Application of a Numerical Method for the Analysis of Metglas 2826 MB Crystallization Kinetics

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Crystallization kinetics of γ-FeNiMo solid solution in Metglas 2826 MB was studied by isothermal differential scanning calorimetry (DSC). The Johnson-Mehl-Avrami (JMA) equation was used to describe the crystallization process. In order to calculate the kinetic parameters, a new model of the numerical analysis of isothermally obtained DSC data was successfully applied. For the purposes of method evaluation, the classical analytical method of data analysis was also performed. The apparent activation energies obtained were (280 ± 22) kJ mol^{-1} and (296 ± 23) kJ mol^{-1} for the analytical and numerical methods, respectively. The Avrami exponents obtained by both methods lie between 1.75 and 1.95.

Key words: crystallization kinetics, differential scanning calorimetry, Johnson-Mehl-Avrami equation, Metglas 2826 MB, numerical model.

INTRODUCTION

One of the purposes of the solid-state crystallization kinetics studies is to obtain an insight into a reaction mechanism. First, the reaction model is postulated on the basis of the rate-determining step. The next goal is to determine the kinetic parameters, which is most often done by analytical

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methods.[1] The shortcoming of this procedure, if the isothermal DSC is employed as the experimental technique, lies in fact that the integral form of data should be calculated. Such a procedure, besides being time-consuming, involves inevitable calculation errors. Due to the increase of computation power, the numerical approach has been introduced and various numerical methods have been presented.[2–4] The essence of numerical methods is the comparison of the experimental curve with the simulated one, obtained using a theoretical function. After the mechanism is assumed and the proper function is chosen, the function is fitted to the experimental curve by parameter adjustment. In this manner, this conclusions regarding the original assumptions used in the calculation can be drawn.[1]

The Metglas 2826 MB alloy is a ferromagnetic, nickel-iron metallic glass. Appropriately annealed, it partially crystallizes developing optimal magnetic properties.[5] An understanding of the crystallization process is essential for its control. On the other hand, information on the thermal stability is important for the conditions of employment, since glass exposure to elevated temperatures leads to loss of some mechanical properties.[5] Metglass 2826 MB has drawn considerable interest in terms of understanding its thermal stability. Several studies[6–8] have indicated that the first phase to crystallize from the glass is γ-FeNiMo s.s. There are discrepancies between activation energies determined by various investigators, *e.g.* values between 270 and 403 kJ mol^{-1} have been reported.[6–9]

The aim of this study is to evaluate our recently proposed numerical model for the analysis of isothermally obtained DSC (DTA) data[10] and to re-examine the kinetics of the first crystallization process in Metglass 2826 MB, *i.e.* the crystallization of γ-FeNiMo s.s.

EXPERIMENTAL

Metglass 2826 MB, of a nominal composition in atomic percentage $Fe_{40}Ni_{38}Mo_4B_{18}$, is a product of Allied Corporation, USA. The analyses were carried out using samples cut from a ≈0.05 mm thick ribbon.

DSC Netzsch 404 was used to obtain the data for kinetic analyses. The scans were performed under a constant airflow of 30 cm^3 min^{-1}. Al pans were used; empty pan was used as a standard. Glasses were heated at a heating rate of 80 K min^{-1} to the temperatures between 683 and 703 K and then kept at the attained temperatures until the end of crystallization.

For kinetic analysis of the obtained data, the Johnson-Mehl-Avrami transformation kinetics equation[11] was used:

$$\alpha(t) = 1 - \exp[-k^n (t - \tau)^n] \tag{1}$$

where k is the reaction constant and it is related to the activation energy, E_a, through the Arrhenian temperature dependence. The Avrami exponent, n, refers to nucleation and growth mechanisms as described by Ranganathan and von Heimendahl,[9] and τ refers to the transient time $(t > \tau)$. By the analytical approach, the DSC data have to be transformed from differential to integral form. The rate constant and the Avrami exponent are then obtained from a plot of $\ln(-\ln(1-\alpha))$ $vs.$ $\ln(t-\tau)$.[13]

A numerical analysis was performed using the computer program recently developed by us.[10] To describe the shape of the DSC exotherm, the following function is proposed as the appropriate differential function of the Johnson-Mehl-Avrami equation:

$$f(t) = \Delta H \frac{d\alpha}{dt} = \Delta H n k^n (t - \tau)^{n-1} \exp[-k^n (t - \tau)^n] \qquad (2)$$

where ΔH is the total enthalpy difference between transformed and untransformed states. The data were fitted to Eq. (2) in such a manner that the originally obtained untransformed data were used. Subsequently, a plot of $\ln k$ $vs.$ $1/T$ was used to determine E_a.

RESULTS AND DISCUSSION

Isothermal DSC data obtained at different annealing temperatures, in the range from 683 to 703 K, are shown in Figure 1. From DSC curves, the
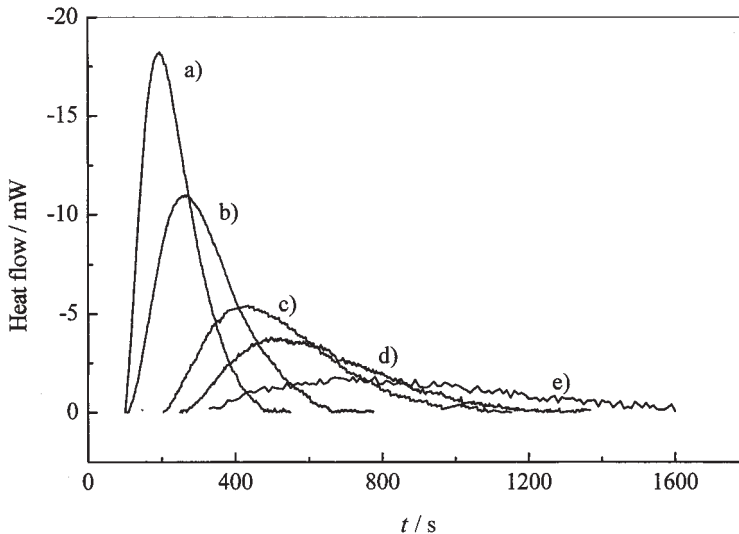

Figure 1. Isothermal DSC scans obtained at various annealing temperatures: a) 703 K, b) 698 K, c) 693 K, d) 688 K, e) 683 K.

volume fractions transformed as a function of time $\alpha(t)$ were calculated. Avrami plots (Figure 2) were used to obtain the rate constants and Avrami exponents; the parameters obtained are given in Table I.

The experimental scans were fitted to the proposed model[10] (Figure 3). As can be seen, a very good match was attained for each curve. The obtained kinetic parameters are given in Table I. The Avrami exponent values are consistent and close to those previously calculated from integrated data.
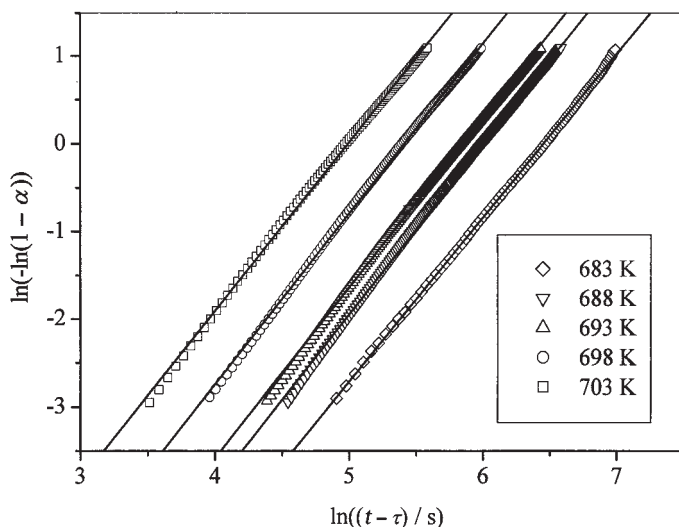

Figure 2. Avrami plots calculated from DSC scans obtained at various annealing temperatures.

TABLE I

Kinetic parameters for γ-FeNiMo s.s. crystallization

T / K	Calculated from Avrami plots			Obtained by fitting to the model[10]		
	$10^3\ k$ / s^{-1}	n	τ / s	$10^3\ k^{\,a}$ / s^{-1}	n	τ / s
683	1.58	1.87	305	1.55	1.76	324
688	2.47	1.94	265	2.63	1.86	288
693	2.89	1.94	210	3.13	1.78	232
698	4.48	1.95	118	4.74	1.79	128
703	6.79	1.92	101	7.36	1.75	111

[a] The error margins of k are smaller than $\pm(3 \times 10^{-5})$.

The Arrhenius plots for both constant rate sets (Figure 4) revealed linearity and enabled calculation of the activation energies. Plots were fitted by the linear least squares regression and the activation energies were derived
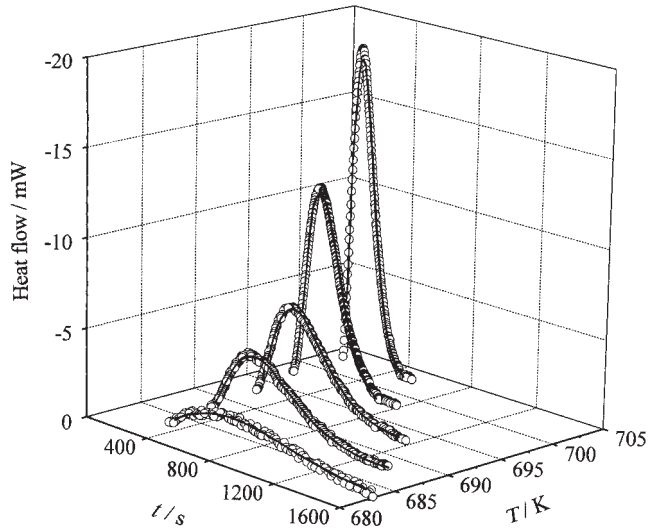

Figure 3. Isothermal DSC scans obtained at various annealing temperatures (ooo) and data fitted to the proposed model (---).
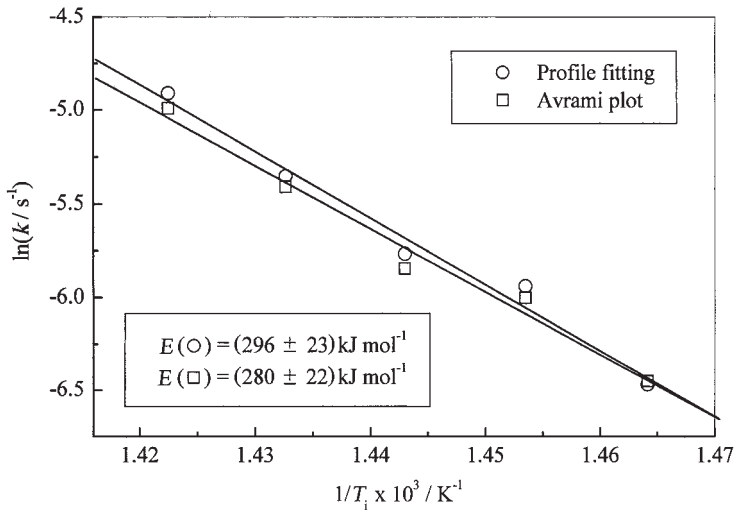

Figure 4. Arrhenius plots for the data obtained from the Avrami plots and by profile fitting.

from their slope. The calculated values were E_a = (280 ± 22) kJ mol^{-1} and E_a = (296 ± 23) kJ mol^{-1} for the rate sets obtained from integrated data and from scans fitting, respectively. Differences between the calculated values are within the calculation error span.

The obtained values are in good agreement with most of the results reported in literature. Antonione *et al.*[6] performed a non-isothermal kinetic study using the Ozawa[14] equation and reported the activation energy for γ-FeNiMo s.s. crystallization to be 296 kJ mol^{-1}. Cumbrera *et al.*[7] obtained 288 kJ mol^{-1} in non-isothermal conditions using the Kissinger[15] equation and exactly the same value under isothermal conditions. Raja *et al.*,[8] using the Kissinger equation, calculated the activation energy to be 270 kJ mol^{-1}.

CONCLUSION

The crystallization kinetics of γ-FeNiMo s.s. in Metglass 2826 MB has been studied in isothermal conditions using DSC.

The activation energies, calculated using the analytical approach and the proposed numerical model, were (280 ± 22) kJ mol^{-1} and (296 ± 23) kJ mol^{-1}, respectively. The very good match between experimental and calculated curves and similarity of the obtained E_a values shows that the proposed numerical model has been successfully applied.

Thus, we conclude that the proposed model, which avoids an unnecessary mathematical transformation of experimental data, offers (at least) the same accuracy in less time.

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SAŽETAK

Uporaba numeričke metode u analizi kinetike kristalizacije Metglas 2826 MB

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Kinetika kristalizacije čvrste otopine γ-FeNiMo, u materijalu Metglas 2826 MB, proučavana je metodom diferencijalne pretražne kalorimetrije (DSC). Proces kristalizacije opisan je jednadžbom Johnsona, Mehla i Avramija (JMA). Za izračun kinetičkih parametara uspješno je primijenjen novi model za numeričku analizu DSC-krivulja dobivenih u izotermnim uvjetima. U svrhu vrednovanja metode, kinetički parametri izračunani su i klasičnom, analitičkom metodom. Energija aktivacije određena analitičkom metodom iznosi (280 ± 22) kJ mol^{-1}, a numeričkom (296 ± 23) kJ mol^{-1}, Avramijevi eksponenti dobiveni primjenom obiju metoda iznose između 1,75 i 1,95.