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Effect of Al and Zr Addition on the Age Hardening Behavior of Bronze Metal

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Abstract

The age hardening behavior of high tin bronze metal due to the addition of Al and Zr has been experimentally investigated. Alloys are prepared conventionally by controlled melting and casting. Age hardening treatment is given to the cast alloys. Samples are isochronally aged for 60 minutes at different temperatures up to 500ºC and isothermally aged at various temperatures up to 350ºC for different period of time ranging from 15 to 240 minutes. To understand the age hardening behavior the hardness values of differently aged alloys have been measured. It is observed that significant hardening takes place in case of Al added alloys due to formation of Al_2Cu *intermetallic precipitates and Zr addition improves the thermal stability of the alloy. Microstructure study of alloy reveals that Al addition creates a new microstructure with relatively large dendritic arms and Zr addition refines the grain structure. The base alloy attained almost fully recrystallized state after ageing at 300ºC for 60 minutes while the other two alloys did not fully recrystallize at that temperature for the given time.*

Keyword: Alloying additions, high-tin bronze, age hardening, microstructure, SEM.

1. Introduction

Copper and copper-based alloys have been utilized in quite a variety of applications since the ancient time. Copper metal in the pure form is so soft and ductile. Adding different materials can change the property of pure copper metal. However, mechanical and corrosion resistance properties of copper can be improved by alloying [1]. Also, copper alloys may be endowed with a wide range of properties by varying their composition and the heat treatment to which they are subjected. For this reason they probably rank next to steel in importance to the engineers [2].Very few metals have a wide range of attractive colors comparable with copper and its alloys. There are more than 400 copper alloys, each with a unique combination of properties, to suit many applications, high quality requirements, manufacturing processes and environment, utilities etc. [3].

Tin is more effective in strengthening copper than zinc, but is also more expensive and has a greater detrimental effect on the electrical and thermal conductivities than zinc. Aluminium, manganese, nickel and silicon can also be added to strengthen copper. Another copper strengthening method is precipitation hardening. The process involves quenching a supersaturated solid solution from an elevated temperature, then reheating to a lower temperature (ageing) to allow the excess solute to precipitate out and form a second phase. This process is often used for copper alloys containing beryllium, chromium, titanium or zirconium. Precipitation hardening offers distinct advantages. Bronze is a tin alloy of copper which is harder than either of the alloy metal ingredients. It is extremely strong and resistant to atmospheric corrosion. It has been used since prehistoric times to forge tools, weapons, statues and ornaments. It has a comparatively low melting point, which metalworkers in ancient times could achieve with charcoal and bellows. This allowed them to cast complex shapes. Other metals such as lead, gold or silver were sometimes added to alter the color, improve the finish or make the molten bronze flow better. Ancient bronze was usually made up of copper, tin and small amounts of noble metals or lead. The amount of tin could reach 40 percent but classic bronze alloy and today's commercial bronze are 10 percent tin and 90 percent copper. Copper alloys with more tin content are technically called high tin bronze alloys. Manganese is added to bronze used for ships' propellers because it resists saltwater corrosion. Iron, nickel, silicon and aluminium are added for strength in tools because bronze will not make a spark when struck. The addition of 0.05-0.15% zirconium to copper, results in maintaining excellent electrical and thermal conductivity. If aluminium is added to copper based alloys, Al_2Cu intermetallic precipitate forms which increases the hardness [4]. In view of the importance of trace additions of zirconium in the high tin bronze, the age hardening studies can also be conducted with quaternary addition. This addition of zirconium increases stability of the material by refining the grains. This study is about improving the properties of high tin bronze by adding fundamental materials. From the literatures it is seen that not many studies have been conducted on the effect of the addition of aluminium and zirconium on the age hardening behavior of the high tin bronze. So investigation on the results of the experiments carried out to study the above mentioned issues related to the age hardening behavior of high tin bronze is the main focus. In this paper the effects of these additions along with the analysis are observed on the evolution of microstructures in the experimental alloys due to change in their chemistry and thermal history.

2. Experimental Procedure

Three samples of high tin bronze, high tin bronze with Al and high tin bronze with the addition of both Al and Zr were fabricated individually through casting process. In the process of preparation of the alloys, the commercially pure copper, tin, aluminium and zirconium were taken. Melting was carried out in a clay-graphite crucible in a natural gas fired pit furnace under suitable flux cover. To make Alloy 1, copper and tin were melted in the clay-graphite crucible. For making the 2nd Alloy pure Al was added by dipping it into another molten metal of copper-tin. Consecutively Al+10wt% Zr master alloy was added to the molten copper-tin for making the 3rd Alloy. All three alloys were casted individually. The final temperature of the melts were always maintained at 1300±15°C. A preheated steel mold (200°C) size of 20× 150 × 150 in millimeter was prepared which was coated inside with a film of water-clay. The melts were then allowed to be homogenized under stirring at 1200°C and poured in that preheated mold. All the alloys were analyzed by spectrochemical method to determine the chemical composition. The chemical compositions of the alloys are given in Table 1.
The cast samples were first machined to skin out the oxide layer from the surface and then different samples were prepared from the castings. The samples of 15 x 15 x 4 mm^3 size obtained and the alloys processed through different routes were aged at different temperatures for different times. The samples were sanded mechanically with emery papers of rough one and the one of 1200 grits. Microhardness of the aged samples was measured with a Micro Vickers Hardness Tester. The knoop indenter was applied with 1Kg load for 10 seconds. At least seven indentations from different locations from each sample were taken.
The optical metallography of the samples was carried out in the usual way. A wet polishing machine with velvet clothed wheel with the addition of alumina powder was used to make scratch free polished surface. Acetone was applied to clean the surface. In case of using metallographic copper etchant a conventionally recommended one of Ammonium Hydroxide+ Hydrogen peroxide (3%) was used where the compounds were taken in 1:1 ratio. The washed and dried samples were observed carefully in optical microscope at different magnifications and some selected photomicrographs were taken. A Scanning Electron Microscope was used for mapping the individual phases in microstructures. The samples used to find the SEM were heat treated to 300°C and etched with same etchant solution used in finding the microstructure.

TABLE 1. Chemical Composition of the Experimental alloys (wt%).

	Sn	**Pb**	**Fe**	**Ni**	**Al**	**Si**	**Cr**	**Zr**	**Mn**	**Cu**
Alloy 1	24.935	0.000	0.000	0.019	0.005	0.001	0.004	0.000	0.001	Bal
Alloy 2	25.444	0.000	0.012	0.018	1.165	0.007	0.003	0.000	0.001	Bal
Alloy 3	25.008	0.010	0.020	0.018	1.170	0.002	0.004	0.240	0.002	Bal

3. Results and Discussion

Age-hardening behavior of the cast alloys

Isochronal Ageing

The results of isochronal ageing of the experimental alloys at different temperature for 60 minutes is shown in Fig. 1. It is seen that all the alloys except Alloy 1 have shown appreciable ageing response. Alloy 1 has however shown a continuous softening at increasing ageing temperatures, with minimum hardness observed beyond 300°C. This happened because of the stress relieving, grain coarsening and recrystallization of the cast alloy. Aluminium added Alloy 2 has shown a better response to the ageing effect, retaining its hardness up to 400°C. The results of the present experiments clearly indicate that the age hardening effect shown by the Alloy 2 was due to the addition of aluminium. Aluminium when added in small concentrations is known to cause precipitation hardening of cast metal and to form a supersaturated solid solution upon solidification [5]. The intermetallic precipitation of Al_2Cu is the reason behind this increasing hardness [6]. There was a steep drop in hardness beyond 400°C, or more specifically at 500°C. This occurred due to precipitation coarsening and recrystallization effect. On close observation of the variation of hardness in overaged situation, it appears that Alloy 3 with 0.2wt% zirconium possessed highest resistance to age softening. Alloy 3 showed its maximum hardness at 400°C and beyond 400°C it retained its overall hardness. It appears from the graph that the presence of zirconium provided thermal stability to Alloy 3. In all cases the peak increase in hardness was observed around 300°C, where the hardness of Alloy 1 was at its least and Alloy 2 and 3 retained their overall hardness. For all three alloys the usual softening due to ageing took place beyond peak hardness.

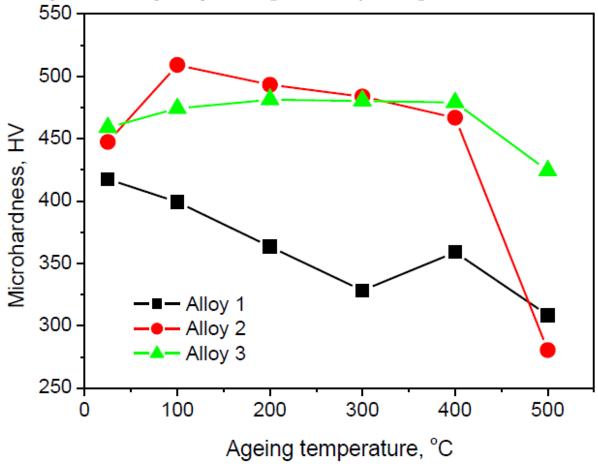

FIGURE 1. Isochronal ageing curve of the alloys, aged for 1 hour

Isothermal Ageing

Figure 2 shows the variation of hardness of the cast alloys when they were isothermally aged at 250°, 300° and 350°C for different time periods. It can be found that the ageing peaks were present for Al added Alloy 2 and Zr added Alloy 3. This was due to formation of the Intermetallic compound, Al_2Cu at this temperature. In the ageing process of the alloys, Al_2Cu intermetallic precipitates can effectively strengthen the alloys and lead to the ageing peak [6, 7]. When the alloys were isothermally aged at different temperatures, the hardness results followed a trend similar to that of isochronal ageing. Figure 2(a) shows the time dependence of age hardening at an ageing temperature of 250°C, which was below the peak hardening temperature of the alloys as observed during isochronal ageing. It appears from the figure that, the base alloy did not respond to such isothermal ageing treatment. The hardness of Alloy 1 dropped with the ageing period and least hardness was found when ageing time was 60 minutes. Alloy 2 and 3 started age hardening from an early time and reached their maximum hardness after 30 minutes of ageing. The extent of this increase in hardness value was relatively low. After attainment of peak hardness values, Alloy 2 and 3 have shown softening and finally their hardness attained more or less constant values. The maximum increase in hardness of Alloy 2 and 3 as compared to Alloy 1 was found to be at 60 minutes of ageing. When the alloys were aged at 300°C, which was the peak isochronal ageing temperature of the alloys (Fig. 1), the ageing response of the alloys were found to be quite appreciable and the extent of age hardening was quite comparable with maximum hardening obtained by isochronal ageing. The peak-aged condition was mostly reached within 60 minutes (Fig. 2.b). No significant softening due to overageing could be observed for Alloy 2 and 3. Under such ageing condition the resistivity of Alloy 2 and 3 are found to reach a plateau after an initial decrease in resistivity up to 60 minutes of ageing (Fig. 2.b). Isothermal ageing at higher temperature (350°C) shows further reduction in the time to reach peak hardness values for Alloy 2 and 3 (Fig. 2.c). In this temperature Alloy 1 shows a continuous trend of decreasing hardness with the ageing time. A small amount of overageing effect was noticed in the alloys.

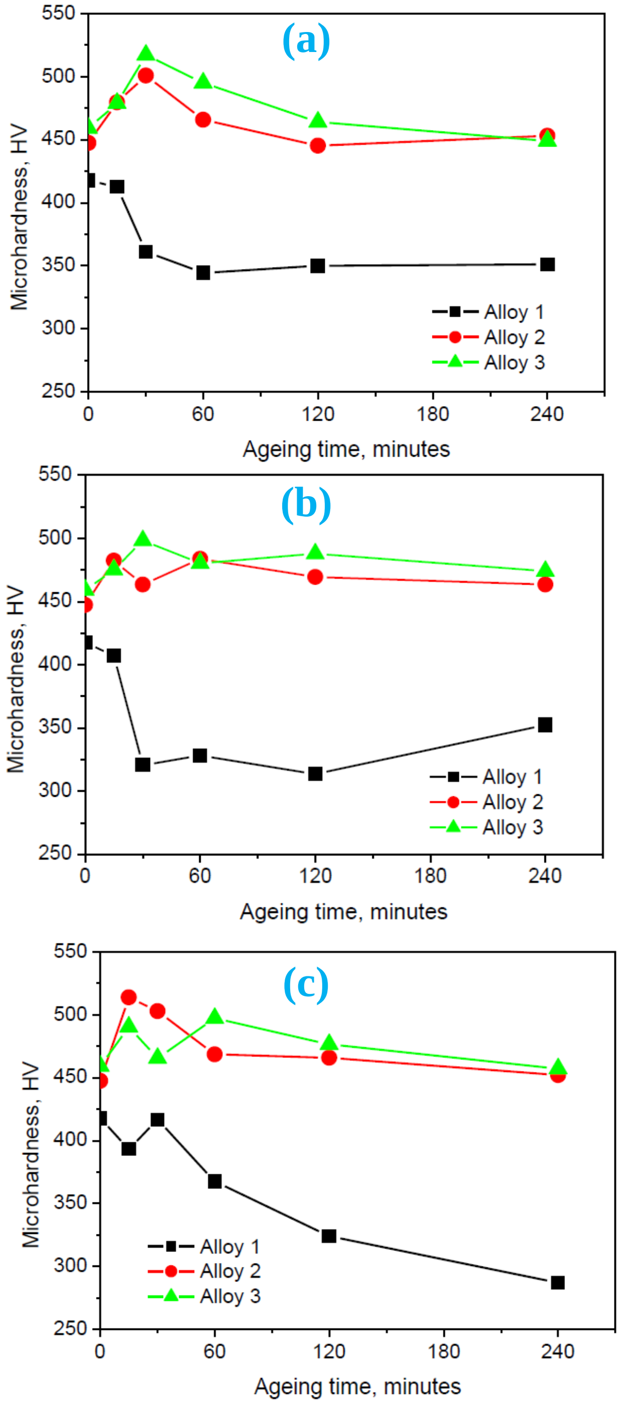

FIGURE 2. Isothermal ageing curve of the alloys, a) aged at 250ºC, b) aged at 300ºC and c) aged at 350ºC

Optical micrographs

Mechanical Properties of alloys are crucially influenced by their microstructural features. The optical micrographs showed visible changes in the microstructure due to change in chemical composition as seen in Fig. 3. The cast alloys showed relatively coarse non-uniform grain structure. The microstructure of Alloy 1 showed islands of α phase and needle like β phase present along the grain boundaries (Fig. 3.a). The high-tin bronze of Alloy 1 contains slightly less than the required amount of tin needed to make a complete β phase [8].There was a complete change in microstructure of the high-tin bronze due to the addition of aluminium (Fig. 3.b). The microstructure of Alloy 2 at room temperature showed long dendritic arms which was completely different from the island-like grain structure of the Alloy 1 microstructure. The presence of the dendritic arms was due to the addition of aluminium [9]. Alloy 3 also showed visible difference in the microstructure. The dendritic arms remained present due to the addition of aluminium, but the arms seemed to be much more refined in shape and structure (Fig. 3.c). This happened due to the grain refining effect caused by the addition of Zr. Zirconium is commonly known to cause grain refinement of copper alloys when added in small amounts. The zirconium present in Alloy 3 reacts with the copper to form an intermetallic Cu_9Zr_2 [10]. It forms another intermetallic compound Al_3Zr with the aluminium present in the alloy. The grain refinement was caused by the presence of Al_3Zr particles that act as effective heterogeneous nucleation point preventing the grain growth during solidification of the Alloy [11]. Grain growths were also restricted by the Cu_9Zr_2 precipitates [12]. The presence of these intermetallic precipitates refined the grains of the microstructure and increased the thermal stability of the alloy [13]. When the alloys were aged to 500°C as presented in Fig. 4, there were some substantial change in the microstructure of Alloy 1 and 2. The grains of the Alloy 1 seemed to be fully recrystallized. Recrystallization of the grains was the cause behind the reduction of hardness during ageing of Alloy 1 (Fig.4.a). Alloy 2 also showed a complete recrystallization of the dendritic arm structure (Fig.4.b), which corresponds to the sudden softening of the alloy at 500°C. The recrystallized grains were much more visible under the microscope as the original grains were replaced by a new set of defect-free grains. Alloy 3 did not show much change in the grain structure (Fig.4.c). The dendritic arms remained refined as before and the grains showed partial recrystallization. This adherence of the grain structure directly corresponds to the thermal stability of Alloy 3 due to the formation of metastable Cu_9Zr_2 and Al_3Zr [12, 14]

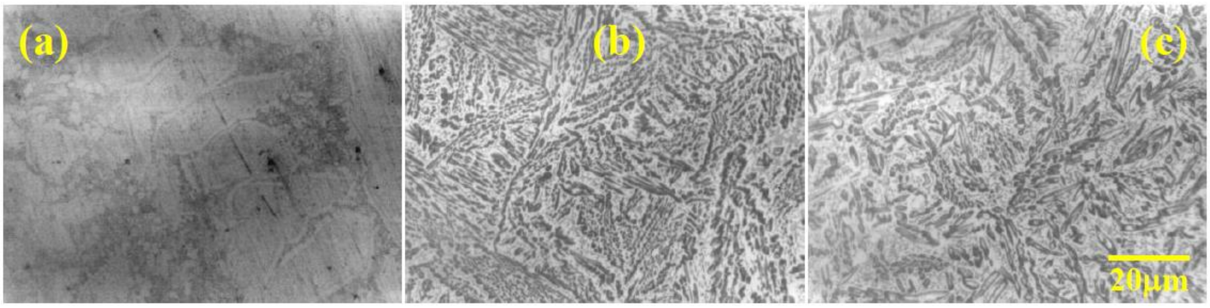

FIGURE 3. Optical micrograph of the experimental cast alloys a) Alloy 1, b) Alloy 2 and c) Alloy 3

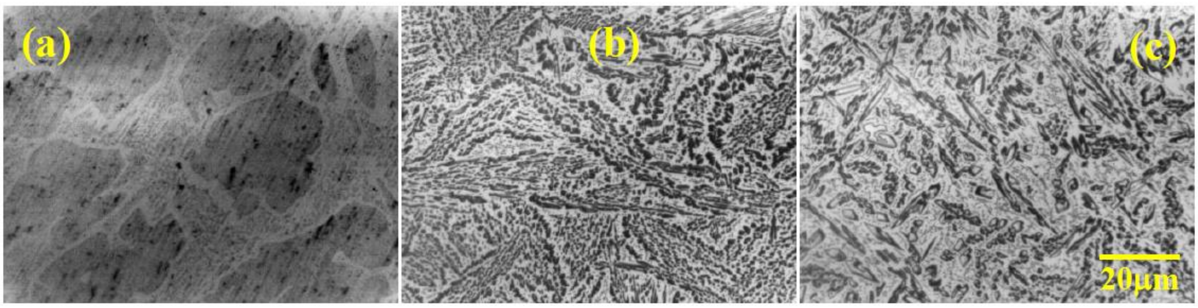

FIGURE 4. Optical micrograph of the experimental alloys aged at 500^{o}C for one hour a) Alloy 1, b) Alloy 2 and c) Alloy 3

SEM micrograph

Figure 5 represents the SEM micrographs of the experimental alloys. The grains of Alloy 1 were visible in the SEM micrograph and appeared to be recrystallized (Fig. 5.a). This observation corresponds to the drastic drop in hardness when Alloy 1 was heat treated to 300°C. The SEM micrograph of Alloy 2 showed coarse dendrites with high quantity of second phase constituents. The second phase was found to be contained in the inter-dendritic space (Fig. 5.b). The coarse dendrites appeared due to the presence of aluminium in Alloy 2. The grain structure of Alloy 2 did not appear to be recrystallized. This is in direct correspondence to the retention high hardness of Alloy 2 at 300°C. The micrograph of Alloy 3, where zirconium was added, it was seen that not only there happened a considerable refinement of dendrites but also the second phase constituent had been reduced in amount (Fig. 5.c). The dendrites, which appeared in the microstructure of Alloy 2, were seen to have refined significantly with the addition of zirconium. The grain refinement of the alloy was mainly caused by its growth restriction effects during solidification, due to the effect of nucleant particles, introduced with the alloying addition of zirconium [15].

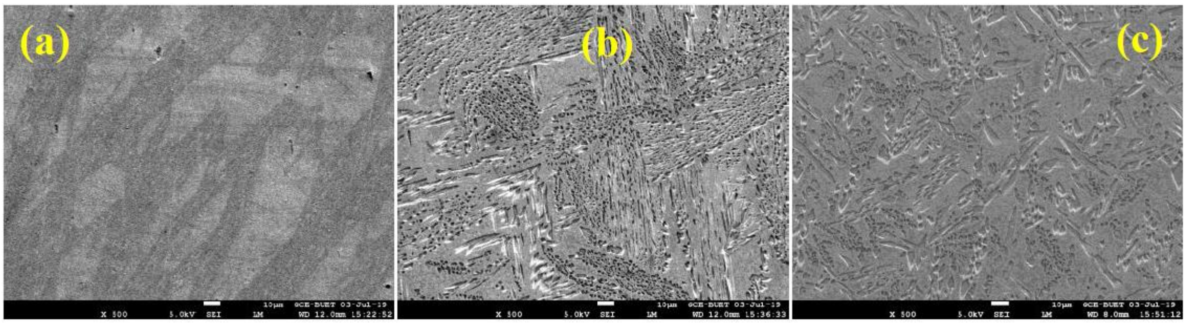

FIGURE 5. SEM micrograph of the experimental alloys aged at 300ºC for one hour a) Alloy 1, b) Alloy 2 and c) Alloy 3

4. Conclusion

The aluminium addition showed the ageing response by increasing the hardness of high tin bronze while addition of zirconium restricted the softening with the increase of temperature. The intermetallic precipitates of Al_2Cu formed in the aluminium added alloys is the reason behind of this increasing hardness. This addition also changed the microstructure of the bronze metal where large dendritic arms formed. The dendrites of the cast base alloy were refined significantly with the addition of zirconium. Trace-added Zr refined the grain structure and hindered the softening due to the precipitation of Cu_9Zr_2 and Al_3Zr, which is very stable against coarsening, redissolution, and pin-grain boundaries and thus this addition of zirconium increased thermal stability. Because of this, while the cast bronze metal and aluminium added bronze were seen to be recrystallized almost fully after ageing at 500°C for 60 minutes, the alloy with trace amount of zirconium did not follow the same trend.

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