# INFLUENCE OF THERMO CYCLIC TREATMENT ON THE ANNEAL HARDENING EFFECT OF A CAST CUAI AND CUZn ALLOYS

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## ABSTRACT

The results of investigations on the influence of thermo cyclic treatment on the anneal hardening effect of a cast Cu-10Al and Cu-10Zn alloys are presented. The cast samples of both alloys were performed to the same thermo mechanical treatment. Quenched samples of both alloys were subjected to cold rolling followed by only annealing and annealing with thermo cycling treatment below the recrystallisation temperature. Anneal hardening effect has been observed with alloys in an annealing temperature range of 180- 300 OC, the hardness and electrical conductivity being increased with the amount of reduction at the prior cold - rolling. These investigations showed that the thermo cyclic treatment increased the intensity of anneal hardening effect some higher at Cu-Zn than at Cu-Al alloy. **Keywords:** anneal hardening effect, thermo cyclic treatment, Cu-10Al, Cu-10Zn

## 1. INTRODUCTION

The last few years have seen a major effort devoted to the exploration of copper-based alloys in the search for improvements of properties such as strength, conductivity, and stress retention at high temperature [1]. One of the processes which has the influence on the increase of mechanical characteristics is thermo cyclic treatment [2-5] consisting of alternating annealing and cooling of the supersaturated solid solution up to the recrystallisation temperature of copper alloys. The mechanism responsible for the increase of strength of cold worked substitutional alloys known as anneal hardening was previously investigated in some copper-based systems containing Al, Ni, Au, Ga, Pd, Rh, Zn [6-11]. The results of that papers 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 [6,7]. This strengthening effect could be applied to copper alloys when producing spring materials for electro-mechanical devices.

The aim of this study is to assess the influence of the thermo cyclic treatment on the anneal hardening effect of a copper-based Cu-10Zn and Cu-10Al alloys.

## 2. EXPERIMENTAL

Two the copper-based alloys containing 10at.% Zn and 10at.% Al as a solute were melted in a laboratory electro resistance furnace and cast into a copper molds. Ingots were protected with a graphite cover and homogenized at 850 0C for 24 h. Samples with dimensions 100x30x7mm were cut from the homogenized materials and then pre finally cold rolled. After that the samples were subjected to a thermo mechanical treatment (TMT), i.e.: after solution annealing (at 700 0C for 1 h followed by an ice-water quenching) samples were subjected to the finally reduction of 20, 40 and 60 % by cold rolling. Then samples were annealed in the temperature range 150-5000C, with holding time at annealing temperature of 30 min. One set of the samples was ice-water quenched following annealing (defined as thermo cycled, TC, samples), whereas another set was air-cooled after full annealing at annealing temperatures (defined as annealed, AN, samples).

Vickers hardness and electrical conductivity were measured following each annealing. Five measurements were performed for each annealing temperature.

#### 3. **RESULTS AND DISCUSSION**

### **3.1.** Cold rolled samples

The hardness of samples increases with the degree of prior cold deformation due to the deformation strengthening (Fig. 1). Higher hardness was obtained for Cu-10Al alloy, than for Cu-10Zn alloy and pure copper. Maximum hardness values after 60 % deformation are 115, 162 and 206 HV of copper, Cu-10Zn and Cu-10Al alloys, respectively.



rolled samples on deformation degree



Fig. 2 shows the change of electrical conductivity after cold rolling. It can be seen that electrical conductivity of pure copper is higher than for Cu-10Zn and Cu-10Al alloy. Fig. 2 also shows that electrical conductivity for all samples slowly decrease with degree of prior deformation.

## 3.2 Thermo cycled (TC) and annealed (AN) samples of Cu-10Zn and Cu-10Al alloys

Change of hardness of TC and AN samples as a function of annealing temperature is shown in Fig. 3. For all samples the hardness increases after annealing in the temperature range of 150-300 °C due to anneal hardening effect.



Figure 3. Hardness of TC and AN samples with annealing temperature

Figure 4. Electrical conductivity of TC and AN samples with annealing temperature

The maximum hardness increases for TC Cu-10Zn samples were achieved after annealing at 240 °C. These increases are about 30, 28 and 25 HV (in comparison with the initial cold-rolled condition) for 60, 40 and 20 % of deformation, respectively. The maximum hardness increases for AN Cu-10Zn samples were achieved after annealing at 240 °C, too. These increases are some lower than these obtained for AN Cu-10Zn samples (about 26, 25 and 19 HV for 60, 40 and 20 % of deformation, respectively).

The maximum hardness increases for TC Cu-10Al samples were achieved after annealing at 200  $^{\circ}$ C. These increases are about 21, 24 and 20 HV (in comparison with the initial cold-rolled condition) for 60, 40 and 20 % of deformation, respectively. The maximum hardness increases for AN Cu-10Al samples were achieved after annealing at 180-200  $^{\circ}$ C. These increases are some lower than these obtained for AN Cu-10Al samples (about 19, 16 and 15 HV for 60, 40 and 20 % of deformation, respectively).

It can be seen that values of hardness of TC samples are some higher than those of AN samples. Thermo cycling treatment at Cu-Zn alloy has more pronounced influence on the anneal hardening effect i.e. on the strengthening than at Cu-Al alloy. The maximum of hardness values for all samples are reached between 180 and 240  $^{\circ}$ C (higher degree of deformation shifts the maximum of hardness to lower annealing temperature, especially in the case of TC samples). After the maximum is reached hardness decreases slowly and at about 350  $^{\circ}$ C an abrupt decrease of hardness occurs. This decrease of hardness near 350  $^{\circ}$ C corresponds to the start of recrystallization. If the recrystallization temperature for the pure copper is reported to be around 200  $^{\circ}$ C [6, 7] then it is obvious that the anneal hardening not only strengthens but also increases recrystallization temperature of Cu-10Zn and Cu-10Al alloys at about 350  $^{\circ}$ C.

Change of electrical conductivity of TC and AN Cu-10Zn and Cu-10Al alloys samples as a function of annealing temperature is shown in Fig. 4. It can be seen that the electrical conductivity of TC and AN samples remains unchanged up to 200  $^{0}$ C and then starts to increase due to the anneal hardening effect. The slow increase above 350  $^{0}$ C is probably due to recovery and recrystallization. Bader et al. [6] obtained the similar results by electrical resistivity measurements.



Figure 5. Hardness of samples after thermo cycling and annealing as a function of annealing time at 200 °C

Figure 6. Electrical conductivity of samples after thermo cycling and annealing as a function of annealing time at  $200 \, {}^{0}C$ 

Figure 5 shows the change of hardness with time during annealing at 200  $^{0}$ C. For both TC and AN samples hardness increases due to anneal hardening effect up to 150 min, 180 min for Cu-10Al, Cu-10Zn alloys, respectively, and then slowly decreases with annealing time.

After 180 min of annealing the maximum of hardness of TC Cu-10Zn samples increases after prior deformation of 20, 40, 60 % for 31, 30 and 38 HV, respectively. The values of hardness of AN Cu-10Zn samples are somewhat lower.

After 150 min of annealing the maximum of hardness of TC Cu-10Al samples increases after prior deformation of 20, 40, 60 % for 25, 26 and 33 HV, respectively. The values of hardness of AN Cu-10Al samples are somewhat lower.

After 5h of annealing the values of hardness are higher compared to the cold-rolled condition for all samples which implies that the recrystallization does not occur. This may be explained by the fact that anneal hardening effect shifts the onset of recrystallization to higher temperatures.

Fig. 6 shows the change of electrical conductivity of TC and AN Cu-10Zn and Cu-10Al alloys samples with time during annealing at 200  $^{\circ}$ C. Generally, electrical conductivity increases with

annealing time showing a relatively small maximum after 150 min for Cu-10Al and after 180 min for Cu-10Zn where and hardness shows maximum. Conductivity of AN samples is some lower.

## 4. CONCLUSIONS

- The alloying elements, Zn and Al were found to have a pronounced effect on the recrystallisation temperature of cold rolled copper alloys increase of hardness due to anneal hardening effect.

- Anneal hardening effect was observed in the cold rolled Cu-10Al and Cu-10Zn alloys, during annealing with and without thermo cycling, in the temperature range between 150 and 300  $^{0}$ C and was followed by an increase in hardness and electrical conductivity.

- Thermo cycling treatment (TC) has more pronounced influence on the anneal hardening effect than annealing (AN) treatment.

- Thermo cycling treatment at Cu-Zn alloy has more pronounced influence on the anneal hardening effect i.e. on the strengthening than at Cu-Al alloy.

## 5. ACKNOWLEDGEMENT

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## 6. REFERENCES

- Morris D.G.: Recent research on advanced copper alloys: possibilities for Osprey spray deposition, Powder Metalurgy, 42 (1) (1999) 20-26.
- [2] Fedokin V.K., Smagorinskij M.E.:Termocikličeskaja obabotka metallov i detalej mašin, Mašinostroenie, Leningrad, 1989 (on Russian).
- [3] Li Z., Shen J., Cao F., Li Q.: A high strength and high conductivity copper alloy prepared by spray forming, Journal of Materials Processing Technology, 137 (2003) 60-64.
- [4] Stobrawa J., Ciura L., Rdzawski Z.: Rapidly solidified strips of Cu-Cr alloys, Scripta Materialia, 11 (1996) 1759-1763.
- [5] Monzen R., Watanabe C.: Microstructure and mechanical properties of Cu-Ni-Si alloys Materials Science and Engineering, 483-484 A (2008) 117-119.
- [6] Bader M., Eldis G. T., Warlimont, H.: The Mechanisms of Anneal Hardening in Cu-Al Alloys, Met. Trans. 7A (1976), 249-255.
- [7] Vitek J. M., Warlimont H.: The mechanism of anneal hardening in dilute copper alloys, Metall. Trans., 10A (1979), 1889.
- [8] Nestorović, S., Marković, D.: Influence of alloying on the anneal hardening effect in sintered copper alloys. Materials transactions JIM, 40 (3) (1999) 222-224.
- [9] [9] Nestorović S., Marković D., Marković I.: Influence of Thermal Cycling Treatment on the Anneal Hardening Effect of Cu-10Zn Alloy, Journal of Alloys and Compounds, 489(2010) 582–585
- [10] Nestorović, S., Milićević, B., Marković, D.: Anneal hardening effect in sintered copper alloys, Science of Sintering, 34 (2) (2002) 169-174.
- [11] 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.