The 8th Pacific Rim International Congress on Advanced Materials and Processing
Edited by: Fernand Marquis
TMS (The Minerals, Metals & Materials Society), 2013

INFLUENCE OF LOW TEMPERATURE ANNEALING ON MECHANICAL BEHAVIOR OF Cu AND Cu-Ge ALLOY PROCESSED BY COLD ROLLING

Y.L. Gong [1], X.X. Wu [2], S.Y. Ren [2], L.P. Cheng [2], Y. Long [2], X.K. Zhu [2]*

[1]Faculty of Science, Kunming University of Science and Technology, Kunming, Yunnan, China.
[2]Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, Yunnan, China.

Keywords: Copper alloys; Cold rolling; Annealing; Mechanical behavior

Abstract

The mechanical properties of ultra-fine grained pure copper and Cu-Ge alloy samples produced by cold rolling followed by annealing in the temperature range between 100 and 250 °C for 1h have been studied. It is found that the strength of pure Cu decreases dramatically, while Cu-0.1at.%Ge alloy reduces slightly and Cu-5.7at.%Ge alloy remains basically unchanged after annealing at 150 °C for 1h. However, the Cu-9.0at.%Ge alloy exhibits unusual anneal hardening. The ductility of pure Cu after annealing increases dramatically, while that of Cu-Ge alloys changes slightly. The effect of solute element content and low temperature annealing on the microstructure and mechanical behavior of alloys is investigated in this paper.

Introduction

Nanostructured/ultrafine grained (NS/UFG) metals produced by severe plastic deformation (SPD) have aroused great research interest around the world and received much development during the past decades because of their superior properties [1]. NS/UFG metals by SPD usually have high strength, however their ductility is relatively low [2]. Many strategies have been applied to improve the tensile ductility of NS/UFG materials [3]. Thermal treatment is one of the effective routes usually used to improve the mechanical properties of NS/UFG materials [4]. Recently, research suggests an increase in the hardness and tensile strength of NS/UFG materials produced by SPD and subsequent recovery annealing, in which annealing is conducted at a temperature below the onset of recrystallization. The anomalous anneal hardening behaviors, which are totally opposite to the typical anneal softening behaviors of conventionally coarse-grained materials, have attracted intensive attention.

It has also been shown that the hardness and tensile strength of nanocrystalline materials can significantly increase while grains remain constant during low-temperature annealing treatment [5, 6]. A dislocation source hardening mechanism has been proposed to explain the annealing-hardening of nanostructured Al produced by accumulative roll-bonding [7]. The anneal hardening effect of nanocrystalline Ni-W alloys can be attributed to the relaxation of non-equilibrium grain boundary structure [8]. The Cu alloys exhibit anneal-hardening behavior as a

---

* Corresponding author. Tel.: +86-871-65198154; fax: +86-871-65161278.
E-mail address: xk_zhu@hotmail.com.

result of the interaction of solute atoms with lattice defects during annealing [9-11]. Enhancing strength with reasonable ductility can be found in Al-Cu-Li alloy processed by SPD together with subsequent annealing treatment, which is associated with fine precipitates [12]. In one study, the anneal hardening of heavily deformed FCC metals arises from annealing twin boundaries strengthening [13]. As has been said, various hypotheses have been proposed to explain a peculiar hardening effect. However, further work is needed to improve our understanding of properties and microstructures of NS/UFG materials during annealing.

In the present study, UFG pure Cu and Cu-Ge alloys with various Ge additions (corresponding to different stacking fault energy, SFE) were fabricated by severe rolling at room temperature and then recovery annealing in the temperature range of 100–250 ^{o}C for 1 h. The effect of low temperature annealing treatment on the microstructures and mechanical properties of Cu alloys and the possible mechanisms of anneal hardening behavior are explored systematically.

Experimental method

Cu (SFE ~ 78 mJ/m^2 [14]) and Cu-xGe (x = 0.1, 5.7, and 9.0 at.%, with SFEs of 54, 15, and 8 mJ/m^2, respectively [15]) in this work were produced by induction vacuum melting using 99.9% Cu and 99.99% purity Ge. The casting was hot-rolled into ~ 7.9 mm thick plates, and then annealed at 600 ^{o}C for 4 h in an argon atmosphere to obtain homogeneous microstructure. The materials were subsequently rolled at room temperature to the final thickness of ~ 0.3 mm. The rolling reduction was approximately 96%. Recovery annealing was applied to the cold-rolled (CR) sheets at temperatures ranging from 100 to 250 ^{o}C for 1 h.

The grain size, micro-strain and dislocation density in the CR and heat treated samples were characterized by means of X-ray diffraction (XRD). XRD was carried out on a Rigaku X-ray diffractometer using Cu-Ka radiation at an acceleration voltage of 40 kV and a current of 200 mA. To make accurate measurements of these parameters, pure Cu powder (99.95% purity) annealed at 700℃ in vacuum was used as an XRD peak-broadening reference.

Dog-bone shaped tensile specimens were machined with the tensile axis parallel to the rolling direction. The gauge length was 15 mm, and the width was 5 mm. The tensile tests were conducted at room temperature on a Shimazu AG-X universal material testing machine with constant crosshead speed of 0.09 mm/min, which corresponded to a strain rate of 1.0×10^{-4} s^{-1}.

Experimental results

The XRD patterns of cold rolled Cu-Ge alloys before and after annealing at 150 ºC for 1 h are shown in Figure 1. It can be seen that XRD patterns contained no appreciable peaks from Ge besides those from Cu, indicating extensive solubility of all germanium compositions. Moreover, there were negligible changes in the patterns before and after annealing. As a result, no second phase presence was found by XRD after annealing.

The micro-strain values and average grain sizes for the CR and annealed samples of Cu alloy can be calculated from the XRD peak broadening. The dislocation density ρ can be calculated from grain size d and micro-strain $(<\varepsilon>^2)^{1/2}$ according to the following relationship [16, 17]:

$$\rho = \frac{2\sqrt{3}\left(\varepsilon^{2}\right)^{1/2}}{d_{XRD}b} \tag{1}$$

where b is the absolute value of the Burgers vector. For FCC metals, $b = \left(\sqrt{2}/2\right)a$, a is the lattice parameter.

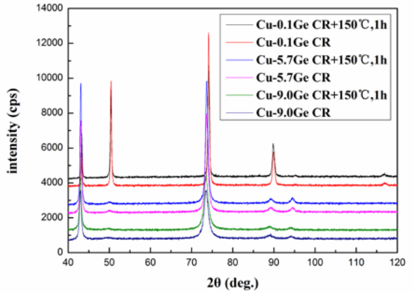

Figure 1. X-ray patterns of Cu-Ge alloys before and after annealing at 150 ºC for 1 h.

The dependence of grain sizes, micro-strains and dislocation densities of CR and annealed alloys estimated by XRD on the solute concentration is shown in Figure 2. It can be seen that no obvious grain growth occurred as the result of heat treatment. It is shown that the microstructure parameters change slightly during annealing at 150 °C, which indicates that the recovery effects are likely to be less pronounced. In particular, for Cu-9.0Ge, micro-strain, grain size and dislocation density remain basically unchanged after annealing at 150 °C, which may be attributed to high solute content.

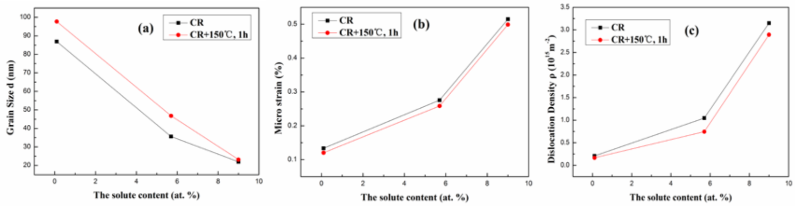

Figure 2. Variation of (a) Grain size, (b) micro-strain, and (c) dislocation density of Cu-Ge alloys with different solute concentration before and after annealing at 150 °C for 1 h.

The tensile engineering stress-strain curves of Cu and Cu-Ge alloys before and after thermal annealing are shown in Figure 3. The tensile behaviors of low temperature annealed Cu and Cu-Ge alloys share several characteristics depending on the germanium contents. It is interesting to note that the tensile strength of Cu-9.0 Ge increased while elongation reduced, exhibiting anomalous anneal-hardening behavior. The strength of CR Cu-5.7Ge remained basically unchanged after annealing at 150 °C. For CR Cu-0.1Ge alloy, the strength decreased slightly and ductility increased in the temperature range of 100–200 °C. The strength and elongation of alloys changed slightly after low temperature annealing at 150 °C, which shows annealing in this temperature corresponding to the recovery process. In contrast, it can be seen from Figure 3 (d), after annealing at 150–250 °C, the strength of CR Cu decreased and the tensile elongations increased dramatically, exhibiting the typical anneal softening behavior. The soften temperature increases with increasing Ge addition, because solute atoms restrict the motion of grain boundaries to retard recrystallization.

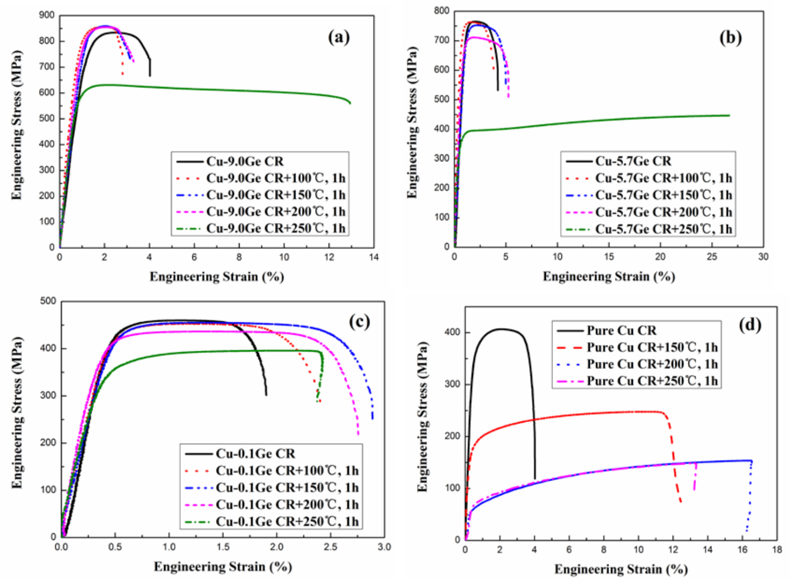

Figure 3. The tensile engineering stress-strain curves of severely cold-rolled Cu and Cu-Ge alloy before and after annealing: (a) Cu-9.0Ge, (b) Cu-5.7Ge, (c) Cu-0.1Ge and (d) pure Cu.

The effect of annealing temperature and Ge content on the tensile properties of low temperature annealed Cu-Ge alloys is summarized in Figure 4. As can be seen, for Cu-9.0Ge, the tensile strength is firstly increased with increasing temperature and then decreased. The anneal-hardening effect appeared on the CR Cu-9.0Ge alloy in the temperature range of 100–200 ^{o}C. The optimal hardening temperature of CR Cu-9.0Ge alloy is 150 ^{o}C, at which the yield strength increases from 736 MPa to 801 MPa and the ultimate tensile strength increases from 834 MPa to 859 MPa. As the annealing temperature increased to 250 ^{o}C, all the Cu-Ge alloys exhibited a considerable strength reduction and increased elongation, which may be attributed to the onset of recrystallization in these alloys. In general, alloy with higher Ge content exhibited higher tensile strength after annealing at the same temperature. The transition from considerable softening to hardening after low temperature annealing occurs as the Ge content increases.

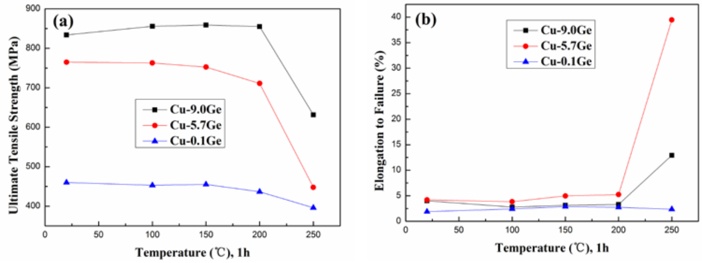

Figure 4. Changes in (a) ultimate tensile strength and (b) elongation to failure as a function of isochronal heat treatment (1 h) for Cu-9.0Ge, Cu-5.7Ge and Cu-0.1Ge.

Discussion

In the SPD-processing materials with grain sizes in a submicron (100-1000 nm) or nanocrystalline (<100 nm) range, high angle grain boundaries of metals account for a significant volume fraction of materials. These grain boundaries with excess dislocations, misfit regions or excess grain boundary energy are often called "non-equilibrium" grain boundaries, which can play a significant role in the development of the mechanical properties of UFG materials [18-21].

Excess defects in these non-equilibrium grain boundaries will annihilate during heat treatment through a so called "grain boundary relaxation" process [8]. There is no obvious change in grain size and texture after low temperature annealing, while gain boundary regions become more ordered. Grain boundary relaxation removes excess grain boundary dislocations and decreases the amount of available dislocation sources, consequently leading to the need of higher applied stress for activating new dislocation sources in the course of tensile deformation [8]. The elevation of strength results from the depletion of available dislocation sources caused by moderate thermal annealing. The decrease in the density of dislocation resources and interior dislocations during annealing may increase the strength and reduce the elongation [7].

As mentioned previously, although NS/UFG pure Cu and Cu alloys were produced under the same conditions, there was a significant difference in the mechanical properties between them. This illustrates solute element plays a curial role in annealing behavior. It is well known that solute element can interact with all kinds of structural defects like vacancies, dislocations, stacking faults and grain boundaries, which have a marked influence on the mechanical properties of materials.

It can be seen that the softening temperature of Cu-Ge alloy is higher than that of pure Cu, and therefore the alloying element Ge causes an increase in recrystallization temperature in comparison with pure Cu. The addition of only 0.1at.% Ge to Cu was found effective at stabilizing the grains in the nanocrystalline state and retaining the strength during annealing. When Ge was added in concentration of 9 at.%, the alloy underwent substantial hardening induced by annealing. The addition of solute atoms has been found useful in reducing grain growth by two basic ways, i.e. the kinetic approach and the thermodynamic approach [22]. First, the grain boundary mobility is reduced by solute drag, consequently preventing grain growth. On the other hand, the solute atoms may diffuse to grain boundaries during annealing, resulting in the reduction of grain boundary energy by solute segregation. Thus, the driving force for boundary migration and grain growth is reduced dramatically [23]. At temperatures below the recrystallization temperature, the change in mechanical properties results from the competition between the softening caused by deformation recovery and strengthening caused by solute. It is likely that at temperatures below 250 ^{o}C, the deformation recovery was sluggish, thus the strength of Cu alloys decreased slightly or even increased after annealing. In general, increasing the amount of alloying elements in the alloy can reduce the dislocation recovery rate during annealing and maintain high strength [24].

As already noted, pure Cu exhibited obvious anneal softening effect. However, the strength of Cu-Ge alloys can be retained or even enhanced during annealing as solute atoms content increases. Cu-9.0Ge with highest solute concentration exhibits the most obvious hardening behavior. It can be seen from XRD analysis that the lattice parameter of CR Cu-Ge alloys changed during annealing, which shows solute clustering at dislocations [10]. Thus, the anneal hardening effect of Cu-Ge alloy may result from solute atoms segregation to dislocations, analogous to the formation of Cottrel atmospheres in interstitial solid solutions, which leads to an increase in the strength of Cu alloys after annealing [9, 10]. The Cu-9.0Ge has high solute segregation rates, which increase with dislocation density [25]. In addition, for Cu-9.0Ge alloy with the lowest SFE, almost all dislocations slip out in partials. The distance between the partials should be several times the Burger's vector, so the segregation process to one partial is hardly affected by the other partial [25]. In a word, the solute segregation effect is the most significant in the Cu-9.0Ge alloy. The dislocations are effectively pinned by solute segregation and cannot glide, climb and annihilate during thermal treatment, which is the main reason for annealing hardening [9, 10]. In addition, a larger amount of solute atoms may segregate to the non-equilibrium boundary after annealing. The driving force for GB segregations is usually the minimization of the grain boundary energy. It seems that GB segregations could also affect the deformation mechanisms, leading to an increase of the strength.

Conclusion

(1) The strength of CR pure Cu reduced significantly after low temperature annealing.
(2) After annealing at temperatures below 250 ^{o}C, the strength of CR Cu-0.1Ge and Cu-5.7Ge alloys changed slightly, while CR Cu-9.0 exhibited unusual hardening behavior.
(3) During annealing at 150 ^{o}C, slight grain coursing occurred in CR Cu alloys, and micro-strain and dislocation density decreased to a small extent.
(4) The concentration of solute plays the most important role in the mechanical properties of metals after low temperature annealing. The hardening by annealing may occur when the solute content reaches the critical value. The anneal-hardening can be attributed to a variety of factors, of which solute segregation may be the most important.

Acknowledgements

The authors would like to acknowledge financial supports by the National Natural Science Foundation of China (NSFC), Grant No. 50874056.

References

1. R.Z. Valiev, R.K. Islamgaliev, and I.V. Alexandrov, "Bulk nanostructured materials from severe plastic deformation", *Progress in Materials Science*, 45 (2) (2000), 103-189.

2. C.C. Koch, "Optimization of strength and ductility in nanocrystalline and ultrafine grained metals", *Scripta Materialia*, 49 (7) (2003), 657-662.

3. E. Ma, "Eight routes to improve the tensile ductility of bulk nanostructured metals and alloys", *JOM*, 58 (2006), 49-53.

4. Yinmin Wang et al., "High tensile ductility in a nanostructured metal", *Nature*, 419 (6910) (2002), 912-915.

5. A.J. Detor, and C.A. Schuh, "Microstructural evolution during the heat treatment of nanocrystalline alloys", *Journal of Materials Research*, 22 (11) (2007), 3233-3248.

6. Y.M. Wang et al., "Effects of annealing and impurities on tensile properties of electrodeposited nanocrystalline Ni", *Scripta Materialia*, 51 (11) (2004), 1023-1028.

7. X. Huang, N. Hansen, and N. Tsuji, "Hardening by Annealing and Softening by Deformation in

Nanostructured Metals", *Science*, 312 (5771) (2006), 249-251.

8. T.J. Rupert, J.R. Trelewicz, and C.A. Schuh, "Grain boundary relaxation strengthening of nanocrystalline Ni–W alloys", *Journal of Materials Research*, 27 (09) (2012), 1285-1294.

9. M. Bader, G. Eldis, and H. Warlimont, "The mechanisms of anneal hardening in Cu-Al alloys", *Metallurgical and Materials Transactions A*, 7 (2) (1976), 249-255.

10. J. Vitek, and H. Warlimont, "The mechanism of anneal hardening in dilute copper alloys", *Metallurgical and Materials Transactions A*, 10 (12) (1979), 1889-1892.

11. S. Nestorović, I. Marković, and D. Marković, "Influence of thermomechanical treatment on the hardening mechanisms and structural changes of a cast Cu–6.6 wt.%Ag alloy", *Materials and Design*, 31 (3) (2010), 1644-1649.

12. M.A. Muñoz-Morris, and D.G. Morris, "Severe plastic deformation processing of Al–Cu–Li alloy for enhancing strength while maintaining ductility", *Scripta Materialia*, 63 (3) (2010), 304-307.

13. N. Jia et al., "On the anomalous hardening during annealing of heavily deformed f.c.c. metals", *Materials Science and Engineering: A*, 527 (4–5) (2010), 1143-1150.

14. M.H. Loretto, L.M. Clarebrough, and R.L. Segall, "Stacking-fault tetrahedra in deformed face-centred cubic metals", *Philosophical Magazine*, 11 (111) (1965), 459-465.

15. A. Vinogradov et al., "Effect of solid solution hardening and stacking fault energy on plastic flow and acoustic emission in Cu-Ge alloys", *Materials Science and Engineering A*, 341 (1-2) (2003), 57-73.

16. G.K. Williamson, and R.E. Smallman, "III. Dislocation densities in some annealed and cold-worked metals from measurements on the X-ray debye-scherrer spectrum", *Philosophical Magazine*, 1 (1) (1956), 34-46.

17. R.E. Smallman, and K.H. Westmacott, "Stacking faults in face-centred cubic metals and alloys", *Philosophical Magazine*, 2 (17) (1957), 669-683.

18. G. Wilde et al., "Plasticity and Grain Boundary Diffusion at Small Grain Sizes", *Advanced Engineering Materials*, 12 (8) (2010), 758-764.

19. G. Nurislamova et al., "Nanostructure and related mechanical properties of an Al–Mg–Si alloy processed by severe plastic deformation", *Philosophical Magazine Letters*, 88 (6) (2008), 459-466.

20. Y.R. Kolobov et al., "Grain boundary diffusion characteristics of nanostructured nickel", *Scripta Materialia*, 44 (6) (2001), 873-878.

21. S. Ranganathan, R. Divakar, and V.S. Raghunathan, "Interface structures in nanocrystalline materials", *Scripta Materialia*, 44 (8–9) (2001), 1169-1174.

22. C.C. Koch, "Structural nanocrystalline materials: an overview". *Journal of Materials Science*, 42 (5) (2007), 1403-1414.

23. M.A. Atwater, R.O. Scattergood, and C.C. Koch, "The stabilization of nanocrystalline copper by zirconium", *Materials Science and Engineering: A*, 559 (0) (2013), 250-256.

24. N.H. Lee et al., "Effect of manganese addition on the tensile properties of cold-rolled and recovery-annealed aluminum alloy sheets", *Materials Science and Engineering: A*, 535 (0) (2012), 297-305.

25. A. Vrschavsky, and E. Donoso, "A calorimetric investigation on the kinetics of solute segregation to partial dislocations in Cu–3.34at%Sn", *Materials Science and Engineering: A*, 251 (1–2) (1998), 208-215.