

[54] **GRAIN REFINEMENT OF COPPER ALLOYS BY PHOSPHIDE INOCULATION**

577,850 6/1959 Canada..... 75/153

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[57] **ABSTRACT**

[52] **U.S. Cl.**..... **75/153; 75/135; 75/154; 75/161; 75/164**

[51] **Int. Cl.²**... **C22C 9/00; C22C 9/02; C22C 9/05; C22C 1/02**

[58] **Field of Search**..... **75/135, 153, 161, 164, 75/154**

A method of refining as-cast grain size of copper alloys by inoculation of the melt, prior to or during pouring, by addition of phosphorus and a transition metal such as zirconium. Certain parameters of the inoculation and casting process are critical.

In particular, the melt with a P content of 0.002 to 1.0% is stirred at 20° to 200°C above the liquidus, then 0.002 to 0.5% of a transition metal such as Zr is stirred into the melt, and finally within a period of 10 minutes or less, the alloy must be poured and solidified. Through the synergistic action of P and Zr, the resulting cast ingot is then characterized by advantages such as improved uniformity, absence of columnar crystals, and finer equiaxed grains, which help prevent difficulties in further processing of the alloy.

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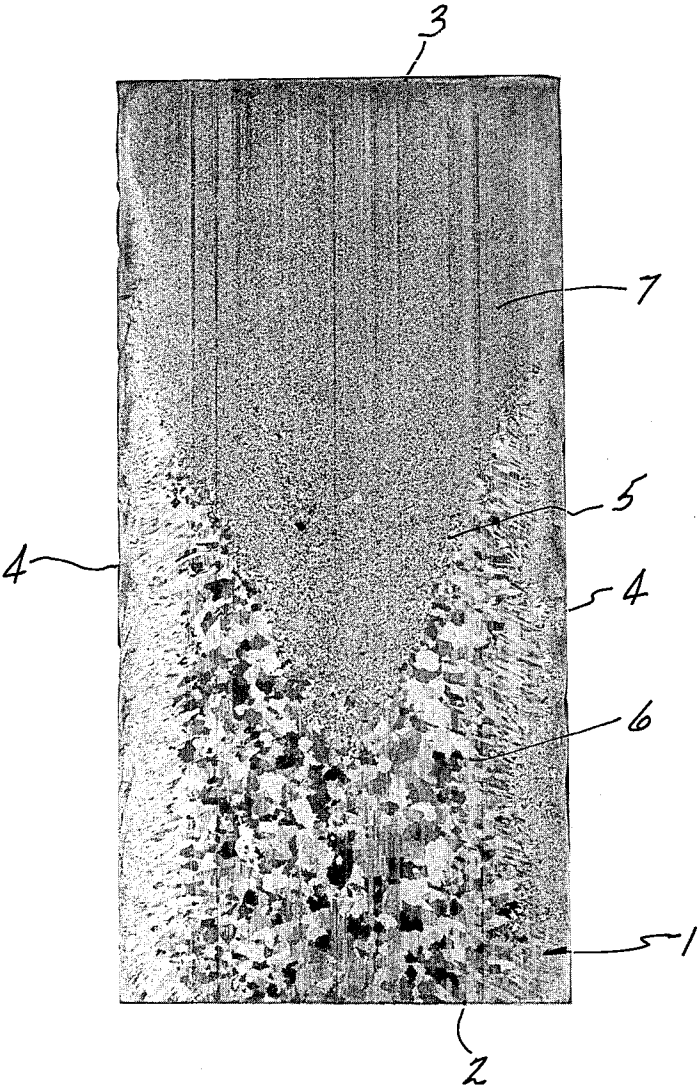
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10 Claims, 1 Drawing Figure



(MAGNIFICATION 1X)

GRAIN REFINEMENT OF COPPER ALLOYS BY PHOSPHIDE INOCULATION

BACKGROUND OF THE INVENTION

Copper base alloys are widely used, particularly in applications where conductivity and ease of fabrication are important. A variety of processing routes are commonly used, the great majority of which employ melting and casting. The alloy may be cast into the desired shape and used in the as-cast condition or following some desirable heat treatment. Alternatively, an ingot may be cast and the final product arrived at by means of hot working, cold working or combinations of these techniques. In all cases, structural uniformity of the original as-cast process ingot or casting has an important influence on the ease or even economic feasibility of further processing and the properties or qualities of the end product. Structural imperfection or non-uniformity in ingots and castings include cracks, porosity, inclusions, and segregation of alloying elements and impurities. Cracked ingots are usually impossible to further process and would, in any case, lead to defective end products. Pores may become filled with gas and lead to blistered sheet products or act as stress risers and hence impair ductility. Inclusions, particularly where they agglomerate or segregate to grain boundaries lead to poor surface finish or appearance and may also act as stress risers. Segregation of both desirable and unwanted elements in solid solution or as precipitates leads to non-uniformity in end products and to difficulties in processing. Such difficulties and others have an important influence on process economics. This is particularly so as these structural non-uniformities and defects are difficult to reduce, much less eliminate in normal casting techniques.

Grain refinement of the original ingot or casting is one means by which all of the above structural non-uniformities and defects may be reduced to some degree. Casting and ingot cracking may be reduced or even eliminated by refinement of the as-cast grain size. The same is true of cracking during hot rolling operations. Porosity may be eliminated or at least reduced in size and spread more uniformly thereby reducing blistering effects and rendering the alloy more ductile during processing and as a final product by grain refinement. Also, the distribution of solute elements and precipitates both desirable and unwanted is rendered more uniform.

Grain refining techniques, both chemical inoculation and mechanical, exist for copper alloys. Existing inoculation techniques are only applicable to a narrow range of alloys either because they are inherently inactive in but a few alloys or, as in the case of iron inoculation, such a high inoculation rate is required as to alter radically the very nature of the alloy concerned. Mechanical grain refinement techniques although perhaps more widely applicable are economically unattractive and hence have found very limited acceptance in the industry.

Accordingly, it is an object of the present invention to provide an effective and economical process for refinement of the as-cast grain size in a wide variety of copper alloy castings and ingots.

A further object is the derivation of the above described advantages of fine grained castings and ingots in terms of uniformity of structure and properties,

economies of processing, and advantageous properties of end products.

A still further object is the provision of an effective and economical process of this type, which may readily be used in available melting and casting installations.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that the foregoing objects are readily and advantageously accomplished by a novel and improved process wherein a copper alloy melt is chemically inoculated by additions of phosphorus and a transition metal such as zirconium prior to or during the normal casting operation. A wide variety of copper alloys treated in this manner demonstrate an unusually fine as-cast grain size and thereby derive the above mentioned advantageous uniformity of structure and reduced incidence of defects.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a section of a D.C. ingot in which the process of the present invention was applied during part of the casting process.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention effective refinement of the cast grain size of a wide variety of copper alloys is accomplished by inoculation of the melt with phosphorus and a transition metal prior to or during transfer of the molten alloy to the mold.

Ti, V, Cr, Mn, Zr, Hf, and other such transition metals may be used according to the teachings of this invention, Zr being the preferred transition element inoculant. Levels of inoculation of below 0.002% generally lead to ineffective grain refinement and are, in any case, difficult to control where chemically reactive transition metals are concerned. Levels higher than 1%, whilst they may be highly effective in grain refinement, are not generally useful because radical changes may be imparted to the properties of the resultant alloy. The latter consideration is, of course, inapplicable where the transition metal is a part of the basic alloy make-up. Accordingly, transition metal inoculation at levels between 0.002 and 1% will generally provide best results, 0.02 to 0.2 being the preferred range.

Levels of phosphorus inoculation below 0.002% have been found to be ineffective in grain refinement and are, in any case, difficult to control. Levels of phosphorus above 0.5% are generally not needed for grain refinement and would influence alloy properties too drastically to be widely useful. In most cases, a maximum of 0.2% phosphorus has been found adequate to produce marked grain refinement and levels in the 0.2 to 0.5% range would normally be used only where called for by the alloy specification. Accordingly, phosphorus inoculation in the range 0.002 to 0.5% will generally provide the best results, 0.02 to 0.2% being the preferred range.

It is hypothesized that phosphides of transition metals are instrumental in the grain refining effects of the transition metal-phosphorus inoculations described in this invention. Generally, however, it has not been found necessary to adhere to the stoichiometric ratio of the transition metal phosphide of concern. In fact, in the case of the preferred transition metal inoculant zirconium; Zr/P ratios of from 0.02 to 2.0 have been investigated and found effective.

The method of grain refinement described herein is applicable to a wide range of copper alloys including those which contain transition metals or phosphorus as part of their standard or specified chemistries. In the case of alloys containing transition metals, it is preferred that the added transition metal have a higher energy of phosphide formation than the transition metal which is a normal alloy constituent. Although it is not generally necessary to consider transition metal phosphide stoichiometry an important factor in grain refinement, in certain alloys it may be desirable to add an excess of the transition metal over stoichiometry in order to minimize the extent of other low melting metal phosphides which may otherwise form. These low melting phases, including Cu_3P , may cause severe cracking problems during hot working of some alloys. In still other alloys, it may be convenient to maintain phosphorus in excess of stoichiometry for the transition metal phosphides of concern in order to benefit from the known attributes of phosphorus in certain copper alloys such as solid solution strengthening.

According to the teachings of the current invention, the form, order, timing and temperature of the inoculations are important considerations. Thus, because phosphorus and certain transition elements are readily oxidized under the condition prevailing in normal copper melting techniques, they are most conveniently added in the form of a master alloy to insure rapid dissolution and dispersion in the melt. For instance, in the case of the preferred combination of Zr and P, a copper - 13% phosphorus and a copper - 6% zirconium master alloy have been found to be suitable.

Also, in order to take advantage of the deoxidizing capabilities of phosphorus, it is usually advantageous to add this element prior to the addition of the transition metal. Attempts at utilizing the reverse order of addition, particularly in the case of the preferred inoculants of Zr and P, have often led to loss of the greater part of transition element to oxidation before the phosphorus could be alloyed. As a consequence, no grain refinement was observed. Because of the tendency to lose certain transition element additions by oxidation, it is also advisable to cast the alloy as soon as possible after the latter addition. In the case of Zr additions, dwell times of less than 1 minute are preferred in order to ensure reasonable recovery rates although dwell times as high as 10 minutes may be feasible in certain instances. High melt temperatures, especially during and also after alloying of phosphorus and reactive transition elements tend to lead to poor recovery of these elements and consequently adversely affect the grain refining process. Superheats between 20° and 200°C above the liquidus have been found to be suitable with 20° to 60°C being the preferred range.

The method of grain refinement described herein, is suitable for a wide range of processes when the above-mentioned factors are born in mind. In general, where small scale melting and casting processes are contemplated, normal batch additions of phosphorus and the transition element to the crucible may be advantageously used. On the other hand, where an alloy is to be melted and cast on a large scale, continuous type alloying additions should be considered. In the case of the preferred elements, Zr and P, it has been found satisfactory to use normal batch addition to melts of less than 150 lbs. weight. Where casting on a larger scale has been undertaken, for instance, in D.C. casting of 300 lb. slabs, it has been found desirable to add the Zr

continuously as a 6% Zr master alloy rod feeding directly into the transfer launder at a predetermined rate. Where desirable, this approach may also be taken with the P addition.

The present invention and its main advantages will be readily understood through consideration of the following illustrative examples.

EXAMPLE I

A 15 lb. charge of CDA alloy 260 having a nominal composition of 70% Cu - 30% Zn was melted in a small induction furnace using standard operating procedures. Five pounds of this melt were cast at a temperature of 1020°C, into a steel mold, the sides of which were insulated with a layer of 1/8 inch thick Fiberfrax paper and which rested on a water cooled copper block or chill which formed the bottom of the mold. The nature of this casting technique is such as to favor growth of large columnar grains vertically upwards from the chill face. The remaining melt, held at a temperature of 1020°C, was then inoculated with 0.1% P, stirred and further inoculated with 0.05% Zr, stirred and another 5 lb. ingot cast at a temperature of 1010°C, into an identical mold 1 minute after the Zr inoculation. Macrostructural examination of the solidified ingots showed that the normal 70/30 brass ingot contained a large percentage of columnar grains of up to 1.5 inches in length, the balance of the grain being equiaxed and up to 0.3 inches in diameter. In marked contrast, the inoculated 70/30 brass ingot had a totally equiaxed grain structure with a mean grain diameter on the order of 0.001 to 0.005 inches. In addition, the untreated ingot contained extensive intergranular porosity which proved to be absent in the casting treated according to the teachings of this invention. Subsequent chemical analysis showed that the inoculated casting contained 0.1% P and 0.03% Zr, a recovery of 60% of the added Zr.

EXAMPLE II

A test similar to that described in Example I was conducted. In this case, however, a charge of CDA alloy 194 having a nominal composition of 2.1% Fe, 0.1% Zn, 0.02% P, balance Cu was melted. One ingot was cast at a temperature of 1150°C without further alloying or inoculation and a second ingot was cast after inoculation with a Cu - 6% Zr master alloy at a level of 0.15% Zr and cast at the above superheat 2 minutes after the Zr was added. A similar difference in grain size was observed between the inoculated and the normal untreated ingot as in Example I. Subsequent chemical analysis showed that the inoculated ingot contained 0.02% P and 0.10% Zr, a recovery of 67% of the added Zr.

EXAMPLE III

Three melts of a nominal 95% Cu, 5% Sn alloy were made under identical conditions using a method and apparatus described in Example I. The first melt was deoxidized by addition of 0.1% P and cast at a temperature of 1110°C into the previously described bottom chill mold. The second melt was deoxidized by inoculation with 0.1% Zr and cast 2 minutes later at the same temperature into the same mold. The third melt was first deoxidized by addition of 0.1% P and further inoculated with Zr at the level 0.1%, held for 2 minutes and cast in an identical manner. Only the third ingot, inoculated according to the teachings of this invention, with

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both P and Zr, had a totally fine equiaxed grain structure with a grain diameter on the order of 0.001 to 0.005 inches. The ingots treated with P and Zr separately showed a mixed coarse columnar plus equiaxed structure similar to that of the uninoculated 70/30 brass described in Example I. Subsequent chemical analysis showed that Ingot 1 contained 0.1% P, Ingot 2 contained 0.05% Zr and Ingot 3 contained 0.1% P, 0.05% Zr.

EXAMPLE IV

A 95% Cu, 5% Sn melt was made up in a like manner to those described in Example III. The melt was inoculated with 0.1% F, followed by 0.1% Zr and held at 1110°C. After 2 minutes a first ingot was cast into the end chilled mold described in Example I. After 10 minutes the melt was restirred and a second ingot cast. Examination of the solidified ingots showed that only the first ingot demonstrated a totally fine equiaxed grain structure, the second ingot having a coarse structure typical of the uninoculated alloy. Subsequent chemical analysis showed that the first ingot contained 0.1% P and 0.06% Zr, whereas the second contained 0.08% and <0.002% Zr. This example illustrates the importance of minimizing the dwell time between inoculation and casting so as to obtain the desired results of inoculation in terms of grain refinement.

EXAMPLE V

Two chill castings of a nominal 5% Sn, 0.2% P, and balance Cu alloy were made in accordance with the procedure described in Example I. The first ingot was cast without further treatment and the second in an identical manner after inoculation with Cr to a level of 1%. The alloy inoculated with both P and Cr proved to have an equiaxed grain structure having a mean grain diameter about 10 times smaller than that of the equiaxed portion of the alloy containing no chromium. In addition, the coarse grained ingot contained significant microporosity whereas the ingot treated according to the present invention was completely free of this serious casting defect.

EXAMPLE VI

Two castings of a nominal 4% Sn - 3% Zn - 4% Pb - 0.1% P, and balance Cu, equivalent to CDA alloy 544, were made according to the method described in Example I. The first ingot was cast at this nominal composition and the second 1 minute after inoculation with 0.05% Zr. A similar decrease in grain size as was described in Example I was noted. This alloy is commonly used for production of bronze bearings. The lead is preferably distributed within the alloy in the form of fine discrete particles and the particle size and uniformity of its distribution is extremely important in the performance of the bearing. It was noteworthy that a much better distribution of fine lead particles was observed in the grain refined alloy as compared to the non-grain refined alloy.

EXAMPLE VII

A 300 lb. melt of a nominal CDA alloy 510 containing 5.4% Sn, 0.2% P, balance Cu was made in a induction furnace using standard melting practices for this alloy. The alloy was transferred to a 3 x 8 inches D.C. casting mold by means of a short transfer launder at a temperature of 1170°C. The first half of the melt was cast in the normal manner whereas a Cu - 6% Zr master

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alloy rod of 154 inch diameter was fed into the metal in the launder at a rate equivalent to 0.05% Zr in the cast ingot during the second half of the casting run. A similar reduction in grain size was observed as in Example I with the added benefit that a much more uniform structure resulted having an average grain diameter of about 0.002 inches.

FIG. 1 shows an etched cross-section of a D.C. ingot 1 cast as described in Experiment VII. In D.C. casting a chilled mold is used which has no bottom. Molten metal is poured into the top of the mold and a solidified or partially solidified ingot is withdrawn from the bottom of the mold. Heat is removed by cooling water applied to the mold and to the metal which has been withdrawn from the mold. In FIG. 1 the section of ingot shown moved through the mold in a direction from surface 3 to surface 2. The cooling effect of the mold was applied to side surfaces 4 and 4. Dotted line 5 shows the transition zone between region 6 where no grain refining treatment was applied and region 7 in which zirconium and phosphorus was added according to the teaching of the present invention. This figure graphically illustrates the beneficial results obtained by the process of the present invention.

The uniformity of structure obtained in this case was the direct result of the more closely controlled conditions with respect to level of inoculation, dwell time and solidification conditions inherent in the above described arrangement. Subsequent chemical analysis showed that the reduced dwell time involved in this case lead to an 80% recovery of Zr. Hot rolling sections of this material at 800°C showed that the extent of edge cracking was reduced by the grain refining effect of the P and Zr inoculations.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A method of casting molten copper base alloys comprising the steps of:
 - A. providing a melt of copper base alloy with a content of 0.002 to 0.5% phosphorus at a temperature of 20° to 200°C. above the liquids;
 - B. then stirring into said melt at said temperature 0.002 to 1.0% of a transition metal selected from the group consisting of Zr, Hf, Ti, V, Cr, Mn and mixtures thereof; and
 - C. then pouring the molten alloy said temperature into a cooled mold within a period of about 2 minutes after the said addition of transition metal, thereby forming a solidified uniform ingot of fine grain size without substantial loss of said transition metal.
2. A method as in claim 1 wherein the phosphorus content is 0.02 to 0.2%.
3. A method as in claim 1 wherein the amount of said transition metal is 0.02 to 0.2%.
4. A method as in claim 1 wherein the said melt is maintained during steps A and B at a temperature of 20° to 60°C above the liquids.
5. A method as in claim 1 wherein the said melt is poured within 1 minute after step B.

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6. A method as in claim 1 wherein the said copper base alloy contains tin.

7. A method as in claim wherein the said transition metal is zirconium.

8. A method as in claim 1, wherein the said sequential steps are effected in continuous manner.

9. A method as in claim 1, wherein the said ingots are

characterized by the substantial absence of columnar grains.

10. A method as in claim 1, wherein the said ingots are characterized by fine equiaxed grains having an average size less than one-tenth of that resulting from the identical sequential steps in the substantial absence of said transition metal.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,928,028
DATED : December 23, 1975
INVENTOR(S) : John C. Yarwood

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 60, the word "case" should read ---cast---.

Column 5, line 7, "011% P," should read ---0.1% P,---;

Column 5, line 14, "0.1% F," should read ---0.1% P,---;

Column 5, line 24, after "0.08%" insert ---P---.

Column 6, line 1, "154 inch" should read ---3/8"---;

Column 6, line 11, the word "solifified" should read ---solidified---;

Column 6, line 54, after the word "alloy" insert ---at---.

Column 7, line 3, after the word "claim" insert ---l---.

Signed and Sealed this

thirtieth **Day of** *March* 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks