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KINETICS OF TRANSFORMATION DURING SUPERSATURATION AND AGEING OF THE Al-4.7 %Cu ALLOY

Abstract

The processes taking place during supersaturation of the Al-4.7%Cu alloy have been studied by the methods of quantitative metallography and dilatometry. The grain growth activation energy was about of 95 kJ/mole, the exponent of time, n, was close to 0.4. Dissolution of precipitates has caused two-stage shrinkage of the sample that activation energies were 90 kJ/mole (first stage, n = 0.8) and 63 kJ/mole (second stage, n = 0.4).The kinetics of the phase transformation during ageing of the Al-4.7% Cu alloy has been studied by the dilatometry and DTA.The activation energy of the precipitation processes within the range of 50–320 ^{0}C varied between 50 and 100 kJ/mole and confirmed the results obtained previously. For the precipitation processes within the range of 320–462 ^{0}C, the activation energy varied from 226–300 kJ/mole. The results obtained have been compared to the literature data.

Key words: transformation kinetics; grain size; supersaturation; ageing, Al-4.7%Cu alloy

1. Introduction

The processes of precipitation in Al-Cu alloys are well known [1,2,3,4]. After supersaturation consisting of annealing at about 520 °C, quick cooling down to room temperature and ageing, G-P zones appear as first, followed by precipitates θ" nucleates on the most stable G-P zones. The other G-P zones dissolve in the solid solution and the Cu atoms diffuse to the growing θ". When ageing temperature increase, the θ" dissolves and θ' nucleates at the defects of solid solution. Finally, the equilibrium phase Al_2Cu - θ nucleates at the boundaries of the solid solution grains, θ' dissolves and the Cu atoms diffuse to the growing θ.

The saturation process precedes ageing and comprises dissolving excess precipitates enriching the solid solution with copper atoms, grain growth and quick cooling to the ambient temperature. The amount of Cu atoms in the solid solution influences the quantity of precipitates during ageing and determines the properties obtained after ageing. The grain boundaries of the solid solution are privileged places of the precipitate nucleation, so the grain size can influence the precipitation kinetics. The processes of dissolving excess equilibrium precipitates and grain growth are interrelated in a sense. Fine grain accelerates precipitate dissolving, due to more ways of easy diffusion; the presence of precipitates decelerate movement of the grain boundaries and the grain growth. The processes are known but their kinetics has not been described in detail. Since the specific volume of the solid solution decreases during its enrichment with Cu atoms [5], the process can be studied by means of a dilatometer while the kinetics of the grain growth by the methods of quantitative metallography. During ageing, the processes of precipitation and dissolution overlap each other. That is why they are often difficult to separate when analysing the transformation kinetics.

The kinetics of phase transformations during the ageing processes can be analysed in isothermal and isochronous experiments. DTA and DSC are applied in isochronous heating because the processes of heat emission during precipitation and heat absorption during dissolving are well visible. Precipitation in Al-Cu alloys is accompanied by the sample volume growth, while dissolution by its decrease [1,5]. The changes are clearly visible in dilatometric investigation and they can be successfully used for the analysis of the kinetics of the transformations taking place during isothermal ageing. The JMA equation can be applied for the analysis of the kinetics of isothermal transformations [3,5]. In addition to the determination of activation energy, the equation can be used to find out the value of the *n* coefficient. The value is helpful in the selection of the nucleation and growth mechanism in the investigated temperature range. The value of the sample elongation can provide some additional information about the quantity of precipitates.

2. Experimental procedure

The Al–4.7% Cu alloy was especially prepared for the studies. The composition the alloy was the following: Al-94.85%, Cu-4.69%, Fe-0.2%, Si-0.08%, and other elements – 0.15 %. Because of decrease of specific volume of the solid solution during its saturation of Cu atoms the process can be studied by dilatometry, whereas grain growth kinetics by quantitative metallography. Presence of the Al_2Cu not dissolved during supersaturation was identified by X-ray method.

For ageing kinetics studies two methods were used: dilatometry (for isothermal studies) and DTA (for continuous heating studies). Dilatometric studies were performed with the use of Adamel – Lhomargy LK02 dilatometer. Samples of rod 2 mm in diameter and 13 mm length were supersaturated at the temperature of 505 °C for 10 h in preliminary vacuum radiation furnace and quenched to room temperature in helium gas jet. Isothermal ageing was performed also in LK 02 dilatometer in temperature range of 120 – 350°C for time necessary to reach no dilatation change stage. DTA studies were performed with use of Mini DTA M5 Setaram. Samples of truncated cone of 4 mm length and diameters of 2 and 3 mm were used. Standard specimen was prepared from electrolytic Al DTA samples were supersaturated in a resistance furnace at 520 °C for 6 h and quenched in water.

3. Kinetics studies - theoretical basis

3.1. Grain growth studies

Before annealing structure of Al-4,7 %Cu consisted of solid solution grains and Al_2Cu. Solid solution grains are big as compared with Al_2Cu gains. Number of the Al_2Cu as compared with number of solid solution gains is small (about 8%). Therefore the grain growth of the alloy during isothermal annealing at 500-540^{0}C temperatures range can be treated as one phase (solid solution) grain growth [2,3] and expressed by:

$$\bar{d} = k(T) \cdot t^n \qquad (1)$$

where:
d - average grain size,
t - time,
n - time exponent which is supposed to be constant at the temperature range for certain kind of transformation,
k(T) - grain growth rate constant;

$$k(T) = A \cdot \frac{-Q}{R \cdot T} \qquad (2)$$

where:
A - a constant,
Q - activation energy for analyzed transformation,
R - gas constant,
T - temperature in K.

3.2. Precipitation and dissolution studies

For isothermal kinetics studies JMA equation [2,3,5,6]] was used in the form of:

$$x = 1 - \exp(-k \cdot t^n) \qquad (3)$$

where:
x - fraction transformed at time t,
k - transformation rate constant for the selected transformation at isothermal temperature,
n - time exponent which is supposed to be constant at the temperature range for certain kind of transformation.
Activation energy Q can be determined from equation (2)

For continuous heating kinetic studies of activation energy Q of the transformations, Kissinger method [6,8-10] was used:

$$Q = -R\left(\frac{dC}{d(1/T_m)}\right) \tag{4}$$

where:

$$C = \ln\frac{V}{T_m^2} \tag{5}$$

V - constant heating rate,
T_m - temperature of the maximum ΔT curve.

4. Results

Examples of structures after annealing at temperatures 510 °C and 540 °C and quenching are shown on figures 1 and 2 (510 °C) and 3 and 4 (540 °C).

Fig. 1. Structure after annealing for 5 h at 510^{0}C. Magnification 100 X

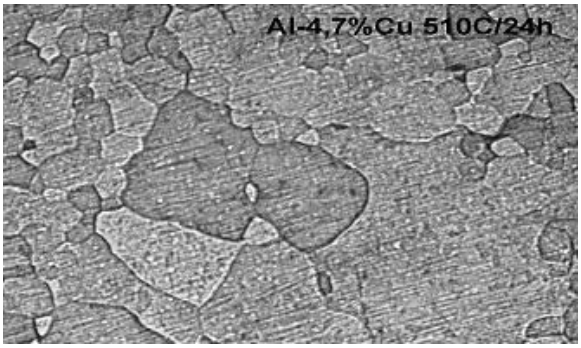

Fig. 2. Structure after annealing for 24 h at 510^{0}C. Magnification 100 X

Fig. 3. Structure after annealing for 5 h at 540^{0}C. Magnification 100 X

Fig. 4. Structure after annealing for 24 h at 540^{0}C. Magnification 100 X

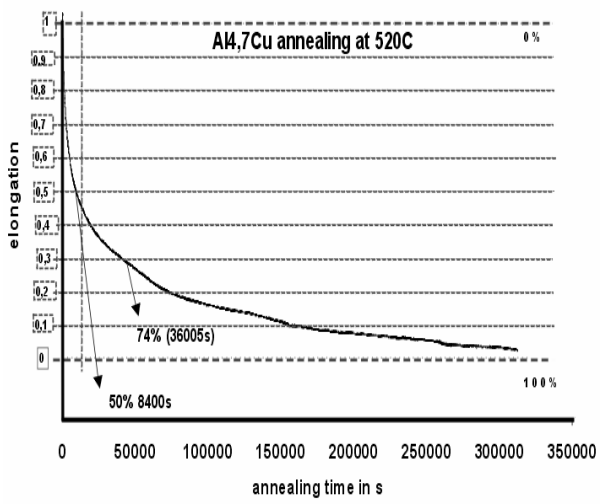

Fig. 5. Example of dilatometric diagram of annealing at 520°C

Changes of average grain size of samples annealed at 510, 525 and 540°C are shown on figure 6.

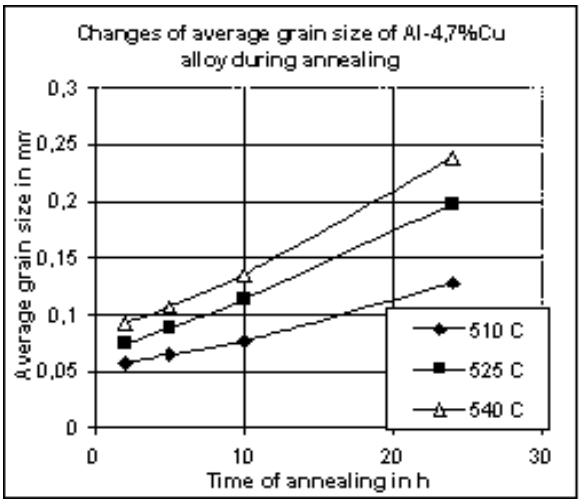

Fig. 6. Changes of average grain size during annealing at 510 , 525 and 540 °C

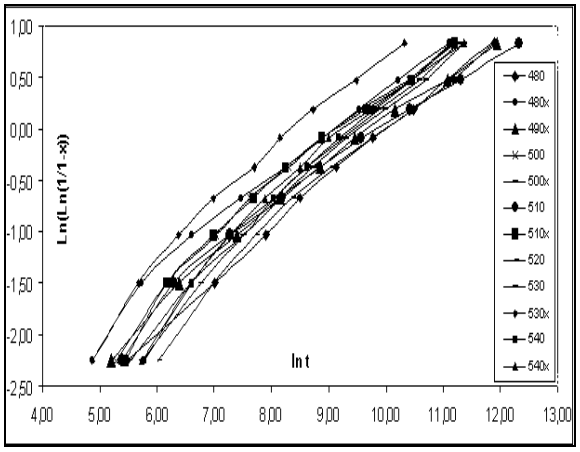

Fig. 7. Dilatometric curves of annealing at temperatures range of 480–540 °C transformed into ln[ln(1/(1-x))]-lnk diagrams

Set of dilatometric curves of annealing at temperatures between 480–540 °C transformed into ln [ln (1/(1-x))]-lnk diagrams is shown on figure 7. Examples of dilatometric diagrams of isothermal ageing at temperatures between 125-305 ^{0}C immediately after supersaturation are collected in figure 8.

DTA diagrams of isochronal ageing immediately after supersaturation are collected in figure 9.

One can calculate activation energy if the mechanism of transformation is the same at certain temperature range [10, 11]. That means the same (or nearly the same) the *n* coefficient. Average values of *n* for the same mechanism of transformation vary from 1.4 to 1.47 [3]. The temperatures of 523 K and 548 K were excluded from the calculation of activation energy due values of n to different much from 1.4-1.47.

Results of kinetic analysis of isothermal (dilatometric) and isochronal (DTA) experiments are collected in table 2.

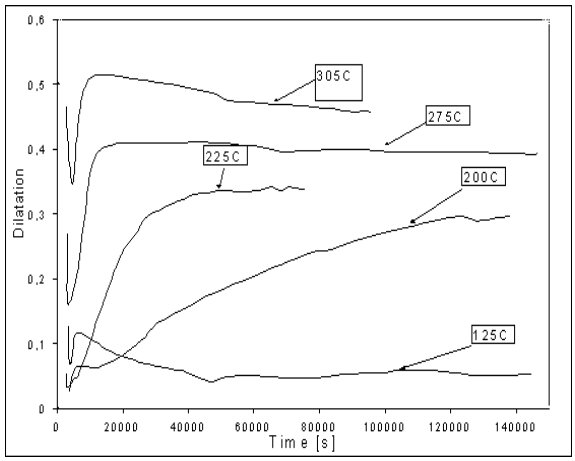

Fig. 8. Dilatation changes during isothermal ageing of supersaturated Al-4.7% Cu alloy

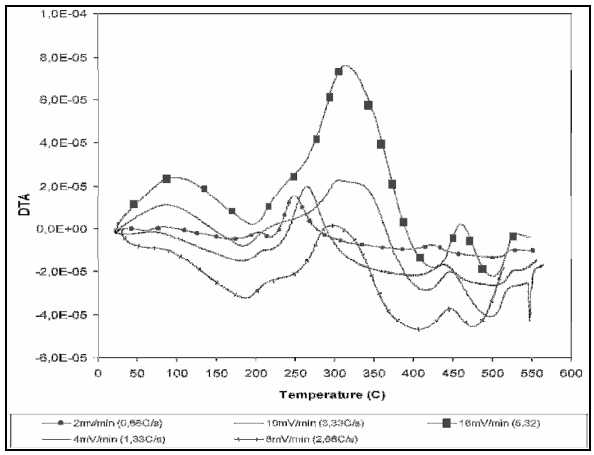

Fig. 9. DTA diagrams of isochronal ageing of the Al-4.7% Cu alloy

Table 1

Results of transformation kinetics analysis during annealing. Isothermal studies

Grain growth kinetics		
Temperature range °C	n value	Activation energy kJ/mole
510- 540	0.4 – 0.43	94.432
Contraction kinetics – JMA analysis (dilatometric studies)		
Temperature range °C	n value	Activation energy kJ/mole
480-540	0.7-0.8	90.010
480-540	0.4-0.45	65.854

Table 2
Results of transformation kinetics analysis during ageing. Isothermal and isochronous experiments

Temperature range [ºC]	Experiment	Value of n	Transformation	Activation energy value kJ/mol
124-175	isothermal	1.4	G-P precipitation	60,700
200-235	isothermal	1.47	θ ” precipitation	100, 767
250 (523K)	isothermal	1.74	Overlap of transformations	
275 (548K)	isothermal	2.08	Overlap of transformations	
290-320	isothermal	1.42	θ’/ Al_2Cu precipitation	300, 200
51-101	isothermal	-	G-P precipitation	47, 536
168-202	isothermal	-	G-P dissolution	106, 120
205-240	isothermal	-	θ ” precipitation	106, 120
251-316	isothermal	-	θ ”/ θ’ transformation	67, 830
395-429	isothermal	-	θ’ dissolution	226, 218
427-462	isothermal	-	Al_2Cu precipitation	303., 864

5. Analysis and discussion of results

Average grain size of solid solution increased during increase of time and temperature of annealing (see fig. 6). At temperature 540 °C grains size increased more than during temperature of 510 °C. Time exponent of kinetic equation value was almost the same at each annealing temperature, this means the similar growth mechanism. The activation energy of growth is about 95 kJ/mole and is close to that obtained for diffusion of Cu in Al [9,11].

During annealing the samples in the dilatometer at temperature range of 480-540 °C a contraction was seen (see fig. 5) because the increase of Cu amount in solid solution [2,5].

From figure 7 one can see faster process at the beginning of annealing (more steep slope of diagram) than latter on. The n values are about 0.8 and decrease to about 0.4 when transformation proceeds. The activation energy value at the beginning of transformation is almost the same for that obtained during grain growth. For the next stage of transformation the activation energy decreases, but still is close to that for Cu diffusion in Al. It means that dissolution of Al_2Cu particles and the Cu clusters existing at annealing temperatures of 480-540 °C limits the grain growth of solid solution. During progress of dissolution Al_2Cu particles and Cu clusters gradually disappear but sill limits the decrease of samples.

Dilatometric diagram of saturation shows continuous decrease of specimen length caused by saturation of solid solution by Cu atoms. In this the case length of the sample decreases.

Dilatometric diagram of ageing at 125 °C (fig. 8) after supersaturation shows a slight increase of specimen length caused by precipitation of small specific volume and smaller amount of Cu in the G-P zones. After a period of about 40 000s a slight decrease of specific volume appear due to dissolution of precipitates and temporary enrichment of matrix by Cu atoms.

What can be seen in the diagram of ageing at 200 ºC (fig. 8) is a slight increase of the sample length due to precipitation followed by a plateau as a result of simultaneous occurrence of changes caused by precipitation and dissolution, and an ultimate sample length growth as a result of formation of precipitates different from the previous ones.

Next dilatometric diagram shows ageing at 225 °C (fig. 8) after supersaturation. Continuous increase of sample length is seen and no changes of length from time about 50 000 s. Diagrams of isothermal ageing at temperatures of 225 and 305 ^{O}C (fig. 8) show increase of sample length because of precipitation processes. Plateau (or slight decrease of length) for aging at 275 °C starts after about 1000 s time, for ageing at 305 °C after about 1000 s time starts decrease of length. The greater increase of samples length is seen at 200 ^{O}C and 225 ^{O}C temperature of ageing.

A set of DTA diagrams of ageing with different heating rates after supersaturation is shown in figure 9. For heating rate of 0.66 Deg/s all stages of ageing are clearly seen. Below of 100 °C G-P zones appear, between 100 C and 150°C dissolution of G-P take place, from about 150 to 225°C transformation of G-P zones to θ” take place, at about 225 starts dissolution

of θ" and its transformation to θ' (the biggest pick), dissolution of θ' begins at about 300 °C and ends at about 400 °C, and precipitation of Al_2Cu starts at about 450 °C and at higher temperatures dissolution of precipitates takes place. Similar DTA pick temperatures for precipitation processes were presented by Thomson [8]. Results of dilatometric and DTA studies correspond each other; the largest increase of length and the largest heat effect at slow heating rates appears at the temperatures range 230-250 °C due to precipitation of θ'. Small changes of length and small heat effects appear at temperatures of G-P precipitation, transformation of G-P into θ" and precipitation of Al_2Cu. The smallest activation energy values (47-60 kJ/mol) determined by both methods are relevant to G-P formation and comply with the results obtained by Smith [9,11] (61-73 kJ/mol), the highest (about 300 kJ/mol) is the value of the Al_2Cu precipitation that starts sooner in isothermal ageing. Activation energy of dissolution process appearing during G-P zone transformation into θ" is the order of 100 kJ/mol. Activation energy of the θ" precipitation process is about 100 kJ/mole according to dilatometric and DTA method. The obtained values are somewhat lower than obtained by Smith [9,11] (93-131 kJ/mol).

Activation energy of θ' precipitation determined by DTA is somewhat lower (about 68 kJ/mol) than those that determined by dilatometric method (about 100 kJ/mol). The value of activation energy of Cu diffusion in Al without any factors accelerating this process is 135, 34 kJ/mol [1,6,10]. Activation energy of diffusion may be lowered by the presence of quenched in vacancies and dislocations [2,4]. Therefore decrease of activation energy is expected at low temperatures of the precipitation where G-P zones appear. A certain number of vacancies and dislocations can be produced by dissolution of precipitates and that can be a reason for decrease of the activation energy values during precipitation processes following up dissolution processes. Activation energy values of the Al_2Cu precipitation about three times higher than those of precipitation of G-P zones was found by Thomson [8]. The increase of the activation energy of the processes taking place above 300 ºC is relevant to both experimental methods and can be caused by small that increases values of activation energy [2]. The *n* values in the JMA equation are close 1.5 and they indicate that, in each of the analyzed processes, nucleation takes place in pre-existing nucleation sites. Those sites are: quenched in dislocations in the case of G-P zones, stable G-P zones which transform into θ" for θ', grain boundaries of solid solution α for Al_2Cu. Nucleation of Al_2Cu at solid solution grain boundaries may indicate lack in solid dislocation suitable for nucleation, or very small number of such dislocations. Small value of undercooling can also increase activation energies of θ' dissolution and Al_2Cu precipitation processes.

6. Conclusion

- Dilatometric and quantitative metallography methods can be applied for analysis of grain growth of solid solution and dissolution of precipitates during saturation annealing of Al-4.7% Cu alloy, where both processes overlap each other.
- Activation energy values of grain growth and dissolution of precipitates in Al-4.7% Cu alloy were determined by quantitative metallography and dilatometric method. The values of the activation energy indicate that both processes depend on diffusion of Cu atoms in solid solution. The differences between values obtained by each method are small and acceptable.
- Both methods (dilatometric and DTA) can be applied for analysis of precipitation and dissolution processes during ageing of supersaturated Al-4.7% Cu alloys.
- Activation energy values of precipitation processes in Al-4.7% Cu alloy were determined by DTA and dilatometric methods. The differences between values obtained by each method are small and acceptable. Results obtained for precipitation of G-P zones and for precipitation of θ" and θ' in principle comply with those obtained before by other authors.

- Activation energies of precipitates dissolution were determined by DTA. Activation energy values obtained for dissolution of the G-P zones comply with those obtained before by other authors. In the case of dissolution of θ' and $CuAl_2$ precipitation the obtained activation energies were higher than the activation energy of diffusion of Cu in solid solution.

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