Improvements in properties of sintered and cast Cu–Ag alloys by anneal hardening effect

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Copper and copper alloys containing 4 at.-% of silver were prepared by the cast method and by the powder metallurgy process. Sintered and cast samples of copper and alloys were subjected to the same thermomechanical treatment. Annealing up to recrystallisation temperature was performed, followed by hardness and electrical conductivity measurement. This investigation shows that the hardness and electrical conductivity of cold deformed Cu–4Ag alloys increase after annealing in the temperature range of 160–400°C due to the anneal hardening effect. It is shown that the amount of strengthening (caused by anneal hardening) increases with the increasing degrees of predeformation and that the increase of strength is more pronounced in the sintered than in the cast Cu–4Ag alloy. The electrical conductivity of the sintered alloy increases with the degrees of cold rolling, whereas the electrical conductivity of the cast alloy decreases. During annealing the electrical conductivity of both alloys slowly increases.

Keywords: Cu-4Ag alloy, Thermomechanical treatment, Copper, Anneal hardening effect

Introduction

The strength properties of cold worked substitutional solid solutions are increased upon annealing up to the recrystallisation temperature in several Cu based alloy systems. This strengthening effect is termed anneal hardening[1,2] and is mainly applied to copper alloys in the production of spring materials for electromechanical devices. Three general trends can be noted which characterise the phenomenon in all alloy systems: the amount of strengthening, which accompanies aging, increases with the increasing degree of predeformation; the strengthening increases with increasing substitutional element concentration and the strengthening due to aging is decreasing the function of the plastic strain at which the strength is measured.[1–4]

The mechanism responsible for this hardening effect has been investigated in several copper based alloys after cold rolling and annealing in the temperature range from150 to 300°C. The effect has been investigated mainly in cast copper based alloys and some observations have been interpreted to indicate that the atomic ordering is primarily responsible for the hardening effect.[1] On the other hand, in a recent detailed investigation of anneal hardening in Cu–Al alloys, it was concluded that the solute segregation to dislocations gives rise to the predominant hardening mechanism.[1,2]

Copper has excellent conductivity, but poor resistance to softening and low strength at moderate temperatures. This presents a considerable problem for engineers and designers of electrical equipment. The last few years have seen a major effort devoted to the investigation of copper based alloys in search of improvements in properties such as conductivity, strength and maintenance of strength at high temperatures. The literature shows a great deal of interest in Cu based alloys, particularly in Cu–Al, Cu–Mn, Cu–Sb.[1,2,4–6] The authors decided in favour of the Cu-Ag system due to its low electrical resistance in the investigations. For commercial use, not only electrical but also mechanical properties are of great importance.[7,8]

The present study shows the results of investigations on sintered and cast Cu–Al alloys conducted for the purpose of improving their properties by the anneal hardening effect and compares them with pure copper mutually.

Experimental

Copper based Cu–4Ag alloys were prepared for a study on the anneal hardening effect using two different ways of preparation: the common way casting and the powder metallurgy process in similar thermomechanical treatments.

The copper based Cu-4Ag alloy was melted in a laboratory electric furnace and cast into $65\times25\times180$ mm prism ingot in a sand clay mould followed by air cooling. Metallic silver and electrolytic copper wire with purity of 99·99% were used as the starting materials. The ingot was protected with a graphite cover and homogenised at 800°C for 24 h. Samples were cut from the homogenised material at a height of 7 mm and then prefinally cold rolled to the thickness of 5, 3·3 and 2·5 mm by a prefinal reduction of 29, 53 and 64%. After solution annealing (at 700°C for 1 h followed by ice water quenching), the samples were subjected to the final reduction of 20, 40 and 60% by cold rolling.

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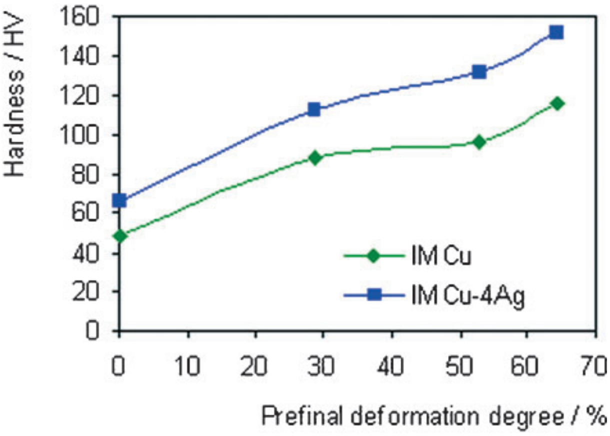
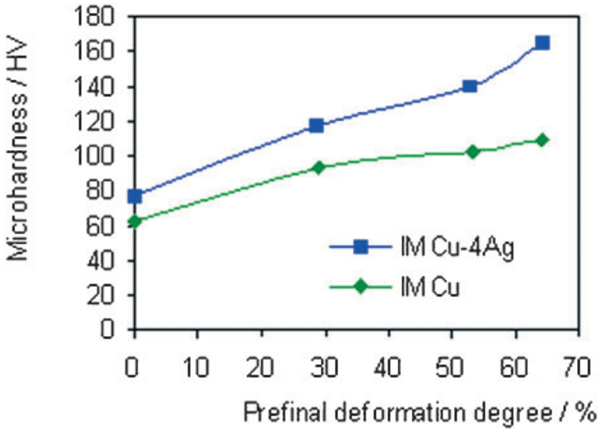


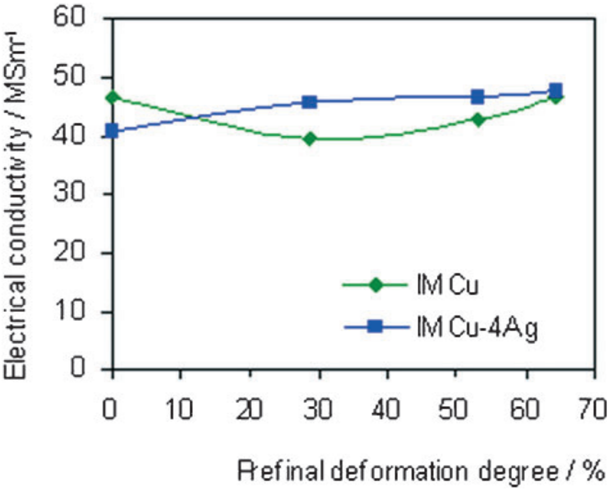
1 Dependence of hardness of cast samples on prefinal deformation degree

In the second phase of the experiment, the Cu–4Ag alloy was prepared by the powder metallurgy process. Electrolytic copper powder and silver powder with purities of 99·7 and 99·9% respectively were used as the starting materials. The silver powder content in the mixture was 4 at.-%. Powder mixture compacts measuring 6–7 mm in height, 30 mm in length and 12 mm in width were prepared by a method of one sided pressing with the pressure of 300 MPa on the hydraulic press. The compacts were sintered at 790°C in a horizontal tube furnace under an atmosphere of high purity dry hydrogen for 1 h. After sintering, the samples were subjected to the final reduction of 20, 40 and 60% by cold rolling. Vickers hardness, microhardness and electrical conductivity were measured following each step of rolling.

In the next stage both sets of samples (cast IM Cu–4Ag alloy samples and sintered PM Cu–4Ag alloy samples) were annealed in the temperature range between 150 and 600°C in 30 min intervals. Vickers hardness (applying load of 50 N) and electrical conductivity (Sigmatest) were measured following each annealing. Five different hardness and electrical conductivity measurements were recorded for each sample to minimise errors. The results were averaged for these measurements and reported as a single dataset with its appropriate standard deviation which was typically in the order of ±1% for hardness, i.e. ±0·2% for electrical conductivity.



2 Dependence of microhardness of cast samples on prefinal deformation degree



3 Dependence of electrical conductivity of cast samples on prefinal deformation degree

In order to compare some of the properties, an ingot of unalloyed Cu (OFHC quality) and sintered Cu were prepared and subjected to the same thermomechanical treatment as IM more exactly PM Cu–4Ag alloys.

Results and discussion

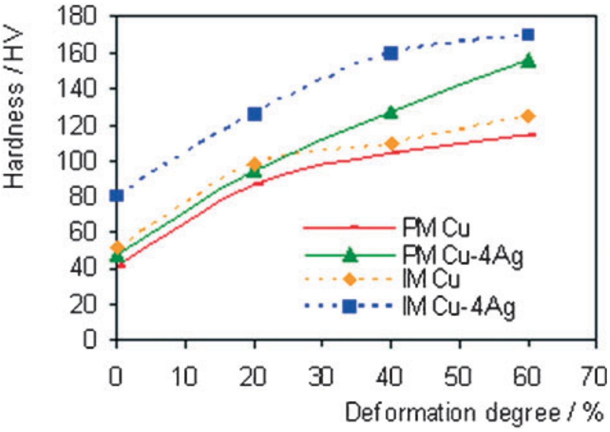
Prefinal rolling

The hardness and microhardness of IM Cu and IM Cu–4Ag alloy samples increases with the degree of prefinal cold deformation due to deformation strengthening (Figs. 1 and 2). Higher hardness values were obtained for the alloy than for copper.

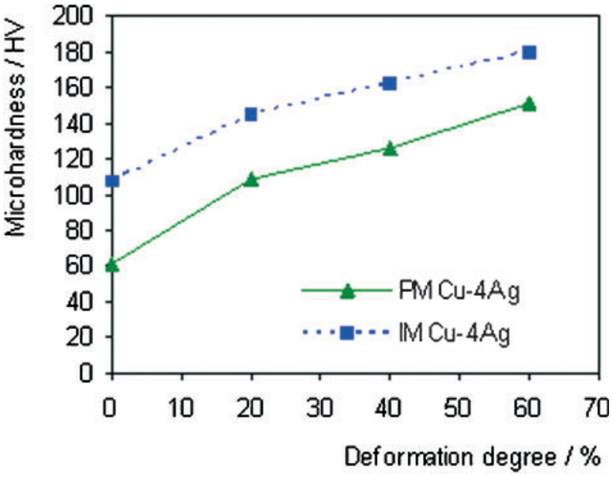
Figure 3 shows the change in the electrical conductivity of IM Cu and IM Cu-4Ag alloy samples after prefinal cold rolling. It can be seen that electrical conductivity slowly increases with the degree of deformation due to porosity decrease. Porosity here is caused by the captivation of gases during the casting.[9]

Final rolling

The hardness and microhardness of all samples increase with the degree of final cold deformation due to deformation strengthening (Figs. 4 and 5).



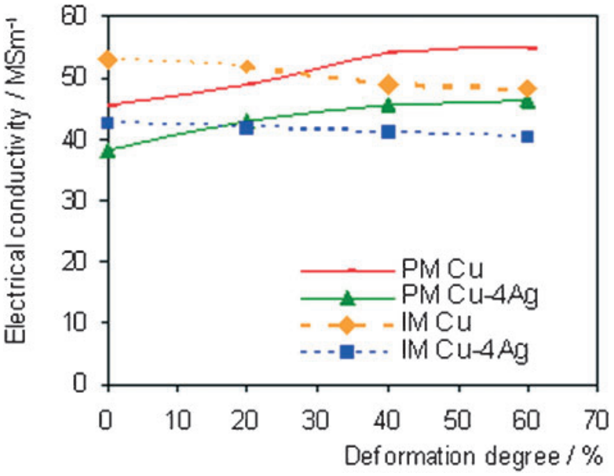
4 Dependence of hardness of IM and PM samples on final deformation degree



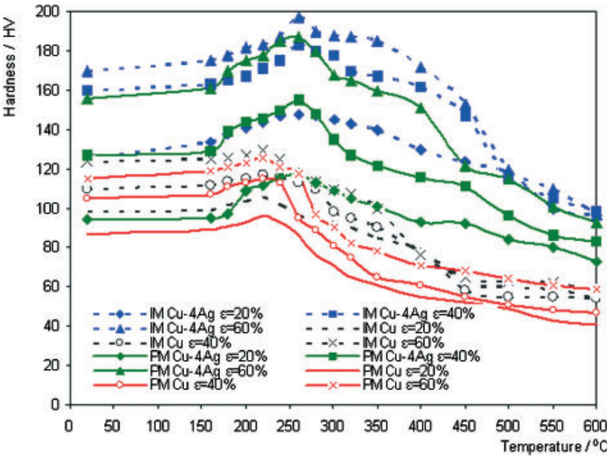
5 Dependence of microhardness of IM and PM samples on final deformation degree

After cold rolling with the same deformation degree, higher hardness values were obtained for Cu–4Ag alloy than for copper. The maximum hardness values after 60% deformation were 170, 156, 124 and 115 HV for IM Cu–4Ag, PM Cu–4Ag, IM Cu and PM Cu respectively. Although PM Cu and PM Cu–4Ag alloy samples which underwent cold plastic deformation still had lower hardness values in comparison with suitable hardness values of IM samples, more intensive hardness increase was achieved in PM samples, because deformation strengthening and porosity elimination were performed simultaneously.[10]

Figure 6 shows the change in the electrical conductivity of IM and PM Cu and IM and PM Cu–4Ag alloy samples after the final cold rolling. It can be seen that the electrical conductivity of Cu is slightly higher than that of Cu–4Ag alloys, because the alloying element silver has a smaller influence on the electrical conductivity than any other alloying element.[11] Figure 6 also shows that the electrical conductivity of PM Cu and PM Cu–4Ag alloy slowly increases with the degree of predeformation, but the electrical conductivity of IM Cu and IM Cu–4Ag alloy slowly decreases with the degree of predeformation. This is the result of two opposing effects.[12] The decrease in the porosity of samples during cold rolling results in an increase in electrical conductivity (effect 1).[12–15] However, it is well known that the increase in cold working results in the decrease in electrical conductivity (effect 2).[16] In the sintered alloy the first effect is stronger than the second one and electrical conductivity increases as a result. On the other hand, in the cast alloy the second effect is stronger than the first one, which results in a decrease in electrical conductivity.



6 Dependence of electrical conductivity of IM and PM samples on final deformation degree



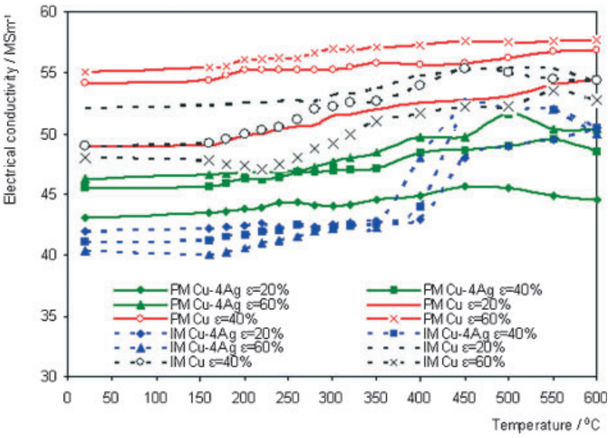
7 Variation of hardness of cold rolled IM and PM Cu and Cu–4Ag alloy with annealing temperature

Anneal hardening effect

After cold rolling with the final height reduction of 20, 40 and 60% all samples were annealed at the temperatures from 160 to 600°C. Figure 7 shows the dependence of hardness on the annealing temperature of the cold rolled sintered and cast alloy samples. It can be seen that the recrystallisation temperature is above 400°C for all deformation degrees, i.e. the alloying element Ag causes an increase in recrystallisation temperature in comparison with pure copper. Figure 7 shows that in the temperature range of 160–400°C the hardness values increase remarkably for all applied deformation degrees of 20, 40 and 60% for both alloys, sintered and cast. This effect has been investigated mainly in dilute copper alloys containing Al, Au, Ga, Pd, Rh, Ni and Zn.[1,2] The results would tend to support the hypothesis that solute segregation to dislocation, analogous to the formation of Cottrel atmospheres in interstitial solid solutions, is primarily responsible for the anneal hardening phenomenon.[1,2] Based on the experiments, after annealing cold deformed IM and PM Cu–4Ag alloy samples in the temperature range of 160–400°C, it was noticed that the anneal hardening effect appeared as a result of solute silver segregation to dislocations, which results in strengthening.[1,2,4,5,12,17]

Figure 7 shows that IM Cu–4Ag alloy deformed samples (20, 40 and 60%) at all annealing temperatures show higher hardness values than PM Cu–4Ag alloy samples deformed by the same deformation degrees. This is due to higher initial hardness values of cold deformed IM Cu–4Ag alloys in comparison with the initial hardness values of cold deformed PM Cu–4Ag alloys.

However, the anneal hardening effect is more intensive in PM Cu–4Ag alloy samples in comparison with IM Cu–4Ag alloy samples. The powder metallurgy process produces a microstructure with smaller grains



8 Variation of electrical conductivity of cold rolled IM and PM Cu and Cu–4Ag alloy with annealing temperature

and larger numbers of defects,[10] which is more suitable for the achievement of the anneal hardening effect in comparison with the microstructure obtained by casting. The maximum hardness increase of about 22 HV was achieved in IM Cu–4Ag alloy samples ($\varepsilon=20\%$) whereas this increase for PM Cu–4Ag alloy samples was about 24 HV. Annealing of IM Cu–4Ag alloy samples ($\varepsilon=40\%$) provided the maximum hardness increase of about 23 HV while this increase for PM Cu–4Ag alloy samples was about 28 HV. The maximum hardness increase, caused by the anneal hardening effect, was obtained in IM and PM Cu–4Ag alloy samples deformed with the highest deformation degree ($\varepsilon=60\%$), and it was about 27 HV, i.e. about 31 HV. Previous data are confirmed by the literature facts[1,2,4,5,12,17,18] that the amount of strengthening, which accompanies anneal hardening, increases with increasing degree of predeformation as result of larger numbers of defects, more intensive partial dislocation recombination and interactions of solute atoms with lattice defects during the annealing.

Cold deformed IM and PM Cu samples behave similarly during the annealing. Hardness drops significantly after annealing above 240–260°C as a result of formation and growth of a new undeformed grain, i.e. recrystallisation occurrence. The most intensive anneal hardening effect in IM and PM Cu–4Ag alloys was obtained at 260°C. However, in IM and PM Cu samples at the same temperature the hardness decreases considerably due to recovery and recrystallisation.

Figure 8 shows the dependence of electrical conductivity on the annealing temperature. The electrical conductivity of IM and PM Cu–4Ag alloys slowly increases with annealing in the temperature range of 160–400°C, where the anneal hardening effect appears, due to the segregation of the atoms of silver to dislocations, which contributed to the solid solution weakening. The copper atomic radius in the pure state is $R_{\mathrm{Cu}}=128$ pm,[19,20] while the silver atomic radius in the pure state is $R_{\mathrm{Ag}}=144$ pm.[20] This suggests that if the silver dissolves into the copper matrix, the copper matrix lattice parameter will be increased. Thus, as silver segregation occurs, the copper lattice becomes similar to that of pure copper and the electrical conductivity is enhanced.[21] During further annealing the electrical conductivity of both alloys increases due to recovery and recrystallisation.

The best combination of strength and electrical conductivity (197 HV, 42 MSm^{-1} for IM Cu–4Ag alloy and 187 HV, 47 MSm^{-1} for PM Cu–4Ag alloy) was achieved after annealing at 260°C cold deformed ($\varepsilon=60\%$) Cu–4Ag alloy.

Conclusions

1. The alloying element silver was found to have a pronounced effect on the increase of the recristallysation temperature of the cold rolled sintered and cast Cu–Ag alloys.
2. The anneal hardening effect has been observed in Cu–Ag alloys in the annealing temperature range of 160–400°C, the hardness being increased with the degree of predeformation.
3. The anneal hardening effect has an important role in the strengthening of Cu–4Ag sintered and cast alloys. The strengthening, caused by the anneal hardening effect of PM Cu–4Ag alloy, is higher than that of IM Cu–4Ag alloy.
4. The strengthening effect in Cu–Ag alloys can be employed in the production of electrical contacts.

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