

Repeated crystallization in undercooled $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ liquids

Jan Schroers^{a)} and William L. Johnson

Keck Laboratory of Engineering Materials 138-78, California Institute of Technology, Pasadena, California 91125

Ralf Busch

Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon 97331

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Isothermal crystallization studies are performed on $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ melts. Undercooling experiments are carried out repeatedly at 907, 860, and 750 K. The scattering of the time to reach the onset of crystallization is investigated. Results from experiments performed at 907 K show a large scatter of the onset time of crystallization. For the experiments carried out at 860 and 750 K, scattering of the onset time is two orders of magnitude smaller. These results indicate that, at high temperatures, the crystallization is governed by the time scale of the statistical nucleation events. At low temperatures, the crystallization is controlled by diffusion, resulting in a well-defined onset time for crystallization. © 2000 American Institute of Physics. [S0003-6951(00)00117-0]

Bulk metallic glasses distinguish themselves from other metallic alloys by a very sluggish crystallization kinetic. This results in low critical cooling rates to avoid crystallization.^{1,2} The well-studied $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$ (Vit 1) multicomponent alloy, for example, has a critical cooling rate of about 1 K/s (Ref. 3) and the isothermal onset time for crystallization is larger than 50 s for the entire supercooled liquid temperature region.⁴ Possible explanations for this sluggishness are given by the “Confusion principle,”⁵ a nucleation model that considers the effect of the number of components on the nucleant fluctuations,⁶ as well as the strong liquid nature of this melt.⁷ This sluggishness in the crystallization behavior makes it somewhat surprising that at low temperatures in the vicinity of the glass transition temperature, Vit 1 crystallizes into a nanocrystalline microstructure from the amorphous state. This suggests a high nucleation rate. By combining results from investigations of microstructures formed at different isothermal heat treatment and crystallization kinetics some insight in the crystallization mechanism could be gained.⁸ These investigations suggested that for a temperature region from the liquids temperature down to 150 K below, crystallization is governed by a classical nucleation and growth mechanism. For lower temperatures, it has been suggested that a chemical decomposition process prior to crystallization influences the resulting microstructure.^{9,10} In this region, the onset time for crystallization is expected to be basically the time required for chemical decomposition.⁸

A useful tool to investigate the crystallization mechanisms are repeated undercooling experiments.¹¹ These experiments have been performed for constant cooling for several different systems like Zr,¹² Al,¹³ and CoPd.¹⁴ A common method is to calculate the preexponential factor in the expression for the nucleation rate from the scattering of the maximum undercooling values.

In this letter, repeating isothermal undercooling experiments at different temperatures on Vit 1 melts are presented.

Annealing temperatures were chosen in such a way that the experiment was carried out above the “nose” in the TTT diagram¹⁵ at 907 K. Additionally, experiments at 860 and 750 K have been performed. The temperature at 860 K is at about the nose and 750 K is below the nose. The evaluation of the scattering of the onset time for crystallization is used to gain a deeper understanding of the crystallization mechanism.

Amorphous samples were prepared by arc melting the constituents (purity 99.5–99.995 at. %) in a titanium gettered argon atmosphere. The investigations were performed in high purity graphite crucibles. It was shown earlier that heterogeneous surface nucleation at the container walls does not effect the crystallization of the bulk Vit 1 sample.¹⁶ The graphite crucibles (machined from POCO Graphite, grade DFP-1, supplied by EDM Supplies Inc.) were heated treated at 10^{-4} Pa and 1300 K for 30 min prior to the experiment. The samples were embedded in the graphite crucible and inductively heated in vacuum of 10^{-4} Pa or in a titanium gettered argon atmosphere. The temperature was measured using a thermocouple (type K) with an accuracy better than ± 2 K. The control algorithm enables isothermal anneals within ± 0.5 K of a setpoint. Details of the experimental setup can be found elsewhere.¹⁷

Figure 1 shows a temperature-time profile for an isothermal undercooling experiment performed to investigate the crystallization behavior during repeated undercooling. The sample was first heated up to about 1200 K and kept there for 150 s. Subsequently, it was cooled with a rate of 10 K/s to the isothermal plateau. The crystallization of the melt during the isothermal treatment is detected by a temperature rise (recalescence), which has its origin in the release of the heat of fusion during crystallization at the solid/liquid interface. The inset in Fig. 1 reveals a closer view of the recalescence. Since at some temperatures, the isothermal time is comparable with the cooling time, a correction procedure for the isothermal time has been applied which is described in Ref. 18.

The results of the repeated undercooling experiments for

^{a)}Author to whom correspondence should be addressed; electronic mail: schroers@hyperfine.caltech.edu

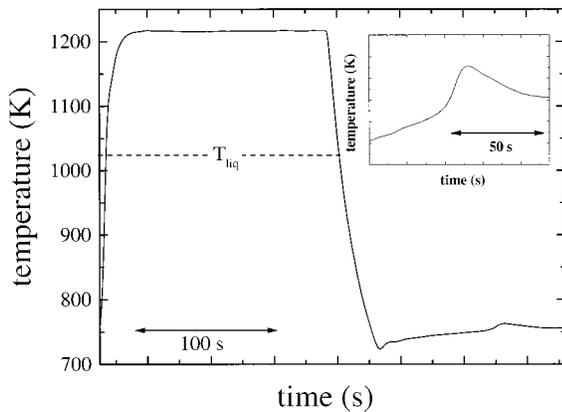


FIG. 1. Temperature-time profile for an undercooling experiment performed to investigate the crystallization behavior during repeated undercooling. The sample was heated for 150 s at about 1200 K. Subsequently, the Vit 1 melt was kept 276 K below the liquidus temperature of the alloy of $T_{\text{liq}} = 1026$ K for 200 s. The inset shows the detection of the onset of crystallization.

an isothermal temperature of 750 K are depicted in Fig. 2. A number of 31 cycles on the same sample have been performed. The time to reach crystallization (in the following, we will refer to it as the onset time) decreases with the cycle number but only little scatter of the onset times from cycle to cycle is observed. The scatter of the onset times for an isothermal temperature of 750 K from one cycle to the other is less than 3% with the exception of the first three cycles. The continuous decrease in the onset times with cycle number is attributed to a slight change of the melts composition. This is due to the fact that a ZrC layer forms between the crucible walls and the liquid. Therefore, the melt becomes depleted of Zr. The phase primarily crystallized at 750 K is a MgZn_2 -type Laves phase,¹⁵ which contains less Zr than the nominal composition of Vit 1. Consequently, the depletion of Zr shifts the composition of the melt towards the composition of the primarily solidified phase and increases nucleation and growth rate, and thus decreases the onset time.

For an isothermal temperature of 860 K, the undercool-

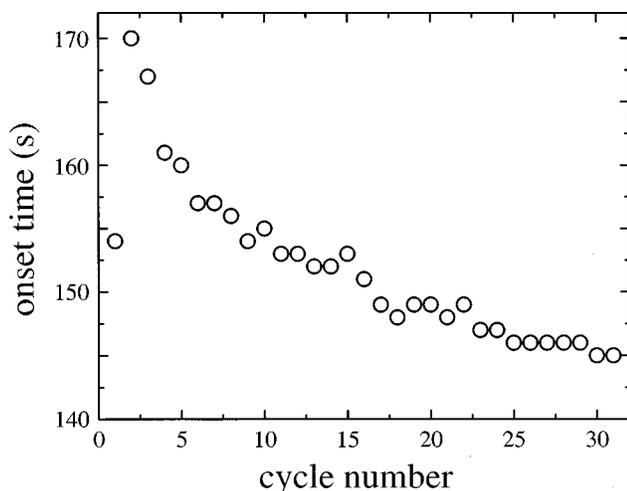


FIG. 2. Summary of 31 isothermal undercooling experiments performed at 750 K. The onset times correlate with the cycle number but only small scatter of the onset times from one cycle to the other is observed. The scatter from one cycle to the other is less than 3% except for the first three cycles. The continuous change of the composition of the melt due to the formation of a ZrC layer leads to a decrease of the onset time.

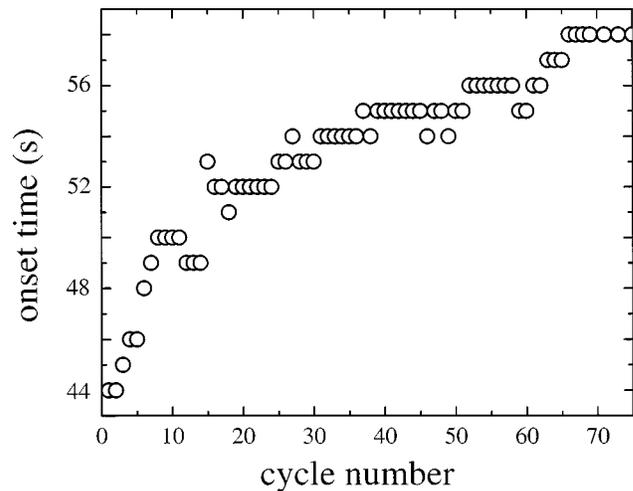


FIG. 3. Results of the repeated undercooling experiments for an isothermal temperature of 860 K. 75 cycles with the same sample have been performed. The onset times scatter less than 10% from one cycle to the other. The continuous change of the composition of the melt due to the formation of a ZrC layer leads to an increase of the onset time.

ing experiments were performed 75 times. The results are shown in Fig. 3. In contrast to the observations at an annealing temperature of 750 K, the onset time increases after 75 cycles by about 30%. After 31 cycles the onset time has increased already by about 20%. Scattering from cycle to cycle of the onset times is less than 10%.

Results of isothermal undercooling carried out at 907 K are shown in Fig. 4. The onset time scatters between 40 and 120 s. On average, the onset time increases with the cycle number. The scatter of the onset times from one cycle to the other is almost 100%. The reason that for the annealing temperatures of 907 and 860 K, the onset times increase with cycle number is that the composition shifts away from the composition of the phase that primarily crystallizes at these temperatures. In contrast to the case discussed for low temperatures, a Zr-rich Zr_2Cu -type phase primarily crystallizes.¹⁵ The depletion of the liquid alloy of Zr shifts the composition away from the composition of the Zr_2Cu -type phase formed at these temperatures. This slows

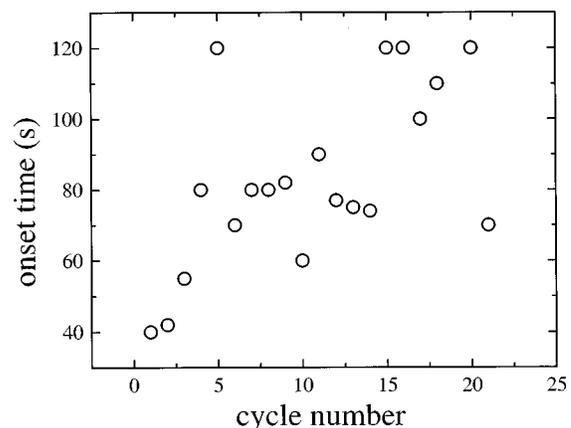


FIG. 4. Results of the repeated undercooling experiments for an isothermal temperature of 907 K. 20 cycles with the same sample have been performed. The onset times scatter between 40 and 120 s and show an average increase of the onset time with the cycle number. The continuous depletion of the melt of Zr is due to the formation of a ZrC layer, which leads to an increase of the onset time.

down the crystallization kinetics and increases the onset times.

In earlier work on $Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23}$,¹⁹ the onset time, τ , has been described according to Uhlmann²⁰ which depends on nucleation and growth rate:

$$\tau = \left(\frac{3x}{\pi I u^3} \right)^{1/4}. \quad (1)$$

Here, I denotes the nucleation rate, u the growth rate, and x the crystallized volume fraction. Nucleation is a statistical process that results from statistical density fluctuations in the liquid.¹¹ Therefore, a large fluctuation of the onset time of crystallization can be expected for a crystallization process that is governed by nucleation. This can be observed at the high temperature experiments carried out at 907 K where the growth rate u is large and the low nucleation rate is the controlling factor for crystallization. The statistical nature of the nucleation process is reflected in the large scattering of the onset times.

Equation (1) was used to describe the large onset time of the time-temperature-transformation diagram of Vit 1 assuming a steady state nucleation process and a diffusion limited growth rate.¹⁹ Parameters were chosen so that the calculated onset times give the best fit with the experimentally determined time-temperature-transformation diagram.¹⁹ Recent microstructure investigations on Vit 1 quenched from different temperatures after isothermal heat treatment suggest a continuous rise of the nucleation rate with decreasing isothermal annealing temperature.¹⁵ The observed microstructures are much finer than would be expected for steady state nucleation. The apparent contradiction of the sluggish crystallization kinetics and the fine microstructure, suggests a high nonsteady nucleation rate. It was shown earlier, that a topological transient time $\tau_{\text{trans}} = 6\pi a^3 \eta / kT$ according to Davies²¹ can be neglected on the time scale of the crystallization process for Vit 1.¹⁵ In this equation, a is an interatomic spacing, η the viscosity, T the absolute temperature, and k is Boltzmann's constant. One explanation for the nonsteady nucleation rate that increases with decreasing temperature is a decomposition process prior to crystallization. In the Cahn-Hilliard theory on spinodal decomposition,²² e.g., the length scale of the phase separated regions is given mainly 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 $\tau = -\lambda^2 / 4\pi^2 D$ (D : diffusion constant). If we assume that nucleation sets in if a certain amplitude is reached and a fixed number of nuclei are formed in one decomposed region, a strong increase of the nucleation rate and of the onset time can be expected with decreasing temperature. The decomposition process in this picture would be diffusion controlled and leads to a nucleation rate that is not constant but initially negligible but finally reaches a very large value. This process was suggested to control the crystallization mechanism, especially at

low temperature up to 860 K.^{8,15} The observation of a very reproducible onset time for crystallization up to a temperature of 860 K supports the suggestion of a well-defined diffusion controlled process that precedes copious nucleation.

In conclusion, repeated isothermal undercooling experiments on Vit 1 melts are presented. For a temperature of 907 K, the isothermal experiment was repeated 20 times. At 860 K, as many as 75 experiments were carried out and at 750 K, a number of 31 experiments were performed. While the scattering of the onset times from one cycle to another is about 100% for the experiments performed at 907 K, a significant lower scatter was observed for the experiments carried out at low temperatures. This indicates that the crystallization process at high temperatures is controlled by nucleation. The statistical nature of the nucleation process results in a large scattering. At lower temperatures, the onset times show very little scattering. This can be explained by the fact that in this temperature region crystallization is controlled by a diffusion controlled process that precedes nucleation.

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