK61 has been investigated. The addition of uranium to these alloys was made in the form of a flux mixture of 40% UF_4, 36% $MgCl_2$ and 24% NaCl. The molten magnesium reduces the UF_4, and the resultant uranium analyses were 0.002% in pure magnesium and 0.014% in the Mg-6% Zn alloys Z6 and ZK61. These amounts produced no change in structural, mechanical or chemical properties and it is considered that there is no potential application of uranium in this system of alloys. The balance of the uranium reduced from the flux formed a sludge at the bottom of the melt.

6. THE EFFECT OF URANIUM ON ALUMINUM AND ITS ALLOYS

The lack of solid solubility of uranium in aluminum, and the stable intermetallic compound formation exhibited in the Al-U equilibrium diagram, restrict the application of uranium in aluminum alloys to three possible types of usage:

(a) Binary Aluminum-Uranium Alloys

These have been of interest to reactor designers, and thus have received considerable attention(16,17), with a view to the development of a corrosion-resistant wrought fuel. Saller(18) indicated that alloys containing from 2% to 17% uranium displayed no properties superior to those of conventional aluminum-base materials, though some slight ageing susceptibility was noted at the lower uranium levels. This may reflect some degree of solid solubility which went undetected in previous researches. Since no data have been uncovered on the properties of as-cast alloys in this range of composition, some experiments were designed to investigate the properties of cast test bars containing up to 13 wt % U (eutectic composition)(19). Some results of this work are reproduced in Table 3, from which it is apparent that the ultimate and yield tensile strengths increase, and the elongation decreases, with increasing uranium content. Metallographic examination of the structures of these alloys showed them to be a matrix of aluminum surrounded by a pearlitic network of $Al-UAl_4$ eutectic. This latter was finer, in general, than an unmodified aluminum-silicon eutectic; which may account for the high level of elongation found in the series.

A number of solution and artificial ageing treatments were carried out on these alloys, but no significant improvement in properties was noted, indicating only limited solid solubility.

(b) Grain Refinement

The usual grain-refining agent for aluminum castings is titanium, either alone or with boron. The work of Cibula(20) and others has shown that the grain refining action is due to particles of titanium carbide, or, when boron is present, of titanium boride. While it was indicated that a number of other transition elements that form stable interstitial compounds (with carbon, boron, nitrogen, and hydrogen) can behave as grain refiners in aluminum alloys, uranium was not considered at that time. In view of its known chemical behaviour with these non-metallic elements, it seemed probable that uranium would exert some grain-refining action.

A comparison was made of the grain structures of an Al-4% Cu alloy treated with 0.5% metallic uranium in one case and 0.1% Ti in the other. The effect of superheat was included in this experiment (see Figure 11), and it was found that, whereas titanium remained effective as a refining agent irrespective of melt treatment, the uranium-bearing alloy was coarse-grained to an extent dependent on the pouring temperature and in this respect showed no improvement on the alloy without grain refinement.

(c) Stress Corrosion

The possibility of improving the stress-corrosion resistance by additions of uranium to the alloy is being examined on the basis of the undoubted reactivity of uranium with impurity elements, and of the fact that in the cast condition it produces a grain boundary phase of unexplored chemical behaviour. As-cast tensile bars of uranium-bearing G10 alloy (Al-10% Mg) will be examined under standardized testing conditions, and the results compared with those for the parent alloy.

7. URANIUM IN NICKEL

Though the uranium-nickel alloy system has received considerable attention(21), due to the interest in developing corrosion-resistant uranium alloys for nuclear reactors, no information has been unearthed on the characteristics of the nickel-rich end of the binary system. The reportedly excellent corrosion resistance of Ni-U intermetallic compounds(22), notably U_6Ni, aroused interest in the chemical behaviour of dilute nickel-uranium alloys containing UNi_5 in a eutectic phase (Figure 12). Initial experiments showed that up to 0.8% U in nickel did not reduce the corrosion attack of mineral acids(23). There was some evidence, however, that under more aggressive conditions, such as "redox" media, the compound phase of the eutectic was behaving anodically toward the nickel matrix in such a way as to alter the type and extent of pitting corrosion. This behaviour is analogous to that of UFe_2 in iron and will be further investigated, particularly with respect to the effect of uranium on the dissolution and polarisation characteristics of nickel anodes.

The solid solubility of uranium in nickel has been investigated for alloys containing 0.3 and 0.8% U. Hardness and metallographic surveys were conducted on forged specimens quenched from a temperature of 1075°C (see Figure 1a). No diminution of the proportion of eutectic phase was observed metallographically after quenching, nor were there any significant hardness or structural alterations in the matrix of the uranium-bearing alloys after ageing for one hour at 150, 250, 370, 500 and 600°C, as can be seen in Table 4. (The reduction in hardness on solution treatment is considered to be due to elimination of residual cold work from the hot-rolling operation, and the initial small increase in hardness occurring with all alloys on ageing is probably due to traces of aluminum from the deoxidation operation.)

The presence of the UNi_5 phase in the matrix does make a contribution to the overall hardness of the alloys, however. In the solution-treated condition (which in this case may be taken as the annealed condition), the nickel-uranium alloys are 30 to 40% harder than an identically prepared uranium-free nickel. This is due, in some measure, to the relatively high hardness of the intermetallic compound (Figure 13).

As with copper, uranium will deoxidize nickel melts to yield sound gas-free castings (although there is some evidence of mould reaction at high ($\sim$1% U) residual uranium levels) and will combine with impurities in nickel such as lead, tin, arsenic, antimony, tellurium, sulphur, selenium and bismuth. A discourse(24) on the effect of these and other elements on the melting and malleability of nickel indicated that the most pronounced deleterious effect of such impurities was a reduction in hot ductility, brought about by brittle films or low melting phases at grain boundaries. It was proposed that uranium, being insoluble in nickel, might react with deleterious impurities during the freezing process to form high-melting-point complexes which would not reduce the high-temperature properties of grain boundaries. The efficiency of such a mechanism would be determined by the relative chemical affinities of nickel and uranium for each other and for the impurity element. Since the heats of formation of the intermetallic compounds Ni-X, U-X and Ni-U are not all known, and could only be used as a guide in any case, the only way of judging the feasibility of the proposal was to determine whether or not uranium restored hot malleability to the contaminated nickel. This has been done initially by conducting rolling tests at different temperatures on sections of chill-cast ingots, and correlating the results with metallographic examination. Although this work is incomplete, the results so far have indicated a malleableizing effect of uranium on the impurities lead, sulphur, selenium, tellurium, arsenic, antimony and tin.

Thus, as in the analogous copper and copper alloy systems, there is the possibility that uranium may be employed to negate the effects of impurity elements harmful to hot ductility.

8. URANIUM IN BEARING METALS

The possibility of using uranium as one constituent of the hard compound in lead-base, tin-base or copper-base antifriction alloys is being studied at the U.S. Bureau of Mines, Rolla, U.S.A. (25). They have shown that relatively hard cubic crystals of UPb_3 are readily obtainable in lead-uranium alloys containing up to 8% U and it is suggested that this and other compounds could be introduced into lead-antimony bearings or similar antifriction alloys that require finely-dispersed hard particles embedded in a soft matrix. Some properties of such compounds are presented in Table 5.

9. CONCLUSIONS

A brief outline of the experimental work carried out to date at the Mines Branch has indicated a lack of possible metallurgical applications of uranium to the alloy systems of aluminum, magnesium and zinc, whereas in copper and nickel and their alloys the introduction of uranium has produced several interesting phenomena.

From theoretical considerations, it appears that there is little chance of forming alloys of greatly improved general mechanical properties, except in the isolated cases of the less common refractory metals. However, the high chemical activity of uranium, and the stability of its compounds with gases, metalloids and metals, can be used to advantage in the deoxidation of molten metals and in improving the malleability of certain alloys--notably of copper and nickel--by converting contaminant elements into harmless compound forms. These promising applications are being investigated further.

10. ACKNOWLEDGMENT

The advice and assistance of R. Jamieson (International Nickel Company of Canada) were most helpful in the preparation and examination of the nickel-uranium alloys.

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RT:JOE:(PES)ls

TABLE 1

Abstract of U-X Phase Diagram

	X	Max Solubility of U in X (wt %)
Type I Intermetallic Compound Formation Figure (1a)	Al	Nil
	Ge	"
	Co	"
	Be	"
	Sn	"
	Ga	"
	Hg	"
	Au	0.6 at 855°C
	Mn	*
	Ni	0.75 at 1100°C
	Si	*
Type II Liquid Miscibility Gap Figure (1b)	Bi	Nil
	Cu	"
	Mg	"
	Pb	"
	Th	"
	Zn	"
	Ag	0.4 at 950°C
Type III Allotropic Solid Solution Figure (1c)	Nb	100% U in Nb
	Ti	100% U in ß Ti
	Zr	100% U in ß Zr
Type IV Peritectic	Mo	12% at 1280°C
	Ta	2.6% at 1175°C
	W	*
Eutectic	Cr	Nil
	V	16.3% at 1040°C

* Slight solubility, unestablished.

TABLE 2

Diagram Illustrating the Relatively High Affinity of Uranium for Oxygen, Sulphur, Carbon and Nitrogen

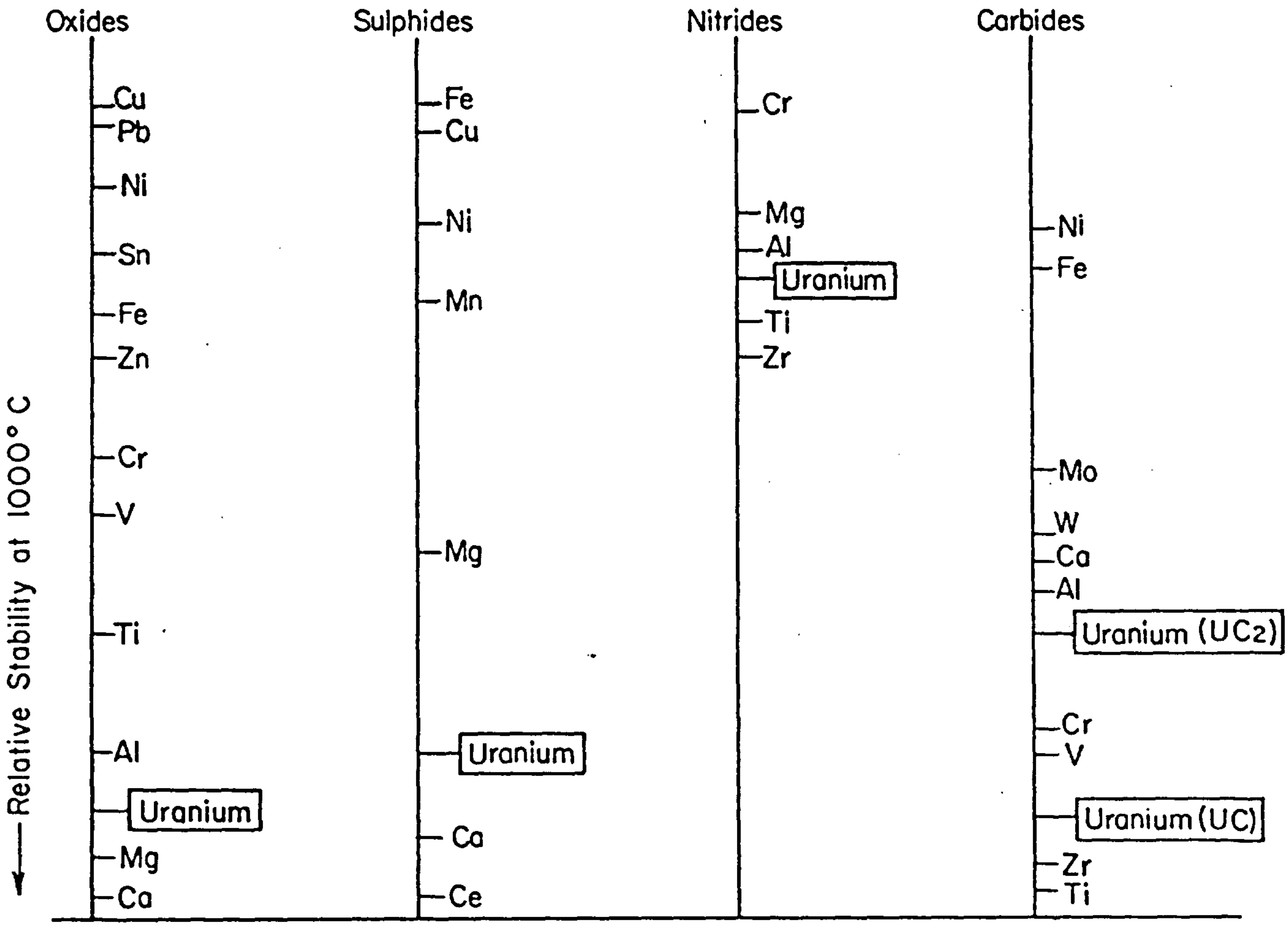


TABLE 3

Tensile Test Results of As-Cast Aluminum-Uranium Alloys

Wt % Uranium	UTS, kpsi	0.2% YS, kpsi	% El. in 2 in.
0.7	9.7	3.0	42.0
3.2	13.2	4.3	30.5
8.1	15.1	5.4	24.0

TABLE 4

Hardness Values of Nickel and Nickel-Uranium Alloys After Various Heat Treatments

Condition	Hardness - Rockwell B		
	Nickel	0.3 U	0.8 U
Hot-rolled	74	84.6	85.5
Solution treated 1 hr. 1075°C	33.1	44.4	50.0
Solution treated and aged 1 hr at (150°C	37.1	51.0	56.4
(250°C	37.9	45.7	56.2
(370°C	38.7	46.8	56.4
(500°C	36.0	44.7	56.8
(600°C	35.0	45.1	56.0

TABLE 5

Properties of Some Uranium Metallic Compounds

X	X-rich Compound with Uranium	Crystal Structure	Melting Point, °C	Hardness VPN
Pb	UPb_3	f.c.c.	1220	?
Sn	USn_3	f.c.c.	1350	?
Sb	USb_2	c.p.h.	?	?
Cu	UCu_5	f.c.c.	1052	120
Ni	UNi_5	f.c.c.	1305	300 (approx.)

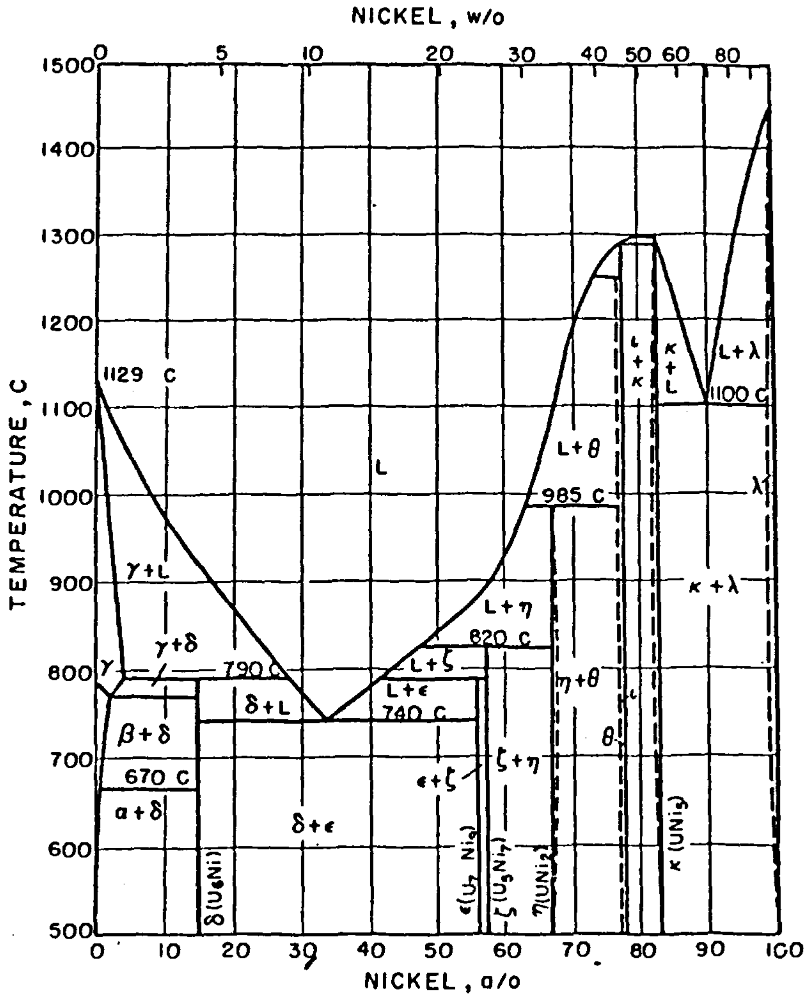
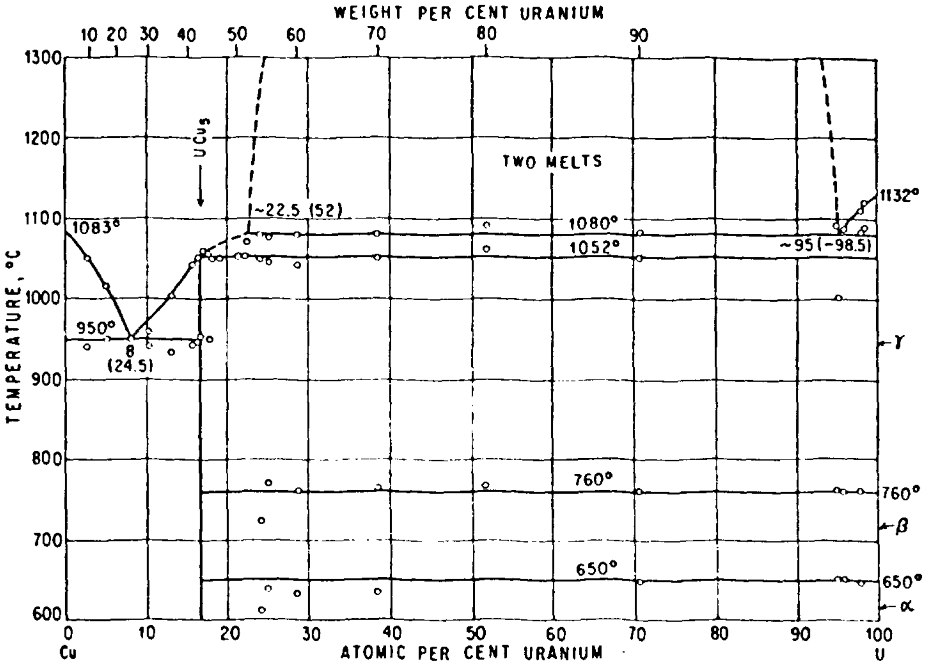


Figure la.

Type 1 - Intermetallics.

Figure lb.

Type II - Liquid immiscibility.



Cu-U

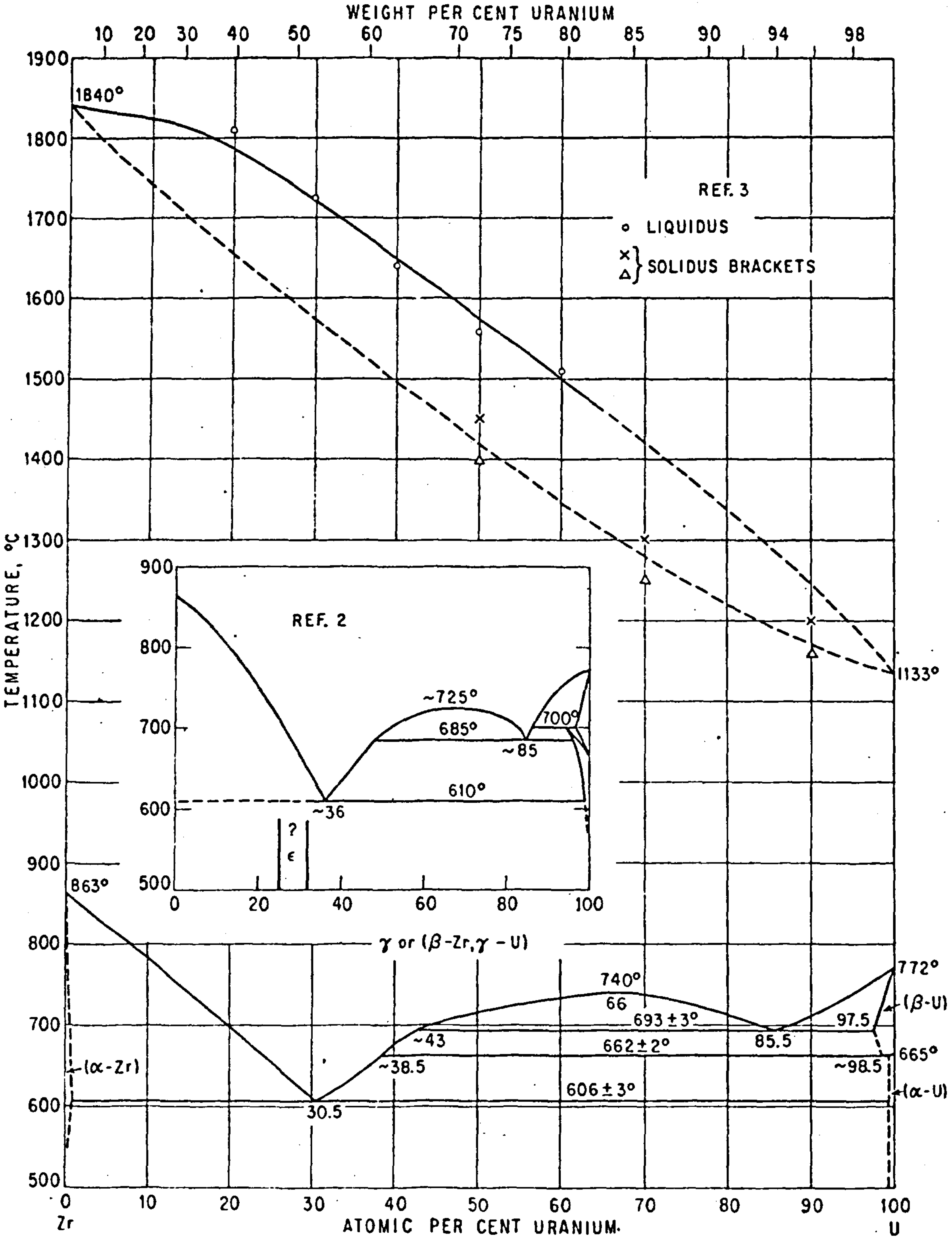


Figure 1c. Type III - Allotropic solid solution.

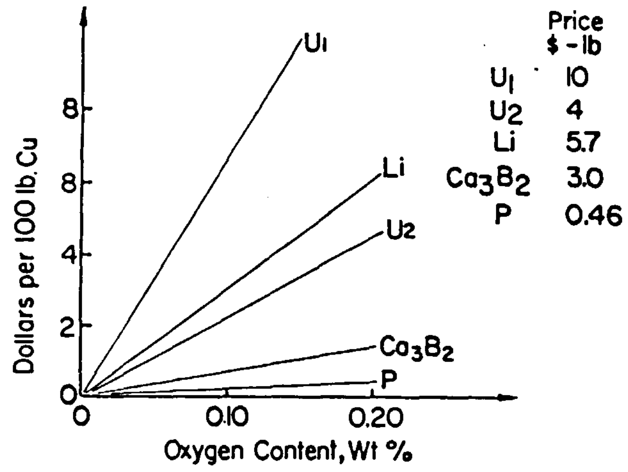


Figure 2. Minimum Deoxidation Costs per 100 lb, Copper.

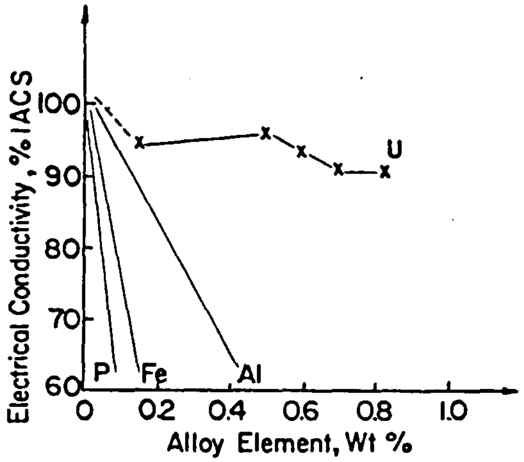


Figure 3. Effect of Uranium on Electrical Conductivity.

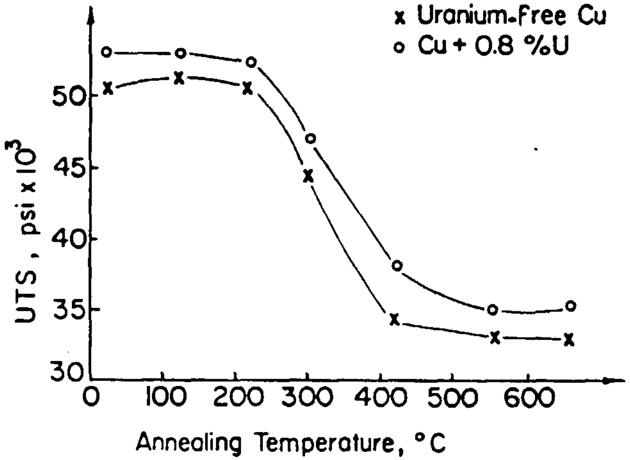


Figure 4. Softening Characteristics of Copper.

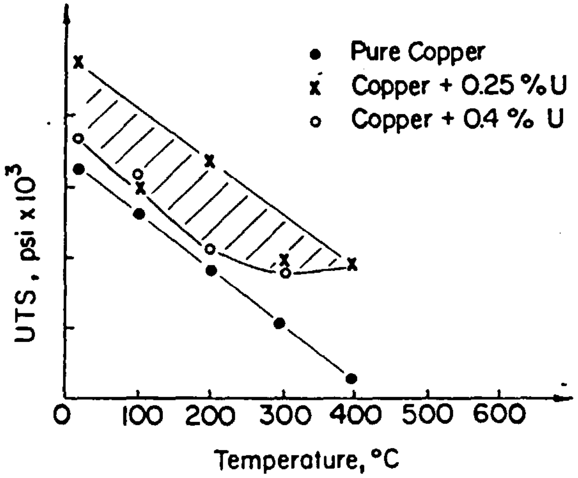


Figure 5. Cast Strength of Pure and Uranium Copper.

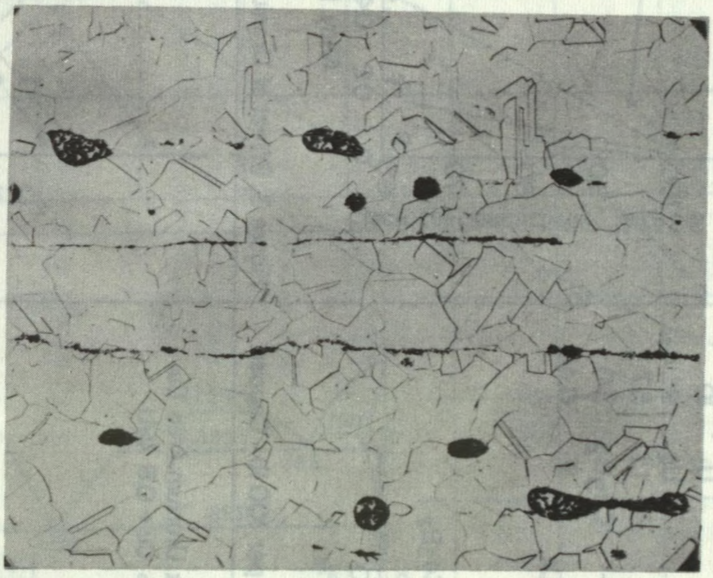
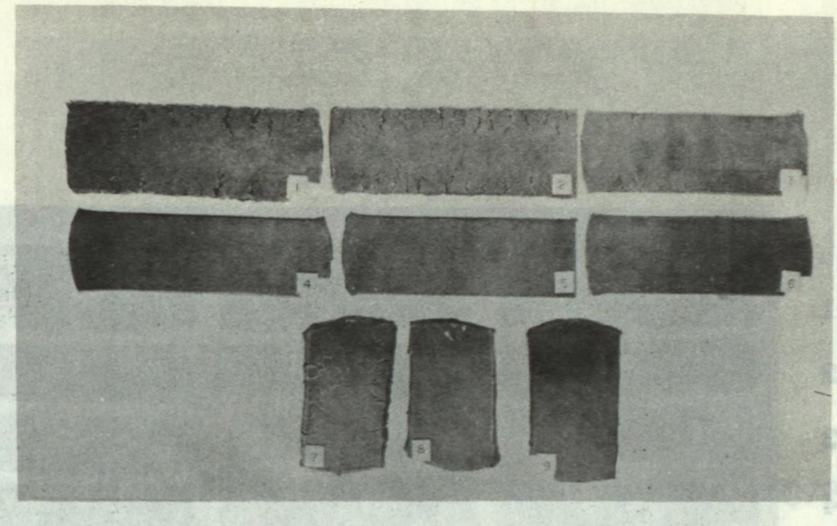


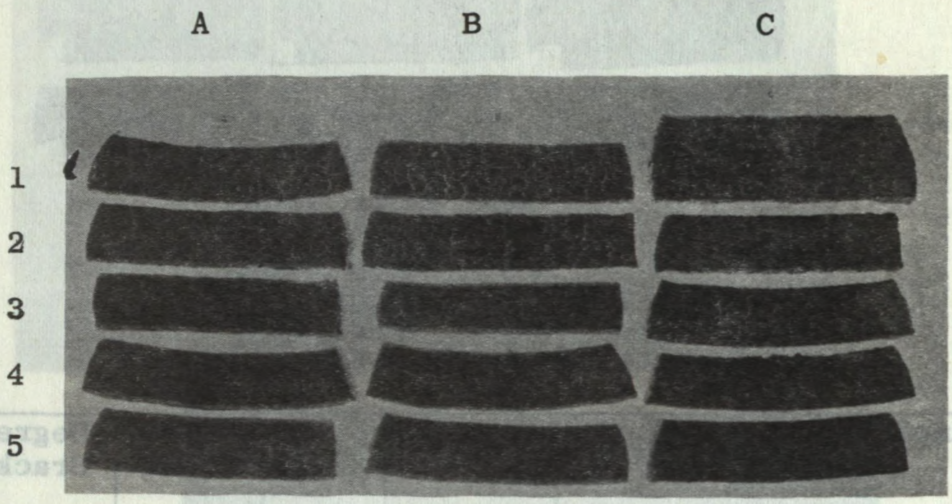
Figure 6. Extruded uranium-deoxidized copper containing 0.5% excess uranium. Etched in ferric chloride. X250



Sample No.	Composition, %		Rolling Temperature, °C	Degree of Cracking*
	Pb	U		
1	0.06	Nil	600	D
2	"	"	725	D
3	"	"	800	B
4	"	0.40	600	A
5	"	"	725	A
6	"	"	800	A
7	0.07	Nil	750	D
8	0.10	0.42	750	A
9	0.19	"	750	A

* A - crack-free
B - few cracks, confined to edges
D - massive cracking

Figure 7. Effect of uranium on the cracking of hot-rolled 70:30 brass. Rolling reduction - 50%.



Sample No.	Composition, %				Degree of Cracking*
	Pb	U	P	U:Pb	
1A	0.13	0.003+	-		D
B	0.49	0.003	-		D
C	1.01	0.003	-		D
2A	0.13	0.003	0.013		D
B	0.49	0.003	0.010		D
C	1.01	0.003	0.015		D
3A	0.11	0.21	-	1.9	A
B	0.32	0.21	-	0.7	B
C	0.55	0.21	-	0.4	D
4A	0.15	0.34	-	2.3	A
B	0.35	0.34	-	1.0	A
C	0.62	0.34	-	0.5	D
5A	0.21	0.99	-	4.7	A
B	0.60	0.99	-	1.6	C
C	1.24	0.99	-	0.8	D

* A - crack-free
B - small number of gross defects
C - fine cracking
D - massive cracking

\+ Residual amount

Figure 8. Effect of phosphorus-deoxidation and U:Pb ratio on hot cracking during rolling of leaded 65:35 brass. Rolling temperature, 750°C; 50% reduction in thickness.

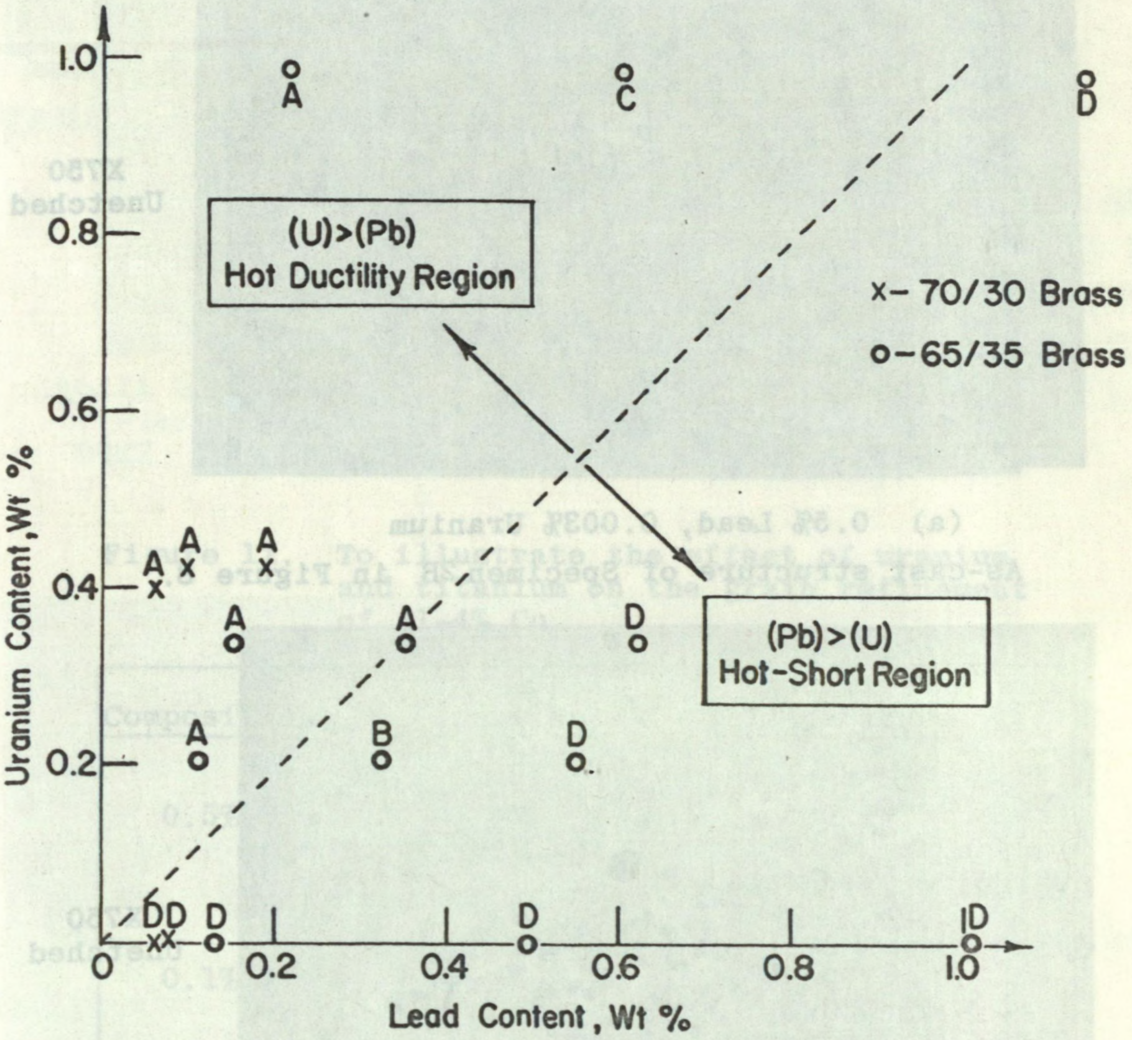
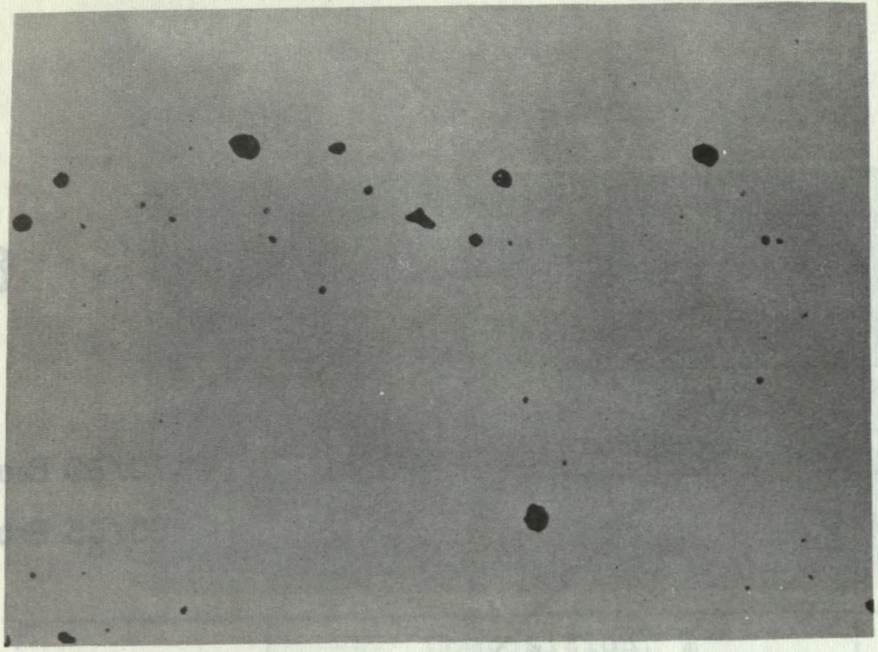
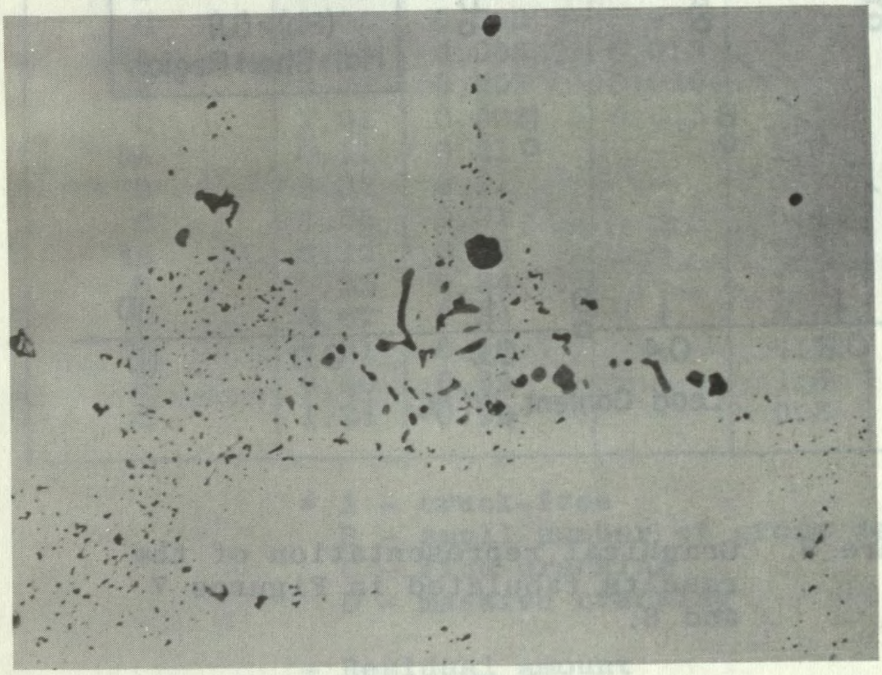


Figure 9. Graphical representation of the results tabulated in Figures 7 and 8.



X750
Unetched

(a) 0.5% Lead, 0.003% Uranium
As-cast structure of Specimen 2B in Figure 8.



X750
Unetched

(b) 1.24% Lead, 0.99% Uranium
As-cast structure of Specimen 5C in Figure 8.

Figure 10. Appearance of lead phase in uranium-free and uranium-bearing 65:35 brass.

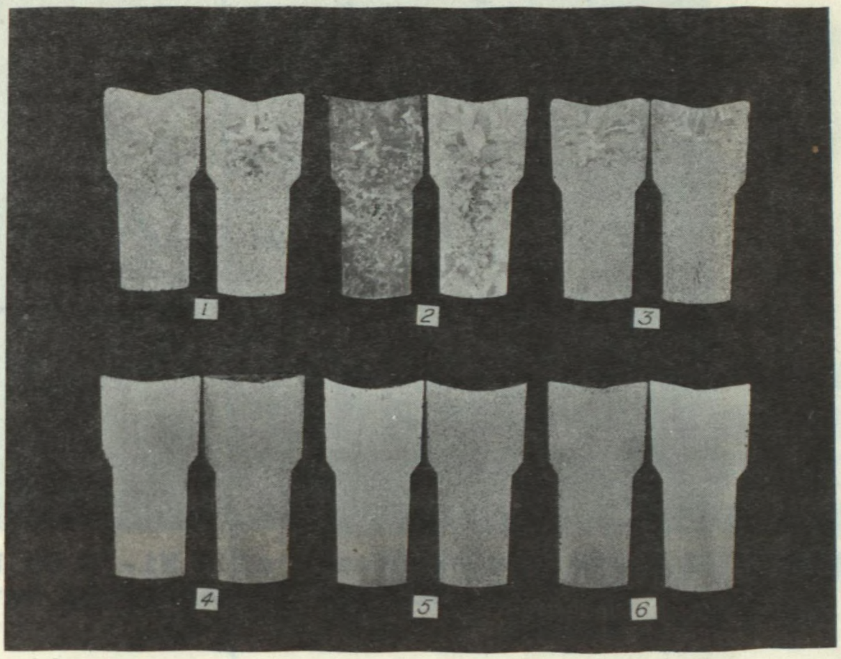


Figure 11. To illustrate the effect of uranium and titanium on the grain refinement of Al-4% Cu.

Composition	Ingot No.	Pouring Temperature
0.5% U	1	670°C
	2	800°C
	3	670°C after superheat at 800°C
0.1% Ti	4	670°C
	5	800°C
	6	670°C after superheat at 800°C

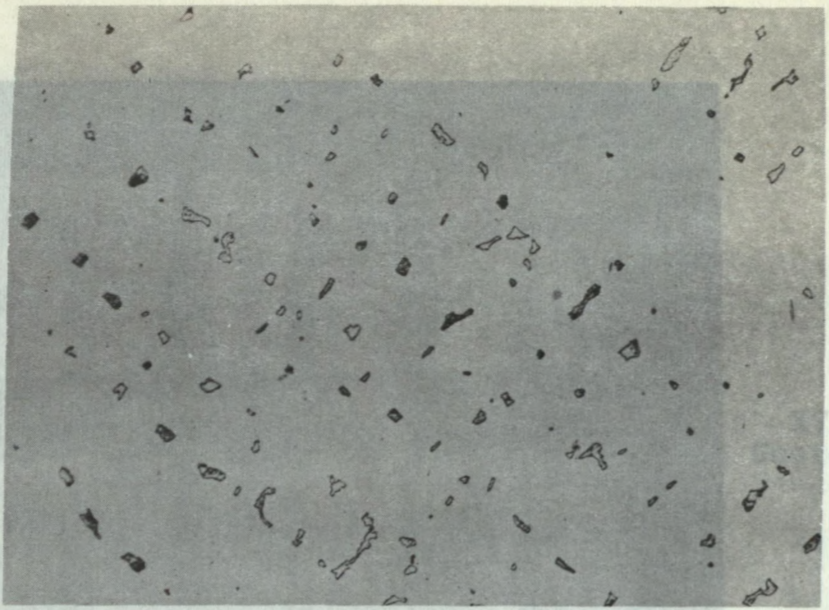


Figure 12. As-cast structure of a Ni- 0.8% U Alloy. Ni-UNi_5 eutectic in dendritic interstices. X250

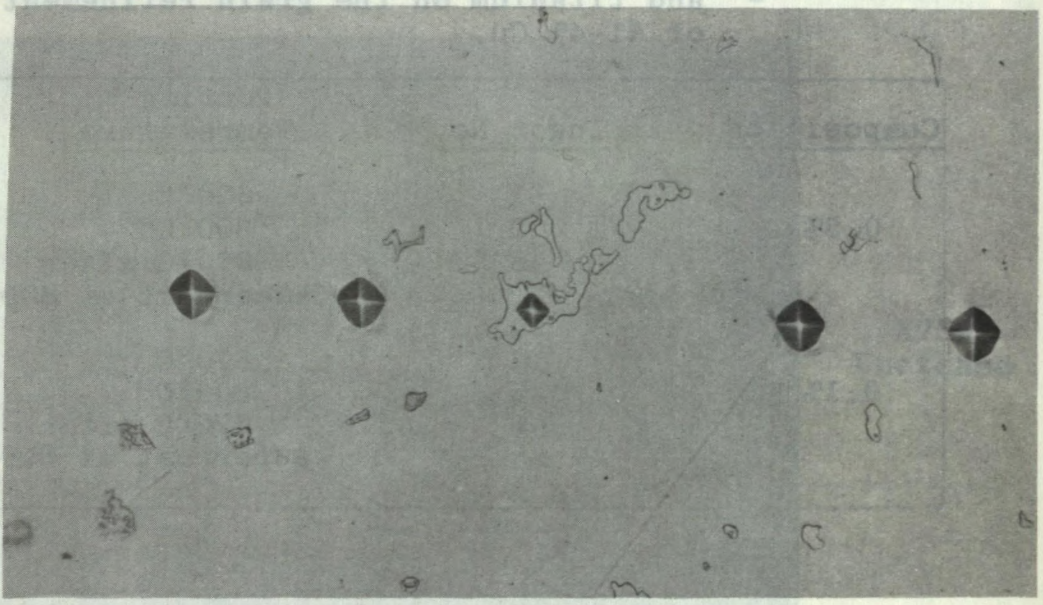


Figure 13. Microhardness indentations on the same alloy as Figure 12. The average value for the nickel matrix was 96 DPH, while the secondary constituent gave values from 220 DPH (as here) to 500 DPH.

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