DSC ANALYSIS OF AN ECAP-DEFORMED Cu-Ni-Si ALLOY

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Abstract

The stored and activation energy of an industrial Copper alloy (SICLANIC S) (Cu-2.5Ni-0.6Si) (% in weight) deformed by Equal-Channel Angular Pressing (ECAP) via route A up to 12 passes at 150°C was studied by Differential Scanning Calorimetry (DSC). The DSC results showed only a single characteristic peak that was attributed to recrystallization. The relatively low SFE of the alloy makes recovery difficult and may explain the absence of the recovery peak so that almost all stored energy of deformation is associated with the accumulation of dislocations. The stored energy increased upon straining up to 4 passes and then saturates at a constant value close to ~0.91 J/g. The activation energy of recrystallization after 12 passes ranged between 123 and 127 kJ/mol (1.28 and 1.32 eV, respectively). The estimated dislocation density from the stored energy is in agreement with that determined from X-Ray Diffraction Line Profile analysis.

Keywords: SPD, ECAP, DSC, CuNiSi alloy

1. INTRODUCTION

Severe Plastic Deformation (SPD) methods are extensively investigated for the purpose of achieving enhanced grain refinement compared to that obtained by classic plastic deformation techniques. Equal-Channel Angular Pressing (ECAP) is a recently developed method for homogeneous deformation processing of materials in bulk form and its principle was described earlier [1, 2]. This promising and attractive technique is increasingly studied because recent improvements make it easy to adapt to large-scale industrial processes. Some microstructural phenomena at solid-state as kinetics of grain growth, post-SPD processing, recovery, and recrystallization can be recorded by monitoring accurate thermal analysis using Differential Scanning Calorimetry (DSC) [3]. It has been long established that the addition of alloying elements lowers significantly the stacking fault energy of most metals [4, 5]. Probably γSFE in the present alloy (Cu-2.5Ni-0.6Si, % in weight) is close to that (γSFE ~ 50mJm−2) found by Alili et al. [6]. Suwas et al. [7] investigated experimentally the thermal stability of two pure metals (Cu and Ag for which γSFE is equal to 78 and 22 mJm−2 [8], respectively) deformed by ECAP following route A with channel angle of 90°. In the case of pure Copper, the recorded DSC thermogram for the first pass showed two distinct peaks attributed to a significant recovery taking place before recrystallization begins. A shoulder before the onset of the recrystallization left-hand side peak was observed for the two-pass deformed Cu sample. Alternatively, for the case of pure Silver (Ag), no recovery took place prior to recrystallization. Usually, under continuous heating regime (static mode) of ECAP-deformed materials, the calorimetric feedback signal evolution contains typically two exothermic peaks corresponding to the solid-state thermal events which are as follows: a first exothermic peak which is attributed to vacancies and is small and not always clearly identified, and a second peak which is more broadened and associated with the annihilation mechanism of dislocation-type lattice defects as with a recovery process by dislocation rearrangement yielding to a decrease in dislocation density and a reduction of the driving force available for recrystallization. The difference between the transformation peak and the
baseline reference is used to evaluate the stored energy [9]. It appears that no such study was previously undertaken on Cu-Ni-Si alloys. The scope of this paper is to evaluate the stored and activation energies of an industrial Copper alloy (SICLANIC S) (Cu-2.5Ni-0.6Si, % in wt.) deformed by ECAP via route A (without rotation around the specimen longitudinal axis between two successive passes) up to 12 passes at 150°C using DSC. Results are discussed and compared to the published data. The X-Ray Diffraction (XRD) technique using the PM2K software [10], a program implementing the method of Whole Powder Pattern Modelling (WPPM), was utilized to estimate the dislocation density of the annealed samples. The procedure was described in more detail in earlier reports [11, 12].

2. EXPERIMENTAL PROCEDURES AND METHODOLOGICAL BASES

The material used in this work is an industrial Copper-based alloy with the commercial nomenclature of SICLANIC S (Cu-2.5Ni-0.6Si, % in wt.). As indicated by the manufacturer (CLAL-FRANCE), after casting the alloy was subjected to hot rolling (800°C) and quenching by spraying water so that the alloy was in a supersaturated solid-solution state. Cylindrical samples of 9.8 mm diameter were cut from the initial plates (~160 x 102 x 11 mm³), the billets were then passed through an ECAP-die with a channel angle of 135° and a corner region with an outer arc of curvature of 20°. In this configuration, one pass corresponds to an equivalent strain of ~ 0.46. Several passes (N =1, 2, 3, 4, 8 and 12) were achieved following route A at a cross head speed of 7 mm/s and using Crown 9105 as a lubricant. The SICLANIC S is a hard-to-deform material, so the die was heated to a temperature of 150°C in order to facilitate the material flow; such a temperature is obviously far below the recrystallization temperature. The amount of stored energy estimated using a DSC Q10 V7.3 calorimeter with temperature scan over the entire range from ambient temperature to 400°C at a constant heating rate of 10 °C per min, in an argon environment to minimize oxidation of the alloy. In order to fit the cylindrical form of the metallic crucibles, samples were cut from the central portions of rods to ensure elimination of the friction-affected zones and were shaped with small size of approximately 9 mm in diameter and 0.3 mm in height so that the final weights were in the range from 120 to 170 mg. The total elastic stored energy per unit volume in the strain field of dislocation structure can be related to their average total density $\rho$ by the following equation [10]:

$$ E_{dis} [J] = AV_c G b^2 \rho \ln \left( \frac{1}{b/\rho} \right) $$

where $A = \frac{1}{4\pi} (f_{\text{screw}} + f_{\text{edge}} \frac{1}{1 - \nu})$ [14, 15], and it stands for the $q$ factor depending on the edge or screw dislocation character determined experimentally from X-Ray Diffraction Line Profile Analysis (XRDLP) [16]. This parameter is required for computing a more realistic value of the stored energy, $f_{\text{screw}} = q - \frac{1.608}{0.69}$ and $f_{\text{edge}} = \frac{2.37 - q}{0.69}$ [14] are the individual fractions of the screw and edge dislocations, $V_c$ is the crystal volume, $\nu$ is the Poisson’s ratio, $G$ is the shear modulus, $b$ is the magnitude of the Burgers vector. By dividing equation (1) by the sample mass, we obtain the following relationship of the weight-normalized stored energy reported in [14]:

$$ E_{stor} [J/g] = AGB^2 \rho m \ln \left( \frac{1}{b/\rho m} \right) $$

where $\rho_m$ is the mass density. The stored energy given in equation (2) is not a linear function of dislocation density, but it shows that the driving force of the recrystallization is greatly influenced by the dislocation structure. It is worth recalling that the dislocation character is dependent on the material internal variables and on the degree and mode of deformation. For example, in the case of Copper ($\nu$, $G$, $b$ and $\rho_m$ are taken
equal to 0.355, 48 GPa, 0.255 nm and 8.96x10^6 g/m³, respectively), the theoretically calculated values of q are 1.608 and 2.37 for pure edge and screw dislocations [16], whereas an incorrect value (1.68) of q for the pure edge case is reported in references [17, 14]. As pointed out [18], for simplicity one can assume that half of the dislocations are screw and half are edge so that q is taken equal to 1.99. To estimate the activation energy, DSC analyses were performed at five different heating rates (5, 10, 20, 30 and 50°C min⁻¹) but only to samples deformed through 12 passes. The activation energy for recrystallization was calculated using the dependence of the peak temperature on the heating rate given by the Kissinger method [19] (see equation 3) and the Chen and Spaepen method (known also as the modified Kissinger method) [20] (see equation 4):

\[
\ln \left( \frac{V}{T_p^2} \right) = A_1 \cdot \frac{\Delta G_1}{RT_p}
\]

\[
\ln \left( \frac{V}{T_p} \right) = A_2 \cdot \frac{\Delta G_2}{RT_p}
\]

where \( V \) is the heating rate, \( T_p \) is the peak corresponding to the temperature of the maximum transformation rate, \( A_1 \) and \( A_2 \) are constants, \( \Delta G \) is the activation energy, and \( R \) is the gas constant. The deformation microstructure parameters (dislocation density, grain size and faulting probability) have been determined by XRDLPA [21]. A full description of the analysis method is reported in this paper.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the prominent peak obtained from continuous DSC thermograms recorded at 10°C/min of ECAP-deformed Cu-2.5Ni-0.6Si (wt.%) samples (from 1 to 12 passes at 150°C via route A). All the thermograms exhibit one exothermal peak within a temperature range from 150 to 270°C. The integrated areas of the peaks give the stored energies. This considerably broadened mono-peak is often associated with the release of the stored strain energy due to dislocations during recrystallization in the microstructure of non-equilibrium grain boundaries [7, 22]. Very similar results have been found for an ECAP-deformed pure Copper [22]. Suwas et al. [7] attributed the first peak of the DSC output signal relative to the case of one-pass ECAP-deformed pure Copper to a recovery process while the second peak was associated with recrystallization. The authors compared this thermogram to the one obtained for pure Silver and exhibiting a single peak attributed to recrystallization. This difference may indicate the impact of stacking fault energy on the nature of the DSC thermograms. In Figure 2, the stored energy evaluated from DSC thermograms are plotted versus the equivalent strain. The released heat starts from 0.72 J/g for the first pass and rises gradually with the increase of deformation up to 4 ECAP passes where it saturates at a constant value of approximately 0.91 J/g. As pointed out by Wang and Ma [23], such evolution may be associated with the increase of the stored energy introduced by ECAP deformation which increased the driving force for nucleation of new strain-free grains, so that copious nucleation is realized at lower temperatures where growth is limited. The activation energy of recrystallization
in Cu-2.5Ni-0.6Si (% in wt.) after 12 ECAP passes was calculated using equations (3) and (4) and the quantities

\[ \ln \left( \frac{V}{T_p} \right) \quad \text{and} \quad \ln \left( \frac{V}{T_p} \right) \]

are plotted versus \( \frac{1000}{T_p} \) in Figure 3.

The activation energy is found to be equal to \( \sim 123 \text{ kJ/mol} \) (1.28 eV) using equation (3) (Kissinger method) and \( \sim 127 \text{ kJ/mol} \) (1.32 eV) by equation (4) (modified Kissinger method). A deep analysis of the published data [3, 7, 14, 22, 25-28] for all routes (mainly route A and Bc were the most studied) showed that the stored energy in Cu-2.5Ni-0.6Si (% in wt.) up to 12 ECAP passes are in good agreement with those found for pure or OFHC (Oxygen-Free High Conductivity) Cu. However, our values are slightly higher than those reported by [7] for OFHC copper but are fairly close to those reported by [22] for pure Copper after processing by route A. Our results are a little in contradiction with the results of Suwas et al. [7] who found that the stored energy amounted to 0.494 and 0.771 J/g after 4 passes of ECAP processing of a commercial purity Cu using route A and Bc respectively. These authors concluded that route Bc was more efficient for grain refinement, and thus in imparting dislocations. Khereddine et al. [21] have evaluated by XRD dislocation analysis the dislocation density for the present alloy (Cu-2.5Ni-0.6Si, % in wt.). Figure 4 presents the evolution of dislocation densities in Cu-2.5Ni-0.6Si (% in wt.) from this work. These values fall within the values reported by [28] for Cu processed through route A, Bc and C. We can notice also that the dislocation densities found by [21] are almost higher than those given by [28] using an XRD technique. A rapid calculation (for the alloy under consideration, the shear modulus is equal to 48.5 GPa, the Poisson ratio value is 0.34 and the mass density \( 8.9 \times 10^6 \text{ g/m}^3 \)) of the dislocation density from equation (2) gives a value around \( 2.95 \times 10^{15} \text{ m}^{-2} \) which is of the same order as dislocation densities derived from XRD LPA [21].

**Fig. 2:** Stored energy versus equivalent strain evaluated by DSC for ECAP-deformed Cu-2.5Ni-0.6Si at 150°C

**Fig. 3:** Kissinger and modified Kissinger graphs for Cu-2.5Ni-0.6Si after 12 ECAP passes. The activation energy is between 123 and 127 kJ/mol (1.28 and 1.32 eV, respectively)

**Fig. 4:** Dislocation densities in Cu-2.5Ni-0.6Si (% in wt.) from reference [21]. Results published in [28] are given for comparison
4. CONCLUSION
The main results can be summarized as follows: After careful inspection of the DSC signature plot of the ECAP-deformed SICLANIC S (Cu-2.5Ni-0.6Si, % in wt.) at the indicated heating rate, the presence of only a single characteristic peak (without shoulder) attributed to recrystallization was revealed. It is anticipated that the absence of a recovery peak is probably due to the fact that the alloy has a low SFE making recovery difficult. The large exothermic peak in the heat evolution is an excellent indicator of the introduction of a substantial dislocation density by severe plastic deformation. This may also lead to the assumption that in this specific material, only dislocations remain after warm ECAP so that no peak is observed due to vacancies. Stored energy was found to continuously increase with strain up to the fourth pass, and thereafter it reaches a constant value of approximately 0.91 J/g. The associated dislocation density is $2.95 \times 10^{15}$ m$^{-2}$. Based on Kissinger and modified Kissinger analysis, the activation energy for recrystallization was found to be between 123 and 127 kJ/mol (1.28 and 1.32 eV, respectively) for the 12-pass deformed alloy. The alloying elements Ni and Si up to 2.6 and 0.5 % in wt.) appeared not to alter the thermochemical response (stored and activation energies) of the Cu matrix.

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REFERENCES


