

CRYSTALLIZATION PATHWAY
IN THE BULK METALLIC GLASS $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$

S. SCHNEIDER¹, P. THIYAGARAJAN², U.GEYER¹ and W.L. JOHNSON³ *Materials Res Soc Pr*
¹I. Phys. Institut and SFB 345, Universität Göttingen, 37073 Göttingen, Germany 455, 1997
²Argonne National Laboratory, Argonne, IL 60439, USA
³California Institute of Technology, Pasadena, CA 91125, USA

RECEIVED
OCT 13 1999
CIN/PR

OSTI

Abstract

A new family of multicomponent metallic alloys exhibits an excellent glass forming ability at moderate cooling rates of about 10K/s and a wide supercooled liquid region. These glasses are eutectic or nearly eutectic, thus far away from the compositions of competing crystalline phases. The nucleation of crystals from the homogeneous amorphous phase requires large thermally activated composition fluctuations for which the time scale is relatively long, even in the supercooled liquid. In the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy therefore a different pathway to crystallization is observed. The initially homogeneous alloy separates into two amorphous phases. In the decomposed regions, crystallization probability increases and finally polymorphic crystallization occurs. The evolution of decomposition and succeeding primary crystallization in the bulk amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy have been studied by small angle neutron. Samples annealed isothermally in the supercooled liquid and in the solid state exhibit interference peaks indicating quasiperiodic inhomogeneities in the scattering length density. The related wavelengths increase with temperature according to the linear Cahn-Hilliard theory for spinodal decomposition. Also the time evolution of the interference peaks in the early stages is consistent with this theory. At later stages, X-ray diffraction and transmission electron microscopy investigations confirm the formation of nanocrystals in the decomposed regions.

Introduction

A unique family of multicomponent metallic glasses exhibits an excellent glass forming ability and a wide supercooled liquid region [1,2]. Their high thermal stability against crystallization has opened for the first time the opportunity to investigate thermodynamic and atomic transport properties in the supercooled liquid state of a metal [3-5]. Since these glasses exhibit high reduced glass temperatures, nucleation of crystalline phases from the homogenous multicomponent systems is suppressed to a great extent. Instead, their thermal stability is probably limited by alternative processes. We have reported phase separation with succeeding polymorphic nanocrystallization in the decomposed regions occurring in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ earlier [6,7]. This paper gives additional information on small-angle neutron scattering (SANS) investigations of the

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

time- and temperature evolution of the decomposition process. In particular, we show that above a critical temperature crystallization behavior changes significantly.

Experimental

Amorphous samples were prepared from a mixture of the pure elements by induction melting on a water-cooled silver boat under Ti gettered Ar atmosphere. The ingots were remelted in a silica tube with an inner diameter of 10mm and then quenched with a cooling rate of about 10K/s. For the SANS investigations disks with a thickness of 2.7mm were cut from the these rods and isothermally annealed at temperatures between 608K and 673K for different times. The SANS measurements were carried out at the Intense Pulsed Neutron Source at Argonne National Laboratory.

Results and Discussion

Figure 1 shows SANS data of an as prepared $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy and samples isothermally annealed for different times at 613K. The data for the as- prepared sample only depict background scattering, for the aged ones broad maxima appear. For early stages a maximum of scattering intensity is observed at $q=0.05\text{\AA}^{-1}$, indicating spatially correlated chemical inhomogeneities in the amorphous state.

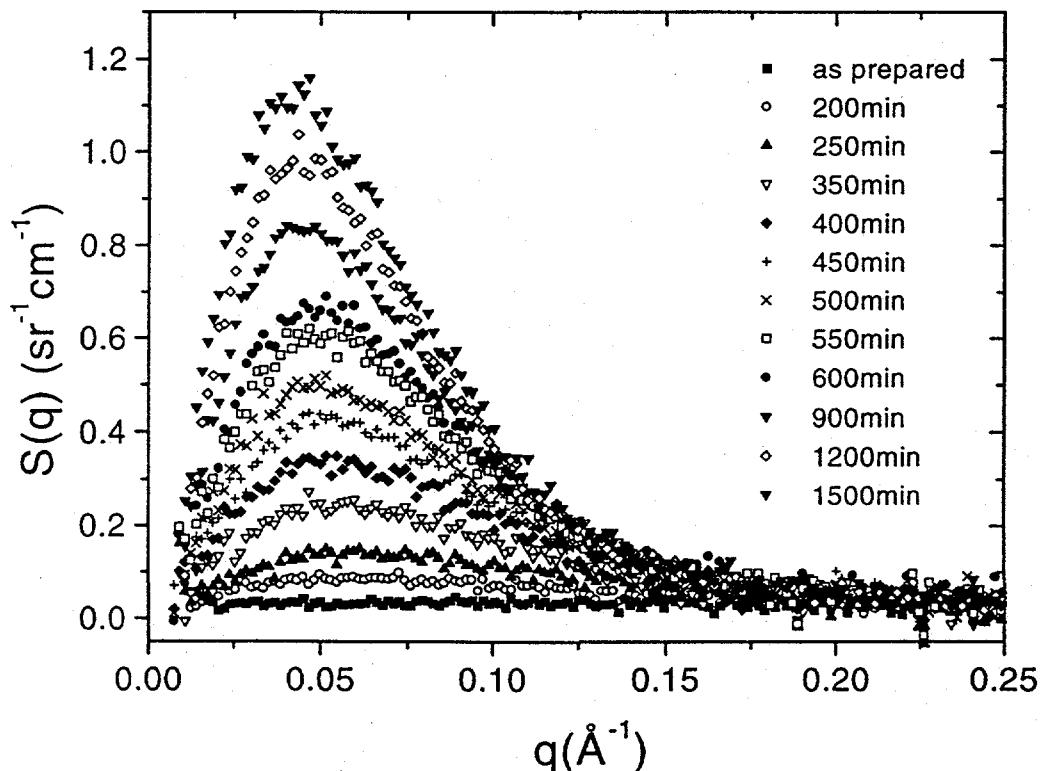


Fig. 1: SANS data of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy aged at 613K for different times.

The wavelength corresponding to the maximum intensities is about 125Å. The position of q_{\max} shifts slightly towards smaller values with increasing annealing duration suggesting a coarsening of the chemical inhomogeneities during isothermal heat treatment. We assume a decomposition process being responsible for the scattering contrast [7]. From estimations of the increase of scattering intensity and ^{62}Ni isotope experiments we conclude that the initial increase is mainly associated with a decomposition process of Ti and Be atoms [8]. Two different time laws are involved in the process (Fig. 2). First, the scattering cross section for a constant q value grows exponentially during annealing, and the interference peak shifts slightly to lower q . In the very early stages of decomposition the slowly rising exponential time law mimics an incubation time of about 150min at 613K. During that time no changes in structure or composition are observed by SANS or thermal analysis [7]. Then the scattered intensity increases very rapidly. Later a much slower process overtakes control on the increase of scattering cross section. It is not clear yet whether the time dependence for the later stages is also exponential or a power law.

Cahn's theory of spinodal decomposition gives such an exponential growth law [9] but does not predict a shift of the interference peak to lower q with increasing time. Such a behavior is proposed in [10]. During phase separation, composition and short-range atomic order [11] in at least one of the decomposed regions approach those of a competing crystalline phase and the nucleation probability increases rapidly. Due to the exponential time law of decomposition and the rapid increase of nucleation probability with composition and structural changes, the onset of polymorphic nucleation of nanocrystals in the Ti-rich regions is very sharp [7]. The second slower time law probably represents the growth of the periodically arranged nanocrystals.

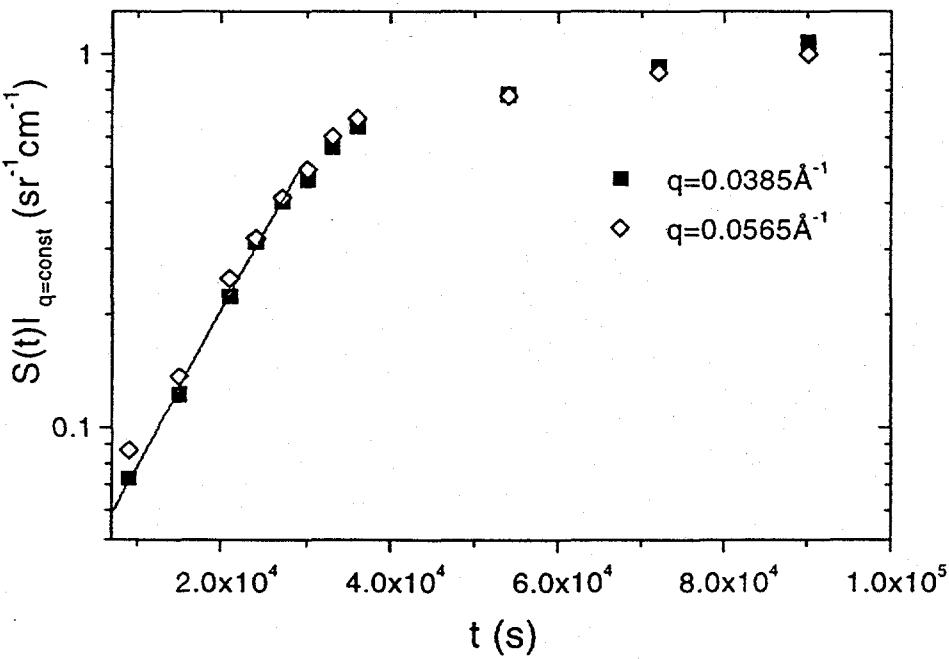


Fig. 3: Annealing time dependence of the scattering cross section of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ samples aged at 613K for two wavenumbers near the maximum.

The crystal size calculated from Guinier analysis increases slightly from 20Å to 40Å after annealing for 600min and 1500min, respectively. The growth of the nanocrystals is related to Ni diffusion [8]. In this stage no further shift of the scattered intensity maximum to lower q is detected. This suggests a primary crystallization of the Ti rich regions occurring in the maxima of the composition wave and the pinning of a certain wavelength in the early stages of decomposition.

SANS spectra of samples annealed at different temperatures below and above the glass transition are shown in Fig. 3. All spectra exhibit an interference peak indicating a quasiperiodic arrangement of scattering inhomogeneities. The peak positions shift to lower q values with increasing temperature and the related wavelengths increase from about 125Å to some 350Å. The wavelengths follow a relation $\lambda^2 \propto T$ (Fig. 4), as suggested by Cahn's linear theory of spinodal decomposition [9]. The extrapolated coherent spinodal temperature T_{cs} for $\lambda \rightarrow \infty$ is about 670K. In accordance with that, samples annealed at 673K do not exhibit an interference peak but a strong increase of intensity with decreasing q , indicating thermally activated crystallization without precursory decomposition of the amorphous matrix. The change of crystallization behavior might be related to the rapidly decreasing viscosity which destabilizes the periodic composition modulation with increasing temperature.

From the SANS data there is evidence that a miscibility gap opens in the undercooled liquid region near the glass transition temperature. Related to the limited mobility in this temperature range the as prepared samples do not show any indications of decomposition with respect to Ti. But during isothermal annealing below the miscibility gap a Ti composition wave can grow with time. Its wavelength is determined by the aging temperature. Samples annealed above the coherent spinodal temperature do not develop quasiperiodic composition waves and do not exhibit SANS interference peaks.

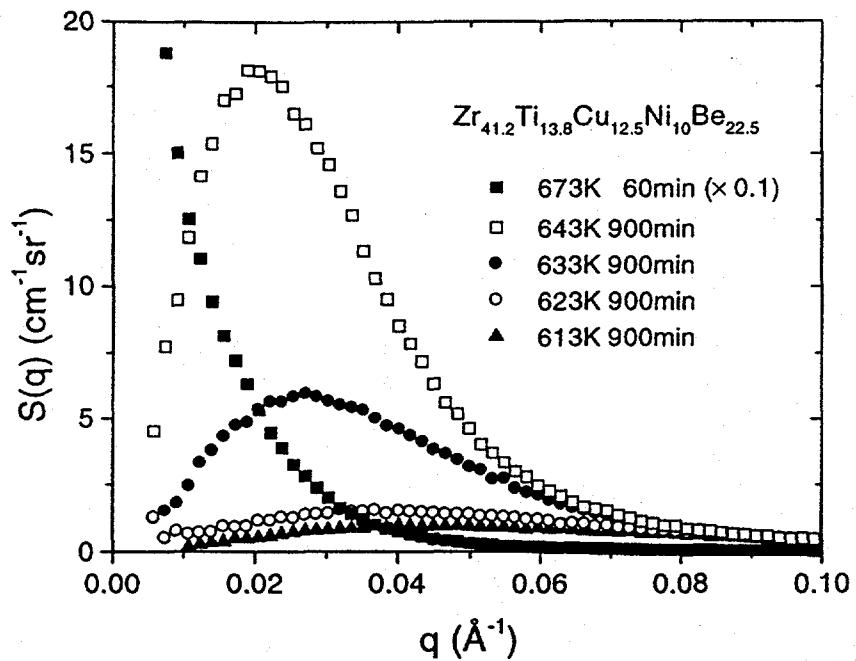


Fig.3: SANS data of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ samples annealed for 900min at different temperatures.

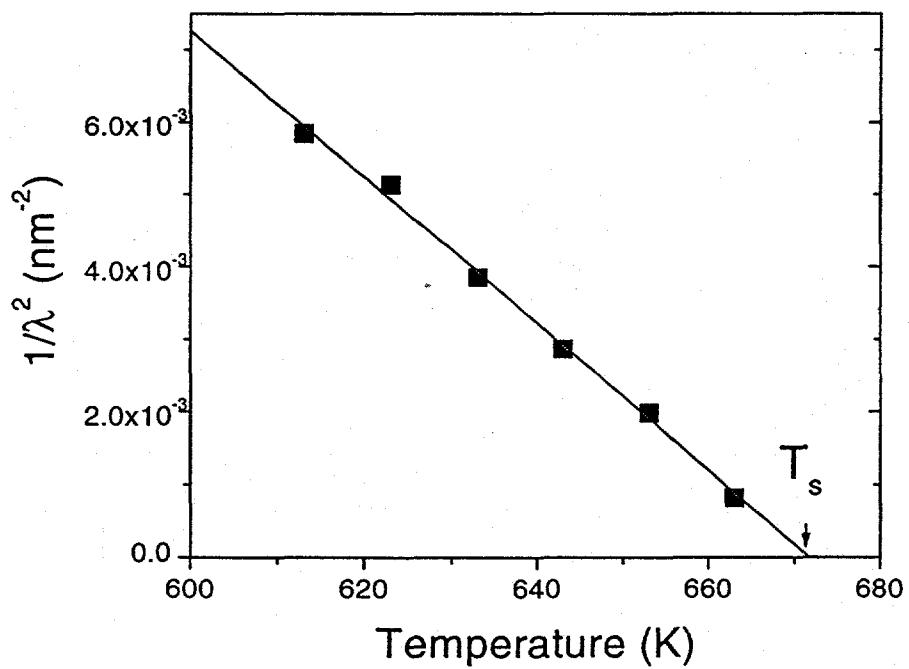


Fig. 4: Temperature dependence of the composition wavelength in $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$

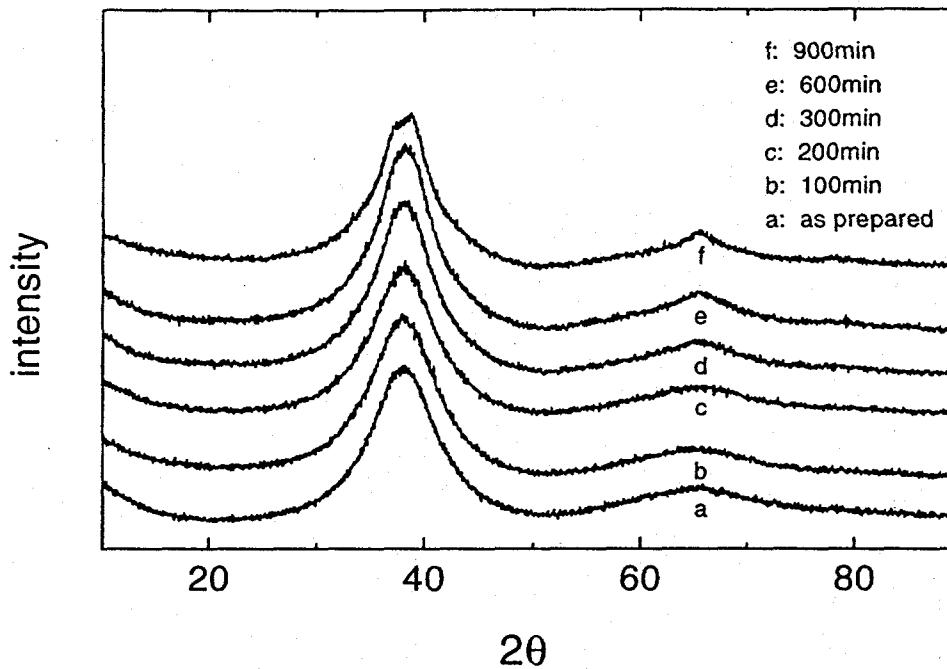


Fig. 5: Wide angle X-ray spectra of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ samples annealed at 613K for different times.

X-ray diffraction analysis of samples annealed at 613K does not show crystalline contributions for aging times below 400min (Fig. 5). After 600min, when according to Fig. 2 the first stage of decomposition is finished and a slower time law is observed, a slight sharpening of the second diffraction maximum occurs. At this time cross section TEM clearly reveals the existence of nanocrystals in the sample. After 900min of heat treatment also the first diffraction peak indicates the nanocrystals.

Summary

Our analysis of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ samples isothermally annealed near the glass transition temperature of the alloy reveals a chemical decomposition, succeeded by the formation of nanocrystals. The decomposition process shows several properties typical for spinodal decomposition: a quasiperiodic arrangement of chemical inhomogeneities, an exponential growth with time of the amplitude of the composition wave, and a critical temperature beyond which the crystallization behavior changes to a different mechanism. With progressing phase separation composition and short-range atomic order in one of the decomposed regions approach those of a competing crystalline phase. Thus the interfacial energy between a crystalline nucleus and the amorphous matrix decreases with time and the nucleation probability increases rapidly.

Acknowledgments

Financial support from the Department of Energy (Grant No. DE-FG03-86ER45242) and the DFG via SFB 345 is gratefully acknowledged. This work has benefited from the

use of IPNS which is funded by U.S. DOE under Contract No. W-31-109-ENG-38 to the University of Chicago.

References

- [1] A. Inoue, T. Zhang and T. Masumoto, Mater. Trans. JIM **31**, 177 (1990)
- [2] A. Peker and W.L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993)
- [3] R. Busch, Y.J. Kim and W.L. Johnson, J. Appl. Phys., **77**, 4039 (1995)
- [4] U. Geyer, S. Schneider, Y. Qiu, et al., Phys. Rev. Lett. **75**, 2364 (1995)
- [5] R. Rambousky, M. Moske and K. Samwer, Mat. Sci. Forum **179-181**, 761 (1995)
- [6] S. Schneider, U. Geyer, P. Thiyagarajan, and W.L. Johnson, Mat. Sci. Forum, in press (1997)
- [7] S. Schneider, P. Thiyagarajan, and W. L. Johnson, Appl. Phys. Lett. **68**, 493 (1996)
- [8] S. Schneider et al., to be published
- [9] E.L. Huston, J.W. Cahn, and J.E. Hilliard, Acta Met.,**14**, 1053 (1966)
- [10] J.S. Langer, M. Baron, and H.D. Miller, Phys. Rev. **A11**, 1417 (1974)
- [11] S. Schneider and P. Schaaf, to be published

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.