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Thermal Stability of Ultrafine Grained CuCrZr Alloy Produced by Continuous Extrusion

Hui Feng[1,2], Haichang Jiang[1,*], Desheng Yan[1], Lijian Rong[1]

[1]CAS Key Laboratory of Nuclear Materials and Safety Assessment, Institute of Metal Research, Chinese Academy of Science, Shenyang 110016, China

[2]CNPC Tubular Goods Research Institute, Shanxi Xi'an 710077, China

*Corresponding author: Haichang Jiang(hcjiang@imr.ac.cn)

Research Article

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Abstract The Cu-0.36Cr-0.15Zr alloy was prepared by solid solution, continuous extrusion and cold deformation. The microstructural evolution, microhardness and the thermal analysis were examined for the alloy after annealing treatment at different temperatures ranging from 300 °C to 700 °C. Experimental results show that the microstructure of the alloy remains stable after annealed below 500 °C due to the pinning effect of dislocations from the nanoscale precipitates. However, recrystallization and grain growth took place after a 600 °C annealing treatment when the precipitates grew up and lose inhibition of movement of dislocations and grain boundaries. Meanwhile, the higher dislocation density and finer grains introduced by continuous extrusion accelerate the recrystallization process compared with that prepared by the traditional rolling process.

Keywords: *thermal stability; continuous extrusion; ultrafine grains; CuCrZr alloy; precipitate*

1. Introduction

Due to the synergistic effect of precipitating strengthening and work hardening mechanisms, CuCrZr alloy possesses high mechanical strength, electrical conductivity and thermal conductivity and therefore are being considered as the candidate material for engineering applications, such as electric contacts, lead frames and trolley contact wires[1-3]. Many researchers have focused on the microstructure, precipitates and the mechanical behaviors of the CuCrZr alloys[4-7]. Feng et. al[8,9] found that the mechanical properties of CuCrZr alloy could be further improved after continuous extrusion by forming ultrafine subgrains while the electrical conductivity does not show a significant decrease.

Thermal stability is another important property for the high strength and high electrical conductivity material. Nevertheless, ultrafine grained materials usually exhibit poor thermal stability. Jiang[10] found that the micro-hardness of copper, prepared by high-pressure torsion (HPT), decreased at as low as 180 °C, which indicates a very low thermal stability. However, the situation would become more complex for CuCrZr alloys with the introduction of precipitates, since these precipitates might block the motion of the dislocations and have a positive effect on the thermal stability. So, the aim of the present work was to analyze the influence of the precipitates and ultrafine grains on the thermal stability of CuCrZr alloys processed by continuous extrusion.

2. Experimental Procedures

In the experiment, The Cu-0.36Cr-0.15Zr alloys were produced in a vacuum induction furnace and extruded into a diameter of 20 mm. After solution treated at 960 °C for 2 h, the CuCrZr rods were continuous extruded on the TLJ400 copper continuous extrusion machine. The wheel speed is 4 rpm and the preheating temperature is 723 K.

Plates with a thickness of 10 mm were cut from the continuous extrusion processed CuCrZr rods and then cold rolled by 90% reduction in thickness. The cold deformed specimens were annealed in a resistance furnace for 1 h at different temperatures.

Microstructural characterization was performed along the rolling direction by optical microscopy (OM) and the FEG-SEM (JEOL 7001F). Transmission electron microscopy (TEM) observation was carried on a JEM 2010 transmission electron microscopy with an operating voltage of 200 kV. The hardness was determined on polished longitudinal section of the specimens using a Vickers hardness tester with a load of 200 g and a holding time of 15 s. The hardness for each sample was taken from the measured average of at least 7 indentations.

X-ray diffraction (XRD) analysis was conducted with CuKa radiation, and the thermal analysis was carried out by differential scanning calorimetry (DSC) with a heating rate of 20 K/min from 300 °C to 700 °C.

3. Results

3.1 Microstructural evolution

Figure 1 shows the microstructure of Cu-0.36Cr-0.15Zr alloy after continuous extrusion and 90% cold deformation and then annealed at different temperatures. The as-deformed microstructure displays a ribbon-like grains elongated along the rolling direction. It has been demonstrated that grains are largely refined to sub-micron scale after continuous extrusion for CuCrZr alloys [8], thus it is reasonable that the grains are very fine after cold rolling, shown in Figure 1(a). The ribbon-like grains are still retained in the alloy after annealing at 500 °C for 1 h. However, annealing at 600 °C produces obvious recrystallization grain growth. Ribbon-like structures vanished while coarse equiaxed grains and annealed twins could be observed. Meanwhile, there are still some very small grains that might be subgrains or recrystallized grains at an early stage. After annealed at 700 °C for 1 h, considerable grain growth took place. The average grain size is about 10 μm and the annealed twins became more obvious.

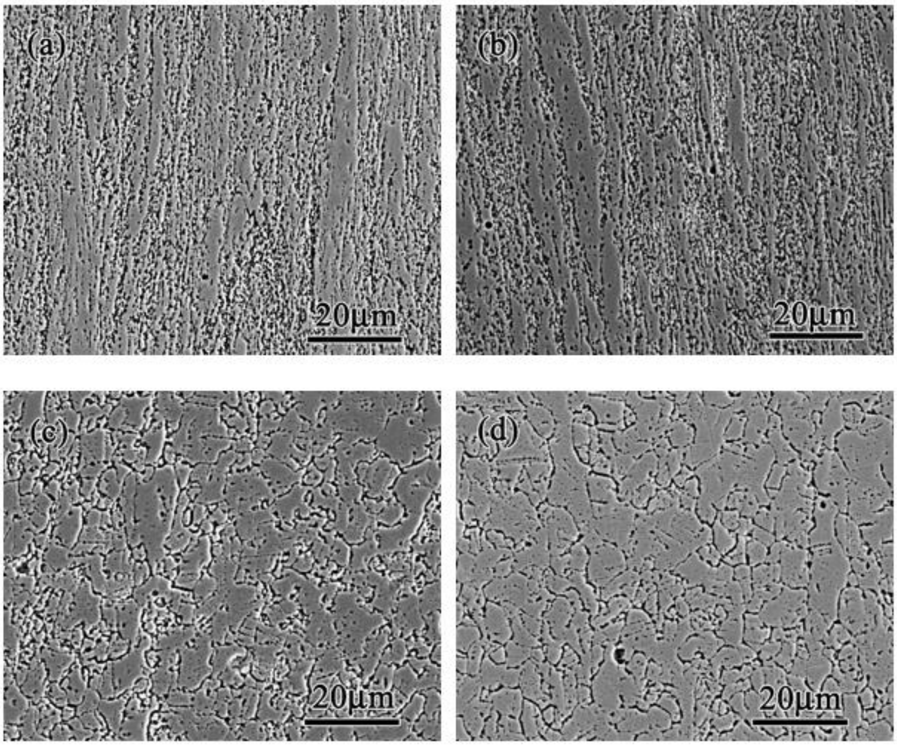

Figure 1. Microstructure of Cu-0.36Cr-0.15Zr alloy after continuous extrusion and 90% cold deformation. (a) as-deformed, (b) annealed at 500 °C for 1 h, (c) annealed at 600 °C for 1 h and (d) annealed at 700 °C for 1 h.

3.2 Microhardness

After continuous extrusion and cold rolling, the CuCrZr samples were annealed at 300 ºC, 400 ºC, 500 ºC, 600 ºC and 700 ºC for 1 h respectively. Figure 2 shows the microhardness of the samples versus annealing temperatures. It can be seen that the microhardness keeps nearly the same with annealing temperature up to 500 ºC. Our previous study has proved that only a small part of solutes precipitate from the matrix, thus during the following annealing treatment below 500 ºC, the remaining solutes precipitate providing the strengthening effect which compensates the softening effect of resulting from the dislocation recovery during annealing treatment. However, after annealed at 600 ºC, the microhardness shows a sharp decrease to 81.7 HV. According to [11-13], the main precipitates in CuCrZr alloys are Cr, $CrCu_2Zr$ and Cu_4Zr. These precipitates would grow up and lose the pinning effect of dislocations, leading to a recrystallized microstructure, as shown in Figure 1(c). When annealed at 700 ºC, most recrystallized grains grow up and the microhardness demonstrates a further decrease to 69.2 HV.

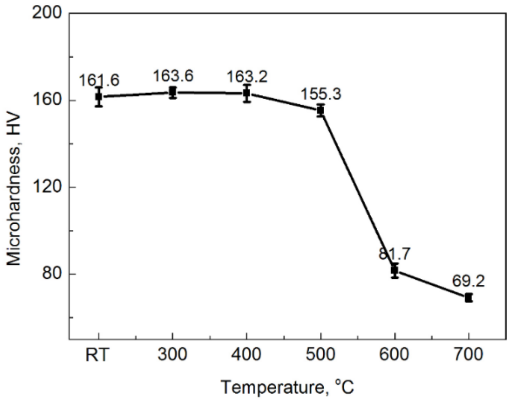

Figure 2. Microhardness of Cu-0.36Cr-0.15Zr alloy after annealing at different temperatures

3.3 DSC result

Figure 3 shows DSC curve of the Cu-0.36Cr-0.15Zr samples processed by continuous extrusion and cold deformation. The curve shows endothermic reaction points in the positive y-direction. It is reported that only the exothermal peak corresponding to recrystallization could be observed for deformed pure metals [14,15]. However, in this experiment, the DSC curve seems to be more complex, which has two exothermal peaks. The first exothermal peak at approximately 400 ºC can be attributed to the recovery of dislocations and the precipitating process [14]. The exothermal peak at the higher temperature corresponds to the recrystallization process when dislocation density significantly decreases, which could be verified by the microstructural evolution shown in Figure 1. Jiang etc.[10,16] have also found the recrystallization induced exothermal peak in ultrafine grained materials. When the scanning temperature is above 700 ºC, the curve shows a descending trend, which might be part of another exothermal peak. We believe that it was caused by the oxidation of the CuCrZr alloys since the sample was colored after the DSC test although protected by the N_2.

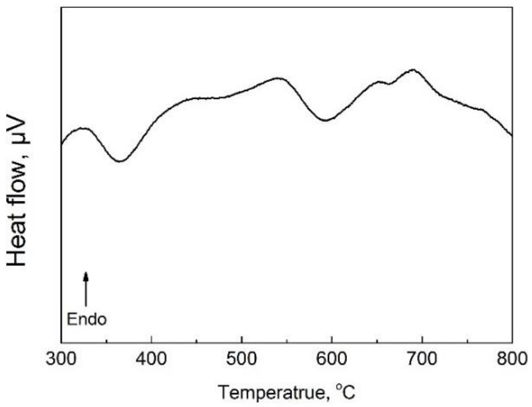

Figure 3. DSC curve of Cu-0.36Cr-0.15Zr alloy processed by continuous extrusion and cold deformation.

3.4 XRD result

Figure 4 shows the XRD results of Cu-0.36Cr-0.15Zr alloy processed by continuous extrusion and cold deformation after annealed at 400 ºC, 500 ºC, 600 ºC and 700 ºC respectively. Although there exists the second phase of precipitates, no diffraction peaks could be observed in the XRD patterns since these precipitates have a nanoscale size and a very low volume fraction. Figure 4 demonstrates not only the peak distribution of Cu matrix, but also the relative intensity variation of certain crystal planes. It can be seen that the $(111)_{Cu}$ intensity is the lowest after annealed at 400 ºC but increase with the increase of annealing temperature while the (200)Cu shows the opposite trend, which indicates that the annealing temperature leads to the change of crystal orientation in the Cu-0.36Cr-0.15Zr alloy.

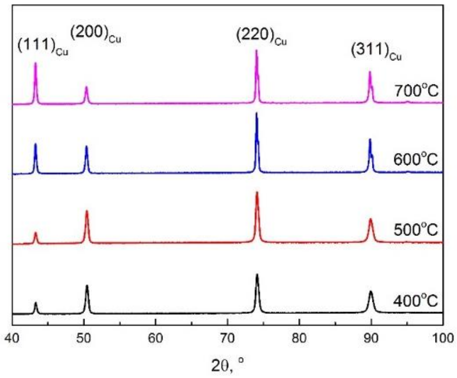

Figure 4. XRD patterns of the Cu-0.36Cr-0.15Zr alloy annealed at different temperatures

The Lotgering factor is used to describe the change of crystal orientation quantitatively. According to [17,18] the Lotgering factor could be given by:

$$L_{(hkl)} = \left(P_{(hkl)} - P^0_{(hkl)}\right)/\left(1 - P^0_{(hkl)}\right)$$

$$P_{(hkl)} = I_{(hkl)}/\sum I_{(hkl)}$$

where $I_{(hkl)}$ illustrates the intensity of (*hkl*) diffraction, and $P_{(hkl)}$ presents the ratio of a (*hkl*) diffraction intensity with the integrated intensity at a certain annealing temperature. $P^0_{(hkl)}$ means that it is calculated under the condition that the samples were fully annealed which is 700 ºC in the experiment.

Figure 5 shows the Lotgering factors of different diffractions with different annealing temperatures for the Cu-0.36Cr-0.15Zr alloy. The fraction of $(220)_{Cu}$ and $(311)_{Cu}$ remains almost unchanged with the increase of annealing temperature while the $(111)_{Cu}$ and $(200)_{Cu}$ demonstrate a significant variation when annealed above 500 ºC. This phenomenon is consistent with the microstructure observation and the microhardness result. In fact, continuous extrusion and cold deformation lead to the formation of deformation texture. The stored energy decreases due to the recovery when annealed at lower temperatures, however the grain orientation remains unchanged, thus, the Lotgering factors at 400 ºC and 500 ºC are almost the same. When annealed at 600 ºC, the deformation texture was greatly weakened by the formation of equiaxed grains and the crystal orientation is gradually approaching that of fully annealed samples.

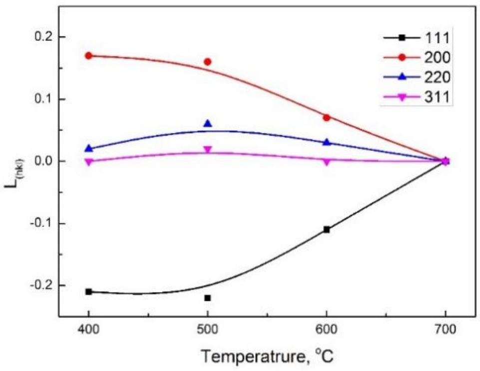

Figure 5. Lotgering factor showing the structural evolution with annealing temperature

4. Discussion

4.1 Effect of precipitates on the thermal stability

Figure 6(a) shows the precipitate morphology of the Cu-0.36Cr-0.15Zr samples annealed at 500 ºC for 1 h. The precipitates have an average size of about 20 nm. It is generally accepted that the very fine nanoscale precipitates make great contribution to the strengthening of the alloy due to the pinning effect of the dislocations during plastic deformation. The restrain of dislocation movements inhibits the process of recrystallization, which actually improves the thermal stability of the alloy. The ultrafine grained Cu process by high pressure torsion recrystallized at as low as around 180 ºC[11] while the CuCrZr alloy in this experiment remains thermal stable even annealed at 500 ºC.

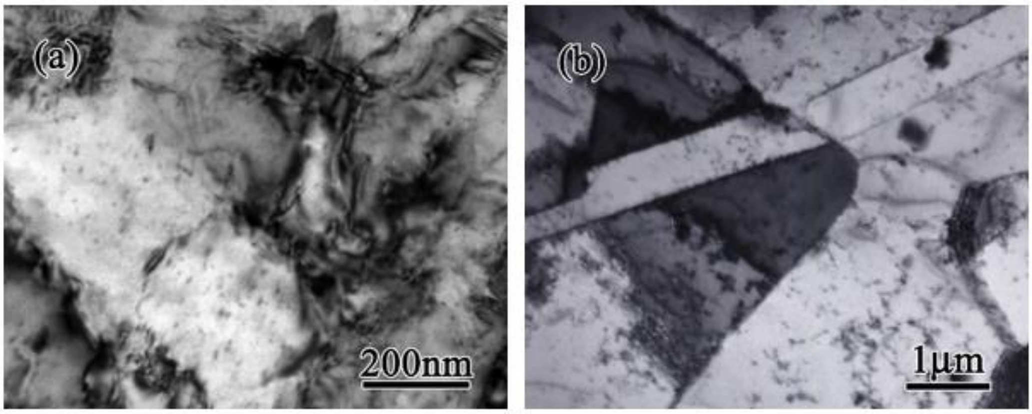

Figure 6. Microstructure of the Cu-0.36Cr-0.15Zr samples annealed at 500 ºC (a) and 600 ºC (b) for 1 h

Actually, there is always the competitive relationship between the driving force and the braking force for deformed CuCrZr alloys subjected to annealing treatments, where the reduction of dislocation density provides the driving force and the pinning effect from precipitates provides the breaking force of recrystallization. According to [19,20] the driving force (F_D) and the braking force (F_B) could be roughly estimated as follows:

$$F_D = \alpha G b^2(\rho_0 - \rho_1)$$
$$F_B = 3f\gamma_b/D$$

where α is a numerical constant, G is the shear modulus, b denotes the Burgers vector of the matrix, ρ_0 and ρ_1 are the dislocation density before and after recrystallization, f presents the volume fraction of the precipitates, γ_b is the boundary energy and D is the diameter of the precipitates.

If $F_D = F_B$, the critical precipitate size can be expressed as:

$$D_{cr} = 3f\gamma_b/\alpha G b^2(\rho_0 - \rho_1)$$

For Cu-0.36Cr-0.15Zr alloy in this experiment, the critical precipitate size is about 50 nm in diameter. Thus, when the samples were annealed below 500 ºC, the size of precipitates is below 20 nm which is smaller than the critical size. Therefore, the braking force is larger than the driving force and the recrystallization process is inhibited. However, when annealed at 600 ºC, nanoscale precipitates grew up to nearly about 100 nm, which is larger than the critical size. In this situation, the precipitates could not pin the dislocations and the subgrain boundaries effectively and recrystallization took place, as shown in Figure 6(b).

4.2 Effect of ultrafine grains on the thermal stability

Figure 7 shows the microstructure of the Cu-0.36Cr-0.15Zr alloy after continuous extrusion. It can be seen that the subgrains have a size of several hundred nanometers with dislocations accumulating at the subgrain boundaries and inside the subgrains. Severe plastic deformation as well as abundant heat was introduced due to the friction between the extrusion die and the CuCrZr rod during the extrusion process, which provides the possibility of dynamic recrystallization. Ultrafine grains help to improve the ductility of the alloy when subjected to large strains in the following cold deformation, which results in a more uniform grain spacing across the radial direction of the rod, just as shown in Figure 1(a).

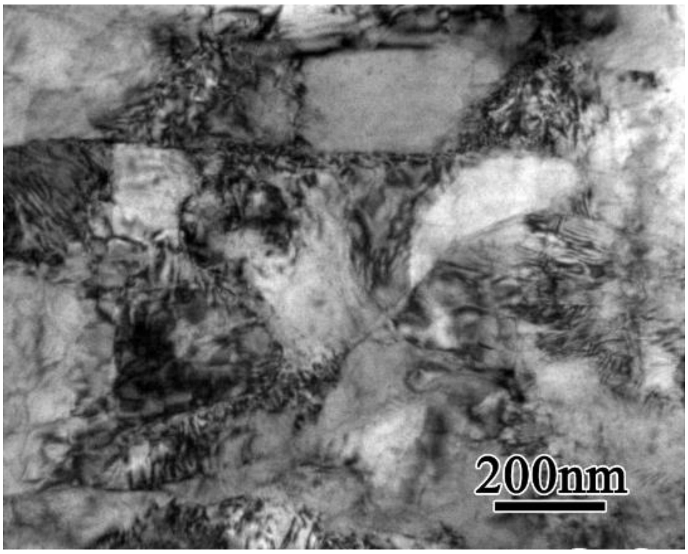

Figure 7. TEM image showing ultrafine grains of Cu-0.36Cr-0.15Zr alloy after continuous extrusion

To clarify the effect of ultrafine grains on the thermal stability produced by continuous extrusion and subsequent cold rolling, the Cu-0.36Cr-0.15Zr samples directly subjected to the cold rolling were adapted as the comparison. The samples prepared by the two processing technologies were annealed at different temperatures and the variation of grain size vs. annealing temperatures is shown in Figure 8. It can be seen that the samples prepared by continuous extrusion demonstrate a notable grain growth after annealed above 500 ºC while it above 600 ºC for the samples prepared directly by cold rolling, which means that the introduction of continuous extrusion results in a relatively poor thermal stability.

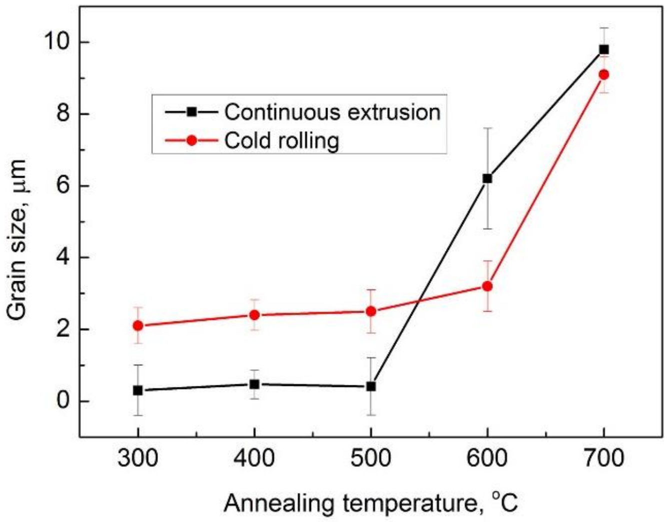

Figure 8. Comparison of variation of grain size of Cu-0.36Cr-0.15Zr alloy fabricated with and without continuous extrusion versus annealing temperature.

Compared to the traditional deformation process, such as rolling, drawing and so on, continuous extrusion introduced dynamic recrystallization, which produced ultrafine grains and relatively higher density of dislocations as well. The driving force for recrystallization from dislocations and grain size can be described as $F_D = \alpha G b^2(\rho_0 - \rho_1)$ and $F_B = 3\gamma/d$ respectively, in which γ represents the boundary energy of grains and d is the size of grains[19,21,22]. It can be deduced that the ultrafine grained CuCrZr alloy has a higher driving force for recrystallization with smaller grain size and higher dislocation density, which explains the relatively poor thermal stability.

5. Conclusions

1. The microstructure and microhardness remained stable when annealed below 500 °C due to the pinning effect of the nanoscale precipitates.

2. The nanoscale precipitates would grow up and lose inhibition of dislocations and grain boundaries after annealed at 600 °C when recrystallization took place. Microhardness shows a sharp decrease and the crystal orientation approaches that of the fully annealed samples.

3. Compared with the samples prepared directly by cold rolling, the ultrafine grained samples demonstrate a relatively poor thermal stability as a result of the higher dislocation density and the finer grains introduced by continuous extrusion.

6. Acknowledgements

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