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Influence of Al content on martensitic transformation behavior in $Zr_{50}Cu_{50-x}Al_x$

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ABSTRACT

Influence of Al content on martensitic transformation temperature in ZrCu phase was investigated by differential scanning calorimetry for a series of $Zr_{50}Cu_{50-x}Al_x$ alloys. The crystallographic structure of the martensite was predominantly a monoclinic Cm, which is a superstructure of B19′. Microstructural observations revealed that a higher Al content above 6 mol% led to a pronounced formation of Zr_2Cu and τ_5 phases forming complex eutectic microstructures. The electron probe microanalysis indicated that the Al atoms in ZrCu phase substitute the Cu atoms up to 6 mol% and the excess Al atoms exist mainly in the τ_5 phase. The increasing Al content from 0 to 6 mol% induced a decrease in the martensitic transformation start temperature, M_s, from 446 K to 311 K, and in the reverse martensitic transformation start temperature, A_s, from 537 K to 468 K. But M_s remained almost constant when the Al content is over 6 mol%. Thus, the substitution of the Cu atoms by the Al atoms in ZrCu phase led to the decrease in M_s and A_s.

1. Introduction

Structure and phase transformation in binary ZrCu intermetallic compound has been studied since the early 1980s [1–5]. ZrCu exhibits two unique characteristics, namely martensitic transformation and high stability of amorphous phase. Koval et al. [6–8] reported that the equiatomic ZrCu intermetallic compound undergoes martensitic transformation (MT) from the cubic B2 structure to two monoclinic martensite phases at 443 K [9], one with a base structure (B19′) with $P2_1/m$ symmetry and the other with its superstructure with Cm symmetry. Shape memory effect associated with the MT has been also observed [9–11].

On the other hands, relatively high glass-forming ability (GFA) in the ZrCu based alloy systems was demonstrated by Inoue et al. [12,13]. The addition of Al significantly improves the GFA with the maximum ΔT_x ($\Delta T_x = T_x - T_g$, T_g: glass transition temperature, T_x: onset temperature of crystallization) of 80 K at the composition of $Zr_{50}Cu_{40}Al_{10}$ [14]. Zr–Cu–Al bulk amorphous can be produced in the form of one centimeter diameter rod [15]. More recently, Zr–Cu–Al metallic glasses (MG) were shown to exhibit pronounced work hardening when the B2 crystals of several hundred nanometers are present in the structure due to the stress-induced martensitic transformation [16–19]. These MG/B2 composites may be a potential method to improve the plasticity of bulk metallic glasses (BMGs) after further adjustment of the structures and MT [20]. For Zr–Cu–Al metallic glasses, the improvement of Al on the GFA has been confirmed by Xing et al. [21]; however, there are few reports about the effect of Al content on the MT behavior in ZrCu intermetallic compound.

In this study, the influence of substitution of Cu by Al on the martensitic transformation temperatures in $Zr_{50}Cu_{50-x}Al_x$ alloys was investigated. The microstructure, crystallographic structure and phase transformation behaviors are presented, and the factors influencing the variation in the transformation temperatures are also discussed.

2. Materials and methods

Ingots of $Zr_{50}Cu_{50-x}Al_x$ ($x = 0, 2, 4, 6, 8, 10$) were prepared by arc-melting the element metals of Zr, Cu and Al in an argon atmosphere. Hereafter, the sample with x mol% aluminum will be referred to as xAl. To maintain a low-oxygen concentration in the alloys, a high purity Zr with the oxygen content less than 0.05 at% was used. The mother ingots of the alloys were remelted at least three times in order to ensure the chemical homogeneity. In the 10Al alloy with the highest glass formability, amorphous phase was observed in the bottom part of the ingots. All the ingots were completely remelted, and cast into cylindrical rods with the diameter of 10 mm. The X-ray diffraction analysis of the as-cast samples revealed that 6Al, 8Al and 10Al alloys were fully amorphous. All the samples were crystallized at 1073 K for 72 h in a sealed quartz tube under an argon atmosphere, followed by water quenching. This treatment was also sufficient to crystallize the amorphous phase in the 6Al, 8Al and 10Al samples. Crystal structures of the samples were characterized by X-ray diffractometry (XRD) with a Cu-Kα radiation (40 kV–300 mA). Differential scanning calorimetry (DSC) was carried out using a TA Instrument DSC Q-10 with a heating/cooling rate of 0.17 K/s to determine the forward and reverse MT temperatures. All the DSC runs

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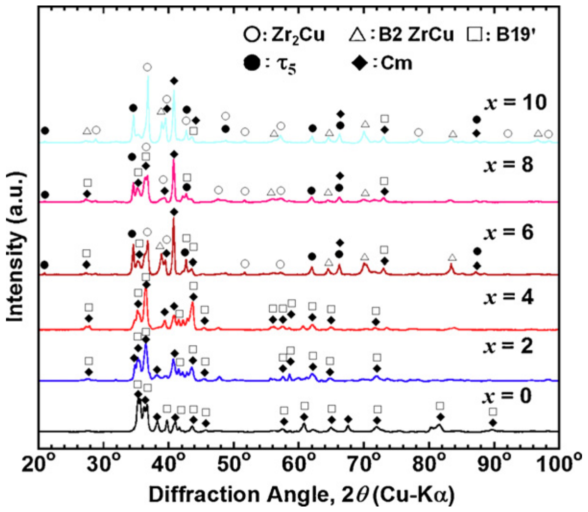

Fig. 1. X-ray diffraction patterns of $Zr_{50}Cu_{50-x}Al_x$ ($x = 0$, 2, 4, 6, 8, 10) after crystallization treatment at 1073 K for 72 h.

were started from a heating run after holding the samples at 193 K for 5 min. The microstructure was investigated by optical microscopy (OM) using a Nikon Eclipse LV150 microscope with a differential interference mode, and by backscattered electrons (BSE) mode on a JEOL 7001F scanning electron microscope (SEM), operated at 20 kV. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2000FX transmission electron microscope operated at 200 kV. The samples for OM and SEM observations were mechanically polished using SiO_2 (0.06 μm) colloidal suspension. Disc samples (⌀3 mm) for TEM observations were mechanically thinned to 150 μm thick and then perforated by electropolishing using a Tenupol-5 with an electrolyte consisting of 20 vol% nitric acid and 80 vol% methanol at a temperature of 253 K. The chemical compositions of different phases were determined by an electron probe microanalyzer (EPMA) using JEOL JXM-8530F.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $Zr_{50}Cu_{50-x}Al_x$ samples after crystallization treatment at 1073 K for 72 h. It can be seen that all the samples have been fully crystallized, and both B19′ and Cm martensite phases are detected in all the samples. For the $x = 0$ and 2 samples, all the peaks can be assigned to the B19′ or Cm martensite phases, and no other phase is detected. As seen in Fig. 1 most of the peaks for B19′ and Cm martensite phases overlap and there are only a few minor peaks that can be solely attributed to B19′ (such as those at around 42 degree in 0Al and 2Al samples).

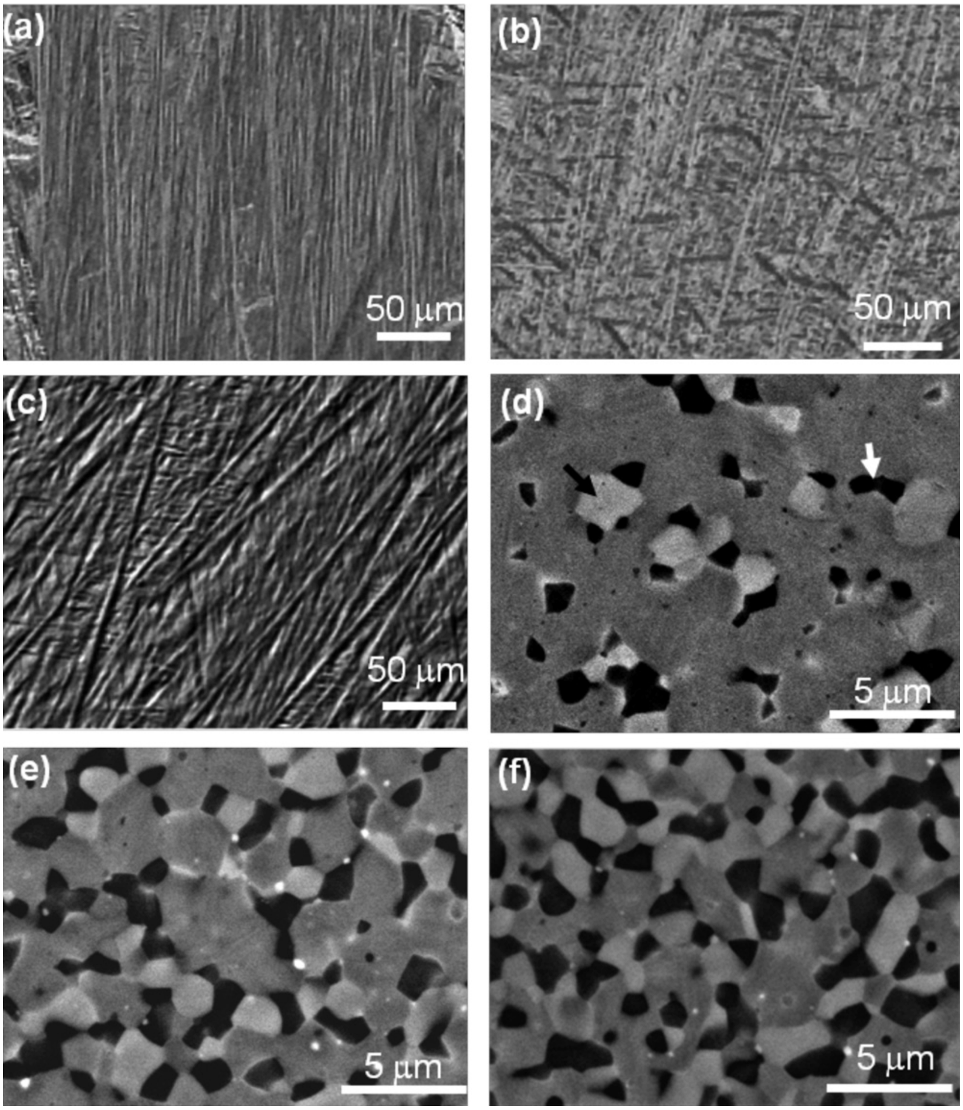

Fig. 2. Optical micrograph of (a) 0Al, (b) 2Al, (c) 4Al, and BSE-SEM micrographs of (d) 6Al, (e) 8Al, (f) 10Al after crystallization treatment at 1073 K for 72 h.