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DSC analysis of commercial Cu−Cr−Zr alloy processed by equal channel angular pressing

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Abstract: Samples of a commercial Cu−1Cr−0.1Zr (mass fraction, %) alloy were subjected to equal channel angular pressing (ECAP) up to 16 passes at room temperature following route Bc. Differential scanning calorimetry (DSC) was used to highlight the precipitation sequence and to calculate the stored energy, recrystallization temperature and activation energy after each ECAP pass. On another hand, electrical properties were correlated with the dislocation density. Results show that the stored energy increases upon increasing ECAP pass numbers, while the recrystallization temperature decreases significantly.

Key words: equal channel angular pressing (ECAP); Cu−Cr−Zr alloy; differential scanning calorimetry (DSC); electrical conductivity; stored energy

1 Introduction

Cu−Cr−Zr alloys attracted growing interests in electric/microelectronics areas and nuclear fusion reactors [1]. These alloys are known to be strengthened by conventional cold working, as well as by precipitation of Cr and complex Cu−Zr phases [1−3]. As long as severe plastic deformation processing was capable of producing strong materials with good ductility, these techniques were also applied to Cu−Cr−Zr alloys [4]. Since the work of VINOGRADOV et al [5] associated with thermal stability after SPD processing of Cu−Cr−Zr, very little work was devoted to highlight the thermodynamic aspects associated with thermal energy (enthalpy changes) that may lead to the improved knowledge of the chemical and microstructural changes that occur during and/or after SPD processing [6].

The mechanical properties such as strength and ductility of Cu−Cr−Zr have been been considerably optimized by combining severe plastic deformation and precipitation [7].

Moreover, serious controversies still exist on the sequence and nature of precipitates that can appear during annealing after conventionally or severely deformed Cu−Cr−Zr alloy [5,7,8].

The present work aims to evaluate some thermodynamics (stored energy) and kinetics (temperature and activation enthalpy) of recrystallization as well as to clarify the sequence of precipitation after ECAP processing of a Cu−1Cr−0.1Zr alloy.

2 Experimental

The material considered in this work is a Cu−1Cr−0.1Zr alloy that was supplied in the form of rod bars by Goodfellow. Billets of 10 mm in diameter and 60 mm in length were then machined for ECAP processing and solution heat-treated for 1 h at 1040 ºC in a protective inert gas atmosphere followed by a subsequent water quenching. The billets were processed by ECAP at room temperature up to 16 passes using route B_c (sample rotation of 90° along their longitudinal axis in the same direction after each pass). The ECAP die used in these experiments had an internal angle of Φ=90° and an outer arc of curvature of ψ=37°. The samples were coated with molykote spray and deformed at a constant cross head speed of 0.02 m/s.

In order to clarify the precipitation sequence and estimate the stored energy and the recrystallization temperature, miniature specimens of 40−50 mg were cut near the axial centre of the as-pressed billets and subjected to DSC analysis using a Labsys Evo (1600 °C) facility under a constant heating rate of 10, 20, 30 and

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40 °C/min in argon atmosphere. The DSC scanning temperature ranged from 30 to 700 °C and at least three specimens were probed for each heating rate. Standard Al_2O_3 samples were thermally scanned to calibrate the calorimeter prior to measurement and to obtain a baseline.

The activation energy of precipitation and recrystallization was calculated for the material processed for 1, 8 and 16 passes based on DSC measurements at heating rates of 10, 20, 30 and 40 °C/min. The dependence of the peak temperature on the heating rate was used to calculate the apparent activation energy for recrystallization based on the KISSINGER's method [9] given by

$$\ln\left(\frac{v}{t_{\mathrm{p}}^2}\right)=A-\frac{\Delta G}{RT_{\mathrm{p}}} \tag{1}$$

where v is the heating rate, t_{p} is the peak temperature, A is a constant, G is the apparent activation energy and R is the gas constant.

An X-ray diffraction profile analysis for each sample was carried out from the flat and polished surface by Brukers D8 Advance X-ray diffractometer using Cu K_α radiation operated at 40 kV and 20 mA. The 2θ Bragg angle varied from 30° to 88°. The step scan was 0.02° and the counting time per step was 7 s. Electrical conductivity measurements were performed ex situ using a four probe set-up (DFP-Research Model from SVSLabs).

The formation enthalpy of Cu clusters, Cu_5Zr and $Cu_{51}Zr_{14}$ precipitating phases were calculated within the framework of density functional theory (DFT) using pseudopotential method as implemented in the pseudo-potential plane wave self-consistent field package (Quantum Esspresso) [10]. The many-body problem of interacting electrons and nuclei was mapped to a series of one-electron equations in the so-called Kohn-Sham (KS) equations [11,12]. The generalized gradient approximation (GGA) of PERDEW et al (PBE) [13] of the local density approximation was considered to include the exchange-correlation energy and ultrasoft pseudopotentials of VANDERBILT [14] were used. A well converged value of the cut-off energy and the k-point mesh over the Brillouin zone were considered for both the structure of both compounds. All systems were allowed to fully relax using Broyden-Fletcher-Goldforb-Shanno (BFGS) scheme [15] until the total energy has converged to less than 10^{-5} eV/atom, the maximum force has converged to lower than 0.004 eV/Å and the maximum displacement was 0.002 Å.

3 Results and discussion

Figure 1 presents a compilation of DSC scans showing the enthalpy release during linear heating at 20 °C/min of the ultra-fine grained Cu−1Cr−0.1Zr alloy subjected to 1, 4, 8 and 16 ECAP passes. Other scans (not shown here) corresponding to 10, 30 and 40 °C/min exhibit almost the same trends.

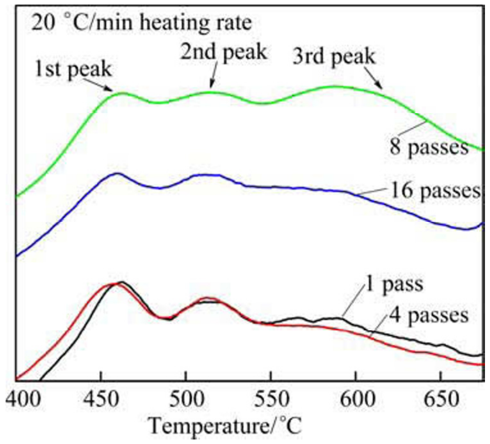

Fig. 1 Enthalpy release rate during linear heating of ultra-fine grained Cu−1Cr−0.1Zr alloy subjected to 1, 4, 8 and 16 ECAP passes

From Fig. 1, the third DSC peak near 600 °C and corresponding to recrystallization is more resolved for scans after 8 passes than for 1, 4 and 16 passes. The preceding peaks around (1st and 2nd peaks) confirm the complex precipitation sequence already mentioned in Ref. [5]. The first two peaks can be associated with Cr clustering and Cu_3Zr (replaced by $Cu_{51}Zr_{14}$ [16]) precipitation, respectively. All the peaks are however slightly shifted towards higher temperatures upon straining. It is worth mentioning that some DSC scans associated with recrystallization exhibit more than one peak (at least two, as shown in Fig. 1 after 1 ECAP pass). The occurrence of multiple peaks, within the recrystallization one, has already been observed in Al−Mg alloy after ECAP processing where the two present peaks are associated with the advent (recovery process) and the completion of the recrystallization process, while only one single peak appears in the cold-rolled alloy and that is related to the completion of the recrystallization [17]. However, the microstructures existing in the two alloys are somewhat different. The Al−Mg alloy after ECAP processing and dynamic aging exhibits a duplex microstructure divisible into areas of unrecrystallized grains and areas where recrystallization is essentially complete [17]. In the present work, the Cu−1Cr−0.1Zr alloy may exhibit a quite different microstructure consisting of not only duplex microstructure as observed above but also fine Cr and $Cr_{51}Zr_{14}$ precipitations [5,16], which interact with recrystallization, resulting in a rather very complex DSC signal.