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Cu–Hf–Ti–Ag–Ta bulk metallic glass composites and their properties

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Abstract

Multi-component $(Cu_{0.50}Hf_{0.35}Ti_{0.10}Ag_{0.05})_{100-x}Ta_x$ ($x = 0$, 1, 3, 5, 8, 12) bulk metallic glass (BMG) composites containing in situ formed dendrites were prepared successfully. With increasing Ta content, both compressive fracture strength (σ_f) and elastic-plastic strain (ε_f) increase from 2180 MPa and 2.1% for $x = 0$, to 2770 MPa and 19.2% for $x = 8$, respectively, but yield strength and elastic modulus decrease. The precipitation of a high volume fraction of the dendrites ($V_{dendrite}$) causes the compositional variation of the dendrites and its counterpart glass matrix. Composition analysis shows that both Hf and Ti elements exhibit an opposite behavior of dissolving into the dendrites during the cooling. About 7–11 at.% component elements (Ti, Cu and Ag) were detected in Ta-rich dendrites, but no Hf element was found. With increasing $V_{dendrite}$, the content of component elements dissolving into Ta-rich dendrites decreases from 11.35 at.% for $V_{dendrite} = 4.3\%$ and 7.97 at.% for $V_{dendrite} = 26.5\%$. Indentation testing was also performed to evaluate the properties of the composites. With increasing $V_{dendrite}$, the hardness of the dendrites decreases from 6.0 GPa for $x = 3$ to 5.21 GPa for $x = 12$, and its elastic modulus increases from 151.2 GPa for $x = 3$ to 156.9 GPa for $x = 12$. The hardness and elastic modulus of the glassy matrix also decrease, respectively, from 9.66 and 148.7 GPa for $x = 0$ to 9.36 and 137.4 GPa for $x = 12$ with increasing precipitation of the dendrites. The variation of the properties is due to the compositional change originating from the opposite behavior of Hf and Ti elements to dissolve into the dendrites.

Keywords: Bulk metallic glass composite; Composition; Dendrite; Mechanical property; Indentation

1. Introduction

Recently, there has been considerable scientific and industrial interest in a variety of bulk metallic glass (BMG) composites as an effective way of further improving mechanical properties compared to monolithic BMGs [1–13]. BMGs are also interesting matrix materials for composites because of their excellent mechanical properties and high resistance against heterogeneous nucleation of crystals [14,15]. Metals, ceramic particles and strong fibers [4–7,11–13] have been introduced successfully into Zr-based BMGs. With further understanding of the formation mechanism of BMGs, Zr–Ti–Cu–Ni–Be–Nb alloys containing in situ formed dendrites have been prepared [3]. The growth of primary dendrite and solute partitioning in the molten state yields a microstructure consisting of a ductile crystalline Ti–Zr–Nb phase, with body-centered cubic (bcc) structure, in the BMG matrix. The dendrites act to seed the initiation of organized shear bands, confine the propagation of individual shear bands, induce the formation of multiple shear bands, and lead to large strain of the composites. Das et al. [8,9] also reported similar results and successful preparation of Be-free Zr-based BMG composites with micro-scale ductile bcc phase reinforcement. Ductile phase-containing metallic glass composites exhibit improved work hardening and ductility compared to monolithic metallic glasses. He et al. [10] reported the mechanical properties and the

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strengthening mechanism of Ti-based composites. The ductile dendritic hexagonal close-packed-Ti (hcp-Ti) solid solution dispersing in the glassy/nanocrystalline matrix also increases the plasticity and fracture strength of the composites. This strengthening behavior is very similar to the results reported by Pekarskaya [3]. More recently, in situ formed Cu-based BMG composites containing the precipitated dendrites have also been reported [16–18]. These composites also display over 10% plastic strain and have much higher fracture strength.

From the above descriptions, it can be seen that the ductile dendrites dispersing in the BMG matrix [3,8,9,16–18] as well as hard/brittle matrix [8,10] play a significant role in improving the plastic strain and inducing the matrix strengthening. In different glassy alloy systems, the dendrites have different composition and crystalline structure, which is decided by the matrix composition, added elements as well as the solid solubility of component elements. Although the effective strengthening role of the dendrites has been reported extensively [3,8,9,16–18], up to now, no sufficient investigation has been made on the properties of the dendritic structure itself, including its composition and properties. As the dendrites are some solid solution phases, like Ti–Zr–Nb bcc structure in Zr-based BMG composites [3], hcp-Ti solid solution in Ti-based composites [8,10] and Ta-rich as well as Nb-rich phases in Cu-based BMG composites [16–18], the precipitation of the dendritic structure is always concomitant with the dissolving process of component elements into the growing dendrites during the cooling. It means that the composition of the precipitated phases is decided by the dissolving as well as dispersing process of component elements from the glassy matrix to the precipitating phases. As the dissolving and dispersing process have a close relation to the solubility, atomic size, atomic concentration, and so on, any change in the above parameters may cause the compositional variation of the precipitated dendrites, and further causes the change in physical as well as mechanical properties. It is very important to investigate the composition of the precipitated dendrites and to clarify the effect of the compositional change on its properties. Due to the special microstructure of the in situ formed BMG composites, indentation testing is a very useful tool for performing this investigation. Actually, the indentation technique has also been used extensively to investigate the properties of BMG and some composites [19–22]. In this paper, we prepared in situ formed Cu–Hf–Ti–Ag–Ta BMG composites containing different volume fractions of the dendrites. Compressive mechanical properties of the composites were investigated and its elastic modulus was measured in detail. By using the indentation technique, we also investigated in detail the hardness and elastic modulus of both the dendrites and its counterpart glass matrix. This will be helpful in further understanding the formation mechanism of in situ formed BMG composites and developing new BMG composites in the future.

2. Experimental procedure

2.1. Preparation and characterization of BMG composites

A group of $(Cu_{0.50}Hf_{0.35}Ti_{0.10}Ag_{0.05})_{100-x}Ta_x$ ($x = 0$, 1, 3, 5, 8, 12) alloy ingots were prepared by arc-melting method. The purity of metals was over 99.9 mass%. At first, both Hf and Ta metals were melted homogeneously in a Ti-gettering argon atmosphere, and then the pre-ingots of Hf-Ta binary alloys were broken or cut into small parts, and mixed homogeneously with other pure metals. The mixtures were re-melted four times by arc-melting in a Ti-gettering argon atmosphere, which ensures that the ingots with the homogeneous composition are obtained. Both Cu–Hf–Ti–Ag BMG and Cu–Hf–Ti–Ag–Ta BMG composites in a cylindrical rod form with the diameters of 2 mm were produced by using copper mold casting. The precipitated phase from the glassy matrix was identified by using X-ray diffraction (XRD) with Cu Kα radiation. The microstructure of the Cu-based BMG composites was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with attached X-ray energy-dispersive spectroscope (EDS). The crystallization enthalpy of Cu–Hf–Ti–Ag BMG and Cu–Hf–Ti–Ag–Ta BMG composites was measured by using differential scanning calorimetry (DSC) in a Seiko DSC 6300 (Exstar 6000, Seiko Instruments Inc.) at a heating rate of 0.33 K/s. The composition of the dendrites and their counterpart glass matrix was analyzed by using EDS. To measure the elastic modulus (Young's modulus) of the composites, the composite rods were cut to specimens of 4 mm length, and were polished carefully. The strain gauge was glued strongly on the surface of the specimens by using the special strain gauge cement. The gauge dimension of specimens was 2 mm in diameter and 4 mm in height. Compressive testing was performed with an Instron testing machine and the strain rate was 5×10^{-4} s^{-1}. After the yielding of the specimen, the strain gauge separated from the surface of the specimen because of the deformation behavior of the specimen; the information obtained from the strain gauge started to deviate from the real values. So, for each material, 3–5 samples were measured again, and were unloaded before yielding. The slope of the stress–strain curves measured by using the strain gauge was estimated as the elastic modulus of the composites.

2.2. Indentation testing

All the specimen surfaces for indentation testing were polished mechanically, subsequently electropolished to