INVESTIGATION OF RECRYSTALLIZATION KINETICS BY DSC ANALYSIS OF Mg-Ce ALLOY AFTER SEVERE PLASTIC DEFORMATION

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Abstract

The recrystallization process of Mg-Ce alloy after high-pressure torsion (HPT) was investigated using differential scanning calorimetry (DSC) technique. The DSC results show that the recrystallization peak temperature increases with increasing the heating rate which confirms that recrystallization is thermally activated and kinetically controlled. The recrystallized volume fraction, the rate of recrystallization, the transformation function and the kinetic parameters (activation energy and Avrami exponent) for Mg-Ce alloy were estimated using several analytical approaches.

Keywords: HPT, recrystallization, DSC, Mg-Ce alloy, kinetics

1. INTRODUCTION

In recent years, magnesium alloys have drawn significant attention as attractive lightweight structural materials due to their specific properties adaptable for structural applications [1]. However, due to the hexagonal packed structure of the magnesium alloys, their applications were limited because of their relatively low strength and ductility at low temperatures [2]. In order to improve the plastic formability of these alloys, rare earth elements were used as solute adding which could change the deformation mechanisms during plastic deformation through solute drag that changes the relative boundary mobility [3]. Severe plastic deformation (SPD) such as high-pressure torsion (HPT) [4] has been used to produce materials with ultrafine grains, having satisfactory ductility and high strength [5]. Post-deformation annealing treatment of UFG materials is often used in order to reach a more or less stable state by recovery and recrystallization which may result in grain growth [6]. It is known that, DSC technique is an important tool to investigate some solid state transformation such as recrystallization and precipitation. A strong lack of data associated with recrystallization kinetics in Mg-RE alloys is manifest in the literature, therefore the present investigation aims to evaluate the recrystallization kinetics and related parameters (activation energy, Avrami exponent) using Differential scanning calorimetry (DSC) for Mg-1.44 wt.% Ce alloy after processing by HPT at room temperature up to 10 turns.

2. EXPERIMENTAL PROCEDURE

The Mg-1.44Ce (wt.%) alloy was supplied in an as-cast state by colleagues from the *Institut für Metallkunde und Metallphysik* (IMM), Aachen, Germany. Cylindrical samples with diameter of 10 mm were solution heat-treated in sealed glass tubes at 535 °C for 6 h followed by a subsequent water quenching. Disks with thickness of 1.5 mm were sliced from the cylindrical samples and then carefully polished with abrasive papers to a final thickness of 0.85 mm. The discs were processed by HPT at room temperature at 1/2, 1, 5 and 10 turns with a rotational speed of 1 rpm, using an imposed pressure of 6.0 GPa. All disks were processed by HPT under quasi-constrained conditions [7]. Specimens of 18−20 mg were cut near the centers of the discs and were inserted in an aluminum crucible (6.5 mm inner diameter and 1 mm height) and subjected to DSC analysis

using a 2920 MDSC calorimeter under Nitrogen atmosphere, while an empty Al crucible was used as a reference. The DSC experiments were performed using four heating rates (5, 10, 20 and 30 °C/min) and the scanning temperature ranged from 80 to 500 °C.

3. RESULTS AND DISCUSSION

Figure 1 a) presents DSC plots at different heating rates (5, 10, 20 and 30 °C/min) of a selected exothermic peak corresponding to the recrystallization process in Mg-1.44 wt.% Ce alloy subjected to 1/2 turn by HPT. The more or less wide aspect of the present peaks may be explained by the heterogeneous microstructure. From **Figure 1 a)** the peak temperature of recrystallization increases with increasing heating rate from 144.8 to 177.1 °C for 5 and 30 °C/min respectively. Such observations were reported in the case of hot ECAP-deformed ZK60 following using route A up to 4 passes [6]. As shown in **Figure 1 b)**, the recrystallization peak temperature corresponding to 1, 5 and 10 turns exhibit almost the same trends and decreases with increasing number of HPT turn. The present peak temperature values, in the range 135-177.1 °C, are lower than those reported in the case of conventionally hot rolled Mg-1 wt.% Ce and Mg-1 wt.% Gd alloys [8]. These low values of temperature peak may be explained by the unusual and particular microstructure generated by HPT processing.

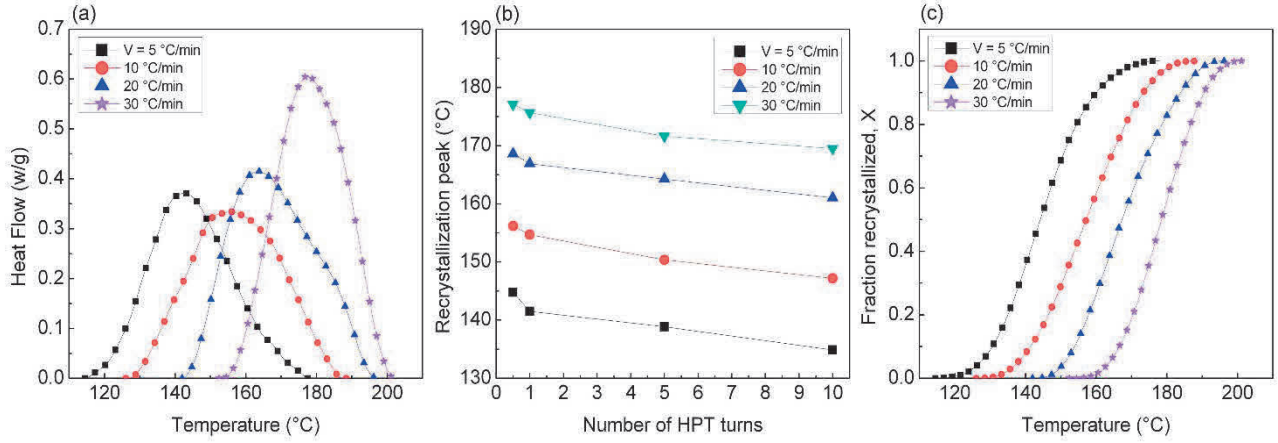

Figure 1 a) DSC curves of an exothermic peak records to the recrystallization process of Mg-1.44 wt.% Ce alloy processed by HPT to 1/2 turn; **b**) Evolution of recrystallization temperature peak of Mg-1.44 wt.% Ce as function of number of HPT turns; **c)** Fraction recrystallized, X versus temperature of Mg-1.44 wt.% Ce alloy processed by HPT to 1/2 turn

The recrystallized fraction X can be calculated using the following equation [9]:

$$X = A_T/A \quad (1)$$

where X is the recrystallized fraction, A is the total area of the exothermic peak and A_T is the area between onset peak and the chosen temperature T, respectively.

The recrystallized fraction is presented in **Figure 1 b)** for the present alloy processed by HPT to 1/2 turn at different heating rates. It is obvious that the recrystallization fraction X plots exhibit characteristic sigmoid shape with a net shift of the peak temperature upon lowering the heating rate. Quite similar observations were obtained in the case of hot ECAP-deformed commercial purity titanium up to 10 passes [10].

In order to determine the activation energy and to highlight the mechanism of recrystallization process in Mg-1.44 wt.% Ce alloy processed by HPT, the Johnson-Mehl-Avrami equation was used [11]:

$$X = 1 - \exp[(-kt)^n] \quad (2)$$

In the literature, a modified Johnson-Mehl-Avrami equation has been proposed as follows [12]:

$$\frac{dX}{dt} = k_0 f(x) \exp\left[\frac{-E}{RT}\right] \quad (3)$$

where X is the fraction recrystallized after time t, k is the reaction rate constant, k_0 is the frequency factor, $f(x)$ is a function of the fraction transformed, E is the activation energy.

The activation energy as well as the kinetic parameters k_0 and $f(x)$ should be then easily deduced from the linearization of equation (3) [12]:

$$\ln\frac{dX}{dt} = \ln[k_0 f(x)] - \frac{E}{RT} \quad (4)$$

Figure 2 a) shows the plots of the transformation rate dX / dt versus recrystallization time of Mg-1.44 wt.% Ce alloy subjected to 1/2 turn by HPT at different heating rates. It is obvious that the rate of recrystallization plot becomes narrower and higher upon increasing heating rate.

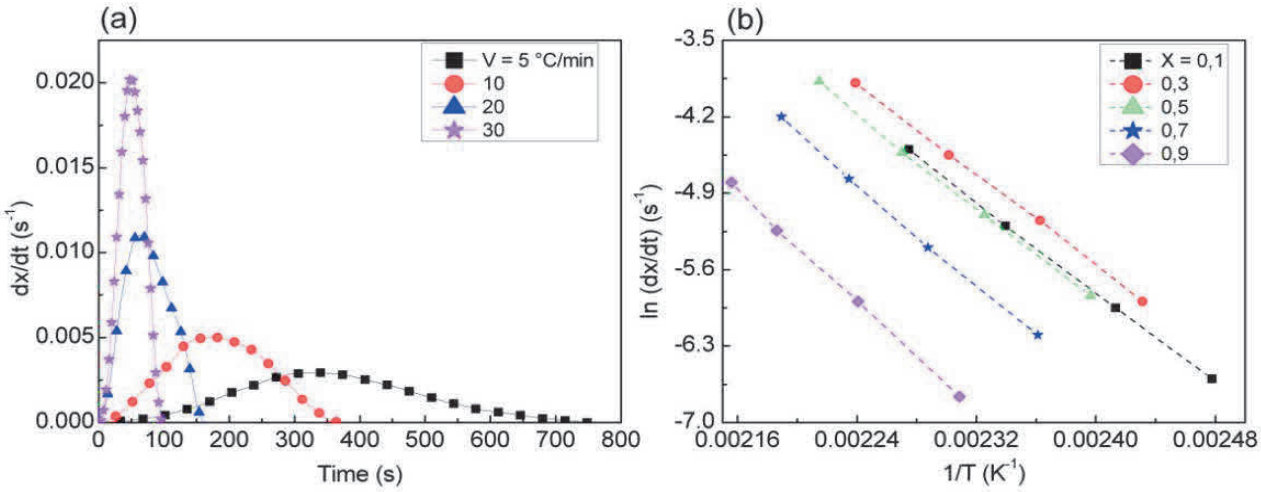

Figure 2 a) Rate of recrystallization process versus time, **b)** Plot of ln (dX/dt) versus $1/T$ of Mg-1.44 wt.% Ce alloy processed by HPT to 1/2 turn

Furthermore, Ligero et al [13] have proposed a mathematical approach that could be applied to non- isothermal experiments conditions. For every DSC and at different heating rates, there should be a linear relationship between ln (dX/dt) and 1/T when plotted for the same value of transformed fraction X. Hence the average slope should give the activation energy E.

Figure 2.b presents the plots of ln (dX/dt) versus $1/T$ of Mg-1.44 wt.% Ce alloy processed by HPT to 1/2 turn. As can be seen, the plots show straight lines and the deduced activation energy was 87.29 kJ/mol for 1/2 turn. The same trends were observed for 1, 5 and 10 turns (not shown here) and the deduced activation energy for all the turns are presented in **Table 1**. Chao et al. [14] reported values of activation energy about 85.9 kJ/mol in the case of AZ31 alloy heavily cold-drawn and annealed. Both this value and those of present work are close but slightly lower than the boundary self-diffusion energy in magnesium (92 kJ/mol) [15].

Knowing the value of the activation and calculating hence the ln[k_0 $f(x)$] evolution. Under a special approximation (ln [$k_0 f(x_1)$]= ln [$k_0 f(x_2)$]), the Avrami parameter n could be determined by the selection of many pairs of x_1 and x_2 that satisfied this condition, from the following equation [12]:

$$n = \frac{\ln[\ln(1-x_2)/\ln(1-x_1)]}{\ln[(1-x_2)/\ln(1-x_2)/(1-x_1)/\ln(1-x_1)]} \quad (5)$$

Figure 3 shows the plot of ln [k_0 $f(x)$] versus the recrystallized fraction, X of Mg-1.44 wt.% Ce alloy processed by HPT to 1/2 turn at heating rate 10 °C/min. By using the expression (5), the deduced average value of the Avrami parameter for 1/2 turn at different heating rates is n =1.37. The obtained average values of n for other HPT turns are presented in the **Table 1**. In the present investigation, the Avrami value is close to 1.5. According to Matusita et al. [16], the recrystallization process in the present alloy is of bulk nucleation character controlled by diffusion with constant number of nuclei.

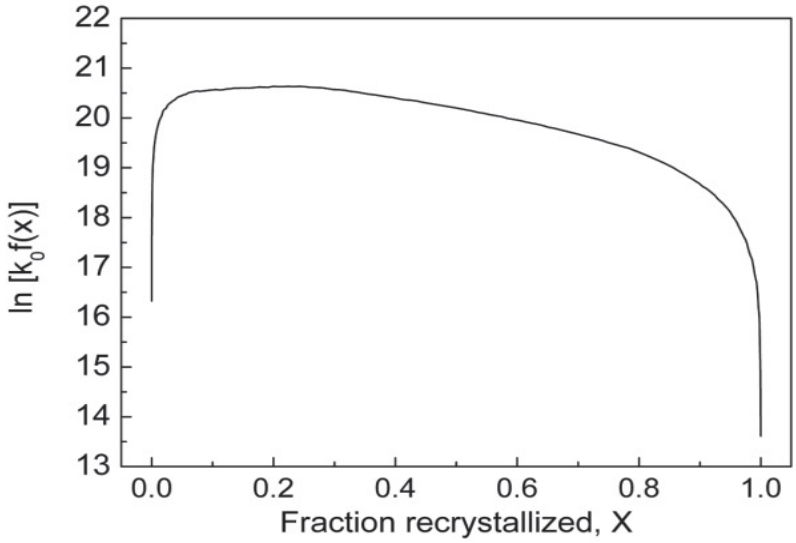

Figure 3 Plot of ln [k_0 $f(x)$] versus recrystallized fraction X

Table 1 Activation energy and Avrami parameter of Mg-1.44 wt.% Ce alloy hyper deformed by HPT up to 10 turns

Number of turn	1/2	1	5	10
Activation Energy, E (kJ/mol)	87.2	84.0	81.4	79.0
Avrami parameter, n	1.37	1.38	1.44	1.46

In order to compare the activation energy with those determined from classical methods used for non-isothermal conditions, Kissinger [17], Boswell [18] and Ozawa [19]) methods were used. They obey the following expressions, respectively:

$$\ln\frac{V}{T_p^{\,2}} = C - \frac{E}{RT} \tag{6}$$

$$\ln\frac{V}{T_p} = C - \frac{E}{RT} \tag{7}$$

$$\ln V = C - \frac{E}{RT} \tag{8}$$

where V is the heating rate, C is a constant, T_p is the peak temperature, E is the activation energy.

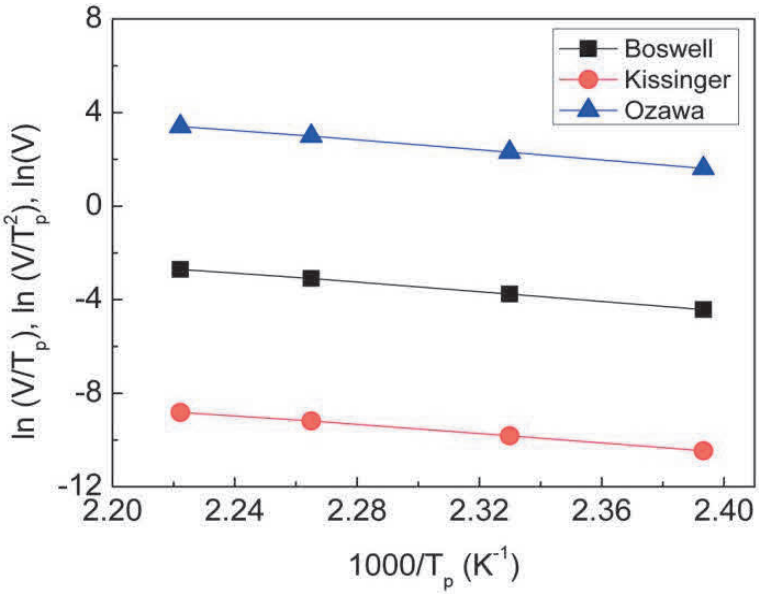

Figure 4 Plots of ln (V/T_p), ln (V/T^2_p) and ln (V) against 1000/T_p of Mg-1.44 wt.% Ce alloy processed by HPT to 1/2 turn

Figure 4 presents the Boswell, Kissinger and Ozawa plots versus 1000/T_p for the recrystallization peak measured by DSC using four heating rates of Mg-1.44 wt.% Ce alloy processed by HPT to 1/2 turn. All the plots show straight lines and the activation energy was calculated from the slope of the plots.

Table 2 Activation energy for the recrystallization using different methods (in kJ/mol) in Mg-1.44 wt.% Ce alloy after HPT processing up to 10 turns

Number of turn	1 / 2	1	5	10
Kissinger	80.27	77.86	72.66	72.33
Boswell	83.8	78.31	76.15	75.82
Ozawa	87.48	85.02	79.78	79.43

Other plots (not shown here) corresponding to 1, 5 and 10 turns exhibit almost the same trends. The obtained values of activation energy are presented in **Table 2**. It is obvious that the values of activation energy calculated by the modified isothermal method of Ligero et al [13] are very close to those calculated by Ozawa method. Therefore, it can be concluded that the Kissinger and Boswell methods underestimate the activation energy for recrystallization of the Mg-1.44 wt.% Ce alloy after HPT processing. Furthermore, **Tables 1** and **2** show that the increase in the number of HPT turns leads to an apparent decrease in activation energy necessary for recrystallization process. This finding may be associated with the strong amount of nucleation sites for recrystallization such as high angle grain boundary, vacancies and their clusters that are progressively introduced into the material upon SPD processing [20].

4. CONCLUSION

The main results deduced from DSC can be summarized as follows:

- The recrystallization temperature is strongly reduced by the HPT processing and the obtained values are in the range of 144.8-169.4 °C.

- The activation energy of the recrystallization decreases with increasing the number of HPT turns and the values range from 72.33 to 87.48 kJ/mol for 10 and 1/2 turns respectively.
- The Avrami parameter *n* is close to 1.5 which indicates a bulk nucleation character of the recrystallization controlled by diffusion with constant number of nuclei.
- The Kissinger and Boswell methods underestimate the activation energy for recrystallization of Mg-1.44 wt.% Ce alloy after HPT processing.

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