



Available online at www.sciencedirect.com



Acta Materialia 61 (2013) 6911-6917



www.elsevier.com/locate/actamat

# Structural property comparison of Ca-Mg-Zn glasses to a colloidal proxy system

R.C. Kramb<sup>a,b,\*</sup>, L.T. Ward<sup>c</sup>, K.E. Jensen<sup>d</sup>, R.A. Vaia<sup>a</sup>, D.B. Miracle<sup>a</sup>

<sup>a</sup> AFRL/RX Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433, USA

<sup>b</sup> UES, Dayton, OH 45432, USA

<sup>c</sup> Department of Material Science and Engineering, Northwestern University, Evanston, IL 60201, USA <sup>d</sup> Department of Physics, Harvard University, Cambridge, MA 02138, USA

Received 25 March 2013; received in revised form 26 July 2013; accepted 2 August 2013 Available online 29 August 2013

#### Abstract

We compare various structural properties of the Ca–Mg–Zn ternary metallic glass system at compositions  $Ca_{60}Mg_XZn_{40-X}$  (where X = 25, 20, 15, 10) to a colloidal proxy system containing "Red", "Green" and "Blue" particles at the corresponding compositions  $R_{60}G_XB_{40-X}$ . The methacrylate-based polymer colloid particles have the same relative radius ratio as their atomic counterparts and surface electrostatic charges are employed to mimic atomic interactions. The structures of these colloidal suspensions are investigated through laser scanning confocal microscopy, with each particle species labeled with red, green and blue fluorescent dyes. We find qualitative agreement with number densities and many characteristics of the partial radial distribution functions and partial coordination numbers between the atomic and colloid systems. In general, coordination numbers agree within experimental error. Total coordination numbers for Red-centered clusters are found to be slightly higher than the corresponding Ca-centered clusters, while Green- and Blue-centered clusters have slightly fewer neighbors than Mg- and Zn-centered clusters. These and other differences are noted and possible explanations of these are offered, as well as ways that the proxy system might be improved to more accurately reproduce the structure of the metallic system.

© 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Metallic glasses; Colloids; Amorphous materials; Ternary glasses

# 1. Introduction

Ternary metallic glasses such as Ca–Mg–Zn exhibit unique and potentially useful properties [1–6]. However, the structure of these systems has rarely been systematically studied. To date, the only comprehensive study of glass structure of a ternary metallic glass to include all partial radial distribution functions (PRDFs) and partial coordination numbers ( $Z_{ij}$ ) over a range of compositions is found in Ref. [1] and includes four compositions: Ca<sub>60</sub>Mg<sub>X</sub>Zn<sub>40-X</sub> (where X = 25, 20, 15, 10). The major reason for this dearth of information on ternary glass structure is the enormous effort needed to define each individual species contribution to the structure. For example, to obtain the PRDF curves for all six pair combinations in Ca–Mg–Zn (i.e. Ca–Ca, Ca–Mg, Ca–Zn, Mg–Mg, Mg–Zn, and Zn–Zn), one needs to do six independent scattering experiments for each composition studied. In addition to experimental difficulties, reverse Monte Carlo (RMC) simulations are required in order to obtain information about the locations of atoms in the system [7]. RMC simulations are often limited to less than 10,000 total atoms, leading to statistical uncertainty in the results. These difficulties have hindered large-scale experimental studies of the structure of ternary (and higher complexity) metallic glasses.

<sup>\*</sup> Corresponding author at: AFRL/RX Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433, USA.

E-mail address: ryan.kramb.ctr@wpafb.af.mil (R.C. Kramb).

<sup>1359-6454/\$36.00 © 2013</sup> Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.actamat.2013.08.003

To eliminate many of the drawbacks of experimental work with metallic glasses, we have developed a proxy system using micron diameter polymer colloid particles that can be used to study glass structure. Important properties of the colloidal system, such as particle shape, relative particles size, interparticle forces and particle packing density, are tuned to match those of the atomic metallic glass system of interest to ensure the proxy system remains relevant for investigating metallic glass structure. This colloidal proxy concept was first developed for a binary system based on Cu-Zr metallic glasses, and showed success in reproducing many structural features of the original metallic system over a wide range of compositions [8]. Agreement was found both with experimental diffraction studies and with molecular dynamics (MD) simulations. In this paper, we present a similar technique based on the Ca-Mg-Zn ternary metallic glass system. Batches of particles are synthesized from a combination of methacrylate polymers in three distinct sizes that closely match the diameter ratio of Ca:Mg:Zn [1]. Each species of particles is modified with a unique surface electrostatic charge, infused with one of three distinct fluorescent dyes (referred to here as Red (R), Blue (B) and Green (G) particles), and suspended in a solvent that matches the refractive index of the copolymers. The colloid suspensions are densified via centrifugation, and samples are imaged in three dimensions by acquiring a sequential series of two-dimensional image stacks with confocal microscopy. Analysis of the images results in particle location information for greater than 10,000 particles per image stack, and this information is used to calculate PRDFs, Voronoi tessellation cells and coordination numbers. We note that this experimental system is significantly larger than simulation studies and thus does not suffer from the finite-size effects seen in simulations.

While the choice of using a positive or negative electrostatic charge was straightforward for the binary system ("A" type particles positive, "B" type negative), the choices for the ternary system are more complicated since there are three choices for each type of particle (positive, negative or neutral). Using the paper by Senkov and colleagues as a guide [1], we chose to incorporate a positive charge on the Red particles (Ca atom proxy), and a negative charge on the Green and Blue particles (Mg and Zn proxies). The reason for this is that the description used to describe the overall structure of clusters in the Ca-Mg-Zn system is "a mixture of Mg- and Zn-centered clusters, with Ca dominating in the first coordination shell of these clusters". In this way, we ensure that there is a preference for forming G- and B-centered clusters with R in the first shell with our proxy system particles.

## 2. Experimental

#### 2.1. Particle synthesis

The details of the particle synthesis procedure have been described in the paper on the Cu–Zr proxy system and will

only be summarized here [8]. The core particles consist of a 61:39 ratio of poly 2,2,2 trifluoroethylmethacrylate (PTF-EMA):polymethylmethacrylate (PMMA). Using a surface initiated atom transfer radical polymerization (SI-ATRP) reaction and an "inimer" (inititator + monomer) molecule used in the core particle synthesis step, the particles are functionalized with either a positive (Red particles) or negative (Green and Blue particles) acrylamide polymer. The zeta potential of the final particles in water are +48, -27,-33 mV for Red, Green, and Blue particles, respectively, with the variation within each sample type  $\pm 5$  mV. The relative ratios of the colloidal particle diameters closely match those of the atomic size ratios, as shown in Table 1. The colloidal sizes reported in Table 1 are determined by the confocal image separation distances, i.e. the location of the first peak in the PRDF. This likely represents close to a hard core particle size as the particles have been highly densified (close-packed) from centrifugation. However, once the centrifugal forces have been removed, the electrostatic charges on the surface of the particles likely influence the particle spacing such that the reported sizes and separation distances are also influenced by attractive (unlike) and repulsive (like) charges on neighboring particles. To ensure that each component of the ternary system consisted of particles with low polydispersity, samples of each type of individual particle were examined with the confocal microscope and the crystal structure examined. Each single-component sample produced large-scale crystals (greater than 90% of the image stack volume), which is only possible with polydispersity less than 7% [9]. Additionally, size monodispersity was verified by manually measuring particle diameters in scanning electron microscopy images and the standard deviation was found to be less than 5%.

Three pyrromethene fluorescent dyes purchased from Exciton, Inc., are used to label the particles so that each species can be tracked independently. The dye compounds are named for the most intense wavelength from their emission spectra: pyrromethene 650, 605 and 546. These are used to label Red, Green and Blue particles, respectively. Samples are prepared by adding 0.1–1 ml of dilute suspensions of each particle type (in deionized formamide solvent) into a cylindrical cell made from copper pipe and a 0.1 mm microscope cover glass. The cell is centrifuged to densify the particle suspension and afterwards excess formamide solvent is removed, as described in Ref. [8]. This technique

Table 1

Absolute and relative sizes for Ca, Mg and Zn atoms [1] and for Red, Green and Blue colloidal particles used in this work. Bold values highlight the similarities in the relative size ratios for the two systems.

	Ca/Red	Mg/Green	Zn/Blue		
Atomic diameter (Å)	3.82	3.05	2.60		
Ratio to Zn	1.47	1.17	1		
Colloid diameter (µm)	3.51	2.82	2.39		
Ratio to Blue	1.47	1.18	1		

is used to make four suspension compositions as described previously  $- R_{60}G_XB_{40-X}$  (where X = 25, 20, 15, 10).

Using a Zeiss model LSM700 confocal laser scanning microscope and a  $63 \times oil$  immersion objective, image stacks are acquired from five locations on each sample and consist of 250  $100 \times 100 \,\mu\text{m}$  images separated by 0.2 µm. A particle finding code developed by Gao and Kilfoil [10] and written for Matlab is used to locate and record the position of each particle in the system. A second Matlab package utilizes Voro++ [11] to analyze the structure and results in an output of PRDF curves, partial coordination numbers and Voronoi cell construction for each particle. An example of the combined image stack for the sample with composition  $R_{60}G_{20}B_{20}$  is shown in Fig. 1. Due to crystallization of the first 3-5 layers of particles caused by the glass cover slip, only images 50-300 of the stack are included in the analysis, similar to what was done previously [8].

### 3. Results and discussion

### 3.1. Number density

We first compare the atomic and particle number densities of the metallic and colloidal systems at each composition. The atomic densities are reported in Ref. [1] in terms of atoms per angstrom. We scale the reported atomic density by the volume of the smallest atom, Zn, in order to compare to the particle number densities scaled to the volume of the smallest, blue particles. This average volume takes into account the ~5% polydispersity of the colloidal particles [12]. We calculate the colloid number densities by calculating the Voronoi volume for each particle in the image stack. The number density for each particle is then the reciprocal of its Voronoi volume (1/Vor). We find the overall number density for the entire sample by taking the average of all individual particle number densities. This



Fig. 1. Three-dimensional reconstruction of sample with composition Red60Green20Blue20. The cover glass and edge of the sample is located at the top of the image. Actual sample continues on in all other directions.

1 4010 2	Table	2
----------	-------	---

Number densities of metal and colloid systems at each composition.

Composition Ca/R:Mg/G:Zn/B	Metal Atoms/Vol(Zn)	Colloid Particles/Vol(B)
60:25:15	0.294	0.272
60:20:20	0.288	0.264
60:15:25	0.284	0.262
60:10:30	0.278	0.259

is done for each of the five samples at a particular composition and the average for each composition is reported in Table 2. Sample-to-sample variations in number density are  $\sim \pm 0.008$  from the reported average. To eliminate edge effects, we exclude any particle whose Voronoi cell is not completely contained within the image volume. This step is important because we found artifacts in the particle locating results where the edge density can appear to be higher than in the center. This is due to particles on the edge being counted as regular, full-sized particles even though some of their volume is outside the image stack boundary.

As expected, the number densities of both systems increase as the fraction of smaller Zn/Blue particles is increased and the fraction of larger Mg/Green particles is decreased. The density of the colloid system is consistently lower than the metal system. There are a number of possible explanations for this. First, there is the possibility of uncounted particles in the image stack. This is a common source of error when using confocal microscopy to track colloidal particles [10]. With  $\sim 20,000$  particles in each image stack, it is not reasonable to visually check that each particle was counted correctly. Second, there is some uncertainty in the diameter measurements used to calculate the average particle volume. The diameter is determined from the separation distances (i.e. the first peak in the pRDFs) for each sample as discussed in the next section. All 20 samples (five samples for each of four compositions) are averaged to get a single mean diameter that is used in the calculations for number density  $(R = 3.51 \,\mu m)$  $G = 2.82 \mu m$ ,  $B = 2.39 \mu m$ ). As seen in Table 3, the variation in particle diameter between compositions is  $\sim 3\%$ , which translates to an uncertainty in the number density of  $\sim \pm 0.03$  in Table 2. Considering these uncertainties,

Table 3

Locations of first peaks from PRDFs for four compositions. The bold values at the bottom compare the average heterogeneous particle separation from PRDFs to the prediction based on the distance half way between the two corresponding homogenous peaks.

First peak location (µm)	R–R	R–G	R-B	G–G	G–B	B–B
$R_{60}G_{25}B_{15}$	3.54	3.00	2.76	2.82	2.48	2.38
$R_{60}G_{20}B_{20}$	3.52	2.96	2.76	2.82	2.48	2.40
$R_{60}G_{15}B_{25}$	3.48	2.90	2.80	2.82	2.46	2.36
$R_{60}G_{10}B_{30}$	3.50	3.04	2.72	2.82	2.48	2.40
Average	3.51	2.98	2.76	2.82	2.48	2.39
"Half distance" prediction		3.17	2.95		2.60	



Fig. 2. PRDF curves for  $R_{60}G_{20}B_{20}$ .

the quantitative similarities in number density is remarkable.

#### 3.2. Partial radial distribution function

The next piece of structural information we obtain from the confocal images is the PRDF. Fig. 2 shows representative PRDF curves for the  $R_{60}G_{20}B_{20}$  sample. All other compositions show qualitatively the same results as in Fig. 1. Within experimental error, no discernible trends in peak height or location are found with composition.

The R-R first peak is the broadest and shortest, while the B-B first peak is the narrowest and tallest. The locations of interspecies peaks (i.e. R-G, R-B, G-B) are shifted to shorter distances than what would be predicted by the distance half way between homogeneous peaks (e.g. between R-R and G-G for the R-G peak). For R-G and R-B this can be explained as being due to an electrostatic attraction between R and G particles and between R and B particles, which acts to squeeze these particles closer together, compared to the repulsion force between two particles of the same species. However, since G and B particles are both negatively charged, this explanation does not fit with the bond shortening also seen with the G-B peak. We do note, though, that G-B bond shortening is the least pronounced (0.12  $\mu$ m shorter compared to 0.19  $\mu$ m). In Table 3, we show the first peak locations for each of the four compositions and compare the predicted peak location to the actual location for the heterogeneous peaks.

To more directly compare PRDF curves from the colloidal particles with the actual metallic glass system, we show data from both systems in Fig. 3. Here, the *x*-axis has been made dimensionless by the radius of Zn/Blue. Each PRDF curve from the colloid data in Fig. 1 is separated and shown with its atomic counterpart on the same plot.

For many of the partial RDF curves, the agreement is very good. The first peak location and height is nearly identical for R–G (Ca–Mg), G–G (Mg–Mg) and R–B (Ca–Zn). The agreement is only slightly worse for R–R (Ca–Ca) and G–B (Mg–Zn), which show opposite disagreements with both peak height and location compared to the metal data. The most obvious qualitative difference between the PRDF curves from the two systems is in the Zn–Zn/B–B plot in Fig. 3f. In the metallic system, there is essentially no first peak, whereas in the colloid system there is a distinctive and tall first peak. The low signal to noise for the metal data likely contributes to the majority of the discrepancy since most other comparisons are in agreement. The bond shortening effect discussed above can be seen here as the peaks for R–B, R–G and G–B are located at shorter distances than the corresponding atomic peaks. However, discrepancies are small. Features of the second peaks seen in Ca–Ca and Ca–Mg curves are missed in the colloid data, but overall, even longer range structure is similar in the two systems.

#### 3.3. Partial coordination numbers

We construct three-dimensional Voronoi tessellation cells around each colloid particle using particle locations obtained from the images and the "radical" Voronoi approach [11]. The Voronoi cells give the number and type of first shell neighbors around each particle, referred to as the partial coordination number  $(Z_{ij})$ . The criteria for defining a first shell neighbor is that the neighboring particle must share at least one face of its Voronoi cell with the central particle and the area of that shared face must be at least 1% of the total surface area of the Voronoi cell. Also, the separation distance between the two particles must not exceed the distance of the minimum in the PRDF curve between the first and second peaks. The Voronoi method is also used to determine coordination numbers in metallic systems, with similar constraints, allowing a direct comparison of results from the two systems. Fig. 4a-c shows the distribution of total coordination numbers around R(Ca), G(Mg), and B(Zn) centered cluster for each of the four compositions.

In comparing the two systems, we see that the distributions largely overlap, with the colloid systems having slightly more first shell neighbors in R-centered clusters and slightly less in G- and B-centered clusters compared to the corresponding metallic clusters. The lower coordination numbers for G and B centered clusters could be due to underdensification as discussed earlier. The degree of overlap is within experimental error. The distributions for colloid systems are more Gaussian than the metallic systems, which tend to have tails in the high coordination number range. The shape and peak locations for colloid systems have less variation than the metallic systems with only a slight shift to higher values as more of the smaller B particles are added in the colloid systems. Asymmetry in total  $Z_{ii}$  distributions is seen for Mg- and Zn-centered clusters in metallic systems, where higher-than-expected total  $Z_{ij}$ values give "overpacked" first coordination shells. The local compressive stresses associated with this overpacking are accommodated by displacing some of the atoms in the first coordination shell from contact with the central atom [1]. The decreased stability from adding free volume is



Fig. 3. (a–f) PRDF curves for each component in both the colloid system (color) and metallic system (black). The x-axis has been scaled by either the size of Blue–Blue separation for colloid data or Zn–Zn separation for metal data in order to compare relative peak locations of the two systems. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

offset by the reduced energy from forming additional Mg–Mg, Mg–Zn and Zn–Zn bonds. In the colloid systems studied here, repulsive forces exist between G–G (Mg–Mg), G–B (Mg–Zn) and B–B (Zn–Zn) pairs, so that non-contacting G–G, G–B and B–B pairs and higher-than-expected total  $Z_{ij}$  values might also be expected. However, the attractive R–G (Ca–Mg) and R–B (Ca–Zn) colloid forces may allow the R particles to bond more tightly to G-and B-centered clusters, thus forcing out competing G and B first neighbors. Since R is larger than both G and B particles, total  $Z_{ij}$  values for G- and B-centered clusters

would be expected to decrease, as is observed in the present work. The small differences between metallic and colloid systems in the present work may therefore come from the absence of attractive forces between all pairs of particles, which is different from typical metallic systems.

Fig. 5a–c shows partial coordination numbers for each composition. From the left to right, the fraction of G(Mg) decreases from 25% to 10%. The mode values of the distributions are used, since the metallic system profiles are not symmetric. Error bars indicate one standard deviation in the distribution for the colloid data; standard





Fig. 5. (a–c) Partial coordination numbers for R(Ca), G(Mg), B(Zn) centered clusters calculated from the mode of the distributions for compositions of ranging from  $Ca_{60}Mg_{25}Zn_{15}$  to  $Ca_{60}Mg_{30}Zn_{10}$  (left to right). Error bars indicate one standard deviation.

Fig. 4. Total coordination number distributions for: (a) R(Ca), (b) G(Mg), (c) B(Zn) centered clusters. Colloid data are solid curves and metallic system data are dashed. Colors indicate composition as indicated in the legend. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

deviations of the partial coordination numbers for the metal data were not available. Again we see agreement in results from the atomic and colloid systems. The overlap of Ca and R coordination numbers is well within experimental error and we see the same trends with changing composition for all R(Ca) centered partial coordination numbers. For G centered clusters, clear composition trends are also seen. However, in the metallic system,  $Z_{MgMg}$  is higher at 15% Mg than at 20%, which is opposite the general trend for both systems. Overall though, the data mostly overlaps within experimental error for Mg and G clusters. The coordination numbers with the least agreement are with the Zn- and B-centered clusters. Here, B-centered clusters in the colloid system have 1–2 fewer nearest neighbors overall, which comes from having both fewer R and other B neighbors in the first shell. Although beyond the scope of this work, additional studies could be done to explore the effects of changing the sign and magnitude of the charges on the surface of the colloidal particles to determine if better agreement can be found. The composition trends for B-centered clusters in the colloid system are similar to the other particles, but do not agree with the metallic system. In Ref. [1], it is argued that the Zn–Zn coordination number minima at 20% and 25% Zn indicate better glass formability at these compositions. We do not see this in the colloid system.

# 4. Summary

We have demonstrated that colloidal particles can serve as useful proxies for atomic metallic glass systems when key parameters are tuned correctly. For the ternary proxy system based on Ca-Mg-Zn, we synthesized Red (R), Green (G) and Blue (B) particles from polymer material that matched the relative radii of the Ca, Mg and Zn atoms, respectively. A fluorescent dye molecule was incorporated into the particles and we acquired particle location information from confocal microscopy experiments. Particle locations were used to calculate PRDFs and  $Z_{ii}$ 's for four compositions and compared to the corresponding structural information for the Ca-Mg-Zn system at the same compositions. We find slight bond shortening of interspecies bonds as noted by the locations of the first peaks from PRDFs. We attribute this to the attractive and repulsive effects of using surface electrostatic charges on the particles for R-G and R-B. There is generally good agreement for the PRDF curves, with the exception of the Zn-Zn, B-B PRDFs, where there is a noticeable lack of a definitive first peak for Zn–Zn. This might be explained by the electrostatic particle interactions we use in the colloid system, but is likely also to be influenced by the low concentration of Zn in the metallic samples which may lead to measurement difficulties for PRDFs. Coordination numbers largely agree within experimental error for both systems, with the largest differences found between Zn and B centered clusters.

The benefit of using a proxy system like the one described here, over doing experiments with actual metallic

glass samples, is the simplicity and speed of the experimental technique. All structural information can be calculated with the particle location information obtained from the image stacks. Instead of needing six scattering experiments to be able to calculate the structural contributions from each component in Ca–Mg–Zn, we are able to calculate the same information from a single experiment using a single sample. In fact, the Ca–Mg–Zn experimental data used to validate our approach is the first and only measured dataset for local coordination in ternary systems. The relative ease and reliability of the colloidal systems make them an attractive alternative for the determination of local atomic structures in ternary metallic glasses.

## Acknowledgements

The authors thank Tom Kodger for discussions on particle synthesis, surface charge and solvent choice, and Oleg Senkov for discussion on Ca–Mg–Zn structure and for providing data for comparison. We also thank David Weitz and Frans Spaepen for discussion and access to their resources. Work at the Air Force Research Laboratory was supported through the Air Force Office of Scientific Research and under on-site Contract No. F49620-02-C-0015 conducted through the National Research Council, Washington, DC.

# References

- Senkov ON, Miracle DB, Barney ER, Hannon AC, Cheng YQ, Ma E. Phys Rev B 2010;82:104206.
- [2] Senkov ON, Miracle DB, Scott JM. Intermetallics 2006;14:1055.
- [3] Senkov ON, Scott JM. Scripta Mater 2004;50:449.
- [4] Senkov ON, Scott JM. J Non-Cryst Solids 2005;351:3087.
- [5] Senkov ON, Scott JM, Miracle DB. J Alloys Compd 2006;424:394.
- [6] Senkov ON, Scott JM, Miracle DB. Mater Trans 2007;48:1610.
- [7] McGreevy RL. J Phys Condens Matter 2001;13:R877.
- [8] Kramb RC, Ward L, Jensen KE, Vaia R, Miracle DB. Acta Mater 2013;61:2025.
- [9] Sciortino F, Tartaglia P. Adv Phys 2005;54:471.
- [10] Gao Y, Kilfoil ML. Opt Exp 2009;17:4685.
- [11] Rycroft CH. Chaos 2009;19:041111.
- [12] Jensen KE, Pennachio D, Recht D, Weitz DA, Spaepen F. Soft Matter 2013;9:320.