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Recrystallization and Precipitation Behavior of Cu-Cr-Zr Alloy

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Recrystallization and precipitation behaviors after cold rolling and aging are investigated for Cu-0.7Cr-0.13Zr alloy. The processed alloy was characterized using the measurement of Vickers hardness, scanning electron microscopy, and transmission electron microscopy. The resultant complex microstructures are interpreted in terms of the interactions between precipitation and recrystallization. Upon aging at 500 °C for 1 h, the 45% rolled alloy exhibits a retarded recrystallization process and therefore an efficient hardening response, which are attributed to the pinning effect of fine dispersed precipitates on the dislocation. When heavily deformed and aged at high temperature, the alloy shows an accelerated process of recrystallization, and precipitates are found to coarsen.

Keywords Cu-0.7Cr-0.13Zr alloy, hardness, precipitation, recrystallization

1. Introduction

There is strong academic and industrial interest in recrystallization, particularly in copper alloys, driven by the need to understand and control this complex phenomenon in order to optimize properties through the careful control of thermo-mechanical processing schedules. In precipitation hardening copper alloys, the situation may arise in which the processes of recrystallization and precipitation occur concurrently. If recrystallization of a deformed supersaturated solid solution is not complete before the start of precipitation, then the material may exhibit complex behavior due to the mutual interaction of recrystallization and precipitation (Ref 1-5). Thus the presence of a deformed microstructure may affect the nature and kinetics of the precipitation, and the presence of precipitates may interfere with the recrystallization processes. In Ref 6 a phenomenon of combined in situ and discontinuous recrystallization has been observed in the rapidly solidified Cu-Cr-Zr-Mg alloy. In Ref 7 during the isothermal aging, the hardness of the deformed Cu-0.61Cr-0.07P alloy showed three distinct stages as a function of aging time; this hardness behavior was associated with the interactions between precipitation, recovery, and recrystallization. Similar work has seldom been reported on solution treated and cold rolled Cu-Cr-Zr alloys. Recently, Cu-Cr-Zr alloys have attracted considerable interest because of its superior combination of high-electrical conductivity and high strength (Ref 7-12). The purpose of the present work is to investigate the interaction between recrystallization and precipitation in the Cu-Cr-Zr alloy. Particular emphasis is placed on the use of scanning electron microscope (SEM) and transmission electron microscopy (TEM) in order to study the evolution of microstructure and a detailed analysis in terms of thermodynamics was also performed.

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2. Experimental Procedure

The alloy investigation was prepared by solution treatment for 1 h at 920 °C in an argon atmosphere and water quenching. Then it was rolled in different extent of deformation. The aging treatments were carried out in a tube electric resistance furnace under a fluid atmosphere of argon with temperature accuracy of ±5 °C. The microhardness was measured on a HVS-1000-type hardness tester under a 100 g load and holding for 10 s. Every sample was tested five times with an accuracy of ±5%. The transmission electronic microscope (TEM) samples were prepared by conventional electro-polishing method using an electrolyte of HNO_3:CH_2OH = 1:3. The electron microscopy for this study was carried out using a H-800 TEM at 200 kV. The evolution of microstructure was observed by JSM-5610 LV scanning electron microscope.

3. Results

Figure 1 shows the relationship between the hardness and time aged at 500 °C. The time to peak hardness decreases with increasing ratio of cold rolling and the peak hardness increases with increasing ratio of cold rolling. Deformation before aging enhances the hardness substantially. At 500 °C in the 60% cold worked condition the peak hardness is 177HV for 0.5 h. Under the same aging condition, with no deformation, the hardness is only 116HV. The dislocations resulting from cold rolling act as diffusion paths for solute atoms and provide nucleation site for precipitation during aging treatment and result in the

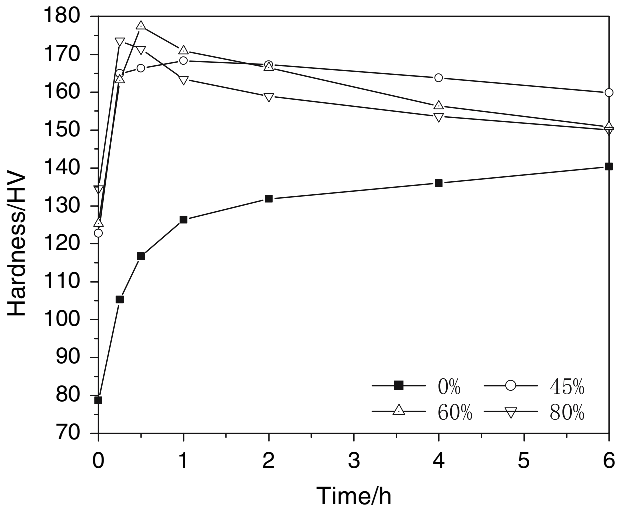

Fig. 1 Hardness with regard to time aged at 500 °C

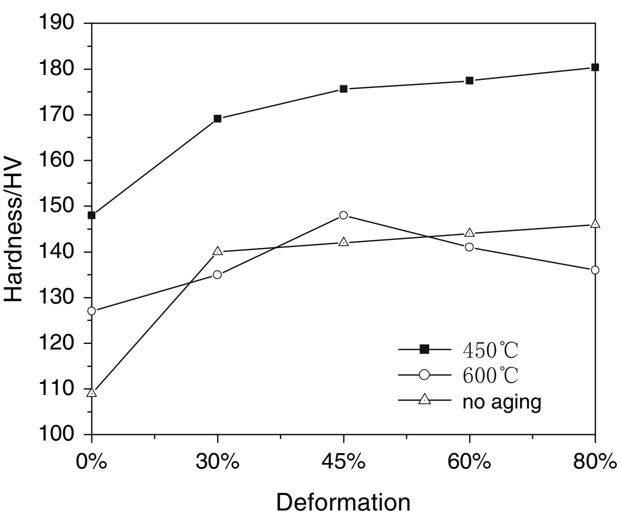

Fig. 2 Hardness with regard to strain aged for 2 h

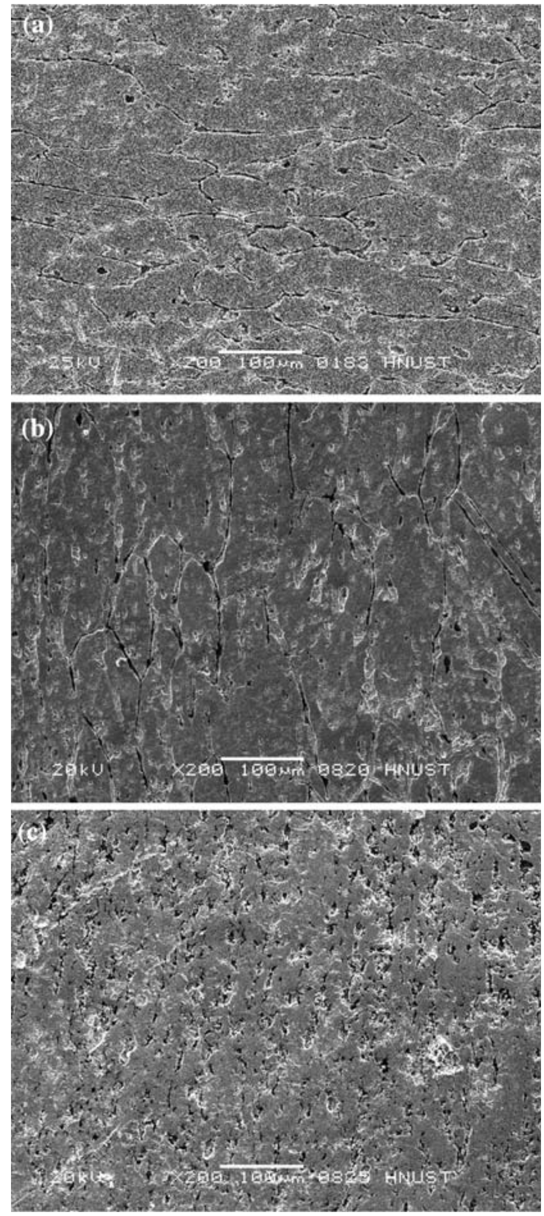

Fig. 3 Scanning electron micrographs showing the microstructures of Cu-0.76Cr-0.13Zr alloy after being: (a) predeformed by 80% cold rolling, (b) predeformed by 80% and aged for 1 h at 500 °C, (c) predeformed by 80% and aged for 4 h at 600 °C

precipitation hardening effect from a finer size of precipitates. The hardness in 80% cold rolling is slightly smaller than that in 60% cold rolling.

Figure 2 reveals the variation of hardness with increasing temperature and ratio of cold rolling at 2 h. With different amounts of cold rolling, at 450 °C, the hardness is higher at 600 °C. The maximum hardness reaches 180.3HV at 450 °C for 2 h with 80% deformation. The hardness is almost the same as that in the deformed conditions with no aging. The recrystallization of the alloy is responsible for the decrease in hardness.

Figure 3 shows the scanning electron micrographs of the Cu-0.76Cr-0.13Zr alloy specimens with the prior deformation of 80%, and aged at different aging process parameters. After deformation, the alloy specimen retains the defect structure. The grains are elongated in the direction perpendicular to the compression axis. No recrystallization is visible in the specimen as seen in Fig.3(a). Aged for 1 h at 500 °C the alloy does not change dramatically the deformed microstructure of the specimen with 80% pre-deformation. It is shown in Fig. 3(b) to consist of many stretched grains aligned in the same direction. Many 'particles' can be seen in this specimen and they appear to be larger and more numerous. The distribution of these particles is not homogenous. This suggests that they might be new grains, which nucleate in the specimen but have no time to grow larger. After being aged for 4 h at 600 °C, the specimen with 80% pre-deformation has a microstructure different from others (Fig. 3c). Many fine recrystallized grains are formed. The elongated grains almost disappear. The structure has a higher recrystallized fraction.

Figure 4 reveals the TEM images of recrystallized samples after 60% deformation and aging at 600 °C for 2 h . The cell substructure formed by dislocation walls can be seen. Dislocation density is also high inside many of the cells. However, the bulging of the boundaries of some cells and annihilation of

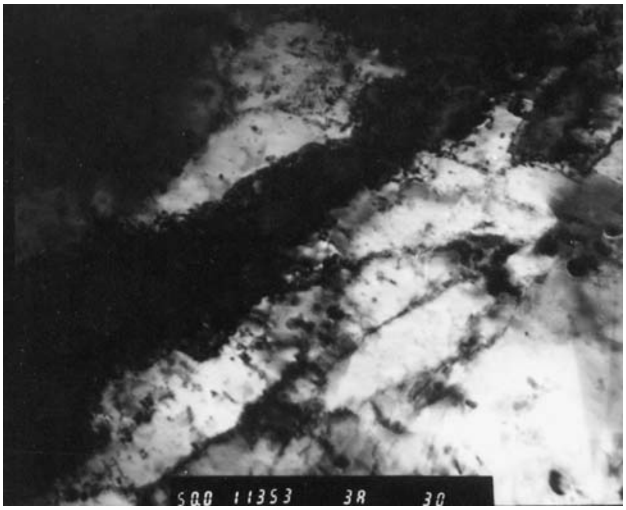

Fig. 4 Recrystallization in a sample with 60% deformation after aging at 600 °C for 2 h

Fig. 5 Dislocations in 45% deformed specimen after aging at 500 °C for 1 h

the dislocations inside the cells indicate the onset of recrystallization. The development of recrystallization softens significantly the pre-deformed alloy, offsetting the hardening increase resulting from the precipitation hardening. The hardness is only 141HV.

4. Discussions

During the nucleation and growth of recrystallization the precipitates might be resolved or coarsened in the front of migrating boundaries. This phenomenon can be analyzed in terms of thermodynamics. At the initial stage of recrystallization, the crystal nuclei are first formed in certain selected sites. These nuclei, almost free of strain, might grow toward the deformed matrix through migration of large angle boundaries to decrease the strain energy. Let the driving force for recrystallization be denoted as F_N, and the boundary migration braking force in unit area caused by the precipitates be Zener force Fv. If $F_N = Fv$, then the critical size of the precipitates can be obtained by

$$D_C = 3f\gamma_b/\alpha Gb^2(\rho_0 - \rho_1) \quad \text{(Eq 1)}$$

where α is a constant; G, the shear elastic modulus; b, Burgers vector; ρ_0 and ρ_1 are the dislocation density after deformation and recrystallization, respectively; f is the volume fraction of the grains; γ_b, boundary energy.

If f = constant and $D < D_C$, then $Fv > F_N$, that is, the braking force is larger than the driving force. In this case, the grain-boundary migration cannot be realized before the precipitates are resolved. However, the resolution of the precipitates might result in the increase of the system's free energy, which, on the contrary, might obstruct the grain-boundary migration. Here, the braking force exerted by the grains on the boundaries should be chemical force F_c (Ref 6):

$$F_c = 2\pi(\Delta G r^2 - 2\pi r' r)/3V_a \quad \text{(Eq 2)}$$

where V_a is molar volume of atoms; r, the size of precipitate; r', the coherent interface energy; ΔG, the free energy. For a Cu-Cr alloy system, suppose the system's free energy is increased by ΔG owing to the resolution of per molar precipitates, and the alloy has a relative lower content of solute. Thus it can be simplified as a dilute solid solution, then there is:

$$\Delta G \approx RT\ln(C_0/C_a) \quad \text{(Eq 3)}$$

where R is the gas constant; T, the absolute temperature; C_0, the composition of the alloy; C_a, the equilibrium solubility at the aging temperature. Substituting Eq 3 into Eq 2, one gets:

$$F_{c0} = \frac{2\pi r^2}{3V_\alpha}RT\ln(C_0/C_\alpha) - 2\pi\gamma' r. \quad \text{(Eq 4)}$$

Therefore, in the premise of $D < D_C$, whether the precipitates in the front of recrystallization zone could be resolved depends on the chemical force F_c. Only when there is $F_c > F_{c0}$ could the precipitates be resolved due to grain-boundary migration. Here a supersaturation is again formed in the recrystallized zones and the alloy will still proceed through aggregation of solute atoms and the nucleation of the precipitates. However, if the condition of $F_c < F_{c0}$ is satisfied, the precipitates cannot be resolved or rapidly coarsened. These precipitates may play a pinning action on the grain boundaries so that the recrystallization is restrained. Figure 5 is a TEM micrograph showing the microstructure characteristics of the Cu-Cr-Zr alloy with 45% rolled and aged at 500 °C for 1 h. A large amount of small precipitates pin the dislocations and retard the rearrangements of dislocations and the movement of subgrain boundaries. The alloy at the thermo-mechanical process is very resistant to recrystallization or softening. The hardness can reach 168.3HV.

If $D > D_C$, the driving force is greater than the braking force. The grain boundary is easy to migrate. The dislocation density decreases in the zones swept by the migrating grain boundaries. If $F_c < F_{c0}$, the recrystallization can still proceed, which forms a big phase inside the recrystallized grains as has been shown in Fig. 6. If $F_c > F_{c0}$, the precipitates can be coarsened or resolved. Since the size of precipitate is increased, it is difficult for the bigger precipitates to resolve. So the recrystallization can proceed by means of the precipitate growth (Ref 13).

Fig. 6 The coarsened precipitates inside the recrystallization grains

5. Conclusions

1. Upon aging, the precipitation process takes place prior to recrystallization for the cold-deformed Cu-Cr-Zr alloy. The pinning of the dispersed fine precipitates on dislocation has shown a restraining effect on the following recrystallization process. With 80% rolled and aged at 450 °C for 2 h, the hardness of the alloy can reach 180.3HV.
2. The heavily deformed and aged at high-temperature alloy showed an accelerated process of recrystallization and precipitates are found to coarsen. Rolled 80% and aged at 600 °C for 2 h, the hardness reduces to 136HV.

Acknowledgments

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