Dilatometric and DSC Study of the Kinetics of Discontinuous Precipitation of Ag2Al Intermetallic in Al – 10% Ag Alloy

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DILATOMETRIC AND DSC STUDY OF THE KINETICS OF DISCONTINUOUS PRECIPITATION OF Ag_2Al INTERMETALLIC IN Al – 10% Ag ALLOY

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The kinetics of discontinuous precipitation of Ag_2Al intermetallic in alloy Al – 10% Ag is studied after 10-h holding in vacuum at 530°C and subsequent water quenching. The DSC and dilatometric curves are plotted for heating rates ranging from 5 to 20 K/min. The activation energy of formation of the Ag_2Al γ-phase is computed from the DSC data with the help of the Boswell equation and by the Kissinger method.

Key words: alloys of the Al – Ag system, kinetics, discontinuous precipitation, activation energy, differential scanning calorimetry, dilatometry.

INTRODUCTION

The most important parameters of the kinetics of continuous precipitation of phases in alloys are the activation energy and the growth rate exponent [1, 2]. Precipitation processes in aluminum [1, 3 – 5] and copper [6 – 9] alloys have been studied extensively by thermal analysis. Discontinuous precipitation in aluminum alloys, when the supersaturated α_0-solid solution decomposes into a depleted α-matrix and a new β-phase [10 – 12], has not been studied exhaustively. In [13], the methods of differential dilatometry and differential scanning calorimetry are applied for studying the kinetics of discontinuous precipitation in alloy Al – 30 wt.% Zn. It is shown that at the temperatures below 180°C the supersaturated solid solution decomposes fully by the reaction of cellular precipitation. The activation energy is 58.7 kJ/mole, the Avrami exponent is 1.83. The kinetics and the mechanism of precipitation in alloy Al – 0.2 wt.% Sc under isothermal holds within 190 – 530°C is studied in [14]. The authors obtain two minimums of the transformation time at about 310 and 410°C and associate them with continuous and discontinuous precipitation respectively. The continuous precipitation of phases and their coarsening in the Al – Zn – Cu system is studied in [15], where the coarsening is shown to occur by the mechanism of dissolution and spheroidization of the laminar structure formed at low temperature (150°C). The discontinuous coarsening of the structure formed under the continuous precipitation occurs above 200°C and causes formation of coarse cells with enhanced laminar distance. The growth rate of the coarse cells rapidly reaches a maximum and then decreases with growth in the hold time and with introduction of cooper into the alloy. It is shown in [16 – 19] that an equilibrium γ-Ag_2Al phase nucleates in Al – Ag alloys over grain boundaries of the solid solution. Guinier–Preston zones are present in the Al – 5 at.% alloy already in quenched condition [20]. Aging of the quenched alloys results in heterogeneous nucleation of γ'-phase platelets on dislocations [21]. Analyzing published data, we established that quite a few works have been devoted to the kinetics of discontinuous precipitation in aluminum-base alloys.

The aim of the present work was to study the kinetics of discontinuous precipitation in the Al – 10 wt.% Ag alloy.

METHODS OF STUDY

We studied alloy Al = 10% Ag[5] containing 0.02% Cu, 0.01% Fe and 0.012% Si as impurities. The alloy was supplied by the Cathay Advanced Materials Ltd Company.

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[5] Here and below in the paper the content of elements is given in weight percent.

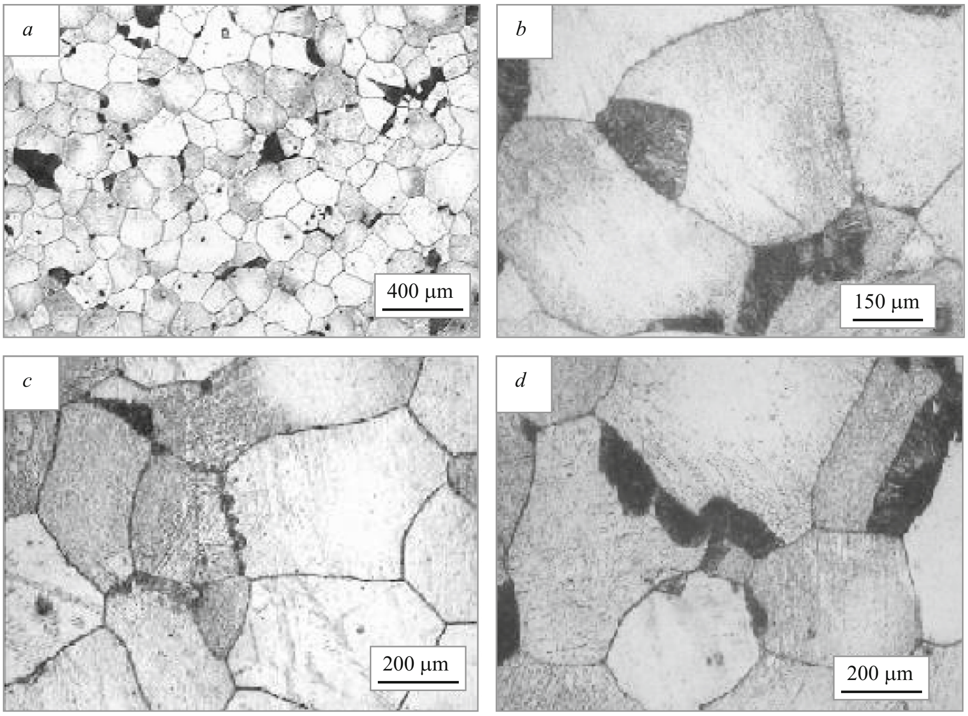

Fig. 1. Structure of alloy Al – 10% Ag after quenching from 530°C in water (*a*) and aging at 150°C for 2 h (*b* – *d*).

The alloy was quenched by homogenizing in vacuum at 530°C for 10 h and water cooling. Disks 3 mm in diameter and 3 mm thick were cut for the differential scanning calorimetry (DSC) and parallelepipeds with a size of 10 × 2.5 × 2.5 mm were cut for the dilatometry. The DSC curves were plotted for a temperature from room one to 450°C at heating rates 5, 10, 15 and 20 K/min in an atmosphere of nitrogen using a NETZSCH 200PC device. The thermal expansion of the specimens was measured with the help of a NETZSCH (DIL 402C) dilatometer at heating rates 5, 10 and 15 K/min. The metallographic analysis was performed with the help of an OPT-B159 optical microscope. The x-ray diffraction patterns were obtained using a PANalytical X'Pert PRO diffractometer in copper radiation with scanning rate 1 deg/min.

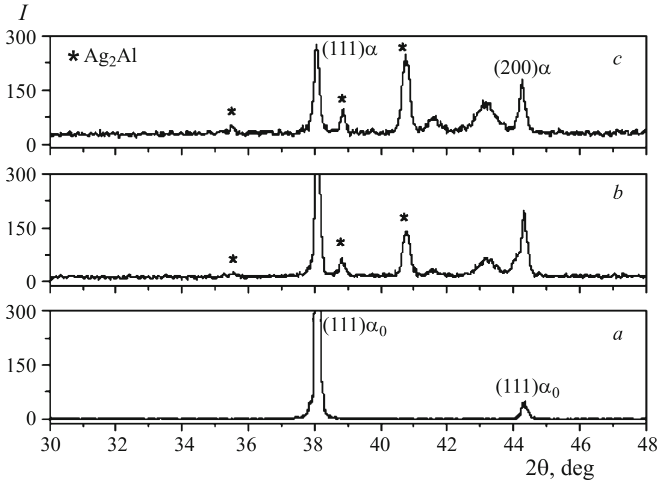

Fig. 2. XRD patterns for alloy Al – 10% Ag after quenching from 530°C (10 h) in water (*a*) and aging at 150°C for 2 h (*b*) and 6 h (*c*).

RESULTS AND DISCUSSION

The microstructure of alloy Al – 10% Ag after quenching and aging at 150°C is presented in Fig. 1. We can observe a typical structure of discontinuous precipitation with numerous cells propagating from grain boundaries into the bulk of the grains. The cells consist of lamellas of a depleted aluminum solution and a γ-Ag_2Al intermetallic (Fig. 1*b*). Two distinct domains nucleate on a boundary and start to grow in opposite directions in neighbor grains. This growth is accompanied by lateral expansion of the domains until they contact each other (Fig. 1*c* and *d*). The resulting S-morphology is described in [22].

Figure 2 presents x-ray diffraction patterns for alloy Al – 10% Ag after water quenching from 530°C and aging at 150°C. After the quenching, the diffraction patterns exhibit only the lines of an aluminum-base supersaturated solid solution. After the aging, we observe additional reflections from an Ag_2Al intermetallic, i.e., a γ-phase matching the phase diagram [23 – 25]. The diffraction data indicate rapid development of discontinuous precipitation, because the location of the reflections from the γ-phase does not change with in-

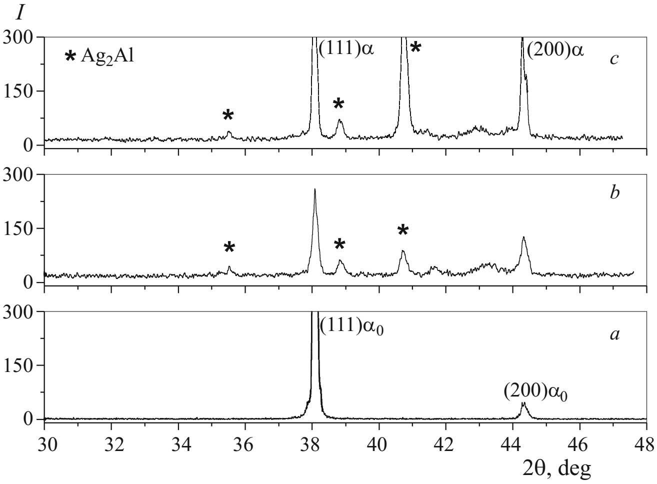

Fig. 3. XRD patterns for alloy Al – 10% Ag after quenching from 530°C (10 h) in water (*a*) and aging at 200°C for 2 h (*b*) and 8 h (*c*).

crease in the aging time. Aging at 200°C is accompanied by similar phenomena (Fig. 3). Growth in the duration of aging results in intensification of the reflections from the γ-phase. The results of the XRD analysis presented in Figs. 2 and 3 agree with the data of [26 – 28].

The thermokinetic curves of the discontinuous precipitation as plotted from the DSC data for different heating rates are presented in Fig. 4. The area under the peak and the position of peak T_p change with growth in the heating rate. In accordance with the XRD data, the only exothermic peak is caused by formation of γ-phase (Ag_2Al). If the temperature in the non-isothermal DSC experiment is changed with time linearly at a rate $V = dT/dt$, the activation energy of the process E_a may be calculated by the equations

$$Y = \ln(V/T_{p_2}) = -E_a/(T_p R) + C \text{ [29];} \quad (1)$$

$$Y = \ln(V/T_p) = -E_a/(T_p R) + C_1 \text{ [30],} \quad (2)$$

where R is the gas constant and C and C_1 are constants.

The maximum rate of the transformation corresponds to the maximum DSC peak at $T = T_p$ when $d^2Y/dt^2 = 0$. In accordance with these equations, the activation energy is determined from the slope of the curves in coordinates $Y - 1/T_p$ (Fig. 5), i.e., $E_a = 64.0$ and 54.3 kJ/mole as determined by the Boswell and Kissinger methods, respectively. Figure 6

TABLE 1. Activation Energy of Precipitation Reaction in Alloy Al – 10% Ag

Test method	Activation energy, kJ/mole, calculated by the method of	
	Boswell	Kissinger
DSC	63.93 ± 0.3	54.25 ± 0.3
Dilatometric	64.15 ± 0.5	53.47 ± 0.5

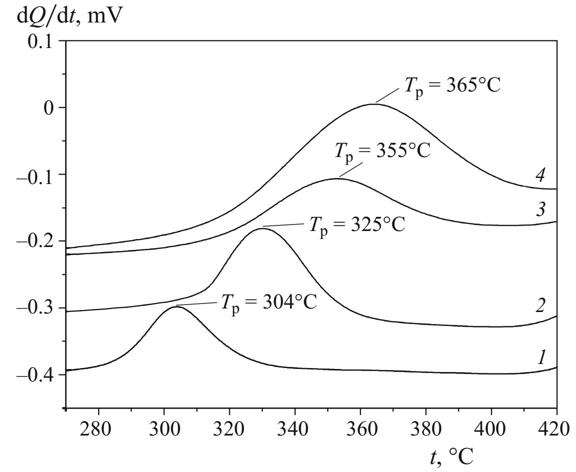

Fig. 4. SDC curves for alloy Al – 10% Ag: *1*, *2*, *3*, *4*) for heating rates 5, 10, 15 and 20 K/min, respectively; T_p) peak temperature dQ/dt.

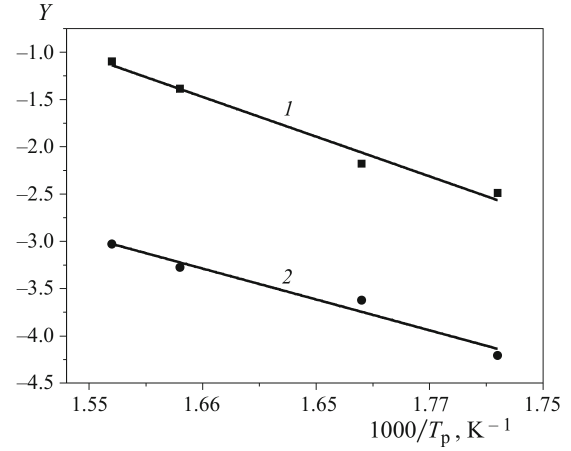

Fig. 5. Y – 1000/T_p curves for alloy Al – 10% Ag as plotted by the methods of Boswell (*1*) and Kissinger (*2*).

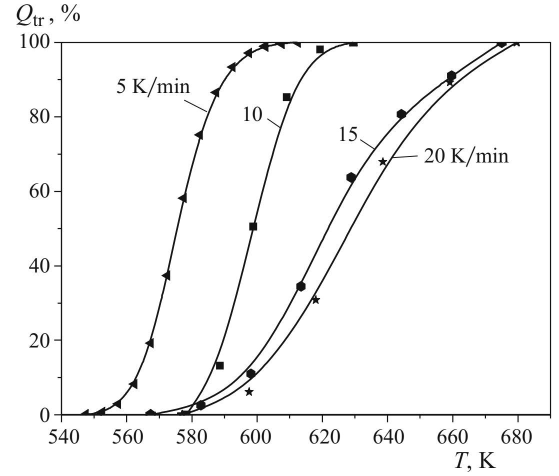

Fig. 6. Fraction of transformed volume Q_{tr} in alloy Al – 10% Ag at different heating rates (given at the curves).

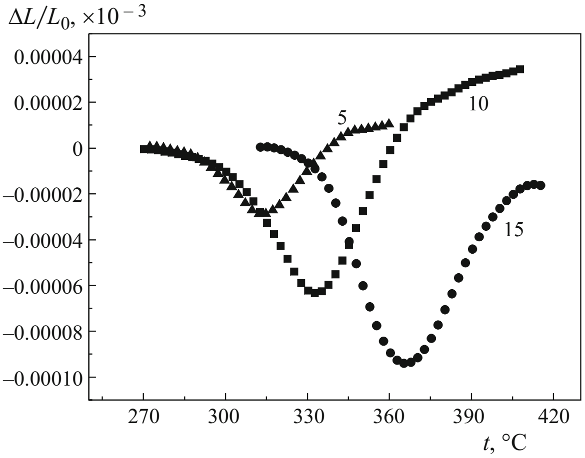

Fig. 7. Derivatives of the dilatometric curves for alloy Al – 10% Ag after quenching from 530°C (10 h) and heating at a rate of 5, 10, and 15 K/min (given at the curves).

presents the dependences of the fraction of the transformed volume on the temperature for different heating rates. It can be seen that the growth in the heating rate shifts the exothermic peaks to higher temperatures.

The derivatives of the dilatometric curves of alloy Al – 10% Ag quenched from 530°C are shown in Fig. 7. The peak corresponding to precipitation of γ-phase (Ag_2Al) shifts toward higher temperatures with growth of the heating rate. The values of the activation energy calculated by the Boswell and Kissinger methods are presented in the Table. These values agree well with the data of [31 – 33].

CONCLUSIONS

The kinetics of discontinuous precipitation of Ag_2Al intermetallic (γ-phase) in alloy Al – 10% Ag was studied by the methods of DSC and dilatometry; the phase composition was determined by x-ray diffractometry. The DSC peaks and the peaks on the dilatometric curves corresponding to maximums of precipitation of γ-phase in alloy Al – 10% Ag shift toward higher temperatures when the heating rate is increased. The activation energy of the process of discontinuous precipitation calculated by the methods of Boswell and Kissinger amounts to 64.0 and 53.8 kJ respectively.

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