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PHASE TRANSFORMATIONS IN Al–Zn ALLOYS SOLIDIFYING AT VARIOUS RATES

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The influence of the alloying elements magnesium, copper and silicon on phase transformations in Al–60 wt% Zn alloy solidified at rates from 0.4 up to 65 deg/s has been investigated by means of DTA method.

The dendritic segregation of zinc in the solid solution manifested itself by changes of the shape of the respective parts of the cooling or heating curves between the solidus and liquidus temperatures. The appearance of non-equilibrium transformations has been recorded as peaks in the last stage of crystallization.

The shift of liquidus and eutectic temperatures in the direction of lower temperatures was observed in dependence on the cooling rate.

Thermal analysis carried out at various cooling rates revealed nonequilibrium transformations at higher velocities. The occurrence of such effects was confirmed using X-ray microanalysis.

Keywords: Al–Zn alloys, phase transformations

Introduction

The advantageous properties of aluminium zinc alloys with magnesium or copper additions have been known and utilized for years. However, numerous transformations occurring during solidification, heat treatment or ageing yield in consequence some instability of dimensions or changes of properties thus requiring their further examination [1, 2, 5].

The phenomena of dendritic segregation in Al–Zn alloys were studied from the theoretical and practical point of view in papers [3] and [9]. Transformations in these alloys with Mg, Cu or Si additions in the equilibrium state were investigated by several authors [6–13] who presented the respective phase diagrams or their parts.

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In order to estimate the influence of nonequilibrium solidification on these transformations the methods of thermal analysis (DTA) as well as X-ray microanalysis and metallographic observations have been employed in the present investigation.

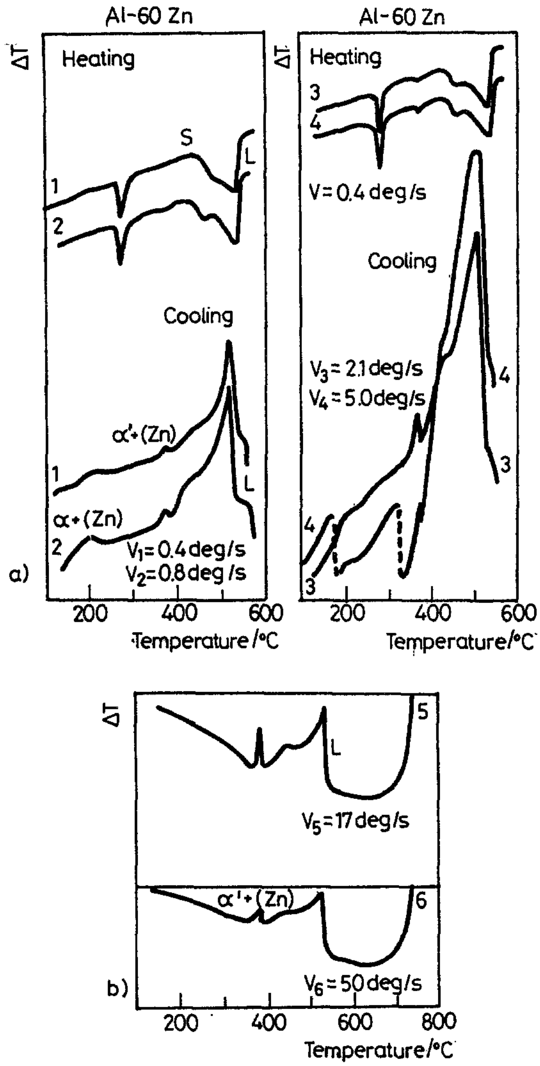


Fig. 1 The complete set of heating (at constant rate) and cooling curves (at various rates) of Al–60 Zn alloy obtained from the thermal analysis. a) at rates 0.4 – 5.0 deg/s, b) at rates 17 and 50 deg/s

Experimental procedure

Four alloys based on Al–60 wt% Zn alloy without or with 0.2% Mg, 2.0% Cu and 1.0% Si addition were cast from high purity metals using conventional methods.

The examination was carried out using thermal analysis (DTA) which enabled registration of thermal effects during heating and cooling in the form of the curve $\Delta T = f(T)$ where ΔT was the difference between the sample temperature and that of the reference material. The experiments were performed at six cooling rates from 0.4 up to

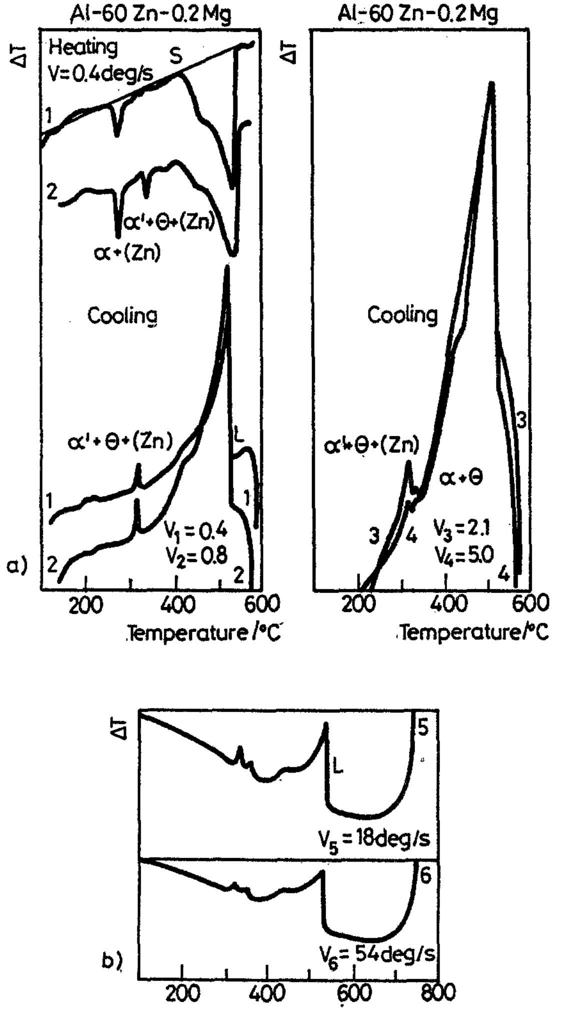


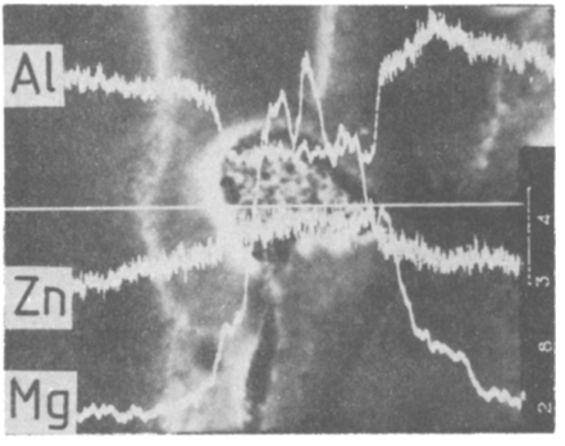
Fig. 2 The set of heating (at constant rate) and cooling curves (at various rates) of Al–60Zn–0.2Mg alloy obtained from the thermal analysis. a) at rates 0.4 – 5.0 deg/s, b) at rates 18 and 54 deg/s

65 deg/s using two different instruments. The samples were heated at a constant rate of 0.4 deg/s.

Results

The set of heating and cooling curves obtained for the Al–60 Zn alloy is collected in Fig. 1 where all typical transformations are indicated. The rest of the results will be referred to these curves in order to estimate the influence of additions of Cu, Mg and Si on the processes going on in the alloy.

a



b

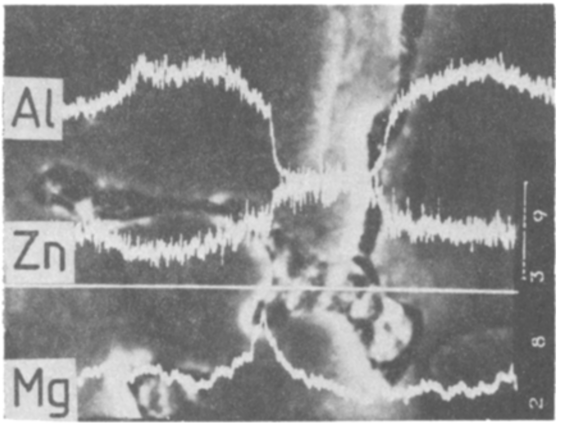


Fig. 3 Two kinds of precipitates in interdendritic areas of Al–60Zn–0.2Mg alloy; SEI image; magnification 2000×: together with concentration profiles of Al, Zn and Mg along the line of analysis. a) ternary eutectics, b) product of peritectic transformation

It is shown in Fig. 2 how the magnesium addition in an amount of 0.2 wt% affects the phase transformations in the Al–60 Zn alloy.

The liquidus temperature has not been influenced in a visible way. Nevertheless, it affected the nonequilibrium eutectic reaction because ternary eutectics built of α', θ (Mg_5Zn_{11}) and (Zn) appeared at 330°C (T_E = 343°C after [6]) during heating and at 325°C during cooling at v_3 = 0.4 and v_5 = 0.8 deg/s. The increase of the cooling rate to

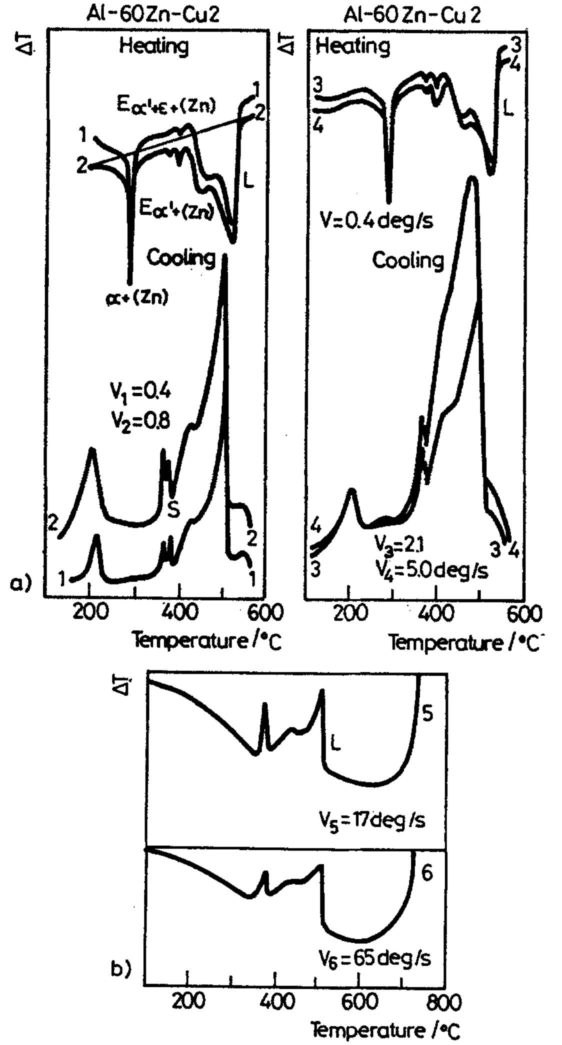


Fig. 4 Thermoanalytical curves of Al–60Zn–2Cu alloy obtained during heating at 0.5 deg/s and during cooling at various rates: a) 0.4 – 5.0 deg/s, b) 17 and 65 deg/s

2.1 deg/s yielded another heat effect at 357°C. It remains a question whether it is the binary eutectic reaction or the peritectic one ($L + \eta \rightarrow \alpha' + \theta$). Both kinds of precipitates are visible in Figs 3a and b obtained using X-ray microanalyzer. Figure 3a shows the

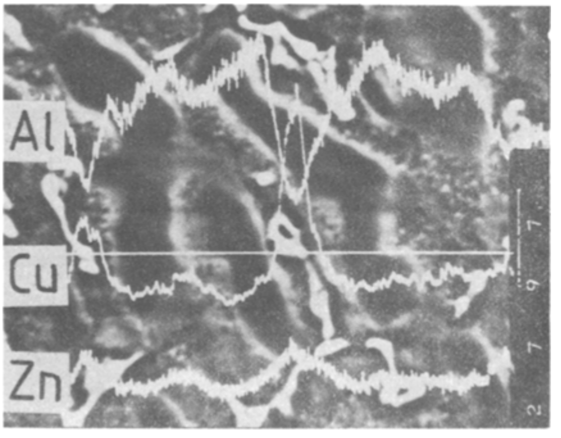


Fig. 5 Microstructure SEI of Al–60Zn–2Cu alloy solidified at rate 65 deg/s; magn. 2000×; with Al, Zn, Cu-concentration profiles along the line of analysis

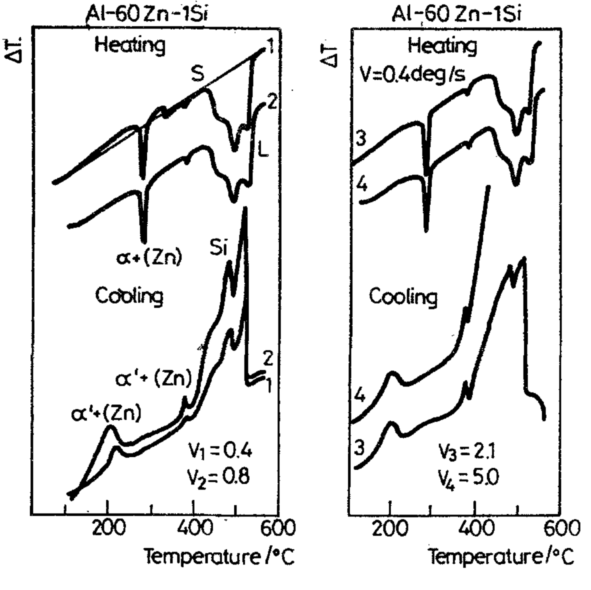


Fig. 6 Thermoanalytical curves of Al–60Zn–1Si alloy obtained during heating at 0.5 deg/s and during cooling at low rates

ternary eutectics. The products of peritectic transformation rather than the precipitate of the binary eutectics are presented in Fig. 3b.

The influence of the cooling rate on the shift of transformation temperatures is evident at higher rates (Fig. 2b) where all the characteristic reactions are shifted in the direction of lower temperatures.

a

b

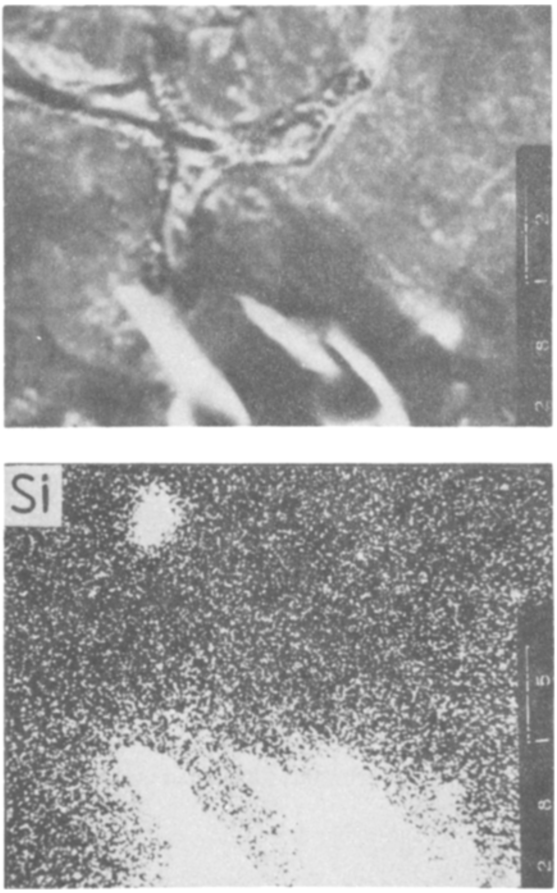


Fig. 7 Si-precipitates (light) in Al–60Zn–1Si alloy solidified at rate 5 deg/s. a) SEI image; magn. 2000 ×, b) distribution of Si on the above image

Figure 4 collects a set of thermoanalytical curves of Al–60Zn–2Cu alloy obtained during heating at 0.5 deg/s and during cooling at various rates. When comparing it with the binary alloy, a shift of the liquidus temperature by about 10°C is visible while that of the solidus temperature is not so evident (Figs 1b and 4b). Nonequilibrium solidification of the solid solution procedures, apart from the binary eutectic α + (Zn) the ternary one with ε-phase. The Cu addition affects also the eutectoidal transformation having entered both solid solutions. It caused a slight shift of the reaction temperatures in the direction of higher temperatures which was more pronounced at cooling.

Unlike the alloy with magnesium addition two heat effects from two non-equilibrium eutectics were registered at low cooling rates which joined into one while the rate increased. The disappearance of the ternary eutectic can be explained by the increase of the solubility of Cu in α–solid solution with the cooling rate. X-ray microanalysis confirmed the existence of one kind of eutectic precipitating in the sample which had solidified at 65 deg/s (Fig. 5). The tendency to shift the characteristic temperatures in the direction of lower ones was preserved in the alloy with copper addition in comparison with the alloy with magnesium.

Silicon was the third element added to the basic alloy. It can be seen from Fig. 6 that it affected visibly neither the temperatures of transformations nor the segregation typical for the binary alloy. X-ray analysis showed, however, the existence of Si in the solid solution as well as in large randomly dispersed precipitates of high Si concentration which appeared during solidification at about 500°C (Fig. 7).

Conclusions

1. The segregation of zinc in the solid solution of Al–60Zn alloys with 0.2% Mg or 2% Cu or 1% Si manifested itself as the change of the shape of the respective parts of the cooling and heating curves between the solidus and liquidus temperatures.

2. Non-equilibrium transformations have been observed in the last stage of solidification of the investigated alloys. The alloys with magnesium revealed eutectics and at higher cooling rates a peritectics, while in the alloy with copper two non-equilibrium eutectics have been found. The contribution of the ternary one decreased with the increasing rate of cooling.

3. The distinctive influence of magnesium on the shift of eutectoidal transformation in the direction of lower temperatures has been observed in comparison with that of copper or silicon additions.

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Zusammenfassung — Mittels DTA wurde der Einfluß der Legierungselemente Magnesium, Kupfer und Silizium auf Phasenumwandlungen in Al-60m% Zn-Legierungen mit Erstarrungsgeschwindigkeiten zwischen 0,4 und 65 K/s untersucht.
Die dentritische Segregation von Zink in Mischkristallen macht sich durch Unterschiede des Verlaufes der jeweiligen Abschnitte der Abkühl- oder Aufheizkurven zwischen Solidus- und Liquidustemperaturen deutlich. Das Auftreten von Nicht-Gleichgewichts-Umwandlungen wurde als Peak im letzten Abschnitt der Kristallisierung aufgezeichnet.
Die Verschiebung von Liquidustemperaturen und Eutektika in Richtung niedriger Temperaturen wurde als Funktion der Kühlgeschwindigkeit beobachtet.
Die bei verschiedenen Kühlgeschwindigkeiten durchgeführte Thermoanalyse deckte das Auftreten von Nicht-Gleichgewichts-Umwandlungen bei höheren Geschwindigkeiten auf. Das Auftreten solcher Effekte wurde durch Anwendung von Röntgen-Mikroanalyse bekräftigt.