Characterization of Bulk Metallic Glasses with the Atom Probe

M. Miller, K. Russell, P. Martin, R. Busch, W. Johnson

► To cite this version:

M. Miller, K. Russell, P. Martin, R. Busch, W. Johnson. Characterization of Bulk Metallic Glasses with the Atom Probe. Journal de Physique IV Proceedings, 1996, 06 (C5), pp.C5-217-C5-222. 10.1051/jp4:1996535 . jpa-00254414

HAL Id: jpa-00254414

<https://hal.science/jpa-00254414>

Submitted on 1 Jan 1996

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Characterization of Bulk Metallic Glasses with the Atom Probe

M.K. Miller, K.F. Russell, P.M. Martin, R. Busch* and W.L. Johnson*

Microscopy and Microanalytical Sciences Group, Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6376, U.S.A.

** W.M. Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, CA 91125, U.S.A.*

Abstract. An atom probe field ion microscopy survey of several bulk metallic glasses including the zirconium-based glasses $Zr_{55}Al_{10}Ni_5Cu_{30}$, $Zr_{46.25}Ti_{8.75}Cu_{7.5}Ni_{10}Be_{27.5}$, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$, and $Zr_{52.5}Ti_5Al_{10}Cu_{17.9}Ni_{14.6}$, together with two non-zirconium-based glasses $Ti_{34}Zr_{11}Cu_{47}Ni_8$, and $Mg_{65}Cu_{25}Y_{10}$ is presented. Non random distribution of solute was observed in all these glasses and crystalline regions were observed in the $Ti_{34}Zr_{11}Cu_{47}Ni_8$ and $Zr_{55}Al_{10}Ni_5Cu_{30}$ materials.

1. INTRODUCTION

Many different types of amorphous alloys have been produced since their introduction in the 1960's. Initially, high cooling rates of more than 10^4 Ks⁻¹ were required to produce amorphous samples and the thickness of the samples was limited to less than ~ 150 μ m. Recently, several families of multicomponent alloys such as La-Al-Ni [1], Zr-Al-Ni-Cu [2], and Zr-Ti-Cu-Ni-Be [3] have been developed that exhibit an extremely high glass-forming ability compared to conventional metallic glasses. In these bulk metallic glasses (BMG), the nucleation of crystalline compounds is suppressed and an amorphous material is formed if relatively slow cooling rates of between 1 and ~ 100 Ks⁻¹ are used. In some of these materials, bulk samples up to several centimeters in extent have been produced. The characterization of these new types of bulk metallic glasses have recently received much attention due to their properties. However, little is known about the local compositional inhomogeneities in these materials.

Several field ion microscopy and atom probe studies have been performed on the Fe- and Ni- and Pd-based metallic glasses. These studies have been reviewed previously [4]. In this paper, an atom probe field ion microscopy survey of several of these new generation bulk metallic glasses is presented.

2. EXPERIMENTAL

The bulk metallic glasses examined in this study included the zirconium-based glasses $Zr_{55}Al_{10}Ni_5Cu_{30}$, $Zr_{46.25}Ti_{8.75}Cu_{7.5}Ni_{10}Be_{27.5}$, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ and $Zr_{52.5}Ti_5Al_{10}Cu_{17.9}Ni_{14.6}$ [5] together with two non-zirconium-based glasses $Ti_{34}Zr_{11}Cu_{47}Ni_8$ [6], and $Mg_{65}Cu_{25}Y_{10}$. All these bulk metallic glasses were examined in the as-prepared state.

Suitable blanks were cut from the interior of the bulk material to minimize the possibility of surface effects. Field ion specimens of the zirconium-based glasses were electropolished with the standard two stage procedure [4, 7] with a mixture of 25% perchloric acid in glacial acetic acid in stage 1 and 2% perchloric acid in 2-butoxyethanol in stage 2. The copper-based $Ti_{34}Zr_{11}Cu_{47}Ni_8$ material was electropolished in a mixture of 2% perchloric acid in 2-butoxyethanol. The magnesium-based $Mg_{65}Cu_{25}Y_{10}$ alloy was electropolished in a mixture of 20% nitric acid in methanol at $\sim 50^\circ$ C.

Neon was used as the imaging gas for all the materials apart from the $Mg_{65}Cu_{25}Y_{10}$ alloy for which argon was used due to its lower evaporation field. Atom probe analyses were performed in the ORNL energy-compensated atom probe with a specimen temperature of either 35K for the $Mg_{65}Cu_{25}Y_{10}$ alloy or 60-70K for

the other alloys. A pulse fraction of 20% and a pulse repetition rate of > 770 Hz were used for most of the analyses. In these analyses, the 30 u peak was assigned to the more abundant $^{90}\text{Zr}^{3+}$ isotope rather than the $^{60}\text{Ni}^{2+}$ isotope. This will have a small effect of the zirconium and nickel results in the statistical analyses of the atom probe data since the natural abundance of the $^{90}\text{Zr}^{3+}$ isotope ranged from 7 to 21 times that of the $^{60}\text{Ni}^{2+}$ isotope in the zirconium and nickel containing alloys.

3. RESULTS

Initial field ion microscopy of the materials revealed that sharp (1 to 5 kV) field ion specimens were prone to failure both during DC field evaporation and also on the application of the field evaporation pulse. In contrast, extensive periods of field evaporation were possible with high voltage specimens (>15 kV). Therefore, the low temperature resistivities of these materials were measured to determine if the amplitudes of the applied voltages were being significantly attenuated. The resistivities of these materials are relatively high compared to most pure metals and are similar to some high resistance alloys. Unlike most metals, these bulk metallic glasses exhibit a small increase in resistivity on cooling to cryogenic temperatures. For example, in the $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ material, the resistivity increases from $199 \mu\Omega \text{ cm}$ at 270 K to $206 \mu\Omega \text{ cm}$ at 50 K.

A series of field ion micrographs of all the as-prepared materials is shown in Fig. 1. Most regions of the materials exhibited a random distribution of spots that is characteristic of an amorphous alloy. However, it should be noted that the absence of a well defined ring structure in the field ion image is not proof of an amorphous material as the ring structure is not always well defined in alloys with high solute contents. In the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ materials clear evidence of regions of different contrast was observed, as shown in Fig. 2. The presence of these regions indicate that some phase separation or crystallization had occurred. In both cases, well defined ring structures were observed and indicated that the precipitates were crystalline. The size of the brightly-imaging precipitates in the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ were less than ~ 4 nm in diameter. The precipitates in the $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ material were up to ~ 20 nm in diameter. These estimates were based on their maximum extent in the field ion micrograph since the normal persistence size measurement cannot be performed in amorphous alloys.

Figure 2: Field ion micrographs of (a) the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ alloy and (b) the $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ alloy in the as-prepared condition. Both micrographs show evidence of crystalline precipitates.

A series of random area analysis composition profiles through the materials are shown in Fig. 3. Although several fine scale fluctuations are evident in these composition profiles, it is difficult to determine whether these fluctuations are due to compositional variations in the material or due to the sampling process. Therefore, the distribution of all the solutes in these materials was investigated by applying several statistical methods to the atom-by-atom data.

The atom-by-atom data chain was examined for ABA, ABBA, ABBBA, etc. sequences. The probability of detecting a chain containing n B atoms is given by [8] $P(n) = p^n q^2$ or $D(n) = N P(n)$, where p is the probability of collecting a B atom, $q = 1 - p$, and N is the number of atoms in the chain. The significance of the experimental value is given by $(D_{\text{experimental}}(n) - D_{\text{expected}}(n)) / \sigma$, where the σ was taken as $\sqrt{N p^n q^2}$. The Johnson and Klotz (J&K) method was also applied to the data. The J&K ordering parameter, θ , was determined from the number of AB and BB pairs in the data chain [9]. The significance is given by $(\theta - 1) / \sigma$,

Figure 3: Random area analysis composition profiles of

a) $\text{Zr}_{46.25}\text{Ti}_{8.75}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$

b) $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$

c) $\text{Zr}_{52.5}\text{Ti}_{5}\text{Al}_{10}\text{Cu}_{17.9}\text{Ni}_{14.6}$

d) $\text{Zr}_{57}\text{Nb}_{5}\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$

e) $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_{5}\text{Cu}_{30}$

f) $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ and

g) $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_{8}$.

Table 1. Summary of the statistical analyses of the atom probe data for the materials analyzed.

$Zr_{46.25}Ti_{8.75}Cu_{7.5}Ni_{10}Be_{27.5}$	Zr	Ti	Cu	Ni	Be
ABA	-1.07	-0.41	0.25	0.24	-0.27
ABBA	0.53	1.50	-0.55	-1.29	-0.73
ABBBA	0.83	<u>-2.57</u>	-0.96	1.10	-0.42
ABBBBA	-0.64		1.33	0.87	0.51
ABBBBBBA	0.50				0.75
ABBBBBBBA					<u>2.05</u>
ABBBBBBBBA	0.52				0.06
J&K (θ)	<u>1.06</u>	<u>1.09</u>	<u>1.02</u>	<u>1.04</u>	<u>1.07</u>
Significance	<u>6.13</u>	1.03	0.22	0.48	<u>3.23</u>
Mean Sep. Sig.	<u>749.1</u>	-0.64	-1.26	0.18	<u>-2.38</u>

$Zr_{55}Al_{10}Ni_5Cu_{30}$	Zr	Al	Ni	Cu
ABA	1.84	1.46	-0.36	0.18
ABBA	0.83	<u>-2.59</u>	1.02	-1.14
ABBBA	-0.62	0.15		0.51
ABBBBA	-0.28	-0.22		1.13
ABBBBBBA	0.24			0.02
ABBBBBBBA	0.19			
ABBBBBBBBA	-0.15			0.73
J&K (θ)	<u>0.99</u>	<u>0.82</u>	<u>1.14</u>	<u>1.01</u>
Significance	-0.62	<u>-2.47</u>	0.60	0.28
Mean Sep. Sig.	-0.09	-1.12	1.10	1.27

$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	Zr	Ti	Cu	Ni	Be
ABA	0.41	0.56	-0.31	1.26	0.21
ABBA	0.85	-0.79	0.52	<u>-2.42</u>	0.22
ABBBA	0.06	0.09	-0.44		-0.14
ABBBBA	-0.38	-0.58	0.09		0.17
ABBBBBBA	-0.74	0.46	0.65		
ABBBBBBBA	0.54				
ABBBBBBBBA	0.30				
J&K (θ)	<u>0.99</u>	<u>0.95</u>	<u>1.03</u>	<u>0.79</u>	<u>1.00</u>
Significance	-0.57	-0.89	0.61	<u>-2.51</u>	-0.10
Mean Sep. Sig.	-0.25	0.25	1.11	-0.87	-0.44

$Mg_{65}Cu_{25}Y_{10}$	Mg	Cu	Y
ABA	-0.86	<u>-4.11</u>	1.69
ABBA	-0.46	<u>2.49</u>	-0.27
ABBBA	-0.58	0.33	<u>-4.85</u>
ABBBBA	1.02	0.11	-1.33
ABBBBBBA	-0.02	0.53	
ABBBBBBBA	0.40	0.65	
ABBBBBBBBA	0.58	1.75	
J&K (θ)	<u>1.01</u>	<u>1.08</u>	<u>0.88</u>
Significance	<u>2.33</u>	<u>4.44</u>	<u>-2.89</u>
Mean Sep. Sig.	0.96	<u>3.27</u>	-0.42

$Zr_{52.5}Ti_5Al_{10}Cu_{17.5}Ni_{14.6}$	Zr	Ti	Al	Ni	Cu
ABA	1.35	-0.10	1.56	1.12	0.54
ABBA	1.17	-0.13	<u>-2.56</u>	-1.33	-0.64
ABBBA	-0.70	0.59	-0.10	-0.82	-0.25
ABBBBA	0.73	0.67	<u>-2.27</u>	-0.58	1.14
ABBBBBBA	-1.22		0.69	0.45	-1.51
ABBBBBBBA	0.27				
ABBBBBBBBA	-1.66				0.69
J&K (θ)	<u>0.98</u>	<u>1.04</u>	<u>0.89</u>	<u>0.92</u>	<u>0.98</u>
Significance	-1.05	0.43	<u>-2.76</u>	<u>-2.16</u>	-0.88
Mean Sep. Sig.	-0.35	1.00	-0.62	0.08	0.55

$Ti_{34}Zr_{11}Cu_{47}Ni_8$	Cu	Ti	Zr	Ni
ABA	<u>-2.57</u>	-0.34	-0.51	0.11
ABBA	-0.24	-0.14	1.43	-1.17
ABBBA	0.31	-0.19	-1.09	1.65
ABBBBA	1.58	0.89		
ABBBBBBA	0.92	0.97		
ABBBBBBBA	-0.09	<u>-2.44</u>		
ABBBBBBBBA	-1.03	-0.71		
J&K (θ)	<u>1.08</u>	<u>1.05</u>	<u>1.09</u>	<u>1.04</u>
Significance	<u>6.59</u>	<u>3.28</u>	1.20	0.36
Mean Sep. Sig.	<u>10.50</u>	<u>10.22</u>	<u>3.67</u>	1.07

$Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$	Zr	Nb	Al	Ni	Cu
ABA	<u>2.65</u>	0.11	1.25	0.87	0.51
ABBA	1.61	0.26	<u>-2.77</u>	-1.10	0.55
ABBBA	-0.19	<u>-2.99</u>	0.84	-1.00	-0.38
ABBBBA	0.24	0.60	0.22	0.25	-1.20
ABBBBBBA	<u>-2.67</u>				<u>-2.15</u>
ABBBBBBBA	-1.29				0.89
ABBBBBBBBA	-0.04				
J&K (θ)	<u>0.96</u>	<u>0.99</u>	<u>0.86</u>	<u>0.90</u>	<u>0.99</u>
Significance	-1.92	-0.15	<u>-2.53</u>	-1.68	-0.32
Mean Sep. Sig.	0.10	-0.01	-0.36	0.55	0.41

Negative significances in the Markov chain (ABA) results indicate less experimental observations than predicted.

Underlined values indicate a deviation from random behaviour.

entries indicate that no chains of that length were experimentally detected.

where the σ is the standard error. Solute clustering was also investigated by applying the mean separation method. In this method, the variances of the experimental and expected mean separation of B atoms are compared [10, 11]. The results from these analyses are summarized in Table 1. Blank entries in this table indicate that no chains of that length were experimentally detected. In each method, significances greater than 2 or less than -2 indicate non-random behavior.

The Markov chain (i.e., ABA sequences etc.) analyses indicated that there was some evidence of a non-random distribution of some of the solutes in all the materials examined. The Johnson and Klotz ordering parameter for Al in all three Al containing materials ($\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$, $\text{Zr}_{57}\text{Nb}_5\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$ and $\text{Zr}_{52.5}\text{Ti}_5\text{Al}_{10}\text{Cu}_{17.9}\text{Ni}_{14.6}$) was statistically significantly less than 1 indicating that chemical short range ordering had occurred in these materials. Solute clustering was detected in the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$, $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ and $\text{Zr}_{46.25}\text{Ti}_{8.75}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ materials by both the mean separation and the Johnson and Klotz method.

The atom probe composition profile data were also examined for cosegregation and antisegregation of the alloying elements with the use of pairwise contingency tables [4]. The use of contingency tables provides a statistical method to examine the atom probe data for longer scale decompositions compared to the atom-by-atom Markov chain methods. Evidence of antisegregation of Zr and Be and to a lower extent of Zr and Ti were found in both the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ and $\text{Zr}_{46.25}\text{Ti}_{8.75}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ materials, antisegregation of Zr and Cu was found in the $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$, $\text{Zr}_{57}\text{Nb}_5\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$ and $\text{Zr}_{52.5}\text{Ti}_5\text{Al}_{10}\text{Cu}_{17.9}\text{Ni}_{14.6}$ materials, antisegregation of Cu and Ti was found in the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ material, and antisegregation of Mg and Cu and of Mg and Y was found in the $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ material.

4. CONCLUSIONS

This preliminary survey of seven of the new generation of bulk metallic glasses has demonstrated that suitable specimens of these materials may be fabricated and subsequently characterized with the atom probe field ion microscope. Non-random distribution of solute was observed in all these glasses and fine-scale crystalline regions were observed in the $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ and $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ materials.

Acknowledgments

This research was sponsored by the Division of Materials Sciences, U. S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., by the U. S. Department of Energy, Grant No. DEFG-03-86ER45242 and by the Alexander von Humboldt Foundation through the Feodor Lynen Program. This research was conducted utilizing the Shared Research Equipment (SHaRE) User Program facilities at Oak Ridge National Laboratory.

References

- [1] Inoue A., Zhang T. and Masumoto T., *Mater. Trans. JIM*, **31** (1991) 425.
- [2] Zhang T., Inoue A. and Masumoto T., *Mater. Trans. JIM*, **32** (1991) 1005.
- [3] Peker A. and Johnson W. L., *Appl. Phys. Lett.*, **63** (1993) 2342.
- [4] Miller M. K., Cerezo A., Hetherington M. G. and Smith G. D. W., *Atom Probe Field Ion Microscopy*, (Oxford University Press, Oxford, England, 1996).
- [5] Lin X.H., *J. Appl. Phys.*, **78** (1995) 6514.
- [6] Lin X.H., PhD thesis, California Institute of Technology, 1996.
- [7] Miller M. K. and Smith G. D. W., *Atom Probe Microanalysis: Principles and Applications to Materials Problems*, (Material Research Society, Pittsburgh, 1989).
- [8] Tsong T. T., McLane S. B., Ahmad M. and Wu C. S., *J. Appl. Phys.*, **53** (1982) 4180.
- [9] Johnson C. A. and Klotz J. H., *Technometrics*, **16** (1974) 483.
- [10] Hetherington M. G. and Miller M. K., *J. de Phys.*, **48-C6** (1987) 559.
- [11] Hetherington M. G. and Miller M. K., *J. de Phys.*, **49-C6** (1988) 427.