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Acta Materialia 60 (2012) 4720–4728

Acta MATERIALIA

www.elsevier.com/locate/actamat

Structural properties of amorphous metal carbides: Theory and experiment

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Received 1 March 2012; received in revised form 24 April 2012; accepted 25 April 2012
Available online 28 June 2012

Abstract

By means of theoretical modeling and experimental synthesis and characterization, we investigate the structural properties of amorphous Zr–Si–C. Two chemical compositions are selected: $Zr_{0.31}Si_{0.29}C_{0.40}$ and $Zr_{0.60}Si_{0.33}C_{0.07}$. Amorphous structures are generated in the theoretical part of our work by the stochastic quenching (SQ) method, and detailed comparison is made regarding the structure and density of the experimentally synthesized films. These films are analyzed experimentally using X-ray absorption spectroscopy, transmission electron microscopy and X-ray diffraction. Our results demonstrate a remarkable agreement between theory and experiment concerning bond distances and atomic coordination of this complex amorphous metal carbide. The demonstrated power of the SQ method opens up avenues for theoretical predictions of amorphous materials in general.

Keywords: Amorphous materials; Ab initio calculations; X-ray absorption spectroscopy; Metal carbide glasses; Atomic structure

1. Introduction

Deposition of thin films from the vapor phase may lead to amorphous structures. A group of materials which often exhibit non-crystalline structure is various transition metal–metalloid films such as Cr–C, Zr–Si and Fe–B [1–3]. Interestingly, they are also important components in metallic glasses formed during rapid quenching from a melt, suggesting that the tendency to form amorphous structure is related to inherent properties of the elements and interactions between these elements. In order to obtain a more detailed understanding of the formation of amorphous structures and glasses we need to develop theoretical methods to model the structure and bonding in these non-crystalline environments. This can be achieved by, for example, molecular dynamics (MD) [4], Monte Carlo (MC) simulation [5] and reverse Monte Carlo (RMC) simulation [6]. These methods, together with experimental techniques, have been used to investigate short-range order in metallic glasses. Sheng et al. studied $Ni_{80}P_{20}$ theoretically by RMC and ab initio MD methods, as well as experimentally by X-ray diffraction and EXAFS [7]. Guerdane and Teichler applied MD to investigate $Ni_{25}Zr_{60}Al_{15}$ alloy [8]. Imafuku et al. described the local atomic structures of $Fe_{90-x}Nb_{10}B_x$ (x being 10, 20, 30) by anomalous X-ray

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http://dx.doi.org/10.1016/j.actamat.2012.04.044

scattering measurements [9]. Qin et al. studied the structure of liquid and amorphous $Fe_{78}Si_9B_{13}$ alloys by ab initio MD [10]. Hostert et al. validated their ab initio MD model for Co–Fe–Ta–B and Co–Fe–Ta–Si metallic glasses by experimental pair distribution functions, densities and elasticity data [11,12]. Unfortunately, the computational methods mentioned above suffer from being computationally expensive or rely on interatomic potentials of sometimes questionable accuracy. In this study we investigate another approach, namely the stochastic quenching (SQ) method [13,14], which combines computational efficiency and accuracy in describing the chemical interaction. This method is based on the single-random-valley approximation in vibration-transit (VT) theory. The VT theory was originally developed for simple metal liquids [15,16]. According to this theory, the atomic motion is described by vibrations within a single valley, interspersed by transits, which carry the system across intervalley intersections. The random class of many-atom potential energy valleys dominates the potential surface, and these valleys have the same macroscopic potential properties. In this method the atoms are placed randomly in the calculation cell, and are then relaxed using first-principles density functional (DFT) calculations until the force on every atom is negligible. It has been shown that it is possible to generate amorphous structures this way [13,14]. However, the present investigation is the first in which a detailed comparison between experiment and the SQ theory is made in terms of structural properties, such as bond length and nearest-neighbor coordination, in particular for a material with complex chemical interactions.

In this study, we have selected the Zr–Si–C system as an amorphous model system, since transition metal carbides and silicides are known to have complex chemistry, with competing metallic and covalent bonds [17]. We deposit amorphous films using magnetron sputtering from elemental targets and confirm the structure experimentally with several techniques. The choice of elements is based on several facts. First, Zr is a well-known base element in many metallic glasses. The atom has a large radius (1.59 Å), favorable for amorphous structure formation when combined with several other elements with smaller radii [18]. Second, the Zr–Si system is well known to produce amorphous thin films with magnetron sputtering for potential use as, for example, diffusion barriers [3]. The addition of carbon to a ternary Zr–Si–C film will create a multicomponent system with different atomic radii favorable for glass formation [18]. Also, in a ternary Zr–Si–C film a wide variety of bond types is formed (metallic Zr–Zr, and covalent Zr–C, Zr–Si and Si–C bonds), which makes it possible to create a network structure which should further favor an amorphous structure. The potential for applications in Zr–Si–C has recently been discussed [19].

The paper is organized as follows. In Section 2, we describe the theoretical methods used in this study, and summarize the most important details of the calculations. The experimental methods are described in Section 3. The theoretical and experimental results are presented in Section 4.

2. Theory

The amorphous structures were generated theoretically by the SQ method. This method is designed to describe amorphous structures in general, although there is less experience with it for complex materials with competing natures of chemical bonding. The amorphous structures are obtained by means of the following two steps of the SQ method. Firstly, the atoms are placed randomly in the calculation cell under the constraint that no pair of atoms are closer together than a small value (typically 0.4 Å). This constraint is required in order to avoid numerical problems in the first few steps in the calculation. Secondly, the positions are relaxed by means of a conjugate gradient method until the force on every atom is negligible. We found that the self-averaging of 150–200 atoms usually properly describes the electronic properties at the thermodynamic limit [14,20–24]. In the present study we used 200 atoms for most of the calculations, and made a few calculations with 400 atoms for comparison.

The first-principles calculations were performed by means of the projector augmented wave [25,26] method as implemented in the Vienna Ab initio Simulation Package (VASP) [27–29]. This method is based on DFT [30,31]. The exchange–correlation energy was calculated using the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional[32]. The calculations were considered converged when the potential energy difference between atomic iterations was less than 10^{-5} eV atom^{-1}, and the forces on each atom were typically less than 0.005 eV Å^{-1}. A plane-wave energy cutoff of 400 eV was employed. The calculations were performed using only the Γ k-point.

3. Experimental

The Zr–Si–C film was deposited by non-reactive, unbalanced, DC magnetron sputtering in an ultra-high-vacuum chamber (base pressure 1×10^{-7} Pa). Separate 2 in. elemental targets (Kurt J. Lesker Ltd.) with a purity of 99.999% for Si and C and 99.2–99.7% (grade 702) for Zr were used. The Ar plasma was generated at a constant pressure of 0.4 Pa with a deposition temperature of approximately 350 °C and bias of −50 V. All depositions were made using a rotating substrate holder to ensure a homogeneous composition. Prior to deposition, the Si and SiO_2 substrates were cleaned in an ultrasonic bath in 2-propanol and ethanol for 5 min each and dried with nitrogen gas. The deposition rate was 40–70 Å min^{-1} depending on composition and the films for X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and resistivity analysis were deposited with a thickness of ~0.3 μm. The chemical composition was analyzed by XPS using a Physical Systems Quantum 2000 spectrometer