Journal of Alloys and Compounds 536S (2012) S65–S69

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# Clustering, microalloying and mechanical properties in Cu/Zr-based glassy models by molecular dynamics simulations and ab-initio computations

Ch.E. Lekka [a], G.B. Bokas [a], G.A. Almyras [b], D.G. Papageorgiou [a], G.A. Evangelakis [b,*]

[a] University of Ioannina, Department of Materials Science and Engineering, Ioannina 45100, Greece
[b] University of Ioannina, Department of Physics, Ioannina 45110, Greece

ARTICLE INFO

*Article history:*
Received 8 July 2011
Received in revised form 20 October 2011
Accepted 7 November 2011
Available online 16 November 2011

*Keywords:*
Amorphous materials
Metallic glasses
Computer simulations
Atomic scale structure
Clusters

ABSTRACT

We present results on the microstructure of Cu–Zr metallic glasses (MGs) at equilibrium and under tensile deformation by means of large scale molecular dynamics (MD) simulations and density functional theory (DFT) calculations. We found that the MGs are composed by interpenetrating icosahedral-like (ICO) clusters forming superclusters (SCs). The deformation accommodation is associated with the destruction and recreation of these ICO clusters and SCs. DFT calculations on the $Cu_{13}Zr_{10}$ SCs with Cu–Cu core atoms revealed the presence of a free of bonds (FoB) plane that could be viewed as analog of a slip plane of the crystalline materials. The microalloying (MA) effect in a similar SC (one of the core atoms substituted by Al) yielded that Al is associated with the formation of a FoB plane. These results provide possible explanations of the experimental findings referring to the short range order, the MA effect and could potentially be used for the design of new MGs.



## 1. Introduction

The lack of crystalline order in metallic glasses (MGs) is closely related to their unique mechanical properties. Due to the amorphous nature of the MGs the deformation accommodation mechanisms are fundamentally different from their polycrystalline counterparts in which individual dislocations and grain boundaries respond plastically under mechanical solicitation. It is now accepted that the MGs' microstructure consists of clusters that are of icosahedral-like (ICO) shape and may be touching and/or interpenetrating [1–14]. Among the various ways that could be envisaged for the clusters' interconnections, simple compositional considerations lead to the prediction of superclusters (SCs) that obey particular sequences of magic numbers [9,10]. It is believed that plastic deformation in MGs occurs through the interconnections of the shear transformation zones (STZs) [1,2,15–17] consisting of tiny clusters, which above certain thresholds of applied stresses respond spontaneously and reorganize their shapes via cooperative movements [1,2,17]. The macroscopic lack of ductility, from which the MGs often suffer, is attributed to the extreme localization of stress into thin bands, of about 10 nm thick, known as shear bands, that are formed when the STZs percolate [5,6,18,19]. In addition, it was found that within the elastic region the deformation accommodation is correlated with a dynamic process of destruction and recreation of these ICO-like clusters [6]. It comes out therefore that the existence of these clusters, their shape and composition and the way they are interconnected may be decisive for the mechanical properties of the MGs. In this mainstream we could include the so-called microalloying (MA) effect, according to which small additions of an element alter significantly the glass forming ability (GFA) and the ductility of the parent alloys [20–24]. Recent studies report that the MA is related with changes in the clusters' compositions [25–27]. Very recently it was reported that MA with a suitable element (typically s or p type) of the ICO clusters alters the bonding characteristics of the cluster's atoms resulting in a free of bonds (FoB) plane [28]. This plane is usually situated at low energy levels; it is one of the dense planes of the ICO, containing the cluster's core atom and could be viewed as analog of the slip planes existing in the crystalline materials. Nevertheless, the clusters' interconnections, their stability, the MA effect and the possible existence and the role of the FoB planes in the SCs that constitute the MGs are still among the challenging issues.

The aim of the present work is to address these issues; the exploration of clustering and the SCs behavior upon mechanical solicitation is done by means of large scale molecular dynamics (MD) simulations, while ab-initio computations based on the density functional theory (DFT) were used for the assessment of the bonding characteristics of SCs, their alterations upon MA and the exploration for possible FoB planes.

## 2. Computational setup

We performed large scale MD simulations for the tensile deformation of Cu–Zr systems using a potential model in analogy

* Corresponding author. Tel.: +30 2651008590; fax: +30 2651008675.
*E-mail address:* gevagel@cc.uoi.gr (G.A. Evangelakis).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.11.038

to the Tight Binding Theory in the second moment approximation. The glass was prepared in slab geometry with free surfaces from a liquid system of 128,000 atoms that was carefully cooled to room temperature at steps of 100 K, each of which lasted 15 ps, while the final configuration was aged for 0.5 ns. For the deformation simulations we used in the lateral direction with boundary conditions a Poison ratio value of 0.34 and a strain rate of $10^8\ s^{-1}$. It has to be noted that due to the usual limitations of the MD simulations, this strain rate is by orders of magnitude faster from those usually applied experimentally and therefore the obtained results have to be considered with caution.

Standard Kohn–Sham self-consistent DFT to local density approximation calculations were performed by means of the SIESTA code for the evaluation of the electronic properties of the CuZr clusters/superclusters found by the MD simulations as well as for the case of substitutions with Al. For all elements core electrons were replaced by norm-conserving pseudopotentials [28] in the fully non-local Kleinman–Bylander [29] form and the basis set was a general and flexible linear combination of numerical atomic orbitals (NAOs) constructed from the eigenstates of the atomic pseudopotentials [30]. The non-local partial core exchange correlation correction was included for Cu and the $Zr^{2+}$ ion pseudopotential was used for the metallic Zr [31]. An auxiliary real space grid equivalent to a plane-wave cutoff of 100 Ry was used, while for the geometry optimization, the structure was considered as being fully relaxed when the magnitude of the forces on the atoms was smaller than 0.04 eV/Å.

Besides the single cluster cases that we used as reference, based on the MD trajectory analysis findings of the binary case of $Cu_{65}Zr_{35}$ we considered the following SCs: (a) $Cu_{13}Zr_{10}$ (Cu–Cu centered), (b) the same composition but with Cu–Zr or, (c) Zr–Zr cluster centers, (d) $Cu_{12}Zr_{10}Al$ (Cu–Al centers), (e) $Cu_{12}Zr_{10}Al$ (Zr–Al centers) and (f) $Cu_{12}Zr_9Al_2$ (Al–Al centers).

## 3. Results and discussion

### 3.1. Molecular dynamics results

The detailed analysis of the MD trajectories yielded abundance of ICO-like clusters, in agreement with previous studies [6–12]. These clusters are interpenetrating forming SCs, the sizes of which obey predicted specific sequence of magic numbers [9]. It came out that under tensile deformation, ICO-like clusters are destructed and recreated [6], while the formation of SCs is also manifested during this dynamical process. A representative example of such a processes is depicted in Fig. 1 in a sequence of snapshots. As it can be seen, the initial amorphous matrix (Fig. 1a), is locally transformed, an ICO cluster is formed at strain of 0.6‰ (Fig. 1b), followed by the creation of an interpenetrating second one, the processes thus resulting in the formation of a SC at strain of 0.8‰ (Fig. 1c). Interestingly, the Cu–Cu SC's core atoms are aligned along the deformation direction persisting until the eventual SC destruction occurring at strain 1.1‰ (Fig. 1d). We note here that due to the size of the simulating system (which is comparable to the thickness of a shear band), the material dilates homogeneously, effect that is not shown in the present study that focuses on the role of clusters and SCs in the mechanical response.

In addition, we found that the application of tensile deformation affects the existing SCs that are forced to reorganize their shapes and orientations, thus contributing in the accommodation of the mechanical solicitation. A schematic representation of this process is depicted in Fig. 2 in a sequence of snapshots. The SC's Cu–Zr core atoms that are initially randomly oriented (Fig. 2a), align along the deformation direction at strain of 0.3‰ (Fig. 2b), principally by means of the Cu core atom's movements. Meanwhile, the SC is

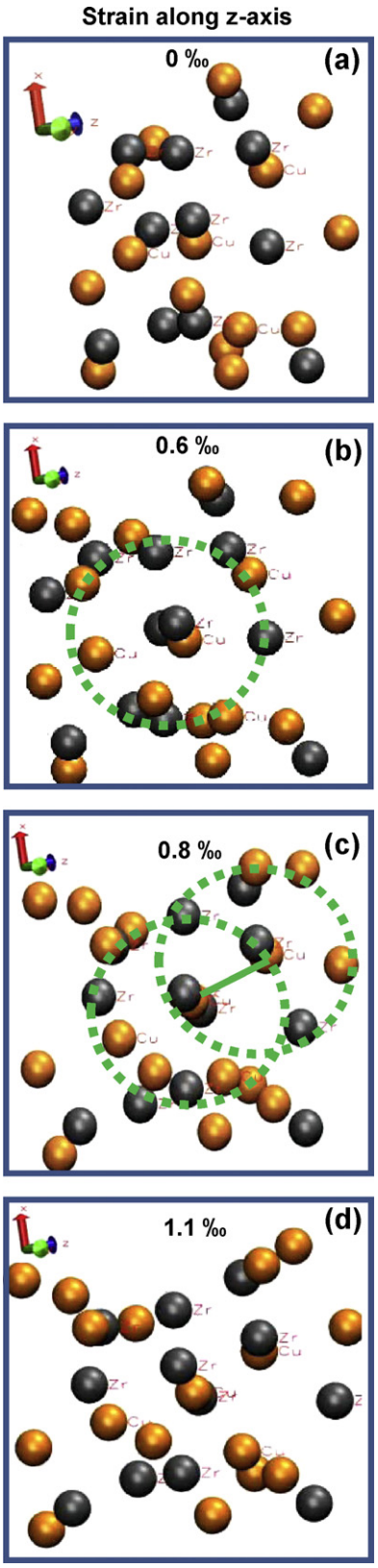


**Fig. 1.** Sequence of snapshots extracted from MD trajectory of $Cu_{46}Zr_{54}$ upon tensile deformation showing (a) the initial amorphous matrix, (b) the creation of an ICO cluster, (c) the SC formation from two interpenetrating ICOs and (d) the destruction of the SC.