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Modelling the atomic structure of Al$_{92}$U$_{8}$ metallic glass

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Abstract

The local atomic structure of the glassy Al$_{92}$U$_{8}$ alloy was modelled by the reverse Monte Carlo (RMC) method, fitting x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) signals. The final structural model was analysed by means of partial pair correlation functions, coordination number distributions and Voronoi tessellation. In our study we found that the most probable atomic separations between Al–Al and U–Al pairs in the glassy Al$_{92}$U$_{8}$ alloy are 2.7 Å and 3.1 Å with coordination numbers 11.7 and 17.1, respectively. The Voronoi analysis did not support evidence of the existence of well-defined building blocks directly embedded in the amorphous matrix. The dense-random-packing model seems to be adequate for describing the connection between solvent and solute atoms.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Al-based metallic glasses have attracted interest during the last two decades because of their good mechanical properties which seem to be better in comparison with the crystalline counterparts [1, 2]. In order to understand their macroscopic properties one should recognize basic phenomena occurring at the microscopic scale level. The principal question of their glass forming ability can be raised. This is especially true in the case of high content Al glassy alloys which usually do not satisfy the atomic size ratio criterion [3]. Metallic glasses do not have a long range atomic order and their properties are strongly determined by the local atomic arrangement. X-ray and neutron diffraction, electron transmission microscopy and x-ray absorption spectroscopy (XAS) are well established methods which are frequently used in order to describe the local atomic structure of disorder systems such as metallic glasses. Reverse Monte Carlo (RMC) and molecular dynamics simulations have been quite extensively employed in recent years to determine a 3D atomic structural model of the glasses investigated [4, 5]. Performing Voronoi tessellation on the 3D atomic configuration obtained helps one to identify basic structural units and thus contributes to better understanding of the glassy state [6, 7]. The general formula of the currently investigated Al-based amorphous systems can be summarized as follows: Al$_{(100-x-y)}$–TM$_{x}$–RE$_{y}$ (5 < x < 10, 2 < y < 10), where TM stands for late transition elements (Ni, Co, Fe) and RE denotes Y or rare-earth elements (La, Ce, Nd, Sm, Gd). The total x-ray structure function \( S(Q) \) of these alloys usually exhibits the presence of a small prepeak located on the left side of the principal diffuse peak. The existence of this prepeak was thoroughly investigated in previous studies [8–10]. It was suggested that the prepeak could be connected with chemical short range order or be due to the distant separation of solute atoms. Another interesting feature of Al-based glasses is the contraction of the Al–TM distance. Zalewski et al confirmed by means of XAS the shortening of Al–TM distances by 10%, suggesting a significant contribution of covalent bonding [11]. Similar TM–Al shortening was also found by other authors [8, 10, 20, 21].

In this paper we present a structural study of amorphous Al$_{92}$U$_{8}$. Only recently, Al-rich metallic glasses, in which a lanthanide element has been replaced with an actinide (namely by U), have been presented [12]. These alloys were studied by...
using high energy x-ray diffraction and EXAFS spectroscopy was performed at the U L₃ edge. Experimental data were fitted by the reverse Monte Carlo simulation technique. The resulting atomic configuration was analysed by means of partial pair correlation functions, coordination number distributions and Voronoi tessellation. Due to the high atomic number of uranium, Al–U and U–U partial structure factors already make a significant contribution to the XRD signal at 8% uranium content. Thus, this composition offers a unique possibility to observe solute–solvent and solute–solute correlations in Al-rich alloys.

2. Experimental details

Glassy alloys with a nominal composition of Al₂₅U₈ (at.%) were prepared by a single-roll melt spinning method. The peripheral velocity of a wheel was 40 m s⁻¹. Casting was performed under an Ar atmosphere. This preparation route yielded samples having the form of thin sheets with a cross section of 3 × 0.025 mm².

X-ray diffraction data measured up to a large wavevector transfer $\mathbf{Q} = 4\pi \sin(\theta)/\lambda$ (in which $\theta$ denotes the scattering angle and $\lambda$ corresponds to the wavelength) are necessary in order to obtain high resolution radial distribution functions which are helpful in the atomic structural investigation of disordered systems. XRD measurements using high energy photon beams were carried out at the experimental station ID15B of ESRF (Grenoble, France). The synchrotron radiation wavelength was set to $\lambda = 0.1429$ Å (equivalent to the photon energy of 86.763 keV). The diffraction experiments were carried out in the transmission geometry. An LaB₆ standard was used to calibrate the sample-to-detector distance and tilt of the imaging plate relative to the beam path. The sample was continually illuminated with a well collimated incident beam having cross section of 0.4 × 0.4 mm². XRD patterns were collected using a fast, large area PIXIUM 4700 detector (2640 pixels × 1920 pixels, having pixel size of 154 × 154 μm²) carefully mounted orthogonal to the x-ray beam. To avoid detector overexposure the maximum exposure time was set to 0.4 s. Summing of 50 consequent two-dimensional diffraction images resulted in an excellent signal-to-noise ratio. The background intensity was subtracted directly from the 2D XRD pattern and the result was integrated into the $\mathbf{Q}$-space. The integrated data were corrected for fluorescence, Compton scattering, polarization and sample absorption and thereafter they were used for calculation of the total structural factor $S(\mathbf{Q})$ applying the Faber–Ziman formula [13].

A great advantage of the XAS method is its element sensitivity which gives an opportunity to study a local atomic surrounding around a selected chemical atom type. The XAS represents a source of complementary structural information with respect to information obtained by using XRD. The x-ray absorption fine structural measurement at the U L₃ edge (energy 17 166 eV) was realized at the bending magnet beamline X1 of the DORIS III positron storage ring at the HASYLAB/DESY (Hamburg, Germany). The EXAFS signal was measured at room temperature in the transmission mode using a fixed exit double-crystal Si(111) monochromator. The size of a beam was 2 × 2 mm². The energy calibration was done by making measurements for a pure Nb reference foil at the Nb K edge (energy 18 986 eV). The experimentally measured x-ray absorption cross section $\mu(E)$ was analysed by the standard procedure of data reduction described elsewhere [14, 15] using the program Viper [17]. Backscattering amplitude $F_r(k)$ and phase shift $\chi_r(k)$ functions were calculated using the FEFF 8.4 code [18].

3. Simulation

The reverse Monte Carlo method is an iterative simulation method offering a way to obtain a 3D model that is in agreement with available experimental data containing structural information. Its main idea is to minimize differences between experimentally measured structural signals (x-ray and/or neutron structural factor $S(\mathbf{Q})$, EXAFS $\chi(k)$ signal) and signals calculated from the optimized 3D atomic configuration. At every step one atom is chosen at random and then slightly shifted. The decision about an acceptance of the new atomic configuration is done on the basis of applying the well known Metropolis algorithm. Detailed information about the RMC method can be found elsewhere [4, 19, 10, 16]. In this work, the simulation box contained 12 000 atoms with the number atomic density $\rho = 0.059$ Å⁻³ estimated theoretically from the chemical composition of Al₂₅U₈. The $\rho$ obtained is in good accordance with previously reported values for similar systems. Saksl et al. used $\rho = 0.055$ Å⁻³ for the amorphous system Al₈₈Y₇Fe₅ [20] and $\rho = 0.0567$ Å⁻³ was reported by Hsieh et al. for the glassy alloy Al₂₅Ce₅Fe₅ [8]. Two experimental data sets (XRD and EXAFS) were fitted simultaneously using the RMC method. The following minimum interatomic distances (cut-offs) were used: 2.4 Å for Al–Al, 2.5 Å for Al–U and 4.4 Å for U–U atomic pairs.

4. Results and discussion

Figure 1 shows an experimentally determined x-ray diffraction pattern and an EXAFS spectrum together with the corresponding model curves obtained by the simultaneous RMC fitting of the two data sets. One can observe a perfect match between the experimental data and RMC fit.

As can be seen from figure 1(a) the total structural factor $S(\mathbf{Q})$ exhibits a highly asymmetric principal peak at $\mathbf{Q} = 2.65$ Å⁻¹ and a relatively intense prepeak located at $\mathbf{Q} = 1.3$ Å⁻¹. Oscillations seen in $S(\mathbf{Q})$ are rather pronounced and they can be observed up to 16.5 Å⁻¹. However no sharp Bragg peaks are detected. XRD measurements confirm a fully glassy state of the alloy investigated. In the case of the binary Al₂₅U₈ alloy the total structural factor $S(\mathbf{Q})$ is a result of the summation of the three weighted partial structural factors, i.e. $S(\mathbf{Q})_{\text{Al–Al}}, S(\mathbf{Q})_{\text{U–Al}}$ and $S(\mathbf{Q})_{\text{U–U}}$. The weighted partial structural factors extracted from a RMC final configuration box of atoms are shown in figure 2. It is readily seen that the partial structural factor $S(\mathbf{Q})_{\text{U–U}}$ exhibits an intense peak at position $\mathbf{Q} = 1.3$ Å⁻¹ which is well correlated with the prepeak position of the total $S(\mathbf{Q})$. It can be concluded that...
Figure 1. (a) The total x-ray structural factor $S(Q)$ and (b) U $L_3$ EXAFS signal of glassy Al$_{92}$U$_8$ obtained experimentally (open circles) and by RMC modelling (full line).

Figure 2. Weighted partial XRD structural factors obtained from the RMC simulation.

the prepeak is caused by U–U pairs due to their relatively large separation.

Partial pair correlation functions (ppcf) extracted from the RMC final configuration box are compared with ones obtained from a hard sphere model (HSM) using the same minimum interatomic distances but without fitting experimental data. They are shown together in figure 3. Partial coordination numbers were obtained from ppcfs after applying the following constraints:

$$r_{\text{min}}(\text{Al–Al}) = 1 \text{ Å},$$
$$r_{\text{max}}(\text{Al–Al}) = 3.8 \text{ Å}; r_{\text{min}}(\text{Al–U}) = 1 \text{ Å}, r_{\text{max}}(\text{Al–U}) = 3.8 \text{ Å}; r_{\text{min}}(\text{U–U}) = 1 \text{ Å}, r_{\text{max}}(\text{U–U}) = 6.8 \text{ Å}.$$

The first peak of the Al–Al ppcf extracted from the RMC final model is shifted to the higher $r$ but no other significant changes are noticed. The position of the peak is at 2.70 Å. This value is significantly shorter than the Al–Al distance in a crystalline Al (2.868 Å) phase (PDF 01-072-3440 4-787). Similar shortening was observed in amorphous Al$_{80}$La$_{17}$N$_5$ and Al$_{80}$Y$_{17}$Fe$_5$ alloys [10, 20]. The Al–Al coordination number $N_{\text{Al–Al}}$ is 11.7, which is higher than the value of 7.7 reported for Al$_{80}$La$_{17}$N$_5$ system. Matsubara et al found for the binary glassy Al$_{80}$Y$_{10}$ alloy $N_{\text{Al–Al}} = 10.7$ but for the ternary Al$_{87}$Y$_3$Ni$_5$ alloy it was only 7.2 [21]. It seems that transition metals have a significant influence on the Al surrounding as was pointed out by Miracle [22, 23]. It is noteworthy that values 11.7 and 10.7 are much closer to the maximal theoretical coordination number 12.6, assuming that all atoms are idealized as hard spheres and they are efficiently packed. Such assumptions form the basis of the dense-random-packing (DRP) model, which is based on the principle of two-dimensional packing of the atomic surface [24]. The equation for calculation of the coordination number $N_{\text{B–A}}$ of a solute atom B with a radius $r_B$ in a matrix of solvent atoms A with a radius $r_A$ has the following form [24]:

$$N_{\text{B–A}} = 4\pi \frac{1 - \frac{r_B^3}{3}}{1 - \frac{r_A^3}{3}}.$$  

(1)

The first peak of the RMC U–Al ppcf is at position 3.1 Å which is quite close to the nearest Al–U distance $r_{\text{Al–U}}$ in orthorhombic Al$_4$U phase (PDF 01-072-3438). Actually, this phase was identified after annealing an Al$_{92}$U$_8$ sample at 600°C (not shown here). If we consider the main peak position of the U–Al ppcf of the final RMC model and the Al atomic radius $r_{\text{Al}} = 1.43$ Å (this value has been frequently used by many investigators studying Al-based glassy alloys [10, 11, 21, 25]) then the atomic uranium radius could be $r_{\text{U}} = 1.67$ Å. Applying equation (1), the theoretically maximal $N_{\text{U–Al}}$ is estimated to take the value of 14.9. When the experimental value $N_{\text{U–Al}} = 17.1$ obtained from the RMC U–Al ppcf is compared with the theoretical one, then one could have the impression that our value is overestimated and some doubts could be raised about the final RMC model. It should be noted here that the main peak position of the U–Al ppcf was stable during the RMC fitting procedure and gently increasing/decreasing the cut-off had no influence on it. Considering the main peak position of the RMC U–Al ppcf located at 2.70 Å suggests shortening of the Al–Al bonds which, in turn, implies an effective radius of 1.35 Å for Al atoms. Furthermore, the closest distance between two Al atoms in the orthorhombic Al$_4$U phase is 2.62 Å and not 2.86 Å. Taking into account the main peak position of the RMC U–Al ppcf (3.1 Å), one obtains the effective radius of 1.75 Å for U atoms. Recalculating the new theoretical $N_{\text{U–Al}}$ according
to equation (1) based on atomic radii of 1.35 and 1.75 Å for Al and U, respectively, one obtains the value of 16.9 which is in much better agreement with the value of 17.1 extracted from the U–Al ppcf. One may conclude here that the DRP model appears to be adequate for describing the U surrounding (if the hard sphere diameters are chosen properly).

During the RMC modelling we supposed that only Al atoms are present in the closest surrounding of uranium atoms. In fact this assumption was directly included in our RMC model, setting the cut-off for U–U pairs to 4.4 Å. For binary and ternary Al-based metallic glasses it is generally accepted that the rare-earth element (La, Ce, Nd, Sm or Gd) or Y is surrounded by only Al atoms in the first shell. Direct evidence of such behaviour was provided by Zalewski et al in their study of glassy Al–Sm and Al–Sm–Ni systems [11]. They measured the EXAFS signal above the Sm L3 edge and found that including either Sm or TM in the first coordination shell strongly decreased the fit quality in comparison with the situation when the fitting of the EXAFS signal was realized for a cluster of only Al atoms surrounding an absorber Sm atom. Another argument supporting the use of a relatively large cut-off (4.4 Å) for U–U pairs could come from the knowledge that the minimal interatomic distance between two U atoms in the indexed phase Al4U is 4.36 Å. After comparison of ppdfs extracted from the final RMC model with ones obtained from the HSM, it is remarkable that the most drastic changes occurred in the case of the U–U ppcf. A broad maximum is formed in the RMC U–U ppcf and is followed by a deep minimum. One may think that the main broad peak observed in the RMC U–U ppcf is composed of the two wide peaks located at 5.4 Å and 6.2 Å, respectively. Additionally two other peaks positioned at ~7.7 and 10 Å are strongly pronounced in comparison with the HSM’s ppcf. It should be mentioned here that the positions of peaks at 6.2, 7.7 and 10 Å are in quite good agreement with the interatomic U–U distances in the orthorhombic Al4U phase.

Figure 3 shows a 3D structure model of Al92U8 amorphous alloy as obtained from the RMC simulation. The extraction of the real 3D structure from the RMC simulation can be very helpful due to the fact that atomic coordinates may be used for more detailed analysis of structural features.

Using this perspective, the presence of building blocks, or ‘clusters’, could be revealed. Sheng et al remarked that despite the large number of geometrically distinct polyhedron types, certain polyhedra appeared with high frequencies [7]. For example they identified polyhedra with Voronoi index <0, 3, 6, 0> and <0, 2, 8, 0> of frequencies 17.8% and 7.1% respectively in the Ni39B4 alloy. The Voronoi index ni in the notation <n3, n4, n5, n6, ...> denotes the number of i-edge faces of the Voronoi polyhedron, which surrounds a central solute atom. ∑ni is the total coordination number of the Voronoi polyhedron (for more details see [26, 27, 6, 7]).
Figure 4. The final 3D configuration box of atoms obtained from the RMC simulation, representing amorphous Al_{92}U_{8}. Grey spheres stand for Al atoms and red ones denote U atoms.

The aforementioned reasons the Voronoi tessellation analysis using the Voro++ program [28] was applied to our final RMC and HSM configuration box of atoms with the aim of separately studying the nearest neighbours of aluminium and uranium atoms. Results are listed in table 1. In the tables, only those polyhedra whose occurrence is higher than 2% are shown. None of polyhedra have a particularly high frequency of appearance but on the other hand in the case of the HSM configuration no type of polyhedron went over the filtering criterion, with only one exception. The Voronoi polyhedron \( \langle 0\bar{3}640 \rangle \) around the Al atom was present in the HSM with a 2.2% frequency. However after applying the RMC method its presence is 5.8%. Results of Voronoi analysis did not support evidence of the existence of well-defined building blocks directly embedded in the amorphous matrix. In addition, coordination numbers \( N_{\text{Al-Al}} \) and \( N_{\text{U-Al}} \) of Voronoi polyhedra were analysed. (\( N_{i-j} \) means the number of \( j \)-type solvent atoms around an \( i \)-type solute central atom of the Voronoi polyhedron.) Their distributions for the RMC final model and HSM are compared in figure 5. It is readily seen that the distribution of \( N_{\text{U-Al}} \) after applying RMC constraints is moved to higher values (the average coordination number increased from 16.4 to 17.6) and becomes narrower. On the other hand, changes of the \( N_{\text{Al-Al}} \) distribution are not so pronounced. Although the peak position is shifted to the left (the average coordination number decreased from 13 down to 12.4), the peak width and height are practically unmodified. So it seems that more severe changes during the RMC modelling occurred in the neighbourhood of uranium atoms.

5. Conclusion

The local atomic structure of the glassy Al_{92}U_{8} alloy was modelled by the RMC method, fitting XRD and EXAFS signals. The final structural model was analysed by means of partial pair correlation functions, coordination number distributions and Voronoi tessellation and was confronted with the HSM. It was found that the closest environment of U atoms consists of 17 well packed Al atoms. The DRP model seems to be sufficient for describing not only the U neighbourhood but also the Al surroundings. These results suggest that U behaves in binary Al-based glassy alloys in a very similar manner to Y and La. The Al–Al and U–Al distances were determined as 2.7 Å and 3.1 Å respectively. After the RMC modelling the most serious modifications of ppcfs compared to the HSM are observed in the case of the U–U ppcf in which four intense peaks appeared. The Voronoi tessellation analysis did not reveal the presence of any polyhedron with a significantly high frequency.

Table 1. The Voronoi index of polyhedra and the frequency of the appearance of polyhedra in the final RMC model.

<table>
<thead>
<tr>
<th>Voronoi index</th>
<th>( n_3 )</th>
<th>( n_4 )</th>
<th>( n_5 )</th>
<th>( n_6 )</th>
<th>( n_7 )</th>
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Figure 5. Distributions of the coordination numbers (a) \( N_{\text{U-Al}} \) and (b) \( N_{\text{Al-Al}} \) extracted from the final RMC model and HSM on the basis of the Voronoi tessellation analysis.
Acknowledgments

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