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NUMERICAL METHOD OF NON-ISOTHERMAL CURVE ANALYSIS BY MEANS OF ELECTRICAL RESISTANCE MEASUREMENT DURING COOLING

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The temperature-dependence of the electrical resistance of Al-Zn 78 wt.% was measured during linear cooling of the samples in the range of eutectoidal decomposition. The resulting resistance *vs.* temperature curves were analysed by:

– deriving the temperature-dependence of the volume fraction $x(T)$ of the η precipitate;

– fitting the theoretical function $x(T) = x_H(T)+x_C(T)$ following from numerical integration of the reaction rate equations for the simultaneously occurring homogeneous (H) and cellular (C) precipitation processes.

As a result, the activation energies E_H and E_C, the JMA exponents n_H and n_C, the rate constants k_H and k_C, and the critical temperatures T_o of the two processes were estimated.

Standard methods of non-isothermal data analysis (Kissinger [1], Ozawa [2], Augis-Bennett [3]) are useful only when relatively simple processes are treated. The analysis of more complex phenomena, such as alloy decomposition, requires more accurate procedures. In this paper, an original method of analysis of cellular decomposition in the Al-Zn system is presented.

Experimental procedure

Samples of the eutectoidal composition Al-Zn 78 wt.% were chosen. The temperature-dependence of the electrical resistance of samples previously homogenized for 48 h at 630 K was recorded by means of the four-probe method. The experiments were performed in a He atmosphere, with cooling rates ranging from 0.1 deg/min to 5 deg/min. All experiments were controlled by an "on-line" computer. The resistance *vs.* temperature curves are shown in Fig. 1.

Analysis of experimental data

From the experimental $R(T)$ curves, the temperature-dependences of the volume fractions of precipitates were derived by means of the following procedure:

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– the linear temperature-dependence of the resistance of both the homogeneous and the fully decomposed alloy was assumed (straight lines $R_1(T)$ and $R_2(T)$ in Fig. 1);

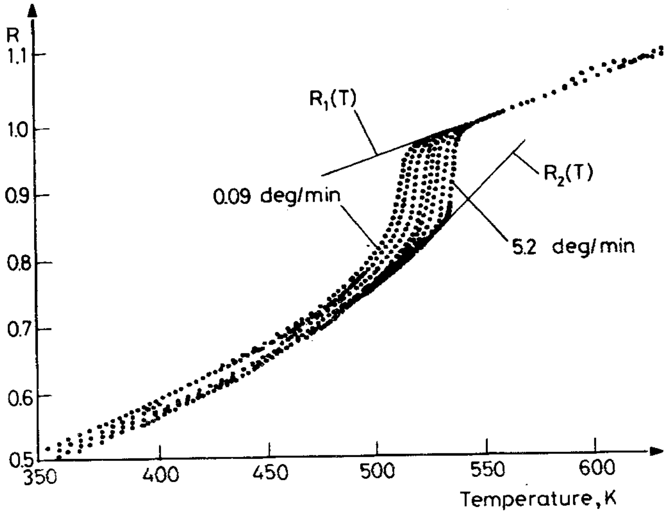

Fig.1 Temperature dependences of the resistance of Al-Zn 78 measured at various cooling rates in the marked range (particular values of cooling rates are presented in Table 1). Straight lines represent the temperature dependences of homogenous and fully decomposed alloy.

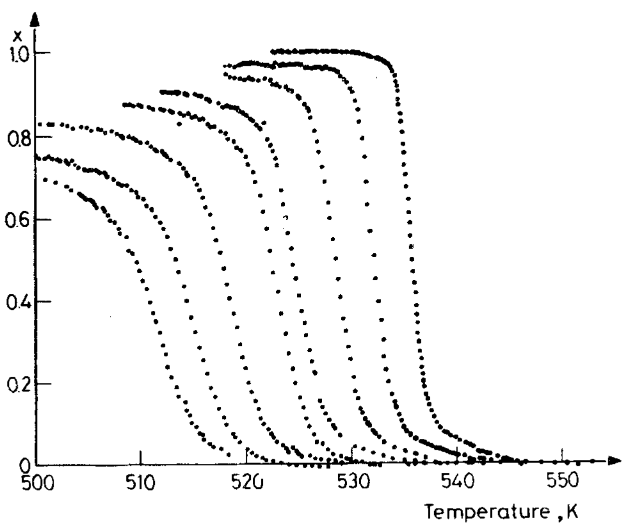

Fig. 2 Calculated temperature dependences of the volume fraction X of η precipitates in Al-Zn 78 at various cooling rates.

– a linear relation was assumed between the change in the alloy resistance and the volume fraction X, and the latter quantity was calculated by means of the following formula:

$$X(T) = (R(T) - R_1(T)/(R_2(T) - R_1(T)) \tag{1}$$

The resulting $X(T)$ curves are presented in Fig. 2.

The supercooled eutectoidal Al-Zn alloy is known to decompose by a cellular mechanism [4, 5]; at temperatures close to the critical one, homogeneous precipitation occurs as well, but the products of homogeneous precipitation are dissolved by the growing lamellae.

Let us denote: P = parent phase, H = products of homogeneous precipitation, C = products of eutectoidal decomposition.

The decomposition scheme can be written as follows:

$$\begin{tikzcd} \mathrm{P} \arrow[rr] \arrow[dr] & & \mathrm{C} \\ & \mathrm{H} \arrow[ur] & \end{tikzcd}$$

The rate equations are derived on the basis of the following assumptions:

– the kinetics of all three processes can be described by the Johnson-Mehl-Avrami (JMA) equation, modified by taking into account the dependence of the growth rate on the degree of supercooling. According to Christian [6], the JMA equation is applicable to eutectoidal reactions.

– Processes P → C and H → C are characterized by the same values of the respective parameters. Therefore, we have

$$\frac{\mathrm{d}x_H}{\mathrm{d}t} = n_H k_H (1 - x_H - x_c)\,[-\ln(1 - x_H - x_c)]^{\frac{n_H - 1}{n_H}} * \\ * \exp\left(-\frac{E_H}{RT}\right) g_H(\Delta T) - \frac{x_H}{1 - x_c}\,\frac{\mathrm{d}x_c}{\mathrm{d}t} \tag{2}$$

$$\frac{\mathrm{d}x_c}{\mathrm{d}t} = n_c k_c\,(1 - x_H - x_c)\,[-\ln(1 - x_c)]^{\frac{n_c - 1}{n_c}} * \\ * \exp\left(-\frac{E_c}{RT}\right) g_c(\Delta T) \tag{3}$$

where

x_H and x_C = volume fractions,
T = temperature,
T_0 = critical temperature (eutectoidal point),
$\Delta_T = T_0 - T$ = supercooling,
n_H and n_C = JMA exponents,
E_H and E_C = activation energies,
k_H and k_C = rate constants,
g_H and g_C = functions representing the supercooling dependence of the rate, and
R = gas constant

The first component in (1) represents the effect of the x_H increment following from the $P \to H$ reaction, while the second component represents the effect of the $H \to C$ reaction. The increase of C follows from both the $P \to C$ and the $H \to C$ processes, but only the fraction of X_C change equal to $X_H/(1-X_C)$ results from the $H \to C$ reaction.

According to the theoretical considerations [7] as well as to the experimental examinations of Al-Zn [5], for the eutectoidal decomposition $g \sim (T)^3$ and for homogeneous precipitation $g \sim \Delta T$ [6]. The latter relation was checked by numerical fitting of $g = (\Delta T)^\nu$, where ν was the free parameter.

Numerical integration of the equations under the conditon of linear temperature decrease gives the parametric relation:

$$X = X_C + X_H = X(T, < T_o, E_H, E_c, n_H, n_c, k_H, k_c >) \tag{4}$$

Table 1 Parameters T_o, n_c, E_c, n_H, E_H, of the decomposition of eutectoidal Al-Zn 78 estimated from the experimental data obtained at cooling rates V

V, K/min	T_o, K	n_C	E_C, 10 kJ/mol	n_H	E_H, 10 kJ/mol
0.09	548.9	4.37	8.39	1.89	19.6
0.22	549.0	3.87	6.74	1.65	11.01
0.44	549.0	3.85	6.73	1.67	10.36
0.88	549.2	3.92	5.39	1.54	7.0
1.30	548.6	3.89	7.90	–	–
2.09	549.1	4.34	7.54	–	–
3.76	549.0	4.42	6.28	–	–
5.20	550.2	4.31	6.30	–	–

The above function was fitted to the experimental data, which resulted in an estimation of the parameters. In Fig. 3, the selected fits are shown. The estimated values of the parameters are presented in Table 1.

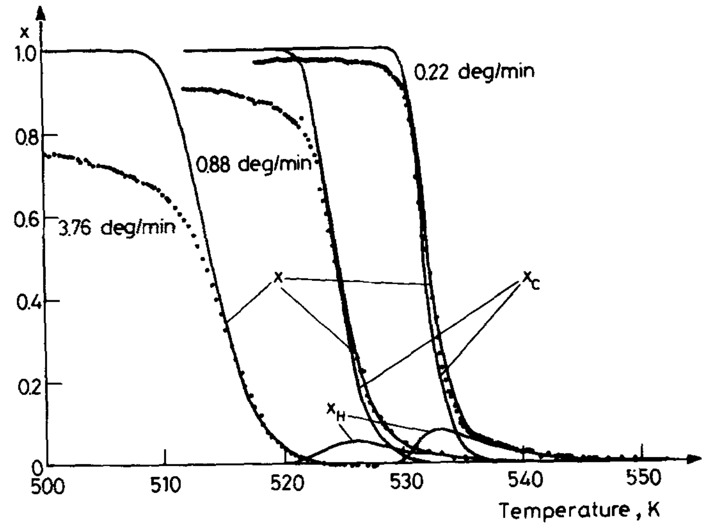

Fig. 3 Selected fits of $x_H(T)$, $x_c(T)$ and $x(T) = x_H(T) + x_c(T)$.

Discussion

1) Satisfactory fits were obtained for all cooling rates in the range $X < 0.5$. The disagreement between model and experiment in the range of higher values of X was due to the limitations of the validity of the JMA equation, which described only the early stages of decomposition, where no interaction between the precipitates took place.
2) The quality of the fits confirmed the assumed mechanisms of the processes (supercooling dependences of reaction rates and values of JMA exponents).
3) The homogeneous precipitation influenced only experiments performed with lower cooling rates $v < 1$ deg/min.
4) The values of T_0 resulting from all fits agreed perfectly with the value of the eutectoidal point [8].
5) The values of the JMA exponents n were in agreement with the model ones predicted for such processes [6].

6) The estimated values of the activation energies of the processes $P \rightarrow C$ and $H \rightarrow C$ were close to those of grain boundary diffusion which controlled these processes [5].
7) The estimated value of the activation energy of the homogeneous precipitation $P \rightarrow H$ was close to that of volume diffusion [9].
8) It should be stressed that with the described method it is possible to estimate the values of all parameters of the examined process by analysing a single $R(T)$ curve.

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Zusammenfassung — Die Temperaturabhängigkeit des elektrischen Widerstandes von Al-78 Masse-% Zn wurde bei linearer Abkühlung im Temperaturbereich des eutektoidischen Zerfalls gemessen. Die erhaltenen Widerstand-Temperatur-Kurven wurden untersucht durch
– Berechnung der Temperaturabhängigkeit des Volumentanteils $x(T)$ der ausgeschiedene n-Phase
– Anpassen der theoretischen Funktion $x(T) = x_H(T) + x_C(T)$, die durch numerische Integration der Reaktionsgeschwindigkeitsgleichungen für die gleichzeitig ablaufende homogene (H) und zellulare Ausscheidung (C) erhalten wurden.
Im Ergebnis werden die Aktivierungsenergien E_H, E_C, die Johnson-Mehl-Avrami-Exponenten n_H, n_C, die Geschwindigkeitskonstanten k_H, k_C, und die kritischen Temperaturen T_o beider Prozesse abgeschätzt.

РЕЗЮМЕ — Измерена температурная зависимость электрического сопротивления образцов Al–Zn (78 вес.%) при линейном температурном охлаждении их в области эвтектического разложения. Полученные кривые анализировались путем дифференцирования температурной зависимости объемной фракции $x(T)$ осадка и подгонкой теоретической функции $x(T) = x_H(T) + x_c(T)$, получаемой числовым интегрированнем уравнений скоростей реакции для одновременно протекающих гомогенных (H) и пористых (C) процессах осаждения. Благодаря этому для обоих процессов были установлены энергии активации E_H, E_C, экспоненциальные множители n_H, n_C, константы скорости κ_H, κ_C и критическая температура T_0.