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Kinetics of Transformation during Supersaturation and Aging of the Al-4.7Mass%Cu Alloy: Grain Size, Dilatometric, and Differential Thermal Analysis Studies

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The processes taking place during supersaturation of the Al-4.7mass%Cu alloy have been studied by the methods of quantitative metallography and dilatometry. The grain growth activation energy was about 95 kJ/mol, and the exponent of time, *n*, was close to 0.4. Dissolution of precipitates caused two-stage shrinkage of the sample, which had activation energies of 90 kJ/mol (first stage, *n* = 0.8) and 63 kJ/mol (second stage, *n* = 0.4).The kinetics of the phase transformation during aging of the Al-4.7mass%Cu alloy has been studied by the dilatometry and differential thermal analysis The activation energy of the precipitation processes within the range of 50-320 °C varied between 50 and 100 kJ/mol and confirmed the results obtained previously. For the precipitation processes within the range of 320-462 °C, the activation energy varied from 226 to 300 kJ/mol. The results obtained were compared with literature data with good agreement.

1. Introduction

The processes of precipitation in aluminum-copper alloys are well known. After supersaturation consisting of annealing at about 520 °C, quick cooling down to room temperature, and aging, G-P (Guinier-Preston) zones first appear, then are followed by Θ″ precipitates, which nucleate on the most stable G-P zones. The other G-P zones dissolve in the solid solution, and the copper atoms diffuse to the growing nuclei. When the temperature increases, because of aging, the Θ″ dissolves, and Θ′ nucleates at defects in the solid solution. Finally, the equilibrium phase Al_2Cu (Θ) nucleates at the boundaries of the solid solution grains, Θ′ dissolves, and the copper atoms diffuse to the growing Θ.[1-4]

The saturation process precedes aging and comprises dissolving excess precipitates enriching the solid solution with copper atoms, grain growth, and quick cooling to the ambient temperature. The amount of copper atoms in the solid solution influences the quantity of precipitates during aging and determines the properties obtained after aging. The grain boundaries of the solid solution are privileged places for precipitate nucleation, so grain size can influence the precipitation kinetics. The processes of dissolving excess equilibrium precipitates and grain growth are interrelated in a sense. A fine-grain microstructure accelerates precipitate dissolution because of an increase in the diffusion path; the presence of precipitates decelerates movement of the grain boundaries and the grain growth. The processes are known, but their kinetics has not been described in detail. Because the specific volume of the solid solution decreases during its enrichment with copper atoms,[5] the process can be studied by means of a dilatometer, and the kinetics of the grain growth can be studied by the methods of quantitative metallography. During aging, the processes of precipitation and dissolution overlap each other, which is why they are often difficult to separate when analyzing the transformation kinetics. The kinetics of phase transformations during the aging processes can be analyzed in isothermal and isochronous experiments. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are applied in isochronous heating because the processes of heat emission during precipitation and heat absorption during dissolving are very visible. Precipitation in aluminum-copper alloys is accompanied by the sample volume growth, whereas dissolution is accompanied by its decrease.[1,5] The changes are clearly visible in dilatometric investigation, and they can be used successfully for the analysis of the kinetics of the transformations taking place during isothermal aging. The Johnson-Mehl-Avrami (JMA) equation can be applied for the analysis of the kinetics of isothermal transformations. In addition to the determination of activation energy, the equation can be used to find 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.

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Fig. 1 Annealing 5 h at 510 °C. Magnification 100×

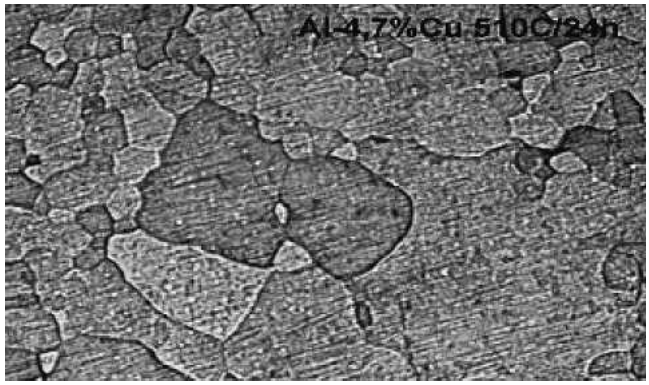

Fig. 2 Annealing 24 h at 510 °C. Magnification 100×

2. Experimental Procedures

The Al-4.7mass%Cu alloy was prepared especially for these studies. The composition the alloy in mass% was 94.85 aluminum, 4.69 copper, 0.2 iron, 0.08 silicon, and 0.15 other elements. Because of the decrease in the specific volume of the solid solution during its saturation of copper atoms the process can be studied by dilatometry, and grain growth kinetics can be studied by quantitative metallography. The presence of Al_2Cu not dissolved during supersaturation was identified by the x-ray method.

For aging kinetics studies two methods were used: dilatometry (for isothermal studies) and DTA (for continuous heating studies). Dilatometric studies were performed with an Adamel-Lhomargy LK02 dilatometer. Samples of rod 2 mm in diameter and 13 mm long were supersaturated at 505 °C for 10 h in a vacuum radiation furnace and quenched to room temperature by a helium gas jet. Isothermal aging was performed also in the LK02 dilatometer at a temperature range of 120-350 °C for the time necessary to reach a no-dilatation change stage. DTA studies were performed using a Mini DTA M5 Setaram. Samples in the form of truncated cones 4 mm long and 2 and 3 mm in diameter were used. Standard specimens were prepared from electrolytic aluminum. DTA samples were supersaturated in a resistance furnace at 520 °C for 6 h and quenched in water.

Fig. 3 Annealing 5 h at 540 °C. Magnification 100×

Fig. 4 Annealing 24 h at 540 °C. Magnification 100×

3. Kinetics Studies: Theoretical Basis

3.1 Grain Growth Studies

Before annealing, the structure of Al-4.7mass%Cu consisted of solid-solution grains and Al_2Cu. Solid-solution grains are big compared with Al_2Cu grains. The number of the Al_2Cu grains compared with number of solid-solution grains is small (about 8%). Therefore, the grain growth of the alloy during isothermal annealing in the temperature range of 500-540 °C can be treated as one phase (solid solution) grain growth[2,3] and expressed by:

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

where d is average grain size, t is time, n is the time exponent, and $k(T)$ is the grain growth rate constant:

$$k(T) = A \cdot \left(\frac{-Q}{R \cdot T} \right) \quad \text{(Eq 2)}$$

where A is a constant, Q is the activation energy for the analyzed transformation, R is a gas constant, and T is temperature in K.

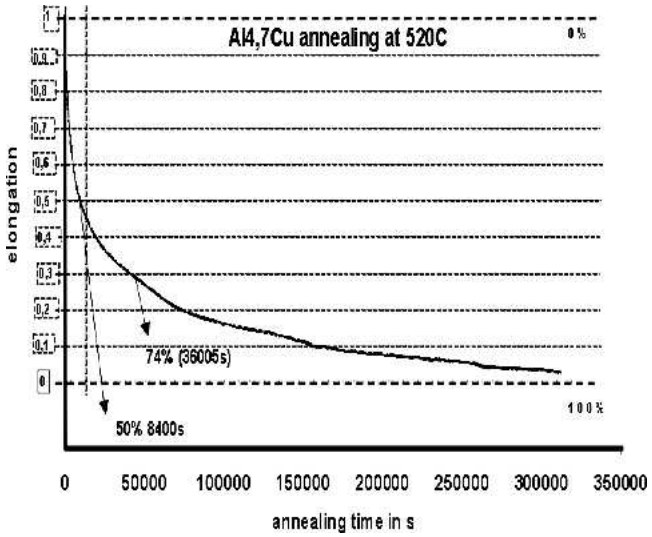

Fig. 5 Example of dilatometric diagram of annealing at 520 °C

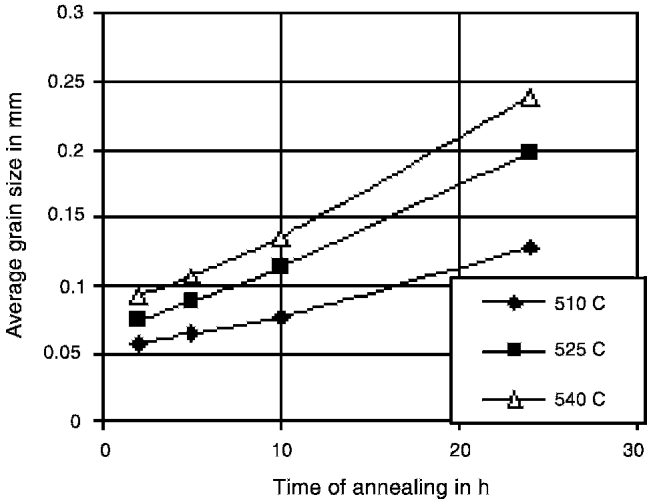

Fig. 6 Changes of average grain size during annealing at 510, 525, and 540 °C

3.2 Precipitation and Dissolution Studies

For isothermal kinetics studies the JMA equation[3,6,7] was used in the form:

$$x(t) = 1 - \exp(-k \cdot t^n) \quad \text{(Eq 3)}$$

where x-is the fraction transformed at time t, k is the transformation rate constant for the selected transformation at isothermal temperature, and n is the time exponent, which is supposed to be constant at the temperature range for a certain kind of transformation.

Activation energy Q can be determined from Eq 2.

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

$$Q = -R \cdot dC/d(1/T_m) \quad \text{(Eq 4)}$$

where

$$C = \ln \frac{V}{(T_m)^2} \quad \text{(Eq 5)}$$

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

4. Results

Examples of structures after annealing at temperatures 510 and 540 °C and quenching are shown in Figs. 1 and 2 (510 °C) and 3 and 4 (540 °C). An example of a dilatometric diagram of annealing at 520 °C is presented in Fig. 5. Changes of the average grain size of samples annealed at 510, 525, and 540 °C are shown in Fig. 6. A set of dilatometric curves of annealing at temperatures between 480 and 540 °C transformed into lnln [1/ (1 − x)] vs ln$k$ diagrams is shown in Fig. 7. Examples of dilatometric diagrams of isothermal aging at temperatures between 125 and 305 °C immediately after supersaturation are shown in Fig. 8. DTA diagrams of isochronal aging immediately after supersaturation are presented in Fig. 9.

One can calculate activation energy if the mechanism of transformation is the same at a certain temperature range,[3,7] which means the same (or nearly the same) n coefficient. Average values of n for the same mechanism of transformation during aging vary from 1.4 to 1.47.[3] The temperatures of 250 and 275 °C were excluded from the calculation of activation energy because the values of n obtained for these temperatures differed too much from the range of 1.4-1.47. Results of transformation kinetics analysis during isothermal annealing (grain size and dilatometric studies) are presented in Table 1. Results of kinetic analysis of isothermal (dilatometric) and isochronal (DTA) experiments are shown in Table 2.

5. Analysis and Discussion

The average grain size of solid solution increased during increasing time and temperature of annealing (Fig. 6). At 540 °C grain size increased more than at 510 °C. The time exponent of kinetic equation value was almost the same at each annealing temperature, which indicates a similar growth mechanism. The activation energy of growth was about 95 kJ/mol and is close to that obtained for diffusion of copper in aluminum.[9,11]

During annealing the samples in the dilatometer at a temperature range of 480-540 °C contracted (Fig. 5) because of the increase in the amount of copper in solid solution.[5]

From Fig. 7 one can see a steeper slope of the diagram at the beginning of annealing (the n values is about of 0.8) than latter on (with an n value of about 0.4), which indicates a faster processing rate at the beginning of the transformations. The activation energy value at the beginning of the

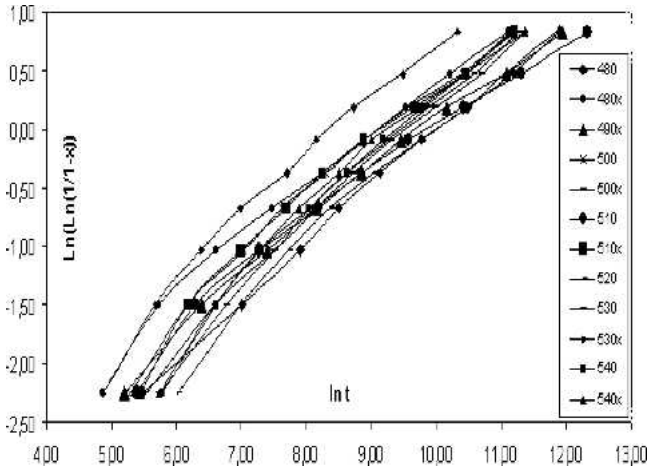

Fig. 7 Dilatometric curves of annealing at 480-540 °C transformed into lnln [1/(1 − *x*)] vs ln*k* diagrams

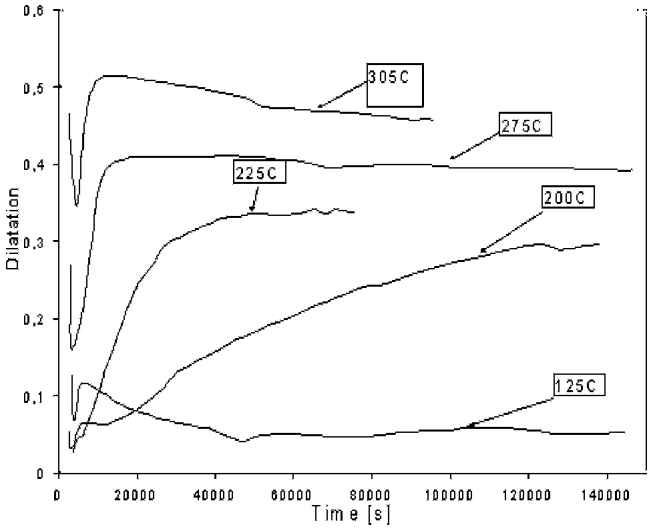

Fig. 8 Dilatation changes during isothermal aging of supersaturated Al-4.7mass%Cu alloy

transformation is almost the same for that obtained during grain growth. For the next stage of transformation the activation energy decreases, but it is still close to that for copper diffusion in aluminum. This means that dissolution of Al_2Cu particles and the copper clusters existing at annealing temperatures of 480-540 °C limits the grain growth of solid solution. During the progress of dissolution number of Al_2Cu particles and copper clusters gradually disappears but sill limits the contraction of samples.

The dilatometric diagram of aging at 125 °C (Fig. 8) after supersaturation shows a slight increase of specimen length caused by precipitation of a small specific volume and a smaller amount of copper in the G-P zones. After a period of about 40,000 s a slight decrease of specific volume appears, resulting from dissolution of precipitates and temporary enrichment of the matrix by copper atoms.

What can be seen in the diagram of aging at 200 °C (Fig. 8) is a slight increase of the sample length caused by precipitation followed by a plateau as a result of the 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.

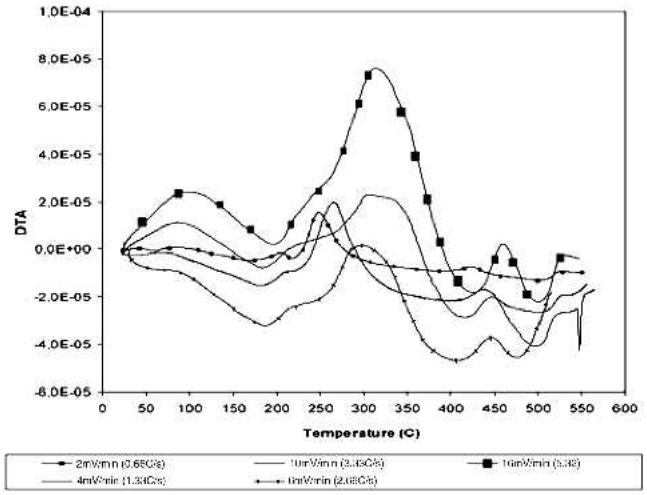

Fig. 9 DTA diagrams of isochronal aging of the Al-4.7mass%Cu alloy

Table 1 Results of transformation kinetics analysis during annealing: isothermal studies

Grain growth kinetics		
Temperature range, °C	***n* value**	**Activation energy, kJ/mol**
510-540	0.4-0.43	94,432
Contraction kinetics: JMA analysis (dilatometric studies)		
Temperature range, °C	***n* value**	**Activation energy, kJ/mol**
480-540	0.7-0.8	90,010
480-540	0.4-0.45	65,854

Next, the dilatometric diagram shows aging at 225 °C (Fig. 8) after supersaturation. A continuous increase of sample length is seen and no changes of length from about 50,000 s in time. Diagrams of isothermal aging at temperatures of 225 and 305 °C (Fig. 8) show an increase of sample length caused by precipitation processes. A plateau (or slight decrease of length) for aging at 275 °C starts after about 1000 s; for aging at 305 °C after about 1000 s a decrease in length begins. The greater increase of sample length is seen at 200 and 225 °C temperatures of aging.

A set of DTA diagrams of aging with different heating rates after supersaturation is shown in Fig. 9. For a heating rate of 0.66 °C/s all stages of aging are clearly seen. Below 100 °C, G-P zones appear; between 100 and 150 °C, dissolution of G-P takes place; from about 150 to 225 °C, transformation of G-P zones to Θ″ take place; at about 225 °C dissolution of Θ″ and its transformation to Θ′ (the

Table 2 Results of transformation kinetics analysis during aging: isothermal and isochronous

Temperature ranges, °C	Experiment	*n* value	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 (523 K)	Isothermal	1.74	Overlap of transformations	…
275 (548 K)	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 precipitaion	303,864

biggest peak) begin. Dissolution of Θ′ begins at about 300 °C and ends at about 400 °C. Precipitation of Al_2Cu starts at about 450 °C, and at higher temperatures dissolution of precipitates takes place. Similar DTA peak temperatures for precipitation processes was presented in Ref 8. Results of dilatometric and DTA studies correspond to each other; the largest increase of length and the largest heat effect at slow heating rates appear at the temperatures range of 230-250 °C because of 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 reported in Ref 9 and 11 (61-73 kJ/mol). The highest (about 300 kJ/mol) is the value of the Al_2Cu precipitation that starts sooner in isothermal aging. The activation energy of dissolution process appearing during G-P zone transformation into Θ″ is on the order of 100 kJ/mol. The activation energy of the Θ″ precipitation process is about 100 kJ/mol according to dilatometric and DTA methods. The obtained values are somewhat lower than obtained in Ref 9 and 11 (93-131 kJ/mol).

Activation energy of Θ′ precipitation determined by DTA is somewhat lower (67.8 kJ/mol) than those determined by the dilatometric method (100.7 kJ/mol). The value of the activation energy of copper diffusion in aluminum without any factors accelerating this process is 135.34 kJ/mol.[1,6,10] The activation energy of diffusion may be lowered by the presence of quenched in vacancies and dislocations.[2,4] Therefore a decrease of activation energy is expected at low temperatures of precipitation where G-P zones appear. A certain number of vacancies and dislocations can be produced by dissolution of precipitates, which can be a reason for a decrease of the activation energy values during precipitation processes after dissolution processes. Activation energy values of Al_2Cu precipitation about three times higher than those of precipitation of G-P zones are found in Ref 8. The increase of the activation energy of the processes taking place above 300 °C is relevant to both experimental methods and can be caused by small undercooling that increases values of activation energy.[2] The *n* values in the JMA equation are close to 1.5, and they indicate that in each of the analyzed processes, nucleation takes place in preexisting nucleation sites. Those sites are: quenched in dislocations in the case of G-P zones, stable G-P zones that transform into Θ″, for Θ′ defects of solid solution α, grain boundaries of solid solution α for Al_2Cu. Nucleation of Al_2Cu at solid-solution grain boundaries may indicate a lack in solid dislocation suitable for nucleation or a very small number of such dislocations. A small value of undercooling can also increase activation energies of Θ′ dissolution and Al_2Cu precipitation processes (Table 2).

6. Conclusions

- 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-4.7mass%Cu alloy, where both processes overlap each other.
- Activation energy values of grain growth and dissolution of precipitates in Al-4.7mass%Cu alloy were determined by quantitative metallography and dilatometric methods. The values of activation energy indicate that both processes depend on diffusion of copper atoms in solid solution. The differences between the 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 aging of supersaturated Al-4.7mass%Cu alloys.
- Activation energy values of precipitation processes in Al-4.7mass%Cu alloys were determined by DTA and dilatometric methods. The differences between the 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 precipitate 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 copper in solid solution.

References

1. D. Altenpohl, *Aluminium und Aluminiumlegirungen,* Springer Verlag, Berlin, 1965, p 120-165 (in German)
2. D.A. Porter and K.E. Easterling, *Phase Transformations in Metals and Alloys,* Van Nostrand Reinhold Company, New York, 1981, p 291-316
3. J.W. Christian, *The Theory of Transformations in Metals and Alloys,* 2nd. ed. Pergamon Press, London, 1975, p 729-759
4. L. Lochte, A. Gitt, G. Gottstein, and I. Hurtado, Simulation of the Evolution of G-P Zones in Al-Cu Alloys: Extended Cahn-Hillard Approach, *Acta Mater.,* Vol 48, 2000, p 2969-2984
5. P. Nowak, *Badania Procesów Starzenia Stopów Al-5%Cu. Próba Symulacji Komputerowej,* Politechnika Poznańska WBMiZ, Praca Dyplomowa, 2002, p 10-31 (in Polish)
6. E.J. Mittemeijer, "Analysis of the Kinetics of Phase Transformations," Annual Report, Delft University of Technology, 1990, p 6-10
7. I.A. Wierszyłowski, The Effect of the Thermal Path to Reach Isothermal Temperature on Transformation Kinetics, *Metall. Trans. A,* Vol 22, 1991, p 993-999
8. D.S. Thomson, The Calorimetric Observation of Solid State Reactions in Aluminum Alloys, *Thermal Analysis,* ASM, 1970, p 1147-1170
9. G.W. Smith. Precipitation in an Air-Cooled Aluminum Alloy: A Comparison of Scanning and Isothermal Calorimetry Methods, *Thermochim. Acta,* Vol 313, 1998, p 27-36
10. W.N. Wendland, *Thermal Methods of Analysis,* A. Wiley-Interscience Publications, John Wiley & Sons, New York, 1974, p 145-209
11. G.W. Smith, Precipitation Kinetics in Solutionized Aluminum Alloy: Determination by Scanning and Isothermal Calorimetry, *Thermochim. Acta,* Vol 317, 1998, p 7-23