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Applying composition control to improve the mechanical and thermal properties of Zr–Cu–Ni–Al thin film metallic glass by magnetron DC sputtering

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ABSTRACT

This study is intended to investigate the amorphicity region of Ni + Al content in Zr–Cu–Ni–Al thin film. The thermal and mechanical performances of Zr–Cu–Ni–Al thin film metallic glass (TFMG) are also addressed. By adjusting target power, thin film metallic glass with various (Zr + Cu)/(Ni + Al) ratio were fabricated. The composition of the Zr–Cu–Ni–Al thin films was analyzed by field emission electron probe micro-analyzer (FE-EPMA). Via Grazing Angle X-Ray Diffractometer (GIXRD), all Zr–Cu–Ni–Al thin films show the hump peak, implying the amorphous feature. To further identify the amorphous characteristic, a differential scanning calorimetry (DSC) is used and the amorphicity region of (Ni + Al) in Zr–Cu–Ni–Al thin film is as wide as 54 at.%. Besides, the glass transition temperature Tg, for all Zr–Cu–Ni–Al TFMGs are above 700 K, and the △T ranges from 50 K to 70 K. With the aid of nano-indention, hardness and elastic modulus were measured in which the hardness reaches 7.5 GPa for $Zr_{23}Cu_{23}Ni_{27}Al_{27}$ TFMG. The value of △T increases with (Ni + Al) contents in Zr–Cu–Ni–Al TFMG across the whole amorphous region, indicating that the thermal stability is improved and higher hardness is thus achieved. For a better intrinsic viewpoint, the average interatomic distance is calculated. The calculated distance gets closer with Ni + Al content, which might result from the increase of short range order (SRO) structure with good thermal stability. From the positive correlation of elastic modulus and Ni + Al content, the improved hardness is explained in the viewpoint of energy. In summary, the thermal and mechanical performances of Zr–Cu–Ni–Al TFMG with 54 at.% (Ni + Al) content are among the best in the class of Zr–Cu–Ni–Al metallic glass, implying that Zr–Cu–Ni–Al TFMG with improved performance can be fabricated in lower cost.

1. Introduction

Metallic glass (MG) is one of the most promising materials that can be utilized in novel fields due to the extraordinary strength, superplasticity, and surface roughness in atomic scale [1–3]. In the past decades, the challenge lies in the fabrication of bigger bulk metallic glass (BMG), which is deterred by the decrease of thermal conductivity when forming amorphous solid [4]. This makes the expense in cooling process extraordinary high. Fabrication of metallic glass by sputtering can make the cost much lower than that by BMG process. By sputtering, the cost is largely reduced in two ways. First, the gas state condensing makes cooling no longer a problem, and the material system can be replaced by cheaper elements despite less amorphous intention in thermodynamics, which resulted from ~10^{12} K/s cooling rate in sputtering [5,6]. Thus, the magnetron sputtering technique is widely used to fabricate thin film metallic glass (TFMG) in the recent years [7,8]. Besides, by adjusting the sputtering parameters, the search of less expensive MG composition with moderate performance and new material class of MG with improved performance becomes the focus of study [9,10].

Zr–Cu based MG is a milestone in the development of MG not only because of its superior glass forming ability, but for its much lower material cost. Wang et al. once applied selected Zr–Cu ratio clusters as the base and doped various amounts of Al into the bulk metallic glass. The addition of Al would improve both the mechanical properties and thermal stability [11–13]. Owing to the negative mixing enthalpy between Al–Zr and Al–Cu pairs, the addition of Al stabilizes the cluster structure. With Al as the bridge of electron cloud between Cu and Zr atoms, the icosahedral structure increases. Furthermore, the addition of Ni into Zr–Cu bulk material glass would improve the mechanical properties, corrosion resistance and glass transition temperature [14]. Several studies have also reveal the principle of designing new Zr–Cu–Ni–Al bulk metallic glass by analyzing critical dimension (Z_{max}), electron concentration (e/a) ratio, and average atomic radius (R_a) [15,16]. Besides, Zr-based TFMG has been widely investigated for its good thermal

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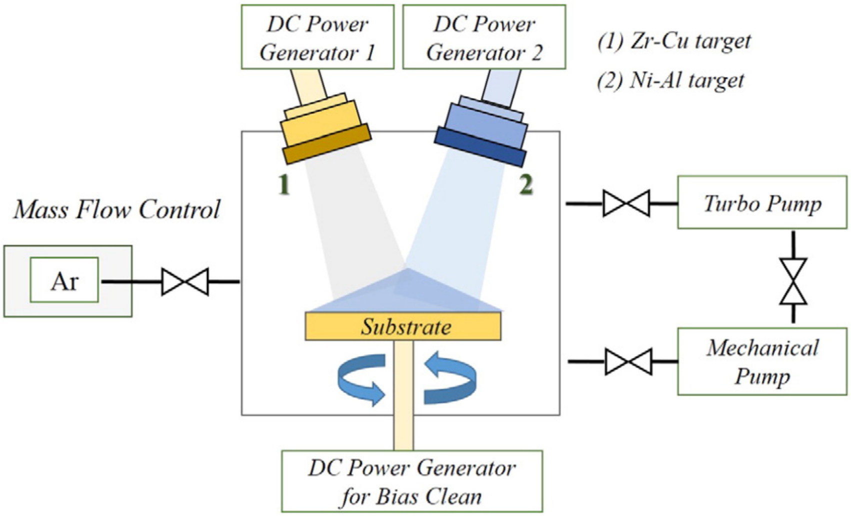

Fig. 1. Schematic diagram of magnetron DC co-sputtering system.

stability and corrosion resistance [17,18]. By controlling the process temperature, a Zr–Cu–Ni–Al TFMG with enhanced hardness and antimicrobial property could be tailored [19].

In this study, various contents of Ni and Al are alloyed into Zr–Cu TFMG until the Zr–Cu–Ni–Al thin film is no longer amorphous. Three targets are expected to be reached: 1. less expensive Zr–Cu–Ni–Al TFMG with higher Ni, Al contents; 2. the extension of amorphicity region of Ni + Al in Zr–Cu–Ni–Al TFMG; and 3. the improved thermal and mechanical performances of Zr–Cu–Ni–Al TFMG.

2. Experimental procedure

The Zr–Cu–Ni–Al TFMGs were fabricated by a magnetron DC co-sputtering system. The samples were ultrasonically cleaned by acetone then fixed on the rotating substrate of the vacuum chamber. Further, a −500 V bias was applied to the substrate in 30 min for cleaning purpose. The Zr–Cu (1:1 at.%), and Ni–Al (1:1 at.%) alloys were chosen as the sputtering targets. Two targets were connected to DC power supply (Advanced Energy, MDX-500) with the power fixed at 240 W for Zr–Cu target and with power ranged from 0 to 320 W for Ni–Al target. The vacuum chamber was pumped to background pressure of 2.6×10^{-4} Pa by a turbo pump. Then 30 sccm of argon was let in to maintain a working pressure of 0.9 Pa. The thin film was deposited on the substrate under argon atmosphere after a 10-minute pre-sputter process. By manipulating the working power of the DC power supply, various thin films with different chemical compositions can be fabricated. The overall schematic diagram of the co-sputtering process used in this study is shown in Fig. 1.

The chemical composition of thin films was analyzed by a field emission electron probe micro-analyzer (FE-EPMA, JXA-8500F, JOEL, Japan). Three quantitative analysis was conducted for each thin film and the distance between neighboring signal sources is 20 mm. The crystallographic structure was determined by a grazing incidence X-ray diffractometer (TTRAX III, Rigaku, Japan) using Cu Kα radiation with a wavelength of 1.54 Å operated at 50 kV and 300 mA from a Cu target. The field emission scanning electron microscopy (JSM-7600F, JOEL, Japan) operated at 10 kV was used to check the thickness of thin films around 1.5 um. The thermal properties were evaluated using a

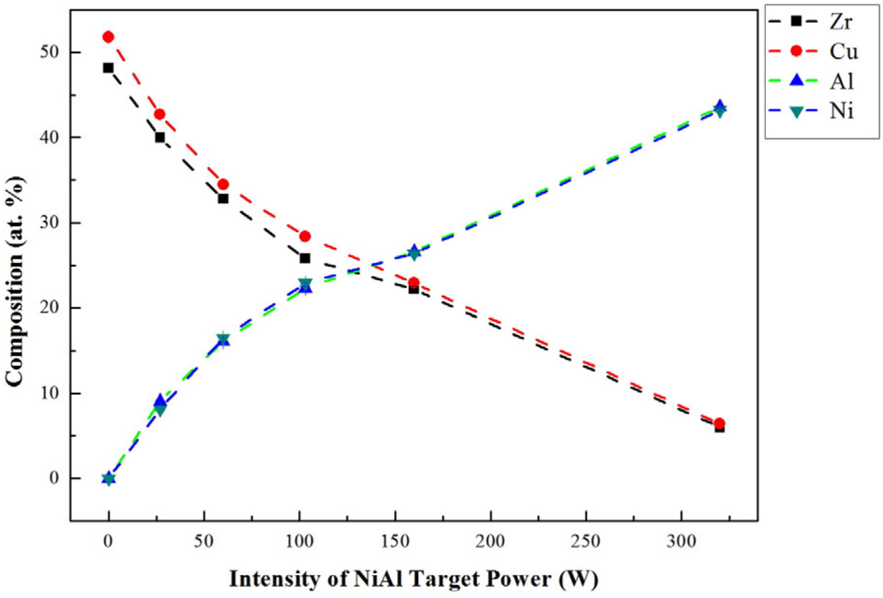

Fig. 2. The variation of Zr–Cu–Ni–Al thin film composition with intensity of NiAl target power.