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PROCESS FOR IMPROVING THE QUALITY OF COPPER-ZIRCONIUM ALLOY CASTINGS

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Fig. 2.

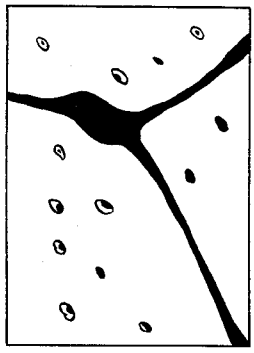


Fig. 3.

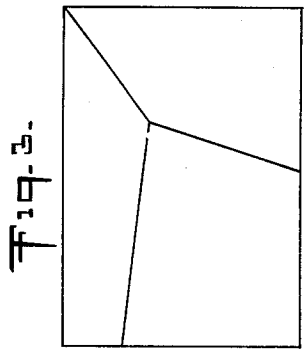


Fig. 4.

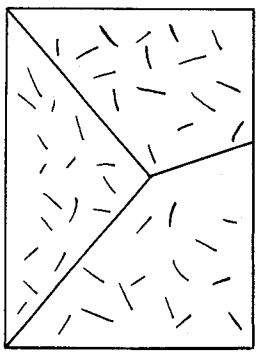
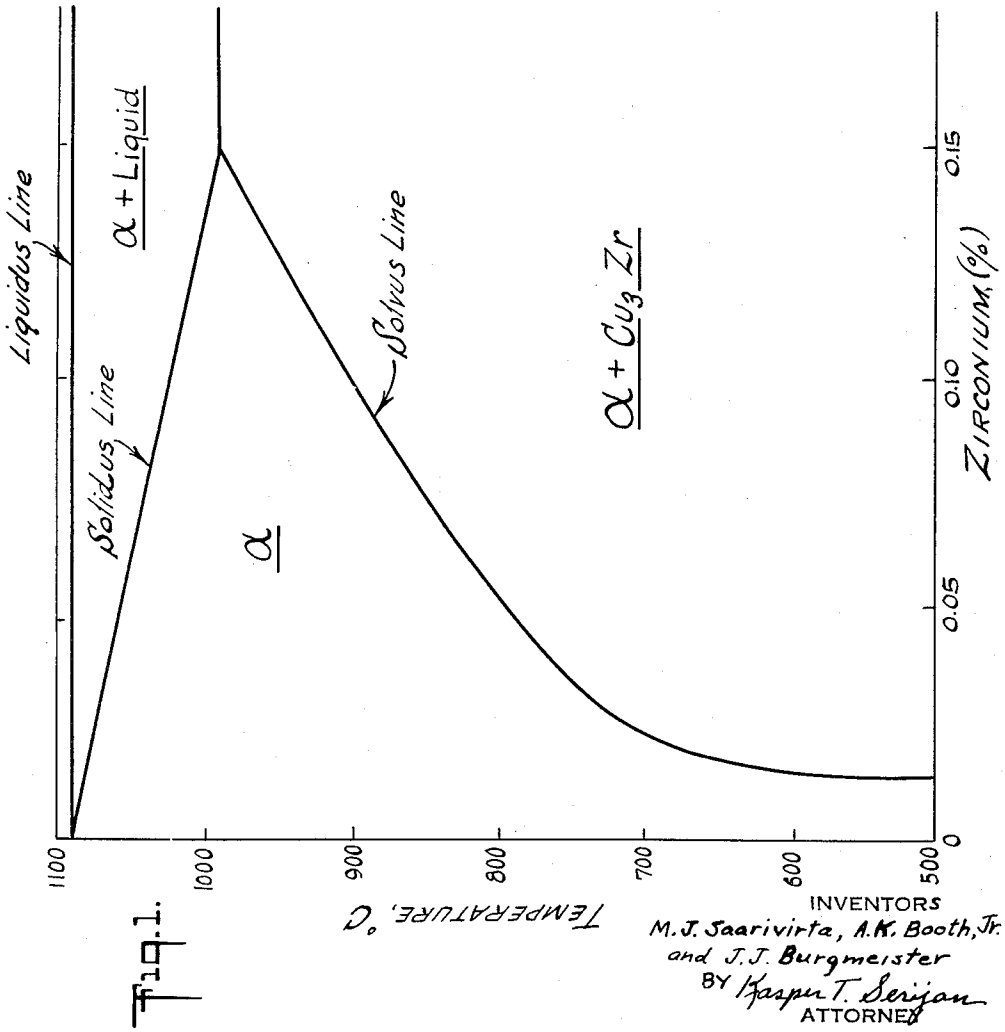


Fig. 1.



INVENTORS
M. J. Saarivirta, A. K. Booth, Jr.
and J. J. Burgmeister
BY Kaspar T. Serijan
ATTORNEY

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PROCESS FOR IMPROVING THE QUALITY OF COPPER-ZIRCONIUM ALLOY CASTINGS

Matti J. Saarivirta, Plainfield, Archibald A. K. Booth, Jr., Elizabeth, and John J. Burgmeister, New Brunswick, N.J., assignors to American Metal Climax, Inc., New York, N.Y., a corporation of New York

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5 Claims. (Cl. 148—3)

This invention relates to improvements in the thermal treatment of castings and relates more particularly to a process for the treatment of freshly poured castings made of copper and containing preferably within the maximum solid solubility limit of zirconium in said copper. The invention is useful for eliminating or greatly reducing the occurrence of intercrystalline cracking which has been heretofore encountered particularly in connection with the making of relatively large castings such as ingots, billets, bars, cakes and the like.

Castings of most copper alloys are generally considered as being relatively free from residual stresses. However, some stresses are set up during solidification and subsequent cooling and, in some instances, these may be sufficiently high to cause intercrystalline cracks, primarily near the center line of the casting and occasionally on the casting surface. In the case of certain copper-base alloys, particularly where constituents present have either a low solubility in the alloy or a freezing point that differs appreciably from the major phase or phases, the occurrence of segregation is not uncommon. Usually a homogenizing treatment of the metal is essential or desirable before subjecting such material to working.

In the case of copper-zirconium alloys made preferably with initially oxygen-free copper and containing up to the maximum solid solubility of zirconium, which alloys are described in detail in U.S. Patent No. 2,842,438, little or no difficulty is encountered in the making of relatively small size castings using conventional casting procedures utilizing, for example, a water-cooled mold. It has been found, however, that the making of sound castings of relatively large size as is commonly required in commercial practice presents a serious problem in that the formation of intercrystalline cracks becomes extremely difficult to avoid. With the occurrence of intercrystalline cracking in the cast condition, the resulting casting becomes highly susceptible to failure particularly during hot working of the material. This, of course, imposes a serious limitation on the widespread use of the alloy notwithstanding the excellent combination of properties possessed by the material notably with respect to resistance to softening at elevated temperatures and good electrical conductivity among other highly desirable properties.

Once intercrystalline cracking in the cast condition occurs, subsequent processing of the casting to effect homogenization within the cast structure as by solution heat treatment of the alloy is of little or no benefit concerning the aforesaid susceptibility of the material to failure upon hot working. Hot topping applied in accordance with conventional practices has also proven ineffective with respect to intercrystalline. Although it has been long recognized that for some copper base materials slow cooling which may be achieved in various ways as by using a heated mold or a well insulated mold is beneficial for producing improved casting soundness and good surface finishes, the conventional slow cooling cycles requiring generally under two hours have been found to provide no satisfactory solution of the problem in the

case of copper-zirconium alloys. With the use of such slow cooling cycles in the case of some copper-base alloys, internal stresses may be minimized but frequently such treatment adversely affects the mechanical properties. For this reason slow cooling is generally avoided whenever possible in the making of copper-base alloys.

It has now been discovered that when copper-zirconium alloys of the type herein designated are subjected to relatively prolonged slow cooling to provide ample time for substantially complete homogenization of the zirconium in the copper and to enable gradual cooling of the alloy over an appreciably longer period of time than heretofore provided in the so-called "slow cooling" processes, the castings made thereby are practically entirely free of intercrystalline cracks regardless of the size of the casting. It has been further found that notwithstanding the use of a substantially prolonged cooling cycle, there is, surprisingly enough, no impairment with respect to any of the mechanical properties of the alloy.

It is therefore a principal object of this invention to provide an improved process for casting copper-zirconium alloys whereby the internal stresses are relieved to the extent practically necessary for completely eliminating the occurrence of intercrystalline cracking notwithstanding the size or mass of the casting being produced.

Another object of this invention is to provide an improved process for the thermal treatment of freshly poured castings consisting of initially oxygen-free copper containing within the maximum solid solubility limit of zirconium in said copper whereby the cast product is made completely free from intercrystalline cracks without impairment of the mechanical properties of the alloy.

For a clearer understanding of the present invention, reference is made to the accompanying drawing in which:

Fig. 1 is a phase diagram of the binary alloy of copper-zirconium made with initially oxygen-free copper;

Fig. 2 is an enlarged schematic representation of the alloy structure showing undissolved second phase accumulated in the crystal boundary region;

Fig. 3 similarly illustrates the crystal boundary region with the residual second phase completely dissolved within the matrix material; and

Fig. 4 represents the cast structure upon further cooling to temperatures below the solvus line wherein precipitation of the second phase is seen to be uniformly distributed throughout the entire casting.

As used herein the term "initially oxygen-free copper" refers to a high purity copper which has been substantially freed of its oxygen content by any of the known methods commonly employed for the purpose before addition of the alloying substance thereto. Although copper which has been produced in a reducing atmosphere such as "OFHC" brand copper is particularly suitable for making the copper-zirconium alloys in accordance with the process herein disclosed, copper prepared in an inert atmosphere, a vacuum or in accordance with any other of the conventional practices used for making oxygen-free copper is included within the meaning of the term. The invention is also applicable to copper-zirconium alloys made with chemically deoxidized copper wherein the copper is freed of its oxygen content by the addition of small amounts of a deoxidizer such as phosphorus, lithium and the like.

The maximum solid solubility of zirconium in initially oxygen-free copper is seen from Fig. 1 to be close to 0.15% by weight at about 980° C. Depending upon the properties desired, the amount of zirconium in the alloy may be varied generally between 0.01 to 0.15% or thereabouts with about 0.13% being preferred for production of alloys which are particularly suitable for most electrical and electronic applications of the alloy. Where maximum resistance to softening at elevated temperatures

is desired, the amount of zirconium is increased accordingly.

The preliminary steps involved in making the aforesaid alloys are carried out by melting the copper using a protective atmosphere such as carbon monoxide. After heating the oxygen-free copper or oxygen-freed copper preferably to about 1170–1200° C., a sufficient quantity of zirconium either as metal, sponge, master alloy or in any other form suitable for use in making the alloy is added to provide the desired zirconium content in the alloy. At the alloying stage, it is desirable to maintain a protective atmosphere of an inert gas such as argon in place of a reducing gas under which the copper is generally melted. Following an alloying period of about 2 to 5 minutes during which time the melt is stirred with a graphite plunger, the alloy is ready for casting within 5 to 10 minutes thereafter. The preferred casting temperatures are between 1150 and 1225° C. in connection with the use of either bottom pouring or lip pouring procedures which are equally satisfactory. Bone ash and silicone mold dressings are satisfactory for use in casting copper-zirconium alloys of the type referred to herein.

For improving the quality of the copper-zirconium alloy castings in accordance with the present invention, the freshly poured alloy casting of desired zirconium content is maintained at a sufficiently high temperature for a prolonged period of time to permit maximum dissolution of the zirconium in the copper upon solidification of the casting. This may be readily accomplished by avoiding conditions conducive to rapid cooling of the casting following solidification thereof. To obtain virtually complete homogenization of the alloy thereby avoiding the presence of any appreciable residual phase in the crystal boundaries as depicted in Fig. 2, it has been found essential to maintain the freshly poured solidified casting within a temperature range preferably between about 850 and 1000° C. for a minimum period of 10 to 15 minutes and preferably for about 15 to 30 minutes or even longer depending upon the size of the casting and the zirconium content of the alloy. This treatment coupled with further controlled slow cooling of the alloy at an average rate not exceeding 180° C. per hour starting at not lower than about 850° C. and continued until the casting reaches a temperature of about 400° C. and preferably closer to 300° C. has been found to be both critical and essential to the reliable production of sound castings. Thereafter, the casting may be quenched in accordance with conventional practices.

Time-wise, the aforesaid controlled slow cooling of the casting after effective homogenization thereof requires a minimum period of at least 2½ hours to effect lowering of the temperature from about 850° to 400° C. or thereabouts. Experience has shown, however, that it is generally advantageous to employ a slow cooling cycle of from 3 to 5 hours or even longer especially in the case of the relatively large size castings containing more than 0.1% zirconium. Generally speaking, sound castings in all instances are assured with the use of controlled slow cooling cycles such that the average cooling rate within the designated range of temperature actually falls between 100 and 160° C. per hour.

It will be readily apparent from the phase diagram of the copper-rich binary alloy system (Fig. 1) that the aforesaid homogenization can be more readily achieved within the alpha temperature range (between the solidus and solvus lines) at the relatively low zirconium concentrations of the alloy than at the higher zirconium content values. For this reason, it is important that the alloys containing more than 0.10% zirconium be kept at elevated temperatures somewhat above 900° C. and preferably about 950° C. for as long as possible and for at least 15 to 30 minutes, or even a longer period of time as previously stated. This ensures practically complete homogenization although the desired diffusion leading to the completely homogenized state schematically depicted in Fig. 3 apparently proceeds toward completion though at a much slower rate at temperatures below the solvus line. Such continued slow cooling controlled to provide a cooling rate of below 180° C. after substantially complete homogenization of the alloy results in minimizing shrinkage stresses while effecting precipitation of the second phase uniformly within the crystals as schematically illustrated in Fig. 4. The latter obviously occurs only at temperatures below the solvus line and at a sufficiently high zirconium content to render the alloy precipitation hardenable.

In practice, the critical slow cooling is satisfactorily accomplished by stripping the sufficiently solidified casting from the mold while still hot and immediately burying the same in vermiculite, ashes, lime, magnesia or any other suitable insulating material capable of preventing heat losses at an excessive rate. The same purposes, namely, obtaining substantially complete homogenization while minimizing shrink stresses in the casting to the extent that virtually no intergranular cracking is encountered may be alternatively effected by the use of molds adapted to provide the prerequisite temperature control through the use of insulation, radiation shields and the like or the use of furnaces wherein the temperature can be properly controlled to provide the desired cooling rate. In commercial practice, however, it is preferred to use the stripping procedure with the controlled slow cooling being effected by the provision of adequate insulation around the casting being started above at least 850° C. as previously stated, and preferably above 880° C. and somewhat higher in the case of the relatively high zirconium content alloys. It should be readily apparent from the foregoing that the longer the holding time at temperatures within or close to the alpha solid solution temperature range for any particular alloy composition after sufficient solidification thereof, the more efficiently and effectively is the required homogenized condition achieved.

Parallel or tapered well molds of steel and cast iron treated with bone ash mold wash have proven satisfactory for use in the process herein described but in commercial practice graphite molds are preferred. No difficulty was experienced in stripping castings from either type of mold at temperatures as high as 900 to 1030° C.

Numerous castings were made using either lip or bottom pouring methods, said castings consisting of 6, 8 and 10 inch diameter billets ranging in weight from 300 to 1000 pounds. In making 8" billets weighing 300 pounds, for example, the melts of initially oxygen-free copper were made using a graphite crucible in a 300 pound capacity induction furnace. Alloying was achieved in some instances by the addition of a master alloy consisting of 30% zirconium, balance copper; other melts were successfully made using zirconium platelets. The melts maintained under a protective atmosphere of argon, nitrogen or carbon monoxide were cast into steel, iron and also graphite molds with either parallel sides or tapered sides (⅛" taper per foot). Castings containing 0.005, 0.03, 0.08, 0.10, 0.13, 0.14, and 0.15% zirconium were perfectly sound in every instance where immediately upon solidification of the casting (at the temperature indicated by the solidus line in Fig. 1) sufficient time was allowed for effective homogenization following which controlled slow cooling was used. The same proved true in the case of the 1000 pound billets. The procedure used consisted of maintaining the solidified casting for from 10 to 30 minutes and generally from 15 to 25 minutes at above 850° C. and, in the case of the castings containing 0.08% or more zirconium, above 900° C. after which the castings were removed from the mold and insulated in vermiculite. The subsequent slow cooling was varied to the extent that from 2½ to 12 hours was required to lower the temperature to 400° C. or thereabouts after which the

castings were quenched. Some of the surface roughness caused by contacting the hot casting with vermiculite is removed by water quenching the alloy.

Although castings of the alloy containing generally below 0.05% zirconium were not extremely susceptible to cracking in the absence of one or both of the above precautions, an appreciable number of such castings were nevertheless sub-standard as to their quality due to the presence of some intergranular cracking. With castings of a zirconium content above 0.08%, however, the results proved unfavorable in nearly all instances in that unsound castings were consistently obtained when (*a*) initial cooling of the solidified casting to about 850° C. or somewhat higher from the solidification temperature which is generally over 1000° C. was permitted to occur in less than 10 minutes, and (*b*) less than a 2½ hour minimum period was allowed for the subsequent slow cooling of the casting down to a temperature of at least 400° C. That both expedients are essential especially where the zirconium content exceeds 0.08% is illustrated by the failure of prolonged homogenization treatment in the absence of the subsequent slow cooling to produce sound castings. Experience has also shown that the aforesaid subsequent controlled slow cooling is not particularly beneficial where the prior homogenization of the alloy at the elevated temperatures is circumvented by allowing the initially solidified casting to cool to below 900–850° C. too rapidly.

It will be seen from the foregoing that the production of sound castings of copper-zirconium alloys requires avoidance of any processing conditions which fail to substantially completely homogenize the alloy since subsequent shrinkage stresses normally encountered in the relatively large-sized castings invariably cause cracking at the zirconium-rich phase which freezes out last at the grain boundaries. Only by providing sufficient time for the alloy to become completely homogenized and thereby freeing the crystal boundaries from the second phase and improving cohesion between the crystals particularly near the center region of the casting and by the utilization of continued slow cooling under controlled conditions to prevent excessive shrinkage stresses has it been found possible to produce completely sound relatively large sized castings of this extremely useful alloy.

Having thus described this invention, it will be apparent to those skilled in the art that other modifications are possible. It should therefore be understood that within the scope of the appended claims, this invention may be practiced otherwise than as specifically described.

We claim:

1. In a process for making sound castings of a precipitation hardenable copper-zirconium alloy, the improvement comprising the steps of maintaining the cast molten alloy immediately following solidification thereof at a temperature above 850° C. for at least ten minutes and thereafter controlling the cooling of the casting down to a temperature of at least 400° C. to provide an average cooling rate below 180° C. per hour.

2. In a process for making sound castings of a precipitation hardenable alloy containing between 0.08 and 0.15% by weight zirconium with the balance being oxygen-free copper, the improvement comprising the steps of maintaining the cast molten alloy immediately following solidification thereof for from ten to thirty minutes at a temperature above 880° C. and thereafter subjecting the casting to controlled slow cooling down to at least 400° C. at an average rate below 180° C. per hour.

3. The process of claim 2 wherein the controlled slow cooling is at an average rate between 100 and 160° C. per hour.

4. The process of claim 2 wherein the casting is quenched following the controlled slow cooling thereof down to at least 400° C.

5. The process for making sound castings of a precipitation hardenable alloy made with initially oxygen-free copper containing within the maximum solid solubility limit of zirconium, comprising the steps of casting the molten alloy under a protective atmosphere, homogenizing the cast solidified alloy for at least 10 minutes at a temperature above the solvus line in the phase diagram of Figure 1 of the accompanying drawing for any particular zirconium content and thereafter slow cooling the substantially completely homogenized casting from a temperature of at least 850° C. such that the progressive cooling thereof down to 400 to 300° C. requires a minimum period of at least two and one-half hours.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,842,438	Saarivirta et al.	July 8, 1958