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The bulk metallic glass formation in Zr–Al–Ni–Ti quaternary system

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Abstract

The optimum metallic glass compositions are located close to the intersecting line of the *e*/*a*-constant and atomic size-constant planes in a quaternary composition chart. According to these criteria, a series of Zr–Al–Ni–Ti quaternary alloys have been designed and prepared by suction casting. The electron concentration and average atomic size of two ternary glass forming alloys, $Zr_{60}Al_{20}Ni_{20}$ and $Zr_{53}Al_{23.5}Ni_{23.5}$, have been used. Pure glass state is reached only within a small composition range of Ti. Ti addition deteriorates the thermal stabilities, but maintains the same glass forming abilities of bulk metallic glasses.

Keywords: Bulk metallic glasses; Zr–Al–Ni–Ti alloys; Electron concentration; Average atomic size

1. Introduction

Many bulk metallic glasses (BMGs) have been found in Zr–Al–TM and Zr–Ti–TM (TM=transition metals) multi-component systems. Inoue group first determined the BMG composition region of the Zr–Al–Ni ternary system [1]. Later, we further optimized the Zr–Al–Ni BMG compositions by using composition criteria developed by us, i.e. the *e*/*a*-constant line with *e*/*a*=1.5 constant line and the icosahedron Zr_9Ni_4–Al cluster line. It was pointed out that the $Zr_{53}Al_{23.5}Ni_{23.5}$ BMG has the largest reduced glass transition temperature T_{rg} [2]. Many Zr–Ti-based multi-component amorphous alloys, such as Zr–Ti–Cu–Al–Ni, Zr–Ti–Cu–Ni–Be, Zr–Ti–Cu–Ni–Be–Fe were also proved to produce BMGs. For instance, Johnson and Pecker discovered a Zr–Ti–Cu–Ni–Be alloy which can be made into an amorphous ingot with the size of 10 cm in diameter and 20 kg in weight [3]. However, no quaternary Zr–Al–Ni–Ti bulk amorphous alloy has ever been reported so far. In this paper, the glass formation in the Zr–Al–Ni–Ti quaternary alloy system is investigated using our composition criteria, the *e*/*a*-constant criterion and the average atomic size (R_{av})-constant criterion, which has been used successfully in the Zr–Al–Ni–Cu system [4]. In the following, we first review the existing alloy design principles for amorphous alloys and introduce our own composition design principles (Fig. 1). Then the criteria are to be used in the composition optimization of the Zr–Al–Ni–Ti BMGs.

2. Composition design

BMGs have been found in many systems. However the formation mechanism is still unclear. Inoue has pointed out that the BMGs' forming systems satisfy the three factors [5]. That is, 1) multicomponent alloy systems consisting of more than three elements; 2) difference in atomic size ratios above 12% among the main three constituent elements; and 3) negative heats of mixing among their elements. The Mg-, Ln-, Zr-, Fe-, Co-based bulk glassy alloys for the achievements of large GFAs all follow the three rules. However this is only an empirical rule and can not tell the ideal amorphous alloy composition. To date, there is no quantitative criterion for determining the BMG formation composition. This hindered the further development of new BMGs.

Recently, several rules have been proposed to design amorphous alloys' composition. The glass former is always associated with deep eutectic. Li has studied the glass forming ability around eutectic composition and pointed out that the glass forming ability

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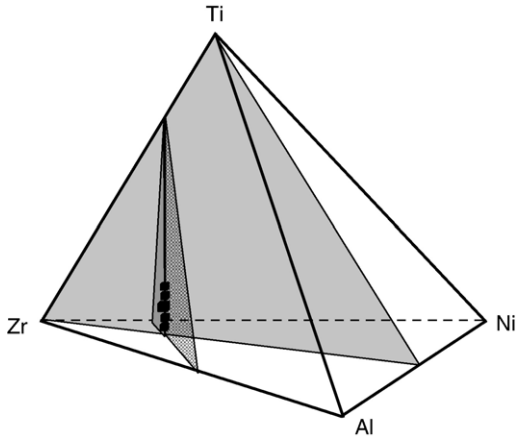

Fig. 1. Zr–Al–Ni–Ti Quaternary composition chart Gray plane: 1.5 *e*/*a*-constant plane; white plane: 0.1496/0.1479 nm atomic size-constant plane.

of a eutectic alloy system depends on the type of the eutectics, i.e. symmetric or asymmetric coupled zone. For the alloy systems with symmetric eutectic coupled zone, the best composition should be at or very close to the eutectic composition. For the alloys with asymmetric eutectic coupled zone, the best composition should be at an off-eutectic composition, probably towards the side of the faceted phase with high entropy in the phase diagram. The competitive process between the formation of glass and the growth of the eutectic and primary phases can well explain the microstructure change of these cast rods, which suggests a good way to pinpoint the best glass forming alloy within the binary Cu–Zr alloy and La-based ternary system [6–8].

Amorphous alloys with high glass forming ability can be regarded as alloy phases with specific compositions. The amorphous formation is sensitively dependent on electronic and atomic structure [9]. Nagel and Taue have examined the electronic structure of metallic glasses consisting of noble and polyvalent metals [10]. They showed that metallic glasses are a group of Hume–Rothery phases, like many crystalline intermetallics. The optimum *e*/*a* ratio, *e*/*a* being the average valence electron number per atom, is about 1.8. Later, Haussler further termed the optimum metallic glasses "ideal amorphous state" [11]. Atomic size factor is also an important factor in determining the glass forming compositions. Amand and Giessen pointed out that atomic size difference influences liquid viscosity and hence amorphous alloy formation [12]. Mizutani and Massalski attempted to combine the contributions of electronic and size effects as two main parameters in judging the glass forming ability [13]. Dong indicated that the GFAs and thermal stabilities of BMGs are closely related to the conduction electron concentration *e*/*a* and the atomic size factors. Recently, we assigned the effective values for the transition metal constitutes in BMGs, and their related phases and proposed the *e*/*a*-related criteria to locate the multi-compositions with high GFAs. The empirical criteria in combination with phase diagram characteristics have been used to predict the large GFA regions in Zr-based Zr–Al–Ni (Co) and Zr–Al–Ni–Cu systems [14,15,4].

A BMG and its crystalline counterparts have nearly constant *e*/*a* ratios specific to a given alloy system. In a binary system, the specific *e*/*a* ratio determines the composition of the best glass forming composition. In a ternary system, *e*/*a*-constant composition corresponds to an *e*/*a*-constant line. In a quaternary system, it is an *e*/*a*-constant plane. Atomic size is also an important factor in forming amorphous structure. The constant atomic size (R_a-constant) phenomenon also existed in BMGs. Zr–Al–Ni–Cu is a typical quaternary BMG forming system. Lots of amorphous

Table 1
Compositions of the alloys designed according to $Zr_{60}Al_{20}Ni_{20}$with constant *e*/*a*=1.5 and R_{av}=0.1496 nm and to $Zr_{53}Al_{23.5}Ni_{23.5}$with constant *e*/*a*=1.5 and R_{av}=0.1479 nm

Number	Alloys
$Zr_{60}Al_{20}Ni_{20}$–Ti	
0	$Zr_{60}Al_{20}Ni_{20}$
1	$Zr_{58}Al_{18.8}Ni_{18.8}Ti_{4.4}$
2	$Zr_{56.5}Al_{17.96}Ni_{17.96}Ti_{7.58}$
3	$Zr_{55}Al_{17.1}Ni_{17.1}Ti_{10.8}$
$Zr_{53}Al_{23.5}Ni_{23.5}$–Ti	
a	$Zr_{53}Al_{23.5}Ni_{23.5}$
b	$Zr_{52.54}Al_{22.73}Ni_{22.73}Ti_2$
c	$Zr_{51.62}Al_{22.19}Ni_{22.19}Ti_4$
d	$Zr_{50.70}Al_{21.65}Ni_{21.65}Ti_6$

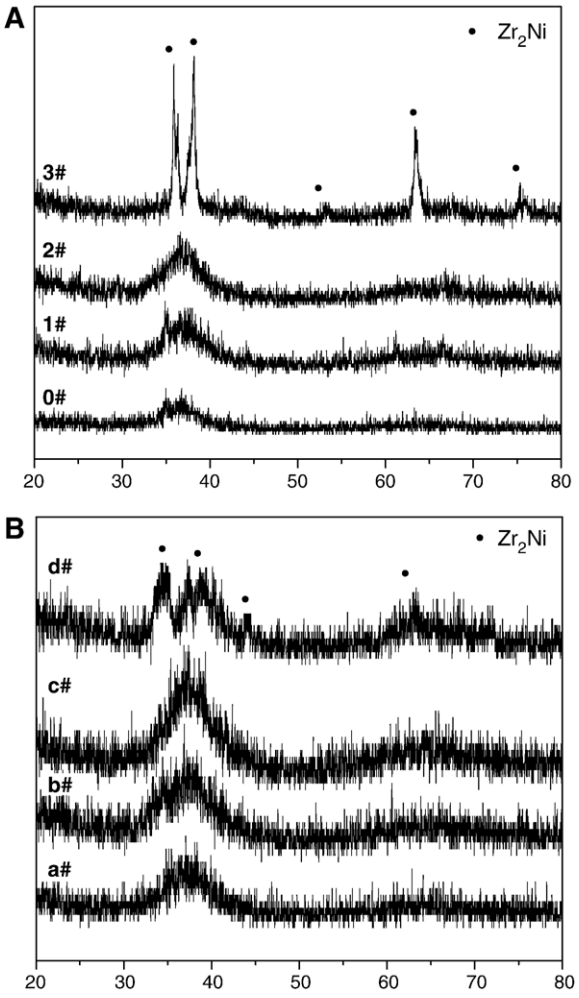

Fig. 2. X-ray diffraction spectrum of suction-cast Zr–Al–Ni–Ti system alloys (A): designed according to the $Zr_{60}Al_{20}Ni_{20}$ alloy; (B) designed according to the $Zr_{53}Al_{23.5}Ni_{23.5}$ alloy.