CRYSTALLIZATION, MAGNETIZATION AND SCALING:
STUDY OF MAGNETIC RELAXATION IN AMORPHOUS $Fe_{83}B_{12}Si_5$

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We have investigated the crystallization of amorphous $Fe_{83}B_{12}Si_5$ by measuring the time evolution of the magnetization for isotherms 634 K $\lesssim$ T $\lesssim$ 666 K. The rate of growth of the crystalline phase increases with increasing temperature but all growth curves collapse to a universal function when the time is scaled by a factor $\tau(T)$. The shape of the universal curve, which is consistent with the Kolmogorov-Johnson-Mehl-Avrami model for nucleation and growth, suggests a diffusion-controlled growth mechanism for this amorphous system.

Scaling concepts have recently been applied to the description of the process of nucleation and growth at first order phase transformations |1-7|. It is the purpose of the present communication to demonstrate the success of the scaling concepts for the crystallization kinetics of magnetic metallic glasses.

Metallic glasses are nonequilibrium metallic solids with structural characteristics similar to frozen supercooled liquids, formed by very rapid solidification from the molten state |8|. The metastable glassy state is gradually transformed into a stable crystalline structure. The transformation and its kinetics are traditionally measured by calorimetry techniques which yield the activation energy of the process |9|. Another frequently used technique is based on measuring changes in electrical resistivity during the crystallization process |6|. In the present work we focus attention on a magnetic metallic glass $Fe_{83}B_{12}Si_5$ for which we study the crystallization process by measuring the time evolution of the magnetization at different isotherms. We find that the measured time t can be scaled by a single, temperature-dependent parameter $\tau(T)$ in such a way that all isothermal time evolution data of the magnetization collapse into a single, "universal" growth curve. The functional form of this curve implies, in the framework of generally accepted models |10|, a diffusion-controlled growth of the transformed volume.

Metallic glasses of $Fe_{83}B_{12}Si_5$ in the form of long ribbons were produced by the melt-spinning technique |8|. The measurement process is the following: One chip of the ribbon typically 12×1×0.075 mm³, is mounted in a vibrating sample magnetometer (VSM) at room temperature (RT) with the longest edge along the

magnetic field H. The magnetization M is measured versus temperature T up to a certain, previously defined temperature where temperature is stabilized to better than 0.5 K for 3-30 H during which frequent isothermal measurements of the magnetization are taken. A new specimen is used for each run and all magnetization data is normalized to its room temperature (RT) value.

Figure 1 exhibits typical M(T) data measured at field H = 250 Oe. The key points for understanding the complex structure exhibited in this Figure are the following: (1) Crystallization in $Fe_{83}B_{12}Si_5$ takes place in two stages |11|. At first α - (FeSi) phase is formed. Then, at higher temperatures, the crystallization is completed by formation of
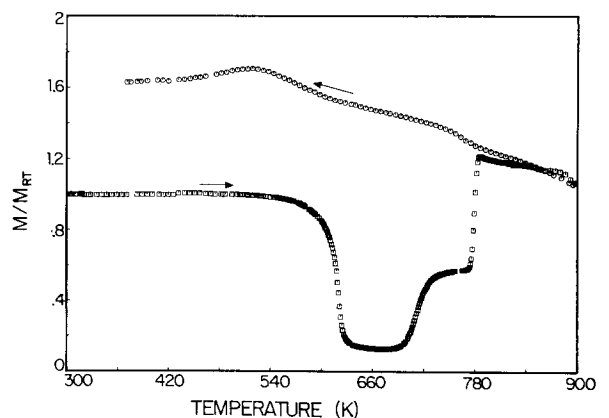
Figure 1   Temperature dependence of the magnetization for $Fe_{83}B_{12}Si_5$.

the Fe_3B phase. (2) The ferromagnetic-paramagnetic (FM-PM) transition temperature T_c^a for glassy materials is usually lower than the FM-PM transition temperature T_c^x for the equivalent crystalline material. Similarly the average magnetic moment for the ordered state is bigger than that of the disordered phase. With these points in mind, the interpretation of Figure 1 is straightforward. On warming up from RT, the magnetization features are characteristic of a glassy ferromagnet with $T_c^a \simeq 610$ K. Any increase in temperature above T_c^a should yield a paramagnetic Curie-Weiss drop in the magnetization of the paramagnetic untransformed volume. On the other hand, transformed α-(FeSi) crystalline volume contributes an increase in the magnetization. The competition between these two processes causes the apparent deviations from a Curie-Weiss behaviour and the shallow minimum around 650 K. As temperature increases, the crystallization rate is accelerated and the α-(FeSi) growth dominates the features of the M(T) curve. This is most apparent at $T_1 \simeq 700$ K where M increases sharply and then saturates, signalling saturation in the growth of this phase. Similarly, the abrupt rise at $T_2 \simeq 785$ K signals the growth of the Fe_3B phase. On further warming, the crystallization process ends and M(T) reaches a maximum, then drops towards the crystalline FM-PM transition. The crystallization process is, of course, irreversible hence the upper curve in Figure 1, which was taken during cooling. (The broad maximum observed around 500 K probably stems from crystalline anisotropy forces which, at low temperatures, rotate the magnetic moment away from the direction of the field thus causing a reduction in the measured moment. This maximum in the magnetization is washed out by fields of order 10 kOe).

In isothermal measurements of the magnetization in the amorphous phase, M increases with time due to growth of the ordered phase. We assume that the changes in the bulk magnetization are linear with the volume of the transformed sample, and define the fraction of volume transformed at time t by

$$X(t) = \frac{M(t) - M(0)}{M(\infty) - M(0)} \qquad (1)$$

where M(0) is the magnetization of the "pure" glassy material (i.e., before any transformation has occurred) and $M(\infty)$ is the magnetization of the bulk after the crystallization process of α-(FeSi) has reached saturation.

The time evolution of the magnetization measured in 30 Oe and normalized to its saturation value is exhibited in Figure 2 for five isotherms. The qualitative similarity between isotherms is apparent. Thus, for each isotherm we can experimentally find the time $\tau(T)$ for which dM/dt is maximum, and redefine the time scale of each isotherm to be t/τ. Following this procedure, all isotherms collapse into a single curve, as illustrated in Figure 3. The importance of this scaling procedure has been discussed at some length in Reference 5. We confine ourselves here to the temperature dependence of the scaling parameter τ. Figure 2 demonstrates the slowing down of the crystallization process as temperature is
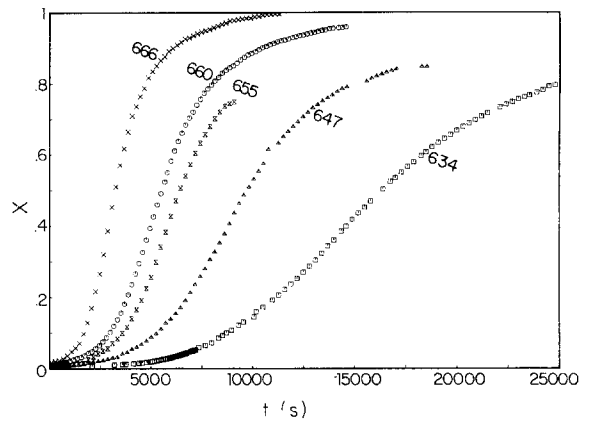

Figure 2   Time evolution of isothermal transformed volume. Numbers in this figure indicate absolute temperature value for the relevant data points.
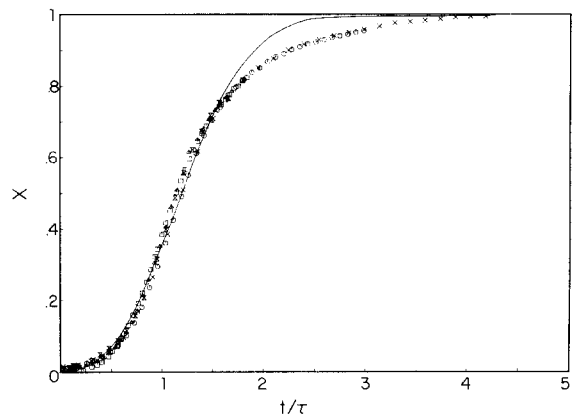

Figure 3   The isothermal curves of transformed volumes plotted in terms of the scaled time t/τ. All curves fall into a single universal line. The solid line is the curve calculated for the KJMA model |10| with the exponent n = 2.5. Symbols have the same meaning as in Fig. 2.

decreased. This slowing down is characteristic of relaxation phenomena of the glassy states and several models have been suggested for explaining experimental data. (A summary of most common models can be found in Reference 12). Arrhenius law

$$\tau^{-1} = \tau_o^{-1} \exp\left[-E_a/kT\right] \qquad (2a)$$

with $E_a = 1.85$ eV and $\tau_o^{-1} = 2.65 \times 10^{10} s^{-1}$ fits the data quite satisfactorily. This is demonstrated by the solid line in Figure 4. We stress, however, that the present data is limited to a relatively narrow temperature range and we are therefore not able to eliminate other possibilities. For example, a Vogel-Fulcher law

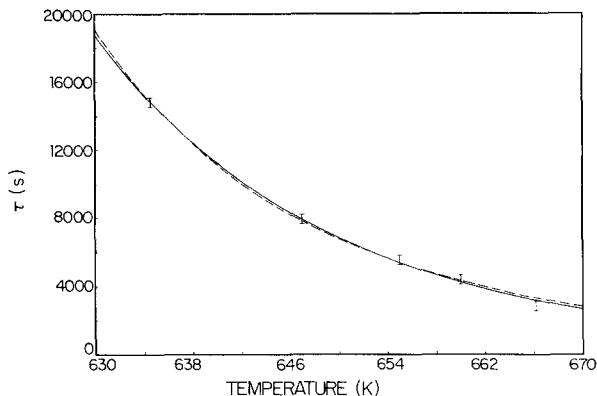$$\tau^{-1} = \tau_o^{-1} \exp\left[-E_a/k(T-T_o)\right] \qquad (2b)$$

Figure 4   The scaling parameter $\tau(T)$. The solid and broken lines are the results of   least-squares fits to Arrhenius and Vogel-Fulcher laws respectively. (See text for the relevant fitting parameters.)

which implies a critical-like slowing down, fits the data as well (broken line in Figure 4) with T_0 = 400 K and E_a = 0.27 eV.

Phenomenological models for nucleation and growth were suggested decades ago |10|. In these models, infinitesimal grains of crystalline phase which are randomly produced at a constant rate $\Gamma(T)$ are the nuclei for a transformed volume. The transformed volume is given by

$$X(t) = 1-\exp\left[-\Gamma\int_0^t V(t')dt'\right] \quad (3)$$

where $V(t')$ is the volume occupied by a grain at time t' after nucleation. Since $V(t') \propto (vt')^d$ where d is the growth dimensionality and v is the growth velocity, it is clear that

$$X(t) = 1-\exp\left[-(kt)^n\right] \quad\quad (4)$$

with n = d+1. Thus in the simplest approach one would expect n to be an integer. This is indeed the case in several of the recent experiments |5,7|, where n is found to be 4 and 3 respectively. The solid line in Figure 3 is our least-square fit of the data to Eq. (4) which yields a non-integer value n = 2.5±0.2. One interpretation of this result is to assume anisotropic velocity growth, i.e., effectively d is between 1 and 2. We do not feel, however, that this assumption is supported by independent structural information. We suggest a more plausible interpretation. For a diffusion-controlled process one expects $V(t') \propto (t')^{\frac{1}{2}d}$, and this yields for a 3d process n = 5/2. Our results therefore suggest that in $Fe_{83}B_{12}Si_5$ the growth of the stable phase is a diffusion-controlled process in 3 dimensions. This description is consistent with the activation energy of 1.85 eV |6,11| which is typical of atomic diffusion processes. It is also consistent with previous claims |11| that diffusion-controlled processes are expected for hypoeutectic (low metalloid) alloys.

Towards the final stages of this work we learned of an independent similar measurement and scaling analysis on an amorphous Fe-Ni-P system |7|. The gross features of both experimental data agree, although we find some subtle disagreements which will be discussed elsewhere. Also, we have completed a set of isothermal magnetic relaxation measurements for several fields. The effect of the field on the crystallization process will be published separately.

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