

History dependent crystallization of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ melts

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(Received 17 January 2000; accepted for publication 30 March 2000)

The crystallization of $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ (Vit 1) melts during constant heating is investigated. (Vit 1) melts are cooled with different rates into the amorphous state and the crystallization temperature upon subsequent heating is studied. In addition, Vit 1 melts are cooled using a constant rate to different temperatures and subsequently heated from this temperature with a constant rate. We investigate the influence of the temperature to which the melt was cooled on the crystallization temperature measured upon heating. In both cases the onset temperature of crystallization shows strong history dependence. This can be explained by an accumulating process during cooling and heating. An attempt is made to consider this process in a simple model by steady state nucleation and subsequent growth of the nuclei which results in different crystallization kinetics during cooling or heating. Calculations show qualitative agreement with the experimental results. However, calculated and experimental results differ quantitatively. This difference can be explained by a decomposition process leading to a nonsteady nucleation rate which continuously increases with decreasing temperature. © 2000 American Institute of Physics. [S0021-8979(00)04813-1]

I. INTRODUCTION

The critical cooling rate, R_c , defines the lowest rate by which a liquid can be cooled to avoid crystallization of a detectable amount.¹ For monoatomic metallic systems R_c is of the order of 10^{12} K/s. The bulk metallic glass forming alloy $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ has a critical cooling rate of about 1 K/s.² In general, to prove that cooling results in a fully glassy sample, x-ray, differential scanning calorimetry, transmission, and scanning electron microscopy are performed. However, these methods fail to detect a crystalline fraction less than 1% of the sample volume. It has been shown several times that slightest partial crystallization can lead to a loss of desired properties of an amorphous material. Slightly partial crystallized $Fe_{80}B_{20}$ loses its high permeability and low coercive force. Mechanical properties are sensitive to the amount of the smallest amount of crystals in the amorphous sample. The fracture toughness of fully amorphous Vit 1 of $K_{Ic} = 55$ Mpa \sqrt{m} drastically decreases in a partially crystallized sample to $K_{Ic} \sim 1$ Mpa \sqrt{m} , a value comparable to silica glass.³

Several experiments suggest that nuclei get quenched in during cooling the melt into the amorphous state (see, e.g., Refs. 4 and 5). The expected volume fraction of these nuclei is much smaller than the detectable fraction with x-ray. Therefore, nuclei formed during cooling would not be detected. For example, Al-Sm alloys prepared by melt-spinning and solid-state processing exhibit a different crystallization behavior upon reheating.⁵ The authors conclude from this result that nuclei formed during quenching. The number of quenched-in nuclei would then depend on the temperature as well as on the cooling rate by which the liq-

uid sample cooled into the amorphous state. Investigations on the nonmetallic glass former lithium disilicate⁶ as well as on $Fe_{80}B_{20}$ (Ref. 4) support the assumption of quenched-in nuclei.

In the present work, the onset temperature of crystallization, T_x , during constant heating was investigated for different preprocess conditions. The influence of T_x on the cooling rate by which Vit 1 melts were cooled into the amorphous state as well as the minimum temperature, T_{min} , to which the sample was cooled prior to reheating was investigated. The results are discussed within a model that is based on a different crystallization mechanism during cooling or heating. The resulting asymmetry in the crystallization mechanism within this model stems from the fact that the maximum in the nucleation rate is at lower temperatures than the maximum in the growth rate.

II. EXPERIMENT

Samples were prepared by arc melting the constituents (purity ranging from 99.5 to 99.995 at. %). The investigations were performed in high purity graphite crucibles. It was shown earlier that the container walls do not alter the crystallization of the bulk Vit 1.⁷ Samples were embedded into the graphite crucibles and inductively heated in vacuum or in a titanium atmosphere. The temperature was measured using a thermocouple (type K) with an accuracy better than ± 2 K. The experimental setup is described in more detail elsewhere.⁸

III. RESULTS

A schematic depiction of the experiments to study the influence of the cooling rate on the crystallization temperature upon reheating Vit 1 with a constant rate is shown in Fig. 1. The Vit 1 melt was cooled with rates between 4 and

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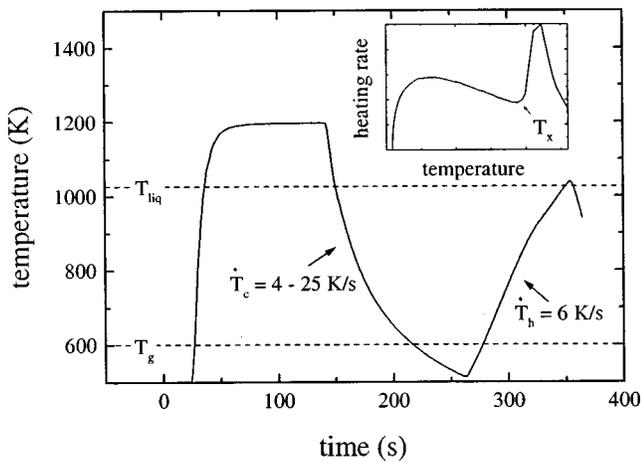


FIG. 1. A temperature–time profile for the experiments where the influence of the cooling rate on the onset temperature of crystallization upon reheating was studied. Prior to cooling, the liquid sample was kept for 100 s at 1150 K before it was cooled with rates between 4 and 25 K/s below the glass transition temperature. Subsequently, the sample was heated with a rate of 6 K/s. The inset depicts the derivative of the temperature–time profile that was used to detect the onset temperature of crystallization.

25 K/s from about 1150 K to a temperature below the glass transition temperature, T_g . Upon subsequent heating with a constant rate of 6 K/s the crystallization was detected. Results are summarized in Fig. 2. The crystallization temperature increases with increasing cooling rate. For a Vit 1 melt that is cooled with 4 K/s into the amorphous state, the crystallization temperature measured upon reheating is 752 K. A crystallization temperature that is 27 K higher of $T_x = 779$ K was measured on a sample that was cooled with 25 K/s.

A schematic illustration of the experiments in Fig. 3 shows the influence of the minimum temperature to which the sample was cooled prior to reheating on T_x . Therefore, Vit 1 melts were cooled with a constant rate of 12 K/s from 1150 K to different T_{min} and subsequently heated with either 6 or 15 K/s. The results are summarized in Fig. 4. The crystallization temperature depends

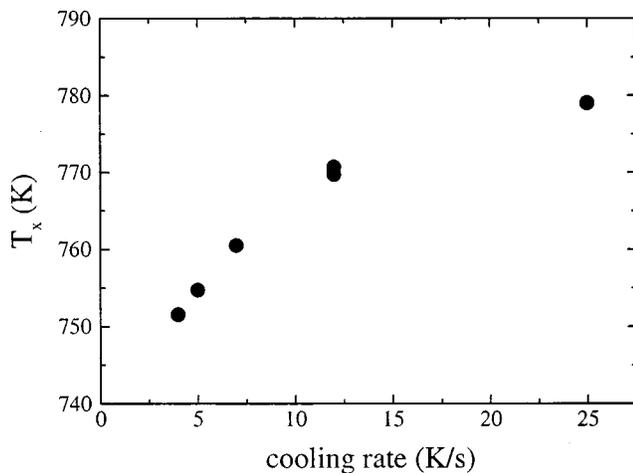


FIG. 2. Onset temperature of crystallization measured while heating amorphous Vit 1 samples with 6 K/s. The amorphous samples were cooled with different rates between 4 and 25 K into the amorphous state.

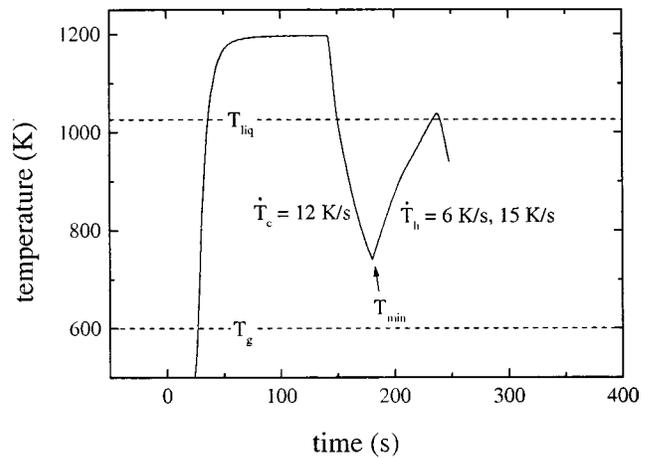


FIG. 3. An illustration of the experiments to study the influence of the minimum temperature, T_{min} to which the sample was cooled prior to reheating on the crystallization temperature. In this case the cooling rate of 12 K/s as well as the heating rate of either 6 or 15 K/s are constant but the minimum temperature varies.

on the minimum temperature to which the melt was cooled prior to reheating. For temperatures below 600 K the influence of the minimum temperature on T_x is very small and this influence increases with increasing temperature. Heating with 15 K/s results in higher T_x than heating with 6 K/s. For a heating rate of 6 K/s the crystallization temperature increases from 773 K for $T_{min} = 295$ K to $T_x = 862$ K for $T_{min} = 857$ K. For $T_{min} > 857$ K no crystallization took place at all. If the sample was heated with 15 K/s from a minimum temperature of 300 K crystallization is detected at 800 K, whereas heating from $T_{min} = 817$ K leads to crystallization at 840 K.

IV. DISCUSSION

According to our experiments, the onset temperature of crystallization for Vit 1 samples upon reheating with a constant rate depends on the cooling rate by which the Vit 1

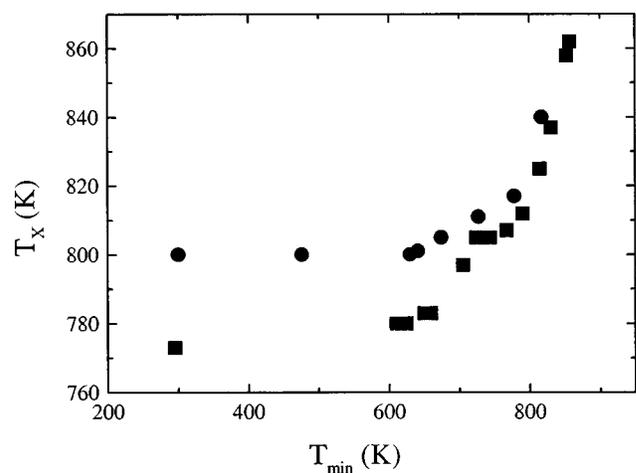


FIG. 4. Influence of the minimum temperature to which the melt was cooled on the crystallization temperature during reheating with either 6 (■) or 15 K/s (●).

melt was cooled below T_g , as well as the minimum temperature to which the melt was cooled prior to reheating. These results suggest that during cooling and subsequent reheating an accumulating process takes place which results in different crystallization temperatures. Crystallization of the supercooled liquid requires the formation of nuclei and their subsequent growth. In an experiment, the onset of crystallization is somewhat arbitrarily defined as the point in time where the crystalline volume fraction within the melt reaches some small but finite value. With the present setup a crystallized volume fraction of about 10^{-3} can be detected. The exact value of the detectable volume fraction has, however, marginal influence on the present discussion. Within classical nucleation theory, the steady state nucleation rate,

$$I_{ss} = AD \exp\left(-\frac{\Delta G^*}{kT}\right) \quad (1)$$

is written as the product of an effective diffusivity, D , times a constant, A , and the thermodynamic Boltzmann factor to overcome the nucleation barrier. T denotes the absolute temperature and k is Boltzmann's constant.

The activation energy to form a critical nucleus is given by

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G^2} \quad (2)$$

Here σ denotes the energy of the interface between the melt and a nucleus and ΔG the difference in Gibbs free energy between the solid and the liquid phase. Assuming diffusion limited growth, the crystalline growth velocity can be described by

$$u = \frac{D}{a} \left[1 - \exp\left(-\frac{\Delta G}{kT}\right) \right] \quad (3)$$

with a as an interatomic spacing. Considering three dimensional growth and a steady state nucleation rate, the time-dependent volume fraction x , of crystallized material is obtained by

$$x(t) = \frac{4\pi}{3} \int_0^t I(T, \tau) \left[\int_\tau^t u(T, t') dt' \right]^3 d\tau \quad (4)$$

The double integral sums over all nucleation centers, appearing at time, τ , and their growth from τ to time, t . The integral was numerically solved for linear cooling with a rate R described by $T(t) = T_{liq} - R \times t$ (T_{liq} : liquidus temperature) and heating with a rate $R' = T_g + R \times t$. Data for $\sigma = 0.04$ J/m² and $A = 10^{11.1}$ were taken from a least square fit to the isothermal temperature-time-transformation (TTT) diagram.⁹ For the effective diffusivity, a temperature dependence according a hybrid equation which considered the parallel development of atomic-like jumps at low temperatures and a viscous flow at high temperatures was used, which was proposed earlier.⁹ Differential scanning calorimetry results from Ref. 10 were taken as an estimate for ΔG . With these parameters the nucleation rate according to Eq. (1) and the growth rate according to Eq. (3) are calculated and shown in Fig. 5. The maximum in the growth rate at 985 K is at much higher temperatures than the maximum in the nucleation rate

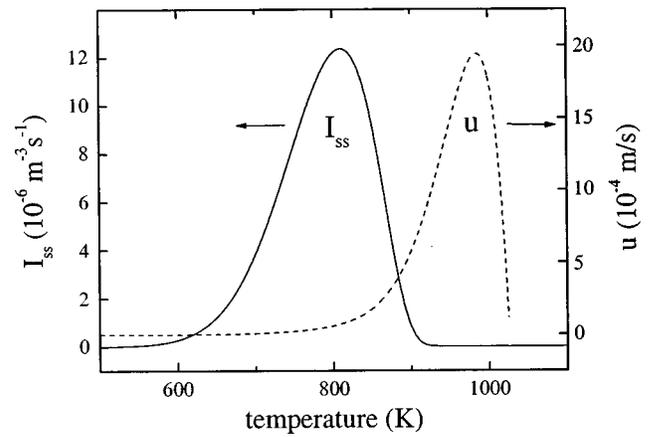


FIG. 5. Nucleation rate according to Eq. (1) and growth rate according to Eq. (3) as a function of temperature calculated with the above mentioned parameters. The maximum of the growth rate at 985 K is at much higher temperatures than the maximum in the nucleation rate at 840 K.

at 840 K. It has been shown earlier that in any metallic system the maximum in the nucleation rate can be expected to be at lower temperatures than the maximum in the growth rate.¹¹ With the nucleation and growth rate shown in Fig. 5 the volume fraction according to Eq. (4) was calculated and depicted in Fig. 6 as a function of temperature. While cooling with 5 K/s the crystallized volume fraction continuously increases and stays about constant below 600 K. The calculation was terminated at 500 K due to the freezing of the crystallization kinetics. The crystallized volume fraction of about 5.4×10^{-7} would not be detected with the present experimental setup. The simulation was subsequently continued by heating with a rate of 1 K/s. At 871 K the crystallized volume fraction reached the detectable level of the present setup of 10^{-3} . These calculations were performed for different cooling rates between 1 and 1000 K/s. Figure 7 depicts the temperature where the crystallized volume fraction reaches the detectable level for the different rates. The calculated

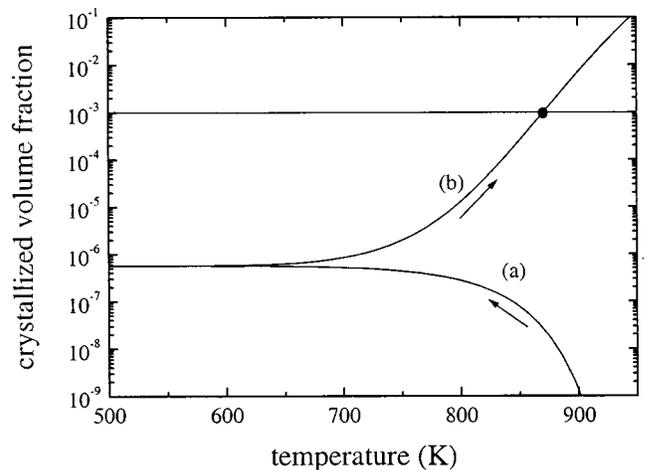


FIG. 6. Calculated crystallized volume fraction as a function of temperature according to Eq. (4). Upon cooling (a) with 5 K/s a volume fraction of 5.4×10^{-7} crystallized. While reheating the sample with a rate of 1 K/s (b) crystallization would be detected at 871 K, where the crystallized volume fraction reaches the detectable level of 10^{-3} .

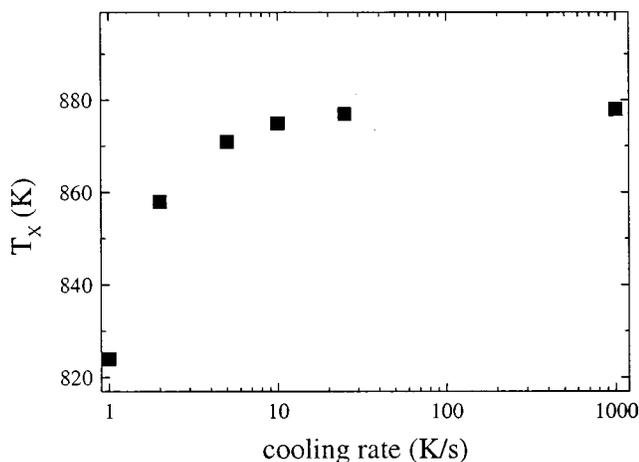


FIG. 7. Calculated crystallization temperature for different cooling rates. The simulations were performed for rates between 1 and 1000 K/s by which the system was cooled from T_{liq} to 500 K. Subsequently, the system was heated with 1 K/s. The dots denotes the temperatures where the crystallized volume fraction according to Eq. (4) reach the detectable level of 10^{-3} .

onset temperatures of crystallization increase from 824 K for a cooling rate of 1 K/s to 878 K for a cooling rate of 1000 K/s. The key assumption that leads to the strong history dependent is that the maximum in the growth rate is at higher temperatures than the maximum in the nucleation rate, which was shown earlier that this can be expected for any metallic system.¹¹ This suggests, that the history dependent crystallization process should be present in any metallic system.

Figure 8 shows calculated crystallization temperatures for different minimum temperatures. Calculations were performed in such a way that the system was cooled with 1 K/s to different T_{min} . Upon reheating with 1 K/s the dots denotes the temperature where the crystallized volume fraction according to Eq. (4) reached a value of 10^{-3} and crystallization would be detected.

A comparison of the calculated minimum temperature dependence on T_x with the experimentally determined T_x shows qualitative agreement. However, the calculated abso-

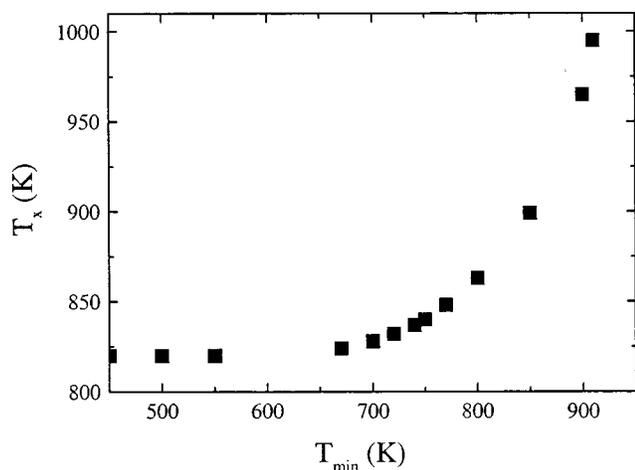


FIG. 8. Calculated crystallization temperatures for different minimum temperatures to which the sample was cooled prior to reheating. The solid squares denote the temperature where the crystallized volume fraction reaches the detectable level of 10^{-3} .

lute values for T_x are about 100 K higher than the measured values. Calculation of the T_x dependence on the cooling rate as well agrees qualitatively with the measured crystallization temperature. The absolute values are, however, about a 100 K larger than the measured ones. In the calculations, T_x increases strongly for cooling rates between 1 and 10 K/s. For cooling rates about 10 K/s the crystallization temperature stays about constant. This is in agreement with the experimental finding, that no significant variation of the crystallization temperatures upon heating amorphous samples prepared by splat quenching or in an arc furnace were observed.¹² The cooling rate achieved by splat quenching is about 10^6 K/s whereas samples with a mass of several grams prepared in the arc furnace are exposed to a cooling rate of about 10 K/s.

The reason that the calculated T_x are about 100 K higher than the measured ones can be explained by the fact that the nucleation rate in the Vit 1 system is underestimated by the steady state nucleation rate. In a complex system like Vit 1 an adequate description of the nucleation process will certainly have to go beyond the concept of steady state nucleation.¹³ It was reported earlier¹⁴ that the microstructures developed at different degrees of undercooling are much finer than suggested by the steady state nucleation rate. This apparent contradiction of a high nucleation rate derived from the fine microstructure and the sluggish crystallization kinetics suggested from the TTT diagram can be explained by a nonsteady nucleation rate which is initially negligible but finally reaches a very large value. This could be a result of a decomposition process prior to nucleation which was indicated in several experiments.¹⁵⁻¹⁷

At this point it should be mentioned that the crystallization in the presented heating experiments is faster than in isothermal experiments. For example, in an isothermal experiment performed at 780 K, the time to reach crystallization is about 250 s.¹⁸ For a sample which is cooled to 650 K and subsequently heated to 780 K, where it crystallizes, the cumulative time for the process gives only 53 s. This suggest that the assumption in the calculation about the maximum in the growth rate at 985 K and the maximum in the nucleation rate at 840 K which already leads to a history dependent crystallization process is not appropriate. To explain this difference in the crystallization kinetics, a nucleation rate has to be considered which continuously increases with decreasing temperature down to a temperature of about 600 K. Then, while cooling to a lower temperature a larger number of nuclei is formed, greater than the number of nuclei formed at the isothermal treatment. Upon reheating, this large number of nuclei are exposed to the same growth rate as the nuclei formed during the isothermal heat treatment. Therefore, the sample which was first cooled to a lower temperature and subsequently heated, which has a larger number of nuclei, will crystallize faster than the isothermal treated sample. Below 600 K the crystallization temperature no longer depends on the minimum temperature (see Fig. 4). This suggests, that the maximum of the nucleation rate is at about 600 K.

A process that is likely to result in continuous increment of the nucleation rate with decreasing temperature down to about 600 K is a decomposition of the homogeneous melt. In

this case, the homogeneous liquid decomposed prior to nucleation into regions of different compositions. The nucleation probability in the decomposed regions is then strongly increased since the composition is locally closer to the composition of the primary solidified phase. In the Cahn–Hilliard theory on spinodal decomposition,¹⁹ e.g., the length scale of the phase separated region, λ , is mainly given by the ratio of the gradient energy and the curvature of the free energy curve. The wavelength, λ , follows the relation $1/\lambda^2 \propto -(T - T_s)$, with T_s as the critical temperature. The composition fluctuations in the regions with a diameter λ grow exponentially with a time constant $\tau = -\lambda^2/4\pi^2 D$. If we assume that nucleation sets in if a certain composition amplitude is reached and a fixed number of nuclei are formed in one decomposed region, a strong increase of the nucleation rate can be expected with decreasing temperature. The decomposition process in this picture would lead to a nucleation rate that is not constant but initially negligible but finally reaches a very large value. In the past, decomposition in liquid Vit 1 prior to crystallization has been observed.^{15–17}

A model that would also result in a continuous increment of the nucleation probability with decreasing temperature is based on an idea of Rusell²⁰ established for partitioning systems like Vit 1. Kelton²¹ takes into account the linked stochastic fluxes of atom attachment at the cluster interface and longrange diffusion in the liquid to the cluster neighborhood. If the effective diffusion rate of a solute atom is comparable to the interfacial rate this should cause the solute concentration in the neighborhood of small clusters to rise above that of the homogeneous phase and therefore result in a higher nucleation probability. Large under critical clusters result in the largest increment of the nucleation rate within this model. Since the number of large under critical clusters increase with decreasing temperature this model would also result in an increase of the nucleation probability with decreasing temperature.

Whether the Cahn–Hilliard theory for spinodal decomposition is appropriate to describe the decomposition or the linked-flux approach is yet unclear.

V. CONCLUSION

Crystallization temperature upon reheating was investigated for different preprocess conditions. Vit 1 melts were cooled to different minimum temperatures and during reheating the crystallization was detected. Also, the crystallization temperature was investigated for samples which were cooled with different rates into the amorphous state. It turns out that the crystallization is strongly history dependent. This result suggests, that an accumulating process takes place in the

undercooled liquid during cooling and subsequent heating. The accumulating process was considered in a model by integrating nuclei—and their subsequent growth—according to steady state nucleation. Although steady state nucleation is an oversimplification of the complex nucleation process of Vit 1 melts, the calculations leads to a history dependent crystallization process that shows qualitative agreement with the experimental results. The fact that the absolute values of the crystallization temperature exhibit some discrepancy as well as that the crystallization kinetics in isothermal experiments are slower than in cooling and heating experiments show that the assumptions in the calculations are not sufficient for the Vit 1 system. To explain the experimental results a position of the maximum in the nucleation rate at about 600 K has to be assumed. Such a low position of the maximum in the nucleation rate suggest a decomposition process prior to nucleation.

ACKNOWLEDGMENTS

This work was supported by the National Aeronautics and Space Administration (Grant No. NCC8-119) and the Department of Energy (Grant No. DEFG-03086ER45242).

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