CRYSTALLIZATION AND NANOCRYSTALLIZATION KINETICS OF Fe-BASED AMORPHOUS ALLOYS

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ABSTRACT

In this work we describe crystallization kinetics as inferred from time-dependent magnetization studies and thermal analysis for an Allied Signal amorphous Fe-based METGLAS® 2605SA-1 alloy and a NANOPERM ($Fe_{88}Zr_7B_4Cu_1$) alloy. We illustrate and contrast several phenomena important to understanding crystallization kinetics in particular to the NANOPERM alloy system. In METGLAS® 2605SA-1 primary and secondary crystallization events are observed in differential scanning calorimetry data (DSC) at temperatures of 504 ^{0}C and 549 ^{0}C, respectively for data taken at a 10 ^{0}C/min scan rate. Both temperatures are greater than the Curie temperature of the amorphous alloy. For the NANOPERM alloy primary crystallization (as determined from differential thermal analysis (DTA)) occurs at 500 ^{0}C and secondary crystallization at 730 ^{0}C and M(t) at temperatures near the primary crystallization temperature is dominated (at short times < 1 hour) by the primary crystallization event. Using the Johnson-Mehl-Avrami equation for isothermal transformations and the Kissinger equation for constant heating transformations, we find corresponding models for the crystallization kinetics of the NANOPERM alloy.

INTRODUCTION

The understanding of the crystallization kinetics of magnetic amorphous alloys is of scientific interest as it represents a phase transformation occurring under extreme conditions far from equilibrium. The subject is also of technological interest because of the drastic deterioration of promising magnetic properties in amorphous alloys upon crystallization. Yet by controlling crystallization, amorphous alloys can be used as precursor starting materials for producing desirable fine microstructures. The mechanisms involved in the transformation from the metastable amorphous state to the stable crystalline state and their kinetics depend on various parameters, such as composition, concentration of nucleation sites, diffusion coefficients, and thermal history of the sample [1]. Crystallization kinetics is often determined from differential scanning calorimetry (DSC) where the onset of crystallization, the temperature of crystallization, and secondary crystallization events can all be revealed. In amorphous ferromagnets the magnetization can also change upon crystallization making it an appropriate probe of crystallization kinetics.

As an example of the manifestation of crystallization events in thermal analysis, Figure 1(a) illustrates a DSC scan and Figure 1(b) illustrates magnetization vs. time for a METGLAS® 2605SA-1 amorphous Fe-based sample. METGLAS® is a Fe-based magnetic alloy trademarked by Allied Signal. It has applications as sensors, high frequency cores, and transformers. Its characteristics include low core loss and the ability to be annealed for very high DC permeabilities. The DSC scan shows a primary crystallization and a secondary crystallization event at 504°C and 549^{0}C, respectively. Both of these crystallization events occur at temperatures above the Curie temperature of the amorphous alloy. As a result, the magnetization

Mat. Res. Soc. Symp. Proc. Vol. 577 © 1999 Materials Research Society

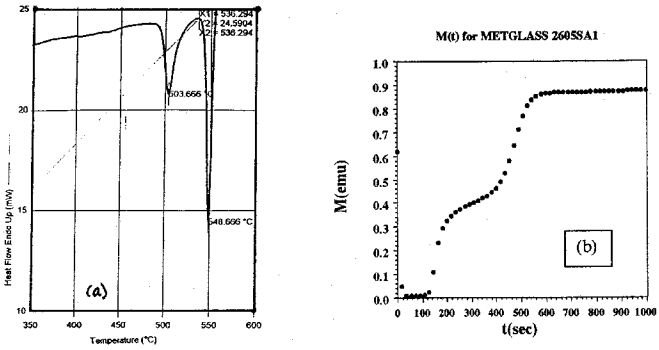


Figure 1: (a) DTA trace and (b) magnetization vs. time for Allied signal METGLAS alloy

is nearly zero below the crystallization temperature but increases upon primary and then again upon secondary crystallization.

NANOPERM is among one of the premiere soft magnetic materials of interest for AC magnetic and high temperature aircraft applications. It is a trademark for the amorphous alloy composition $Fe_{88}Zr_7B_4Cu_1$, which possesses nanocrystalline microstructure in its solid state. Its crystallization process occurs as:

$$\text{Amorphous I} \rightarrow \text{BCC } \alpha\text{-Fe} + \text{Amorphous II (777 K)} \rightarrow \alpha\text{-Fe} + Fe_3Zr \text{ (977 K)} \qquad (1)$$

Target properties for soft magnetic materials for high temperature applications include a working temperature of 500 °C, induction of greater than 2 Tesla, thermal stability at 600 °C for 5000 hours, and a core loss of 480 W/kg at 5 kHz and 500 °C. In alloys of Fe-Zr-B, Fe-Hf-B, and Fe-Nb-B, permeabilities of up to 3.2×10^5, core losses of 0.066 W/kg at 1 Tesla and 50 Hz, inductions of up to 1.63 Tesla, and magnetostrictions as low as -1×10^{-6} were observed [2].

This paper presents two methods for observing the crystallization kinetics of NANOPERM. The DSC is a standard way of measuring the heat flow versus temperature or time of the crystallization process. The heat flow, whether endothermic or exothermic, is related to the volume of the solid transformed. A novel way of measuring the crystallization process is by Vibrating Sample Magnetometry (VSM). This method observes the magnetization versus temperature or time. Figure 2 illustrates a characteristic of the NANOPERM material, which makes the VSM an excellent method for modeling crystallization kinetics. Since the Curie temperature T_c of the amorphous precursor phase is below the crystallization temperature, T_p, of NANOPERM, the alloy initially has zero magnetization when heated to its crystallization temperature. As the alloy crystallizes, the magnetization is directly proportional to the volume fraction of BCC α-Fe that forms. Thus the time dependence of the magnetization is directly proportional to the volume fraction transformed in the isothermal case.

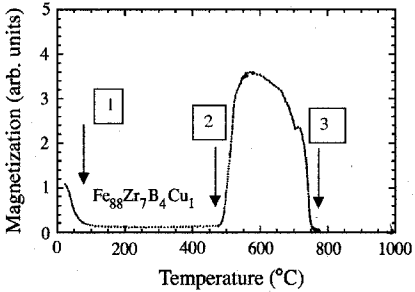


Figure 2: Magnetization vs. temperature for the NANOPERM alloy $Fe_{88}Zr_7B_4Cu_1$

EXPERIMENT

The Kissinger method is one way of quantifying the crystallization kinetics of a continuous heating process[8]. The Kissinger equation:

$$\ln (\alpha/T_p^2) = -Q/RT_p + \text{constant} \quad (2)$$

relates the natural log of the heating rate (α) divided by the square of the crystallization temperature (T_p) to the activation energy (Q) divided by the ideal gas constant (R) and T_p.

A Perkin-Elmer DSC was used to carry out crystallization occurring under continuous heating conditions. Melt-spun ribbons of NANOPERM were cut into pieces weighing approximately 10 mg, put into an aluminum dish, and heated from 50°C to 580°C at varying rates of 2°C/min, 5°C/min, 10°C/min, 20°C/min, 40°C/min and 60°C/min.

The Johnson-Mehl-Avrami (JMA) model is one common way of describing the crystallization kinetics of an isothermal process. JMA transformation kinetics are described by the equation:

$$X(t) = 1 - \exp(-kt^n) \quad (3)$$

Here the volume fraction transformed (X) as a function of time (t) is related by the exponential of the rate constant (k) and time (t) to a power of the morphology index (n). The value of the morphology index depends on the specific nucleation and growth mechanisms of the process. The rate constant can be written as:

$$k(T) = k_o \exp(-Q/RT) \quad (4)$$

where k_o is a rate constant coefficient and Q is the activation energy. The JMA equation can be rearranged into an Arrhenius-like equation, which is useful experimentally.

$$1/t_1 - 1/t_2 \sim -Q/R \exp(1/T_1 - 1/T_2) \quad (5)$$

A Lakeshore Cryogenics VSM was used to carry out crystallization occurring under isothermal conditions. Pieces from the same melt-spun ribbon of NANOPERM were placed into a quartz holder and subjected to a magnetic field of 500 Oersteds for at least one hour at varying temperatures of 490°C, 500°C, 520°C, 550°C, and 570°C.

Given the JMA model and the Kissinger model, it is of interest to compare important values such as activation energy (Q), which can be calculated from experimental data for each model. The morphology index (n) calculated from isothermal experiments on the VSM and the DSC can be compared also. These experimental values serve to describe the kinetics and provide new information to be added and compared to current literature published on magnetic amorphous alloys used for high temperature aircraft applications.

RESULTS AND DISCUSSION

The DSC for continuous heating showed one primary crystallization peak within the range of 50°C to 580°C. It is known that NANOPERM has a secondary crystallization peak at 704°C, but the DSC was limited to 600°C so it could not detect the second peak. At 2°C/min,

Figure 3: NANOPERM Recrystallization Using the DSC

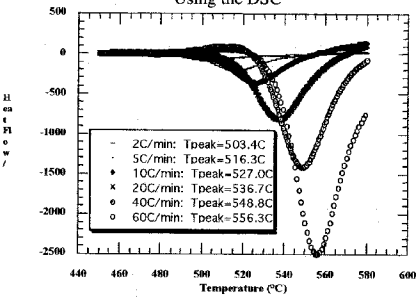
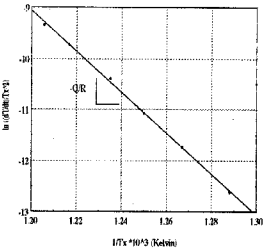


Figure 4: Kissinger Plot (DSC) Q = 3.45 eV



the experimental value for the crystallization peak temperature is 503 °C, which is comparable to the value found in literature. In Figure 3, T_p increases as the heating rate increases suggesting a dependence of the crystallization temperature upon the heating rate. This suggests that the Kissinger model of transformation can be used to relate the rate of heating to the activation energy and temperature. The activation energy from the Kissinger model was found to be 3.5 eV as shown in Figure 4. This is the fitted value for the slope of a Kissinger plot, where the regression coefficient was R^2=0.999.

The magnetization as determined by the volume fraction transformed (dX/dt) from isothermal heating on the VSM also indicates that the primary crystallization temperature is in the range of 500°C to 520°C. Figure 5(a) shows that at temperatures higher than the actual T_p, the magnetization reaches saturation within an hour. At temperatures below the actual T_p, saturation does not occur even after two hours. Figure 5(b) shows the inflection point as the maximum rate of volume transformed. The activation energy from isothermal heating was found to be 3.5 eV or 340 kJ/mole between 490-500°C. The activation energy values at higher

temperatures are observed to increase. This suggests that a sample heating correction may be important where the kinetics are fast. The activation energy for Fe self-diffusion in pure BCC α-Fe is 239.7 kJ/mole [7] at atmospheric pressure. Fe-diffusion, as the majority constituent, is thought to have an important contribution to the kinetics of primary crystallization.

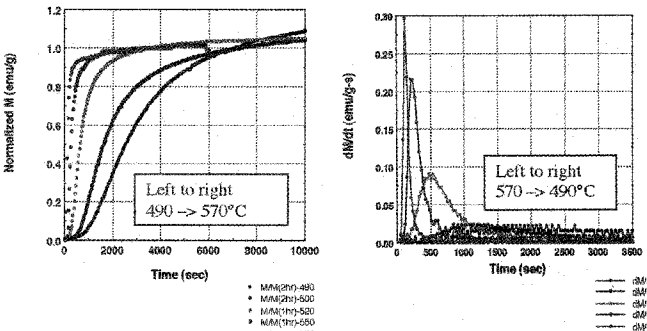


Figure 5: (a) Magnetization vs. Time (b) dM/dt during crystallization of a NANOPERM alloy

Table 1 shows the values of the morphology index calculated experimentally. When the morphology index, n=3/2, the reaction is three-dimensionally diffusion limited with immediate nucleation. This suggests that other mechanisms besides self-diffusion of α-Fe, perhaps contributed by the additional atoms, is occurring during the transformation. Values of Q and n are comparable to those published in literature on similar amorphous magnetic alloys. Table 2 indicates that kinetic analysis has been done either using the JMA model or the Kissinger model, but never both. However, for the similar alloy, FINEMET, experimental values of Q lie in the range of 3.5 - 4.0 eV as well, and the morphology index compares with n = 3/2.

	Volume Fraction Transformed	Morphology Index (n)
490°C	0.33 ± 0.15	1.95 ± 0.70
500°C	0.23 ± 0.08	1.37 ± 0.18
520°C	0.32 ± 0.07	1.66 ± 0.26
550°C	0.38 ± 0.10	2.19 ± 0.70
570°C	0.31 ± 0.17	1.86 ± 0.63

Table 1: Morphology Index of NANOPERM crystallization JMA kinetics

Alloy	Kinetic Analysis	Reference	Q (eV)	JMA index (n)	Experiment
FINEMET	JMA	L.K. Varga, Mat. Sci. and Eng. **A179/A180**, 567, (1994).	3.84-4.08		Vickers Hardness
FINEMET	Kissinger	Same as above	3.7-4.5		DSC
FINEMET	JMA	J. Bigot, J. Mag.Mag. Mat. **133**, 299, (1994).	4.3	n=1.5-2.0	Thermomagnetic gravimetry
FINEMET	Kissinger	C.F. Conde and A. Conde, Mat. Lett. **21**, 409, (1994)	3.8		DSC

Table 2: Activation Energies and Morphology Indices for FINEMET alloys

CONCLUSION

The time dependence of the magnetization is a direct and accurate probe for understanding NANOPERM crystallization kinetics. The DSC is a useful tool for characterizing crystallization temperatures of amorphous alloys. The Kissinger (constant heating) and Johnson-Mehl-Avrami (isothermal heating) models were compared, resulting in similar values for the activation energy. Values of activation energy and morphology index are comparable to those found in the literature for similar amorphous magnets.

ACKNOWLEDGMENTS

Effort sponsored by the Air Force Office of Scientific Research, Air Force Material Command, USAF, under Grant No. F49620-96-1-0454.

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