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Kinetic aspects of the solidification of aluminium–zinc alloys

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A method for determination of the kinetics of linear and volumetric dendritic growth on the basis of a model of dendritic solidification process referred to one mole of alloy has been presented. The model parameters have been derived using Krupkowski's equation of dendritic solidification for the case of Al–40 wt % Zn alloy solidified at a definite rate. The constructed kinetics curves have been analysed using the Johnson–Mehl relation and compared with that of Chalmers. The results of calculation concerning the maximum microsegregation have made it possible to define the linear and volumetric dendritic growth rates. The relationships between these rates and the experimental cooling rate of ingot have been discussed.

1. Introduction

The kinetics of the solidification process of metals and alloys has already been studied fairly closely with regards to the solidification of an ingot on a macroscopic scale [1–3], whereas the problems of the role played by microsegregation and the rate of dendritic growth still present many difficulties and call for further studies. The theoretical principles and experimental investigations carried out in this field are described by Kattamis and co-workers [4–6], but only from the aspect of the kinetics of linear dendritic growth. The objective of the present work is to study the kinetics of the solidification process on the basis of the general theory of dendritic segregation presented by Scheil [7], Pfann [8], Brody and Flemings [9] and Krupkowski [10, 11].

According to the theory of microsegregation, the equalization of the partial chemical potentials of the given component in a liquid and in a solid brings about the formation of solid solution dendrites of varying composition and the occurrence of non-equilibrium phases. The solidification rate which is accompanied by complete diffusion in the liquid and no diffusion in the solid is assumed to be the optimum rate for the occurrence of maximum microsegregation. The parameters characteristic of the course and effect of dendritic solidification in Al–Zn alloys in these conditions were analysed by Dukiet-Zawadzka [12] and Ciach *et al.* [13]. It should be mentioned that the effects of segregation observed under casting conditions deviate from the results of model calculations. A 10% difference was observed in the case of an Al–40 wt % Zn cast alloy [12]. This difference results from the assumed theoretical conditions of the dendritic model of solidification and can also be ascribed to the nucleation process of successive dendrites, which can be initiated by fluctuations in the concentration of definite atoms in the liquid. Both these causes decrease the degree of microsegregation of cast alloys in comparison with the model.

The present paper proposes a method for analysing the kinetics of the formation and course of dendritic segregation on the basis of Krupkowski's equations for dendritic solidification [11]. The segregation parameters calculated for Al–40 wt % Zn alloy by Krupkowski *et al.* [14] are applied in this method. In this study, the speed of volumetric changes during the solidification of Al–40 wt % Zn alloy, at various rates of heat extraction, has been determined by the method based on the spherical solidification model [10, 13]. The influence of the cooling rate on the numerical relations between the linear dendritic growth and the volumetric one has been pointed out.

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2. Model of dendritic growth

2.1. Quantitative approach to dendritic segregation according to Krupkowski

As has already been mentioned, this conception refers to the optimum cooling rate during solidification, when the assumed conditions of diffusion in the solid and liquid cause a maximum dendritic segregation.

The solidification equation derived for one mole of solidifying aluminium–zinc alloy is

$$K = \frac{N^{x}_{(\mathrm{Zn})}}{N^{x}_{\mathrm{Zn}}} = \frac{\mathrm{d}n^{x}_{(\mathrm{Zn})}(1-x)}{\mathrm{d}x\,n^{x}_{\mathrm{Zn}}} \qquad (1)$$

where K is the distribution coefficient, $N^{x}_{(\mathrm{Zn})}$ is the mole fraction of zinc in the solid formed on the dendrite surface at a given stage of solidification, N^{x}_{Zn} is the mole fraction of zinc in the liquid at a given stage of solidification, x is the amount of dendrite constituent in one mole of alloy at a given stage of solidification, $n^{x}_{(\mathrm{Zn})}$ is the amount of zinc in the solidified dendrite at a given stage of solidification, and n^{x}_{Zn} is the amount of zinc in the liquid at a given stage of solidification in one mole of alloy.

The final form of the general solidification equation, obtained by certain transformation and substitutions [11], is

$$-\mathrm{d}\ln(1-x) = \frac{1}{1-K}(\mathrm{d}\ln N^{x}_{\mathrm{Zn}}). \qquad (2)$$

In order to solve this equation the following function must be defined:

$$\frac{1}{1-K} = f(-\ln N^{x}_{\mathrm{Zn}}) \qquad (3)$$

The foregoing function describes the changes in the distribution coefficient that are dependent on the composition of the liquid at successive stages of solidification. For Al–Zn alloys it has the particular form:

$$\frac{1}{1-K} = 1.254 - 0.1012\ln N^{x}_{\mathrm{Zn}} - \frac{0.383}{\ln N^{x}_{\mathrm{Zn}}} \qquad (4)$$

By putting Equation 4 in Equation 2 and integrating both sides, the equation of Al–Zn alloy solidification is obtained for assumed conditions in which the maximum dendritic segregation arises:

$$\ln(1-x) = -1.254\ln N^{x}_{\mathrm{Zn}} + 0.0506(\ln N^{x}_{\mathrm{Zn}})^2 + 0.383\ln(-\ln N^{x}_{\mathrm{Zn}}) + C \qquad (5)$$

The integration constant C has been obtained from the initial conditions of the solidification process, i.e. when $N^{x}_{\mathrm{Zn}} = N^{0}_{\mathrm{Zn}}$ and $x = 0$. Then

$$C = -1.254\ln N^{0}_{\mathrm{Zn}} + 0.0506(\ln N^{0}_{\mathrm{Zn}})^2 + 0.383\ln(-\ln N^{0}_{\mathrm{Zn}}) \qquad (6)$$

where N^{0}_{Zn} is a mole fraction of zinc in the initial liquid, equivalent to the composition of the homogeneous alloy examined. This equation was used to determine, in an earlier study [14], the following parameters, S, of Al–40 wt % Zn alloy (Table I). In this work the optimum cooling rate was found to be 50° C sec^{-1} for the Al–40 wt % Zn alloy. In the present work the following suboptimum rates of cooling will be analysed: $V_1 = 75$ K sec^{-1}, $V_2 = 55$ K sec^{-1} and $V_3 = 45$ K sec^{-1} (Fig. 1). The calculated parameters of maximum segregation can therefore be utilized in this case as well. The changes in some of the parameters with the progress of solidification of one mole of Al–40 wt % Zn alloy are presented in Fig. 2.

3. The kinetics of dendritic growth

3.1. A description of the method for determining kinetics curves

The kinetics curve that represents the arising of dendritic segregation during the solidification of one mole of alloy has been constructed on the

TABLE I

Temperature (° C)	Microsegregation parameters S				Solidification times t (sec) for cooling rates V (K sec^{-1})		
	N^{x}_{Zn}	$N^{x}_{(\mathrm{Zn})}$	x	R^{x*}	$V_1 = 75$	$V_2 = 55$	$V_3 = 45$
590	0.216	0.089	0	0	1.7	2.6	3.0
575	0.25	0.1025	0.2199	0.370	2.1	3.0	3.5
525	0.45	0.1822	0.7141	0.564	2.5	3.6	4.2
470	0.65	0.3445	0.8557	0.628	3.3	4.5	5.6
435	0.75	0.4725	0.8952	0.650	4.2	6.0	7.4
382	0.887	0.6652	0.9375	0.680	5.8	7.3	10.0

*R^{x} is the radius of spherical dendrite cell.

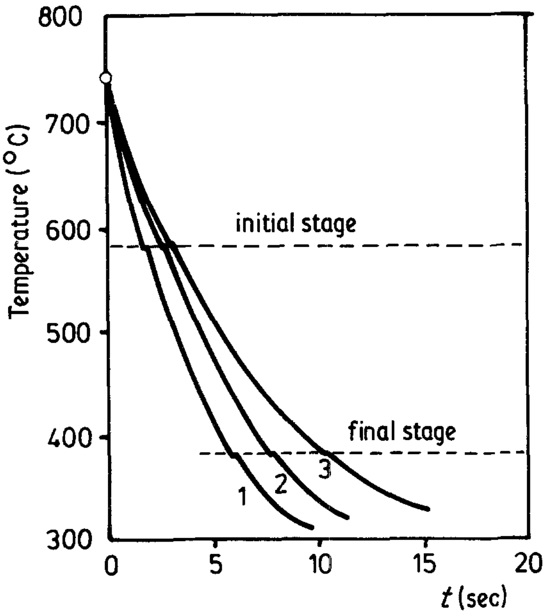


Figure 1 Cooling curves of Al–40 wt % Zn alloy solidified at different rates: curve 1, 75 K sec^{-1}; curve 2, 55 K sec^{-1}; curve 3, 45 K sec^{-1}.

basis of the changes of a mole fraction of zinc in the outer layer of the dendrite at a definite stage of solidification of a spherical model dendrite.

The solidification stages corresponding to a given time have been obtained from the cooling curve (Fig. 1). The definite alloy composition read on the liquidus and solidus lines, N^x_{Zn} and $N^x_{(\text{Zn})}$, respectively, corresponds to an alloy temperature at the given stage of solidification. The knowledge of these values permits the construction of the curve of the function $N_{(\text{Zn})} = f(t)$ and the curves of all the above mentioned segregation parameters which are functions of the alloy composition. The kinetics curves representing the occurrence of dendritic segregation in an Al–40 wt % Zn alloy cooled at three different rates, from 45 to 75 K sec^{-1}, have been constructed (Fig. 2).

For the construction of the kinetics curves representing the changes of the zinc concentration in the dendrite at definite times of solidification the coefficient ξ has been used (Fig. 3). ξ was obtained from the Equation

$$\xi = \frac{N^t_{(\text{Zn})} - N^0_{(\text{Zn})}}{N^f_{(\text{Zn})} - N^0_{(\text{Zn})}} \tag{7}$$

where $N^t_{(\text{Zn})}$ is the mole fraction of zinc in outer layer of dendrite after time t, $N^f_{(\text{Zn})}$ is the mole fraction of zinc in final layer of solid solution dendrite, and $N^0_{(\text{Zn})}$ is the mole fraction of zinc in dendrite at the beginning of solidification. The further analysis of the kinetics will be based on the curves described above.

3.2. Quantitative analysis of the kinetics of the dendritic segregation process

The Johnson–Mehl equation [15] is applied in the analysis of the kinetics of the process under discussion. The use of this equation is justified by the ascertainment that the kinetics curve, defined

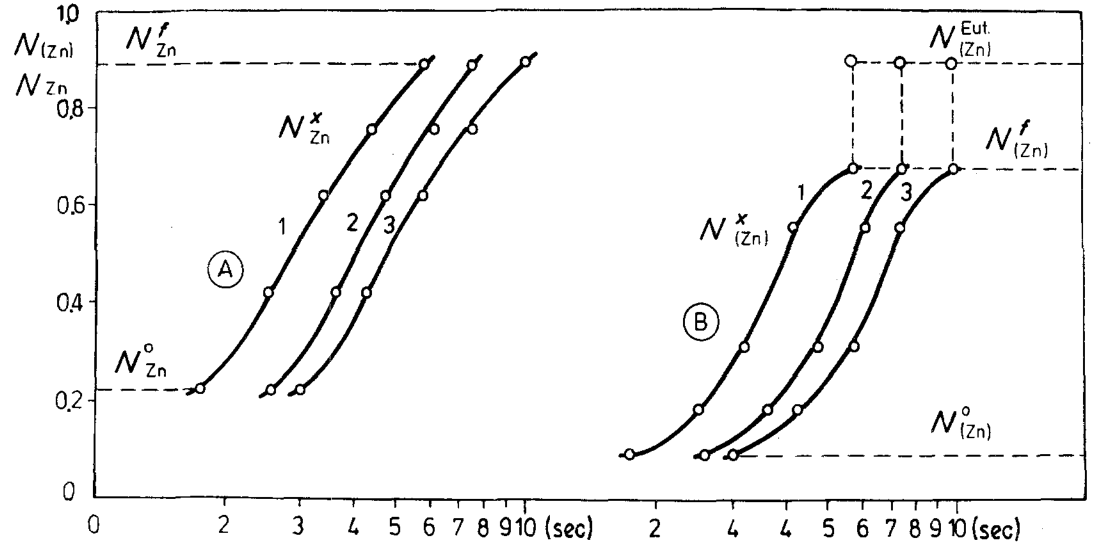


Figure 2 Changes in the zinc concentration during solidification of Al–40 wt % Zn alloy, cooled at the following rates: curve 1, 75 K sec^{-1}; curve 2, 55 K sec^{-1}; curve 3, 45 K sec^{-1}. (A) mole fraction of zinc in liquid (N^x_{Zn}); (B) mole fraction of zinc in a dendrite $N^x_{(\text{Zn})}$.

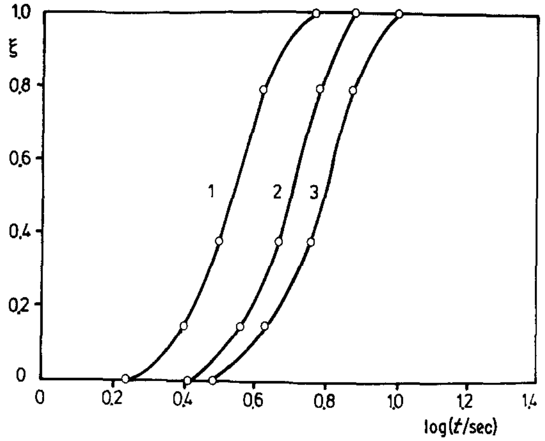


Figure 3 Kinetics curves of solidification of Al–40 wt% Zn alloy.

by $\xi = f(\log t)$ (Fig. 3), illustrates the changes in the mole fraction of zinc in the outer α solid solution dendrite layer formed in the process of the liquid–solid alloy transformation. The obtained kinetics curves, therefore, are defined by the following formula

$$v = \frac{d\xi}{dt} = nkt^{n-1}(1-\xi) \qquad (8)$$

where the coefficients k and n are constant and independent of time in the definite interval in which only one solidification mechanism occurs. By integrating this equation the relationship

$$-\ln(1-\xi) = kt^n \qquad (9)$$

or

$$\log[-\log(1-\xi)] = \log k - 0.362 + n \log t \qquad (10)$$

is obtained.

The kinetics of the liquid–solid transformation governed by one mechanism (e.g. the process of dendritic growth in the liquid in the course of solidification) can be described by only one section of the line in the system of coordinates $\log[-\log(1-\xi)]$ and $\log t$. The other mechanism occurring in the process of solidification, i.e. the formation of solidification nuclei should be represented by another section of the line. The coefficient n is the tangent of the inclination angle of these sections to the axis of abscissae. This method of analysis is shown in Fig. 4. It has been found that there are two ranges of changes in the rate of the dendritic solidification. The first range, up to the 30% advancement of the solidification process, is characterized by the coefficient $n = 7.0$ and may be identified with the continuous appearance of new nuclei of solidification. The second range or that of expansion of the already formed dendrites is indicated by the coefficient $n = 3.5$. The process of nucleation of new dendrites is a separate problem. In this paper we deal only with the period of growth of the existing nuclei and determine the velocity of changes in the zinc concentration in the outer layer of the dendrite at a given stage of solidification of one mole of the alloy. Hence this velocity is referred to as the volumetric one in contradistinction to the rate of linear growth of the spherical dendrite radius and to the rate of heat extraction or cooling.

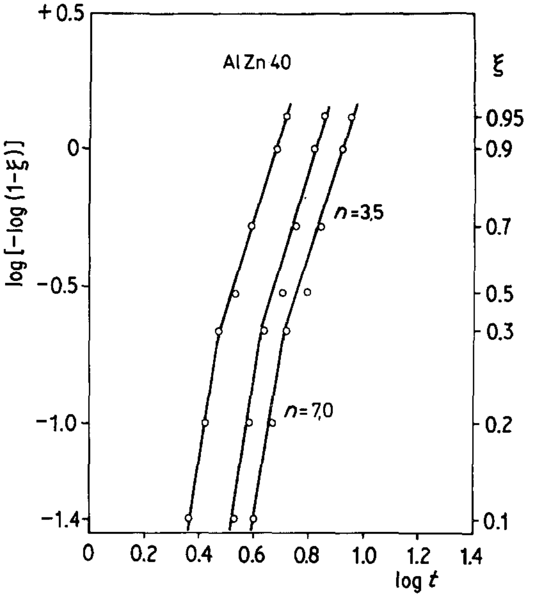


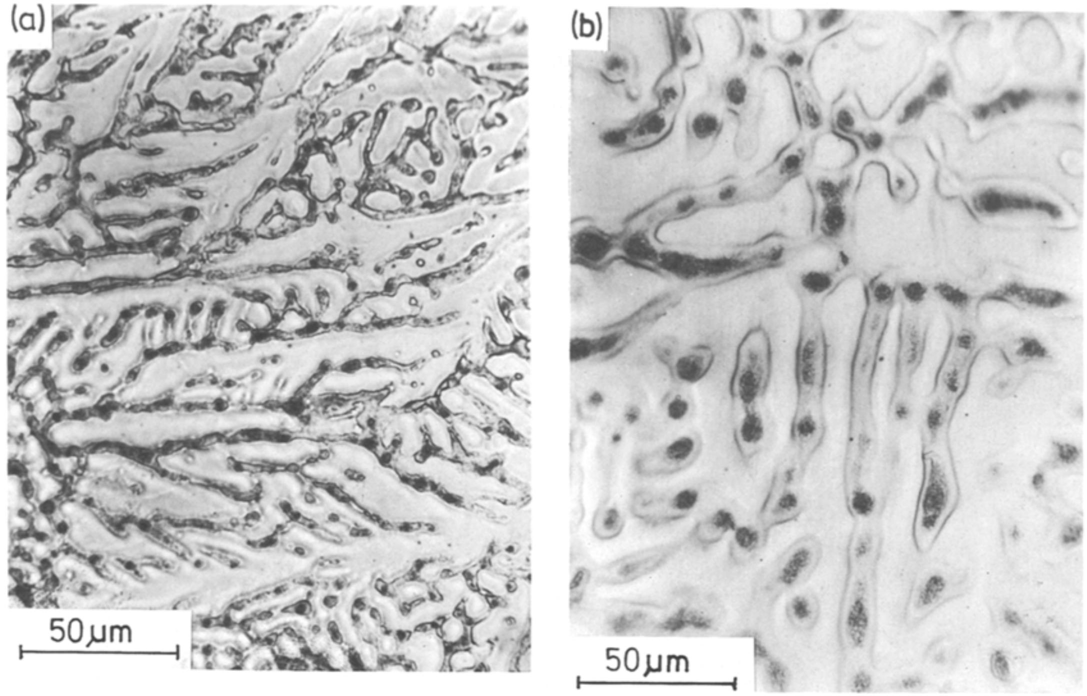
Figure 4 Analysis of the solidification kinetics of Al–40 wt% Zn alloy on the basis of Johnson–Mehl equation.

3.3. The kinetics of linear dendritic growth

The first type of solidification rate determined in this study is the rate of the linear growth of the dendrite radius $V_R = dR/dt$. It was calculated on the basis of the relative radius R^x of the spherical model of dendritic cell (Table I). The values obtained were multiplied by the real radius D, measured from the structures of the Al–40 wt% Zn alloy solidifying at the three different rates.

$$R = R^x D. \qquad (11)$$

The dendritic structures of these alloys are shown in Fig. 5. The time t of the radius growth in the course of solidification was read from the proper cooling curves presented in Fig. 1. The changes of the calculated dendritic radius R with the time of solidification process t are presented in Fig. 6.



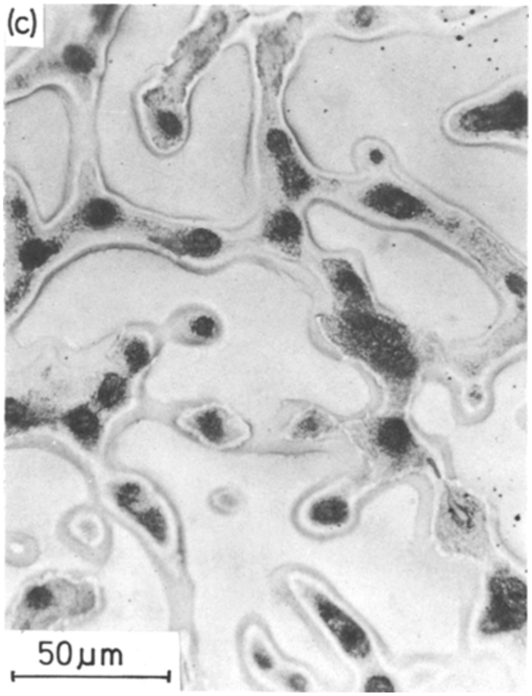


Figure 5 Dendritic microstructures of Al–40 wt % Zn alloy solidifying at rates: (a) 75 K sec^{-1}, (b) 55 K sec^{-1}, (c) 45 K sec^{-1}.

3.4. The kinetics of volumetric dendritic growth

The volumetric growth rate V_N was calculated by substituting the data given in Table I in the formula describing the volumetric changes resulting from the increase in the zinc concentration in the new phase, i.e. in the α solid solution dendrite. In the case under consideration

$$V_N = \frac{d\xi}{dt} = 3.5\,kt^{2.5}(1-\xi) \qquad (12)$$

since $n = 3.5$. The value of the constant k, according to Equation 9 has been read from the graph of $-\ln(1-\xi)$ against t^n.

The dependence of velocity changes in the solidification process on the time of cooling $V_N = d\xi/dt = f(t)$ can be seen in Fig. 7. The three curves in this graph correspond to the cooling rates considered. The initial increase followed by a decrease in the flux of diffusion of aluminium and zinc atoms, which is a function of the composition of the outer dendrite layer and liquid at a given time of solidification, is responsible for the occurrence of the maximum rate of solidification. The distance between the solidus and liquidus lines at a given temperature is decisive for this type of solidification kinetics. The highest value of the volumetric dendritic growth rate occurs at the highest rate of cooling $V_1 = 75$ K sec^{-1}, because it is then that the diffusion flux of atoms in liquid per unit time is the highest.

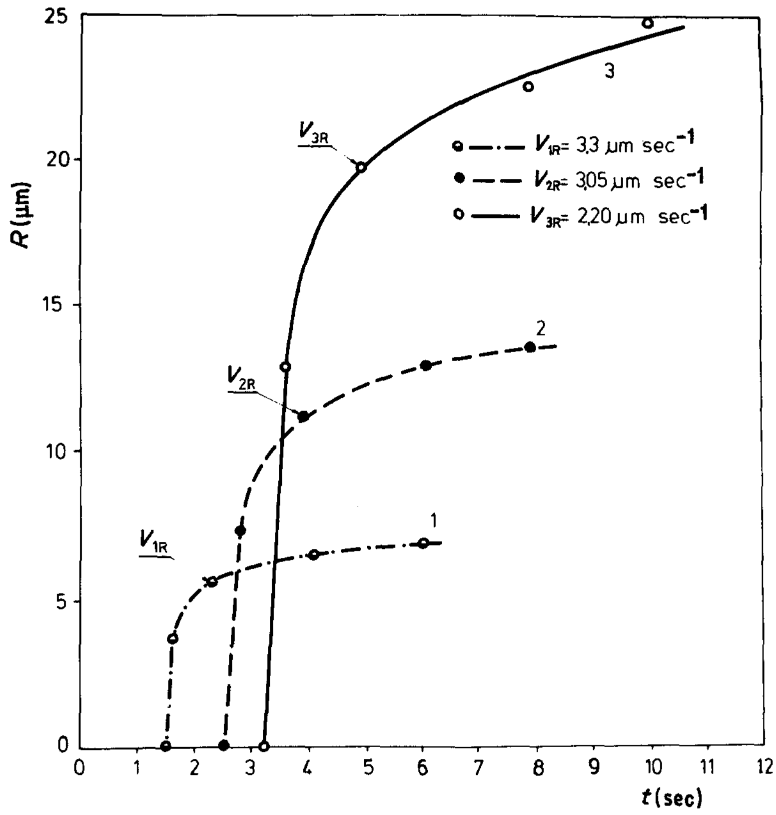


Figure 6 Dependence of dendrite radius R on time of solidification time of Al–40 wt% Zn alloy.

4. Discussion

The process of dendritic solidification is a diffusion process and so it depends on changes in the composition of the dendrite, diffusion path and speed of the process and, according to Chalmers [16], it can be expressed by the equation:

$$D\frac{\mathrm{d}^2c}{\mathrm{d}x^2}+R\frac{\mathrm{d}c}{\mathrm{d}x}=0 \qquad (13)$$

where x is the unit surface of phase boundary, D is the interdiffusion coefficient, c is the concentration, and R is the linear rate of migration of phase boundary. This expression much resembles the diffusion processes that control these two transformations are also similar. It consists, as in the discontinuous precipitation process, of two parts: diffusion at the phase boundary $D(\mathrm{d}^2c/\mathrm{d}x^2)$ and migration of the interface boundary $R(\mathrm{d}c/\mathrm{d}x)$. Therefore, the application of the Johnson–Mehl equation for the transformation liquid → solid seems to be well grounded.

The parameter ξ, being a function of the zinc concentration in the dendrite at a given solidification stage, has been used for the construction of the kinetics curves. The changes of ξ with time of freezing appropriately describe the kinetics of dendrite solidification and can be compared with those given by Chalmers [17]. It is to be noted that the shape of both curves are very similar as shown in Fig. 8.

According to Fisher's theory [18], the linear solidification rate is given by the following relationship:

$$V=\frac{H}{L\rho\pi r^2} \quad \text{or} \quad \frac{2K}{L\rho r}(T_1-T_2) \qquad (14)$$

where ρ is the density of the alloy, K is the heat conduction, H is the cooling rate, r is the radius of rounded tip of dendrite, and L is the latent melting heat.

Kattamis and co-workers [5, 6] distinguished two types of linear solidification rate, namely, the rate of changes in length of dendrite arms $\mathrm{d}l/\mathrm{d}t$ and rate of increase of dendrite radius $\mathrm{d}R/\mathrm{d}t$ given by the Equations

$$\frac{\mathrm{d}l}{\mathrm{d}t}=-\frac{2\sigma DT}{HC_L(1-K)m}\left(\frac{2}{a}-\frac{1}{R}\right)\frac{1}{a} \qquad (15)$$

$$\frac{\mathrm{d}R}{\mathrm{d}t}=\frac{\sigma DT}{HC_L(1-K)m}\left[\frac{2R-a}{R^2(R+L)}\right] \qquad (16)$$

where H is the heat of fusion, C_L is the liquid

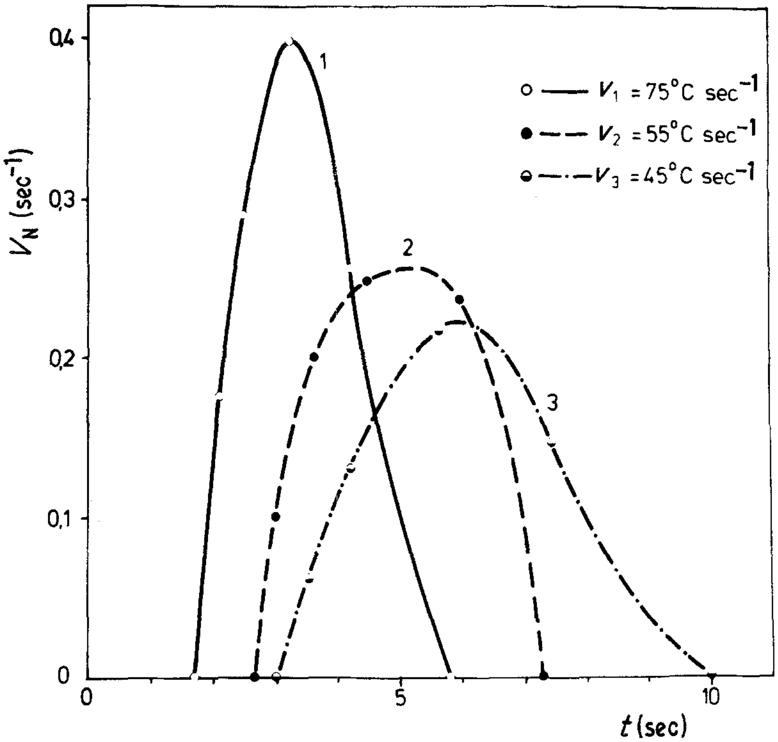


Figure 7 Changes of volumetric growth rate V_N against solidification time of Al–40 wt % Zn alloy freezing at: curve 1, 75 K sec^{-1}; curve 2, 55 K sec^{-1}; curve 3, 45 K sec^{-1}.

composition at T in equilibrium with phase interface, K is the equilibrium distribution coefficient, m is the slope of liquidus, D is the diffusion coefficient in liquid, σ is the solid–liquid interfacial energy, a and l are the radius and length of the small dendrite arm, respectively, and R and L are the radius and length of large dendrite arm, respectively. The above-mentioned authors also point out the fact that there is an utter agreement between the theoretical rate calculated from the foregoing relationships and the rate obtained experimentally.

Another important factor occurring in the solidification process is a rate of heat extraction

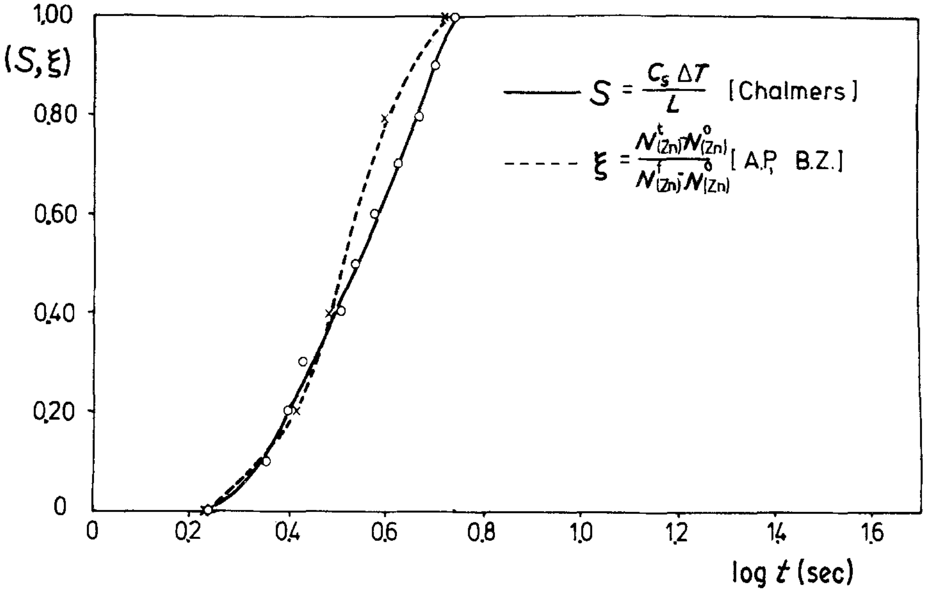


Figure 8 Kinetic curves of solidification given by Chalmers [17] and the authors. S is the fraction of solidified phase; T is the supercooling; L is the latent melting heat.

$\partial Q/\partial t$, which Chalmers [16] difines by means of formula

$$\frac{\partial Q}{\partial t} = -K\left[\frac{\partial \theta}{\partial x}\right]_{x=0}, \quad \text{whereas} \quad \frac{\partial \theta}{\partial t} = \frac{K}{\gamma C}\frac{\partial^2 \theta}{\partial x^2} \tag{17}$$

where Q is the heat of a volume unit at time t, θ is the temperature of a volume unit at time t, γ is the density, K is the thermal conductivity, and C is the specific heat.

In the present paper the cooling rate (heat extraction) V_C has been obtained experimentally from the curve $T = f(t)$, Fig. 1, constructed on the basis of measurements of temperature changes in the cooling ingot. This rate decreases in the course of the solidification process. The volumetric and linear solidification rates have been read from the kinetics curve.

The method for the determination of the rate of the linear dendritic growth presented in this paper refers only to the optimum cooling rate. However, after being verified experimentally, its range could be extended appropriately. The established relationships between the newly introduced concept of the rate of volumetric dendritic growth V_N and the linear rate V_R as well as the rate of heat extraction V_C make a simple and comprehensive analysis of the solidification kinetics possible. The logarithmic graph showing the relationships of these rates is given in Fig. 9. They are linear relationships occurring, however, only within the analysed range of cooling rates approaching the optimum rate of solidification. The numerical relationships between particular functions are

$$\log V_N = 2.20 \log V_R - 1.70 \tag{18}$$

$$\log V_R = 0.39 \log V_C - 0.11 \tag{19}$$

$$\log V_C = \log V_N + 2.20 \tag{20}$$

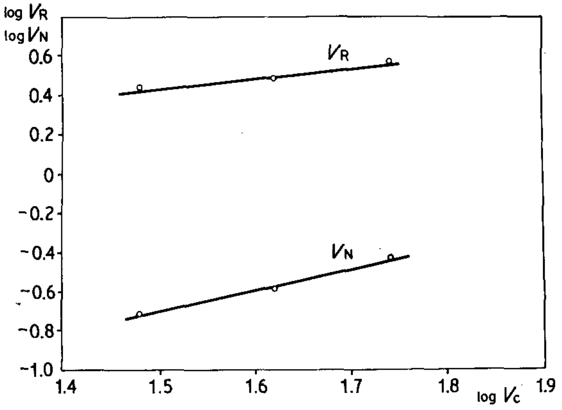


Figure 9 Plot of linear solidification growth rate V_R and volumetric growth rate V_N against the cooling rate V_C.

5. Conclusions

The following conclusions concerning the kinetics of the solidification of Al–40 wt % Zn alloy solidified with the cooling rates approximating those of the optimum conditions for the occurrence of maximum segregation have been drawn:

1. The Johnson–Mehl equation may be applied to the quantitative analysis of the solidification kinetics curve, because the process of solidification corresponds with the model process of the phase transformation in the solid consisting of diffusion at the phase boundary and the migration of the interface.

2. An analysis of the kinetics of solidification showed that the parameter

$$\xi = \frac{N^t_{(\mathrm{Zn})} - N^0_{(\mathrm{Zn})}}{N^f_{(\mathrm{Zn})} - N^0_{(\mathrm{Zn})}}$$

can be used as a measure of the process advance.

3. The kinetics of the solidification of Al–40 wt % Zn alloy can be described by the equation $V_N = 3.5\,kt^{2.5}(1-\xi)$ which expresses the dependence of volumetric growth rate of dendrite V_N on varying composition and time of freezing.

4. The linear rate of dendritic growth V_R decreases during solidification, whereas the volumetric rate shows a characteristic maximum. The maximum values of solidification rates V_N increase with increasing rate of cooling V_C.

5. At such a characteristic moment of the solidification process as the occurrence of the maximum volumetric growth rate V_N, quantitative relationships between the analysed types of solidification rates have been established.

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