RESEARCH PAPER

IMPACT OF COLD PLASTIC DEFORMATION AND THERMAL POSTTREATMENT ON THE PHYSICAL PROPERTIES OF COPPER BASED ALLOYS AI-BRONZE AND $\alpha\text{-}BRASS$

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ABSTRACT

The copper based alloys Al-bronze and α -brass containing each of 10wt% aluminum and zinc were prepared by casting. Afterwards, the specimens were cold-rolled with various percentages of deformation and the cold-rolled samples were aged subsequently at the varied time for four hours and temperatures ranging up to 500°C. Samples underwent characterizations by microhardness testing, electrical resistivity, optical properties, differential scanning calorimetry as well as microstructure analysis using an optical micro scope. The results showed that the hardening of Cu-based alloys was taken place due to solid-solution hardening. Al addition accelerated the hardness through ageing due to the formation of various intermetallic copper aluminites into the aged alloy which was hard and brittle in nature. The resistivity decreased marginally through heat treatment due to the stage of stress relieving, recovery, precipitation coarsening as well as recrystallization and increased for arranging different intermetallics into the alloys. The microstructural study revealed that the cold rolled alloys content the different phases of elongated grain at the rolling direction. Meanwhile higher ageing temperatures at 500°C for one hour led to recrystallization and grain growth especially in pure copper and Cu-loZn alloys.

Keywords: Cu-alloys; plastic deformation; age hardening; microstructure

INTRODUCTION

Copper at the pure state is one kind of soft material. It is also malleable and ductile in nature with extremely high conductivity both in thermal and electrical properties [1, 2]. As a conductor of heat and electricity, building material; Copper is being used. It is also used as a constituent of various metal alloys like sterling silver which is used in jewelry, cupronickel used to make marine hardware and coins, and constantan used in strain gauges and thermocouples for temperature measurement [3-6]. There are different types of methods for strengthening pure copper. The most important mechanisms of strengthening are solid solution strengthening via alloying, work hardening by cold working and precipitation hardening through thermal heat treatments [7, 8]. The common elements such as zinc, nickel, manganese, aluminum, tin, and silicon, etc. are used for solid-solution hardening of copper. The Commercial alloys show the entire range of available solid-solution compositions of each element which is up to 35% Zn, 50% Ni, 50% Mn, 9% Al, 11% Sn, and 4% Si [1, 9]. Work hardening is the most important strengthening method which depends on the degree of deformation applied to most copper alloys. Precipitation hardening of the alloys depends on the type and amount of alloying element and if the element remains in solid solution or

else forms a dispersoid precipitate phase [10, 11]. Even those alloys which are commercially age hardenables are often provided in the mill hardened tempers; which have been processed with cold working after ageing heat treatment [12]. Copper alloys also sensitive to heat treatment, which change the grain size and allocation of the intermetallic precipitates into the microstructure [11]. The effects on copper vary greatly based on the type of trace elements and the quantities that are present in the alloys. These elements play an important role not only in the strengthening behavior but also in other properties like conductivity, corrosion, wear etc. The trace elements too form segregation at the surface of the copper which can change the copper's color and outward appearance [13, 14].

The above studies propose that heat treatment control the different properties as well as the microstructural features of copper and copper alloys. This process is applied to these materials to achieve the preferred properties for every application. However, there no significant comparison of deferent properties has been made in the literature for these particular copper and its alloys. The motivation for these lessons is to found the influence of Al and Zn under different strengthening methods like the solid solution, work hardening and ageing simultaneously because it is important to know the dislocation behavior under strain. More specifically, this paper aims to

demonstrate experimentally the dependence of the hardness, electrical resistivity, optical well as microstructural properties under different heat treatments. Plain binary alloys by ten weight percent of each alloying element were chosen to segregate the influence of individual alloying elements on those properties of the alloys.

MATERIAL AND METHODS

Commercially pure Copper, Cu-10A1 alloy as Al-bronze and Cu-10Zn alloy as α -brass were used in the current study. In the development of the alloys, commercially pure copper, aluminum and zinc were taken. Melting was carried out in a clay-graphite crucible in a natural gas fired pit furnace under suitable flux cover. The final temperature of the melts was always maintained at 1300±15°C. A preheated steel mould (200°C) size of $20 \times 100 \times 150$ 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 into that preheated mould. The chemical compositions of the experimental alloys were analyzed by the spectrochemical method as listed in following **Table 1**.

Table 1 Chemical composition by weight percent of investigated alloys

Al	Zn	Pb	Sn	Fe	Ni	Si	Cr	Cu
0.001	0.000	0.010	0.004	0.033	0.001	0.000	0.001	Bal
9.601	0.023	0.013	0.009	0.078	0.007	0.004	0.007	Bal
0.013	10.300	0.012	0.007	0.057	0.005	0.004	0.007	Bal
	Al 0.001 9.601 0.013	Al Zn 0.001 0.000 9.601 0.023 0.013 10.300	Al Zn Pb 0.001 0.000 0.010 9.601 0.023 0.013 0.013 10.300 0.012	Al Zn Pb Sn 0.001 0.000 0.010 0.004 9.601 0.023 0.013 0.009 0.013 10.300 0.012 0.007	Al Zn Pb Sn Fe 0.001 0.000 0.010 0.004 0.033 9.601 0.023 0.013 0.009 0.078 0.013 10.300 0.012 0.007 0.057	AI Zn Pb Sn Fe Ni 0.001 0.000 0.010 0.004 0.033 0.001 9.601 0.023 0.013 0.009 0.078 0.007 0.013 10.300 0.012 0.007 0.057 0.005	Al Zn Pb Sn Fe Ni Si 0.001 0.000 0.010 0.004 0.033 0.001 0.009 9.601 0.023 0.013 0.009 0.078 0.007 0.044 0.013 10.300 0.012 0.007 0.057 0.005 0.004	Al Zn Pb Sn Fe Ni Si Cr 0.001 0.000 0.010 0.004 0.03 0.001 0.000 0.000 9.601 0.023 0.013 0.009 0.078 0.007 0.004 0.007 0.013 10.300 0.012 0.007 0.057 0.005 0.004 0.077

The cast samples were first machined with the help of a horizontal shaper machine to skin out the oxide layer from the surface and 12×20×20 mm3 size obtained from the cast alloys. Cold rolling of the alloys in an as-cast state was carried out with a laboratory scale rolling mill of 10HP capacity at different reduction percentages. The deformation given was about 1.0 mm per pass. Samples size of 4 x 15 x 15 mm was obtained for studying microhardness and electrical conductivity measurement. The alloy samples were isochronally aged at different temperatures for one hour and isothermally aged at various temperatures for different periods up to 240 minutes. For this purpose, an Electric Muffle Furnace JSMF-30T ranging 900± 3.0°C was used. The samples were sanded mechanically with emery papers of rough one and finally one of 1500 grits. Automatic Turret Micro Vickers Hardness Tester, model: HV-1000DT was used for measuring the microhardness of the aged samples where the Knoop indenter was applied with a 1Kg load for 10 seconds. At least ten indentations were practised from different locations on each polished sample. Electrical conductivity of the different heat-treated alloys was carried out with an Electric Conductivity Meter Type 979. Then the conductivity was converted to resistivity for plotting the graphs. Moreover, powder of the experimental alloys was prepared for measuring the reflectance by using UV Visible Spectrophotometer device. Differential scanning calorimetry (DSC) studies were carried out using DSC131 EVO Analyser. Inert N2 gas atmosphere was used during DSC experiments. The samples for DSC studies were a lump of 70 mg in weight. The samples were loaded in the DSC at room temperature, and each scan was conducted over a temperature range from 30°C to 600°C. A fixed heating rate of 10°C/min was used in all scans

The optical metallography of the samples was carried out in the usual way. In the case of using metallographic copper etchant a conventionally recommended one of Ammonium Hydroxide + Hydrogen peroxide (3%) was used where the compounds were taken in a 1:1 ratio. The cold rolled and aged samples were cautiously observed to take the photomicrographs by using an

Invert Metallurgical Microscope with Polarization USB Camera model SKU: ME1400TC-10MT.

RESULTS AND DISCUSSION

Cold deformation behavior

Fig. 1 illustrates the deviation of hardness on the degree of cold deformation of commercial pure Cu, Cu-10Al and Cu-10Zn alloys. It can be seen that all the experimental alloys achieve some hardness with the level of deformation because of the effect of strain hardening. That means the dislocation density increases with the rolling level, so the hardness as usual increases. Higher hardness values are gained for the Cu based alloys than that of commercially pure copper because the solid solution strengthening takes place through the dissolved Al and Zn atoms into the alloys [15, 16]. These solute atoms hamper the dislocation movement by pinning the grain boundary and therefore the cold rolled alloy keep a stable supersaturating density of dislocations, as a result, high work hardening rate [11]. In the case of Al-bronze, it appears the highest rate of work hardening. It may be attributed that during cold rolling some heat may be generated into the alloy which may form some intermetallics of copper aluminites to responsible for higher hardness. From the graph, it appears the minimum variation of hardness values of the experimental material is the higher scale used in the graph. Apart from the casting quality also dominates the different hardness behavior of the materials.



Fig. 1 Dependence of hardness of the alloys on the degree of deformation $% \left(f_{1}, f_{2}, f_{3}, f_{3},$



Fig. 2 Dependence of electrical resistivity of the alloys on the degree of deformation

The results of electrical resistivity on the level of cold deformation of the above commercial pure copper, Al-bronze and α -brass experimental alloys are presented in **Fig. 2**. The observed slowly increase in the electrical resistivity with the degree of

deformation is attributed to the results of two opposing effects. The reduced porosity of casted alloys during cold deformation results in a decrease the electrical resistivity. However, coldworking results in an increase in the electrical resistivity as it distorts the whole crystal lattice and makes it more difficult for electron flow into the materials. It appears that the first effect is lower than that of the second effect, and the electrical resistivity increases as a result. The earlier investigator also reported similar behavior for other copper alloys under different degrees of cold deformation [17]. Also, it is shown that the electrical resistivity of commercially pure copper is lower than in other alloys. Because alloying elements increases the electrical resistivity of the alloys. These circumstances electronscattering dislocations, as well as second phase particles, might be responsible for the higher resistivity. Al has the most notable influence than Zn on the increased electrical resistivity of copper as discussed earlier the formation of different intermetallics of aluminites during casting and rolling [11, 17].

Ageing behavior of cold deformed alloys

Isochronal Ageing

Isochronal age hardening curves of the cold deformed at 60% experimental alloys aged at different temperatures for one hour are demonstrated in Fig. 3. It is seen from the figure that in the initial stage of ageing all the alloys show a small softening. It is due to stress relieving and recovery of the cold deformed alloys. It may also be seen from the figure that at the 300°C temperature range, the hardness increases for Al added alloy. This data exhibited the age hardening effect of the alloy is due to the addition of Al. During solidification and ageing, various intermetallic phases are formed by the reaction of Al and Cu, such as CuAl2, AlCu, Cu4Al3, Cu3Al2, Al4Cu9. The most important intermetallic phases which influence the hardness of the alloy are Al4Cu9 and Cu3Al2 [18]. There is no age hardening effect in the Cu-10Zn alloy because less than 35 wt.% Zn exhibit a single a-phase FCC state Cu-Zn alloy which is not capable of age hardening effect; above this Zn content, the intermetallic β-CuZn would be formed, which may induce precipitation strengthening. At the intermediate stage of ageing, Al added alloy shows a modest decrease of the hardness for the reason that dissolve of GP zones before the formation of metastable phase into the alloys [19, 20].



Fig. 3 Change of microhardness of the 60% cold deformed experimental alloys when isochronally aged at different temperatures of one hour

On the other hand, the hardness of pure Cu and Cu-10Zn alloy decreases beyond the temperature at 300°C. The reason for this hardening phenomenon was segregation to dislocations and recrystallization. Precipitation coarsening and partial recrystallization responsible for this softening in the case of Cu-10Al alloy.

Cu-10Zn alloy demonstrates small variation with the reason advanced for this hardening phenomenon is solute segregation to dislocations, analogous to the formation of Cottrell atmospheres in interstitial solid solutions [17].

The electrical resistivity changes of the cold deformed at 60% commercially pure copper and its alloys with ageing temperatures are displayed in Fig. 4. At the initial period of ageing the small reduction of resistivity is shown owing to combined effects of stress relieving and recovery of the experimental alloys. During ageing at the lower temperature of the cold worked experimental alloys only dislocation rearrangements are taking place into the deformed grains. The electrical resistivity slowly increases with ageing temperature due to the formation of fine precipitates into the alloys and at the higher ageing temperature, the decrease of resistivity take place for precipitate coarsening and recrystallization of the experimental alloys [21]. These phenomenons are more prominent basically for the Al-bronze alloy. This is already stated that a lot of intermetallic phases are formed by Al and Cu during casting and ageing. These precipitated are accountable for the nature of variation of resistivity.



Fig. 4 Change of resistivity of the 60% cold deformed experimental alloys when isochronally aged at different temperatures of one hour.

Isothermal Ageing

Figs. 5 to **7** show the variation of the hardness of the 60% cold deformed commercially pure Cu, Cu-10Al and Cu-10Zn alloys aged at 250°C, 300°C and 350°C isothermally for different times respectively. No age hardening effect can be seen for Cu and Cu-10Zn alloys but two consecutive aging peaks are there for Cu-10Al alloys and achieve a higher hardness.



Fig. 5 Change of microhardness of the 60% cold deformed experimental alloys when isothermally aged at 250 °C for different time

The Cu and Cu-10Zn alloys always show the nature of continuous softening due to stress relieving, recovery and recrystallization respectively. The drop in hardness becomes more distinct with increasing ageing temperature. It is already stated that less than 35 wt.% Zn does not form the intermetallic β-CuZn in the Cu-10Zn alloy so it is not capable of precipitation hardening effects. In the course of ageing, the formation of GP zones and the metastable phases strengthen the Cu-10Al alloy efficiently and attain peak hardness. During aging of the Cu-10Al alloy metastable phases form through the dissolution of GP zones. Therefore, the ageing effect at this transition stage of the alloy must be low and it is supposed that dissolution of GP zones should be responsible for the lower aging value between two age hardening peaks. At the finishing stage of ageing for a long time, the strength of the alloy reduces due to over ageing effects as well as precipitation coarsening. At lower ageing temperatures the two consecutive ageing peaks for all the alloys are prominent. At higher ageing temperatures, the ageing process of the alloys namely GP zones formation, GP zones dissolution, metastable phase formation and grain coarsening occurs earlier. From the figures, it is clear that Cu-10Al alloy attains the peak condition when it is isothermally aged at 300°C for 30 minutes [22].



Fig. 6 Change of microhardness of the 60% cold deformed experimental alloys when isothermally aged at 300°C for different time



Fig. 7 Change of microhardness of the 60% cold deformed experimental alloys when isothermally aged at 350°C for different time

The variation of electric resistivity of the experimental Cu, Cu-10Al and Cu-10Zn alloys is shown in **Figs. 8** to **10**, when isothermally aged at 250°C, 300°C and 350°C for different times respectively. The initial drop in resistivity of the experimental alloys throughout isothermal ageing occurs due to dislocation rearrangement within the cold deformed alloys. The highest resistivity is found in the case of Cu-10Al alloy than that of commercially pure copper followed by Cu-10Zn alloys. Thus fine zones scatter the free electrons incoherently and thus resistivity increases till the time particle coarsening becomes so prominent as to diminish the incoherent scattering of electrons. At these temperatures during the ageing process, the precipitation of various copper aluminates intermetallic is formed, which is responsible for resistivity peaks in Cu-10Al alloy. The finishing decreases in resistivity give the impression of particle coarsening as reduces the number of scattering centres. At the higher ageing temperature since precipitate coarsening is significant so higher resistivity drop is visible. At the lower ageing temperature recovery is taken place as a result drop in resistivity. It is counteracted by the increasing of the ongoing precipitation process. As a result, depending upon the dominance of the particular event, the resistivity whichever remains constant or slightly increases while the alloys are aged at a lower temperature for an extended time [23, 24].



Fig. 8 Change of resistivity of the 60% cold deformed experimental alloys when isothermally aged at 250°C for different time



Fig. 9 Change of resistivity of the 60% cold deformed experimental alloys when isothermally aged at 300°C for different time



Fig. 10 Change of resistivity of the 60% cold deformed experimental alloys when isothermally aged at 350°C for different time

Reflectance properties

The spectrophotometric reflectance spectra of Cu, Cu-10Al and Cu-10Zn samples at room temperature, aged at 300°C and 500°C for one hour are shown in Figs. 11 to 13 respectively. It is found from all the Figures that the reflectance rises with the increase of wavelength and becomes higher in the visible region. This indicates that the low energy light absorbs by the materials. At any given wavelength, Cu-10Zn alloy exhibits the highest intensity of reflectance followed by Cu-10Al alloy whereas the commercially pure Cu shows the lowest (Fig. 11). It is clear from the reflectance spectrum curves that different materials are capable to absorb light at different wavelengths, the dominance of transmittance varies with the wavelength even for the same concentration of Cu. Coarse grain of Cu-10Al alloy causes the variation of reflectance using pure copper. It was figured out earlier that the transition cause increase in energy slightly with Zn concentration. These transitional energies are identical for the alloy in the whole aphase region. This variation is obvious; the reason is that the absorption is the opposite phenomenon of reflectance. The abrass contains a disordered, substitutional, face centred cubic structure and the increase of Zn content causes the color transformation from the reddish hue of pure Cu to the bright yellow of brass [25, 26].



Fig. 11 The reflectance as a function of wavelength of the copper based experimental alloys at room temperature



Fig. 12 The reflectance as a function of wavelength of the copper based experimental alloys after ageing treatment at 300°C for one hour

When 300°C temperature is applied for aging of the experimental alloys for one hour the graphs as presented in **Fig. 12** demonstrated the higher intensity of reflectance of all the alloys. It should be clarified that more strain free defects fewer grains are created through the heat treatment. Cold deformation typically distorts the overall crystal lattice and increases the dislocation density of the materials. These types of material defects play an important role in the reflectance behavior of all the materials. In the case of Al-bronze fine precipitates of different cu aluminites formed by heat treatment decelerate the reflectance behavior compare to pure copper.

Again the alloys when are subjected to the higher ageing temperature at 500°C both copper and Al-bronze show the declining nature of reflectance. **Fig. 13** demonstrates the aforesaid nature of the reflectance. It may be attributed to the pure copper change of grain orientation or crystal structure and for Cu-10Al alloy the higher amount of precipitation as well as precipitation coarsening responsible for this reduction of the reflectance through the Cu-10Zn alloys continue the intensity of reflectance through the uniform defect fewer grains into the alloy. These are created by fully recrystallised grain into the Cu-101Zn experimental alloy.



Fig. 13 The reflectance as a function of wavelength of the copper based experimental alloys after ageing treatment at 500°C for one hour

Thermal analyses

The results of DSC curves of the 60% cold deformed commercially pure Cu, 10% Al added Al-bronze and 10% Zn added α brass is shown in **Fig. 14**. From the figures, an exothermic peak is visible around 140°C on every heating curve that corresponds to all the alloys. It is due to stress reliving of the experimental alloys which were achieved by plastic deformation through the cold rolling at 60%. As a result, the release of the stored energy provides new strain-free grains into the alloys [27]. In the case of Cu-10Al alloy, another endothermic peak occurs at 175°C which is happened through the dissolution of some phase as present earlier into the alloys. The followed by a wide exothermic peak around 265°C is indicative of metastable phase formation into the alloy. This is associated with mainly the creation of CuAl₂ and Cu₉Al₄ intermetallics [28, 29]



Fig. 14 DSC heating curve of experimental Cu, Cu-10Al and Cu-10Zn alloys

Optical micrographs

The optical microstructure of 60% cold rolled commercially pure Cu, Cu-10Al Al-bronze and Cu-10Zn α-brass is shown in Fig. 15. The grains of the microstructure of all the alloys become elongated in the rolling direction and these are heavily distorted due to the action of cold rolling. The commercially pure copper microstructure consists of non-uniform grains as its reactivity, porosity, formation of surface cracking and internal cavities are high (Fig. 15. a) [30]. The microstructure of Al-bronze is Cu-10Al alloy is composed of different phases like α -phase, retained β' phase and several K-phases (Fig. 15. b) [31, 32]. The four most important types such as KI, KII, KIII and KIV phases are included in the K-phases. They can be illustrious by elements presents into the phases, location as well as distribution in the microstructures. More specifically KI is a rosette form, KII is the spheroids precipitate at the grain boundary, KIII a lathe-shaped lamellar phase and KIV the fine precipitate surrounded by the grains boundary. The microstructure of Cu-10Zn alloy α-brass reveals the single phase of zinc solid solution in alpha copper (Fig. 15. c). The Cu-Zn phase diagram also confirms that the complete solid solubility of zinc is utmost 35% into copper [33]. A huge amount of shear bands can be observed in all the microstructure. These bands appear on the micrographs voluntarily.



Fig. 15 Optical microstructure of cold deformed at 60% (a) Commercially pure Cu, (b) Al-bronze and (c) α -brass



Fig. 16 Optical microstructure of cold deformed at 60% followed by ageing at 500°C for 1 hour (a) Commercially pure Cu, (b) Al-bronze and (c) α -brass

Fig. 16 shows the optical micrographs of the experimental alloys after ageing treatment at 500°C for one hour. Several annealed twins are present in the copper grains and the elongated grains are almost absent into the microstructure due to recrystallization. The majority of annealed twins pass throughout the grain. (Fig. 16. a) [34]. The microstructure of Cu-10A1 aged alloy contains large numbers of κ precipitates with the elongated grains (Fig. 16. b). But the portion of the α phase is increased into the polyhedral grains. The spaces between the grains begin to irregular network. The polyhedral grains also consist of annealing twins along with the spherical particles of κ precipitates may be precipitates may be a solution of the α phase.

be visible. It can be seen from Fig. 16. c that the grain size of aged Cu-10Zn alloy is higher than the original pure copper because of grain growth under high temperatures. Grains with a few twins and precipitates on boundaries are observed for aged alloy. There is no trace of elongated grain into the microstructure, a homogenized recrystallized microstructure is observed in Cu-10Zn alloy.

CONCLUSION

Commerciality pure Cu, Al-bronze and α -brass were obtained by casting and the properties under different cold deformation and heat treatments were studied. The experimental results are concluded as,

The alloying elements Al and Zn noticeably increase the hardness of pure Cu due to solid-solution hardening. Additionally, Al forms hard and brittle intermetallic during ageing which improves the hardness of the alloy. Al has a pronounced effect on the decrease in the electrical resistivity of copper than that of Zn.

Al and Zn addition improve the reflectance behaviour of Cu and the thermal ageing enhances the reflectance behaviour of the alloys and it is prominent for Zn.

Cold rolled microstructures show the elongated grain parallel to the rolling direction. For a one-hour time duration at 500°C aging temperature, the microstructure of Cu-10A1 alloy reach a mixture of recrystallized and coarse non-recrystallized grains but a homogenized recrystallized microstructure is observed in Cu-10Zn alloy as well as in pure copper

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