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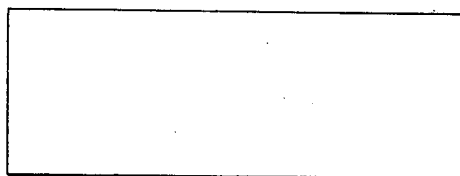
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TREATMENT OF COPPER AND NICKEL AND THEIR ALLOYS

Filed April 22, 1963

2 Sheets-Sheet 1



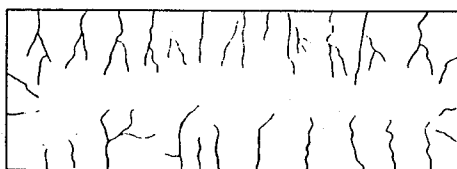
A - Crack-free

FIG. 1A



B - Small number of gross defects

FIG. 1B



C - Fine cracking

FIG. 1C



D - Massive cracking

FIG. 1D

INVENTORS

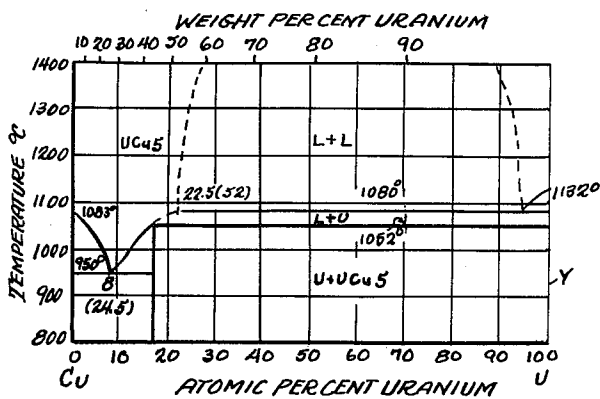
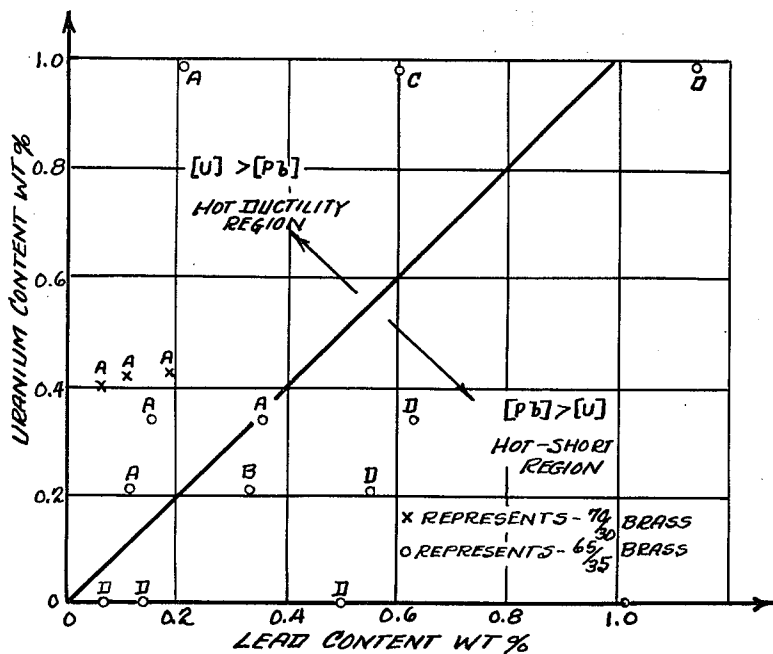
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3,216,821

TREATMENT OF COPPER AND NICKEL AND THEIR ALLOYS

John O. Edwards, Ottawa, Ontario, and Robert Thomson, Hull, Quebec, Canada, assignors, by direct and mesne assignments, to Her Majesty the Queen in Right of Canada as represented by the Minister of Mines and Technical Surveys

Filed Apr. 22, 1963, Ser. No. 274,591
18 Claims. (Cl. 75-76)

This is a continuation-in-part of copending application S.N. 188,817, filed April 19, 1962 and now abandoned.

The present invention relates to the treatment of copper, copper alloys, nickel and nickel alloys to improve their properties.

From one aspect the invention is concerned with the deoxidation of copper and nickel and their alloys. Deoxidation of these metals and their alloys has in the past normally been carried out by using lithium or calcium boride at a deoxidant. The use of these deoxidizers has, however, been rather troublesome since they are relatively unstable materials so that precautions have to be taken to prevent them from being oxidized by atmospheric oxygen. Also, if too much of such a deoxidizer is used the residual materials remaining in the melt may have a seriously detrimental effect on the properties of the product and in particular, may seriously reduce the electrical conductivity.

It has been found that copper and nickel and alloys of these metals can be readily deoxidized by an addition of uranium to a molten bath of the metal or alloy; any oxygen present is converted into a deoxidation product which accumulates at the surface of the bath and can be removed. By using uranium the difficulties encountered due to instability when storing the deoxidizers of the prior art is avoided. Furthermore, any excess of the uranium deoxidant has a relatively small effect on the electrical conductivity of the metal or alloy being produced. Indeed the excess uranium appears to form particles of an intermetallic compound of uranium and copper or nickel which serves to improve the strength of the product. Finally, the presence of the excess uranium improves the anti-oxidation characteristics of the product.

The deoxidation of a molten bath of nickel or a nickel alloy can readily be carried out by adding to it small pieces of uranium metal. This is feasible because nickel and nickel base alloys have normal refining temperatures from about 1500 to about 1600° C. This temperature is high enough to ensure that the uranium quickly melts and passes into the bath, the melting point of uranium being about 1134° C. It may, however, be preferable to effect deoxidation of such a bath by adding to it, rather than metallic uranium, an alloy of nickel and uranium having a lower melting point than either nickel or uranium. The ratio of uranium to nickel in the alloy is not critical and can be determined in accordance with prevailing practical requirements. However, it is convenient to make use of the eutectic of uranium and nickel which contains 30% by weight of uranium and which melts at 1110° C., by comparison with the melting points of uranium and nickel which are respectively about 1134° C. and about 1455° C.

When deoxidizing copper alloys it is preferable, according to the present invention, to effect the deoxidation by adding an alloy of copper and uranium rather than by adding metallic uranium. This is because such baths have a low melting point, the melting point of pure copper being about 1083° C. Since uranium has a melting point of about 1134° C. and since it is much heavier than the material of which the bath is composed the addition of pieces of uranium metal to such a bath is not effective because the pieces tend to sink rapidly to the

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bottom of the bath where they normally remain solid or at best form a liquid/liquid mixture only one component of which is miscible with the copper alloy of the temperature involved. By contrast, when an alloy of copper and uranium is added to the bath it goes much more readily into solution since it melts at a lower temperature than uranium metal and has a lower density. The proportions of copper and uranium in the alloy can be varied in accordance with prevailing practical considerations. In order to ensure that the alloy has a sufficiently low melting point and a sufficiently low density to achieve ready solution in the bath it is desirable that it should contain not more than about 40% of uranium. For example, the alloy used may be UCu_5 which corresponds to about 59% by weight copper and about 41% by weight of uranium. Preferably the copper-uranium alloy is the eutectic of copper and UCu_5 which contains about 78% by weight of copper and about 22% by weight of uranium.

As is well known, the removal of oxygen from copper and nickel and alloys of these metals is most desirable. The presence of oxygen in the liquid metal or alloy gives rise to the formation of holes in the cast metal of such size and shape as to cause cracking and rupture of the casting during fabrication. The deoxidizing effect which is exerted by the addition of uranium is by virtue of the formation of uranium dioxide. It has been found that the deoxidation product agglomerates at the surface of the molten bath and can be removed.

The amount of uranium which should be added to the copper or nickel or alloy thereof is clearly dependent on the amount of oxygen contained in the bath. If all of this oxygen is to be removed sufficient uranium should be added to convert the oxygen into uranium dioxide in accordance with the equation $U + O_2 = UO_2$. However, it is generally not important to attempt to match the amount of uranium with the amount of oxygen present. It is more convenient to add an excess of uranium since the additional uranium does not impair the characteristics of the metal like the lithium and calcium boride additives of the prior art.

The amount of oxygen contained in a melt of copper or nickel or an alloy of one of these metals, will seldom exceed 0.5% and in general is lower than this when modern refining techniques are used. Thus, for practical purposes, the minimum amount of uranium which should be added to such a melt to effect complete deoxidation corresponds to the amount of uranium required in order to convert an amount of oxygen equal to 0.5% by weight of the melt into uranium dioxide.

In a specific test 1.0% by weight of uranium was added to a melt of a nickel base alloy containing 99.8% nickel, 0.1% oxygen and traces of other impurities. The addition of the uranium was effected by adding to the bath small pieces of metallic uranium. A scum containing uranium dioxide formed on the surface of the bath and was skimmed off. Samples of the melt deoxidized in this manner were hot rolled and samples were taken from the melt prior to deoxidation were also hot rolled. The samples from the un-deoxidized melt displayed perceptible signs of cracking while the samples from the deoxidized melt were free from cracks.

In another test also carried out on a nickel bath containing 0.1% of oxygen a similar procedure was followed but instead of adding pieces of metallic uranium the addition of uranium to the nickel bath was effected by adding pieces of an eutectic of nickel and uranium containing 30% of uranium. The amount of this eutectic added was sufficient to give a uranium content again equal to 1.0% by weight of the bath. Hot rolling tests carried out on samples from the un-deoxidized and deoxidized melts showed that the un-deoxidized samples showed

cracks whereas the deoxidized samples were free from cracks.

In a further test, a melt of copper containing 99.8% copper, 0.1% of oxygen and 0.1% of other impurities was deoxidized by adding thereto an alloy of copper and uranium consisting of 78% by weight of copper and 22% by weight of uranium corresponding to the eutectic of copper and UCu_5 . The amount of copper-uranium alloy was such as to provide an amount of uranium equal to 1% by weight of the bath. A scum containing uranium dioxide formed on the surface of the melt and was removed. Hot rolling tests carried out on samples taken from the un-deoxidized melt and samples taken from the deoxidized melt indicated that the un-deoxidized samples showed signs of cracking whereas no cracking occurred in the deoxidized samples.

This invention is also concerned with the improvement of the workability of copper, copper alloys, nickel and nickel alloys contaminated with elements which adversely affect the inherently good working properties of the refined substance. It has particular reference to the incorporation of uranium in these alloys and to an advantageous method for the incorporation of the uranium.

It is recognised that the presence of minor amounts of certain elements deleteriously affect the workability of copper and nickel and their alloys, particularly contaminants such as lead, arsenic, antimony, selenium, tellurium, sulphur and bismuth in copper and copper alloys, and lead, tin, arsenic, antimony, bismuth, sulphur, selenium, and tellurium in nickel and nickel alloys. Contamination by these impurities can readily occur when scrap is used as a source of raw material.

To the present time, the known ways of avoiding loss of workability due to contamination in these metals and alloys have been the imposing of severe restrictions on impurity content or by close control and by limitation of temperatures and the extent of working of the metal.

The necessity for very close control on foundry and working techniques leads to an increase in the costs of production, both because of the care required with consequent higher labour and apparatus costs, and because of increases in scrap costs.

It is an object of the invention to overcome these drawbacks of the prior art by teaching how these effects of contaminants in copper and nickel and their alloys may be negated without the attendant difficulties experienced in the past.

The invention will now be explained in more detail having reference to the drawings, in which:

FIGURES 1A, 1B, 1C and 1D show the appearance of four hot worked specimens to be described;

FIGURE 2 shows a graph of uranium against lead content for the tested alloy samples of Tables I and II; and

FIGURE 3 shows a uranium/copper phase diagram.

Uranium is an element which has practically negligible solid solubility in copper and nickel and their alloys. This is also generally true of those detrimental elements lead, tin, arsenic, antimony, bismuth, sulphur, selenium, and tellurium traces of which can reduce the workability of all or some of these alloys. Thus sulphur is of paramount significance in reducing the hot workability of nickel and nickel alloys, but in nickel-free copper alloys, certain sulphur bearing copper alloys can be fabricated successfully without the appearance of defects or cracks due to the presence of sulphur provided excessive working temperatures are not used. The mechanism by which the insoluble contaminant elements, of the class recited, embrittle copper and nickel and their alloys is one in which during the freezing of the contaminated alloy, the impurity elements segregate to crystal boundaries where they remain, interrupting the coherency of the metal or alloy crystals. The form of these contaminants at the grain boundaries may be globular or film-like, having a composition close to that of the elemental impurity, or they may be combined as a compound with the parent metal

or other elements present. This impurity phase at the grain or crystal boundary is in general of low melting point, but may be brittle and friable, and in either case leads to failure of coherency of the metal along the crystal boundaries at economic hot-working temperatures. It has been found that when uranium is present in a liquid metal or alloy containing such a deleterious impurity, it reacts with the contaminant at some stage during the freezing process in such a way as to create a new phase or compound of the impurity whose melting point and structure are not deleterious to the strength of crystal boundaries at hot working, or lower temperatures.

Some exemplary embodiments of the invention will be described with respect to bismuth and lead contaminated copper alloys and lead, sulphur, selenium, tellurium, antimony, and tin contaminated nickel alloys.

As shown in Table I a batch of nominal 70:30 cartridge brass (samples 1 to 6) containing 0.06% lead was examined with and without uranium additions. These samples were hot worked by rolling to 50% of the original thickness and yielded products exemplified by drawings A to D in FIGURE 1, showing the degree of cracking experienced. The uranium-free alloy exhibited hot shortness at rolling temperatures of 600° C., 725° C. and less extensively at 800° C. However, the same alloy with a uranium content of 0.40% was successfully given a 50% reduction in thickness at all three temperatures. The 0.06% lead present in the alloy is considerably in excess of the maximum normally specified for hot-working cartridge brass. Further tests on a second batch of 70:30 cartridge brass with additions of 0.07% lead without uranium and 0.10% and 0.19% lead each with 0.42% uranium respectively showed that the sample with the lead content of below 0.07 by weight cracked extensively under hot working, whereas the 0.4% uranium added to the samples with 1.5 and nearly 3 times that quantity of lead yielded good metal. It is apparent from this that the influence of lead in a copper alloy can be greatly reduced or eliminated by uranium.

Tests were then carried out on a 65:35 Cu:Zn alloy (yellow brass) in which the amounts of lead and uranium were varied. Table II sets out the compositions of the specimens tested against the degree of cracking produced on hot rolling. The reduction was again 50% in thickness at 750° C., and the classification of the samples follows FIGURE 1. The table shows (samples A1, B1 and C1) that quantities of lead of 0.13 to 1.01% by weight induce hot cracking which is not offset by the residual quantities of uranium (.003%) found to be present. In samples A2, B2 and C2 the presence of phosphorus in quantities indicating complete deoxidation by that element, does not improve matters at the phosphorus levels indicated. However, samples A3, B3, C3, A4, B4, and C4 show that U:Pb ratios of 1.0 or greater produce perfect or greatly improved rolled products. At a uranium level of 0.99%, U:Pb ratios of 4.0 and 0.8 give satisfactory and unsatisfactory products, respectively, while a ratio of 1.5 gave mediocre results. These findings are represented graphically in FIGURE 2.

While the mechanism by which the uranium removes the hot shortness introduced by lead is not yet fully interpreted, it appears that the uranium addition renders the lead innocuous by forming alloy phases with it whose notch forming capacities under stress at high temperatures are not detectable. Microscopic examination of the structures of the series of alloys in Tables I and II revealed that the appearance and degree of dispersion of lead is altered by the uranium additions and that the nature of the alteration is dependent on the ratio of uranium to lead. The grey globular constituent (lead) found in uranium free leaded brasses darkens in colour and tends to become angular in association with the uranium bearing Cu-Zn-U phase in alloys having a U:Pb ratio greater than unity. In alloys where the uranium to lead ratio is less than or equal to unity, the distinctive

uranium bearing eutectic phase is replaced by groups of dark discrete particles whose distribution suggests the intimate mixing of eutectic structures.

As shown therefore by FIGURE 2, uranium additions, if made in amounts approximately equal to or greater than the lead content of the brass negate the deleterious effect of the lead on its hot workability. Further tests have been made as set forth in Table III showing by way of example the effect of alloying additions of uranium to copper in the presence of lead and bismuth and to nickel in the presence of lead, sulphur, selenium, tellurium, antimony, tin and oxygen. The specimens of copper were hot worked at 750° C. and those of nickel at 1070° C. all with a 50% reduction in thickness. The degree of cracking once more follows the classification of FIGURE 1. It is seen that uranium is effective in all cases in improving the quality of the product.

It has been found that a particularly satisfactory way of introducing uranium into contaminated melts containing copper is by first preparing the uranium as an alloy of copper and uranium whose constitution is within the range from pure copper (with a small amount of uranium) up to 59% by weight copper uranium to 41% by weight uranium. This latter alloy is UCu₅. Preferably the copper uranium alloy should be prepared as the eutectic of copper and UCu₅ of 78% by weight copper to 22% by weight uranium. Alloys in this range have the advantage that they melt at lower temperatures than the pure uranium and do not form the complex mixture of melts or solid and melt of alloys richer in uranium (as shown in the graph of FIGURE 4 to the right of the composition for UCu₅). If uranium or a uranium rich alloy is added directly to the copper alloy melt the additive tends to sink very rapidly to the bottom of the melt. It normally remains solid, since the temperature of the copper bath is generally below or close to its melting point or at best it forms a liquid/liquid mixture only one component of which is mixible with the copper alloy at the temperatures involved. The eutectic of copper and UCu₅ is particularly advantageous as an additive because of its low melting point of 950° C. and its density of 9.7 gm./cc. This density is almost the same as that of the copper alloy bath, c. 9.0 gm./cc., as opposed to that of uranium of 19.0 gm./cc.

In those alloys from which copper is absent, i.e. nickel and nickel base alloys, the metal baths to be treated with a malleablising addition of uranium have normal refining temperatures of 1500-1600° C., so that uranium metal, cut into small pieces, may be used as the additive with satisfactory results and recoveries. Alternatively if a lower melting point additive is desired, an alloy of nickel and uranium may be used, the eutectic of 30% by weight uranium being the simplest to fuse and melting at 1110° C., as compared with the melting points of uranium and nickel at 1134° C. and 1455° C. respectively.

Table I

Effect of uranium on the cracking of hot rolled 70-30 brass, 50% reduction in thickness.

Sample No.	Composition, wt. Percent				Rolling Temperature, ° C.	Degree of cracking
	Cu	Zn	Pb	U		
1-----	72.7	27.0	0.06	-----	600	D
2-----	72.7	27.0	0.06	-----	725	D
3-----	72.7	27.0	0.06	-----	800	B
4-----	72.7	27.0	0.06	0.40	600	A
5-----	72.7	27.0	0.06	0.40	725	A
6-----	72.7	27.0	0.06	0.40	800	A
7-----	69.2	30.6	0.07	-----	750	D
8-----	69.2	30.6	0.10	0.42	750	A
9-----	69.2	30.6	0.19	0.42	750	A

Table II

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.

Sample No.	Composition, wt. percent					Ratio U:Pb	Degree of cracking
	Cu	Zn	Pb	P	U		
10 A1-----	64.9	34.9	0.13	-----	0.003	-----	D
B1-----	64.7	34.2	0.49	-----	0.003	-----	D
C1-----	64.7	34.8	1.01	-----	0.003	-----	D
A2-----	64.9	34.9	0.13	.013	0.003	-----	D
B2-----	64.7	34.2	0.49	.010	0.003	-----	D
C2-----	64.7	34.8	1.01	.015	0.003	-----	D
15 A3-----	63.8	36.1	0.11	-----	0.21	2.0	A
B3-----	64.1	35.6	0.32	-----	0.21	0.66	B
C3-----	63.8	35.6	0.55	-----	0.21	0.5	D
A4-----	63.9	35.5	0.15	-----	0.34	2.0	A
B4-----	63.9	35.5	0.35	-----	0.34	1.0	A
C4-----	63.9	35.5	0.62	-----	0.34	0.5	D
A5-----	66.8	33.0	0.21	-----	0.99	4.0	A
B5-----	65.2	34.1	0.6	-----	0.99	1.5	C
20 C5-----	65.2	33.0	1.24	-----	0.99	0.8	D

Table III

Further examples of malleabilisation of contaminated alloys.

Sample No.	Cu	Composition, wt. percent				Contaminant	Degree of cracking
		Ni	P	Al	U		
30 M1-----	99.75	-----	.04	-----	-----	Pb 0.14	D
M1A-----	99.75	-----	.04	-----	0.15	Pb 0.14	B
M3-----	99.62	-----	.04	-----	-----	Bi 0.05	D
M3A-----	99.8	-----	.03	-----	0.3	Bi 0.05	A
M13-----	99.6	-----	0.1	-----	0.05	Pb 0.1	D
M13A-----	99.6	-----	0.1	-----	0.14	Pb 0.1	C
M15-----	99.8	-----	0.1	-----	-----	S .017	D
M15A-----	99.5	-----	0.1	-----	0.34	S .016	A
M21-----	99.8	-----	0.14	-----	-----	Se .06	D
40 M21A-----	99.5	-----	0.14	-----	0.76	Se .04	A
Nominal Compositions, wt. percent							
45 M20-----	99.8	-----	0.1	-----	-----	Te 0.1	D
M20A-----	99.6	-----	0.1	-----	0.3	Te 0.1	B
M24-----	99.5	-----	0.1	-----	-----	Sb 0.1	B
M24A-----	99.5	-----	0.1	-----	0.3	Sb 0.1	A
M17-----	99.8	-----	0.1	-----	-----	Sn 0.1	B
M17A-----	99.5	-----	0.1	-----	0.3	Sn 0.1	A

Experiments were carried out to ascertain the effect of addition of uranium on the hot rolling characteristics of a sulphur-contaminated nickel. A first such nickel contained .044% of sulphur. When hot rolling was carried out at temperatures of 800° C., 1000° C. and 1070° C. massive cracking occurred. Addition of 0.1% by weight of uranium substantially reduced hot cracking and addition of 0.28% by weight completely eliminated hot cracking. Similar tests were carried out on a nickel containing 0.1% of sulphur which cracked badly on hot rolling. Addition of 0.51% of uranium substantially reduced hot cracking and addition of 0.72% of uranium completely eliminated it.

The effect of adding uranium to bismuth-contaminated 70:30 brass was investigated as follows. Bismuth was added to two heats of 70:30 brass, each heat being split into uranium-free and uranium-treated portions. Samples of the four products thereby obtained were tested by rolling at four different rolling temperatures. The results of these tests are shown in Table IV below. In this table samples 11A to 14A are samples of a uranium-free material containing 0.02% of bismuth while samples 11B to 14B are of a similar material containing 0.09% of uranium. It will be observed that although the uranium-

free material could be rolled without cracking at a rolling temperature of 20° C. (samples 11A), massive cracking of this material took place when rolling at temperatures of 600° C., 700° C. and 800° C. as indicated in respect of samples 12A, 13A and 14A. By contrast, all of samples 12B to 14B of the uranium-containing material could be rolled without cracking at these higher rolling temperatures. Samples 11C to 14C are of a uranium-free material containing 0.07% of bismuth. Here again, the material could be rolled at 20° C. without cracking but massive cracking took place when rolling was effected at 600° C., 700° C. or 800° C. The inclusion of 0.36% of uranium permitted hot rolling to be carried out at 600° C., 700° C. or 800° C. without cracking as indicated by samples 12D to 14D.

Table IV.—Bismuth contamination

Alloy No.	Bi	U	Rolling Temp., °C.	Degree of Cracking*
11A	0.02	Nil	20	A
12A	0.02	Nil	600	D
13A	0.02	Nil	700	D
14A	0.02	Nil	800	D
11B	0.02	0.09	20	A
12B	0.02	0.09	600	A
13B	0.02	0.09	700	A
14B	0.02	0.09	800	A
11C	0.07	Nil	20	A
12C	0.07	Nil	600	D
13C	0.07	Nil	700	D
14C	0.07	Nil	800	D
11D	0.07	0.36	20	A
12D	0.07	0.36	800	A
13D	0.07	0.36	700	A
14D	0.07	0.36	800	A

*A, crack-free; B, fine cracking of rolled surface; C, few cracks mostly at edges; D, massive cracking.

It will be appreciated that when malleablising copper or nickel or a copper alloy or a nickel alloy according to the present invention by the addition of uranium the benefits of the invention can be achieved purely by a trial and error approach. It is scarcely feasible to lay down hard and fast numerical ranges within which the benefits of the method can be obtained. However, as an indication of the relative numerical proportions of uranium and contaminants the following observations may be made.

When the contaminants are present in very small amounts malleabilisation of the metal is frequently unnecessary. The proportion of the contaminant or mixture of contaminants which has to be present before the workability of the metal is significantly impaired depends on the nature of the contaminants and of the composition of the metal. However, as a practical guide it can be taken that the workability of copper and copper alloys is substantially unaffected by the presence of lead, arsenic, antimony, sulphur, selenium and tellurium in amounts of less than 0.01% and is substantially unaffected by the presence of bismuth in an amount of less than 0.001%. In the case of nickel and nickel alloys the workability of these metals is substantially unaffected by the presence of lead, sulphur, selenium, and tellurium in amounts of less than .002%, by the presence of arsenic, antimony and tin in amounts of less than 0.005% and by the presence of bismuth in amounts of less than 0.001%. Thus, the malleabilisation of copper, nickel and alloys of these metals by the method of the present invention is in general concerned only with metals which have an amount of contamination greater than the minima represented by the foregoing figures, although in special cases it could, of course, be applied to metals concerning smaller amount of such contaminants. It will be appreciated that

if the metal contains a number of the contaminants in smaller proportions than those quoted above the combination of the effects of these contaminants may be such as to make malleabilisation according to the present invention desirable notwithstanding that each of the individual contaminants is present in an amount less than that which is mentioned above.

It is also of interest to mention the normally encountered maximum limits of the contaminants present in the metals treated by the method of the present invention. In copper and copper alloys the normal maximum of arsenic, antimony, sulphur, selenium and tellurium is about 1.0%, the normal maximum of lead is about 1.5%, and the normal maximum of bismuth is about 0.2%. In nickel and nickel alloys the normal maximum of lead, arsenic, antimony, sulphur, selenium, tellurium and tin is about 0.5% while the normal maximum of bismuth is about 0.1%.

With regard to the amount of uranium which should be added to the metal it is generally found that a significant improvement in workability is achieved by adopting a minimum uranium to contaminant ratio, on a weight percentage basis, as indicated in Table V.

Table V

Impurity X	Copper and Copper Alloys, Minimum U:X ratio	Nickel and Nickel Alloys, Minimum U:X ratio
Pb	0.5	2.0
Bi	1.0	2.0
As	2.0	2.0
Sb	2.0	2.0
S	5.0	5.0
Se	2.0	4.0
Te	2.0	4.0
Sn		2.0

The maximum U:X ratio is of course much less critical than the minimum although it is desirable, once malleabilisation has been effected, to minimise the volume of the secondary phases introduced into the parent metal constitution. Also, an economic limit exists on the amount of uranium that can be introduced. In general a practical maximum U:X ratio may be quoted at about 5 times the minimum given in the above table. Practical consideration will have considerable bearing on the U:X ratio. For instance, if it is desired to malleablise a copper alloy containing 1% of sulphur the figures quoted above would suggest that uranium might be used in an amount of from 5% to 25%. As a practical matter the inclusion of such a large amount of uranium as 25% would not be considered since it is clear that the desired malleabilisation could be achieved by adding at most 5% of uranium. On the other hand when malleablising an alloy which contained only 0.2% of sulphur it would be not at all inconvenient to make use of a high U:X ratio, for example as high as 10.0. Also, it has to be kept in mind that if the proportion of uranium added to the metal gets too high the product obtained is one which would be classed as a copper-uranium alloy or a nickel-uranium alloy rather than a copper or nickel alloy to which uranium has been added solely for the purpose of malleabilisation. Such alloys may have properties which make them quite desirable but the purpose of the present invention is not to provide alloys of this type. From this standpoint, an alternative practical upper limit for the use of uranium in malleablising nickel and copper and alloys of these metals according to the present invention may be taken as about 5% by weight of the product.

It will be appreciated that when considering what amount of uranium should be added for the purpose of

malleablising the copper or nickel or alloy of these metals account should be taken of the fact that more than one of the recited contaminants may be present. Sufficient uranium should be added to overcome the deleterious effects of all of the contaminants. The minimum uranium requirement will be the sum of the minimum requirements in respect of each of the contaminants.

The malleablising of copper, nickel and alloys thereof according to the method of the invention is applicable to a wide range of such alloys. For purposes of illustration the following may be mentioned. Some of the copper alloys which can be successfully malleablised according to the invention are:

(1) coppers containing up to 5% of at least one of cadmium, silver, chromium, beryllium, zirconium, phosphorus, and nickel

(2) brasses containing up to 45% zinc and from 0 to 5% of at least one of tin, aluminium, manganese and iron

(3) bronzes including:

(a) tin bronzes containing up to 15% of tin and from 0 to 10% of at least one of phosphorus and nickel

(b) silicon bronzes containing up to 5% of silicon and from 0 to 5% of at least one of manganese, zinc, iron and tin

(c) aluminium bronzes containing up to 15% of aluminium and from 0 to 5% of at least one of nickel and iron

(4) cupro-nickels containing up to 50% of nickel

(5) nickel silvers containing up to 25% of silver and up to 50% of zinc

Among the nickel alloys which can be successfully malleablised according to the method of the invention are:

(1) Nickels containing from 0 to 10% of at least one of aluminium, manganese and silicon

(2) Monels containing up to 50% of copper and from 0 to 5% of at least one of iron, manganese, silicon and aluminium.

We claim:

1. A method of deoxidizing a molten bath of metal selected from the group consisting of copper, substantially uranium-free copper alloy, nickel and substantially uranium-free nickel alloy, which method comprises: adding uranium to the bath in an amount sufficient to convert substantially all of the oxygen in the bath into uranium dioxide, and removing the deoxidation product from the surface of the bath.

2. The method according to claim 1 wherein the uranium is added in the form of pieces of metallic uranium.

3. The method according to claim 1 wherein said bath is composed of copper and wherein there is added to the bath a uranium-copper alloy containing not more than 40% by weight of uranium.

4. A method according to claim 3 wherein said uranium-copper alloy contains about 78% by weight of copper and about 22% by weight of uranium.

5. The method according to claim 1 wherein said bath is composed of substantially uranium-free copper alloy and wherein there is added to the bath a uranium-copper alloy containing not more than 40% by weight of uranium.

6. The method according to claim 5 wherein said uranium-copper alloy contains about 78% by weight of copper and about 22% by weight of uranium.

7. The method according to claim 1 wherein said bath is composed of nickel and wherein there is added to the bath a uranium-nickel alloy.

8. The method according to claim 7 wherein the uranium is added in the form of pieces of an alloy of nickel and uranium containing about 30% by weight of uranium and about 70% by weight of nickel.

9. The method according to claim 1 wherein said bath is composed of substantially uranium-free nickel alloy and wherein there is added to the bath a uranium-nickel alloy.

10. The method according to claim 9 wherein the uranium nickel alloy contains about 30% by weight of uranium

and about 70% by weight of nickel.

11. A method of improving the hot workability of copper, the copper containing at least one of the following impurities in the proportions specified:

Bi: from 0.001 to 0.2% inclusive

As: from 0.01 to 1.0% inclusive

Sb: from 0.01 to 1.0% inclusive

S: from 0.01 to 1.0% inclusive

Se: from 0.01 to 1.0% inclusive

Te: from 0.01 to 1.0% inclusive

Pb: from 0.01 to 1.5% inclusive

said method comprising adding uranium to the copper in an amount sufficient to reduce the effect of said impurity on the hot workability.

12. A method of improving the hot workability of substantially uranium-free copper alloy, said alloy containing at least one of the following impurities in the proportions specified:

Bi: from 0.001 to 0.2% inclusive

As: from 0.01 to 1.0% inclusive

Sb: from 0.01 to 1.0% inclusive

S: from 0.01 to 1.0% inclusive

Se: from 0.01 to 1.0% inclusive

Te: from 0.01 to 1.0% inclusive

Pb: from 0.01 to 1.5% inclusive

said method comprising: adding uranium to said alloy in an amount sufficient to reduce the effect of said impurity on the hot workability.

13. A method of improving the hot workability of nickel, said nickel containing at least one of the following impurities in the proportions specified:

Bi: from 0.001 to 0.1% inclusive

Pb: from 0.002 to 0.5% inclusive

S: from 0.002 to 0.5% inclusive

Se: from 0.002 to 0.5% inclusive

Te: from 0.002 to 0.5% inclusive

As: from 0.005 to 0.5% inclusive

Sb: from 0.005 to 0.5% inclusive

Sn: from 0.005 to 0.5% inclusive

said method comprising adding uranium to said nickel in an amount sufficient to reduce the effect of said impurity on the hot workability.

14. A method of improving the hot workability of substantially uranium-free nickel alloy, said alloy containing at least one of the following impurities in the proportions specified:

Bi: from 0.001 to 0.1% inclusive

Pb: from 0.002 to 0.5% inclusive

S: from 0.002 to 0.5% inclusive

Se: from 0.002 to 0.5% inclusive

Te: from 0.002 to 0.5% inclusive

As: from 0.005 to 0.5% inclusive

Sb: from 0.005 to 0.5% inclusive

Sn: from 0.005 to 0.5% inclusive

said method comprising adding uranium to said alloy in an amount sufficient to reduce the effect of said impurity on the hot workability.

15. A method according to claim 11 wherein the amount of uranium added is not greater than 5% by weight of the metal.

16. A method according to claim 12 wherein the amount of uranium added is not greater than 5% by weight of the metal.

17. A method according to claim 13 wherein the amount of uranium added is not greater than 5% by weight of the metal.

18. A method according to claim 14 wherein the amount of uranium added is not greater than 5% by weight of the metal.

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