Formation and Mechanical Properties of Bulk Glassy and Quasicrystalline Alloys in Zr-Al-Cu-Ti System

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Summary: The glass-forming ability (GFA) of Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ alloy can be improved effectively by a certain amount of Ti addition. Bulk glassy samples of 3 mm in diameter were obtained in the compositions containing 3–7 at% Ti by copper mold casting, while further Ti additions will deteriorate GFA and lead to the formation of quasicrystals at (Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$)$_{90}$Ti$_{10}$. Meanwhile, the addition of Ti in the Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ alloy was found to alter the crystallization behavior of the metallic glasses; thus bulk quasicrystalline alloy can also be achieved by glass devitrification of Ti-containing BMGs. Room-temperature compression testing showed that bulk quasicrystalline alloy, fabricated either by mold casting or by glass devitrification method, exhibited higher fracture strength and Young’s modulus than that of the relative monolithic BMGs.

18.1 Introduction

An icosahedral short-range order (ISRO) has been suggested to be the intrinsic local structure of metallic glasses [1]. It creates a thermodynamic barrier to the formation of periodic crystals. Therewith, the enhanced stability of such a local atomic configuration leads to improved glass-forming ability (GFA) of an alloy [2–4]. Meanwhile, icosahedral atomic clusters are the building blocks of icosahedral quasicrystals (I-phases) and their crystalline approximants [5]. Under favorable preparation conditions, the icosahedral order could be extended orderly in real space to form an I-phase. And the formation of I-phase is available during the alloy melt cooling down path or on the subsequent heating of these Zr-based BMGs [6, 7]. In most cases, nanometer scaled I-phases revealed as the primary precipitation phases when annealing the BMGs within their undercooled liquid regions. These I-phases are metastable and their grains can not grow easily into a large size [8, 9]. Recently, Kühn et al. found that, in the Zr-Ti-Nb-Cu-Ni-Al BMG-forming alloy system, a large-grained I-phase was formed directly from the melt at low cooling rates [10]. The above experimental evidence implies certain relations in the formation of BMGs and I-phases in these alloys. Generally, I-phases have strict structures and a limit
compositional stability as well [11, 12]. BMG formation is also compositional sensitive [4]. Thus in a given system, it is worthwhile to systematically examine the compositional effect on their formations. In a previous work, we reported that the addition of early transition metals as Ti, Nb, or Ta in the Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$ alloy triggered the I-phase formation via crystallization [13]. In the present work, we will make a thorough investigation on the compositional dependence of BMG and I-phase formation in the Zr-Al-Cu-Ti alloy system. The mechanical properties of the bulk glassy and quasicrystalline alloys are also studied.

18.2 Experimental

Alloy ingots of compositions (Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$)$_{100-x}$Ti$_x$ ($x = 0, 2, 3, 5, 7, 10, 12,$ and 15 at%) were prepared by arc melting the constituent elements under a Ti-gettered high purity argon atmosphere. The purities of metals are 99.9 wt% for Zr and Ti, 99.999 wt% for Al, and 99.99 wt% for Cu. The ingots were remelted four times to improve homogeneity. The alloy ribbons with a cross section of about $0.05 \times 1.0\, \text{mm}^2$ were prepared by using a single roller melt-spinning apparatus with a wheel surface velocity of $40\, \text{m}\, \text{s}^{-1}$. Alloy rods with different diameters were made by means of copper mold suction casting.

X-ray diffraction (XRD) for phase identification was conducted on a Rigaku RINT-ultima IIIsp diffractometer with Cu K$_\alpha$ irradiation ($\lambda = 0.15406\, \text{nm}$). TA-DSC Q100 type differential scanning calorimetry (DSC) and TA-STD Q600 type differential thermal analysis (DTA) were employed to study the thermal stability. The constant heating rates for DSC and DTA measurements were 40 and 20 K min$^{-1}$, respectively. Isothermal annealing treatment was done in the DSC sample chamber under a continuous flow of Ar.

Rod specimens with a length/diameter ratio of 6/3 were adopted for the uniaxial compression testing. Quasi-static loadings (strain rate of $5 \times 10^{-4}\, \text{s}^{-1}$) were conducted on an Instron at room temperature, and the strain was measured by using a strain gauge. The fracture morphology of the broken samples was observed by scanning electron microscopy (SEM).

18.3 Results and Discussion

18.3.1 Formation of BMG and QCs by Liquid Cooling

XRD analysis indicated that all the melt-spun (Zr$_{65}$Al$_{7.5}$Cu$_{27.5}$)$_{100-x}$Ti$_x$ ($x = 0, 2, 3, 5, 7, 10, 12,$ and 15 at%) samples were metallic glasses. The constant heating rate DSC traces of them were shown in Fig. 18.1. Ti-addition is found to lead to a shift of the onset crystallization temperature ($T_x$), while the change glass transition temperature ($T_x$) is very subtle. The under-cooled