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COPPER-BASE ALLOYS CONTAINING CHROMIUM AND IRON

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The present invention relates to the copper-base alloys and this application contains subject-matter in common with my application, Serial No. 696,918 filed November 6, 1933.

Copper-tin alloys, sometimes containing other elements such as phosphorus, zinc, manganese, and nickel, are well-known to the art and are formed into various shapes by casting and by various known processes for working metals in the cold state. However, it has heretofore been difficult to hot work tin bronzes containing above about 3% tin. For instance, in order to form wire or sheets from the so-called phosphor bronze, it has been necessary first to heat the cast ingot to a high temperature of not less than 700° C., hold it at this high temperature for many hours for the purpose of homogenizing the ingot by diffusion, break the ingot down cold, anneal it, roll it down cold to a certain extent, again anneal it, and to repeat the alternate cold working and annealing steps until the metal has attained the desired size and shape. At no stage has hot working been used, because the metal cannot withstand the application of a forging hammer or hot rolls without cracking and breaking to pieces.

I have discovered that copper-tin alloys can be made forgeable and rollable at elevated temperatures by introducing into the alloys certain additional elements which are only slightly soluble in the crystals of solid copper and of solid alpha-tin bronze, and which in addition have a much higher melting point than the bronze. Such additional elements are the first constituents to crystallize out of the molten mass on cooling and thus effect favorable distribution of crystal nuclei and influence the atoms of copper and tin to crystallize in a more constant proportion than is the case with normal binary tin bronzes and with ternary tin bronzes in which the third element forms a component of the alpha solid solution.

Suitable additional elements are chromium and vanadium and, to a lesser degree, iron and cobalt. Vanadium is the most effective of these elements but it is difficult and expensive to introduce into molten copper or molten bronzes. For this reason chromium is preferred, this element being effective as soon as about 0.5% is added. If iron or cobalt alone were to be used, at least 4% would be necessary to produce the desired effect of improving the hot workability of the bronze.

According to the present invention, hot workability is imparted to copper-tin alloys containing about 3% to about 10% tin by the addition of effective amounts of one or both of the elements chromium and vanadium and the further addition of substantial amounts of iron or cobalt. If desired, the chromium or vanadium, or both, may be added in the form of ferro alloys, for instance, a commercial low carbon ferro-chromium containing about 50% to 95% chromium, or a low carbon ferrovanadium containing about 30% to 90% vanadium, or a ferro alloy containing both vanadium and chromium.

When both iron and chromium or vanadium are added, the iron crystallizes chiefly with the chromium or vanadium so that a tin bronze containing say 2% of 50% ferrochromium appears under the microscope, more like an alloy containing 1.75% to 2% chromium than like one containing 1% of chromium as would have been the case had the iron gone into solid solution in the alpha tin bronze.

Tin bronzes made according to the present invention and containing 3% to 10% tin, 0.5% to 2% chromium or 0.2% to 1% vanadium and up to about 2% iron may be taken from the ingot mold as soon as they are sufficiently cold to handle, reheated to 700° to 800° C., forged to about one-half of the area of the original cross-section, and finished into the desired shape by hot rolling.

Vanadium is somewhat difficult to introduce and in addition quite expensive, for which reasons the use of an amount exceeding that which is necessary for the development of the capacity for hot work (about 1%) is not usually desirable. The situation in the case of chromium is different: it can be introduced into molten bronze easily enough, and its excess above the really necessary amount of 1.5% does not seriously affect hot workability but develops interesting and industrially desirable antifriction characteristics.

It is well known, for instance, that the usual bearing bronzes, working without a lining of a low melting antifriction alloy and containing tin in amounts sufficient to produce as a second constituent the delta eutectoid or bronzite, do not work well if the bearing happens to become overheated. In fact, the bearings of hot rolling mills as used in steel making cannot be made at all of such duplex (alpha plus delta) bronzes. The latter fail rapidly when their temperature approaches 500° C.

To cope with this handicap special bronzes have been introduced containing less than 8% tin and therefore containing no delta phase. In place of the delta phase a hard constituent, quite stable at high temperatures, is introduced into the structure of such bronzes by adding up to 0.3% of phosphorus and up to 3% nickel, the

latter producing to some extent at least, fine grains of nickel phosphide of the supposed formula Ni_3P.

I have found, however, that by increasing the amount of chromium added to the copper-tin base bronze, the phosphide can be replaced by a far larger and far more efficient amount of chromium which crystallizes in the shape of irregular single crystals or their star-like aggregates. While the actual hardness of these chromium crystals is not well known, it can be safely assumed to be in the neighborhood of 200 Brinell, while the hardness of nickel-phosphide, a definite intermetallic compound, must be considerably higher. Therefore, the probability of scratching the journals of the rolling mill is far less in the case of a chromium containing bronze.

The amount of chromium present in such a tin bronze may be as high as 10%, but not more than 4 or 5% is desirable. Likewise, the amount of iron or cobalt may be as high as 10%.

The method of making such chromium or vanadium containing bronzes may vary to a great extent, as to raw materials, type of furnace, material of the crucible, etc. The only essential thing is that the metal should be properly deoxidized before the introduction of the chromium and protected from further oxidation by a layer of a liquid flux. For the latter I prefer a mixture of fluorides of sodium and calcium, to which other fluorides may be added. I may employ a flux of commercially pure fused boric acid and borax and its mixtures with glass also may be used, but with less convenience.

To illustrate a way of preparing such alloys, I shall state the following:

I take commercial bronze ingots and melt them in the usual graphite-clay crucibles. I add to them enough copper to bring the content of tin down to the desired level. I cover the molten alloy with a layer of fluorides about one-eighth inch in thickness in the molten state. I add just enough phosphor copper to make the melt quite fluid, usually not more than 0.05% phosphorus. Then I add chromium metal or ferrochrome or ferrovanadium or ferrochrome-vanadium in pieces large enough to be produced conveniently and without much expense and small enough to allow them to be fully covered by the liquid fluoride in those parts which protrude above the level of the molten bronze due to the difference in the specific weights.

Next, I raise the temperature in the metal either by feeding more fuel and air to the furnace, or increasing its current input until it comes to about 1250° C. At this point chromium dissolves rapidly as does ferrovanadium. From time to time the pieces of the metal or of the ferro-alloy are pushed down under the surface of the molten bronze and the latter stirred to check the supersaturation of the top-layers with dissolved chromium or vanadium.

The liquid flux is next removed, by adding dry sand to it. In this manner a pasty mass of fluoride soaked sand forms, and it can be easily kept from flowing down into the mold.

The final casting proceeds as usual, whether it is the manufacture of sand castings, ingots for forging, or castings in permanent molds. In the latter case about 0.2% aluminum may be added to inhibit the welding of the molten metal to the metal of the permanent mold.

It is to be understood that the copper-base alloys of the present invention may contain, in addition to tin and one or more of the elements chromium, vanadium, and iron in proportions within the limits specified herein, one or more of the elements, nickel, manganese, and aluminum in proportions up to say 10%. These elements do not contribute to the workability of the alloy in the hot state, but may be added for their known improvement effects in other respects. Small amounts of the usual deoxidizers, such as phosphorus, magnesium, and the like may also be present.

I claim:—

1. A hot workable copper-base alloy containing about 3% to 10% tin, about 0.2% to 10% mixtures of chromium and vanadium, about 0.2% to 10% iron, and the remainder substantially all copper.

2. A hot workable alloy containing about 5% to 10% tin, about 0.5% to 5% of mixtures of chromium and iron, about 0.5% to 5% iron, and the remainder substantially all copper.

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