The Annal Hardening and Deformation Softening Behaviors of Nanocrystalline Cu-Zn Alloys

Jian Yang1,*,1, Yanzhao Pang1,*,1, Peng Li1,*,1, Zhe Yin1,*,1, Yulan Gong2 and Xinkun Zhu1,*,2

1 Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, China
2 Faculty of Science, Kunming University of Science and Technology, Kunming, Yunnan 650093, China

The changes in the mechanical properties and microstructure of nanocrystalline Cu-Zn alloys deformed by cryorolling during low temperature annealing and the post-process deformation were studied. The deformed Cu-Zn alloys exhibited uncommon anneal hardening and deformation softening behaviors. The degree of anneal hardening and deformation softening increased with the addition of the solute atoms. X-ray diffraction analysis and transmission electron microscopy were employed to reveal the microstructure of the samples in different states. The annealing hardening effect is ascribed to the contribution of solute segregation to dislocation and short range ordering.

Keywords: anneal hardening, cryorolling, copper-zinc alloys, deformation softening, mechanical properties, microstructure

1. Introduction

In recent years, the bulk ultrafine grained (UFG) or nanocrystalline (NC) metals fabricated by severe plastic deformation (SPD) have been widely researched due to their outstanding physical and mechanical properties.1,2,11 Under relatively low temperatures condition, SPD methods such as high-pressure torsion (HPT),3,4 equal channel angular pressing (ECAP),5 accumulative roll bonding (ARB)6 and cold rolling7,8 can efficiently refine grains and improve the mechanical properties of raw materials by heavy deformations. A higher dislocation density and consequently higher strength could be obtained by suppressing the dynamic recovery in the cryorolling process.9,10 It can be concluded that heavy cold rolling is efficient and economical to generate UFG materials compared with other SPD processing techniques.

It is well known that the softening behavior of cold working metals can be achieved by annealing treatment, which can be used to relieve the residual stress and homogenize the microstructure and composition in metals and alloys. Nevertheless, it has been observed that the hardening behavior of the cold deformation coarse-grain copper-based alloys can be induced by low temperature annealing treatment.1,11 Previous studies indicated that the effect of anneal hardening in metal and alloys can be attributed to the solute segregation,12,13 short range ordering (SRO),14 annealing twins,15-17 and dislocation source limited strengthening.18 A softening behavior induced by the deformation after low temperature annealing has been found in some metals and alloys.18,19 Huang et al. has recently put forward a dislocation source limited strengthening mechanism to interpret the phenomenon of deformation softening in nanostructured metals (pure aluminum and IF steel).18,20 Besides, Yang et al. found the behaviors of work-softening in two fine grained eutectoid-type Zn-Al alloys.21 The work-softening behavior can be attributed to the absorption of dislocation by grain boundary according to their study.

The mechanisms of the anneal hardening and deformation softening in NC Cu-Zn alloys could be more complicated and still ambiguous to comprehend by now. And there is very few detailed information about these phenomena. Hence, in this paper, three kinds of single-phase Cu-Zn alloys were processed by heavy cryorolling technology (CR) before low temperature annealing to obtain NC samples. And we explored the mechanism of hardening behavior by low temperature annealing and the softening effect of post-process deformation after the annealing treatment in these deformed NC samples.

2. Experimental Procedure

In this paper, Cu-Zn alloys (Cu-10mass% Zn, Cu-20mass% Zn and Cu-30mass% Zn) with fairly low stacking fault energy (SFE) (35 mJ/m², 18 mJ/m² and 14 mJ/m²) were employed,22,23 and they were casted by induction vacuum melting. Then, these ingots were deformed into plates with a thickness of 7.9 mm by hot-rolling, and the plates were annealed at 700°C for 4 h in argon atmosphere to homogenize the ingredient and microstructure. Before each rolling pass, the samples were soaked into the liquid nitrogen for approximately 5 minutes, and the total plasticity strain of these specimens was about 90% (from a thickness of 7.9 mm to 0.8 mm) with approximately 0.1 mm thickness reduction in each pass during the cryorolling process (referred as CR). Several of the as-rolled specimens were annealed at different low temperature (100, 150, 200 and 250°C) for 1 hour, respectively. The samples were divided into four groups according to the annealing temperature (100, 150, 200 and 250°C). The groups of specimens annealed at low temperature were rolled from a thickness of 0.8 mm to 0.4 mm at room temperature (RR). The rolling process after low temperature annealing is called post-process deformation.

Dog-bone samples of all groups with a gauge width of 5 mm and length of 15 mm were manufactured for the uniaxial tension test. A Shimazu Universal Tester was used to perform the tensile tests with a constant strain rate of 10⁻⁴ s⁻¹ at room temperature.
X-ray diffraction (XRD) was performed at room temperature to analyze the samples using an X-ray diffractometer equipped with a Cu target, operating at 40 kV and 200 mA, with 2-theta angle scans ranging from 20° to 120° to record the XRD patterns, with a scan rate 4°/min.

The average grain size ($d_{XRD}$) and microstrain ($\langle \varepsilon^2 \rangle^{1/2}$) were measured using XRD peak broadening. And Scherrer-Wilson method can be used to calculate the dislocation density $\rho$, given by:

$$
\rho = \frac{2 \sqrt{3} \langle \varepsilon^2 \rangle^{1/2}}{d_{XRD} b}
$$

where $b$ is the Burgers vector, for copper alloys, $b = (\sqrt{2}/2)a$, $a$ is the lattice parameter of each sample. The twin density $\beta$, defined as the probability of detecting a twin boundary between any two neighboring [111] planes, can be calculated based on the equation:

$$
\beta = \frac{\Delta C \cdot G \cdot (2\theta)_{111} - \Delta C \cdot G \cdot (2\theta)_{200}}{11 \tan \theta_{111} + 14.6 \tan \theta_{200}}
$$

where $\Delta C \cdot G \cdot (2\theta)_{111}$ and $\Delta C \cdot G \cdot (2\theta)_{200}$ are the angular deviations of gravity center from the peak maximum of the [111] and [200] XRD peaks, respectively.

Microstructural investigations of specimens were carried out using a FEI Tecnai G-2 TF30 S-Twin transmission electron microscope (TEM) operated at 300 kV. Thin TEM foils were prepared by TenuPol-5 twin jet polishing using voltage about 13.5 V, flow rate of 41 and temperature of 21°C, with a solution of 25% CH₃CH₂OH, 25% H₃PO₄ and 50% H₂O.

3. Experiment Results and Discussion

Figure 1 shows the engineering stress-strain curves of all the samples. Both the yield strength (YS) and the ultimate strength (UTS) of CR processed Cu-10%Zn samples annealed at 100°C, 150°C and 200°C are lower than their counterparts without annealing, as shown in Fig. 1(a). Hence, there is no anneal hardening for CR processed Cu-10%Zn. It can be found that the strength of CR processed Cu-20%Zn sample annealing at 150°C is slightly higher than their counterparts without annealing in Fig. 1(b). Thus, a weak anneal hardening behavior appears in CR processed Cu-20%Zn samples during annealing at 150°C. As is shown in Fig. 1(c), the CR processed Cu-30%Zn specimen annealed at 200°C has the highest YS and UTS. So, the strengthening effect is clearly observed during low temperature annealing. The values of both YS and UTS of the specimens annealed at 250°C are lower than those of the counterparts without annealing, and the result is consistent with previous studies. The annealing temperature of 250°C is close to the recrystallization temperature of Cu-Zn alloys. Thus, the softening behavior of annealing at 250°C can be explained by larger grains induced by recrystallization during annealing. Besides, it is clear that this annealing treatment can decrease the density of defects (dislocation, vacancy and stacking fault) and eliminate deformation stress.

Figure 2 presents the stress-strain curves of Cu-20%Zn and Cu-30%Zn specimens annealed at 150°C and 200°C, which followed by post-process deformation. A significant reduction in strength is clearly observed in the specimens by post-process deformation after annealing. Thus, a deformation softening behavior can be induced by the post-process deformation after annealing at low temperature. Meanwhile, the UTS of samples increases significantly. Furthermore, the strength is practically the same as the CR ones. It is concluded that the mechanical properties as observed in the RR samples are better than that of the CR samples and the annealed samples.

Figure 3 shows the XRD patterns of the samples of CR processed Cu-30%Zn before annealing, annealing at 200°C and RR processed Cu-30%Zn samples after annealing at 200°C. As is shown in Fig. 3, we can found that the XRD patterns of different kinds of samples coincide with each oth-
These agree well with the near-identical grain sizes and microstrains of these samples. These patterns also indicate that the textures in three kinds of samples are essentially the same. Thus, the behaviors of anneal hardening and deformation softening cannot be attributed to the change in texture.

Table 1 and Fig. 4 show that the CR processed Cu-30%Zn samples and the annealed (at 200°C for 1 hour) counterparts have the same grain size. In the sample of RR after 200°C annealing, the grain size decreases slightly as compared to the annealed (at 200°C for 1 hour) counterpart. There is no obvious difference in dislocation density between the before annealing samples and the 200°C annealing ones. While, for the sample annealed at 200°C, the dislocation density increased after RR processing compared to that of its counterpart without RR processing. The twin density in these three kinds of samples are nearly invariable. Wen et al. reported the relationship between the strengthening mechanisms and the yield
Thus, the total strength increments \( \Delta \sigma \) due to twin can be defined by:

\[
\Delta \sigma_T = K \text{TB} \lambda^{-\frac{1}{2}}
\]

(5)

Thus, the total strength increments \( \Delta \sigma^* \) of the samples from the contribution of dislocation, grain size and twin can be defined by:

\[
\Delta \sigma^* = M \alpha G b \rho^\frac{1}{2} + K \text{HP} d^{-\frac{1}{2}} + K \text{TB} \lambda^{-\frac{1}{2}}
\]

(6)

where \( M, \alpha, G, b, K \text{HP}, K \text{TB} \) are constants, \( \rho \) is the dislocation density, \( d \) is the cell or sub-grain size and \( \lambda \) is the twin spacing.

The mechanism of anneal hardening is not consistent with fine grain strengthening and dislocation strengthening. The effect of anneal hardening induced by twinning can also be excluded. In addition, Fig. 5 and Fig. 6 present the microstructures of Cu-30%Zn samples deformed by CR and its counterparts annealing at 200°C after deformed by CR, respectively. There are no remarkable differences between these two kinds of structure. The characteristics of twins in Fig. 6(a) are in accordance with the ones of deformation twins. Therefore, annealing twin cannot be obtained after annealing at 200°C. It is reasonable to conclude that the anneal hardening behavior may not be attributed to the annealing twins. The effect of deformation softening in these Cu-Zn alloys is also hard to be explained by the increased dislocation density, changeless twin density and the decreased grain size.

It was also evident, from the engineering stress-strain curves in Fig. 1, that a more obvious phenomenon of anneal hardening can be achieved, with the increase of Zn atom content. It is well known that an increase in Zn content leads to an increase in the solute atoms and a decrease in SFE. The low SFE could lead to the wide stacking faults generated in samples during the CR process. Wide stacking faults, which facilitates the perfect dislocations transform into partial ones, lead to a higher dislocation density. This has been confirmed in our previous studies.\(^{28}\) During annealing, a large number of vacancies induced by CR can be eliminated to provide enough room for the activities of solute atoms. Pipe diffusion of solute atoms can take place among the partial dislocations and becomes the dominating diffusion mode of solute segregation in Cu alloy during low temperature annealing. The solute segregation rate increases with dislocation density. While, pipe diffusion to partial dislocations may in turn be hindered by its own dislocation migration. Thus, partial dislocations are pinned by the solute atoms. The interaction of solute atoms and dislocations can significantly increase flow stress. This is consistent with the earlier studies.\(^{30-32}\)

Besides, the SRO can appear due to the stacking faults which can serve as preferential nucleation locations for solute atoms to develop ordered regions during annealing.\(^{31}\) Owing to the existence of SRO, glide of the first dislocation in a fresh atomic plane can be hindered by the regional regularity of Zn atoms. In other words, this interaction of SRO and dislocations leads to an extra energy barrier to the glide of dislocations in each original slip plane.\(^{34}\) The occurrence of cross-slip of dislocation can also be restricted with the effect of SRO. The interaction of SRO and dislocations can contribute to the promotion of flow stress, which further lead to anneal hardening behavior. In the previous discussions, we rule out the effects of annealing twins and dislocation saturation and then the low SFE and SRO can appear to form dislocation cell. Thus, we speculate that the anneal hardening behavior of NC Cu-Zn alloy can predominantly be elaborated by solute segregation to dislocation and is related to the effect of SRO. The influence of solute segregation and SRO on anneal hardening behavior need further study and investigation.

Figure 2(a) and Fig. 2(b) show that the strength of the samples processed by post-process deformation is lower than that of the annealing counterparts. This indicates that a softening phenomenon is induced by the post-process deformation. On one hand, it may impair the effect of solute segregation to dislocation and SRO by changing the morphology of dislocations. On the other hand, it can lead to fractured twins, as shown in Fig. 7(b). Whole twins, in comparison with frac-

---

**Fig. 5** Typical bright TEM image of CR processed Cu-30%Zn sample: (a) large-scale microstructure; (b) tangling of dislocations and deformed twins.

**Fig. 6** TEM images of Cu-30%Zn annealing at 200°C after deformed by CR for microstructure: (a) large-scale microstructure; (b) HRTEM shows a high density of stacking faults in samples of Cu-30%Zn annealing at 200°C.

**Fig. 7** TEM micrograph of samples of post-process deformation after annealing at 200°C for Cu-30%Zn showing: (a) large-scale microstructure; (b) the fractured twins and tangling of dislocations.
tured ones, may be more competent to hinder glide of dislocations. A lower flow stress can be achieved by post-process deformation. These may partly explain the deformation softening in NC Cu-Zn alloys. Further systematic investigation is needed to expound thoroughly the softening behavior induced by post-process deformation.

4. Conclusions

A study of the effect of low temperature annealing and post-process deformation on the mechanical properties in deformed NC Cu-Zn alloys was carried out. The following conclusions can be drawn:

(1) For the samples of CR processed Cu-10mass%Zn alloy, there is no low temperature annealing hardening behavior. While the low temperature annealing hardening behavior occurred in the samples of CR processed Cu-20mass%Zn alloy and the samples of CR processed Cu-30mass%Zn alloy. In addition, the anneal hardening behavior in the samples of CR processed Cu-30mass%Zn alloy is more remarkable.

(2) For samples of CR processed Cu-20mass%Zn alloy and CR processed Cu-30mass%Zn alloy, the post-process deformation after low temperature annealing leads to a deformation softening.

(3) The anneal hardening behavior in the NC Cu-Zn alloys cannot be attributed to the effect of annealing twins and dislocation source, and it might predominantly be elaborated by solute segregation at dislocation and the interaction between SRO and dislocations.

Acknowledgment

The authors would like to acknowledge financial supports by the National Natural Science Foundation of China (NSFC) (grant 51561015), and the introduction of talents fund project of Kunming University of Science and Technology (grant KKSY201407100). We also greatly appreciate the Prof. Y.T. Zhu from North Carolina State University (U.S.A) for supporting this research.

REFERENCES