



Structural modeling of liquid and amorphous Al₉₁Tb₉ by Monte Carlo simulations



M. Ovun^a, M.J. Kramer^b, Y.E. Kalay^{a,*}

^a Department of Metallurgical and Materials Engineering, METU, Ankara 06800, Turkey

^b Ames Laboratory US DOE, Ames, IA 50011, USA

ARTICLE INFO

Article history:

Received 27 June 2014

Received in revised form 13 August 2014

Available online 6 September 2014

Keywords:

Monte-Carlo simulations;

Medium-range ordering;

Phase separation;

Chemical and topological configuration;

Al–RE metallic glass

ABSTRACT

Evolution of the chemical and topological inhomogeneities within the Al₉₁Tb₉ amorphous system from liquid to glass was investigated using Monte Carlo (MC) simulations. The interatomic potential for Al–Tb system was developed and three-dimensional atomic configurations of liquid and amorphous structures were modeled. The simulations coupled with Voronoi Tessellation and Warren–Cowley chemical short-range order analysis revealed a high degree of chemical inhomogeneity at nanoscale composed of pure Al clusters which were found to be increasing in number and size with decreasing temperature in the supercooled liquid region. These chemically isolated prenucleation clusters are thought to be the origin of extreme number.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Marginal glass forming alloys have been regarded as promising structural materials due to their continuous fine grain structure attributed primarily to their ability of forming very high number density of nuclei upon crystallization [1,2]. Marginal glass forming alloys, unlike bulk metallic glasses, require high cooling rates $\sim 10^5$ K/s to form a fully amorphous structure [3–5]. Lightweight high-strength Al–RE based alloys [1] and magnetically soft and hard Fe–RE (RE: Rare-earth element) based alloys [3] are two well-known examples for marginally glass forming alloys. The devitrification process of marginally amorphous metals quite often results in formation of very high number densities of primary crystals (10^{21} – 10^{24} m⁻³) with sizes of less than 50 nm. An extensive research in this area has still been in progress to give an exact explanation for the mechanism underlying the formation of such high density of nanocrystals. As the large percentage of bulk amorphous metals do not result in the formation of nanocrystals when subjected to similar heat-treatments; the answer for this enigmatic behavior may lay hidden within the structure of the as-quenched marginal glass forming alloys.

The previous studies on Al–RE and Al–RE–TM amorphous alloys have resulted in two main speculations on the formation of highly populated nanocrystals after low-temperature annealing process. The first one relies on the fact that small fractions of crystallite nuclei already exist in the as-quenched solid [6]. The growth of these nuclei is suppressed by the rapid increasing viscosity near the glass transition

temperature (T_g) during quenching. Therefore some nuclei are trapped in the amorphous matrix and subsequent annealing below T_g results in the growth of these “quenched-in nuclei”. This hypothesis was tested by using melt-spun and cold-rolled Al–Sm amorphous specimens [6]. The existence of highly populated Al-nanocrystals, as observed for melt-spun specimens, was not detected in the cold-rolled specimens upon similar heat treatment processes. Moreover, fluctuation electron microscopy signals [7] indicating an fcc like medium-range order (MRO) for Al atoms in melt-spun alloy were absent for cold-rolled specimen. This agrees well with the hypothesis of having Al crystals being frozen during the quench of the as-spun ribbons. Cold-rolled specimens represent a different type of chemical and topological arrangement where fcc-like order is missing. The second approach is based on phase separation [5,8] effective in amorphous matrix by a mechanism similar to spinodal decomposition [8]. The origin of the phase-separation was explained through a time-independent homogeneous nucleation theory called coupled-flux nucleation [8,9]. According to this argument amorphous phase resulted by rapid-solidification phase separates into Al-rich and RE-rich regions prior to crystallization. Al-rich amorphous regions which extend to 74–126 nm [5] are held responsible for the nucleation of fcc-Al nanocrystals. Both approaches were questioned on different aspects [10–12]. For instance, a phase separation was reported for Al₈₈Gd₆La₂Ni₄ [8] alloy but not observed for Al₈₈Gd₆ErNi₄ [13] where a two-stage fcc nanocrystallization was indicated for several Al–TM–RE amorphous which does not agree with “quenched-in” nuclei hypothesis [14].

Recently, it has been stated that the phase separation in Al may actually be present at nanoscales in the as-quenched state [5,8–12,15] as well as in other systems such as Fe-based, Pd-based and Zr-based

* Corresponding author. Tel.: +90 312 210 2525; fax: +90 312 210 2518.

E-mail address: ekalay@metu.edu.tr (Y.E. Kalay).

metallic glasses [16]. By using atom probe tomography (APT), Kalay et al. have demonstrated regions of 1 nm of pure Al in as quenched $\text{Al}_{90}\text{Tb}_{10}$ [11]. An approximate number density for these regions was calculated as 10^{25} m^{-3} . APT results collected from the specimens annealed to temperatures just before the crystallization temperature point out coalescence of pure Al regions which reduce the population of pure Al clusters to $10^{21-22} \text{ m}^{-3}$. According to small angle X-ray scattering studies, there occurs a phase separation in $\text{Al}_{91}\text{Tb}_9$ as well as in some other Al–rare-earth amorphous alloys prior to devitrification [17]. SAXS/WAXS measurements show that the further coarsening of these chemical fluctuations eventually triggers the nanocrystallization of primary fcc-Al phase [18,19]. Fluctuation electron microscopy (FEM) studies from both as-quenched and annealed specimens of Al–rare-earth alloys clearly reveal medium-range order up to some degree. Therefore, the phase-separated Al and RE rich regions may possess their own atomic structure at a first place in the as-quenched state. These structures do not have conventional crystal configurations, but still hold medium-range correlations.

While above-mentioned experimental approaches are only able to probe the microstructural features resulting from the phase separation in nanoscale, the phase separation itself in Al–rare-earth system can only be investigated by using appropriate computational approaches at the present time. In this study, by investigating the short to medium range correlations, we demonstrate a possible kinetic pathway for the chemical and topological evolution of pure-Al regions during vitrification of $\text{Al}_{91}\text{Tb}_9$ alloy and their role as prenucleation clusters prior to primary crystallization of fcc-Al nanocrystals by using Monte Carlo (MC) simulations.

2. Experimental procedure

The $\text{Al}_{91}\text{Tb}_9$ ingots were produced by electric arc melting under Ar atmosphere by using highly pure Al (99.99 wt.%) and Tb (99.9 wt.%) elements. The diffraction studies of liquid $\text{Al}_{91}\text{Tb}_9$ were previously performed by using the high-energy transmission synchrotron X-ray diffraction (HEXRD) at the Advanced Photon Source at Argonne National Laboratory. Specimens for liquid $\text{Al}_{91}\text{Tb}_9$ analysis were cast into 2 mm diameter rods, inserted into quartz capillaries and sealed under Ar atmosphere. Capillaries were lined with carbon to reduce the interaction between the quartz and the molten alloy at elevated temperatures. The sealed carbon-lined quartz capillaries were heated up to 1208 K and exposed to 100 keV of X-rays corresponding to a wavelength of 0.0124 nm. The diffraction data from molten alloy were collected in transmission (Debye–Scherrer) geometry by a MAR charge coupled device (CCD) with 60 s of exposure time. Similar diffraction patterns were collected from the blank holder and empty carbon-lined quartz capillary for background corrections. The raw HEXRD data collected from the liquid $\text{Al}_{91}\text{Tb}_9$ were corrected for polarization, absorption, multiple, Compton scattering and converted to the total structure factor function, $S(Q)$ by a procedure described in [15]. The ab-initio molecular dynamics (AIMD) simulations were performed by using Vienna ab-initio Simulation Package (VASP). Periodic boundary conditions were applied with constant number of particles, volume and temperature (NVT) by using Nosé–Hoover thermostat to control the temperature [20–23]. Initial number densities for $\text{Al}_{91}\text{Tb}_9$ were estimated by using linear combination of pure Al and Tb elements. The exchange–correlation function has been described with generalized gradient approximation (GGA) of Perdew–Burke–Erzernhof formulations. 200 atoms were distributed randomly in a periodic cell with correct stoichiometry of the produced alloys. Initially, the system was heated up to 2500 K to erase the memory effects for preparing the liquid Al–Tb alloy then subsequently cooled down to 1208 K and to room temperature (300 K). Reverse Monte Carlo (RMC) simulations of the experimental data were conducted by using RMC++ simulation package [24] in order to obtain partial pair correlation functions of liquid $\text{Al}_{91}\text{Tb}_9$. Lacking experimental data for the partial pairs, the RMC was constrained using the density and the partial pair-

correlation functions from the AIMD simulation [24,25]. The resulting fit of the experimental data is shown in Fig. 1a. The combination of the RMC and AIMD provides a robust determination of the longer range partial pair correlations that cannot be obtained by AIMD alone due to the limited size of the system [26].

Inverse Monte Carlo (IMC) algorithm [27] was utilized with a reliable atomic model, to develop an interatomic potential for the Al–Tb system. Partial pair distribution functions obtained from RMC were used as input in the algorithm. Using the interatomic potentials, sequential Monte Carlo simulations were conducted using NVT ensemble from 1200 K to 300 K with temperature decrements of 100 K. For each temperature, the volume of the simulation cell is determined by the number densities that are obtained from AIMD simulation. In order to reach to a relatively stable state, the $\text{Al}_{91}\text{Tb}_9$ system of 32,000 atoms was initialized in fcc configuration and equilibrated for 100,000 steps at 1200 K. At subsequent temperatures, the initial atomic configuration for the next simulation is taken from final atomic configuration of the previous one, and equilibrated 50,000 steps sufficient for the system to reach a relatively stable state. After the energy minimization is complete, the structural data was collected for 5 sets between intervals of 1000 steps.

3. Results and discussion

The interatomic pair potentials obtained from IMC algorithm are shown in Fig. 1b. The relatively limited representation of Tb–Tb interactions resulted in a wavy $E(r)$ - r behavior. On the other hand, the resulting partial $g(r)$ functions obtained from MC simulation at 1200 K governed by the developed interatomic pair potentials almost perfectly fit with partial $g(r)$ functions obtained from RMC (red-dotted line) as shown in Fig. 2a–c. Therefore, we believe that the interatomic pair potentials developed using IMC are successfully represent the paired Al–Tb interactions. Evolution of the partial $g(r)$ functions obtained from subsequent isothermal MC simulations 1200 K to 300 K is shown in Fig. 2a–c. The trend of the change in average atomic volume with respect to temperature in AIMD simulation and that of corresponding MC simulations is given in Fig. 3a. It can be deduced that the system undergoes a glass transition near 600 K due to the rapid decrease in the rate of volume change.

The evolution of the local atomic configuration of Al-centered clusters was initially investigated using Voronoi Tessellation [15]. In Voronoi Tessellation analysis of topologically disordered systems, each atom in the space can be represented by a Voronoi polyhedron while the number of faces forming a polyhedron corresponds to the coordination number of the given atom. Every single face of the polyhedron determines the border between the central atom and one of its neighboring atoms, and the number of edges forming the face gives the number of common neighbors of the corresponding atom pair. All polyhedrons were defined by 5-digit Voronoi indices in the form of $\langle N_3 N_4 N_5 N_6 N_7 \rangle$ where each digit represents N_i number of i -edged faces. The Voronoi polyhedra can be roughly separated into three categories: icosahedral-like, crystal-like and mixed [30]. Within these categories $\langle 0 0 12 0 0 \rangle$, having 12 neighbors, each represented by N_5 faces, represents the nearly perfect icosahedral structure, $\langle 0 1 10 2 0 \rangle$ is a commonly observed icosahedral derivative, and $\langle 0 2 8 4 0 \rangle$ can be interpreted as either a highly distorted icosahedral-like or a mixed-type cluster. The $\langle 0 3 6 \times 0 \rangle$ represents a common mixed-type cluster family, and clusters relatively dominated by N_4 and N_6 faces such as $\langle 0 4 4 6 0 \rangle$ are considered as crystal-like. As shown in Fig. 3b, the population of certain Al-centered clusters considerably increases during vitrification which is the first sign of particular ordering. Icosahedral-like clusters such as $\langle 0 1 10 2 0 \rangle$ and $\langle 0 0 12 0 0 \rangle$ steeply dominated the topology near glass transition, and $\langle 0 3 6 4 0 \rangle$ clusters among the other mixed-type clusters become more preferred with a steady increase in number with decreasing temperature, while $\langle 0 2 8 4 0 \rangle$ exhibits a behavior in between. The amount of crystal-like $\langle 0 4 4 6 0 \rangle$ slightly increases in the amorphous state, whereas some other populous clusters

Download English Version:

<https://daneshyari.com/en/article/1480967>

Download Persian Version:

<https://daneshyari.com/article/1480967>

[Daneshyari.com](https://daneshyari.com)