Retardation of Softening of Ultrafine-Grained Copper during Low Temperature Annealing under Uniaxial Tensile Stress

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It is known that pure metals having ultrafine grains (UFGs) exhibit softening and grain coarsening at temperatures about one third of the melting temperatures. When such low-temperature annealing (LTA) of UFG copper is conducted under uniaxial tensile stress, the retardation of the softening is found to occur compared with that without stress. Observations of the microstructure and texture analysis indicate that the softening and the grain coarsening are attributed to recrystallization, and the presence of uniaxial tensile stress during LTA retards recrystallization. High voltage transmission electron microscopy revealed that the dislocation density of UFG copper annealed under uniaxial tensile stress is lower than that after LTA without stress. The retardation of recrystallization is associated with the reduction of the dislocation density of unrecrystallized UFG copper induced by dynamic recovery.

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1. Introduction

Metals and alloys having ultrafine grains (UFGs) less than one micrometer show several times higher strength than that of pure metals having coarse grains.\textsuperscript{1} Severe plastic deformation (SPD) processes are one of the techniques to produce bulk UFG metals. It has been reported that UFG aluminium (Al)\textsuperscript{2} and copper (Cu)\textsuperscript{3} show grain coarsening at temperatures less than one third of the melting temperature $T_m$.

In most studies, such low temperature annealing (LTA) less than $T_m/3$ have been performed without stress. On the other hand, hydrostatic pressure during annealing is known to retard the softening of the cold rolled coarse grained Cu.\textsuperscript{4} The grain sizes after annealing with the hydrostatic pressure were smaller than those without stress. It was also reported that the presence of shear stress during annealing suppresses the softening of cold rolled Al–Mg alloy.\textsuperscript{5}

It is well known that grain boundary migration occurs during annealing without stress due to the recrystallization. However, even external stress can directly induce the grain boundary migration\textsuperscript{6–9} in addition to dislocation motion and diffusion of atoms via plastic deformation. Thus, in the present study, we investigated the effect of the external stress on the annealing behaviour of UFG Cu during LTA.

2. Experimental Procedure

99.99\% (4N) pure Cu sheets with the thickness of 1 mm were chosen as a starting material for an accumulative roll bonding (ARB) process, which is one of the SPD processes.\textsuperscript{1,9,10} The Cu sheets were annealed at 873 K for 1.8 ks in ambient condition using a furnace, and then the oxidized surface layer was removed by nitric acid. The ARB process was applied up to 6 cycles with lubrication at room temperature (R.T.), of which details can be found elsewhere.\textsuperscript{1,10–12}

The 4N-Cu sheets ARB processed with six cycles, hereafter denoted as ARB 6c, were annealed at 398 K, 423 K, and 448 K in an oil bath as LTA with and without loading, and these are treated as LTA under uniaxial tensile stress and that without stress. A testing machine NMB TG-50kN (Minebea) was used to apply the uniaxial stress of 100 MPa in the case of LTA under uniaxial tensile stress. Here, it should be noted that the 0.2% proof stress of ARB 6c at R.T. was 367 MPa, and therefore the uniaxial tensile stress of 100 MPa was well below the tensile yield stress.

A micro Vickers hardness test machine, MXT-1 (Matsuzawa), was used to measure the Vickers hardness at R.T. with the applied load of 0.3 kgf (2.94 N). The specimens were mechanically polished to be the mirror surface prior to the Vickers hardness measurements. The evolution of Vickers hardness of ARB 6c samples after LTA under and without uniaxial tensile stress of 100 MPa were measured using samples with identical preparation treatments. Vickers hardness of a sample was measured by frequently interrupting LTA. Annealing time was properly selected so that the change of the Vickers hardness can be displayed with a logarithmic time scale. The LTA was restarted after the measurements of the Vickers hardness. To understand overall deformation behavior during LTA under stress, creep tests at 398 K, 423 K, and 448 K under 100 MPa were also performed for ARB 6c samples. In the creep tests, strain gauges for high temperatures were used to measure strains.

Electron backscattered diffraction (EBSD) pattern measurements in a scanning electron microscope with a field emission type gun (FE-SEM) was carried out using a JSM-6500FK (JOEL) with a CCD camera controlled by a
program, OIM Data Collection ver. 4.6 (TSL). EBSD measurements were carried out on a section normal to the transverse direction (TD). EBSD specimens were cut from sheets using an electrical arch discharge wire cutting machine. The surface was polished mechanically and then finished by electrolytic etching. The measurement area was either 20 µm (ND) × 10 µm (RD) or 50 µm (ND) × 25 µm (RD) and the step size was 0.05 µm or 0.25 µm. Here, ND either 20 µm (RD) and the step size was 0.05 µm or 0.25 µm. Here, ND denote normal and rolling direction, respectively. An orthotropic symmetry was assumed when pole figures (PFs) and orientation distribution function (ODF) maps were constructed from the EBSD data.

A high voltage transmission electron microscope (HVEM), H-1250 (Hitachi), operated at 1000 kV was used to quantify the dislocation density. Dislocations were visualised with optimum tilting angles using a dual tilt holder. Ham’s intersection method and a thickness evaluation method using thickness fringes at high angle grain boundaries (HAGBs) were applied for the quantification of dislocation density.12) The specimens for HVEM observations were also carried out on the TD sections, which were prepared with the procedure as those for EBSD specimens except for the final electrolytic etching with a Tenupol twin jet polisher (Struers).

3. Experimental Results

Figure 1 shows the creep curves of ARB 6c annealed at 398 K, 423 K, and 448 K under uniaxial tensile stress of 100 MPa. The evolution of the strain $\epsilon$ is different among these temperatures after the initial increase of $\epsilon$ after about 1 ks. The strain rate $\dot{\epsilon}$ after 1 ks increases with increasing the annealing temperature $T_a$.

Figure 2 shows the evolution of the Vickers hardness of the ARB 6c annealed at (a) 398 K, (b) 423 K, and (c) 448 K without and under uniaxial stress of 100 MPa. The measurements of the Vickers hardness were performed five times each, and the average values are indicated as data points in Fig. 2. The maximum and the minimum values are expressed as an error bar. It takes less annealing time $t_a$ to start the reduction of the Vickers hardness with increasing $T_a$. Furthermore, the retardation of the softening can be seen during LTA under uniaxial tensile stress compared with LTA without stress at all $T_a$.

The Vickers hardness of as ARB 6c is about 140 HV, which reduces down to about 70 HV after both LTA under and without uniaxial tensile stress. The presence of the uniaxial tensile stress during LTA increases the Vickers hardness about 5 HV after the Vickers hardness values saturate at 423 K and 448 K, which is more than the experimental error except for the case of 398 K.

Figure 3 shows the inverse pole figure (IPF) maps along ND of ARB 6c; (a) as ARB 6c, annealed at 448 K without stress for (b) 300 s and (c) 1200 s, and under uniaxial tensile stress (100 MPa) for (d) 300 s and (e) 1200 s. It can be seen that the grain size increases with increasing $t_a$, which explains the reduction of the Vickers hardness. It should be noted that the annealed sample under uniaxial tensile stress after 1200 s still contains more UFGs [Fig. 3(e)] compared with the annealed sample without stress [Fig. 3(c)].

Figure 4 shows the change in the mean separation of HAGB along ND ($d_{\text{HAGB}}$) in the ARB 6c annealed at 448 K without and under uniaxial tensile stress of 100 MPa. The $d_{\text{HAGB}}$ increases with increasing $t_a$ for both without and under uniaxial tensile stress compared with the initial value of 310 nm. It should be noted that LTA under uniaxial tensile stress results in smaller $d_{\text{HAGB}}$ compared with that without stress after $t_a$ of 300 s and 1200 s.

Figure 5 shows (111) PFs of ARB 6c; (a) as ARB 6c, annealed at 448 K without stress for (b) 300 s and (c) 1200 s, and under uniaxial tensile stress (100 MPa) for (d) 300 s and (e) 1200 s. As ARB 6c [Fig. 5(a)] shows the typical rolling texture as reported previously.13) The ideal orientations of rolling texture along $\beta$-fiber for fcc metals (S {112} (634), Brass {100} (112), and Copper {112} (111)) and Cube component [100] (001) are shown in Fig. 5(f). The texture of as ARB 6c composes of strong S and Copper components in addition to the weak Brass components. The observed
intensity was normalised by the random texture, thus, the intensity equal to unity is the same as the intensity observed in a polycrystalline metals with random texture.

When an ARB 6c sample is annealed without stress for 300 s, weak poles of the Cube component appear due to recrystallization, but still rolling texture components remain as shown in Fig. 5(b). It should be noted that the intensity of the S component slightly increases at this stage. Eventually, recrystallization progresses and the strong cube texture appears with weak remaining Brass and S components at 1200 s as shown in Fig. 5(c).

When the ARB 6c was annealed under stress for 300 s, the Cube component became almost undetectable and the S component became stronger as shown in Fig. 5(d). It should be noted that the intensity of the Brass component is also slightly stronger than the initial texture. Furthermore, rolling texture still remains at 1200 s as the mixture of relatively weak Cube component and the rolling texture components (S, Brass, and Copper) as shown in Fig. 5(e).

Figure 6 shows the annealing time dependence on the intensity of the Cube component evaluated from ODF. The intensities of the Cube component are negligible until $t_a$ of 300 s after both LTA without and under uniaxial tensile stress, whereas, the intensity is almost ten and 24 for $t_a$ of 1200 s without and under uniaxial tensile stress, respectively. Here, the definition of intensity of ODF is the same as that of PF.
The annealing time dependence on the intensity of cube component.

![Fig. 6](image)

**Fig. 6** The annealing time dependence on the intensity of cube component.

![Fig. 7](image)

**Fig. 7** HVEM micrographs of uncrystallized UFGs in (a) as ARB 6c, annealed at 448 K (b) without stress for 1200 s, and (c) under uniaxial tensile stress of 100 MPa for 1200 s.

Figure 7 shows TEM micrographs of (a) as ARB 6c, annealed at 448 K (b) without stress for 1200 s, and (c) under uniaxial tensile stress (100 MPa) for 1200 s. It can be seen that the dislocations are observable in all the samples. The dislocation density \( \rho \) was evaluated from three HVEM micrographs as shown in Fig. 7. The initial \( \rho \) of as ARB 6c is \( 8.0 \times 10^{14} \text{m}^{-2} \), whereas the remaining unrecrystallized UFG in the annealed ARB Cu at 448 K without and under uniaxial tensile stress have \( \rho \) of \( 5.0 \times 10^{14} \text{m}^{-2} \) and \( 1.5 \times 10^{14} \text{m}^{-2} \), respectively.

### 4. Discussion

The softening of the ARB 6c at around \( 1/3 T_m \), i.e. 398 K, 432 K, and 448 K, was observed in the present study (see Fig. 2). The reduction of the Vickers hardness of the ARB 6c due to LTA was attributed to the grain coarsening (see Fig. 3). The detailed investigation of Fig 2 reveals that the application of stress during LTA retards the softening by about \( 10^2 \text{s} \), \( 10^3 \text{s} \), and \( 10^4 \text{s} \) at \( T_a \) of 398 K, 432 K, and 448 K, respectively. Thus, the retardation itself becomes shorter at higher \( T_a \). This fact indicates that the softening by grain coarsening and its retardation at different temperatures are caused by a thermal activation process. The softening also affects the creep behaviour. In particular, we note that the slope of the creep curve for \( T_a = 448 \text{K} \) changes at about 1.5 ks. This is reasonable since the grain coarsening occurs during softening.

Let us assume that the same amount of softening at different temperatures occurs when the same amount of grain coarsening, say, \( \Delta X_c \), is realized under a thermal activation process with the activation energy \( G^* \). Then, we can generally write

\[
\Delta X_c = A t \exp \left( -\frac{G^*}{kT} \right)
\]

where \( A \) is a constant independent of temperature, \( t \) is annealing time and \( kT \) has its usual meaning. If the same hardness reduction (say, from the initial value of nearly 140 HV to 100 HV) is realized after annealing time \( t_1 \) at \( T_1 \) and after \( t_2 \) at \( T_2 \), we find from eq. (1)

\[
\frac{G^*}{k} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \ln \left( \frac{t_2}{t_1} \right)
\]

Since \( t_1, T_1, t_2 \) and \( T_2 \) are all known from Fig. 2, we can calculate the activation energy \( G^* \) for the present grain coarsening process. Simple calculations show \( G^* = 130 \pm 10 \text{kJ/mol} \) for both LCA without and under stress of 100 MPa.

From these similar values of the activation energy, we can say that the controlling mechanism and, thus, kinetics of the present grain coarsening is not strongly affected by the application of stress during annealing. Although the above \( G^* \) values are close to the activation energy of grain-boundary diffusion of Cu about 100 to 120 kJ/mol(13,14) detailed analysis on kinetics of grain coarsening is outside the scope of this study and will not be made here. On the other hand, it is true that the retardation of the softening due to the presence of the uniaxial tensile stress is caused by the suppression of the grain coarsening as shown in Fig. 4. In fact, the texture evolution in Fig. 6 shows the suppression of the development of the Cube orientation via recrystallization. Then, what causes the suppression of grain coarsening if stress is applied during annealing?

Here, we should note the large difference in the dislocation density \( \rho \) between specimens annealed with and without stress. This difference can be attributed to the easier occurrence of dynamic recovery under uniaxial tensile stress, since \( \rho \) of the unrecrystallized UFG after LTA under stress is smaller than that after LTA without stress and as ARB 6c. In general, external stress induces the dislocation motion and multiplication, which result in the increase in \( \rho \). However, since the UFG metals produced by SPD processes have already high and often saturated dislocation density, it is reasonable to consider that \( \rho \) is lowered due to the annihilation of dislocations and the recovery is promoted by the applied stress during LTA.
In the present experimental conditions at $T_a$ of 448 K, such lowering of $\rho$ was achieved by the strain up to several percentages during LTA under the uniaxial stress of 100 MPa. Since the driving force of grain coarsening is the strain energy accumulation by dislocations, if $\rho$ in the unrecrystallized UFGs is lower during LTA under external stress than that without stress, the coarsening rate of the recrystallized grain could be suppressed.

It is well known that recrystallization is more difficult in metals having higher stacking fault energy (SFE), say Al compared with Cu. This reason is because dislocation annihilation by cross slip plays an important role in recovery and cross slip occurs more easily in metals with higher SFE. When recovery (decrease in dislocation density) takes place extensively, driving force for recrystallization becomes small.

Let us estimate the change in the stored strain energy caused by the difference in dislocation density between annealed specimens with and without stress. We assign the self energy of a dislocation per unit length be $\mu b^2$ with $\mu$ ($=46$ GPa) the shear modulus and $b$ ($=0.255$ nm) the magnitude of the Burgers vector. Since the molar volume of Cu is $V_m = 7.11 \times 10^{-6}$ m$^3$/mol and the difference in $\rho$ of unrecrystallized UFG Cu after LTA without and under uniaxial tensile stress of 100 MPa is $\Delta \rho = 3.5 \times 10^{-14}$ m$^{-2}$, the change in the stored energy per mol of Cu can be estimated to be $\mu b^2 \Delta \rho V_m = 7.4 J$/mol. Here, it should be noted that the stored whole energy in ARB 6c Cu measured by differential scanning calorimetry (DSC) is about 50 J/mol according to Takata et al.\(^3\) which is the same order as and several times higher than the elastic energy corresponding to the reduced dislocation density ($\Delta \rho = 3.5 \times 10^{-14}$ m$^{-2}$). In the present study, there are still remaining dislocations and grain boundaries after grain coarsening, and therefore the estimated change in the stored energy per mol of Cu is reasonable. When the stored elastic is reduced about 7.4 J/mol estimated above, the retardation of recrystallization in UFG Cu occurs.

5. Conclusions

UFG Cu produced by ARB 6c with the 0.2% proof stress of 367 MPa at room temperature was annealed at 398 K, 423 K, and 448 K without and under uniaxial tensile stress of 100 MPa. The softening was observed at all annealing temperatures, which was attributed to the grain coarsening. The retardation of the softening was observed if stress is applied during annealing. This is attributed to the suppression of the grain coarsening due to the reduction of dislocation density. Presence of stress during annealing of UFG Cu reduces the dislocation density by dynamic recovery, and thus, the driving force of softening is also reduced.

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