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Precipitation and Dissolution Kinetics of GP Zones and Metastable Phase in Al-3wt.%Cu Alloy

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The kinetic parameters such as activation energy E and the growth morphology parameters n and m were determined by a non-isothermal method. The microstructure variations of the precipitation and dissolution of GP zone and metastable phase θ' in Al-3wt.% Cu were analyzed by optical microscopy and X-ray diffraction. The kinetics of GP zone and metastable phase θ' in Al-3wt.% Cu was investigated using differential thermal analysis between room temperature and 430 °C at heating rates of 20, 25 and 30 °C min^{-1}. The activation energies of GP zone precipitation, formation of θ'/θ and dissolution of θ' were 26, 105 and 77 kJ mol^{-1}, respectively. The growth morphology parameters n (Avrami parameter which indicates the crystallization mode) and m (a numerical factor which depends on the dimensionality of crystal growth) are both about 1.5.

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PACS/topics: differential thermal analysis (DTA), precipitation, activation energies

1. Introduction

Aluminum alloys have potential applications in various portable devices and vehicles due to their high strength and low weight. Precipitation hardening by heat treatment is critical in optimizing mechanical performance to achieve rational design [1, 2]. The Al-Cu alloy system has one of the most complex precipitation sequences of all age hardenable aluminum alloys [3].

The precipitation sequence observed on aging these alloys is, supersaturated solid solution → Guinier-Preston (GP) I zones (GPI zones) → (GPII zones) → θ' → θ [4]. Guinier-Preston has different morphologies (platelets, spheres, needles) depending on the difference in atomic diameters of solute and solvent elements [5]. The GP zones in Al-Cu alloys still attract much interest and definitive conclusions on their structure, formation and evolution have not yet been reached [5, 6].

The θ' phase of Al-Cu alloys is the favorite model system for studying the theories or mechanisms of phase transformation in aluminum alloys [7]. The structure of the θ phase with the composition Al_2Cu was originally revealed by Friauf [7]. It was found to be tetragonal and stable up to 591 °C according to Murray [8].

Differential thermal analysis (DTA) has been frequently employed in recent times for the determination of kinetic parameters of thermally activated processes like the precipitation reactions and the activation energies. This method is based on the difference in heat required to increase the temperature of a sample and a reference material, respectively [9]. Our present contribution contains various calculated kinetic parameters. The measured parameters have been used the methods of Kissinger, Ozawa and Boswell under non isothermal conditions using the DTA.

2. Materials and experimental procedure

The composition of impurities of the Al-Cu alloy prepared for this work is listed in Table I. These alloys have been prepared in our laboratory by fusion in a high vacuum (10^{-5} Torr) using pure materials.

After melting, the ingots have undergone plastic deformation by cold rolling before the homogenization treatment in order to accelerate the structure homogenization kinetics. The homogenization temperature and aging were chosen from the equilibrium diagrams. For obtaining a super saturated solid solution, the ingots were homogenized in vacuum at 430 °C for 3 h and quenched in water; we have prepared a disc shaped sample of 3 mm in diameter and 1 mm thickness for DTA.

DTA experiments were performed using Setaram Labsys Evo TG-DTA 1600 °C equipment. Representative sections of annealed samples were investigated by means of a JEOL scanning electron microscope (SEM) model JMS 6400. The X-ray diffraction analysis was performed using a diffractometric system XPERT-PRO with scan step size of 0.0167 ($Cu_{K\alpha}$ radiation and a Ni filter), operated at 40 kV and 40 mA.

3. Results and discussion

Figure 1 shows typical DTA curves of Al-3wt.% Cu alloy from room temperature to 400 °C at heating rates of 20, 25 and 30 °C min^{-1}. Two exothermic peaks (A, B)

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and an endothermic peak (C) were observed. The peak (A) from 107 °C to 135 °C is due to the precipitation of GP zone. The peak (B) from 275 °C to 285 °C corresponds to the precipitation of θ'/θ phases and the peak (C) is due to the dissolution of θ' from 304 °C to 319 °C. The temperature of the maximum of the exothermic peak, T_{p}, shifts to a higher temperature as the heating rate increases from 20 to 30 °C min^{-1}.

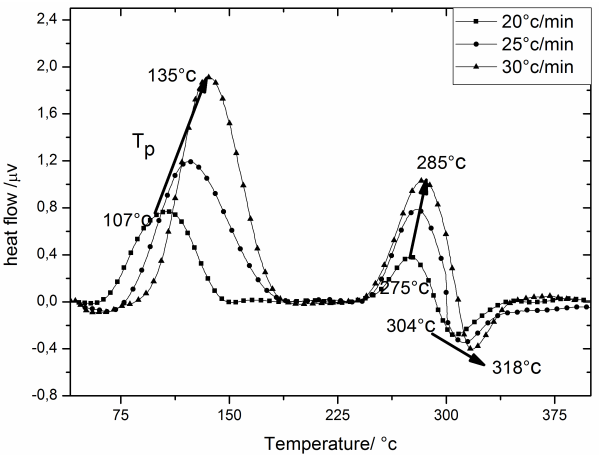

Fig. 1. DTA curves of Al-3wt.% Cu alloy heated at different heating rates.

The X-ray diffraction patterns for Al-3wt.% Cu homogenized during 3 h at 430 °C, quenched and aged at 150 °C are shown in Fig. 2. The θ' phase is present in the matrix. After prolonged ageing of 50 h at 150 °C, the diffraction peaks of θ phase show high intensity and the θ' phase has disappeared. This explains that there are some amounts of precipitated phase. The microstructure of Al-3wt.%Cu alloy, homogenized for 3 h at 420 °C, quenched in water and aged for 6 h at 150 °C is presented in Fig. 3a and b, respectively.

TABLE I

Chemical composition of Al-3wt.% Cu alloy.

Element	Al	Cu	Si	Fe
Composition [wt.%]	96.79	3	<0.10	<0.11

For a non-isothermal DTA experiment, according to Kissinger Eq. (1), Ozawa Eq. (2) and Boswell Eq. (3) methods [10–12]:

$$\ln\left(\frac{\phi}{T_{\mathrm{p}}^2}\right) = -\frac{E_{\mathrm{A}}}{RT_{\mathrm{p}}} + C_3, \tag{1}$$

$$\ln(\phi) = -1.0518\frac{E_{\mathrm{A}}}{RT_{\mathrm{p}}} + C_1, \tag{2}$$

$$\ln\left(\frac{\phi}{T_{\mathrm{p}}}\right) = -\frac{E_{\mathrm{A}}}{RT_{\mathrm{p}}} + C_2, \tag{3}$$

where C_1, C_2 and C_3 are constants, T_{p} is the peak temperature, E is the activation energy and n is the Avrami parameter which indicates the crystallization mode.

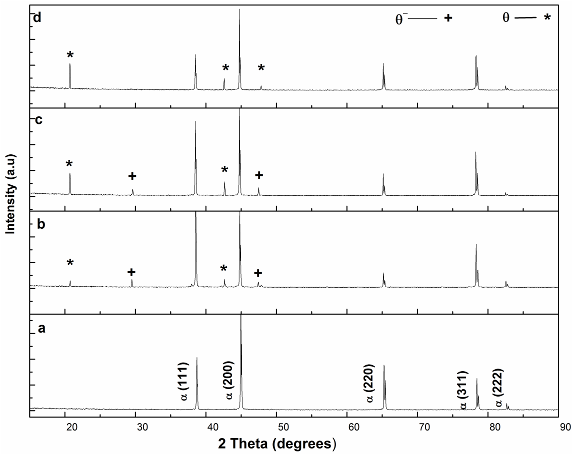

Fig. 2. X-ray diffraction patterns of Al-3wt.%Cu alloy, homogenized at 430 °C for 3 h quenched in water (a), aged for 3 h (b), 6 h (c) and 50 h (d) at 150 °C.

A plot of Y versus $1/T_{\mathrm{p}}$ should be a linear curve, whose slope yields the activation energy E. The plots of Y versus $1/T_{\mathrm{p}}$ according to Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW) Ozawa and Boswell methods of (a) precipitation of GP zone, (b) formation of θ'/θ and (c) dissolution of θ' in Al-3wt.% Cu are visualized in Fig. 4.

The values of the activation energies calculated according to Kissinger, Ozawa and Boswell methods are listed in Table II. The activation energies evaluated through non-isothermal DTA were 26, 109 and 77 kJ mol^{-1} for GP zone precipitation, formation of θ'/θ and dissolution of θ' respectively. These values are in good agreement with those estimated by isothermal DTA treatment [13].

The values of the Avrami parameter n which indicates the crystallization mode for different heating rates are listed in Table III. These values were determined using Eq. (4).

$$n = \frac{2.5T_{\mathrm{p}}^2 R}{\Delta T_{\mathrm{p}} E_{\mathrm{A}}}, \tag{4}$$

where ΔT is the width of crystallization peak at half maximum. The average Avrami parameter is equal to 1.49 for the formation of θ'/θ. This value is closer to 1.5, which suggests that the process of formation of θ'/θ is diffusion controlled. This value is in good agreement with that estimated by isothermal DTA treatment and with the work of M. Fatmi et al. [14].

The dimensionality of crystal growth m calculated from the slope of the function $\ln(\phi_n/T_{\mathrm{p}}^2) = f(1/T_{\mathrm{p}})$, according to Matusita method [15] (see Eq. (5)) is found to be equal to 1.58 for the formation of θ'/θ. This value is closer to 1.5 indicating that bulk nucleation is dominant in θ'/θ formation followed by three-dimensional.

$$\ln\left(\frac{\phi^n}{T_{\mathrm{p}}^2}\right) = C_3 - \frac{mE_{\mathrm{A}}}{RT_{\mathrm{p}}}. \tag{5}$$

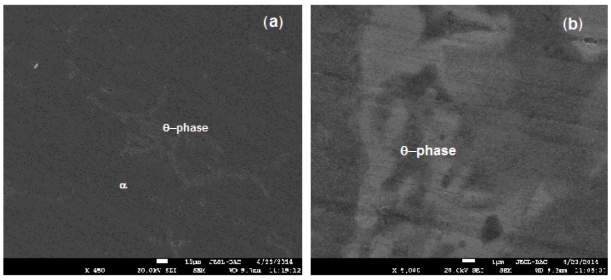

Fig. 3. Microstructure of Al-3wt.% Cu alloy (a) and the same alloy homogenized for 3 h at 420 °C (b), quenched in water and aged for 6 h at 150 °C.

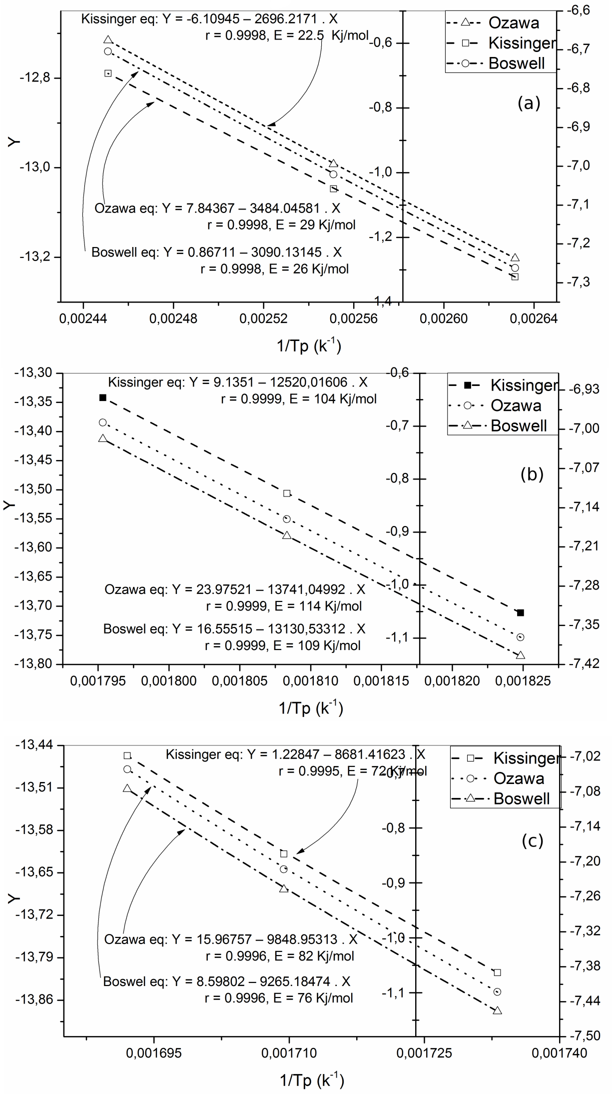

Fig. 4. Plots of Y versus $1/T_\mathrm{p}$ of (a) precipitation of GP zone, (b) formation of θ'/θ and (c) dissolution of θ' in Al-3wt.%Cu, calculated using three different methods.

TABLE II

Activation energies given by Kissinger, Ozawa and Boswell methods (kJ mol^{-1}).

Method	Precipitation of GP zone	Formation of θ'/θ	Dissolution of θ'
Kissinger	22.5	104	72
Ozawa	29	114	82
Boswell	26	109	76

TABLE III

Values of the Avrami parameter n for different heating rates from DTA experiments.

Heating rates	20 °C/min	25 °C/min	30 °C/min
ΔT	38.834	40.882	42.195
n Avrami exponent	1.53	1.48	1.46

4. Conclusions

The kinetics of precipitation and dissolution of GP zone and metastable phase in Al-Cu alloys was determined by a non-isothermal method. The temperature of precipitation of GP zone, formation of θ'/θ and dissolution of θ was found to be around 120, 280 and 312 °C, respectively. The activation energies of GP zone precipitation, formation of θ'/θ and dissolution of θ' were 26, 105 and 77 kJ mol^{-1}, respectively. The growth morphology parameters n and m are both about 1.5.

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