Short Communication

Grain refinement and enhanced precipitation of Cu–Cr–Zr induced by hot rolling with intermediate annealing treatment

D.P. Shen\textsuperscript{a}, Hongbo Zhou\textsuperscript{b}, W.P. Tong\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Key Laboratory of Electromagnetic Processing of Materials, Ministry of Education, Northeastern University, Shenyang 110819, China
\textsuperscript{b} Institute of Materials Physics, University of Münster, Munster 48161, Germany

\textbf{A R T I C L E  I N F O}

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\textbf{A B S T R A C T}

A new process of hot rolling with intermediate annealing is developed to increase the strength and electric conductivity of the Cu-1Cr-0.1Zr (wt.\%) alloy. The process can refine the crystalline structure and accelerate the speed of precipitation simultaneously, and a combination of high ultimate tensile strength of 522 MPa, excellent electrical conductivity of 81.9 IACS\% has been achieved. The results show the higher strain rate and temperature, the higher speed of precipitation. In addition, the microstructure and property of the strip processed by HR-6723 K is non-uniform through the thickness, and the top layer with 0.2 mm thickness shows a higher tensile strength and electrical conductivity than that of the overall rolled sheet.

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1. Introduction

Cu–Cr alloys and their modifications are being widely used in many applications, such as trolley wires, electrodes for resistance welding, connectors of various microelectronic devices and lead frames, due to their excellent electrical conductivity, outstanding tribological behaviour and high mechanical strength [1–5]. As a typical precipitation strengthened Cu alloy, solid solution and annealing treatment is usually used to achieve an optimized combination of strength and electrical conductivity. The high electrical conductivity is due to the low solubility of Cr and Zr in Cu after annealing treatment, whereas the excellent strength is attributed to precipitation and particle-dispersion strengthening mechanisms. In last decades, aging has also been implemented after severe plastic deformations (SPD) to promote grain refinement and precipitation hardening for better mechanical performance [6–8]. It notes that SPD techniques refine grains by deforming a material to an extremely large plastic strain, which would induce high-density dislocations into the as-processed alloys and could be hard to eliminate by annealing without the significant grain growth. Consequently, this increase in strength in the materials produced by the SPD methods is usually accompanied by a loss of electric conductivity even after annealing [9,10]. Therefore, it is still a challenge to improve the strength and electrical conductivity simultaneously for the bulk of UFG materials.

\* Corresponding author.
E-mail: wptong@mail.neu.edu.cn (W. Tong).
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Table 1 – The detailed experimental procedures of HRA.

<table>
<thead>
<tr>
<th>Procedures</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Step 5</th>
<th>Step 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR-6 723 K</td>
<td>AT + HR 30%</td>
<td>AT + HR 30%</td>
<td>AT + HR 50%</td>
<td>AT + HR 50%</td>
<td>AT + HR 50%</td>
<td>AT + HR 50%</td>
</tr>
<tr>
<td>HR-7 53 K</td>
<td>Total annealing</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>HR-3 723 K</td>
<td>AT + HR 50%</td>
<td>AT + HR 75%</td>
<td>AT + HR 50%</td>
<td>AT + HR 50%</td>
<td>AT + HR 7%</td>
<td></td>
</tr>
<tr>
<td>HR-7 53 K</td>
<td>Total annealing</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>HR-3 753 K</td>
<td>time 60 min</td>
<td></td>
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<tr>
<td>HR-7 53 K</td>
<td>AT + HR 50%</td>
<td>AT + HR 30%</td>
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<td>AT + HR 50%</td>
<td>AT + HR 50%</td>
<td>AT + HR 50%</td>
</tr>
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AT: annealed at 723 K or 753 K for 10 min in a furnace.
HR30%, HR50%, HR75%: The samples were taken out of the furnace and rolled rapidly with a reduction of 30%, 50% and 75%, respectively.

Fig. 1 – (a) Variation of micro-hardness along the depth from outer surface to core of HRA samples, (b) the surface microstructure, (c) correspond grain distributions and (d) misorientation distributions of Cu–Cr–Zr alloy subjected to HR-6723 K treatment.

Here, we report an excellent combination of high strength and excellent electrical conductivity produced in Cu–Cr–Zr alloys subjected to multi-pass hot rolling with intermediate annealing (HRA). This work demonstrates the possibility of tailoring the microstructures of ageing hardened alloys by HRA to obtain both high strength and good electrical conductivity.

2. Method

A commercial C18150 alloy was chosen in the present work with 1.0 wt.% Cr and 0.1 wt.% Zr and cut into specimens by wire-electrode cutting (40 × 40 × 80 mm). The specimens were firstly subjected to solid solution treatment at temperatures of 1000 °C, followed by quenching in cold water quickly. Then multi-pass hot rolling combining intermediate annealing treatment (HRA) was carried out to these specimens. And a total reduction of approximately 96.9% with the finally thickness of 0.125 mm was achieved by these procedures. The detailed routes are summarized and labelled in Table 1. The microstructure of the Cu–Cr–Zr alloy was characterized by using SEM, EBSD and TEM, and the electrical conductivity of the samples was measured by an intelligent eddy-current low-resistance tester. Relevant tensile test specimens were designed (schematic diagram shown in Fig. 4) and tested by using an IDW-200H universal testing machine. Three samples were tested for each sample, confirming the excellent repeatability of strength and elongation.

3. Results and discussion

The initial as-soluted sample was characterized by a uniform microstructure with an average grain size of 638 μm with the micro-hardness of approximately 65 HV. The hardness increases after HRA treatments, and the details are shown in
Fig. 2 - (a)(d) Typical orientation maps, (b)(e) correspond grain distributions and (c)(f) misorientation distributions of Cu–Cr–Zr alloy subjected to HR-6723 K and HR-3723 K treatments, respectively. The white and black lines indicate the low-angle (3° > θ < 15°) and high-angle (θ > 15°) boundaries, respectively.

The results show that the hardness is not uniform, which indicate that the microstructure is different between surface layer and the matrix. One of the typical microstructure at the top layer of HR-6723 K can be seen in Fig. 1b. The grain size and misorientation distributions are shown in Fig. 1c and d. The results show that the microstructure evolves toward a granular homogeneous microstructure with small equiaxed crystallites. And the fraction of high angle grain boundaries (HAGBs) is as high as 83.2%. The microstructure in the core area of HR-6723 K is quite different. A higher fraction of the elongation grains along the rolling direction are found, as show in Fig. 2(a). In which, the grain size increases greatly to about 2.982 µm but the fraction of HAGBs decreases dramatically to about 36.7%, as shown in Fig. 2b and c. Compared with HR-6723 K, a higher fraction of small equiaxed grains with the smaller grain size and a higher fraction of HAGBs have been observed in HR-3723 K, as show in Fig. 2d–f, which means that the size distribution and misorientation varies dependent on the different rolling processes.

The engineering tensile stress–strain curves of the Cu–Cr–Zr alloy in the solid-solution state and subjected to HRA are shown in Fig. 3a. The engineering stress and electrical conductivity are summarized in Fig. 3b. The properties of as-quenched alloy subjected to annealing at 723 K, 753 K for 30 min and 60 min was also collected and compared with the HRA samples. It is interesting to found that except for a higher strength, the samples processed by HRA also show higher electrical conductivity under the same annealing temperature and time, in spite of an amount of defects has been induced. Therefore, it is reasonable to believe that the higher electric conductivity is caused by a lower content of solid solution. That means the HRA-processes can accelerate the speed of precipitation. Another important piece of evidence can be seen in Fig. 4a and b. Compared with as-quenched alloy
subjected to annealing at 753 K for 30 min, more chromium particles were precipitated in HR-3723 K. It also should be noted that the conductivity of sample processed by HR-6723 K is much lower than that of sample subjected to HR-3723 K, though the former process have twice as much annealing time as HR-3723 K. As is known, the former process has a higher strain rate. Therefore, a conclusion can be drawn that the higher of strain rate, the higher of the speed of decomposition. This phenomenon can be verified by Fig. 4b and c, in which the size of chromium particles precipitated from HR-3723 K were coarser than those precipitated from HR-6723 K. And further analysis by SEM-EDX showed that the content of chromium in HR-3723 K was 1.55 wt.%, which is higher than that of HR-6723 K (1.49 wt.%). It is well known that the production rate of vacancies during heat deformation is proportional to the strain rate [15]. Therefore, the density of dislocation would increase much effectively during a higher strain rate, which would decrease interfacial and misfit energy and then promoted the nucleation of precipitates. Hence, it can explain why the precipitation is faster under higher strain. Except strain rate, it is looked like that the temperature also has an important effect on precipitation. For example, the conductivities of Cu–Cr–Zr alloys processed by HR-3753 K and HR-6753 K was as high as 83.2 IACS% and 81.9 IACS%, respectively.

It is interesting to find that the strength of the Cu–Cr–Zr alloy subjected to HR-3753 K was lower that the sample subject to HR-6753 K, even the average grain size of HR-3753 K is much smaller, as show in Fig. 2. It was observed that the precipitate size of HR-3753 K was larger than that of HR-6753 K, as shown in Fig. 4c and d, which was expected the main reason to cause such phenomenon. Another interesting phenomenon is that the tensile strength and electrical conductivity of the top 0.2 mm layer are both higher than that of the overall rolled sheet processed by HR-6723 K. As is well known, the friction between the plate and the roller can cause a large shear stress on the surface, which would cause a higher strain rate at the surface. This is the reason why the grain size is smaller at the top surface, as show in Figs. 1c and 2b. Therefore, the increase in tensile strength can be attributed to the smaller average grain size. The increased conductivity can be attributed to the higher strain rate at the top surface, which could accelerate the process of precipitation as talked above. It should be noted that the precipitates are prone to coarsening under higher strain rate, resulting in a drop in precipitation strengthening. Therefore, at the top layer, the decreased of tensile strength caused by precipitates coarsening and the increased caused by grain refinement is a competitive relationship. And the results can be inferred that the tensile properties increased under the combined effects.

4. Conclusion

(1) A new process of hot rolling with intermediate annealing is developed to increase the strength and electrical conductivity of a Cu-1Cr-0.1 Zr (wt.%) alloy. A combination of high ultimate tensile strength of 522 MPa, excellent electrical of 81.9 IACS% has been obtained.

(2) The process can refines the crystalline structure and promote the process of precipitation and could be further accelerated under the condition of higher strain rate and temperature.

(3) The microstructure of the strip is non-uniform through the thickness, from a lower fraction of small equiaxed grains with higher fraction of the elongation grains at the core area to a granular homogeneous microstructure with small equiaxed crystallites at the surface. The top layer with 0.2 mm thickness shows a higher tensile strength and electrical conductivity simultaneously than that of the overall rolled sheet processed by HR-6723 K. And a combination of ultra-high ultimate tensile strength of 685 MPa, excellent electrical conductivity of 75.6 IACS% has been obtained.
Fig. 4 – The SEM micrographs show the distribution of Cr particles in (a) as-soluted samples subjected to annealing at 723 K for 30 min, (b) HR-3723 K and (c) HR-6723 K treatment, respectively; as well as STEM micrographs of (d) HR-3723 K and (e) HR-6723 K.

Conflicts of interest

The authors declare no conflicts of interest.

Uncited references [11,12,13,14].

Acknowledgments

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REFERENCES


