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INVESTIGATION OF EUTECTIC TRANSFORMATION OF Zn–Al ALLOY BY DTA

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Abstract

The paper discusses the investigation of crystallization of metals and alloys by differential thermal analysis (DTA). It was assumed that this method allows determination of the mechanism and kinetics of volumetric crystallization under *iso* conditions (e.g. anisothermal) on the basis of the parameters of the equation expressing an integral form of the DTA curve. From DTA, a course of eutectic transformation was determined for a technical Zn–Al alloy containing 4wt% Al. Investigations were carried out under continuous cooling at various rates and the kinetics parameters were determined with the KEKAM equation: $-\ln(1-x) = kt^n$

Keywords: alloy, DTA, eutectic transformation, Zn–Al alloy

Introduction

Information on the mechanism and kinetics of crystallization of foundry materials is necessary during the design of manufacturing processes if casts are to have a required structure. It was assumed that the necessary information could be obtained from differential thermal analysis (DTA). This has been applied for investigations on phase transitions in the solid state [1–5] for many years.

This paper presents the idea and results obtained with DTA. Kinetic parameters of volumetric crystallization of technical zinc alloy (Zn – 4 wt% Al) were investigated; the composition of the alloy was similar to that of the eutectic in the Zn–Al system [6].

Experiments and results

Specimens of the examined material were melted at 470°C in a furnace of the L/62/30/80 automatic thermal analyser made by LINSEIS. Next, they were cooled to ambient temperature at rates of 0.1, 1, 10 or 50 deg·min^{-1}. During cooling, thermal effects (DTA) occurring during crystallization were registered.

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On the basis of the DTA curves, transition order x was determined *vs.* time t (Fig. 1), the continuous cooling transformation (CCT) curve was obtained (Fig. 2) and crystallization parameters were determined.

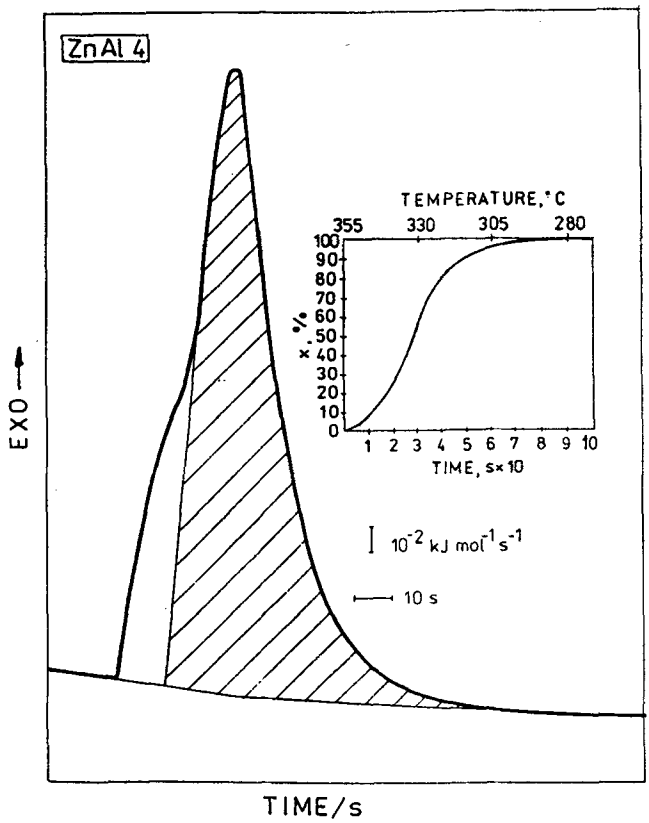

Fig. 1 Diagram DTA and $x=f(t)$ curve for Zn – 4 wt% Al alloy; cooling rate 50 deg·min^{-1}

For determination of the kinetic parameters, it was assumed that curves $x=f(t)$ resulting from DTA could be expressed by means of the KEKAM equation

$$x = 1 - \exp(-kt^n)$$

where $k=A\exp(-E/RT)$ is the transition rate constant and n is a parameter dependent on the transition mechanism [1]. For calculation of n, the KEKAM equation was transformed into its linear form:

$$\ln[-\ln(1-x)] = \ln k + n \ln t$$

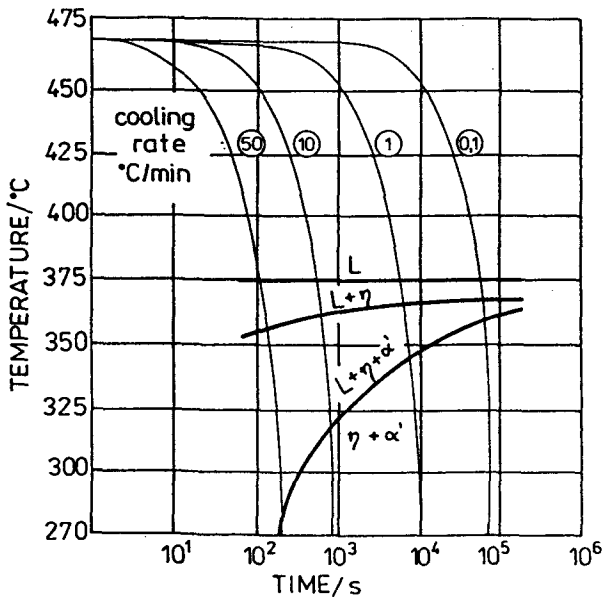

Fig. 2 Diagram CCT

Since k varies with temperature T, and crystallization time $t=\Delta T/v$, under non-isothermal conditions, we have:

$$\ln[-\ln(1-x)] + E/RT = n\ln(\Delta T/v) + \ln A$$

Next, it was assumed that, for a given cooling rate, E/R=constant and n was calculated as a coefficient of simple regression of the least squares in the coordinate system $\{\ln[-\ln(1-x)]\}$—$\{\ln(\Delta T/v)\}$ (Fig. 3). Then, k was determined from $k = -\ln(1-x)/(\Delta T/v)^n$ and the crystallization rate was calculated on the basis of the differential form:

$$\frac{dx}{dt} = nk\left(\frac{\Delta T}{v}\right)^{n-1}(1-x)$$

Conditions for which the transition rate dx/dt was the largest are shown in the Table 1, which also contains the parameters of the KEKAM equation and values of correlation factors r for straight lines from Fig. 3.

Discussion and conclusions

The experiments revealed that solidification of the Zn – 4 wt% Al alloy starts at constant temperature, independently of the cooling rate applied

Table 1 Parameters of the KEKAM equation and values of correlation factor

v / deg·min^{-1}	dx/dt / s^{-1}	T / °C	t / s	x / %	k / s^{-1}	n –	r –
1	11.442	361	330	22.8	0.047	1.89	0.928
10	79.119	340	120	46.9	0.008	2.83	0.989
50	258.943	330	30	54.3	5.337	2.15	0.993

(Fig. 2). The temperature range in which the solidified alloy consists of a mixture of liquid and products of its decomposition increases as the cooling rate increases. This is connected with distinct overcooling of the eutectic transition, especially in its final stage. Kinetic parameters of the eutectic transition of the Zn – 4 wt% Al alloy were determined via the KEKAM equation. It can be said that this equation gives good agreement between the experimental data and the results of calculations, especially for cooling rates of 10 and 50 deg·min^{-1}. This is testified to by the factors of correlation r between the variables in the equations in Fig. 3.

The KEKAM equation was derived on assumptions concerning nucleation. Thus, it can be supposed that for cooling rates of 10 and 50 deg·min^{-1} the total rate of eutectic crystallization was influenced by nucleation. It should be assumed that another mechanism of crystallization predominated during cooling at rates of 0.1 and 1 deg·min^{-1}. Thus, the kinetic parameters shown in the Table 1 seem to be unreliable for these rates. This also explains why it was not

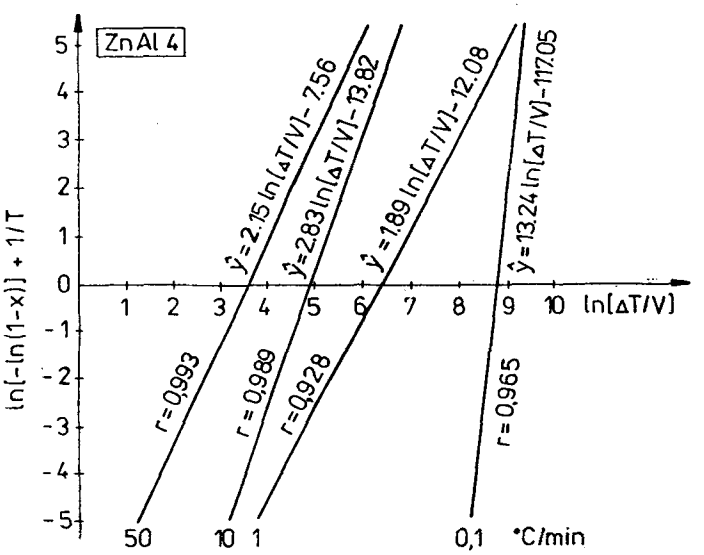

Fig. 3 $x=f(t)$ curves in coordinate system $\{\ln[-\ln(1-x)] + 1/T\}$—$\{\ln(\Delta T/v)\}$

possible to calculate (with the KEKAM equation) a value of dx/dt for crystallization of the alloy cooled at a rate of 0.1 deg·min^{-1}. Assuming that parameter n in the KEKAM equation gives information on the geometry of nucleus growth [1], we can say that during cooling at a rate of 50 deg·min^{-1} the crystallization proceeds mainly by two-dimensional growth ($n=2$). This is indicated by the structure shown in Fig. 4.

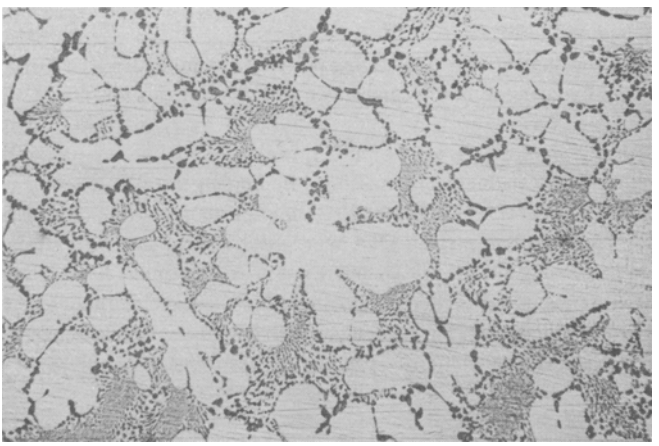

Fig. 4 Structure of Zn – 4 wt% Al alloy cooling at a rate 50 deg·min^{-1}

A similar structure was obtained after cooling at a rate of 10 deg·min^{-1} [7], although in this case n is near 3 (see Table). The difference in the values of n is probably caused by the fact that during cooling at a rate of 10 deg·min^{-1} the crystallization rate was sufficiently low and overcooling before the liquid-solid limit allowed repeated nucleation [8]. Thus, the parameter $n=\beta+\lambda$ depends not only on the geometry of nucleus growth λ, but on β as well. β is usually equal to 1 or 0 [1]. This last case corresponds to immediate nucleation, which could take place during cooling at 50 deg·min^{-1}. $\beta=1$ corresponds to nucleation in many stages, which was possible during cooling at a rate of 10 deg·min^{-1}.

All these questions can be answered after additional investigations. However, at present any conclusions concerning the mechanisms of the considered process on the basis of kinetic parameters should be formulated very carefully. These parameters provide information on the general course of many complicated phenomena occurring during crystallization.

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Zusammenfassung — Man hat eine Auffassung der Untersuchung des Kristallisationsverfahrens von Metallen, Metallegierungen und Legierungen mittells der thermischen Differenzanalyse – DTA dargestellt.
Es wurde angenommen, daß dieses Verfahren den Mechanismus und die Kinetik der Volumenkristallisation unter iso- als auch anisothermishcen Bedingungen in Anlehnung an die Parameter der Gleichung bestimmen läßt, welche die vollständige Form der DTA – Kurve beschreibt.
Auf Grundlage der Untersuchungen von DTA wurde der Ablauf von eutektischer Umwandlung in der technischen Legierung Zn–Al mit Gehalt von 4% Al bestimmt. Die Untersuchungen wurden in Bedingungen der ununterbrochenen Abkühlung mit unterschiedliches Geschwindigkeiten durchgeführt. Mán hat kinetischen Parameter vom Verfahren der eutektischen Kristallisation in Anlehnung an die KEKAM-Gleichung $-\ln(1-x) = kt^n$ bestimmt.