The effect of Mo addition on the microstructural evolution and mechanical properties of Zr-Cu-based metallic glass thin films

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Ternary Zr-Cu-Mo metallic glass thin films (MGTFs) with various Mo contents were synthesized on Si (100) wafers and AISI 304 stainless steel substrates by a magnetron co-sputtering technique, using Zr\textsubscript{64}Cu\textsubscript{36} and Mo targets in an Ar gas environment. The effects of Mo addition in a binary Zr\textsubscript{64}Cu\textsubscript{36} MGTF were investigated, with regard to the microstructural evolution and mechanical properties of Zr-Cu-Mo thin films. Instrumental analyses, such as EPMA, XRD, and HR-TEM revealed that Zr-Cu-Mo films with an Mo content below 38 at.\% maintained the monolithic amorphous phase structure. However, when Mo content is added above 46 at.\%, the Zr-Cu-Mo films begin to have nanocomposite structures of well-distributed Mo\textsubscript{2}Zr and Mo crystallites embedded in an amorphous matrix. The hardness and elastic modulus of amorphous Zr-Cu-Mo films showed nearly constant values of 10 GPa and 166 GPa, respectively, regardless of their Mo content. As Zr-Cu-Mo films have nanocomposite structures at a Mo content of 52 at.\%, their mechanical properties showed increased hardness and elastic moduli of 17 GPa and 240 GPa, respectively. The Mo addition generally reduced the average friction coefficient of the ternary Zr-Cu-Mo thin films regardless of phase structure, which can be attributed to the effect of the Mo addition.

Key words: Zr-Cu-Mo, MGTF, Nanocomposite, Co-sputtering.

Introduction

Metallic glasses (MGs) with unique mechanical and physical properties are one of many potential structural and functional materials for engineering applications. Among existing types of metallic glasses, Zr-based metallic glasses [1-4] have been reported to have a high glass-forming ability, high strength, large elastic limits, and excellent corrosion and wear resistance. Additionally, to avoid the rapid propagation of shear bands and improve mechanical properties, reinforced metallic glass matrix composites (MGMCs) have been developed [5-7] by various methods, such as producing dispersed nanocrystals through the partial devitrification of bulk metallic glasses [3, 5], adding crystalline particles to the melt prior to casting [8], or precipitating a dendritic intermetallic phase from the melt [9]. However, there is a limitation for the fabrication of amorphous phase incorporation with noble metals such as Ta, W, Nb, and Mo by the conventional melting method, due to their high melting points and high densities (Mo (2896 K, 10.2 g/cm\textsuperscript{3}), Ta (3269 K, 16.6 g/cm\textsuperscript{3}), W (3695 K, 19.25 g/cm\textsuperscript{3}) and Nb (2742 K, 8.6 g/cm\textsuperscript{3})).

Recently, the synthesis of thin film metallic glasses (TFMGs) using the sputtering method was attempted, due to the various uses of these metallic glasses as medical tools, implants, or engineering materials [10-12]. Through the sputtering method, the solubility, size, and amounts of the reinforcement elements in amorphous matrices could be controlled by adjusting the deposition parameters. The solubility of constituent elements and the range of glass-forming composition by these sputtering techniques are much higher, and are greater than those of the liquid-quenching process for bulk- or ribbon-type metallic glasses [13, 14]. Chou et al. [6] reported the Zr-Cu-Ti-Ta metallic glass thin films with the refractory element of Ta were synthesized via sputtering and had improved mechanical properties, as compared to Zr-Cu-Ti metallic glass thin films without Ta. Among the refractory metals, molybdenum exhibits superior engineering properties, such as high tensile ductility and high elastic modulus. Also, molybdenum and its compounds show excellent tribological behavior due to the formation of lubricious oxides of MoO\textsubscript{3} during wear processes, such as sliding or machining [15]. Therefore, the fundamental characteristics of refractory-element-based metallic glass thin films (MGTFs) and refractory-element-reinforced metallic glass matrix composite thin films (MGMCTFs) must be further investigated to determine their potential engineering and functional applications.

In this work, Zr-Cu-Mo thin films with various Mo
contents were synthesized by a DC magnetron co-sputtering technique with Zr₆₄Cu₃₆ and Mo targets in an Ar atmosphere. In a previous study, the Zr₆₄Cu₃₆ metallic glass thin film was successfully synthesized, although the Zr-rich metallic glass system had a lower glass-forming ability in the binary Cu-Zr system [4]. The effects of the Mo addition to a binary Zr-Cu metallic glass system on the microstructure and mechanical properties of Zr-Cu-Mo thin films were systematically investigated.

**Experimental Details**

**Film deposition**

Ternary Zr-Cu-Mo metallic glass thin films were deposited on single crystalline (100)-oriented Si and AISI 304 substrates, using a direct current (DC) magnetron sputtering technique with Zr₆₄Cu₃₆ and Mo sputtering targets. The sputter sources were installed in opposite sides of the chamber wall to enable co-sputtering of the elements. A rotational substrate holder was located facing the two sources, with a 100 mm distance from the two sputter sources to the substrate. The Si substrates, with a size of 30 mm × 40 mm × 0.7 mm, were cleaned in an ultrasonic cleaner using acetone and alcohol for 30 minutes, respectively. The chamber was evacuated to less than 6.6 × 10⁻³ Pa, and the chamber temperature was set to room temperature. The Zr-Cu-Mo thin films were deposited at a working pressure of 0.4 Pa. Prior to deposition, the substrates were further cleaned by an Ar ion bombardment at a bias voltage of −700 V for 10 minutes to increase the adhesion between the film and the substrate. In order to synthesize the films with various Mo contents, the DC sputter current for the Zr₆₄Cu₃₆ source was fixed at 1.2 A, while the DC sputter current of the Mo source varied between 0 A and 1.0 A. The film thickness was controlled at approximately 3µm by altering the deposition time.

**Film characterizations**

The surfaces and cross sections of the synthesized films were studied using a scanning electron microscope (SEM, Hitachi, S-4800) operated at 15 kV, and the film thickness was measured using a stylus instrument (α-STEP). Electron-probe micro analysis (EPMA, Shimadzu, EMPA 1600) was carried out to determine the chemical compositions of the as-deposited films. An X-ray diffractometer (XRD; D8, Advance) using Cu Kα radiation was used to characterize the phase structure of the Zr-Cu-Mo films. Relevant XRD analyses were performed by employing the operational mode of sample tilting diffraction (STD; namely, a Bragg reflection measurement in the θ-2θ mode with the θ axis offset by 3° [16]) to avoid signals from a single crystalline Si substrate. This method has been proved to produce XRD results that are as correct as those found with the conventional Bragg-Brentano measurement for the case of non-epitaxial films on single crystalline substrates. The film microstructure was also investigated with a field-emission transmission electron microscope (FE-TEM; JEOL JEM-2010F). The plan-view specimens for TEM analyses were prepared by a standard Ar⁺ ion beam thinning technique. Relevant dark-field TEM (DF-TEM) images, selected-area diffraction patterns (SADP), and high-resolution TEM (HR-TEM) images were obtained to analyze the atomistic structural information. The hardness of films was measured by using nanoindentation (MTS, G200) with depth control (200 nm depth). The friction and wear performance of the synthesized films were investigated using a conventional ball-on-disc tribometer against steel balls as counterparts (diameter 12 mm, 700 Hv0.2). The friction tests were conducted with a sliding speed of 70 cm/s under a normal load of 3 N at an ambient temperature of 24 °C and a relative humidity of 30-40%.

**Results and Discussion**

**Phase structure and microstructure of the Zr-Cu-Mo metallic glass thin films**

Fig. 1 shows the chemical compositions of the Zr-Cu-Mo thin films as a function of Mo contents. Fig. 2 shows the X-ray diffraction patterns of Zr-Cu-Mo thin films as a function of Mo contents.
Cu-Mo thin films measured by EPMA. It is obvious that the Mo content in the film is proportional to the applied DC sputter current of the Mo target. As the sputtering current for Mo increased from 0 to 1.0 A, the Mo content in the Zr-Cu-Mo thin films gradually increased from 0 to 52 at.%, while the ratio of Zr to Cu remained nearly constant and the Zr and Cu contents decreased accordingly, from 64 to 33 at.% and from 36 to 15 at.%, respectively.

Fig. 2 shows the XRD patterns of the Zr-Cu-Mo thin films with various Mo contents. The XRD patterns of the thin films revealed the diffuse broad hump characteristic for the films with Mo content from 0 to 38 at.%, which indicates the amorphous nature of the film. No distinctive diffraction peaks of crystalline phases appeared in the films with Mo content of 38 at.%. When Mo content in such films was higher than 46 at.%, the intensity of the diffuse broad hump peak sharply increased, and peak shift was observed near the diffraction peaks of (311) of the face-centered-cubic (FCC) Mo<sub>2</sub>Zr phase and of (110) of the body-centered-cubic (BCC) Mo phase [17]. The observed peak shift and sharply increased intensities imply that the long-range-order phase in the films occurred due to the high Mo content.

In order to understand the implication of changes in XRD data of the Zr-Cu-Mo thin films, peak shift and full width at half maximum of the main peak has been calculated. Fig. shows a shift and full width at half maximum (FWHM) of main peak positions of the Zr-Cu-Mo thin films as a function of the Mo content. To quantitatively analyze the peak shifts and FWHM, the main peak positions were calibrated by XRD pattern processing software (JADE, Materials Data, Inc). The XRD main peak positions of the Zr-Cu-Mo thin films were shifted to higher 2θ values with increasing Mo content, as shown in Fig. 3(a). When the Mo content in the films was between 0-8 at.%, the main peak positions had a linear tendency to shift. Meanwhile, the sharp shift of the main peak positions were observed with a Mo content up to 46 at.%. As the Mo content increased to between 46 at.% and 52 at.% in the Zr-Cu-Mo thin films, the main peak positions slightly shifted to higher 20 values. Fig. 4(b) shows the variation of FWHM at amorphous Zr-Cu-Mo diffraction peaks, as a function of the Mo content. A continuous dependence of the FWHM versus composition was observed with a maximum at about 27 at.% Mo. When the Mo content in the films reached 46 at.%, a sharply decreasing FWHM was observed. Sudden changes in peak shifts and FWHM with an Mo content between 38 at.% and 46 at.% indicate that a significant structural evolution occurred due to the crystallites’ precipitation in the amorphous matrix. Below an MO content of 38 at.%, the monolithic amorphous Zr-Cu-Mo solid solution was formed with peak shifts and broadening, as Mo atoms were solubilized in the amorphous matrix. The variation of FWHM is caused by the changes in the weights of the partial structure factors and the composition dependence of the parameters of the structure factor, and the atomic pair correlation function points to a solid solution-like behavior of the amorphous structure [18, 19]. As a
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result, the glass-forming-ability is improved, as the addition of Mo leads to enhancement of the structure factors by increasing Mo-Mo pairs and Mo-Zr pairs in the amorphous structure. Above an Mo content of 46 at.%, the sharp peak shifts, peak intensity increments, and FWHM decrements all resulted from the formation of long-range-orders of Mo-Zr pairs and Mo-Mo pairs in the film. At an Mo content of 52 at.%, the peak position shifted from the Mo\textsubscript{2}Zr (311) diffraction position to the Mo (110) diffraction position, due to the Mo-Mo pair increment and Mo-Zr pair decrement in the film. Further increasing the Mo content resulted in the formation of a secondary phase that corresponded to the FCC Mo\textsubscript{2}Zr and BCC Mo crystalline phases in the amorphous matrix.

Microstructural evolutions of the Zr-Cu-Mo thin films with an Mo addition were further investigated by using TEM and HR-TEM analyses. Fig. 4 shows the selected area electron diffraction (SAED) patterns of the whole region, as well as the HR-TEM image in the Zr\textsubscript{49}Cu\textsubscript{24}Mo\textsubscript{27} thin film. The typical amorphous halo diffraction pattern in SAED patterns confirmed that the structure of the Zr\textsubscript{49}Cu\textsubscript{24}Mo\textsubscript{27} thin film is a typical amorphous phase of metallic glass material. As shown in Fig. 4, no lattice fringes were detected in the HR-TEM image, and as a result, the fast Fourier transformation (FFT) of the lattice fringes as shown in the insets revealed a typical amorphous halo diffraction pattern.

Fig. 5 shows the SAED pattern, the dark-field cross-sectional TEM images, and the HR-TEM image of the Zr\textsubscript{33}Cu\textsubscript{15}Mo\textsubscript{52} thin film, respectively. The grains with sizes between 5-20 nm were uniformly distributed in the film, as shown in Fig. 5(a). The SAED pattern (Fig. 5(a) inset) clearly indicated continuous diffraction rings and diffraction patterns of the FCC-Mo\textsubscript{2}Zr phases and the BCC-Mo phases. It was found that each grain was generally composed of many small sub-grains, as depicted in Fig. 5(b). Additionally, it can be seen that sub-crystallites in multiple orientations are embedded in the amorphous phase matrix. As a result, the fast Fourier transformation (FFT) of the lattice fringes, as shown in the insets of Fig. 5(b), revealed diffraction rings of nano-grains of Mo\textsubscript{2}Zr (311) and mist-like spectra of amorphous regions.

As previously described, the microstructure of the Zr-Cu-Mo thin films produced by co-sputtering from Zr\textsubscript{64}Cu\textsubscript{36} and Mo sources in the Ar atmosphere was significantly affected by the Mo contents of the films. XRD and TEM analyses confirmed that increasing the Mo content in the Zr-Cu-Mo thin films resulted in the formation of secondary phases, such as Mo\textsubscript{2}Zr and Mo crystallites.

In the Zr-Cu-Mo thin films, Mo was found to exist interstitially within the nanocrystalline phases (Fig. 5), as well as the amorphous phase (Fig. 4). The crystalline state and the amorphous state of alloys are classified by the pair-correlation functions and the projections of the atomic positions [20], and the glass-forming-ability (GFA) of the amorphous alloys reflects the composition range in a quantitative manner [21]. Therefore, with increasing the Mo content in the Zr-Cu-Mo thin
films, the monolithic amorphous structure changed to composites with metallic glass matrix as the long-range-order of Mo-Zr pairs and Mo-Mo pairs increased in the amorphous matrix and grew into the Mo2Zr and Mo crystallites with an Mo content greater than 46 at.%. Consistent observation from the TEM and XRD results showed that the Zr-Cu-Mo metallic glass thin films and the Zr-Cu-Mo metallic glass matrix nanocomposite thin films were successfully synthesized as a function of the Mo content.

**Mechanical properties of the Zr-Cu-Mo metallic glass thin films**

Fig. 6 shows the friction coefficients of the Zr64Cu36, Zr49Cu23Mo27, Zr41Cu12Mo38 and Zr33Cu12Mo38 films against steel balls (ball-on-disc) as a function of sliding cycles. The friction coefficients of films were obtained from samples having thicknesses above 2 μm. By adding the Mo to the films, the average friction coefficient of the Zr-Cu-Mo film was decreased from 0.44 for the Mo-free Zr64Cu36 film to 0.26 for the Zr49Cu23Mo27 film, and then rebounded to 0.33 for the Zr41Cu12Mo38 film. This finding can be explained by a tribo-chemical reaction, where the film surface reacts with ambient H2O to produce an oxide layer during sliding process. Friction can be reduced due to the formation of the lubricious oxide layer [22]. In a Zr-Cu-Mo system, the lubricious ZrO2, MoO3, and CuMoO4 can be produced by tribo-chemical reactions during wear processes. It has been reported that the MoO3 and CuMoO4 exhibited a lower friction coefficient than ZrO2 [15, 23, 24]. Therefore, the lower friction coefficient of the Zr-Cu-Mo thin films, in comparison with that of the Mo-free Zr64Cu36 thin films, can be attributed to the formation of a beneficial MoO3 and CuMoO4 tribo-layers by the addition of Mo to the films.

Fig. 7 shows the hardness (H) and elastic modulus (E) of the Zr-Cu-Mo thin films as a function of Mo content. The hardness and elastic modulus of the Mo-free ZrCu thin film was 10 GPa and 166 GPa, respectively. As Fig. 7(a) shows, the H and E values for the Zr-Cu-Mo thin films, of which Mo contents are less than 38 at.% and which is identified as the monolithic amorphous structure, are nearly constant. However, sharp and linear increases were observed when the nanocomposite structure was formed with an Mo content of higher than 46 at.%. In the film with the highest Mo content, the hardness and elastic modulus values reached 17 GPa and 240 GPa, respectively. Improved mechanical properties can be explained in terms of strong interatomic bonding pairs between Mo and constituent elements, as well as the nucleation of crystallites in the films. It is well known that the elastic modulus can be determined by the inter-atomic potential and the inter-atomic distance [25]. Also, the melting points of materials are influenced by interatomic bonding [26]. The Mo (2896 K) and Mo-Zr (2193 ~ 2896 K) exhibit a higher melting point in comparison with Zr (2125 K) and Cu (1356 K). As Mo content increases, the Mo-Mo and Mo-Zr bonding pairs with the higher inter-atomic potential and the shorter inter-atomic distance than Zr-Zr, Cu-Cu and Zr-Cu bonding pairs increased in the films. This increased Mo-Mo and Mo-Zr bonding leads to the apparent increase in the elastic modulus.

Additionally, according to the enhancement hardness model [27], an incompatibility of the slip system exists between different structures, such as in an amorphous/crystalline system, and prevents the dislocation and/or transmission when deformation occurs. In a-ZrCuMo/c-Mo2Zr and c-Mo system, the dislocation and/or shear bands that occur in deformation will meet obstacles of heterogeneous structure, and will hardly expand in the system. In a-ZrCuMo/c-Mo2Zr and c-Mo system, the dislocations in the amorphous ZrCuMo phase will meet obstacles at the crystalline Mo2Zr and Mo phases and the shear bands in the amorphous ZrCuMo phase will also hardly expand into the crystalline phases. Therefore, with increasing nanocrystallites and grain-growth, the increasing quantity of interfaces can provide more interference, the structure barrier strengthens, and the hardness is enhanced by strong cohesive energies in interphase boundaries [28, 29].

H/E and H/E^2 values, which are known to be
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proportional to resistance to plastic deformation [30] and the fracture toughness [31], were calculated from the measured results shown in Fig. 7(b). The H/E and H/E^2 values sharply increased, with the same tendencies to those of the hardness and elastic moduli, due to structure transformation from the monolithic amorphous structure to the nanocomposite structure. The higher H/E and H/E^2 values mean a larger elastic strain to failure and higher fracture toughness [32]. Therefore, the Zr-Cu-Mo nanocomposite thin films in this study are promising for engineering applications, such as tribological applications and erosion applications, as compared with the monolithic amorphous films.

Conclusions

The effects of the Mo addition to a binary Zr_{x1}Cu_{90} MGIF were investigated, with regard to the microstructural evolution and their mechanical properties of the Zr-Cu-Mo thin films in this study. The Zr-Cu-Mo films with an Mo content below 38 at.% maintained a monolithic amorphous phase structure. However, when Mo content is increased above 46 at.%, the Zr-Cu-Mo films start to have nanocomposite structures of well-distributed Zr, Cu, and Mo crystallites embedded in an amorphous matrix. The hardness and elastic moduli of amorphous Zr-Cu-Mo films showed nearly constant values, 10 GPa and 166 GPa, respectively, regardless of their Mo content. As Zr-Cu-Mo films have the nanocomposite structures when the Mo content reaches 52 at.%, their mechanical properties showed much increased hardness and elastic moduli, of 17 GPa and 240 GPa, respectively. The Mo addition generally reduced the average friction coefficient of the ternary Zr-Cu-Mo thin films, regardless of their phase structures.

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