

ANNEAL HARDENING EFFECT IN A CAST CuAl4Zn4 ALLOY DEPENDENCE ON THERMOMECHANICAL TREATMENT

Svetlana D. Nestorović, Desimir D. Marković,
Ljubica S. Ivanić, Svetlana Lj. Ivanov
University of Belgrade, Technical Faculty in Bor
VJ 12, 19210 Bor
Serbia

ABSTRACT

The investigations were carried out on the cast samples of Cu-4at%Al-4at% Zn alloy, as well as pure copper samples for the sake of comparison. Cast samples of alloy and copper were subjected to the same thermomechanical treatment. The thermomechanical treatment included the homogenized annealing at 850 °C for 24 h. After that the samples were carried out to the prefinal cold rolling and than to solution annealing at 450 °C for 2 h followed by an ice-water quenching and than cold rolling with 30 %, 50 % and 70 % in final reduction. The alloys in the cold rolled state were primary isochronally annealed up to the recrystallization temperature in purpose of investigation anneal hardening effect. Some of annealed samples of alloys were subjected again to the final cold rolling with 50 % in reduction. After that the cold rolled alloys were secondary annealed up to the recrystallization temperature in purpose of investigation anneal hardening effect after secondary annealing. Influence of thermomechanical treatment on the anneal hardening mechanism of a cast Cu-4at%Al-4at% Zn alloy has been investigated for the hardness and electrical conductivity measurements. The investigations has shown that the anneal hardening effect appeared in the cast Cu-4at%Al-4at% Zn alloy after primary as well as after secondary annealing and was followed by an increase in the hardness and electrical conductivity. The anneal hardening effect appeared in the temperature range of 150-400 °C after primary annealing as well after secondary annealing but with some lower of intensity.

Keywords: copper alloy, thermomechanical treatment, anneal hardening effect

1. INTRODUCTION

Copper is an important engineering material since it is widely used in its pure state and also in alloys with other metals. In its pure state it is the most important material in the electrical industry because the copper has excellent conductivity but poor resistance to softening and low strength at moderate temperatures. It has reasonable tensile strength, controllable annealing properties and general soldering and joining characteristics. For commercial use, both electrical and mechanical properties are of great importance. Alloyed copper in the form of brass, and bronze is used extensively throughout the mechanical engineering industry. Copper-beryllium alloys can be precipitation hardened to the highest strength levels attainable in copper-base alloys.

The strength properties of cold-worked substitutional solid solutions are increased upon annealing up to the recrystallisation temperature in several Cu based alloys systems. This strengthening effect is termed *anneal hardening* and is mainly applied to copper alloys when producing spring materials for electro-mechanical devices. Three general trends can be noted which characterize the phenomenon in all alloys systems. The amount of strengthening, which accompanies ageing, increase with increasing degree of prior cold work, the strengthening increase with increasing substitutional element

concentration, the strengthening due to ageing is decreasing function of the plastic strain at which the strength is measured [1-3].

The mechanism responsible for this hardening effect is investigated in several copper based alloys after cold rolling and annealing at 150 to 300 °C. The effect has been investigated mainly in cast copper base alloys and some observations have been interpreted as indicating that atomic ordering is primarily responsible for the hardening effect [3]. On the other hand, in a recent detailed investigation of anneal hardening in Cu-Al alloys [1], it was concluded that solute segregation to dislocations gives rise to the predominant hardening mechanism. However, the mechanism responsible for this hardening effect is incompletely understood [2-14].

The present paper shows the results of investigations on a cast Cu-4at%Al-4at% Zn alloy conducted for the purpose of improving their properties by the anneal hardening effect after primary and after secondary ageing, and compares them with pure copper.

2. EXPERIMENTAL

Investigated cast copper base alloy containing 4 at% Al and 4 at% Zn of a solute, produced in laboratory for casting. For comparison, parallel specimens made from cast pure copper (chemical composition: Cu>99,95%, O₂<0,04%, Bi<0,0005% and the rest impurities < 0,03%). The copper and copper base alloy containing 1,74 wt% Al and 3,9 wt% Zn as a solute were cast into a sand-clay mould with dimensions 80x80x30 mm, followed by air cooling. The cast alloy was homogenized at 850 °C for 24 hours in graphite and cut to dimension 80x30x7 mm on the erosimat aperture. After that the cold rolling was carried out on the samples and obtained prefinal dimensions of 2.1; 3.5 and 4.9 mm. The samples were solution annealed at 450 °C for 2 h followed by an ice-water quenching. After that the copper and copper alloy were subjected to cold rolling with 30, 50 and 70 % reduction on the final thickness of 2 mm for all samples. Following each step of TMT (thermo mechanical treatment) Vickers hardness and electrical conductivity were measured. After that the cold rolled copper and copper alloy samples were isochronally annealed in the temperature range between 150 and 600 °C up to the recrystallisation temperature, during which the values of hardness and electrical conductivity were measured. At last the samples of recrystallised alloys were subjected to cold rolling with deformation of 50 %. After measuring the hardness and electrical conductivity they were annealed again in the same temperature range of 150-600 °C in order to investigate the anneal hardening effect again after secondary annealing.

3. RESULTS AND DISCUSSION

3.1. Hardness and electrical conductivity of cold rolled cast samples

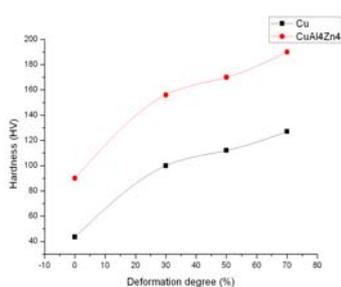


Figure 1. Dependence of hardness of cold rolled samples on deformation degree

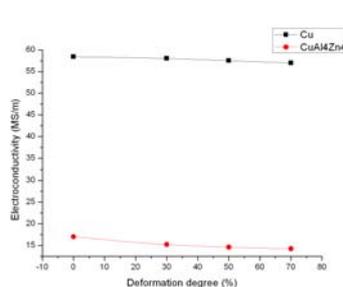


Figure 2. Dependence of electrical conductivity of cold rolled samples on deformation degree

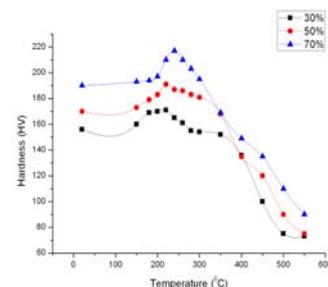


Figure 3. The change of hardness of cold-rolled samples of a cast CuAl4Zn4 alloy with annealing temperature

The hardness (Fig.1) of the samples during cold rolling increases with deformation degree due to deformation strengthening. Some higher hardness values were obtained for alloy, than for pure copper. Maximum values for hardness of copper is 127 HV but for alloy is 170 HV (deformation degree 70 %) i.e. maximum of work hardening was attained for the CuAl4at%Zn4at.% alloy.

Fig. 2 shows the changes of electrical conductivity during cold rolling i.e. the dependence of electrical conductivity on deformation degree. It can be seen, that the electrical conductivity for pure copper is higher than for alloy CuAl4at%Zn4at%. Also Fig. 2 shows that electrical conductivity for both samples slowly decreases with the deformation degree. It is known that the increase in cold working results in a decrease in electrical conductivity [5].

3.2. Anneal hardening effect

After cold rolling with the final height reduction of 30, 50 and 70%, all samples of alloy were annealed at the temperatures from 150-600⁰C. Fig. 3 shows the dependence of hardness on the annealing temperature of the cold rolled cast copper alloy samples. It can be seen that the recrystallisation temperature for all applied deformation degrees is above 450⁰C. Fig. 3 also shows that in the temperature range of 150-450⁰C, for the alloy, the hardness values increase remarkably for all the applied deformation degrees (30, 50, 70 %). On the temperature of 220⁰C the hardness values increase for 15 HV for deformation degree of 30 %, for 21 HV for deformation degree of 50 % and for 27 HV for deformation degree of 70 %. Previous data are confirmed by the literature fact [1-3] and by our investigation [4-11] that the amount of strengthening which accompanies anneal hardening i.e. *anneal hardening effect* increases with increasing degree of prior cold work as a result of larger numbers of defects, more intensive partial dislocation recombination and interaction of solute atoms with lattice defects during the annealing. This effect has been investigated mainly in the cast copper-base alloys containing Al, Ni, Au, Ga, Pd, Rh and Zn [1-3]. The results would tend to support the hypothesis that solute segregation to dislocation, analogous to the formation of Cottrell atmospheres in interstitial solid solutions, is primarily responsible for anneal hardening phenomenon [1,2].

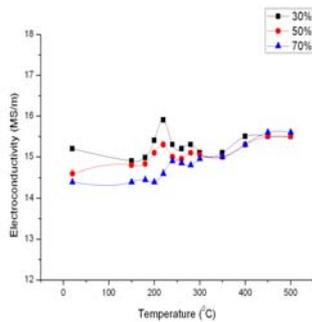


Figure 4. The change of electrical conductivity of cold-rolled samples of a cast CuAl4Zn4 alloy with annealing temperature

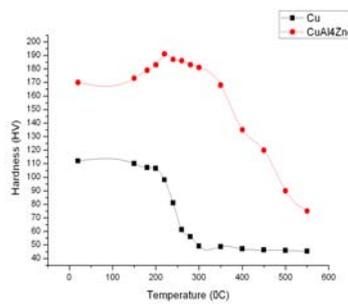


Figure 5. The change of hardness of cold rolled samples (50 %) of copper and alloy with primary annealing temperature

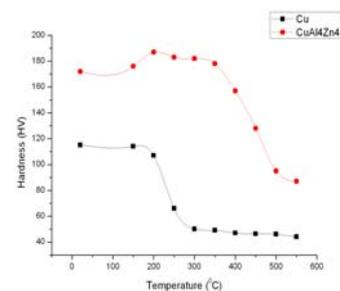


Figure 6. The change of hardness of cold rolled samples (50 %) of copper and alloy with secondary annealing temperature

Fig. 4 shows the influence of the annealing temperature on the electrical conductivity. During annealing, the electrical conductivity of the deformed Cu-Al-Zn alloy slowly increased due to anneal hardening effect. In the previous investigation of anneal hardening of a Cu-Al alloy [1], it was shown that the major decrease in electrical resistivity during annealing cannot be accounted for by short range ordering. It was concluded that segregation to dislocations is the only consistent interpretation for the major portion of the change in resistivity [6-14].

The influence of primary annealing temperature on the hardness of the CuAl4at%Zn4at% alloy and pure copper after final cold rolling of 50 % reduction is shown in Fig. 5.

Fig. 5 shows that in temperature range of 150-400⁰C, at the alloy the hardness values increase remarkably for applied deformation degree of 50 %. Peak hardness was reached after annealing CuAl4at%Zn4at% alloy at the temperature of about 220⁰C. Also it was noticed that anneal hardening effect appeared in the alloy as a result of solute segregation to dislocations. After annealing above 450⁰C the hardness considerably decrease due to mainly grain increase (coarse microstructure), i.e. due to the recovery and recrystallisation. After primary annealing, the recrystallized samples of copper and alloy were again subjected to cold rolling with 50 % in reduction and than secondary annealed. Fig 6. Shows the dependence of hardness on secondary annealing temperature. It can be seen that the

recrystallisation temperature for copper is above 220 °C, but for alloy above 450 °C. It can also be seen that the hardness increases for the alloy. In the first case (Fig. 5), the maximum hardness value increase in CuAlZn alloy samples about 15 HV at a temperature of 200 °C. Anneal hardening effect is more evident after primary annealing than after secondary annealing (Fig. 6).

The anneal hardening effect is well known for Cu base solid solutions alloys. This is due to the fact that these alloys are widely used as spring contact materials where strength in the elastic / plastic limit is of primary significance and has, therefore, been investigated intensively. Anneal hardening has also been found in the Al-Cr system where a size misfit of about 5 pct exists, similar to the magnitude of the misfit in the Cu-Rh system [2].

4. CONCLUSIONS

1. The alloying elements Al and Zn was found to have a pronounced effect on the increase of the recrystallisation temperature of the cold rolled CuAlZn cast copper alloy.
2. The anneal hardening effect has been observed in CuAlZn alloy in the annealing temperature range of 150-450 °C, The amount of strengthening increases with increasing the degree of prior cold work, the maximum values of hardness was established at 70 % deformation degree.
3. The strengthening, caused by anneal hardening effect were established after primary and after secondary annealing of cold deformed cast copper alloy, but some higher values after primary than after secondary annealing were obtained.

5. ACKNOWLEDGMENT

The authors are grateful to the Ministry of Education and Science of the Republic of Serbia for the financial support under Project TR 34003

6. REFERENCES

- [1] Vitek M., Warlimont H.: The Mechanism of Anneal Hardening in Dilute Copper Alloys, *Metallurgical Transactions A*, 10 (1979) 1889-1892.
- [2] Bader M., Eldis G.T., Warlimont H.: The Mechanisms of Anneal Hardening in Cu-Al Alloys, *Metallurgical Transactions A*, 7 (1976) 249-255.
- [3] Watanabe I., Watanabe E., Cai Z., Okabe T., Atsuta M.: Effect of Heat Treatment on Mechanical Properties of Age-hardenable Gold Alloy at Intraoral Temperature, *Dental Materials* 17 (2001) 388-393.
- [4] Rosner H., Kuhlmann O., Nembach E.: Dislocation Configurations in Ordered Copper-10 at.% Gold Solid Solutions, *Materials Science and Engineering A*, 242 (1998) 296-298.
- [5] Liu Q., Zhang X., Ge Y., Wang, J., Cui, J. Z.: Effect of Processing and Heat Treatment on Behavior of Cu-Cr-Zr Alloys to Railway Contact Wire, *Metallurgical and Materials Transactions A*, 37 (2006) 3233-3238.
- [6] Lekka C., Bernstein N., Mehl M., Papaconstantopoulos D.: Electronic Structure of the Cu₃Au(111) Surface, *Applied Surface Science*, 219 (2003) 158-166.
- [7] Nestorovic S., Markovic D., Markovic I., Influence of Thermal Cycling Treatment on the Anneal Hardening Effect of Cu-10Zn Alloy, *Journal of Alloys and Compounds*, 489 (2010) 582-585.
- [8] Nestorović S., Marković I., Marković D.: Influence of Thermomechanical Treatment on the Hardening Mechanisms and Structural Changes of a Cast Cu-6.6wt.%Ag Alloy, *Materials and Design*, 31 (2010) 1644-1649.
- [9] Nestorović S., Rangelov I., Ivanić Lj., Influence of Thermomechanical Treatment on the Anneal Hardening Mechanism of a Cast Copper-Silver Alloy, 11th International Research/Expert Conference, "Trends in the Development of Machinery and Associated Technology" TMT 2007, Hamamet, Tunisia, Proceedings, 259-263.
- [10] Nestorović S., Marković D.: The Strengthening by Anneal Hardening Effect in a Cast CuAl10 and CuZn10 Alloys, 12th International Research/Expert Conference, "Trends in the Development of Machinery and Associated Technology" TMT 2008, Istanbul, Turkey, Proceedings p. 1297-1301.
- [11] Nestorović S., Marković I., Marković D., Ivanić Lj.: Influence of Thermo cyclic Treatment on the Anneal Hardening Effect of a Cast CuAl and CuZn Alloys, 15th International Research/Expert Conference, "Trends in the Development of Machinery and Associated Technology" TMT 2011, Prague, Czech Republic, Proceedings, 153-157.
- [12] Nestorovic S., Markovic D., Ivanic Lj.: Anneal Hardening Effect in a Cast CuAl4Zn4 Alloy Dependence on Primary and Secondary Annealing and Deformation Degrees, 9th International Conference on Advanced Manufacturing Systems and Technology, AMST 2011, Proceeding, 439-446.