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Preparation of Zr-Al-Mo-Cu Single Targets with Glass Forming Ability and Deposition of Thin Film Metallic Glass

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Abstract: Generally, thin-film metal glass (TFMG) is deposited using two or more elemental targets. Thus, achievement of a homogeneous coating during mass production is difficult. As a new method of TFMG deposition, a single target with high glass-forming ability (GFA) has been used to improve the sputtering process, facilitating easy processing and broad application of sputtering targets. In this study, three kinds of targets (i.e., cast, amorphous, and crystalline targets) are prepared via casting and powder processes. The thermal and mechanical properties of the three targets prepared using the various methods are investigated, and the crystalline target is found to be the most thermodynamically and mechanically stable of the three alternatives. In addition, for TFMG deposited using the microcrystalline target, excellent compositional uniformity between the target and coating is achieved. Therefore, this study experimentally demonstrates that a fine crystalline target is most suitable for use as a multi-component single target in GFA manufacturing methods. These findings are expected to facilitate commercial use of TFMGs.

Keywords: thin-film metal glass; glass-forming ability; crystalline target; compositional uniformity; coatings

1. Introduction

Since its discovery in 1960, metallic glass (MG) has become one of the most studied metal materials [1]. MG, which has an amorphous structure, has excellent properties compared with crystalline materials of the same composition. However, researchers have not yet fully explained the effect of the unique structure of MG on its material properties [2,3]. Moreover, MG is not industrially used because it is difficult to manufacture. To overcome these disadvantages of MG, a new alloy system with high glass-forming ability (GFA) has been developed [4]. Inoue [5] reported achievement of MG with thickness exceeding 1 mm from high-GFA alloys at slow cooling rates, called bulk metallic glass (BMG). The same author proposed three simple empirical rules for BMG manufacture [6]; however, the manufacturing conditions were very limited. BMG was initially expected to be actively applied in industry, but this has not occurred because of size limitations in manufacturing. In general, a fast cooling rate is required to overcome these size limitations. However, the conventional method of BMG manufacture involves liquid–solid quenching with a maximum cooling rate of 10³–10⁸ K/s [7–9], which is not achievable using currently available equipment.



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A recently developed alternative is thin-film metallic glass (TFMG) [10], which is produced through deposition of MG as a thin film on a material surface. In the sputtering process, the vapor is cooled to a solid state at a very high cooling rate of $\sim 10^{12}$ K/s [11]. The powerful quenching techniques employed in the sputtering process can yield MG from immiscible metals [12], and can also provide MG with a wider compositional range compared to that obtained through production under low cooling speed [13]. In contrast to BMG, TFMG exhibits thermodynamic and kinetic stability without composition restrictions. Many studies on application of TFMG in various fields have been conducted [14–18]. However, further investigation of the sputtering target for TFMG deposition is still required. Such research is very important because the quality of the target significantly affects the properties of the deposited coating.

In general, the targets used for TFMG deposition are as follows: Crystalline targets formed via arc casting [19], BMG ingot targets or crystalline targets formed by annealing BMG ingot targets [20,21] and divided targets [21]. In addition, a co-sputtering method can be employed in which two or more targets are used simultaneously. When targets produced by arc melting are used, the composition of the deposited film is different from that of the target [22]; therefore, this technique may be difficult to apply to fields requiring an exact composition. Furthermore, as BMG ingots cannot be manufactured in large sizes, the corresponding targets are only applicable in the laboratory. Finally, the co-sputtering method requires simultaneous control of two or more targets, which is disadvantageous, and it is difficult to control the thin-film composition because the sputtering yield is different for each element in the case of a separated target. For TFMG commercialization, the sputtering method should be simple and there should be low compositional difference between the deposited film and target. The production methods for metal, alloy, and ceramic targets are well established; i.e., melting, powder metallurgy, and powder hot pressing methods, respectively [23]. However, the most appropriate method for production of GFA material targets is currently unknown.

In this study, we investigate the production of a single target with a GFA that can deposit TFMG. A GFA material generally consists of a metal element and a metal bond, but has a unique (e.g., amorphous) structure with a low metal-element diffusion rate [24]. Further, if the target is manufactured as a single target, the sputtering process becomes very simple. Therefore, in this work, GFA single targets are prepared through various manufacturing methods and the most suitable method of target production is experimentally confirmed.

2. Materials and Methods

2.1. Manufacture of GFA Single Target

The target was fabricated using a Zr-base system ($Zr_{62.5}Al_{10}Mo_5Cu_{22.5}$) known to have GFA. Figure 1 illustrates the target manufacturing method used in this experiment. In this study, we considered three kinds of single alloy targets: a cast (Figure 1b), amorphous (Figure 1e), and crystalline target (Figure 1f). The cast target was prepared by melting the designed composition in an arc melting furnace in an Ar atmosphere, i.e., Zr-based elementals were melted together to produce a homogeneous ingot; then, the Al, Cu, and Mo were melted together with the Zr alloy ingot. The ingot was melted and flipped several times, thereby ensuring sample chemical homogeneity.

The amorphous and crystalline targets were prepared through powder metallurgy. The amorphous target was prepared through creation of an ingot in an arc melting furnace. Then, an atomizer was used to prepare MG powder (Figure 1d). In this work, the produced amorphous target had a diameter of 5 in and a height of 3.3 in. A crystalline target was prepared by annealing an amorphous target at 800 °C, the temperature at which the crystallization was complete.



Figure 1. Schematic of target manufacture. (**a**) Preparation of alloy compositions with high glass-forming ability. (**b**) Manufacture of cast targets via arc melting method. (**c**) Manufacture of ingots via arc melting method. (**d**) Metallic glass powder preparation using an atomizer. (**e**) Use of spark plasma sintering equipment to create amorphous targets. (**f**) Preparation of the crystalline target by annealing the amorphous target. (**g**) Thin-film metallic glass deposition using the fabricated sputter target.

2.2. Coating Process

Zr–Al–Cu–Mo TFMG was deposited via a direct current unbalanced magnetron sputtering technique using a single Zr–Al–Cu–Mo sputtering target. Before deposition, Si wafer substrates were cleaned in ethanol via ultra-sonication. The 5 in Zr–Al–Cu–Mo target and the substrates were loaded into the chamber in the appropriate positions. Before deposition, the vacuum chamber was evacuated to $< 1.5 \times 10^{-5}$ Torr. The chamber deposition pressure was 2 mTorr, and high-purity Ar gas (grade-1) was used as the sputtering gas. The deposition sputtering power was 300 W, and the deposition duration 30 min.

2.3. Analysis Techniques

X-ray diffraction (XRD, Malvern Panalytical, X'Pert Pro MPD, Almelo, The Netherlands) and scanning electron microscopy (SEM, FEI Hong Kong Company, NNS-450, Hong Kong, China) analyses were performed to evaluate targets manufactured using the three manufacturing methods. A crystalline target was chosen for mechanical property evaluation. To investigate the mechanical changes with grain size, targets heat-treated at various temperatures (600, 700, 800, and 900 °C) were subjected to Vickers hardness testing. The characteristics of the TFMG deposited via the heat-treated crystalline targets were analyzed using differential scanning calorimetry (DSC, Perkin Elmer, STA 6000, Waltham, MA, USA), glow discharge optical emission spectroscopy (GDOES, Spectruma, GDA 750, Hof, Germany), electron probe microanalysis (EPMA, CAMECA, SX100, Gennevilliers, France), and transmission electron microscopy/energy dispersive X-ray spectroscopy (TEM /EDS, Thermo Fisher Scientific, TALOS F200X, Waltham, MA, USA).

3. Results and Discussion

3.1. Analysis of Target According to Manufacturing Method

The glass transition temperature (Tg) and crystallization temperature (Tx) of the MG powders were determined via differential scanning calorimetry (DSC) analysis (Figure 2). A dense (99.9%) amorphous target was fabricated using hot press equipment at 400 °C, which is within the superplastic zone of 367 to 452 °C (Tg and Tx, respectively). At this temperature, the MG is present as a high-viscosity liquid, and the fluidity increases as the temperature increases. This highly viscous liquid can undergo

significant plastic deformation under the applied pressure, and, in this region, super plastic formation is possible [25].

Figure 3 presents the differences in the target microstructural properties according to the manufacturing method. The XRD peak of the amorphous target constitutes a wide hump in the region of $2\theta = 37.5^{\circ}$. This broad peak indicates that the sample is a completely amorphous structure, consistent with those obtained for Zr-based BMGs [26]. In contrast, sharp peaks are apparent for both the cast and crystalline targets, with the former having a more obvious peak than the latter.



Figure 2. DSC curve of ZrAlCuMo MG powder used in target manufacture.



Figure 3. XRD results for targets prepared using different manufacturing methods. (Inset) Amorphous target XRD results between 20° and 50°.

Figure 4a–f presents SEM images and photographs, respectively, before TFMG deposition of the cast, amorphous, and crystalline target surfaces. It is apparent that the cast target is very rough with large grain sizes, whereas the crystalline target has fine, uniform grain sizes. In contrast, no crystalline phase is apparent in the SEM image of the amorphous target. These results correspond to the XRD result in which the amorphous phase was confirmed (Figure 3).

The modification of the target structure occurring after sputtering is represented by the SEM images presented in Figure 5. The surface morphology of the casting target and the amorphous target was changed to appear as a large crater structure, and the microcrystalline target retained crystalline grains (Figure 5a–c). Figure 5d–f shows the optical microscope images of each target after sputtering. The cast target (Figure 5d) has a rough surface, while the amorphous target (Figure 5e) is completely destroyed. In contrast, the surface of the crystalline target after sputtering is very smooth (Figure 5f). Returning to the cast target after sputtering, it is apparent that many nodules are formed on the surface. In magnetron sputtering, many small protrusions called "nodules" are formed on the target surface [27]. These nodules become larger as the sputtering proceeds, and dense nodule formation degrades the various properties of the film.



Figure 4. (**a**–**c**) SEM results for surfaces before TFMG deposition of the (**a**) cast target, (**b**) amorphous target, and (**c**) crystalline target, respectively. (**d**–**f**) Surface photographs before TFMG deposition of (**d**) cast target, (**e**) amorphous, and (**f**) crystalline targets, respectively.

Amorphous alloys have the following superior characteristics when compared with crystalline alloys: (1) higher σ_f and lower E; (2) much larger elastic strain of approximately 2%, exceeding the yield limit of 0.2% for crystalline alloys; (3) considerably higher elastic energy up to yielding; (4) absence of distinct plastic elongation at room temperature because of the inhomogeneous deformation mode; and (5) a relatively high impact fracture energy of approximately 70 kJ/m [28]. Despite these excellent mechanical properties, however, when an amorphous alloy is used as a target, it is destroyed, as shown in Figure 5e. Generally, amorphous alloys are thermally unstable; therefore, during a high-power sputtering process, partial crystallization may be possible. Thus, formation of a brittle intermetallic phase may have resulted in the amorphous target's destruction observed in this study. This is because the high power of the sputtering process sharply increases the temperature of the sputter target. As an amorphous alloy exhibits a metastable phase, which is a thermodynamically high-energy state, when the temperature rises through atomic collision or receipt of external energy, crystallization proceeds. This is one of the reasons why MG cannot be used as a sputtering target despite its excellent properties.

In contrast, no surface nodules were identifiable on the crystalline target surface in this study, and the surface itself was very smooth and shiny (Figure 5f). This is because the target composition was transferred uniformly to the coating. In addition, the crystalline target, due to the heat treatment, has better mechanical properties than the sample having the same particle size [29]. As shown in Figure 5f, when the TFMG was deposited at the same power as the amorphous target, target destruction was not observed. These results indicate that the cast and amorphous targets are not suitable for use as GFA targets. It is also apparent that the crystalline target is more stable than the other targets for TFMG deposition.



Figure 5. (a-c) SEM results for surfaces after TFMG deposition of the (a) cast target, (b) amorphous target, and (c) crystalline target, respectively. (d-f) Surface photographs before TFMG deposition of (d) cast target, (e) amorphous, and (f) crystalline targets, respectively.

3.2. Optimization of GFA Crystalline Target

The results reported in the previous section experimentally confirm that amorphous and cast targets are unsuitable for the production of GFA alloy targets. In this section, to investigate the appropriate sintering conditions for crystalline targets, the targets were fabricated by annealing an amorphous target at various temperatures. The annealing temperature was based on the DSC results of the MG powder shown in Figure 2, which indicated that the temperature at which crystallization terminated completely was 500 °C. Figure 6 shows the XRD pattern of the target according to the heat treatment temperature. ZrCuAlMo targets consist of a ZrCu(B2) phase, a Zr₂Cu phase, and a ZrCu martensite phase (ZrCu(M)). The Zr₂Cu and ZrCu(M) phase peaks are most clearly displayed at 800 °C, and additional formation of the ZrCu(B2) phase is confirmed at a higher temperature of 900 °C.



Figure 6. XRD results according to the annealing temperature of the target.

Figure 7a–d clearly shows that the grain size increases linearly with temperature. The grain sizes identified based on the SEM images are 0.07, 0.2, 0.5, and 1.54 µm at 600, 700, 800, and 900 °C, respectively. This is because, at higher temperatures, the crystals are subjected to energy that exceeds the interfacial tension. SEM images of the crystalline targets annealed at 600, 700, 800, and 900 °C after Vickers hardness testing are shown in Figure 7e–h, where loads of 5, 20, and 30 kg were used. Cracks occurred at the lowest load (5 kg) in the specimens annealed at 600 °C. The specimens annealed at 700 and 900 °C were broken under loads of 20 and 30 kg, respectively, but those annealed at 800 °C were not destroyed.

The results of this Zr–Al–Cu–Mo experiment are consistent with those reported for a previous experimental study by Paradkar et al. [30], in which fracture toughness changes with grain size were examined. Very similar behavior was observed in this study, as shown in Figure 7e–h, which indicates fracture toughness variation with grain size. Initially, the fracture toughness increased with increasing grain size and reached a maximum at a medium grain size. A low fracture toughness then appeared at a very coarse grain size. It has been reported that the formation of the Zr_2Cu phase and ZrCu(M) contributed to high fracture strength and plastic deformation of the material [31]. Thus, the results of this study indicate that the grain size and crystal phase are important factors that influence alloy fracture toughness, and experimentally confirm that increased fracture toughness is achieved at a specific particle size (0.5 μ m).



Figure 7. (**a**–**c**) SEM images of grain size difference according to annealing temperature in crystallization targets after heat treatment at (**a**) 600, (**b**) 700, (**c**) 800, and (**d**) 900 °C. (**e**–**h**) SEM images after hardness testing of crystallization targets subjected to different annealing temperatures: (**e**) 600, (**f**) 700, (**g**) 800, and (**h**) 900 °C.

Figure 8 shows analysis results for TFMGs deposited using crystalline targets annealed at 800 °C, which exhibited superior thermal stability and mechanical properties in the previous analyses. Figure 8a presents the DSC curve of the TFMG deposited using the crystalline target. The glass transition region, which only appears for TFMG, can be identified. Analysis of the DSC curve yields Tg and Tx values of 391 °C and 444 °C, respectively. This glass transition region is similar to that determined from the MG powder DSC curve in Figure 2. Further, there is only one crystallization peak in the DSC curve. Thus, it can be deduced that eutectic crystallization occurred inside the material [32].

TEM and selected area electron diffraction (SAED) patterns were used to determine the crystal structures of the deposited films, as shown in Figure 8b. Hence, the Zr–Al–Cu–Mo TFMG deposited using the crystalline target was found to have the broad, diffuse diffraction pattern of a typical amorphous phase. Figure 8c presents compositional analysis results for the crystalline target and deposited TFMG obtained via glow discharge optical emission spectroscopy (GDOES). Comparison of the results for the crystalline target and deposited TFMG in Figure 8c presents compositional

uniformity. Hence, it can be seen that the target stoichiometry was very similar to that of the film. Based on a study by Yamamura [33], we calculated the sputter yields of the Zr–Al–Cu–Mo target elements. The sputter yields of the Zr, Al, Cu, and Mo elements were found to be 0.26, 0.43, 1.04, 0.36, respectively, for Ar⁺ ions of 260 eV. In practice, however, a TFMG deposited using a fine crystalline target does not conform to the calculated sputter yields. This result is consistent with findings reported by Thomann et al. [34].



Figure 8. Analysis results for TFMG deposited using a crystalline target annealed at 800 °C. (**a**) DSC curve of TFMG. (**b**) TEM plane-view micrograph of ZrAlCuMo TFMG with inset SAED. (**c**) GDOES results of target and deposited TFMG at 300 W.

In the case of a pure solid element, each element is sputtered at the expected yield. However, the sputtering behavior for an alloy target is not well known and is difficult to predict. As reported by Thomann et al. [34], sputtering of alloyed targets can be seen as a global phenomenon that depends on the base element behavior. Those researchers found that when depositing a thin film using a Zr-based crystalline target, the added elements did not follow the sputter yield but transferred to give the same stoichiometry as the target. Hence, they concluded that the target stoichiometry was transferred to the film because the base elements of different sizes were linked to the Zr.

The TFMG deposited using a fine crystalline target in this study can be regarded as a kind of cluster–assembled metallic glass (CAMG). To form a CAMG, which is one of the MG structural models, atoms are first released from the bulk material (target) and then accumulate to form clusters in the gaseous state. According to Kartouzian and Antonowicz [35], the TFMGs developed to date are not CAMGs. Further, the gas phase entities used in the TFMG production are atoms. The main advantage of a CAMG over a TFMG is that the building blocks of the former can be altered without changing the composition of the final metal film. This is because the fine crystalline target was formed using a composition having GFA.

Figure 9 shows a comparison of the composition of TFMG deposited by the casting, the amorphous, and the microcrystalline targets. The TFMG deposited using a fine crystalline target are more similar to the designed composition than other targets. However, the amorphous target was completely destroyed by high power of the sputtering. The microcrystalline target is more similar to the designed composition than the cast target. This is because the Zr atom and other linked elements (Al, Cu, and Mo) are closer to each other in the microcrystalline target since TFMG, having the same composition as the target, can be deposited easily because it exists as an atomic cluster in the gas phase and has a slow diffusion rate.



Figure 9. Electron probe microanalysis results of TFMG deposited by casting, and fine crystal targets.

4. Conclusions

In this study, we attempted to improve the sputtering process for TFMG deposition by using a single target with a GFA. Various targets, i.e., a cast, amorphous, and crystalline, were used to fabricate a novel GFA sputtering target. The thermodynamically metastable amorphous target was destroyed after sputtering, while the cast target exhibited coarse crystal grains. In contrast, the crystalline target was not only thermodynamically stable, but also exhibited excellent mechanical properties.

The mechanical properties of the crystalline target were further enhanced by annealing. A Vickers hardness test on the micro-crystalline scale (approximately 50 μ m) did not show cracking under a high load of 30 kg. However, cracks were observed for a coarse grain size when the same load was applied. Therefore, a crystal target having a crystal grain size of 50 μ m has thermal and mechanical durability without crack generation, even when high sputtering power is applied. In addition, as the elements are present in cluster form, the use of a single GFA target can ensure TFMG composition uniformity. For industrial applications, the use of a TFMG deposited using a single target could reduce process costs or simplify the process. However, further studies on the atomic behavior of a single target-deposited-TFMG are still needed.

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