Journal of Non-Crystalline Solids 400 (2014) 67–71

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Prediction and fabrication of Ti–Zr–Co ternary metallic glasses based on effective atomic radius in Ti solid solution from first-principles calculations

Naoya Shirasawa *, Ren Ito, Yorinobu Takigawa, Tokuteru Uesugi, Kenji Higashi

Department of Material Science, Osaka Prefecture University, Gakuen-cho 1-1, Sakai 599-8531, Japan

ARTICLE INFO

Article history:
Received 5 February 2014
Received in revised form 14 April 2014
Available online 23 May 2014

Keywords:
Metallic glasses;
Amorphization;
Computer simulations;
Cluster

ABSTRACT

New Ti-based metallic glasses were designed and fabricated in the ternary component alloy system Ti–Zr–Co. The constituent elements of the alloy system were selected based on three empirical rules proposed by Inoue, Turnbull, Senkov and Miracle, and by a new parameter called the effective atomic radius, which is based on the first-principles calculations for 2.78 at.% hcp Ti alloys. The reported scheme based on the concept of binary eutectic clusters was applied to predict the alloy composition that shows a glass transition, $Ti_{44}Zr_{30}Co_{26}$. We prepared $Ti_{44}Zr_{30+x}Co_{26-x}$, $Ti_{46}Zr_{28+x}Co_{26-x}$, and $Ti_{48}Zr_{26+x}Co_{26-x}$ ($x = 0, 4, 6, 8$) alloy sheets using a single roller method. The new Ti-based ternary metallic glasses exhibited vitrification for many compositions around the predicted composition of $Ti_{44}Zr_{30}Co_{26}$. The greatest value of the super-cooled region ΔT_x was 34 K for $Ti_{48}Zr_{32}Co_{20}$.

1. Introduction

Ti-based metallic glasses exhibit low density, high specific strength, good corrosion resistance, low Young's modulus, and biocompatibility [1,2]. The unique properties of these alloys make them extremely attractive for biomedical applications [3]. Most Ti-based metallic glasses reported to date are variations of three basic systems (Ti–Cu–Ni, Ti–Cu–Zr, and Ti–Zr–Be) [4–6]. Adding active elements to these systems to increase their ability to form a glass has already been studied by many researchers (for example, Ti–Cu–Ni–(Zr) [7,8], Ti–Zr–Be–(Fe, Cr) [9,10], and Ti–Zr–Cu–Pd–(Sn) [11,12] alloys). However, many of these alloys contain toxic elements such as Ni and Be or noble metals such as Pd, which prevent their practical use. Therefore, it is of scientific and technological interest to design and fabricate a new Ti-based ternary metallic glass free from harmful elements and noble metals.

Since the discovery of the Au–Si system, many empirical rules have been proposed for designing metallic glasses, and some of these are shown below. First is the component rule of glass type alloys proposed by Inoue [13,14], where the metallic glass should fulfill the following conditions: 1) multicomponent system consisting of more than three elements, 2) significant atomic size mismatches (above 12% among the main three elements), and 3) negative heats of mixing among the main elements. The second rule was proposed by Turnbull [15], who pointed out that amorphous alloy compositions tend to be close to a very low eutectic melting point in the equilibrium phase diagram. The third rule is a topological approach proposed by Senkov and Miracle [16], based on the analysis of atomic size distribution obtained by plotting atomic concentrations versus atomic radii of the constitutive elements. There are also criteria based on thermodynamic and electronic models besides these rules [17,18]. However, it is difficult to use thermodynamic and electronic models to design metallic glasses because interatomic reaction data is insufficient. Methods of design based on short range clusters and e/a ratio have also been reported [19–21]. However, since there has been no report applicable to Ti-based alloys, it is difficult to use these methods for the design of new Ti-based ternary metallic glasses.

The existing ternary metallic glasses are classified into three types using the third rule among the criteria mentioned above. The first type is the large element-based (L-based) type. The base alloying element in this type has the largest atomic size and the smallest atom has the next highest concentration, and Ln-, Zr-, Pd-, and Pt-based ternary metallic glasses are included in this type. Atomic size distributions of L-based type glasses, which are known for having high glass forming ability (GFA), have a concave upward shape with a minimum at the middle atomic size [16]. Therefore, the model of short and medium range atomic packing is proposed for this type [22]. The second type is the middle element-based (M-based) type. The base alloying element in this type has the middle atomic size and Mg-, Ti-, Fe- and Co-based ternary metallic glasses are included in this type. Atomic size distributions of representative compositions of M-based type are shown in Fig. 1. As can be observed, alloy systems in the M-based type show significant atomic size mismatches (atomic radius ratios differ more than 24% between the largest and smallest element), and certainly fulfill

* Corresponding author. Tel.: +81 72 254 9313; fax: +81 72 254 9912.
E-mail address: st110024@edu.osakafu-u.ac.jp (N. Shirasawa).

http://dx.doi.org/10.1016/j.jnoncrysol.2014.05.005
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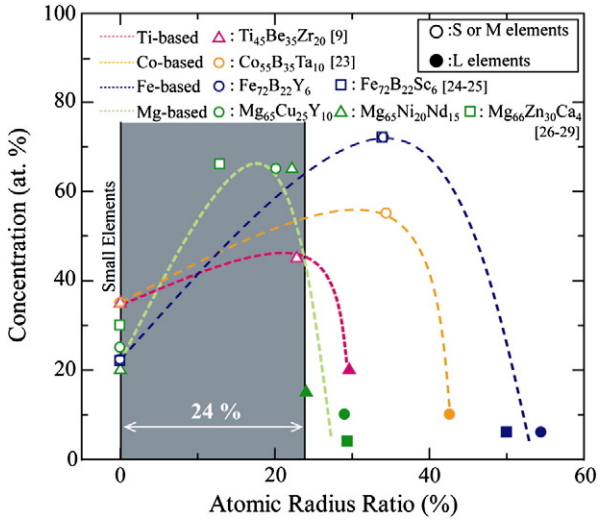

Fig. 1. Atomic size distributions in ternary metallic glasses of M-based type [6,23–29].

the semi-empirical rule proposed by Inoue. So in this type, atomic size is considered to be an important factor of GFA. The third type is the two-element-based (T-based) type. There are two base alloying elements in this type (for example, $Ti_{50}Cu_{42}Ni_8$ [24], $Cu_{50}Ti_{40}Zr_{10}$ [25], $Zr_{47}Cu_{47}Al_6$ [26], $Pd_{40}Ni_{40}P_{20}$ [27,28], and $Ni_{60}Nb_{37}Sn_3$ [29] alloys). Atomic size distribution of T-based type does not have a regular shape. Moreover, the atomic radius ratios between the largest and smallest element of this type are below 24%. Therefore, it is thought that another factor other than atomic radius contributes to GFA in this type.

In the Ti-based ternary metallic glasses, the Ti–Zr–Be system included in the M-based type shows the highest GFA. But Be is so toxic that it is necessary to search for an alternative element to Be using the atomic radius, which is considered to be an important factor in GFA in M-based type glasses. However, atomic radius varies depending on the crystal structure and combination of elements. Therefore, in this study, a new parameter called the effective atomic radius of the elements in the Ti solid solution (calculated by first-principles calculations) is used along with the three empirical rules mentioned above, which are the component rules of glass-type alloys proposed by Inoue, the rule of favorable conditions for amorphous formation in metallic systems suggested by Turnbull, and the topological approach proposed by Senkov and Miracle to design a new Ti-based ternary metallic glass free from toxic elements and noble metals.

2. Theory

2.1. First-principles calculations of effective atomic radius

First-principles calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) [30]. CASTEP is an ab initio pseudopotential method code for solving the electronic ground state of periodic systems in which wave functions are expanded in a plane-wave basis that is set using a technique based on density functional theory (DFT). The electronic exchange-correlation energy used in the DFT was given by the generalized gradient approximation proposed by Perdew et al. (PW91) [31]. Ultrasoft pseudopotentials [32] were used. A cut-off energy of 350 eV was used for the plane-wave basis in all the calculations.

The (hcp)-$Ti_{35}X_1$ solid solution was modeled using supercells containing 36 atoms that are periodic in all three directions, as in our previous studies [33]. The (hcp)-$Ti_{35}X_1$ supercells were hexagonal cells with $3 \times 3 \times 2$ primitive unit cells. The supercells contained only one substitutional solute atom per supercell, which corresponded to a 2.78 at.% solid solution. The energy integration over the Brillouin zone was undertaken using k-points in accordance with the Monkhorst–Pack grid [34] with sets of $6 \times 6 \times 5$ k-points. As introducing the substitutional solute atom leads to local lattice distortion and change in the cell volume, full structural relaxation of the atomic configurations and lattice constants was taken into account for the calculations.

Empirically, the atomic radius of metallic materials is the metallic radius, which is defined as half the distance between neighboring atoms. It is desirable to use the so-called Goldschmidt radius that converts the radii to values with a coordination number of 12 [35] for the atomic radius of metallic materials. The effective atomic radius can be determined by quantitative comparison of the size of the solute atom from the hard sphere approximation as in our previous studies [36]. The effective atomic radius of solute atoms in a solid solution, r_X, is given by

$$r_X = d - d_0/2, \tag{1}$$

where d is the interatomic distance between a solute X atom and a solvent Ti atom in the Ti–X solid solution, and d_0 is the interatomic distance for the first nearest-neighbor atoms in pure Ti. The interatomic distances between the solute and solvent atoms were readily obtained using first-principles calculations by relaxing both the lattice constants of the supercell and atomic configurations.

2.2. Selection of elements

First, the element which replaces Be of the Ti–Zr–Be system included in the M-based type was selected using the atomic radius, which is considered to be an important factor in GFA in this type. It is needed for an alternative element to Be to have a small atomic sizes with an atomic radii ratio differing 24% or more from Zr. Atomic radii are shown in Fig. 2 [35,37].

As can be observed in Fig. 2, Si, P, and S fulfill the conditions, but these elements do not have a low melting eutectic point in their equilibrium phase diagram with Ti. The eutectic temperatures with Ti are 1330 °C, 1495 °C, and 1212 °C for Ti–Si, Ti–P, and Ti–S systems, respectively [38]. Generally, good glass forming compositions in a given system are often at or near deep eutectic points, which has been clearly demonstrated in many alloy systems [5,39–41]. From these studies, a critical eutectic temperature in a phase diagram for forming a glass phase is considered to be around 1000 °C. So the element that fulfills these conditions does not exist when selected by the conventional method based on atomic radii. Hence, the constituent elements were selected for this study based on the values of effective atomic radii in the Ti solid solution. The calculated effective atomic radii from first-principles calculations are shown in Fig. 3. It can be seen that Zr has the largest atomic size and fulfills the empirical rules and purpose of

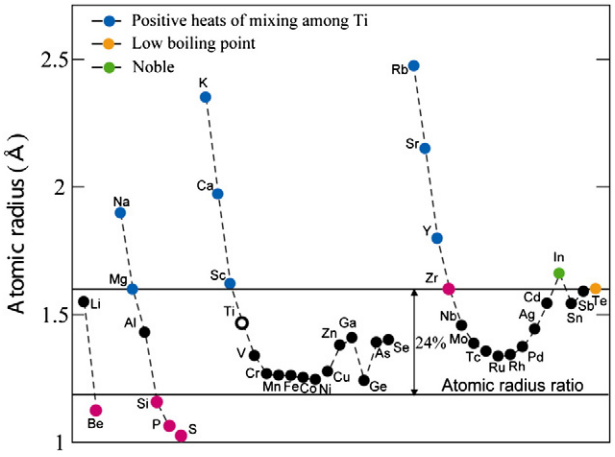

Fig. 2. Atomic radius from Li to Te [40,42].