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Strengthening mechanisms of ultrafine grained copper alloys

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Abstract. Cu-Cr-Zr alloys are characterized by an excellent combination of strength and electrical conductivity and are applied as structural materials in various electrical/electronic devices. The microstructure design of Cu-Cr-Zr alloys, the effect of thermomechanical treatment based on severe plastic deformation, and physical mechanisms providing high strength and electrical conductivity are investigated. The main structure-property relations in Cu-Cr-Zr alloys are considered. The dissolution of the dispersed particles during severe plastic deformation and an increase in the dislocation density, as well as the effect of heat treatment after deformation on the mechanical and electrical properties are discussed.

1. Introduction

Nowadays, Cu-Cr-Zr alloys attract the attention of researchers and engineers due to the unique combination of strength and electrical conductivity. Many works concentrate on investigation of the effect of severe plastic deformation (SPD) at room temperature on the microstructure and properties of the alloys, because deformation at room temperature produces smaller grain size and higher dislocation density in comparison with warm deformation. However, deformation at elevated temperature can provide optimal properties of Cu-Cr-Zr alloys. SPD at elevated temperature can promote dynamic aging, i.e., particle precipitation during deformation that can improve strength by dispersion strengthening and increase electroconductivity due to the decomposition of a supersaturated solid solution. Moreover, the kinetics of dynamic recrystallization is accelerated with an increase in the deformation temperature, so, grain refinement can be realized after relatively small strain. In addition, deformation at elevated temperature can be carried out under low pressure, decreasing the wear of the forming device. Subsequent aging after SPD improves electrical conductivity in Cu-Cr-Zr alloys.

The aim of the present work is to study the microstructure evolution, the mechanical properties, the strengthening mechanisms and the electrical conductivity of Cu-Cr-Zr alloys subjected to SPD at elevated temperature and aging.

2. Experiment

The investigated alloys were Cu-0.1%Cr-0.1%Zr (hereafter 0.1Cr-0.1Zr) and Cu-0.3%Cr-0.5%Zr (hereafter 0.3Cr-0.5Zr). 0.1Cr-0.1Zr was forged at 800 °C to a total strain of 2, then annealed at 920 °C during 1h with subsequent water quenching and aged at 550 °C during 4 h. 0.3Cr-0.5Zr was annealed at 920 °C for 0.5h with subsequent water quenching and aged at 450 °C during 1 h. The alloys were subjected to equal channel angular pressing (ECAP) at 400 °C via route B_C to 1, 2, 4, 8, 12 passes. Then, 0.1Cr-0.1Zr was annealed at 500 °C for 1 h and 0.3Cr-0.5Zr was annealed at 450 °C for

1 h. The microstructures were investigated using a Nova NanoSEM 450 scanning electron microscope (SEM) equipped with an EBSD analyzer and a Jeol Jem 2100 transmission electron microscope (TEM). The average grain size and the fraction of ultrafine grains (the grains with a size of below 2 micron) were estimated using the OIM Software. The dislocation density was determined by counting the number of intersections of individual dislocations located within the grains/subgrains interiors with the foil surfaces in at least 5 arbitrary selected TEM images. The specimens for SEM and TEM investigations were prepared by a Tenupol 5 with an electrolyte consisted of 25% HNO_3 and 75% CH_3OH at a temperature of -20 °C under a voltage of 10 V. The mechanical properties were evaluated using tensile tests at room temperature at a starting strain rate of 2×10^{-3} s^{-1}. The electrical conductivity was measured by the eddy current method using a Constant K6 device.

3. Results and discussion

3.1. Microstructure evolution of Cu-Cr-Zr alloys

After aging, the Cu-Cr-Zr alloys contained nanoscale particles. Fine ellipsoid Cr-rich precipitates with a bcc-lattice were 10-15 nm in the long direction and 5-7 nm in the transverse direction in 0.1Cr-0.1Zr. Spherical fcc-Cr particles with a diameter of about 4-5 nm precipitated in 0.3Cr-0.5Zr. The Cu-Cr-Zr alloys consisted of coarse grains with a size of 100-120 μm and 180-200 μm in 0.1Cr-0.1Zr and 0.3Cr-0.5Zr, respectively.

Plastic deformation at elevated temperature was accompanied by grain refinement (figure 1). After the 1st ECAP pass, new strain-induced low-angles boundaries (LAB) formed in the Cu-Cr-Zr alloys. Parallel long high-angle boundaries (HAB) developed in coarse initial grains and formed deformation microbands. An increase in strain led to the appearance of new grains with a size of less than 1 μm inside the deformation microbands. The formation of new grain resulted from an increase in the misorientations of LAB during deformation. After 8 ECAP passes, a uniform ultrafine grain structure with a grain size below 1 μm was formed.

The kinetics of grains refinement can be estimated using the modified Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation [1]:

$$F_{UFG} = 1 - \exp(-ke^n) \quad (1),$$

where F_{UFG} is the fraction of ultrafine grains, e is the logarithmic strain, k is the constant characterizing incubation period for grain refinement, and n is the kinetic constant.

The kinetic constant, n, was almost the same for 0.1Cr-0.1Zr and 0.3Cr-0.5Zr of 1.99 and 1.72, respectively. The incubation period of grain refinement of 0.1Cr-0.1Zr was longer than for 0.3Cr-0.5Zr alloy, so the grain size was smaller in 0.3Cr-0.5Zr alloy after the same ECAP strain. The change in the average grain size was good approximated with following equitation [1]:

$$D = D_{UFG}\,(1 - \exp(-ke^n)^{-0.5} \quad (2),$$

where D is the current grain size, D_{UFG} is the average size of ultrafine grains.

The dislocation density in 0.3Cr-0.5Zr was very high for copper alloys and achieved about 10^{15} m^{-2} after the 8th ECAP pass. In 0.1Cr-0.1Zr, smaller dislocation density of about $(2\text{-}4)\times10^{14}$ m^{-2} was observed. The change in the average dislocation density, ρ, can be expressed by the following equations [2]:

$$\rho = (1 - F_{UFG})\,\rho_{wh} + F_{UFG}\,\rho_{rec} \quad (3a),$$

$$\rho_{wh} = h/r + (h/r - \rho_0)\exp(-re) \quad (3b),$$

$$\rho_{rec} = h/r' + (h/r' - \rho_0)\exp(-r\,(e - e_C)) \quad (3c),$$

where ρ_{wh} is the average dislocation density in work hardened grains, ρ_{rec} is the average dislocation density in recrystallized grains, h is the athermal work hardening rate, r is the dynamic recovery rate in work hardened grains, r' is the dynamic recovery rate in recrystallized grains, ρ_0 is the initial dislocation density e_C is the onset recrystallization strain.

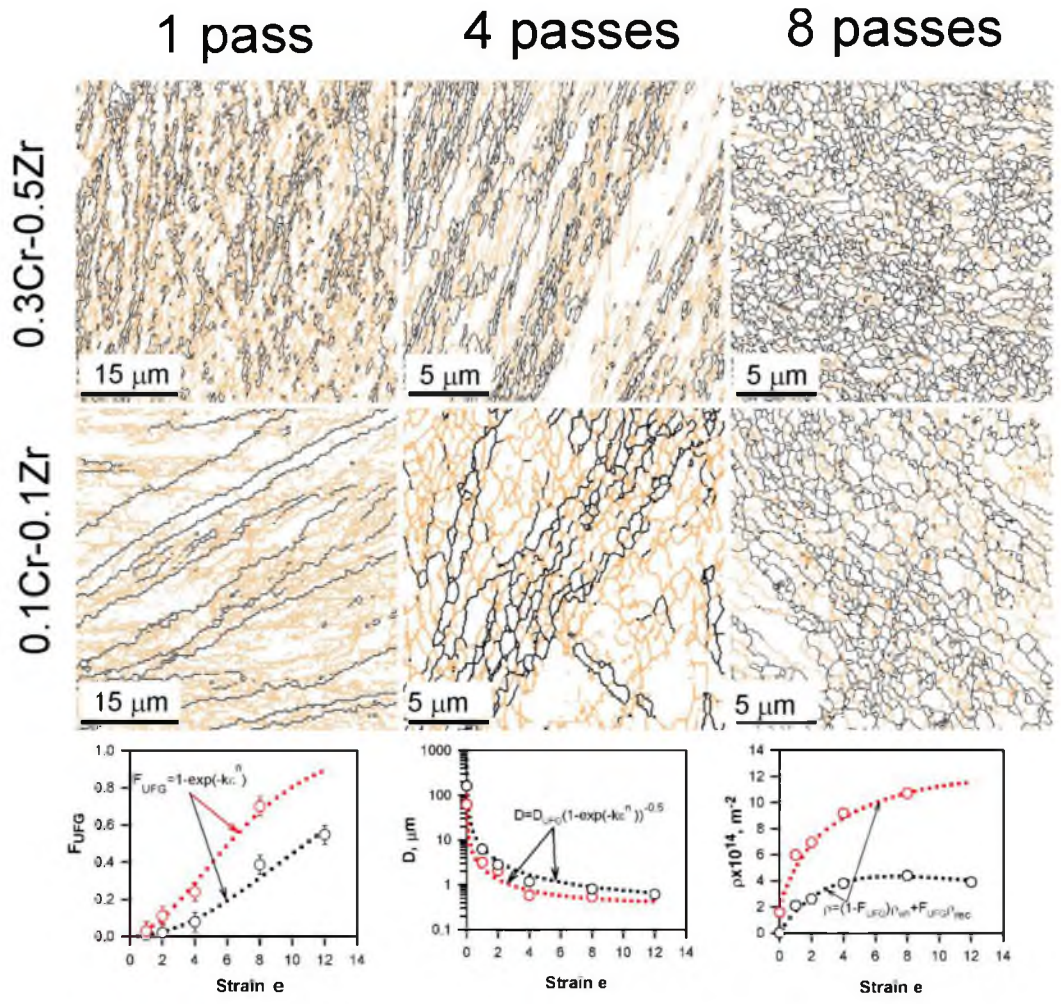

Figure 1. Microstructure evolution during ECAP in the Cu-Cr-Zr alloys. Black and brown lines represent HAB and LAB, respectively. Grain refinement and dislocation density in 0.1Cr-0.1Zr shown by black points and those in 0.3Cr-0.5Zr by red points.

The rate of dynamic recovery was higher, and the work hardening rate was lower in 0.1Cr-0.1Zr than in 0.3Cr-0.5Zr. The difference in the kinetics of grain refinement, dynamic recovery and work hardening can result from the difference in the structure, shape and size of Cr-particles in the initial states. Also, in the 0.3Cr-0.5Zr alloy, additional precipitation of particles during deformation was observed, leading to an increase in the volume fraction of particles from 0.0015 to 0.0027.

3.2. Properties of Cu-Cr-Zr alloys

ECAP led to an increase in the strength and a decrease in the elongation (figure 2). In 0.1Cr-0.1Zr after 8 passes, the ultimate tensile strength achieved 430 MPa. Significant strengthening was observed after the 1st ECAP pass. Then, the strength increased slowly with further straining. In 0.3Cr-0.5Zr the strength increased gradually with straining. 8 ECAP passes resulted in the ultimate tensile strength above 700 MPa. The elongation in the Cu-Cr-Zr alloys degraded with strengthening, although after 4 ECAP passes, the change in plasticity slowed down. The elongation was about 15% and 20% for 0.1Cr-0.1Zr and 0.3Cr-0.5Zr, respectively. In 0.1Cr-0.1Zr, the deformation led to a slight decrease in the electrical conductivity. In contrast, pressing of 0.3Cr-0.5Zr was accompanied by an increase in the electrical conductivity from 47% IACS to 65% IACS that could result from the precipitation of Cr-particles.

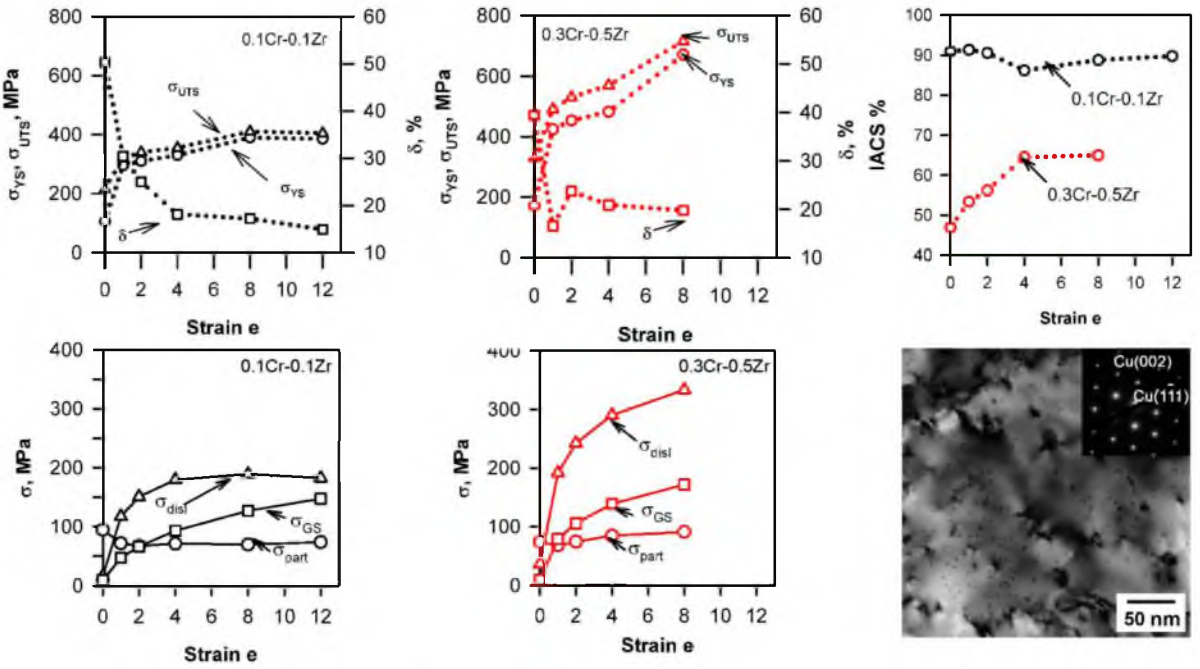

Figure 2. Effect of strain on the yield strength (σ_{YS}), ultimate tensile strength (σ_{UTS}), elongation (δ), electrical conductivity (IACS %), and particle (σ_{part}), dislocation (σ_{disl}) and grain size (σ_{GS}) strengthening of the Cu-Cr-Zr alloys, and the fine microstructure of 0.3Cr-0.5Zr after 4 ECAP passes.

The contribution of the different strengthening mechanisms to the total yield strength can be estimated as [1]:

$$\sigma_{YS} = \sigma_0 + \sigma_{part} + \alpha M G b \rho^{0.5} + k_y D^{-0.5} \quad (4),$$

where σ_{YS} is the yield strength, σ_{part} is the Orowan strengthening, α=0.24, k_y=0.12 are constants, M is the Taylor factor, G is the shear modulus.

The dislocation strengthening ($\alpha M G b \rho^{0.5}$) dominated in the studied deformation range. The particle strengthening (σ_{part}) was nearly the same with the grain size strengthening ($k_y D^{-0.5}$) after small strains. In the 0.3Cr-0.5Zr alloy, the dislocation density and the dislocation strengthening were significantly higher than in the 0.1Cr-0.1Zr alloy that can be associated with the high volume fraction of particles in the initial state in the 0.3Cr-0.5Zr alloy.

Aging of the Cu-Cr-Zr alloys led to increase in electrical conductivity to 93%IACS and 72% IACS for 0.1Cr-0.1Zr and 0.3Cr-0.5Zr, respectively, with a minor decrease in strength to 400 MPa for 0.1Cr-0.1Zr and to 650 MPa for 0.3Cr-0.5Zr that can be associated with the compensation of a decrease in dislocation strengthening by particle strengthening.

References

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[2] Quelennec X and Jonas J J 2012 *ISIJ international* **52** 1145