Analysis of precipitation kinetics in Al-Ge and Al-Ge-Si alloys by dilatometry

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Abstract

The present work is concerned with the precipitation kinetics of Al-Ge(Si) alloys with different amounts of Ge and Si. Continuous heating and isothermal dilatometry are used successfully to identify the formation and dissolution of Ge or Si-Ge precipitates. Differential scanning calorimetry on the same samples confirms the temperatures of precipitation and dissolution. The formation and dissolution of precipitates are studied after different thermal histories. The precipitation kinetics of AlGe1 samples is significantly slower than that of alloys containing more Ge. The apparent activation energy determined from thermal expansion peaks during heating is 20 % smaller for AlGe3 than for AlGe1.

K e y   w o r d s: Al alloys, precipitation kinetics, thermal expansion, differential scanning calorimetry, isothermal dilatometry

1. Introduction

Al-Ge and Al-Si alloys are simple binary eutectic systems, and have historically been used as model systems to study mechanisms of precipitation. Both alloying elements have limited and strongly temperature dependent solubility in Al [1, 2]. Si and Ge form diamond cubic (dc) precipitates in face centered cubic (fcc) Al [3]. The formation of the diamond structure of Si and Ge in Al matrix is associated with a transformation from metallic to covalent bonding [4]. Crystallographic data of fcc Al-based solid solutions and of the dc structure of Si show a relative change of atomic volume of about 28 %. The atomic radius of Ge is slightly bigger than that of Si and it will produce a relative change of 30 % in atomic volume due to precipitation [3, 5, 6]. The Ge and Si atoms have limited solubility in Al of the ternary system, but both atoms are interchangeable in the dc precipitates. Prior work on precipitation in Al-Si-Ge alloys has shown that the dispersion of dc precipitates in the ternary alloy is almost an order of magnitude finer than that in the binary Al-Si and Al-Ge alloys [7].

In the present work, samples were subjected to

T a b l e 1. Major alloying elements in the studied alloys (wt.%)

Alloys	Al	Ge	Si	Fe
AlGe1	97.9	1.9	–	0.2
AlGe3	96.6	3	0.2	0.2
AlGe5Si1	94.15	4.25	1.25	0.35

dilatometry during continuous heating and isothermal holding. The thermal expansion of these alloys is enhanced with respect to pure Al due to the precipitation of supersaturated Ge or Ge-Si identified by differential scanning calorimetry (DSC) thermograms.

2. Experimental procedure

The composition of the Al-Ge and Al-Ge-Si alloys prepared for this work is given in Table 1. All specimens used for the experiments were solution-treated at 430 °C/30 min achieving a complete solid

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solution and quenched in water (w.q.). The dilato-
metric samples were prepared as parallelepiped pieces
of $10 \times 3 \times 3\,\mathrm{mm}^3$ size. The thermal expansion of
the studied material has been analysed by means of a
TMA (Thermo-Mechanical Analyser) 2940 CE equip-
ment from TA Instruments.

The dilatometric cycle consists of heating from
room temperature to 430 °C with heating rates of 1, 5
and $20\,\mathrm{K\,min}^{-1}$, holding of 5 min at 430 °C and cool-
ing down to room temperature with $20\,\mathrm{K\,min}^{-1}$. Im-
mediately afterwards, the samples are reheated at the
same rate as in the first cycle to compare the effects
of cooling rate on the precipitation. The instantaneous
coefficient of thermal expansion (CTE) at a temperat-
ure T was calculated from the ΔL versus temperature
curves smoothed within intervals of $T \pm 12.5\,\mathrm{K}$ by

means of the numerical derivative

$$\mathrm{CTE}(T) = \frac{1}{L}\frac{\mathrm{d}L}{\mathrm{d}T} \qquad (1)$$

where L is the length of the sample at the re-
spective temperature T. The achieved accuracy was
$< \pm 1\,\mathrm{ppm/K}$.

Isothermal dilatometric measurements were car-
ried out on AlGe1 and AlGe3 alloys and the calcu-
lated percent change in length $\Delta L/L_0$ (%) is plotted
versus time. The time elapsed between quenching and
transfer of the sample into the dilatometer was about
15 min. The isothermal measurements consist of heat-
ing from room temperature with a heating rate of
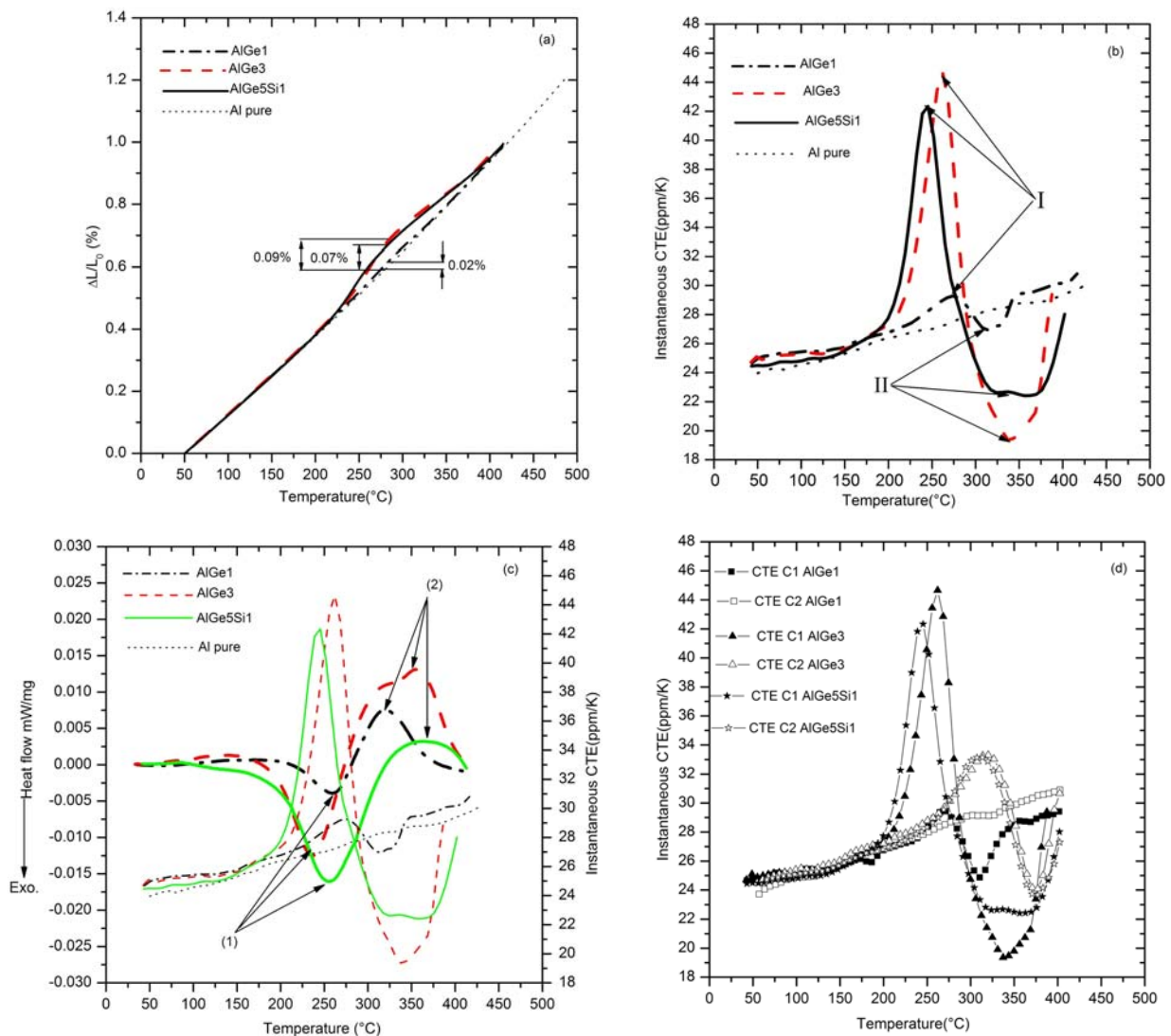$20\,\mathrm{K\,min}^{-1}$ to 240, 290, 310 and 330 °C, then holding

Fig. 1. (a) Typical plot of $\Delta L/L_0$ (%) vs. (T) for w.q. AlGe1, AlGe3 and AlGe5Si1 samples, recorded at a heating rate of $5\,\mathrm{K\,min}^{-1}$, (b) corresponding CTE(T) curves, (c) comparing CTE and DSC results of the samples, (d) comparing first cycle (C1) with second cycle (C2) of CTE(T), after cooling by $20\,\mathrm{K\,min}^{-1}$.

different periods at these temperatures. After allowing the length of the samples to stabilise, the temperature was again changed and kept for a further holding period. The relative change in length, ΔL, was measured and interpreted as the superposition of thermal expansion ΔL^{Al} of pure Al and precipitation or dissolution ΔL^p. The same temperature program was applied to samples of pure Al to calculate $\Delta L^{Al}/L_0$:

$$\frac{\Delta L(\Delta T)}{L_0} = \frac{\Delta L^{Al}}{L_0} + \frac{\Delta L^p}{L_0}, \qquad (2)$$

where L_0 is the original length. The scatter of the relative length change was less than 10^{-4}. Instantaneous or time dependent deviations from the length change of pure Al are assigned to precipitation effects in the alloy at the corresponding temperature. DSC measurements were carried out in a DSC2920 equipment. DSC samples of 6 mm diameter and 1 mm thickness ($\sim$ 100 mg mass) were cut and tested vs. 99.99 wt.% pure-Al of similar weight. The output of enthalpy change was mW per mg.

3. Results and discussion

3.1. Continuous heating results

During continuous heating, the change in length (ΔL) as a function of temperature (T) was recorded, from which the percent change in length $\Delta L/L_0$ (%) vs. T was plotted. A typical plot of $\Delta L/L_0(T)$ for the quenched samples is shown in Fig. 1a. The deviation from pure Al increase in the order AlGe1, AlGe5Si1, AlGe3. The deviations of the instantaneous coefficients of thermal expansion (CTE) are more pronounced as shown in Fig. 1b with the acceleration peaks marked (I) and the retardation minima (II).

The corresponding DSC thermograms in Fig. 1c show exo- and endothermic peaks (numbered 1, 2) indicating formation and dissolution of the precipitates, respectively.

The expansion effect (I) for AlGe1 appears in the temperature interval 240–290 °C with a peak at 270 °C, which coincides with the precipitation effect (1) in the DSC thermogram. CTE(T) curves and DSC thermograms of AlGe3 and AlGe5Si1 confirm each other also. Comparing the first and second cycle of CTE(T) in Fig. 1d, precipitation and dissolution effects are smaller in the 2nd cycle and displaced to higher temperature. The instantaneous CTE(T) of AlGe1, AlGe3 and AlGe5Si1 seems to be sensitive to the cooling rate from solution treatment temperature to room temperature.

Figures 2a–c show the CTE(T) curves of AlGe1, AlGe3, AlGe5Si1 alloys obtained at different heating rates after water quenching. The main precipitation peak shifts to higher temperatures with increasing
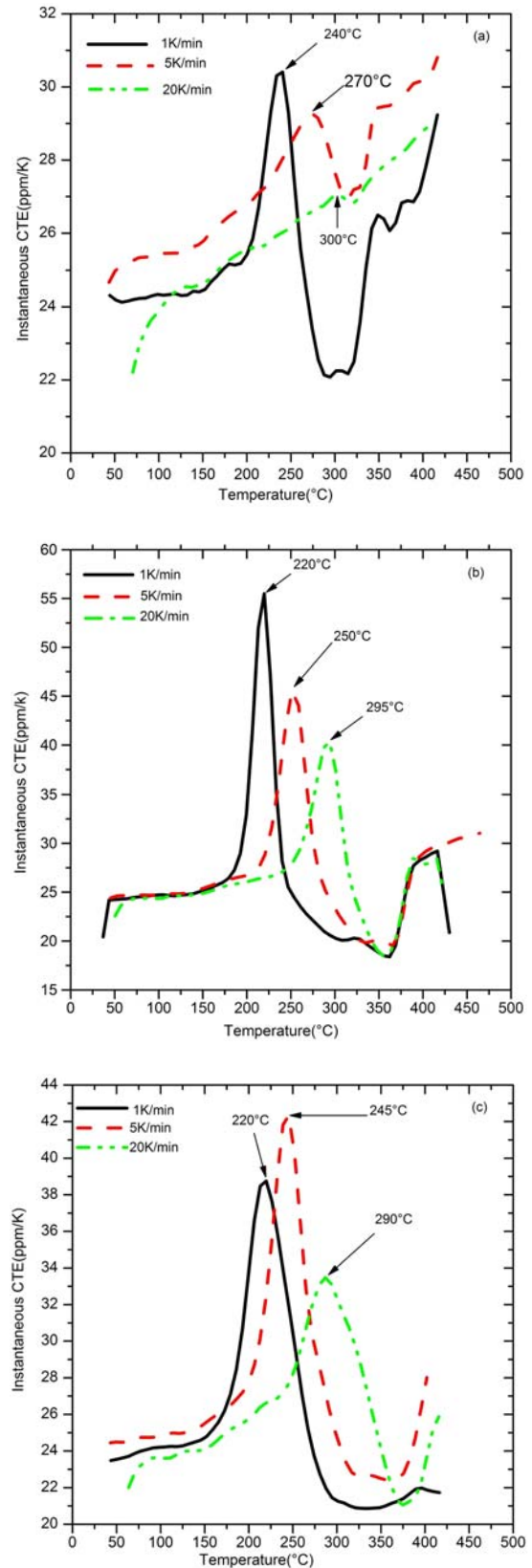

Fig. 2. CTE(T) curve of (a) AlGe1, (b) AlGe3, (c) AlGe5Si1 obtained at different heating rates.
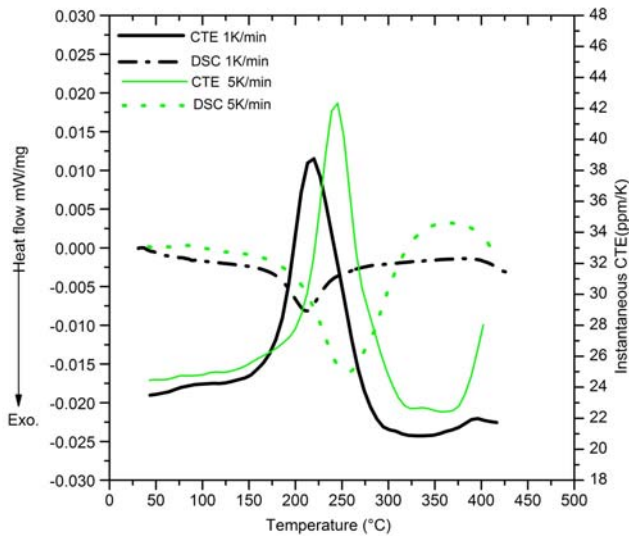
Fig. 3. Comparing CTE curve and DSC thermograms of AlGe5Si1 at different heating rates.

heating rate. In Fig. 2a, the precipitation peak shifts from 240 °C at 1 K min^{-1} to 270 °C at 5 K min^{-1} and disappears almost at 20 K min^{-1} (300 °C). The other alloys show a clear precipitation peak at all 3 heating rates. Figure 2c shows the highest precipitation peak for 5 K min^{-1} heating rate of AlGe5Si1 indicating the sensitivity of the kinetics. Figure 3 shows the CTE and the DSC of AlGe5Si1 alloy, where the main precipitation peaks also shift to higher temperature with increasing heating rate in both experiments.

3.2. Isothermal dilatometry results

Isothermal experiments were carried out at 240, 290, 310, 330 °C on AlGe1 and at 240, 290, 330 and 370 °C on AlGe3 with different holding periods. The highest temperature represents solution treatment of each alloy. From there, the samples were cooled at 20 K min^{-1} to 240 °C and after 20 h holding reheated to 290 °C. The results of w.q. AlGe1 and AlGe3 alloys are depicted in the overview in Fig. 4a,b. The relative length change of pure Al submitted to the same temperature-time exposure is presented as a reference. The expansion of both as quenched alloys at 240 °C indicates that precipitation of Ge proceeds for a few hours. Heating further, the rate of dissolution of Ge precipitates increases with temperature. Complete dissolution of Ge is achieved at 330 °C for AlGe1 within 2 h and at 370 °C in less than 1 h for AlGe3. The relative length change of Al in each temperature step can be taken as reference to quantify the relative length change due to changes in precipitation. Cooling at a rate of 20 K min^{-1} from the solution treatment temperature to 240 °C and holding at that temperature shows less and slower precipitation for both alloys

than from their as quenched condition (see Fig. 4c,d). Figure 5 compares the percent change in length of AlGe3 with that of pure Al. It illustrates the isothermal expansion due to precipitation at 240 °C and the slow return to the Al-curve by progressive dissolution of Ge precipitates with increasing temperature. Some precipitation takes place in AlGe3 during cooling at 20 K min^{-1} from 370 °C to 240 °C as the contraction is less than that of pure Al. Reheating again does not reach the same length change as in the first run, indicating reduced precipitation according to the decrease in supersaturation.

3.3. Apparent activation energy

The apparent activation energy for precipitation can be determined according to the method developed by Kissinger. According to this method we can use the following equation [8] without a precise knowledge of the reaction mechanism:

$$\ln\left(\frac{\phi}{T_{\mathrm{p}}^2}\right) = C - \frac{E_{\mathrm{a}}}{RT_{\mathrm{p}}} \tag{3}$$

and Ozawa

$$\ln(\phi) = C - \frac{E_{\mathrm{a}}}{RT_{\mathrm{p}}} \tag{4}$$

where ϕ is the heating rate, T_{p} is the temperature of the CTE(T) peak, E_{a} is the apparent activation energy, R is the universal gas constant and C is the integration constant.

Figure 6 shows the relationship of $\ln\left[\dfrac{\phi}{T_{\mathrm{p}}^2}\right]$ vs. $1000/T_{\mathrm{p}}$ (Kissinger) and $\ln(\phi)$ vs. $1000/T_{\mathrm{p}}$ (Ozawa). The average values for the activation energy for precipitation of Ge are depicted in Fig. 6. The results for AlGe3 and AlGe5Si1 are very close yielding an activation energy in the range of 90–110 kJ mol^{-1}, whereas that for AlGe1 is ca. 20 % higher yielding 105–125 kJ mol^{-1}. The results according to Ozawa are about 10 % higher than those according to Kissinger.

4. Conclusion

The precipitation and dissolution processes of Ge in the Al matrix can be observed by dilatometry. The precipitation and dissolution produce additional expansion and contraction, respectively. This can be explained by the fact that precipitation of Ge in diamond structure in Al matrix causes a change in volume of 30 % more than that of Al, which would yield a length change of 0.1 % per 1 % Ge precipitated, but we can observe only an extra expansion of about 0.03 %. Dissolution produces the corresponding extra contraction
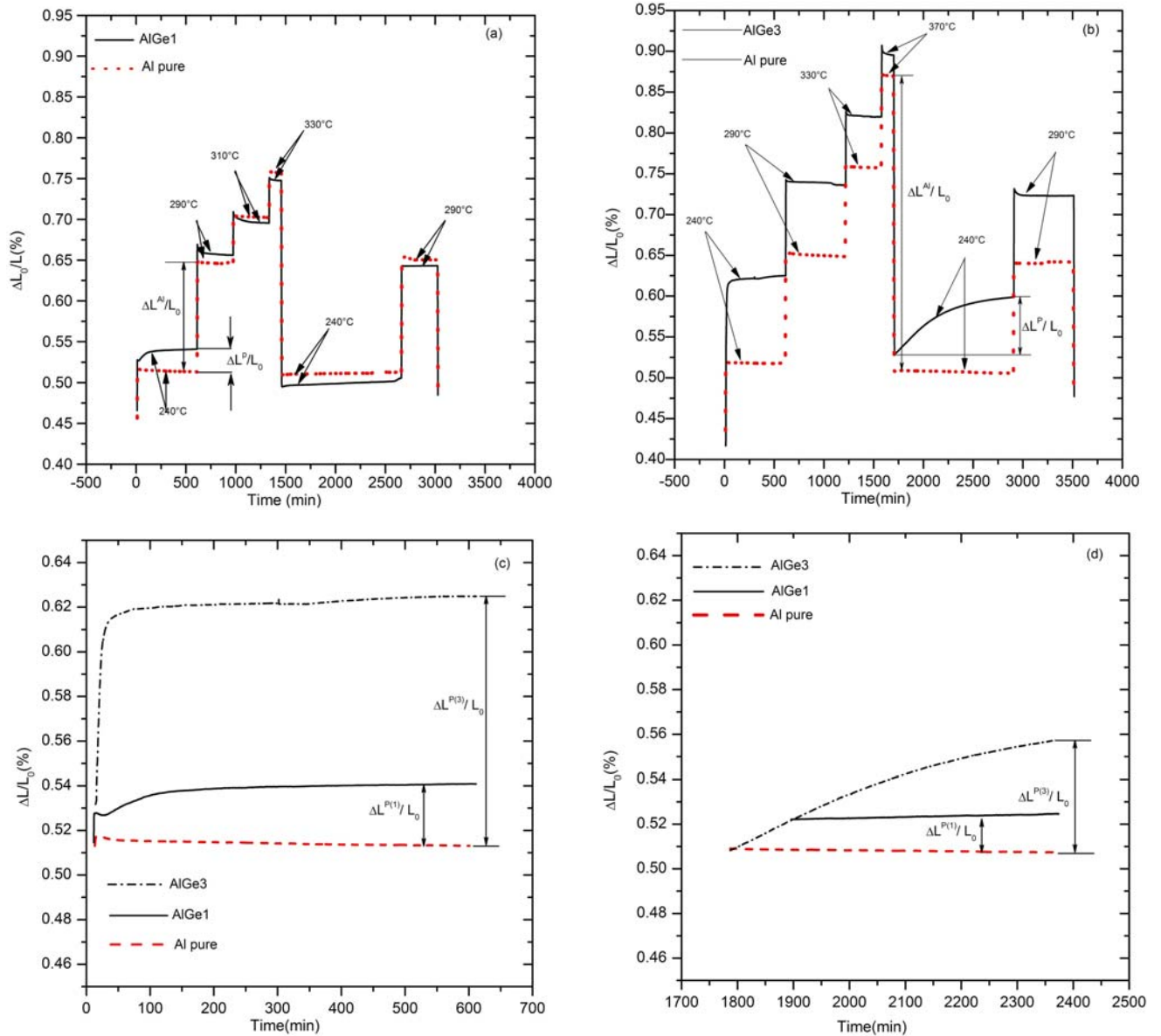
Fig. 4. Isothermal dilatometry after heating from the quenched condition to different temperatures (temperature changes at 20 K min^{-1}): (a) AlGe1 and (b) AlGe3, comparing the amount of Ge precipitation at 240 °C in (c) of water quenched condition, (d) after cooling with 20 K min^{-1} from 330 °C and 370 °C for AlGe1 and AlGe3, respectively.

in the dilatometry diagrams. Isothermal dilatometry measurements of AlGe1 and AlGe3, both in w.q. condition and after complete dissolution at 330 °C for AlGe1 and 370 °C for AlGe3, reveal that the kinetics of Ge precipitation at 240 °C is faster in water quenched samples than in samples moderately cooled directly to 240 °C. In addition, the precipitation kinetics are generally faster in AlGe3 than in AlGe1, as the latter requires about a 20 % higher apparent activation energy than AlGe3. DSC and dilatometry results confirm each other. The dilatometry method has the advantage, that it can be used to investigate the isothermal kinetics of Ge precipitation. Based on the combined results of dilatometry and DSC, the following conclu-

sions can be drawn:

(i) Ge and Si precipitation produce an additional expansion during heating which corresponds to the exothermal DSC effects.

(ii) Dissolution of Ge and Si precipitates reduce the temperature dependent expansion corresponding to endothermal DSC effects.

(iii) Precipitation in w.q. samples is promoted by the high quenched in vacancy concentration. The precipitation of Ge is retarded to higher temperatures after cooling at 20 K min^{-1} analogous to that of the Al-Si system [9]. The solute and vacancy supersaturation are reduced and larger critical radii are required with increasing temperatures.
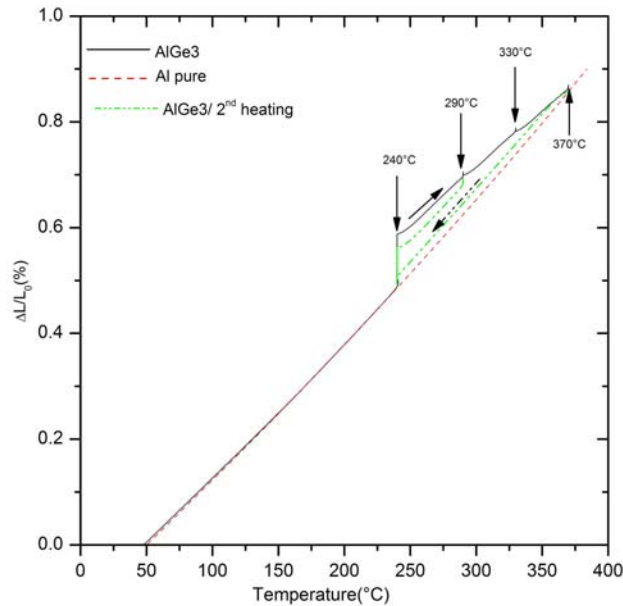
Fig. 5. Comparison of change in length of AlGe3 with pure Al during the temperature changes according to Fig. 4b.
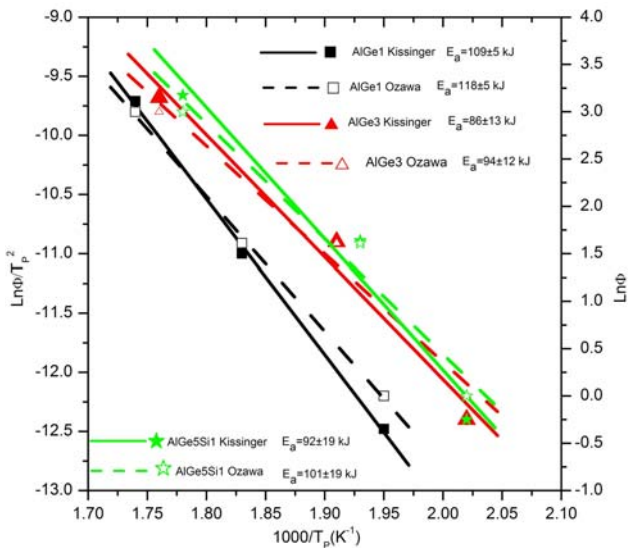

Fig. 6. Calculation of apparent activation energy of precipitation in AlG1, AlGe3 and AlGe5Si1 alloys according to Ozawa and Kissinger [8].

(iv) The dependence of the peak in thermal expansion on the heating rates allows the calculation of an apparent activation energy for precipitation.

(v) Precipitation of Ge in AlGe1 is significantly slower than in AlGe3 and AlGe5Si1. The precipitation of Ge is suppressed in AlGe1 when the heating rate exceeds $20\,\mathrm{K\,min^{-1}}$. The apparent activation energy for Ge precipitation in AlGe1 is about 20 % higher than that of the higher alloyed samples.

(vi) Isothermal dilatometry reveals the time required for precipitation at a temperature within the miscibility gap or the time required for their dissolution in the solid solution range. Precipitation is significantly faster and bigger for AlGe3 (2 h) than for AlGe1 (4 h).

(vii) For the AlGe3 sample, dissolution of the precipitates begins immediately during heating at $20\,\mathrm{K\,min^{-1}}$ from $240\,\mathrm{°C}$. Just above the solubility limit at $370\,\mathrm{°C}$ for AlGe3 and $330\,\mathrm{°C}$ for AlGe1, complete dissolution requires almost 2 h.

Acknowledgements

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