Crystallization of glassy Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$ alloy on heating and the melt amorphization during melt-spinning processing

V I Tkatch$^1$, S G Rassolov, V V Popov and S A Kostyrya

$^1$A A Galkin Donetsk Institute for Physics & Engineering of the NAS of Ukraine, 72 R. Luxemburg Str., 83114, Donetsk, Ukraine

vit@depm.fti.ac.donetsk.ua

Abstract. Crystallization of amorphous Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$ melt-spun ribbons has been studied and analyzed using the classical theory equations. It was established that crystallization of this glass occurs by non-steady state homogeneous nucleation and interface controlled crystal growth. All parameters controlling the rates of crystal nucleation and growth including the temperature dependence of the transient time were estimated from comparison of the calculated kinetic curves with those experimentally measured. By substitution of these parameters and experimentally determined values of the heat transfer coefficient into the numerical approach describing crystallization in a melt-spinning technique amorphization of the Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$ melt has been analyzed. The dominant role of the heterogeneous nucleating in this melt crystallization under rapid cooling in the majority of experiments has been confirmed and the most probable values of the heterogeneous sites density and wetting angle have been estimated by comparing of the experimental and calculated “temperature-time” cooling curves.

1. Introduction

Knowledge of the thermal prehistory of melt-quenched materials is of prime importance because their structure and the majority of physical properties are strongly dependent on the processing conditions. The main process which determines the structural state of materials during rapid quenching is crystallization of undercooled melt occurring in very short time (about $10^{-4}$-$10^{-3}$ s). In view of great experimental difficulties of the direct studies of the solidification process at cooling rates typical for the most common techniques of melt-quenching, computer simulation provides a particularly good opportunity for quantitative studies of structures formed at certain cooling conditions. The most correct models of crystallization during rapid melt cooling are based on self consistent solution of heat transfer and crystallization kinetic equations [1,2], however, the calculations involve a large set of parameters governing the rates of crystal nucleation and growth in undercooled melt, which are unknown for the most of materials.

As it has been shown in [2] the critical thickness of the Fe$_{80}$B$_{20}$ melt-spun ribbons may be correctly predicted under assumption that melt crystallization occurs by homogeneous nucleation and linear growth described by the classical theory formalism [3] with the parameters which have been extracted from studies of devitrification of the glass [4]. However, it has been recently shown that heterogeneous nucleation play a dominating role in melt crystallization [5-7]. Besides, it has been established that variations of the main melt-spinning process parameters results in simultaneous changing of the ribbons thickness and the heat transfer coefficient, $h$, which determines the cooling
regime [8,9]. In this paper we report the results of experimental studies of the well-known Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ glass crystallization and that of calculations of this melt amorphization by melt spinning processing carried out within the modified numerical model presented in [2].

2. Experimental and description of the model

2.1. Experimental

Amorphous ribbons of the Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ alloy (2 mm wide and ~ 20-70 μm thick) were prepared by melt-spinning from a silica glass crucible onto a commercial aluminium bronze wheel in air. The structural characterization of the as-quenched and heat treated specimens was performed by X-ray diffraction (XRD) using Fe-filtered Co Kα radiation in a DRON-3M automated diffractometer. The experimental “temperature – time” curves during melt-spinning processing were measured by original thermoelectric method [9]. The ribbons with different thickness were produced at different wheel velocities and their critical thickness did not exceed 60 μm. Kinetics of the isothermal crystallization was investigated by electrical resistivity measurement method (a standard dc four-probe technique) by annealing in the NaNO$_3$ salt bath at 600-690 K with temperature controlled ± 0.5 K. The ribbons about 25 μm thick were chosen for crystallization investigations in the glassy state.

2.2. Description of the model

The temperature changes both in the solidifying thin melt layer and the semi-infinite substrate are described by the one-dimensional heat conduction equations with the initial and boundary conditions presented elsewhere [1,2]. The crystallization kinetics both in liquid and glassy states is assumed to follow the Kolmogorov’s equation of mass crystallization [10]

\[ X(t) = 1 - \exp \left( -\frac{4\pi}{3} \int_0^t I(t') \left[ U(t') \right]^3 dt' \right) \]  

(1)

where \( X \) is the volume fraction crystallized, \( I \) is the nucleation frequency, \( U \) is the rate of interface crystal growth, and \( t \) is the time. For description of the temperature dependencies of the rates of transient crystal nucleation (both homogeneous and heterogeneous) and growth the equations of the classical crystallization theory were used in the form [3,11,12]

\[ I_{\text{ns}}(t) = I_{i} \left[ 1 + 2 \sum_{m=1}^{\infty} \left( -1 \right)^m \exp \left( -\frac{m^2 t}{\tau_{\text{ns}}} \right) \right] \]  

(2)

\[ I_i(T) = \frac{N_i D_0}{a^2} \exp \left( -\frac{Q}{T} \right) \exp \left( -\frac{W^*}{RT} \right) \]  

(3)

\[ U(T) = \frac{D_0}{a} \exp \left( -\frac{Q}{T} \right) \left[ 1 - \exp \left( -\frac{\Delta G}{RT} \right) \right] \]  

(4)

where \( D_0 \) is the pre-exponential factor and \( Q \) is the activation energy which determine the diffusivity at the crystal-melt interface, \( \tau_{\text{ns}} = \tau \left( \frac{T}{T^*} \right) \) is a transient time of the nucleation, \( a \) is the average atomic diameter (jump distance), \( W^* \) is the activation energy barrier for nucleation, \( \Delta G \) is the Gibbs free energy difference between liquid and crystalline phases, \( R \) and \( T \) are the gas constant and temperature, respectively. The subscript \( i \) in equation (3) refers to the mode of nucleation (homogeneous or heterogeneous) with \( N_{\text{hom}} \) being the number of atoms per volume and \( N_{\text{het}} \) being the volume density of surface nucleation sites. The energy of the critical nucleus formation by homogeneous nucleation is given by

\[ W^*_{\text{hom}} = \frac{16\pi \sigma^3 V^2}{3(\Delta G)^2} \]  

(5)
where $\sigma$ is the specific crystal-liquid interfacial energy, and $V$ is the molar volume, while for the case of heterogeneous nucleation spherical nuclei at planar catalytic sites \[3,11\]
\[
W_{\text{het}}^* = W_{\text{hom}}^* \left(2 - 3\cos\theta + \cos^3\theta\right)/4
\] (6)
with $\theta$ being the wetting angle. The value of the thermodynamic driving force for crystallization was estimated from the Thompson-Spaepen approximation \[13\]
\[
\Delta G = \frac{2\Delta H_m T(T_m - T)}{T_m(T_m + T)}
\] (7)
where $\Delta H_m$ and $T_m$ are the molar heat and the temperature of fusion, respectively.

In calculations for the case of transient homogeneous nucleation we used the values of $D_0 = 1 \times 10^{11} \text{m}^2\text{s}^{-1}$, $Q = 43800 \text{K}$, $\sigma = 0.145 \text{J m}^{-2}$, $\tau_0 = 3.08 \times 10^{23} \text{s}$ extracted from the analysis of Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ glass crystallization based on the classical theory \[4\], while the thermodynamic quantities ($\Delta H_m = 10.3 \text{kJ mol}^{-1}$ and $T_m = 1180 \text{K}$) were taken from \[14\]. The two quantities required for description of heterogeneous nucleation ($N_{\text{het}}$ and $\theta$) were used as adjustable parameters. To account for the dependence of the interfacial heat transfer coefficient on the melt-spun ribbon thickness the data reported in \[8,9\] were plotted and approximated by an exponential decay function $h \approx 9.18 \times 10^{4} + 1.14 \times 10^{7} \exp(- d/7.11)$.

3. Results and discussion

The experimental isothermal crystallization kinetic curves are shown in figure 1. It has been established that crystallization of glass investigated occurs by transient homogeneous nucleation (inset on figure 3) of the eutectic ($\alpha$(Fe,Ni)$+$(Fe,Ni)$_3$(P,B)) crystals and interface controlled growth. The results of matching of the calculated (solid lines) by set of the equations (1-4) to experimentally determined kinetic curves for 608 and 670 K are presented in figure 1. It is also noteworthy, that the proposed approach correctly describes the experimentally observed changing of the Avrami exponent with annealing temperature (inset on figure 2) and gives possibility to extract a temperature dependence of the transient time $t_n$ (figure 2).

**Figure 1.** Experimental (points) and calculated (lines) isothermal kinetic crystallization curves of amorphous Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ alloy for different annealing temperatures: (from left to right) – 670, 640 and 608 K.

**Figure 2.** The fitted values of the transient nucleation times $t$ as a function of the annealing temperatures. The dependence of the Avrami exponent $n$ on annealing temperatures is shown in inset.
At the initial stage the volume fraction crystallized in the Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ melt formed by homogeneous nucleation was calculated as a function of the melt-spun ribbon thickness. Note that in these estimations no free parameters were used. The calculations have shown that the critical thickness of the Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ melt-spun ribbon predicted is about 250 µm. However, in the real experimental conditions the maximum reported thickness of the glassy ribbons does not exceed 60-65 µm. This difference may imply that the input parameters of the model underestimate the rate of crystallization and/or that of heat extraction. On the other hand, purification of the Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ melt with B$_2$O$_3$ recently allowed obtaining the glassy rods with a diameter of 1 mm [5]. These results clearly indicate that the values of the parameters used in the calculations are realistic and that heterogeneous nucleation contributes significantly to the crystallization of the melt. In order to clarify this effect the calculations of critical ribbon thickness were carried out under the assumption that the crystal nucleation rate is the sum of $I_{\text{hom}} + I_{\text{het}}$.

In view that both parameters (N$_{\text{het}}$ and $\theta$) which govern the heterogeneous nucleation rate [11] are unknown, the aim of the simulations was to estimate their values for which the minimum thickness of the fully crystallized melt-spun ribbon is about 65 µm. In these calculations the value of $2 \times 10^{18}$ m$^{-3}$ was taken as an upper limit of N$_{\text{het}}$ which corresponded to concentration of $10^{13}$ m$^{-3}$ of impurity particles with a diameter of 50 nm [15]. Note that this estimation of N$_{\text{het}}$ agrees with that reported in [7]. The calculations have shown that the required critical ribbon thickness may be reached at various combinations of N$_{\text{het}}$ and $\theta$ (e.g., ranging from $10^9$ to $10^{18}$ m$^{-3}$ and from about 60 to 85°, respectively) which does not allow their unambiguous choice. On the other hand, the combination of the N$_{\text{het}}$ and $\theta$ values influences appreciably the shape of the calculated cooling curves of the crystallizing melt as shown in figure 5, i.e. an increase in N$_{\text{het}}$ leads to a decrease in the initial melt undercooling. From a comparison of the calculated $T(t)$ curves with the experimental one (symbols in figure 3) it may be concluded that Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ melt contains a population of about $10^{10}$ m$^{-3}$ of surface nucleation sites (the most probably P$_2$O$_5$ particles [5]) with the wetting angle at particle-melt interface of about 66.5°.

**Figure 3.** Comparison of the cooling curves of Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ melt layer 65 µm thick calculated for N$_{\text{het}} ^{\text{expt}}$ = $2 \times 10^{10}$ m$^{-3}$ and $\theta$ = 66.5° (solid line), N$_{\text{het}} ^{\text{sim}}$ = $2 \times 10^{16}$ m$^{-3}$ and $\theta$ = 79.8° (dashed line) and N$_{\text{het}} ^{\text{sim}}$ = $2 \times 10^{18}$ m$^{-3}$ and $\theta$ = 87.8° (dotted line) with the experimentally determined $T(t)$ curve (●). The horizontal line shows the melting temperature.

**Figure 4.** Comparison of the nucleation and growth rates values in Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$ alloy calculated using the parameters extracted from the studies of glass crystallization kinetics with those experimentally determined [12] (●, ○) and [5] (■, □). (The dashed line represents $I_{\text{het}} ^{\text{expt}}$, dotted line refers to $I_{\text{hom}} ^{\text{expt}}$ and solid line represents $I_{\text{hom}} ^{\text{sim}} + I_{\text{het}} ^{\text{sim}}$; solid and symbols refer to the rate of nucleation and to the rate of growth, respectively).
Note that the latter value is in agreement with the experimentally determined contact angles (66-70°) between the carbide particles and Ni-Si-B glass [11]. It should be also noted that taking into account the heterogeneous nucleation contribution does not influence the calculated density of the quenched-in nuclei in the melt-spun ribbon (about 10^{14} m^{-3}), but essentially increases the critical cooling rate necessary to avoid Fe_{40}Ni_{40}P_{14}B_{6} melt crystallization (from about 10^4 to 1.4×10^5 K/c). All these estimations are in accordance with the published data [4,6,12] thus lending further support to the correctness of our approach. Moreover the presence of the transient nucleation stage in glassy state does not influence on critical ribbon thickness and shape of the nucleation curve (figure 4) in the melt rapid cooling. The possible reasons are both convergence to zero processing time \( t \) and transient time \( t_{ns} \) in equation 2.

4. Conclusion

Crystallization of amorphous Fe_{40}Ni_{40}P_{14}B_{6} melt-spun ribbons has been studied by electrical resistivity measurement method (a standard dc four-probe technique) under annealing in the NaNO_3 salt bath in 600 – 690 K temperature range with temperature controlled ± 0.5 K and analyzed using the classical theory equations. It was established that crystallization of this glass occurs by transient homogeneous nucleation of the eutectic (\( \alpha(\text{Fe,Ni})+(\text{Fe,Ni})_3(\text{P,B}) \)) crystals and interface controlled crystal growth. All parameters controlling the rates of crystal nucleation and growth including the temperature dependence of the transient time were estimated from comparison of the calculated kinetic curves with those experimentally measured. Substituting these parameters and experimentally determined values of the heat transfer coefficient into the numerical approach describing crystallization in a melt-spinning technique amorphization of Fe_{40}Ni_{40}P_{14}B_{6} melt has been analyzed. The dominant role of the heterogeneous nucleating in this melt crystallization under rapid cooling in the majority of experiments has been confirmed and the most probable values of the heterogeneous sites density and wetting angle have been estimated by comparing of the experimental and calculated “temperature – time” cooling curves.

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