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Authors

Holland, T B
Loffler, J F
Munir, Zuhair A

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Crystallization of metallic glasses under the influence of high density dc currents

Troy B. Holland, Jörg F. Löffler, and Zuhair A. Munir^{a)}

Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616

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The effect of a dc current on the crystallization of Vit1A ($Zr_{42.6}Ti_{12.4}Cu_{11.25}Ni_{10}Be_{23.75}$) and PCNP ($Pd_{40}Cu_{30}Ni_{10}P_{20}$) metallic glasses was investigated. Samples were isothermally annealed with and without the current, at 623 and 577 K for the two glasses, respectively. Small-angle neutron scattering analyses showed that in the absence of a current, the annealed Vit1A samples were amorphous, but the imposition of a current enhanced the crystallization process, increasing both the size and volume fraction of the crystallites. Similar general observations were seen for the PCNP glass. Differential scanning calorimetry patterns of Vit1A samples indicate a lower thermal stability of samples annealed with a current. © 2004 American Institute of Physics.
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I. INTRODUCTION

The crystallization and phase separation processes of several bulk metallic glasses (BMGs) have been investigated recently by various techniques including differential scanning calorimetry (DSC),¹⁻³ x-ray diffraction (XRD),¹⁻³ electron microscopy,^{1,3,4} and small-angle neutron scattering (SANS).⁴⁻⁶ The role of diffusion in the decomposition and/or nucleation and growth phenomena near the glass transition temperature, T_g , has been characterized and models have been suggested.⁶ In all of these investigations crystallization and decomposition were effected by thermal means, i.e., by annealing the samples typically at temperatures between T_g and the crystallization temperature, T_{x1} . In prior work, Matyja and co-workers used pulsed heating with a current to effect crystallization. Since heating rate influences the crystallization temperature, the authors concluded that pulse heating creates a different condition than conventional heating.⁷ The difference in the observed final microstructure is, therefore, not directly related to the current but to the rate of heating. Microstructural evidence provided by the authors show that the structures of glasses heated by a pulsed current and those heated conventionally are qualitatively identical if the heating (and cooling) rates are taken into account.⁸ The extent, if any, to which decomposition and crystallization can be influenced by the nonthermal contributions of the current is of fundamental and practical interest and is the topic of this communication. The aim of this work is to investigate the role of high-density dc currents on the crystallization of two bulk metallic glasses (BMGs). The selected BMGs exhibit differing crystallization behaviors during isothermal annealing. One undergoes decomposition before crystallization on a nanometer length scale, while the other is thought to crystallize by classical nucleation and growth.⁹ Since bulk

metallic glasses have a high resistance to crystallization, the mechanism of devitrification can be studied on experimentally accessible time scales.

The imposition of a current has an influence on mass-transport processes and has been amply demonstrated in recent investigations.¹⁰⁻¹³ Of special relevance to the present work are recent studies on the effect of high-density currents on the nucleation and growth of intermetallic layers in diffusion couple experiments.^{12,13} It was shown that the imposition of dc currents increased the growth rate of the product layers significantly. Furthermore, these results indicated that the observed growth rate enhancement is not due to electromigration, implying the existence of other possible roles for the current. Other possible effects which the current can have include an increase in vacancy concentration, as has been observed by Asoka-Kumar,¹⁴ or an alteration of the diffusivity of the participating species, as has been proposed recently by Zhang *et al.* and Zhou *et al.*^{15,16}

Thus, the imposition of a high-density current can affect crystallization in two possible ways: by increasing the flux of the diffusing atoms or by lowering the energy barrier for devitrification. Takemoto *et al.* have recently investigated the effect of a dc current on the elastic properties of amorphous alloys and concluded that the current results in enhanced diffusion rates due to a cooperative diffusion mechanism.¹⁷ Although the detailed nature of the effect of the current on the atomic processes in amorphous alloys is not understood,¹⁷ the effect of the current on the crystallization process as a whole is an intriguing possibility and it is the subject of this communication.

II. PROCEDURE

The effect of a dc current on crystallization was investigated on two metallic glasses: $Zr_{42.6}Ti_{12.4}Cu_{11.25}Ni_{10}Be_{23.75}$ (Vit1A, a derivative of Vit1 that has the composition $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$) and $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (PCNP). The Vit1A samples were supplied by Howmet (Whitehall,

^{a)} Author to whom correspondence should be addressed; electronic mail: zamunir@ucdavis.edu

MI). The Pd-based glass was prepared by induction melting of Pd, Cu_{73.4}P_{26.6}, Ni₂P, and P in vacuum of 10⁻³ mbar inside a silica tube of 5 mm diameter, using B₂O₃ oxide flux, and subsequent water quenching. The constituents used were Pd metal pieces (99.95% purity), Ni₂P powder (99.5%), copper phosphorus shots (Cu:P; 85:15 wt %), and additional phosphorus lumps (99.999+%). Details of this synthesis are provided elsewhere.⁹ These metallic glasses have a critical cooling rate of 1 K/s (Vit1A) or less (PCNP). Their high thermal stability with respect to crystallization makes them ideal for such an investigation, in addition to the fact that these glasses have been well characterized in many other experiments. The glass transition temperatures, T_g for Vit1A and the PCNP glass are 628 and 582 K, respectively, for a heating rate of 10 K/min.⁷ Also, Vit1A was chosen instead of Vit1 because it has a higher thermal stability with $\Delta T = T_{x1} - T_g = 97$ K as compared to $\Delta T = 72$ K for Vit1.¹⁸

The Vit1A glass sample was sectioned into rectangular sheets with dimension of 3.25 × 3.80 × 0.5 mm. The PCNP glass was sectioned into circular disks of 0.5 mm thickness (5 mm diameter). All samples were annealed for 210 min with and without a dc current. The current densities utilized were 0, 810, and 1620 A/cm² for the Vit1A samples and 0, 509, and 1018 A/cm² for the PCNP samples.

To separate the intrinsic effects of the current from that of Joule heating, we utilized a specially designed apparatus. It consists of two copper electrodes surrounded by a cylindrical furnace made from tantalum sheets cut in serpentine design. Details of the apparatus are given in previous publications.^{12,13} The metallic glass samples were placed between the electrodes, and dc currents with the indicated densities were applied. Copper foils, placed between the samples and the electrodes, were added to ensure good contact. When a current is applied, the temperature of the sample increases, due to Joule heating up to a steady-state value for that current density. Regardless of the level of current applied, this temperature was always lower than the desired annealing temperatures, 623 K for the Vit1A and 577 K for the PCNP sample. The annealing temperatures were chosen to be ~5 K below the laboratory T_g values of the two glasses. The temperature stabilized from Joule heating is ~5 min, after which the furnace was activated to achieve the target annealing temperature. The annealing temperatures of 623 and 577 K were controlled to within approximately ±2 K of the target. Temperatures were measured using a shielded and grounded type K thermocouple placed in direct contact with the center of the samples. The thermocouple was calibrated by determination of the melting points of Zn and Sn.

III. RESULTS AND DISCUSSION

After annealing, the samples were analyzed by small-angle neutron scattering (SANS) at the Paul Scherrer Institute (Villigen, Switzerland). Using a wavelength of $\lambda = 6$ Å and sample-detector distances of 1.8 and 8 m, and 20 m in the case of PCNP, the Q range covered was 0.1–3.5 nm⁻¹ for Vit1A and 0.03–3.5 nm⁻¹ for PCNP ($Q = 4\pi \sin \theta/\lambda$, with $\theta =$ half the scattering angle).

Figure 1 shows the SANS results of Vit1A after different

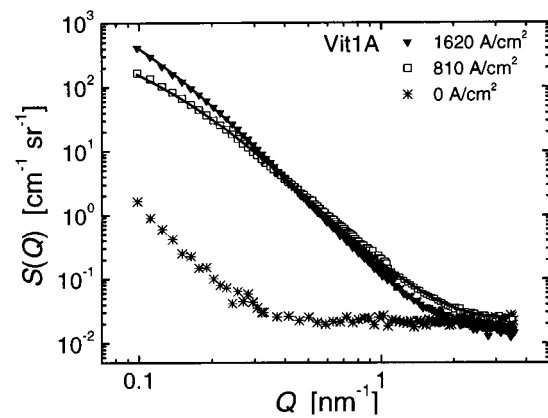


FIG. 1. SANS intensity data of Vit1A annealed for 210 min at 623 K without dc current (stars) and with dc currents of densities 810 and 1620 A/cm², respectively. The straight lines are fits to the data, assuming the SANS scattering to occur from spherical particles with log-normally distributed diameters.

annealing treatments in a log-log presentation. After annealing the Vit1A sample for 210 min at 623 K in the absence of a dc current, only a very small scattering contribution in the low Q region is observed. This shows that the sample is essentially amorphous after this heat treatment and still homogeneous in composition. In contrast, samples annealed at the same conditions, but under the influence of a current, exhibit a strong scattering contribution in SANS. This shows that the imposition of a current has a strong influence on phase separation and/or crystallization in metallic glasses.

For an analysis of the SANS data, we assumed the SANS intensity to occur from spherical particles with log-normally distributed particle diameters. In this case, the scattering intensity is

$$S(Q, R) = (\Delta \eta)^2 \int_R F_p^2(Q, R) V_p(R) N(R) dR, \quad (1)$$

where $\Delta \eta$ is the scattering length density contrast, F_p is the particle form factor, $V_p(R)$ is the volume of the (spherical) particle, and $N(R)dR$ is the incremental volume fraction in the size interval between R and $R + dR$. Assuming a log-normal distribution, $N(R)$ can be parametrized by the amplitude A , width σ , and position R_0 of the log-normal distribution (see, for example, Ref. 19). The three parameters are obtained from fitting (see solid lines in Fig. 1) the scattering curves with Eq. (1). From the resulting log-normal distribution, a (volume-weighted) particle diameter is obtained which is 10 nm for the sample annealed with a current of 810 A/cm², and 20 nm for the sample annealed with a current of 1620 A/cm². The scattering invariant $\bar{Q} = \int_0^\infty Q^2 S(Q) dQ$ of the sample annealed with 1620 A/cm² is ~25% larger than that of the sample annealed with 810 A/cm². This shows that the larger current affects not only the size of the crystallizing particles, but also the overall volume fraction of the crystalline phase.

Figure 2 shows the SANS results of PCNP after annealing for 210 min at 577 K. As for Vit1A, annealing near the glass transition only leads to a small scattering contribution at low Q when no dc current is applied. In contrast, anneal-

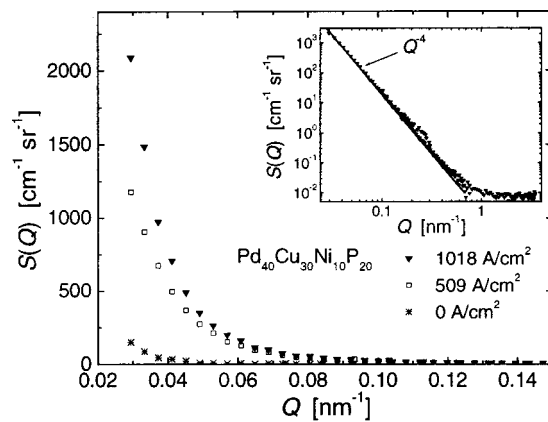


FIG. 2. SANS intensity data of $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ annealed for 210 min at 577 K without dc current (stars) and with dc currents of densities 509 and 1018 A/cm^2 , respectively. The log–log representation in the inset illustrates the Q^{-4} dependence of the scattering intensity.

ing at the same conditions leads to a stronger SANS intensity when the process was carried out in the presence of an external dc current. The log–log presentation of the sample annealed with a current of 1018 A/cm^2 (inset) shows that the SANS intensity mainly follows a Q^{-4} law. The Porod exponent of -4 indicates that most of the structure information is at very low Q , outside the resolution of the present SANS experiment. Although no information can be given about the crystal size (only that it is larger than 100 nm), it is clear that the crystallization behavior changes when an external current is applied.

To obtain further information about the crystallization behavior, we performed differential scanning calorimetry (DSC) on samples processed and annealed in the same way as the SANS samples. Figure 3 shows DSC scans performed on Vit1A with a heating rate of 10 K/min. While the glass transition with $T_g = 625 \pm 3$ K is the same within experimental error for the different annealing conditions, the crystallization behavior is obviously different. The sample annealed without external current shows crystallization peaks centered at 731 and 737 K, with the main crystallization peak being at

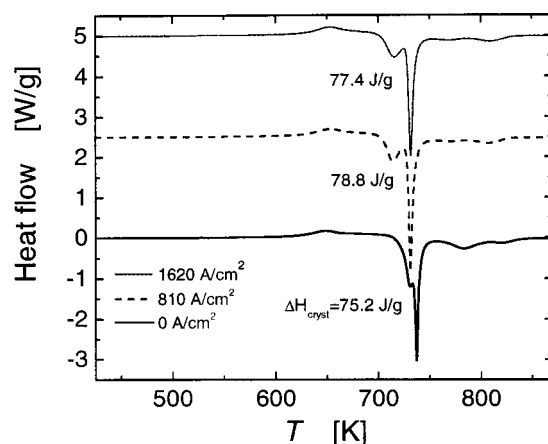


FIG. 3. DSC scans performed with a heating rate of 10 K/min on Vit1A annealed for 210 min at 623 K without dc current and with dc currents of densities 810 and 1620 A/cm^2 , respectively.

737 K. In contrast, the samples annealed with a current show a lower thermal stability. The crystallization peaks are now centered at 715 and 731 K, with the main crystallization peak being at 731 K. Furthermore, the overall crystallization enthalpy of the sample annealed with a current of 1620 A/cm^2 is 77.4 J/g, which is slightly smaller than that of the sample annealed with 810 A/cm^2 ($\Delta H_{\text{cryst}} = 78.8$ J/g). Similar observations are made in the PCNP case. While the glass transition does not change, modifications in the crystallization behavior are observed.

The present results show that current has a strong influence on the crystallization behavior of BMGs. When the alloy Vit1A, for example, is annealed with a dc current, the SANS intensity increases by two to three orders of magnitude compared to that of a sample annealed in the absence of a current. Such an increase in scattering intensity can only be explained by crystallization of a significant volume fraction of the amorphous phase. Indeed, the average crystal size determined from SANS is 10 nm for a current density of 810 A/cm^2 and doubles when the current density is doubled. Furthermore, the crystal volume fraction increases by 25% after increasing the current density from 810 to 1620 A/cm^2 .

Interestingly, the samples annealed with current show no interference maxima, which is in contrast to SANS results on samples annealed in the absence of current. In Vit1A, for example, interference maxima, implying a phase separation process on the nanometer scale, occur in a temperature range between 603 and 643 K, when the samples are annealed for 15 h.¹⁸ Only at temperatures above 643 K do these interference maxima vanish. Apparently, in the presence of the current the glass crystallizes without a prior decomposition process on the nanometer scale. Thus, the current has a similar effect on crystallization as an increase in temperature.

While the sample annealed without current still shows the DSC pattern of an as-prepared Vit1A sample (for the latter, see Ref. 18), the DSC patterns of the samples annealed with current exhibit different patterns (Fig. 3). The patterns show that the thermal stability of the samples annealed with a current is lower, with the first crystallization peak being at 715 K. Interestingly, the DSC patterns are now reminiscent of those of as-prepared Vit1. This would imply that a (Zr,Be)-rich crystalline phase has formed, shifting the composition of the remaining glassy matrix towards that of Vit1. The phase Be_2Zr is known to be one of the stable primary phases that precipitate in Be-bearing Zr-based bulk metallic glasses. The crystallization enthalpy calculated from the area of the crystallization peaks decreased slightly when the current density is increased. This shows that additional crystallization occurs when the current density is increased, in agreement with our SANS data.

As observed earlier,⁹ PCNP forms micrometer-sized crystals even in the deeply undercooled liquid regime and does not decompose on the nanometer scale. In this case, SANS can only give qualitative results on the current-induced crystallization behavior. The strong increase of the SANS intensity at low Q shows, however, that the current also influences the crystallization in Pd-based alloys.

IV. CONCLUSIONS

In summary, we have shown that current has a large influence on the volume fraction and crystal size in metallic glasses. High current densities facilitate crystallization. This may be a kinetic effect, since the current may increase the flux of the diffusing atoms, or a thermodynamic effect, since the current may increase the free volume in the glass. For certain applications, composites consisting of crystals in a glassy matrix are preferred over monolithic glass. The disadvantage of low plasticity of glassy alloys can, for example, be alleviated by the production of two-phase microstructures consisting of a ductile reinforcement material in a glassy matrix.²⁰ In many cases, crystallization results, however, in the formation of intermetallic phases that lead to an embrittlement of the alloy (see, for example, Ref. 21). The present method of crystallization by using high dc currents may be an alternative way of obtaining nano- or microcomposites with desired properties.

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¹B. S. Murty, D. H. Ping, K. Hono, and A. Inoue, *Acta Mater.* **48**, 3985 (2000).

- ²V. I. Tkatch, A. M. Grishin, and S. I. Khartsev, *Mater. Sci. Eng., A* **337**, 187 (2002).
- ³Z. Zhang, L. Xia, R. J. Wang, B. C. Wei, M. X. Pan, and W. H. Wang, *Appl. Phys. Lett.* **81**, 4371 (2002).
- ⁴S. Schneider, P. Thiyagarajan, and W. L. Johnson, *Appl. Phys. Lett.* **68**, 493 (1996).
- ⁵U. Gerold, A. Wiedenmann, U. Keiderling, and H. J. Fecht, *Physica B* **234–236**, 995 (1997).
- ⁶J. F. Löffler and W. L. Johnson, *Appl. Phys. Lett.* **76**, 3394 (2000).
- ⁷H. Matyja and A. Zaluska, *Philos. Mag.* **61**, 701 (1990).
- ⁸T. Kulik, D. Bucka, and H. Matyja, *J. Mater. Sci. Lett.* **12**, 76 (1993).
- ⁹J. F. Löffler, W. L. Johnson, W. Wagner, and P. Thiyagarajan, *Mater. Sci. Forum* **343–346**, 179 (2000).
- ¹⁰Z. A. Munir, *Z. Phys. Chem. (Munich)* **207**, 39 (1998).
- ¹¹Z. A. Munir, *Mater. Sci. Eng., A* **287**, 125 (2000).
- ¹²N. Bertolino, J. Garay, U. Anselmi-Tamburini, and Z. A. Munir, *Scr. Mater.* **44**, 737 (2001).
- ¹³N. Bertolino, J. Garay, U. Anselmi-Tamburini, and Z. A. Munir, *Philos. Mag. A* **82**, 969 (2002).
- ¹⁴P. Asoka-Kumar, K. O'Brien, K. G. Lynn, P. J. Simpson, and K. P. Rodbell, *Appl. Phys. Lett.* **68**, 406 (1996).
- ¹⁵W. Zhang, M. L. Sui, K. Y. Hu, D. X. Li, X. N. Guo, G. H. He, and B. L. Zhou, *J. Mater. Res.* **15**, 2065 (2000).
- ¹⁶Y. Zhou, W. Zhang, M. Sui, D. Li, G. He, and J. Guo, *J. Mater. Res.* **17**, 921 (2002).
- ¹⁷R. Takemoto, M. Nagata, and H. Mizubayashi, *Acta Mater.* **44**, 2787 (1996).
- ¹⁸J. F. Löffler, P. Thiyagarajan, and W. L. Johnson, *J. Appl. Crystallogr.* **33**, 500 (2000).
- ¹⁹J. F. Löffler, W. Wagner, and G. Kostorz, *J. Appl. Crystallogr.* **33**, 455 (2000).
- ²⁰C. C. Hays, C. P. Kim, and W. L. Johnson, *Phys. Rev. Lett.* **84**, 2901 (2000).
- ²¹J. F. Löffler, *Intermetallics* **11**, 529 (2003).