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COPPER-ZINC ALLOYS

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ABSTRACT OF THE DISCLOSURE

Improved copper-zinc alloys containing titanium together with aluminum or nickel or both. If the amounts of titanium, aluminum, and nickel are kept within certain limits, the alloys are age-hardenable and a method is provided for heat treating such alloys to achieve a significant increase in hardness and strength properties. By increasing the amounts of titanium, aluminum, and nickel, it is possible to achieve alloys that are extremely hard after solution heat treating or casting.

This invention relates to heat treatable copper-zinc alloys and more particularly to copper-zinc alloys containing small amounts of titanium together with aluminum and/or nickel, and to methods for heat treating such alloys to achieve an appreciable increase in hardness and strength properties.

Copper-zinc alloys, commonly referred to as "brasses," are of considerable engineering and commercial importance and are utilized widely in both the wrought and cast condition for tubing, fittings, etc. used for carrying water and other fluids. Brass alloys are characterized by good corrosion resistance combined with a high ductility which permits them to be easily formed by rolling, stamping, drawing, etc. Brasses are significantly less expensive than copper; however, they are also marked by relatively low strength properties which, for many applications, negates their economic advantage.

Prior art attempts to increase the strength of brasses have included the addition of one or more specific alloying elements: Sn, Mn, Ni, Al, Si, and Co. Such alloying elements may retain their elementary identity or enter into solid solution, depending on the specific amounts present and the composition of the alloy. Additions of aluminum and/or nickel to brasses, for example, render the alloy heat treatable though only to a limited extent, and the resulting increase in strength is achieved only by the presence of relatively large quantities of nickel. The resulting alloy is thus considerably more expensive than conventional brasses. Brass alloys containing small amounts of cobalt also can be thermally hardened; however, here too the increase in strength is limited and for numerous applications is offset by the higher cost of the alloy. As a result, there exists a definite need for low-cost yet high-strength and corrosion-resistant alloys.

Such a need can be specifically exemplified in the construction of water purification plants where tremendous volumes of condensate tubing are required. While the importance of corrosion-resistant materials in such an application is obvious, material cost is also significant due to the large volume of tubing involved. Efforts to satisfy the requirements for low cost, high strength corrosion-resistant alloys have involved consideration of a number of metal materials. One such material is titanium itself, which is more costly than pure copper but very corrosion-resistant. Another is an aluminum brass containing copper, zinc and aluminum, plus about 0.05 weight percent arsenic. Although less costly than titanium, this alloy does not have the strength of titanium and cannot be age hardened. It also does not have the high

corrosion resistance of titanium or conventional copper alloys such as 70 wt. percent Cu-30 wt. percent Ni. A third material is cupronickel which consists of copper with about 10 weight percent nickel and 1 weight percent iron. This alloy also is less expensive than titanium, but its strength and corrosion-resistant properties are not as high.

Accordingly, it is the principal object of the present invention to provide an inexpensive and corrosion-resistant brass alloy which can be hardened by heat treatment.

Another important object is to provide improved brass alloys that can be hardened after fabrication, thereby achieving economies of manufacture.

Another object is to provide a series of heat treatable brass alloys and a method of heat treating such alloys so as to significantly increase their hardness and strength properties.

Another object is to improve the hardness and strength characteristics of copper-zinc alloys through the addition of selected alloying elements.

Another object is to provide a series of copper-zinc alloys which (a) can be strengthened by a solution heat treatment followed by an age hardening heat treatment, (b) can be readily cold worked after solution treating and prior to age hardening, and (c) when age hardened, have excellent resistance to corrosion and can be easily machined.

Still another object is to provide a brass alloy which will be very strong after casting and which will not soften after prolonged heating.

The foregoing objects are achieved by incorporating in selected copper-zinc alloys selected amounts of (1) titanium and (2) aluminum and/or nickel. Other features and advantages are set forth or rendered obvious in the following detailed description of the invention.

I have now found that small additions of titanium in combination with small amounts of aluminum and/or nickel will render copper-zinc alloys age hardenable (i.e. capable of being hardened by heat treatment alone). Further, when heat treated, these new alloys exhibit a significant increase in hardness and strength with no appreciable loss of machinability or corrosion-resistant characteristics. The alloy optionally may include small amounts of other alloying elements such as tin, lead, manganese, or iron. It also is appreciated that the alloy may include impurities in very small amounts, i.e. trace quantities, without affecting the properties of the alloy and particularly its ability to be age hardened by heat treatment. I have also found that if the amount of titanium is increased sufficiently, the resulting alloy is extremely hard even after solution heat treatment or casting, and that further increase in hardness can be achieved by increasing the amounts of aluminum and/or nickel. Essentially the improved age-hardenable brass alloy of the present invention is comprised by weight of about 5 to 40 percent zinc, 50-80 percent copper, 1.5-5 percent titanium, 2-7 percent nickel and/or 2-7 percent aluminum, 0-1 percent tin, 0-1 percent lead, 0-1 percent manganese, and 0-1 percent iron. Preferably the total amount of titanium, nickel and/or aluminum is less than about 15%. Tin has been found to improve the corrosion resistance of the alloy while lead and manganese improve the machining properties of the alloy. A low zinc content (e.g. 5-15%) is recommended for maximum corrosion resistance while a higher zinc content provides a decrease in cost.

Increasing the relative amount of titanium above about 5 weight percent but no more than about 10% is found to produce an alloy that is very hard even after casting or solution heat treatment but does not harden additionally when subjected to heat treatment at the same

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temperatures used to age harden the age-hardenable brass alloys made in accordance with this invention. Still further increases in hardness of alloys having above about 5 but no more than about 10 wt. percent titanium can be achieved by increasing the amount of aluminum and/or nickel to above about 7% but no more than about 10 wt. percent. Such alloys are particularly suited for the manufacture of objects such as propellers that are used in the cast condition.

The alloys may be made in the same manner as brass except for the addition of titanium and aluminum and/or nickel which may be made by introduction into the molten mass or preferably to the copper before the zinc is added. The alloys may be cast in either permanent or sand molds and those that are age-hardenable may be hot or cold rolled to sheet, rod, or other forms when in their soft condition.

The age-hardenable alloys made in accordance with the present invention may be hardened by a process comprising (1) solution heat treatment, (2) quenching or cooling at a rapid rate, and (3) age-hardening at a selected elevated temperature. During the solution heat treatment the titanium, nickel and/or aluminum constituents are dissolved in the brass solid solution. The quenching or rapid cooling lowers the temperature fast enough to preserve the solid solution at room temperature. It is to be noted that the temperature selected for solution treating is high (i.e. 700° C. or more) but below the temperature at which excessive grain growth or melting of one of the constituents will occur. After the solution treatment and quench, the hardness of the alloy is higher than when the alloy is annealed by slow cooling. Full hardness is developed by precipitation hardening. This involves reheating the alloy to a temperature where the precipitation of the dissolved constituents (Ti, Ni and/or Al) commences and maintaining this temperature for a time sufficient to achieve a suitable dispersion of the precipitate.

The exact temperature of the solution treatment will depend on the specific composition of the alloy but should be between 750° C. and the melting point of the alloy. I have found that best results are achieved when the temperature is about 50 to 150° C. under the melting point for the alloy, i.e. in the general range of 750 to 950° C. depending upon particular alloy compositions, and the alloy is held at that temperature one hour. Minor variations within this range will have no significant effect on the properties of the heat treated alloy, and for a specific alloy composition, may be best determined empirically. For alloys containing about 5 to 25 weight percent zinc, I prefer a solution temperature within the range from about 750° to 850° C.; for alloys with from 25 to 40 weight percent zinc, the preferred range is about 725° C. to 825° C. The optimum time at solution temperature will depend on the thickness of the alloy specimens being treated and will typically vary from a few minutes to several hours. If the specimen is not over 2-inches in thickness, I have found a soaking period of about 90 minutes contributes favorably to the development of optimum properties. Extending the soaking period at the solution treatment temperature to more than about 3 hours may produce an undesirable growth in grain size.

The quenching is preferably carried out in a water bath; however, other quenching media (e.g. oil) also may be used if desired. The temperature of the quench medium may vary within a wide range. Typically, the alloy will be cooled to room temperature. However, under certain conditions it may be advisable to quench directly from the temperature of the solution treatment to the temperature of the age-hardening precipitation treatment. This may be accomplished by heating the quench bath to the desired precipitation temperature or slightly below, provided the volume of the bath is sufficient to prevent the hot specimens from heating the bath above the desired temperature range.

Precipitation hardening is induced by holding the speci-

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mens to a selected intermediate temperature, preferably between 400° C. and 600° C., for a period between about 10 minutes and several hours. A temperature of 500° C. or less is preferred as there appears to be a tendency for higher strength properties to develop from lower aging temperatures. The time period required for producing maximum strength and hardness will depend on the thickness of the specimen and whether or not it has been cooled to room temperature after the solution treatment. This too may be determined empirically. For specimens up to about 2 inches in thickness, I prefer to precipitation-harden at a temperature of 500° C. for about 100 minutes. Overaging, i.e., extending the precipitation hardening heat treatment for a time substantially in excess of about 100 minutes, will result in a decrease in strength, similar to annealing.

To achieve maximum strength and hardness, it is recommended that the age-hardening treatment immediately follow the solution treatment and quench. However, it is recognized that in some instances, for example in the drawing of tubing, it may be desirable to cold work the alloy after quenching when it is most ductile. If the alloy is cold worked after quenching, the age-hardening treatment should be carried out at a somewhat lower temperature as precipitation is accelerated by cold working.

The hardness of alloys made in accordance with the present invention is illustrated by the following specific examples:

EXAMPLE I

Three identical specimens (¼-inch long by ½-inch diameter) of an alloy having the composition of about 73 weight percent copper, 22 weight percent zinc, 2 weight percent titanium, and 3 weight percent aluminum were prepared for testing purposes.

The alloy was made by preparing a copper-zinc melt, dissolving the titanium and aluminum in the melt, and then slowly cooling the melt to room temperature. All of the specimens were solution heat treated in a conventional air atmosphere furnace at a temperature of 850° C. for a period of 60 minutes, then quenched in a water bath to a temperature of 25° C. Hardness measurements were made with a Rockwell machine on several specimens. These specimens were found to have an average Rockwell B hardness value of 56. Less than 15 minutes after being quenched, the remaining specimens were reheated to 500° C. for about 20 minutes, and then air-cooled to room temperature and hardness measurements taken. Thereafter the specimens were repeatedly reheated to 500° C. for additional periods of time, air-cooled and measured for hardness. They were found to have on the average a maximum Rockwell B hardness value of 79 acquired after 127 minutes of heating at 500° C.

EXAMPLE II

Another alloy was prepared and specimens made and tested in accordance with the procedure of Example I. The alloy consisted by weight of 69% Cu, 20% Zn, 2% Ti, 5% Ni, and 4% Al. After quenching, the specimens had an average Rockwell B hardness of 58. A maximum Rockwell B hardness of 81 was achieved after 1623 minutes of aging at 500° C.

EXAMPLE III

A third alloy was prepared and specimens made and tested in accordance with the procedure of Example I. The alloy consisted by weight of 70.5% Cu, 21% Zn, 7% Ni, and 1.5% Ti. After quenching, the specimens had an average Rockwell B hardness of 58. A maximum Rockwell B hardness of 80 was achieved after 160 minutes of aging at 500° C.

Although the reason for the significant increase in hardness is not known with certainty, it is believed to be due to precipitation of the Ti, Ni, and Al constituents throughout the Cu-Zn phase. During the solution treatment, the aforesaid constituents are dissolved into the copper-zinc

solution. Quenching preserves this solution at room temperatures. Aging of titanium-aluminum brass alloys causes the titanium and aluminum to coprecipitate as small particles which are dispersed throughout the matrix of the alloy thereby causing it to be strengthened. Similarly, for brasses containing titanium and nickel the coprecipitate is titanium-nickel, and for alloys containing all three elements the precipitate is titanium-aluminum-nickel.

EXAMPLE IV

A fourth alloy was prepared and specimens made, solution heat-treated and quenched according to the procedure of Example I. The alloy consisted by weight of 67% Cu, 18% Zn, 7% Ti, and 8% Al. It had a Rockwell B hardness of 102 after quenching. The alloy was heat-treated for periods up to 48 hours at temperatures between 500° C. and 700° C. and periodically air-cooled and tested for hardness. The hardness was found to be substantially unchanged by the heat treatment.

The essential difference in properties of the alloy of Example IV as compared to the alloys of Examples I, II, and III is that the former did not soften during solution heat treatment and did not acquire additional hardness when aged at 500–700° C. It has been found that if the relative amount of titanium is increased over 5%, its hardness after quenching is also increased; however, little or no further increase in hardness will result by aging it at 400° C. or higher. If at the same time the amount of nickel and/or aluminum is increased over 7%, the initial hardness will be even higher than if only the titanium content is increased and again little or no further change in hardness will result from further heat treatment. By way of further example, if the alloy of Example II is modified by increasing the titanium content to 7% and decreasing the amounts of copper and zinc to 66% and 18% respectively, it will typically show after quenching a Rockwell B hardness of about 90, and aging at 500° C. for as much as 48 hours will cause the hardness to increase to no more than about 94 on the Rockwell B scale. Although the reason for the difference in behavior and properties of the foregoing alloy and the alloy of Example IV as compared to those of Examples I–III is not known with certainty, it is believed to result from the fact that the titanium and aluminum and/or nickel are present in such quantity that they cannot be fully dissolved by the solution heat treatment.

A consequence of the difference in properties resulting from increasing the content of titanium (and optionally the nickel and/or aluminum content as well) is that the alloy cannot be fabricated in the soft condition and subsequently hardened. However, this apparent limitation is actually an advantage for applications (such as large castings) which do not require fabrication by plastic deformation and where it is desirable that the alloy have a required hardness without need for subsequent heat treatment. In any event, the amount of titanium, aluminum, and nickel individually present in the alloy should not exceed about 10 wt. percent; otherwise the alloy will be too brittle for use. For the same reason it is preferred that collectively the Ti, Ni, and Al should not exceed about 20%. A further reason for these maximum limits on the amounts of Ti, Ni, and Al is cost.

Advantages of the age-hardenable alloys made according to the present invention are several. For example, they exhibit substantially greater hardness and tensile strength than brass alloys heretofore available. Additionally, because of the significant increase in strength, it is possible

to produce tubing having a reduced wall thickness compared to tubing fabricated of conventional brasses. Furthermore, these age-hardenable alloys are easy to shape and, because they have low strength and hardness values after solution treatment, they can be readily cold worked and then hardened thermally. Additionally, alloys made and treated according to the present invention are competitive in cost with conventional brasses in view of their favorable properties. The advantages of alloys made according to the present invention which contain more than about 5% titanium and optionally more than about 7% aluminum and/or nickel is that they have exceptionally high strength without the need for aging heat treatment and thus are suitable for making parts where for one reason or another further heat treatment is not desirable, e.g., large propellers for ships.

What is claimed is:

1. An alloy consisting essentially of 5 to 40% zinc, 50 to 80% copper, in excess of about 5 but no more than 10% titanium, and at least one member of the class consisting of nickel and aluminum with the amount of each present being in the range of 2–10%, the combined amounts of titanium, nickel and aluminum not exceeding 20%.
2. An alloy according to claim 1 containing at least 7% nickel and 2–10% aluminum.
3. An alloy according to claim 1 containing at least 7% aluminum and 2–10% nickel.
4. An alloy according to claim 1 containing at least 7% aluminum and at least 7% nickel.
5. A method of providing an improved brass comprising preparing an alloy consisting essentially of by weight 5 to 40% zinc, 50–80% copper, in excess of 5% but no more than 10% titanium, and at least one member of the class consisting of nickel and aluminum with the amount of each present being in the range of 2 to 10%, the combined amounts of titanium, nickel, and aluminum not exceeding 20%, solution-treating said alloy by heating it to a temperature between 750° C. and its melting point, and cooling said alloy to room temperature by quenching.
6. A method according to claim 5 wherein said alloy includes both nickel and aluminum each present in an amount equal to 2–10% by weight.

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