Original Article

Work softening behavior of Cu–Cr–Ti–Si alloy during cold deformation

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A R T I C L E   I N F O

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A B S T R A C T

Work hardening is a common method of strengthening copper-based alloys. However, softening behavior is observed in Cu–Cr–Ti–Si alloy during cold rolling processes. Cold deformation greater than 85% can induce softening behavior. We used an electron backscatter diffraction system, X-ray diffraction, and transmission electron microscopy to analyze the microstructure of alloy samples subjected to different degrees of cold deformation. A greater proportion of high-angle grain boundaries, a lower dislocation density, and certain dislocation configurations indicated that the recovery takes place during heavy cold deformation leading to softening phenomenon.

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1. Introduction

In general, when a metal alloy is plastically deformed at room temperature, the strength and hardness of the alloy increase as the degree of cold deformation increases; however, plasticity and toughness typically decrease and work-hardening behavior also occurs. When the metal is plastically deformed, the dislocation density increases owing to dislocation entanglement. Grains are elongated and break into fibers. In this situation the Hall–Petch formulae, \( \sigma_y = \sigma_0 + K_d^{-1/2} \) and \( \sigma_y = \sigma_0 + K_p^{-1/2} \), describe the effects of a finer grain size or a higher dislocation density on the greater yield strength of the alloy [1–3]. However, a phenomenon with opposing effects to those of work-hardening occurs in many alloys; with increased cold-rolling deformation, the strength and hardness of the alloy decrease.

Li et al. found that in terms of the large stacking-fault energy of Al–Fe alloy, different amounts of Fe could be added to pure aluminum and the alloy softened when cold deformed. This effect is explained by the formation of a second phase, which absorbs impurities in the matrix to increase the stacking fault energy. When deformed, dislocations might undergo cross-slip and this process is more likely to occur.
for multilateral recovery [4-8]. The same effect occurs in large-stacking-fault energy alloys and when Zn alloys deform they become softened [9,10]. Yang et al. studied the work-softerning behavior of Zn-Al alloys. The rolled Zn-Al alloy retained a steady grain size of approximately 0.4 µm and an equiaxed grain structure instead of an elongated grain structure. Alloys might recover or only partially recrystallize. The structure of the alloy was observed by electron backscatter diffraction (EBSD). The proportion of high-angle grain boundaries increased; thus, a model of grain boundaries combining with stacking dislocation was proposed. Grain boundaries absorb dislocations, such that the grain boundary misorientation angle increases and the dislocation density decreases, which in turn cause the hardness of the alloy to decrease [11]. Xie et al. also studied softening phenomenon in Fe-0.65 wt.% Si alloy. When the cold rolling reduction reached 60%, dislocation cells were formed. At 80%-deformation, the dislocation cell size increased and subgrains developed, such that the alloy dynamically recovered as the dislocation density decreased. At the same time, the ordered phase in the alloy transformed into a disordered phase. They concluded that deformation-induced disorder and dynamic recovery are the main mechanisms of the work softening [12,13]. In addition, [14] also found this phenomenon in alumina-dispersion strengthened copper (ADSC) alloys. The hardness of the alloy increased when oxygen-free copper was cold rolled with different degrees of cold-rolling reduction. However, when Al2O3 powders were adding to the oxygen-free copper at 0.23 vol.%, the hardness of the alloy decreased when the deformation reached 80%. At an Al2O3 powder content of 0.54 vol.%, the alloy was softened at 85% deformation. Transmission electron microscope (TEM) observations and analysis have shown that when ADSC alloys are subjected to a higher degree of cold rolling deformation, dislocations move and encounter Al2O3 particles to form dislocation loops. When the amount of deformation is large enough, these small dislocation units coalesce with each other to form larger dislocation units. Thus the dislocation density of the alloy decreases, resulting in a decrease in the hardness of the alloy [14].

Although work-softenening phenomena have been found in many alloys, there have been few reports on Cu alloys. Therefore, in this paper, we study the effects of microstructure and properties of the solid solution-aging treatment of Cu-Cr-Ti-Si alloy after cold rolling deformation. We found that when the cold rolling deformation of Cu-Cr-Ti-Si alloy reaches 85%, the alloy is softened. The microstructure and properties after cold rolling are observed and analyzed by different methods to investigate the mechanism of work-softenening in Cu-Cr-Ti-Si alloy.

Table 1 – Cu-Cr-Ti-Si alloy chemical composition (wt.%).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cr</th>
<th>Ti</th>
<th>Si</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal composition</td>
<td>0.35</td>
<td>0.07</td>
<td>0.03</td>
<td>Bal.</td>
</tr>
<tr>
<td>Actual composition</td>
<td>0.32</td>
<td>0.059</td>
<td>0.017</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

![Fig. 1 – Hardness of Cu-0.32Cr-0.059Ti-0.017Si alloy subjected to different degrees of cold-rolling reduction.](image)

**2. Experimental procedure**

Pure copper (99.5 wt.%), pure titanium (99.9 wt.%), Cu-8 wt.% Cr alloy and pure Si (99.0 wt.%) were used as raw materials. We used a medium frequency induction furnace (DS-7-003, Wuxi Doosan electric furnace) to smelt and cast a Cu-Cr-Ti-Si alloy ingot, with a thickness of 20 mm, under an air atmosphere. The composition of the Cu-Cr-Ti-Si alloys was determined with an inductively coupled plasma emission spectrometer (ICP-ES, Thintent) (Table 1). The ingot was milled to a thickness of 18 mm. After a homogenization-annealing heat treatment at 850 °C for 2 h, the ingot was hot rolled to a thickness of 7.5 mm by a two-roll hot rolling mill (320 × 500, Wuxi Lianxing Machinery Factory). The ingot subjected to hot rolling was solution treated (910 °C for 60 min followed by water quenching) and aged (450 °C for 6 h). The samples were then cold rolled in one direction at room temperature, ranging from 0% to 90%.

The hardness and electrical conductivity of the alloy were tested by Vickers hardness tester (200 HVS-5) and a digital conductivity meter (Sigma 2008 B/C). The microstructure of the alloys was studied with a metallographic microscope (OM, Axioskop 2, Zeiss, Germany), EBSD (MIA650F, FEI, USA), X-ray diffraction (XRD, Empyrean type, Dutch PANalyt) and TEM (Tecnai F2-20).

3. Results and discussion

3.1. Work softening behavior

The hardness of Cu-0.32Cr-0.059Ti-0.017Si alloy after cold rolling is shown in Fig. 1. Initially, the hardness of the alloy increased as the cold-rolling deformation increased. When the cold-rolling reduction reached 80%, the hardness of the alloy was 191.8 HV0.2. However, when the amount of deformation exceeds 85%, the microhardness of the alloy begins to decrease. When the cold-rolling reduction reached 90%, the hardness of the alloy decreased to 178 HV0.2. When the deformation was increased to 95%, the microhardness of the alloy hardly changes. This phenomenon is known as work-softening behavior.
Fig. 2 – Longitudinal microstructures of Cu–0.32Cr–0.059Ti–0.017Si alloy treated at different degrees of cold-rolling reduction: (a) 30%, (b) 60%, (c) 80%, and (d) 90%.

3.2. Microstructures devolution

Fig. 2(a)–(d) shows the metallographic microstructures of the Cu–0.32Cr–0.059Ti–0.017Si alloy after cold rolling. After cold rolling at 30%, the grains of the alloy were crushed and elongated [Fig. 2(a)]. The structure exhibited obvious directionality and was rod-like. As the amount of deformation increases, the alloy elongated to a greater extent and the grains become more elongated [Fig. 2(b)–(d)]. When the deformation increased to 90%, the alloy was fibrous, the microstructure of the alloy was fibrous in the rolling direction, and grains were severely broken, making it difficult to identify grain boundaries. We found no recrystallized grains and the alloy did not recrystallize.

The grain boundaries of Cu–0.32Cr–0.059Ti–0.017Si alloy with different cold rolling deformation are shown in Fig. 3. The red and black lines in the figures are the low-angle grain boundaries (2° < θ < 10°) and high-angle grain boundaries (θ > 10°). The alloy before deformation contained mainly high-angle grain boundaries. As the cold reduction was increased, the proportion of the low-angle grain boundary increased. When deformation increased to 80%, the proportion of the low-angle grain boundary decreased, such that the high-angle grain boundary showed a relative increase. However, a large proportion low-angle grain boundaries remained in the ingots cold rolled at 80%.

The right column shows the misorientation distributions of the alloy samples after different degrees of rolling reduction. The low-angle grain boundary before deformation was only 4%. After cold rolling 30%, the proportion of low-angle grain boundaries increased greatly to approximately 78%, and the proportion of high-angle grain boundaries was relatively small. As the deformation was increased to 60%, the proportion of low-angle grain boundaries increased slightly to 78.4%. When the deformation reached greater than 85%, the proportion of low-angle grain boundaries in the alloy shows a tendency of decreasing, – as low as 44.7% with 95% deformation.

At the initial stage of deformation, the grains gradually turned in a direction that enabled easy slippage as the cold rolling reduction was increased. In this way, the misorientation between the grains became smaller and the volume fraction of the low-angle boundary gradually increased; however, when the degree of deformation was increased to 80%, the volume fraction of the low-angle grain boundary became lower, and the volume fraction of the high-angle grain boundaries was greater. At this time, the proportion of high-angle grain boundaries was small. When the metal plastically deformed, dislocations were absorbed by subgrain boundaries such that the misorientation between subgrains gradually increased and the low-angle grain boundaries gradually transformed into high-angle grain boundaries. Thus, the conversion process consumed some misplacement.

The microstructures of Cu–0.32Cr–0.059Ti–0.017Si alloy after cold rolling are shown in Fig. 4. The microstructure of the peak aging sample before deformation showed almost no dislocations [Fig. 4(a)]. After the cold rolling deformation 60% there was a high density of dislocations in the alloy sample and dislocation lines entangled with each other to form a dislocation wall [Fig. 4(b)]. When deformation increased to 80%, the internal structure of the alloy exhibited a strip-like and cellular substructure after slip deformation [Fig. 4(c)]. Most of the dislocation lines entangled to form dislocation
cell boundaries. Some dislocation lines were entangled in the dislocation cells and the dislocation density remained high. When the deformation increased to 90% [Fig. 4(d)] the dislocation cell structures of the alloy changed and the dislocation cells become thin, relative to the 80% deformation. Additionally, the intracellular dislocations moved toward the dislocation cell boundary, the dislocation density in the dislocation cells decreased, and dislocations were flattened, to form sub-grains with clear interfaces and large dimensions. The subgrain size was approximately 200–300 nm.

In the initial stage of deformation, the dislocations become entangled and the hardness of the alloy increased.

Fig. 3 – Grain boundary diagrams and misorientation distributions of Cu–0.32Cr–0.059Ti–0.017Si alloy treated at different degrees of cold-rolling reduction: (a1, b1) 0%, (a2, b2) 30%, (a3, b3) 60%, (a4, b4) 80%, (a5, b5) 85%, (a6, b6) 90% and (a7, b7) 95%.
continuously increases as the dislocation density is gradually increased. Under continued deformation, a large number of dislocation cells formed. At 90%-cold rolling, distortion accumulated to a certain extent, dislocations became smoothly multi-laterally restored by slip and cross-slip, releasing a large amount of distortion energy to alleviate the residual stress generated during deformation. At the same time, the dislocation density in the dislocation cell decreased, such that the resistance to continued deformation decreased. The adjacent dislocation cells reacted with each other to merge into larger dislocation cells. Owing to dislocation interaction, subgrains formed inside the structures; however, the subgrains were not equiaxed and did not form a recrystallized nucleation core. The alloy recovered; however, no dynamic recrystallization occurred after 90% deformation.

During plastic deformation, the moving dislocations can interact with each other to hinder their own motion. Generally, a higher dislocation density results in higher hardness of the alloy. The dislocation density can be measured by XRD (Fig. 5), and calculated by Eq. (1) [15]:

$$ \rho = 2\sqrt{3} \cdot \frac{\varepsilon}{D \cdot b} $$

(1)

where $D$ is the crystallite size and $\varepsilon$ is the microstrain, which is obtained by linear fitting of the formula (2), $b$ is the Burger vector (for the FCC structure of alloy, $b = (\sqrt{2}/2)a$):

$$ \beta \cdot \cos \theta = \frac{K \lambda}{D} + (4 \sin \theta) \cdot \varepsilon $$

(2)

where $\beta$ is the half-peak width, $\theta$ is the Bragg angle of a certain peak, $K$ is a constant (~0.9), and $\lambda$ is a wavelength of CuKα radiation (0.15405 nm).

The dislocation densities calculated after cold rolling of Cu-0.32Cr-0.059Ti-0.017Si alloy with different cold-rolling reduction are presented in Table 2. As the cold rolling deformation increased, the dislocation density of the alloy initially
increased. When the deformation was increased to 80%, the dislocation density became lower. As the deformation was increased further to 90%, the dislocation density decreased further. After cold rolling 95%, the dislocation density of the alloy decreased to $4.5599 \times 10^{14}$ m$^{-2}$. This result is consistent with the changes in dislocation density [Fig. 4(c, d)]. Furthermore, after cold-rolling deformation at 80%, the grain breakage is severe; although the dislocation density of the alloy decreases at this time work hardening occurs. The hardening effect is higher than the softening effect caused by the decrease of the dislocation density, such that the hardness of the alloy does not decrease. However, when the deformation was increased to 90%, large subgrains formed because the alloy recovered and the dislocation density of the alloy decreased; thus, the hardness of the alloy decreased.

### 4. Conclusions

We examined cold-rolling of the Cu–0.32Cr–0.059Ti–0.017Si alloy at room temperature. As the cold-rolled reduction increased, the hardness of the alloy first increased. When the amount of deformation exceeds 85%, the hardness of the...
alloy decreased. According to our microstructural analysis, the hardness change is the result of competition between recovery and work hardening. When the deformation was 90%, recovery occurred and the low-angle grain boundaries transformed into high-angle grain boundaries; hence, the dislocation density decreased. The softening effect caused by room-temperature recovery was greater than the effects of work hardening; hence, softening of the alloy occurred.

**Conflicts of interest**

The authors declare no conflicts of interest.

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**REFERENCES**


