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ANNEAL HARDENING EFFECT IN SINTERED COPPER ALLOYS DEPENDENCE ON ALLOYING ELEMENTS AND DEFORMATION

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ABSTRACT
This paper reports results of investigation carried out on sintered copper alloys: Cu-8at%Ni, Cu- 8at %Zn, Cu-8at%Al, Cu-8at%Ag, Cu-4at%Ni-4at%Sn, Cu-4at%Ni-4at%Zn and Cu-4at%Au. For comparison, investigation carried out on the sintered copper. The sintered alloys, as well as pure copper, were subjected to the same thermomechanical treatment. Thermomechanical treatment included cold rolling of 30,50 and 70% in reduction. Isochronal and isothermal annealing up to the recrystallization temperature were performed, followed with hardness and electrical conductivity measuring. This investigation shows that hardness and electrical conductivity of cold deformed copper-alloys increase after annealing in the temperature range of 160 - 400°C, due to anneal hardening effect. Electrical conductivity decreases with increasing the amount of alloying elements. During the annealing the electrical conductivity slowly increases for both set of the samples copper and alloys due to recovery and recrystallization
Keywords: copper, copper alloys, thermo mechanical treatment, anneal hardening effect

1. INTRODUCTION

The last few years have seen a mayor effort devoted to the exploration of copper based alloys in the search for improvements in properties such as strength, conductivity and maintenance of strength at high temperature [1].

The strength properties of cold-worked substitional solid solutions are increased upon annealing up to the recrystallization 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 substituional element concentration, the strengthening due to ageing is decreasing function of the plastic strain at which the strength is measured [1- 4].

The mechanism responsible for this hardening effect is investigated in several copper based alloys after cold rolling and annealing at 150 to 300^{0}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, it was concluded that solute segregation to dislocations gives rise to the predominant hardening mechanism [3, 4].

The hardening has been ascribed to different mechanisms such as hardening by Cottrell and Suzuki locking, solute clusters, ordered clusters and precipitation hardening. The phenomena have been investigated in some papers, particularly on the model systems Cu-Zn and Cu-Al, but detailed studies of the underlying processes are still locking. Previous studies on *anneal hardening* showed that the amount of strengthening increases with increasing degree of prior cold work and with increasing substitutional element concentration [4-11].

This paper presents part of our research relating to the *anneal hardening* on a number of copper base alloys. The aim of this study is to assess the influence of copper alloying with 8at % of: Ni, Al, Zn, Ag, Ni + Sn, Ni+Zn and 4at%Au on the intensity of anneal hardening effect. The goal were improvements in properties of sintered copper alloys by anneal hardening mechanisms which occurs in this alloys.

2. EXPERIMENTAL

Sintered copper base alloys and sintered copper (for the sake of comparison), have been prepared for a study on anneal hardening effect using powder metallurgy treatment.

The basic electrolytic copper powder and powders of Ni, Al, Zn, Ni+Sn, Ni+Zn, Ag, Au, purity 99.7% and 99.9% respectively were used as the starting materials. The content of the alloying powders in the mixture was constancy of 8at. %. Compacts of powder mixtures with 6-7mm in height, 30mm in length and 12mm in with, were prepared by a method of one-sided pressing with the pressure of 300MPa on the hydraulic press. The compacts were sintered at 790^{0}C (for Cu-Ag) and at 850^{0C} (for the Cu-Ni, Cu-Ni-Sn, Cu-Ni-Zn, Cu-Au alloys) in a horizontal tube furnace under an atmosphere of high purity dry hydrogen for 1h. After sintering, samples were subjected to the reduction of 30, 50 and 70% by cold rolling.

In the next stage after cold rolling the sets of samples were annealed in the temperature range between 150 and 600^{0}C (in steps of 20^{0}C up to 320^{0}C, and 50^{0}C after 320^{0}C) with holding time at annealing temperature of 30min. Vickers hardness (applying load of 5kp) and electrical conductivity ("Sigmatest") were measured following each annealing.

In order to compare some of the properties sintered copper were prepared and subjected to the same thermo mechanical treatment as copper base alloys.

3. RESULTS AND DISCUSSION

3.1. Cold rolling

The hardness and micro hardness of all sintered samples after cold rolling increased with deformation degree due to the deformation strengthening (Fig. 1 and Fig. 2).

Some higher hardness values were obtained for alloys than for pure copper. Maximum hardness was about 190HV, of deformation degree of 70% for CuNi4at%Sn4at% alloy i.e. maximum of work hardening was attained at the same alloys by micro hardness tested.

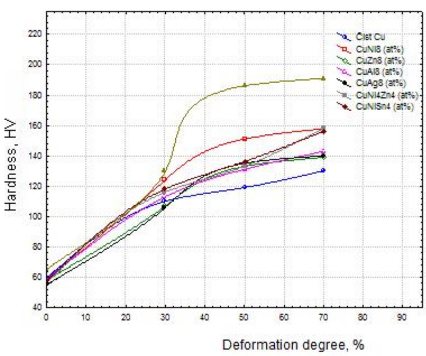

Figure 1. Dependence of hardness of sintered samples on deformation degree

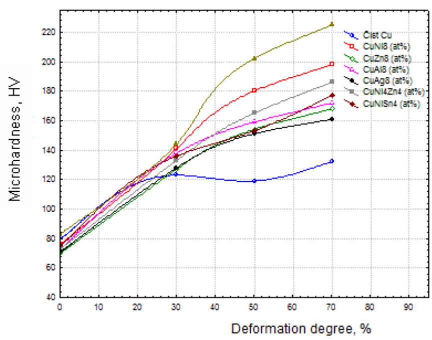

Figure 2. Dependence of micro hardness of sintered samples on deformation degree

Fig. 3 shows the change in electrical conductivity of Cu and Cu–8at%Ni, Cu–8at%Al Cu–8at%Zn, Cu–8at%Ag, Cu–4at%Au, Cu-4at%Ni +4at%Sn, Cu-4at%Ni+4at%Zn, alloys samples after cold rolling. It can be seen that the electrical conductivity of Cu is higher than for copper alloys, because the alloying elements decreases in electrical conductivity but Au and Ag lass than any with any other alloying elements (Ni, Al and Zn) [11]. Fig. 3 also shows that electrical conductivity of P/M Cu and

P/M alloys slowly increases with the degree of prior deformation. This is the result of two opposing effects [5,11]. Decrease in the porosity during cold rolling results in increase in electrical conductivity (effect 1). However, it is known that the increase in cold-working results in decrease in electrical conductivity (effect 2). The first effect is bigger than the second, and electrical conductivity increases as a result. Therefore the contents of alloying elements must be less, because the alloying elements decrease in electrical conductivity.

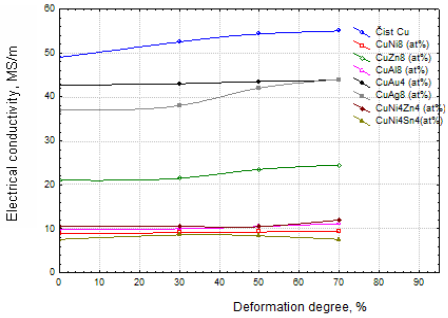

Figure 3. Dependence of electrical conductivity of sintered samples on deformation degree

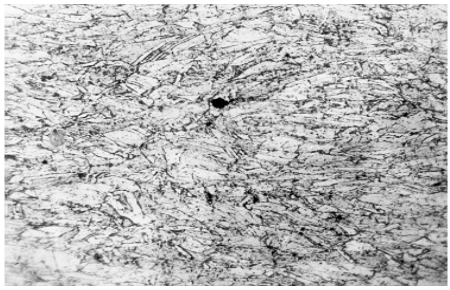

Figure 4. Optical microphotograph of a microstructure of CuNi4Sn4 alloy(deformed 70%)x600

3.2. Anneal Hardening Effect

The influence of annealing temperature on the hardness of the copper and copper alloys after cold rolling with 50% of deformation degree is shown in figure 5. The samples were annealed in the temperature range of 150-500^{0}C. Fig.4. shows that in the temperature range of 200-350^{0}C, the hardness values increase remarkably for all alloys for applied deformation degree of 50%, but for pure copper decrease above 200^{0}C. The maximum hardness increase of about 20HV at Cu-Au alloy, and for 17HV at Cu-Ni-Sn alloys the other alloys were also strengthening but about 10 HV. It can be seen that the recovery and recrystallisation temperature for pure copper sample are above 200^0 C, but above 350 ^{0}C (Cu-Ni; Cu-Zn; Cu-Al; Cu-Ag; Cu-Au and Cu-Ni-ZN) alloys, and above 450^{0}C for Cu-Ni-Sn alloy. The alloying elements cause in increase in the recovery and recrystallisation temperatures in comparison with pure copper. After annealing above 200^{0}C for copper and above 450^{0}C for all the alloys the hardness considerably decrease due to recovery and recrystallisation and hardness values is about for sintered condition.

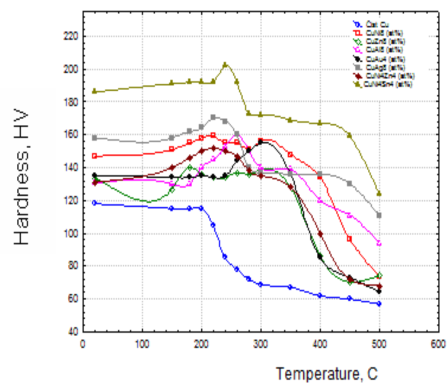

Figure 5. Variation of hardness of cold rolled (50%) P/M (Cu and Cu- alloys) with annealing temperature

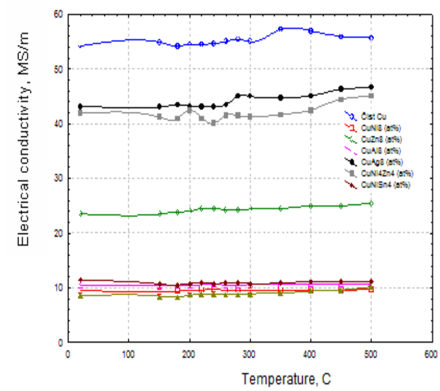

Figure 6. Variation of electrical conductivity of cold rolled (50%) P/M (Cu and Cu- alloys) with annealing temperature

The anneal hardening behavior of copper alloys solid solutions with a constant 4at%, of solute content of Al, Au, Ga, Ni, Pd, Rh, and Zn was previously reported [3,4]. If we assume solute segregation to dislocations, analogous to the formation of Cottrell atmosphere, as the mechanism of anneal hardening effect, the flow stress should be increased by the binding of solute atoms to dislocations [3, 4]. The contribution of anneal hardening to the flow stress was shown to decrease rapidly with increasing plastic strain [4]. The interactions of solute atoms with lattice defects such as dislocations, vacancies and stacking faults introduced during rolling, however, may also cause a considerable increase in flow stress. Solute interactions with vacancy clusters could possibly contribute to the strengthening too [3, 4].
Figure 8 shows the dependence of electrical conductivity on the annealing temperature. During annealing the values of electrical conductivity of copper and alloys slowly increases with annealing in the temperature range of 150-400^{0}C, where anneal hardening effect appears, due to the segregation of the atoms of silver to dislocations which is contributed to the depleting of solid solution on alloying element. Above 450^{0}C electrical conductivity increase at all alloys is contributed to recrystallization.

4. CONCLUSIONS

1) The alloying elements nickel, aluminum, zinc, tin, silver and gold were found to have a pronounced effect on the increase of recovery and recrystallization temperature of cold rolled sintered copper alloys.
2) Anneal hardening effect was attained in the temperature range of 180 – 450^{0}C.
3) The amount of strengthening increased with increasing degree of prior cold work.
4) The electrical conductivity slowly increases during cold working because the porosity decreases. After annealing above 450^{0}C, the hardness considerably decreases but the electrical conductivity increases due to recovery and recrystallisation.
5) The most improved properties were at Cu-Ag and Cu-Au alloys with the best electrical conductivity in comparison with the other alloys.
6) The strengthening effect in Cu-Ag alloys can be employed in the production of electrical contact.
7) Anneal hardening effect is more expressive in ternary than binary systems.

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5. REFERENCES

[1] Morris D.G.,: Recent research on advanced copper alloys: possibilities for Osprey spray deposition, Powder Metalurgy, 42, 1(1999) 20.
[2] Varschavsky A, Donoso E.: A calorimetric investigation on the kinetics of solute segregation to partial dislocations in Cu–3.34at%Sn, Mater. Sci. Eng. A 251 (1998) 208-215.
[3] Bader M., Eldis G. T., Warlimont, H.:The Mechanisms of Anneal Hardening in Cu-Al Alloys, Met. Trans. 7A (1976), 249-255.
[4] Vitek J. M., Warlimont H.: The mechanism of anneal hardening in dilute copper alloys, Metall. Trans., 10A (1979), 1889.
[5] Nestorović, S.D., Marković, D.D.: Influence of alloying on the anneal hardening effect in sintered copper alloys. Materials transactions JIM, 40 (3) (1999) 222-224.
[6] Lee S. J., Lee S. W., Kim K. H., Hahnb J. H., Lee J. C.: A high strength Cu-based alloy containing superlattice structures, Scripta Materialia, 56 (2007) 457-460.
[7] Varchavsky A., Donoso E.: Modelling the kinetics of solute segregation to partial dislocations in cold-rolled copper alloys Materials Letters, 31 (1997) 239-245.
[8] Nestorović S., Marković D., Tančić D., European Congress and Exibition on Powder Metallurgy, EPMA, 2001, vol 2, 158-164.
[9] Nestorović, S.D., Milićević, B., Marković, D.: Anneal hardening effect in sintered copper alloys. Science of Sintering, 34 (2) (2002) 169-174.
[10] Liu J. B.,. Meng L, Zeng Y. W. : Microstructure evolution and properties of Cu–Ag microcomposites with different Ag content, Materials Science and Engineering A, 435-436 (2006) 237-244**.**
[11] Nestorovic S., Markovic D., Ivanic Lj., Influence of degree of deformation in rolling on anneal hardening effect of a cast copper alloy, Bull.Mater.Sci., 26 (6) (2003) 601-604.