Anneal hardening effect dependence on thermal cycling of copper base alloys

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Anneal hardening effect dependence on thermal cycling of Cu-Zn and Cu-Al alloys is studied in this paper. The cast samples of both alloys were performed to the same thermo mechanical treatment which included thermal cycling. The cast Cu-Zn and Cu-Al alloys are quenched and then subjected to cold rolling followed only by annealing or annealing with thermal cycling, below the recrystallization temperature. Anneal hardening effect has been observed in both alloys in an annealing temperature range of 180-300 ^oC, where the hardness and electrical conductivity being increased with the amount of reduction of prior cold rolling. These investigations showed that the thermal cycling increased the intensity of anneal hardening effect some higher at Cu-Zn than at Cu-Al alloy.

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1. Introduction

Copper base alloys have good combination of properties, high electrical and thermal conductivity. resistance to corrosion and good machinability [1,2]. These properties make them suitable for many applications e.g. electro mechanical devices. The main strengthening mechanisms in copper base alloys are work hardening, solid-solution strengthening and precipitation strengthening. Basic methods used to strengthen copper alloys generally also cause a pronounced decrease in electrical conductivity, so that a tradeoff must be made between electrical conductivity and mechanical strength [3]. Some other methods are often needed to increase the strengthening effect without bad effect on electrical conductivity [4,5]. Anneal hardening is genuine hardening mechanisms, that occurs alloying of pure copper with low solubility elements forming pre-saturation solid solution, and then making alloying elements to segregate on dislocation after cold deformation and annealing below the recrystallization temperature [6,7]. Consequently, the strength improves and the electrical conductivity of alloys is still high. Anneal hardening was previously investigated in some copper based systems containing Al, Ni, Au, Ga, Pd, Rh, Zn [6-12]. 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].

During the thermal cycling metals are alternately cooled and heated to optimize the particulate structure of the material throughout relieving stresses and making the metal denser and more uniform [13]. Among all heat treatment methods, thermal cycling treatment is the most effective means to reduce residual stress and improve dimension stability of the alloys [14]. However, the effects

of thermal cycling on the anneal hardening effect of copper alloys are not documented jet and this study provides experimental findings on this subject on two copper based alloys.

2. Experimental

The copper based alloys Cu-10at.%Zn (Cu-10Zn) and Cu-10at.%Al (Cu-10Al) used in the present work were produced in the laboratory electro resistance furnace and cast into a still molds with dimensions 100x100x30 mm. After ingot homogenization at 850 °C for 24 h, samples with dimensions 100x30x7 mm were cut and then pre-final cold rolled to pre-final height of 2.5, 3.3 and 5 mm. After solution annealing (at 700 °C for 1 h) and an ice water quenching, samples were final rolled to final height of 2 mm by rolling degrees of 20, 40 and 60 %. One set of samples was annealed in the temperature range 150-500 ⁰C, with holding time at annealing temperature of 30 min (defined as annealed, AN, samples). Another set of samples was thermal cycled (defined as thermal cycled, TC, samples) involved repeatedly cycling between temperature from temperature range 150-500 °C and 2 °C (ice-water) with a sufficient dwell time at either extreme to allow thermal equilibrium to be attained [15]. The samples underwent 3 cycles, while one cycle consisted of 10 min heating and ice-water quenching, so the total duration in which the TC samples are exposed to the high temperature is the same as AN samples.

The Vickers hardness and electrical conductivity of alloys samples were measured at room temperature after each step of experiment. Five measurements were performed for each annealing temperature. Hardness measurements were made using the Vickers hardness tester (VEB Leipzig) with a load of 50 N and a dwell time of 15 s. Electrical conductivity was measured following each annealing using electrical conductivity measuring instrument - Sigmatest. The instrument uses eddy currents to establish the resistance to the flow of current in the material and hence the conductivity [16].

3. Results and discussion

3.1 Strain hardening

The graph of hardness against strain hardening is shown in Fig. 1. The hardness values were increased by strain hardening i.e. deformation hardening. Deformation occurs principally by the motion of existing dislocation and creation of many additional dislocations [17, 18]. As the dislocation density increases with the cold deformation, it becomes more difficult for the dislocation to move through the existing mass of dislocation, hence the strain hardening increases with increasing cold deformation. The initial hardness values were 70 HV for Cu-10Zn alloy and 103 HV for Cu-10Al alloy. Maximum hardness values after 60 % deformation are 162 and 206 HV for Cu-10Zn and Cu-10Al alloys, respectively.

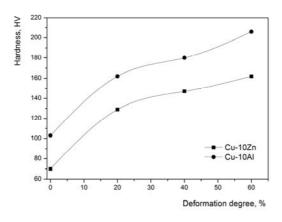


Fig. 1. Hardness dependent on deformation degree

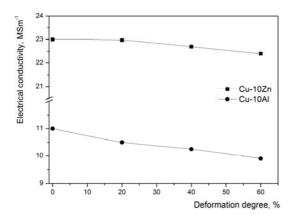


Fig. 2. Electrical conductivity dependent on deformation degree

Fig. 2 shows the change of electrical conductivity after cold deformation. Electrical conductivity slowly decreases with deformation degree, due to the increase of electronic scattering from lattice distortion or internal fault structure [19]. The initial electrical conductivity values were 23 MSm⁻¹ for Cu-10Zn alloy and 11 MSm⁻¹ for Cu-10Al alloy, and decreased to 22,4 MSm⁻¹ and 9,9 MSm⁻¹ after 60 % deformation, for Cu-10Zn and Cu-10Al, respectively. It can be seen that electrical conductivity of Cu-10Zn alloy is higher than for Cu-10Al alloy for all applied deformation degrees.

3.2 Anneal hardening effect

Change of hardness of TC and AN samples of Cu-10Zn and Cu-10Al alloys as a function of annealing temperature is shown in Fig. 3. For all samples the hardness values increase after annealing in the temperature range of 150-300 $^{\circ}$ C due to anneal hardening effect.

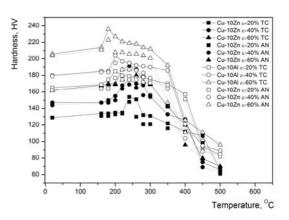


Fig. 3. Hardness of TC and AN samples of Cu-10Zn and Cu-10Al alloys with annealing temperature

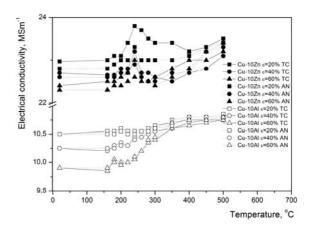


Fig. 4. Electrical conductivity of TC and AN samples of Cu-10Zn and Cu-10Al alloys with annealing temperature

The maximum hardness increases for TC Cu-10Zn samples were achieved after annealing at 240 $^{\circ}$ C. These increases are about 30, 28 and 25 HV (in comparison with the initial cold deformed condition) for 60, 40 and 20 % of deformation, respectively. The maximum hardness increases for AN Cu-10Zn samples were achieved after annealing at 240 $^{\circ}$ 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 deformed 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. In fact, thermal cycling may produce additional dislocations and accumulation of crystalline defects [20-22]. These dislocations might be responsible for shifts in the values of the hardness. Thermal 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 °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 °C an abrupt decrease of hardness occurs. This decrease of hardness near 350 °C corresponds to the start of recrystallization. If the recrystallization temperature for the pure copper is reported to be around 200 ^oC [23] 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 °C.

Change of electrical conductivity of TC and AN samples of Cu-10Zn and Cu-10Al alloys as a function of annealing temperature is shown in Fig. 4. For the TC and AN samples of Cu-10Zn and Cu-10Al alloys, annealing up to 250-300 °C slightly improves electrical conductivity by anneal hardening process while annealing at 300-400 °C rapidly increases electrical conductivity by recrystallization beginning. The increasing tendency becomes gentle as annealed at higher than 400 °C only by grain propagation [24]. Bader et al. [6] obtained the similar results by electrical resistivity measurements.

Figs. 3 and 4 show that hardness and electrical conductivity increase gradually with annealing temperature and come to hardness peak at 200-240 $^{\circ}$ C. Thus, these annealing conditions (i.e. annealing at 200 $^{\circ}$ C for 5h) were chosen as the base for isothermal annealing process for TC and AN samples of Cu-10Zn and Cu-10A1 alloys.

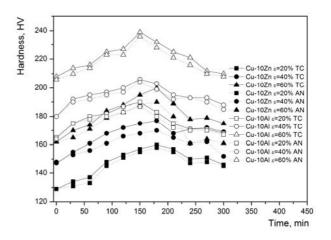


Fig. 5. Hardness of TC and AN samples of Cu-10Zn and Cu-10Al alloys with annealing time at 200 °C

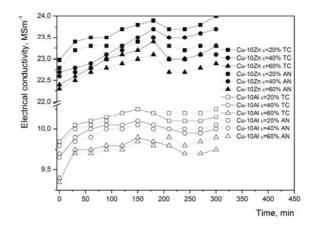


Fig. 6. Electrical conductivity of TC and AN samples of Cu-10Zn and Cu-10Al alloys with annealing time at $200^{\,0}C$

The effect of annealing at 200 ^oC on the hardness of TC and AN samples of Cu-10Zn and Cu-10Al alloys is shown in Fig. 5. For both TC and AN samples hardness increases due to anneal hardening effect up to 150 minutes for Cu-10Al or up to 180 minutes for Cu-10Zn alloys and then slowly decreases with annealing time. Even after annealing for 300 minutes the values of hardness are still higher in comparison with cold deformed condition i.e. recrystallization is not occurs for both set of samples (TC and AN).

The hardness values of TC Cu-10Zn alloy have reached a peak after annealing at 200 0 C for 180 minutes and continuously decreased afterwards. The highest hardness increases are about 31, 30 and 38 HV for 20, 40 and 60 % deformation degrees respectively. The values of hardness of AN Cu-10Zn samples are somewhat lower. After annealing at 200 0 C for 150 min the hardness values of TC Cu-10Al samples increase 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 reaching maximum, hardness of all cold deformed samples gradually decreases with the progress of annealing and after 5 h of annealing there is incomplete recrystallization because the hardness values are still higher compared to the cold deformed state.

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 ^oC. Electrical conductivity of TC samples increased with annealing time and it was about 23-24 MSm⁻¹ for Cu-10Zn alloy after 180 minutes, and about 10 MSm⁻¹ for Cu-10Al alloy after 150 minutes. Electrical conductivity of AN samples is some lower than electrical conductivity of TC samples.

4. Conclusions

Annealing in the temperature range between 150 and 300 °C after cold rolling was developed to optimize the combination of strength and electrical conductivity of Cu-10Zn and Cu-10Al alloys due to anneal hardening effect.

Thermal cycling (TC) has more pronounced influence on anneal hardening effect than annealing treatment (AN) according to the same thermo mechanical treatment of the alloys.

Thermal cycling at Cu-Zn alloy has more pronounced influence on anneal hardening effect than at Cu-Al alloy.

The strength properties are retained for long time of both set (TC and AN) of Cu-Zn and Cu-Al alloys after thermo mechanical treatment.

Anneal hardening effect have a pronounced effect on the increase of the recrystallization temperature of cold rolled Cu-Zn and Cu-Al alloys.

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References

- E.A. Ashour, B.G. Ateya, Electrochim. Acta, 42(2), 243 (1997).
- [2] S. Nagarjuna, K.K. Sharma, I. Sudhakar, D.S. Sarma, Mat. Sci. Eng. A-Struct. 313, 251 (2001).

- [3] L. Lu, Y. Shen, X. Chen, L. Qian, K. Lu, Science Magazine, **304**(5669), 422 (2004).
- [4] D. Lu, J. Wang, W. Zeng, Y. Liu, L. Lu, B. Sun, Mat. Sci. Eng. A-Struct. 421, 254 (2006).
- [5] Z. Dachuan, T. Ke, S. Mingzhao, T. Mingjing, Trans. Nonferrous Met. Soc. China, 16, 459 (2006).
- [6] M.Bader, G. T. Eldis, H. Warlimont, Met. Trans. A, 7, 249 (1976).
- [7] J. M. Vitek, H. Warlimont, Metall. Trans. A, 10, 1889 (1979).
- [8] S. Nestorović, D. Marković, Mater. T. JIM, 40(3) 222 (1999).
- [9] S. Nestorović, D. Marković, I. Marković, J. Alloy. Compd. 489, 582 (2010).
- [10] S Nestorovic, D. Markovic, Lj. Ivanic, Bull. Mater. Sci. 26(6), 601 (2003).
- [11] S. Nestorović, I. Marković, D. Marković, Mater. Design, 31, 1644 (2010).
- [12] S. Nestorović, I. Rangelov, D. Marković, Powder Metall. 54(1), 36 (2011).
- [13] C. Lingfei, W. Mingpu, L. Zhou, X. Ben, S. Yuchang, Trans. Nonferrous Met. Soc. China, 12(4), 716 (2002).
- [14] M. Zhao, G. Wu, D. Zhu, L. Jiang, Z. Dou, Mater. Lett. 58(12-13), 1899 (2004).
- [15] N. L. Hancox, Mater. Design, 19(3), 85 (1998).
- [16] D.J. Thewsey, Y.Y. Zhao, Phys. Status Solidi, 205, 1126 (2008).
- [17] A. G. Guy, J. J. Hren, Elements of physical metallurgy, 5th Edition, Addison-Wesley Publishing Co., California, U.S.A. (1994).
- [18] F.J. Zerilli, R.W. Armstrong, J. Appl. Phys. 61, 1816 (1987).
- [19] J.B. Liu, L. Meng, Y.W. Zeng, Mat. Sci. Eng. A-Struct. 435-436, 237 (2006).
- [20] L.A. Matlakhova, E.C. Pereira, A.N. Matlakhov, S.N. Monteiro, R. Toledo, Mater. Charact. 59(11), 1630 (2008).
- [21] Y. Nakata, T. Tadaki, K. Shimizu, Trans. Japan Inst. Metals, 26(9), 646 (1985).
- [22] H. Jiang, T.S. Rong, D. Hu, I.P. Jones, W. Voice, Intermetallics, 14(12) 1433 (2006).
- [23] Y. Zhang, J. Tao Wang, C. Cheng, J. Liu, J. Mater. Sci. 43, 7326 (2008).
- [24] L. Zhang, L. Meng, Mater. Lett. 58, 3888 (2004).

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