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Study of the reversible intermetallic phase: B2-type CuZr

X. Cui, F.Q. Zu*, Z.Z. Wang, Z.Y. Huang, X.Y. Li, L.F. Wang

Institute of Liquid/Solid Metal Processing, School of Materials Science & Engineering, Hefei University of Technology, No. 193 Tunxi, Anhui 230009, Hefei, People's Republic of China

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ABSTRACT

B2-type CuZr phase is a ductile intermetallic phase which is beneficial to the excellent plasticity of CuZr-based bulk metallic glass (BMG) composites. Studying the crystallization process of CuZr-based BMGs will be helpful in understanding the forming mechanisms of CuZr phase. In the present paper, electrical resistivity measurement and X-ray diffraction were carried out to study the crystallization behaviour of $Cu_{50}Zr_{50}$ amorphous alloy. The B2 CuZr phase forms at 997 K, intriguingly, the inverse process shows a temperature hysteresis of 117 K. The hysteresis temperature during cooling process is believed to be beneficial in stabilizing B2 CuZr phase when fabricating B2 CuZr reinforced BMG composites. Knowing the characteristics of B2-type CuZr phase will be helpful in exploring CuZr-based BMG composites.

1. Introduction

The unique mechanical properties of BMGs such as large elastic limit, high fracture strength and hardness make BMGs more potential predominance on scientific research and industrial application [1–4]. Although some BMGs with large plasticity have been reported by now [5,6], most BMGs macroscopically exhibit obvious brittleness, such as no yielding and no work-hardening behaviour during room temperature deformation, which limits their development to a great extent [7]. Therefore, improving the plasticity is of importance for the potential engineering application of BMGs. One of the most effective ways on improving the plasticity of BMGs is to introduce a second phase into the metallic matrix. The second phase can be introduced by in-situ ways such as in-situ precipitation of microlevel or nanolevel ductile intermetallic phases [7–10], or ex-situ ways such as dispersing spherical particles into the master alloy [11,12]. B2-type CuZr phase is a ductile intermetallic known as the shape-memory compound [13], and it usually in-situ precipitate in a series of Cu–Zr–Al and Cu–Zr–Ti BMG composites [7,9,14–17]. These BMG composites usually show obvious plastic deformation and work-hardening behaviour under room temperature compression, even in tensile test conditions [16,17]. B2 CuZr is also known as a reversible intermetallic phase concerning the reversible reaction: B2 CuZr ↔ B19′ CuZr (where B2 is austenite and B19′ is martensite). The martensite transformation of CuZr phase can be induced by deformation, and it was reported [17] that the deformation induced martensite transformation in BMG composites can increase the rate of strain hardening and suppress early necking, which being the controlling mechanism for the observed strain hardening and ductility.

As it is known that [7,8] the B2 CuZr phase is an equilibrium phase at temperature higher than 988 K, it will decompose to $Cu_{10}Zr_7$ and $CuZr_2$ with the temperature descending. $Cu_{50}Zr_{50}$ BMG, which has the same atomic ratio as CuZr phase, is the base alloy for a series of CuZr-based BMGs. Knowing the crystallization behaviour of $Cu_{50}Zr_{50}$ metallic glass (MG) and the forming mechanism of B2 CuZr phase will be important for exploring BMGs or BMG composites with excellent plasticity for engineering applications. In aims of seeking the basic characteristic of the reversible intermetallic phase: B2-type CuZr, electrical resistivity measurement was employed to study the crystallization process of $Cu_{50}Zr_{50}$ MG with a constant heating and cooling rate of 10 K/min. The crystallization products of $Cu_{50}Zr_{50}$ MG are $Cu_{10}Zr_7$ and $CuZr_2$. The forming temperature of CuZr begins at 997 K, which relates with the reversible reaction formula: $Cu_{10}Zr_7 + CuZr_2 \leftrightarrow CuZr$. However, the inverse process shows a wide temperature hysteresis, the hysteresis is believed to be significant for stabilizing B2 CuZr phase when fabricating B2 CuZr phase reinforced BMG composites.

2. Experimental

The alloy ingot of nominal composition $Cu_{50}Zr_{50}$ was prepared by arc melting mixture of ultrasonically cleaned Zr and Cu with a purity of 99.9 at%, 99.999 at%, respectively. The arc melting was performed in a Ti-gettered high purity Argon atmosphere. The

* Corresponding author. Tel./fax: +86 551 2905057.
E-mail address: fangqiuzu@hotmail.com (F.Q. Zu).

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ingot was re-melted five times in the arc melter and accompanied with electromagnetic stirring in order to insure chemical homogeneity, and then crushed into pieces. Amorphous ribbon with a thickness of about 50 μm was prepared by the single roller melt-spinning method under a high purity argon atmosphere. The circumferential velocity was about 28.8 m/s. The electrical resistivity was measured using the direct current four-probe method as a function of temperature, the voltage was measured by Keithley-2182 nano-voltmeter and the constant current was provided by the PF66M sourcemeter. The structures were checked using X-ray diffraction (XRD) (D/MAX-2500V Cu Ka radiation).

3. Results and discussions

The XRD pattern of as quenched $Cu_{50}Zr_{50}$ MG is shown in Fig. 1, and it exhibits only broad diffuse diffraction peak characteristic which implies that the structure of as prepared $Cu_{50}Zr_{50}$ MG is fully amorphous. Electrical resistivity measurement upon heating and cooling will provide us fine detailed information about the structural change of as-quenched $Cu_{50}Zr_{50}$ MG, as shown in Fig. 2(a). The glass transition temperature T_g and crystallization temperature T_x are determined using the method proposed by Guo et al. [18], which are 665.4 K and 719.6 K, respectively.

The resistivity–temperature curve of $Cu_{50}Zr_{50}$ MG shows two stage of decrease of the resistivity. The first decrease of the resistivity begins at T_x. And the secondary decrease appears at 997 K, which is close to the forming temperature of B2 CuZr phase related with the reaction formula: $Cu_{10}Zr_7 + CuZr_2 \leftrightarrow CuZr$, which had been reported earlier [14,19]. Intriguingly, a reversible phenomenon at a much lower temperature is observed from the cooling curve of resistivity, apparent increases of the resistivity begins at 880 K and finishes at 796 K, after that then, the resistivity decreases nearly linearly with the temperature descending. Fig. 2(b) shows the second thermal cycling of the crystallized $Cu_{50}Zr_{50}$ MG with heating and cooling rate of 10 K/min. The starting temperature of the decrease of the resistivity is 997 K, and the inverse process begins at 871 K.

The method of changes in resistivity is sensitive to structure change but it is quantitative, and the X-Ray diffraction method allows one to make qualitative analysis. In order to get detailed information of the crystalline phases at different stage, the samples were treated as follows: (1) Quenched into water after the primary decrease of resistivity (primary precipitated phases); (2) Quenched into water from 1100 K (transformed crystal phases) (3) Cooled with the vacuum furnace from 1100 K (final crystal phases). The results of the phase identification are shown in Fig. 1. As it can be seen that, the primary precipitated phases are identified to be $Cu_{10}Zr_7$ and $CuZr_2$, the transformed crystal phase is identified to be CuZr, while, the final crystallization phases are the same as the primary crystallization phases. The experimental results confirm that the secondary crystallization process is the reversible CuZr phase formation process, which concerning the reaction [20]: $Cu_{10}Zr_7 + CuZr_2 \leftrightarrow CuZr$.

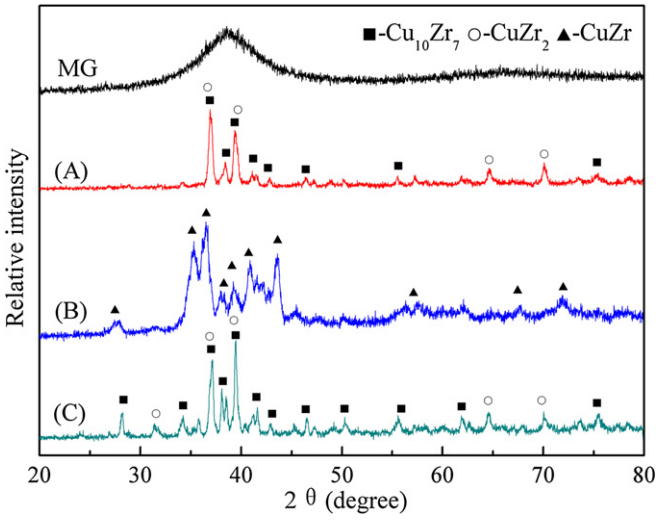

Fig. 1. XRD pattern of $Cu_{50}Zr_{50}$ metallic glass ribbon(MG), and the phase identification results which include: (A), primary crystal phases; (B), transformed crystal phases; (C), final crystal phases.

Referring to Cu–Zr binary alloy phase diagram (Fig. 3, the phase diagram of CuZr alloy was drawn referring to the references [20,21]), the constituent phases of $Cu_{50}Zr_{50}$ alloy at room temperature are $Cu_{10}Zr_7$ and $CuZr_2$. On heating $Cu_{50}Zr_{50}$ alloy, the starting point of B2 transformation begins at 997 K, which is quite in accordance with the phase diagram. Here, it should be emphasized that the inverse process is proved by electrical resistivity measurement to be 880 K, 117 K lower than the transition temperature. It was reported [22] that as the atomic distance in $CuZr_2$ phase is far different from that of CuZr phase, and formation of $CuZr_2$ phase need long range diffusion during the phase separation process of CuZr phase, which is believed to be the reason for the hysteresis in this work. Consequently, the $Cu_{10}Zr_7$–$CuZr_2$ eutectic system in CuZr phase diagram should be revised: an extended temperature region of CuZr phase on cooling process is shown by the dot line in Fig. 3. It should be pointed that T_1 represents the forming temperature of CuZr on heating, and T_2 represents the decomposing temperature on cooling. The existence of the hysteresis temperature can remarkably suppress the decomposition process of B2 CuZr phase upon cooling. Especially, when fabricating austentic CuZr phase reinforced BMG composites, the existence of the hysteresis temperature during cooling will be important for stabilizing the B2 CuZr phase.

It had been reported that [7,8] by micro element addition or element substitution to $Cu_{50}Zr_{50}$ alloy, the glass forming ability could be improved distinctly. Although some ductile CuZr-based BMG had been reported [23,24], excellent mechanical property was mainly achieved in many CuZr-based BMG composites which composed of BMG matrix containing dispersive ductile B2 CuZr intermetallic phase [7,9,13,14]. The plasticity of BMG composites was believed to be caused by the precipitation of in-situ microlevel spherical CuZr phase which reinforces the BMG matrix. It was also reported [16,17] that B2 CuZr is a reversible phase and the phase transformation from B2 CuZr to B19′-CuZr was responsible for suppressing the tensile work-softening and affording ductility of these CuZr-based BMG composites. As a result, the rapid propagation of shear bands would be blocked, which requires further stress to move the shear bands and consequently inhibits the early necking and work-softening [16]. So, the precipitation of B2 CuZr phase is important for achieving excellent mechanical properties of CuZr-based BMG composites, knowing the characteristic and forming mechanism of B2 CuZr will be of significance for exploring new BMG composites with outstanding mechanical property for engineering applications.

Zhang et al. [22] reported that the Zr–Cu distance in CuZr-based BMGs is 0.286 nm, being very close to the distance (0.279 nm) of the nearest neighbour Cu–Zr pair in B2-type CuZr phase. It is indicated that the local structure of CuZr-based BMGs have certain similarities with CuZr phase in terms of the inter-atomic distances and atomic coordination. On quenching the Alloy melts, as the local structure of CuZr phase and the melt structure have certain similarities, CuZr phase would precipitate on primary cooling process of the melt. As the cooling rate on copper mould casting process is usually very high, the hysteresis temperature of the B2 phase which related the reaction: $CuZr \rightarrow Cu_{10}Zr_7 + CuZr_2$, could stabilize B2