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A direct extension of the Avrami equation to describe the non-isothermal crystallization of Al-base alloys

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Abstract

A direct extension of the Avrami equation considering the temperature dependence of the frequency factor is applied to describe the crystallization of a series of Al–Mm–Ni–Co amorphous alloys (Mm is a mischmetal). For high Al content, a nanocrystalline microstructure (fcc α-Al embedded in an amorphous matrix) is formed during the first crystallization process. However, for the alloy with 85 at.% of Al, the devitrification process consists of two strongly overlapped stages, which yield the formation of intermetallic metastable phase(s) without the detection of any amorphous residual matrix. Results are compared with those obtained using other kinetic approaches.

Keywords: Amorphous materials; Kinetics; Calorimetry

1. Introduction

Although Johnson–Mehl–Avrami–Kolmogorov theory (JMAK) [1] was developed to describe the crystallization phenomena in isothermal regimes, several models were proposed to extend its validity to non-isothermal regimes. These models usually imply the comparison of several calorimetric scans (by differential scanning calorimetry, DSC, for example) obtained at different heating rates, β. Among these approximations, Gao–Wang method [2] supplies average values of the activation energy, Q, and the Avrami exponent, n, calculated from the variation of the peak temperature, T_p. On the other hand, Ozawa method yields local values of n as a function of the temperature [3]. This dependence of $n(T)$ implicitly assumes that the kinetic parameters are constant along the transformation process for thermally activated processes. In fact, Ozawa method supplies a value of n for a given value of T but it is clear that, for different values of β, the transformation will be at different stages (more evolved as the heating rate used is lower). Recently, the authors proposed a new method [4] from which it is possible to obtain a local value of n as a function of the transformed fraction, X. These $n(X)$ values were independent of β under the assumption of isokinetic transformation in the frame of Nakamura theory [5]. Consequently, it is possible to obtain a continuous value of $n(X)$ with the use of a single DSC scan and a raw estimation of the activation energy [4]. This method was successfully applied to describe the crystallization of Nb-containing HITPERM alloys [4].

Although other theories, different to JMAK, have been developed to describe non-isothermal crystallization processes trying to overcome the limitations of this theory [6,7], the aim of this study is to analyze the crystallization process in the frame of JMAK theory, using a direct extension of this theory to non-isothermal regimes. The approach developed [4] is applied to the devitrification process of a series of Al-base alloys. The amorphous and nanocrystalline Al–RE–TM alloys (RE is a rare earth metal or Y and TM is a 3d transition metal, generally Ni, although small additions of Fe and Co can be also found in quaternary alloys) are interesting for their excellent mechanical properties [8–10].

2. Description of the method

The proposed method consists on a direct extension of the Avrami equation:

$$X = 1 - \exp\{-[k(t - t_0)]^n\}. \quad (1)$$

where X is the transformed fraction (normalized to 1 at the end of the process), k the frequency factor, t the time and t_0 is the

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incubation time. The direct extension to non-isothermal regimes implies the following relationship:

$$X = 1 - \exp\left\{-\left\{\left[k_0 \exp\left(\frac{-Q}{RT}\right)\right]\left[\frac{T - T_0}{\beta}\right]\right\}^n\right\}. \qquad (2)$$

where the dependence of k with the temperature, T, has been explicitly considered, thus k_0 is independent of T, R is the gas constant and T_0 is the onset temperature. Under this consideration, it is possible to obtain local values of $n(X)$ [4]:

$$\frac{\mathrm{d}(\ln[-\ln(1 - X)])}{\mathrm{d}(\ln[(T - T_0)/\beta])} = n\left\{1 + \frac{\mathrm{d}(\ln(k))}{\mathrm{d}(\ln[(T - T_0)/\beta])}\right\}$$
$$= n\left\{1 + \frac{Q}{RT}\left(1 - \frac{T_0}{T}\right)\right\}. \qquad (3)$$

3. Results and discussion

As-cast samples of $\mathrm{Al_{88}Mm_4Ni_5Co_3}$, $\mathrm{Al_{88}Mm_5Ni_5Co_2}$, $\mathrm{Al_{87}Mm_5Ni_5Co_3}$ and $\mathrm{Al_{85}Mm_8Ni_5Co_2}$ alloys were studied by differential scanning calorimetry in a Perkin-Elmer DSC7. Fig. 1 shows the DSC scans (normalized to the same area for comparison) of the as-cast amorphous alloys obtained at two different heating rates. The alloys with 88 and 87 at.% of Al show a primary crystallization which yields the formation of a nanocrystalline microstructure [11] (α-Al nanocrystals embedded in a

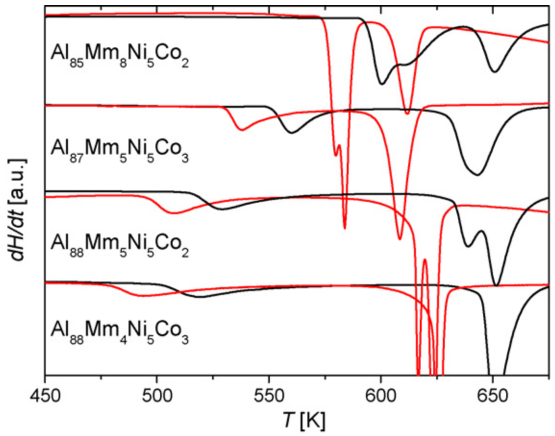

Fig. 1. DSC scans at 10 and 80 K/min (shifted to higher temperatures) of the studied alloys. Plots have been normalized to an equal value of the whole area in order to compare the different samples and heating rates.

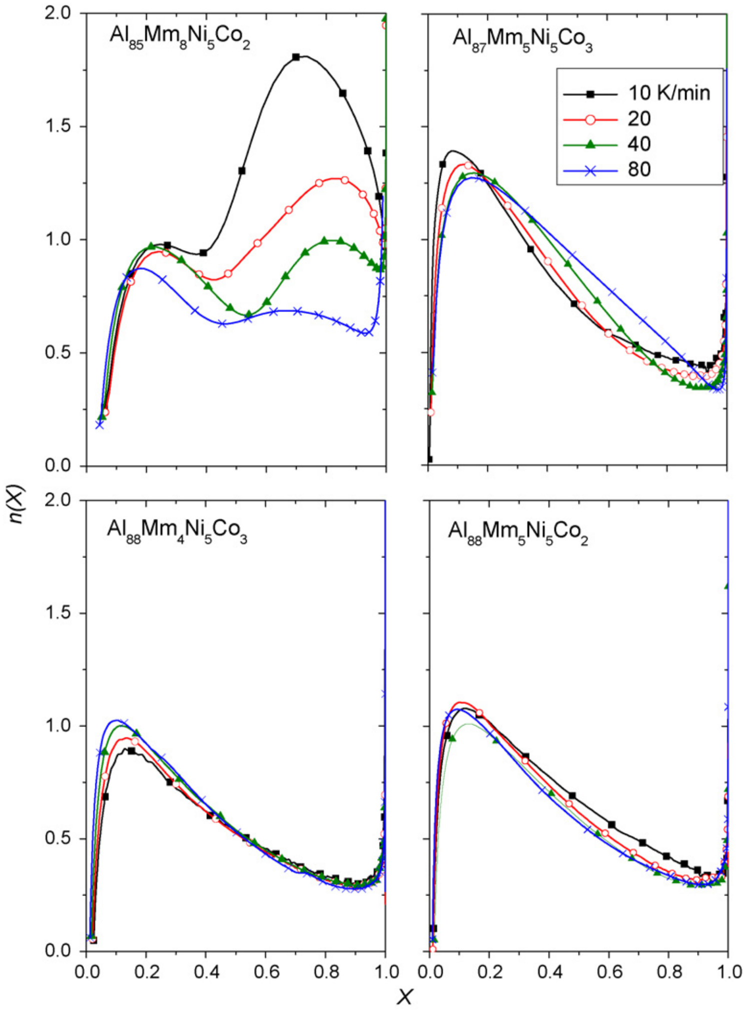

Fig. 2. $n(X)$ values after applying Eq. (3) to DSC scans of the studied alloys obtained at 10, 20, 40 and 80 K/min.

residual amorphous matrix). However, the alloy with the lowest Al content does not form any nanocrystalline microstructure and after the first two strongly overlapped crystallization processes, the main phase is a metastable intermetallic [12]. This alloy exhibits a clear dependence of the shape of the first DSC peak with the heating rate.

After applying Eq. (3) to the first stage of devitrification (first and second in the case of 85 at.% of Al where they cannot be resolved), it is possible to obtain $n(X)$. Fig. 2 shows the $n(X)$ values obtained for different values of β for all the studied alloys, Q values were obtained from refs. [11,12]. It can be observed that $n(X)$ values are independent of β for the alloys with 88 at.% of Al (differences less than 0.1), for which the first transformation stage is well separated from the second stage of transformation. For the alloy with 87 at.% of Al, the difference between the results of n obtained for different β values increases (up to 0.2) with respect to the alloys with 88 at.% of Al. The higher overlapping between the nanocrystallization and the second stage (see Fig. 1) could explain such behavior in two ways: due to an indetermination of the baseline or due to a real effect of the formation of intermetallic nuclei during the nanocrystallization as the first and second crystallization stages become closer, which would mean a deviation from the isokinetic hypothesis. However, it is worth noting that the differences between scans are very small (<0.2). For the alloy with 85 at.% of Al, a very strong dependence of the $n(X)$ values with β can be observed. In fact, the independence with β of the $n(X)$ values obtained by the direct extension of the Avrami equation to non-isothermal regimes was a consequence of the assumption of isokinetic behavior of the transformation. Therefore, if this requirement is not fulfilled (the devitrification depends on β) we cannot trustfully apply the method to the devitrification of this alloy.

As it was pointed above, Ozawa method supplies also a local value of n, although as a function of T. This value of $n(T)$ can be obtained through the following expression [3]:

$$\ln[-\ln(1-X)] = \ln[Z(T)] - n\ln[\beta] \tag{4}$$

where $Z(T)$ is the crystallization function. This method was applied to the alloys with 88 and 87 at.% of Al. Ozawa method needs a common temperature range in which the process occurs for different β values but this requirement cannot be found for the alloy with 85 at.% of Al at 10 and 80 K/min (see Fig. 1) and thus this alloy was excluded from the calculation. Results are shown in Fig. 3. It is worth noting that the error bars decrease till the value of n becomes constant. In fact, as it was said above Ozawa method implicitly assumes that the kinetic parameters are constant along the process, as $n(T)$ is obtained after comparing scans obtained at different β values and, therefore, at different stages of the transformation. Both methods Ozawa and the direct extension of JMAK theory to non-isothermal regimes agree describing a strong impingement of the transformation process characterized by a very low value of n at the final stages (~0.5). The $n(X)$ values at low values of X ($n \sim 1$) obtained by the direct extension of JMAK agree with those values obtained by the Gao–Wang approach [11]. In fact, this method supplies n values at T_p and $X(T_p) \sim 0.3$ is independent of β.

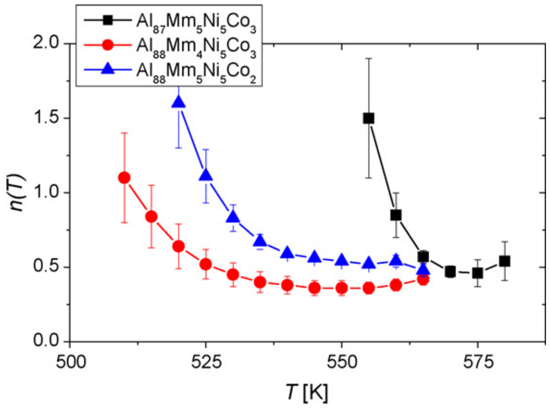

Fig. 3. $n(T)$ values obtained by Ozawa method for the different studied alloys. The heating rates used were: 10, 20, 40 and 80 K/min.

4. Conclusions

Summarizing, the direct extension of the JMAK theory to non-isothermal regimes shows several advantages with respect to other methods developed to describe non-isothermal crystallization processes: a local value of the Avrami exponent as a function of the transformed fraction, which is a richer information than that obtained from average-information methods as Gao–Wang approach and a more self consistent information than that of Ozawa, for which a non-constant value of n is contradictory with the fact that the kinetic parameters must be constant in order to compare the transformation at different stages. As far as the method was theoretically justified for isokinetic processes in the frame of Nakamura equation, the results cannot be trustful if a strong β dependence of n is observed, as it occurs for the alloy with 85 at.% of Al.

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