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Microstructure, mechanical and anti-corrosion property evaluation of iron-based thin film metallic glasses

Li-Ting Chen [a], Jyh-Wei Lee [b,c,*], Yung-Chin Yang [a], Bih-Show Lou [d], Chia-Lin Li [e], Jinn P. Chu [f]

[a] Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC
[b] Department of Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan, ROC
[c] Center for Thin Film Technologies and Applications, Ming Chi University of Technology, New Taipei, Taiwan, ROC
[d] Chemistry Division, Center for General Education, Chang Gung University, Taoyuan, Taiwan, ROC
[e] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan, ROC
[f] Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, ROC

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ABSTRACT

Thin film metallic glasses (TFMGs) represent a class of promising engineering materials for structural applications. Despite the effort that has been made in the development of TFMG materials, the iron-based thin film metallic glasses fabricated by sputtering have gained limited attention. In this work, five iron-based Fe–Zr–Ti thin film metallic glasses with different Fe contents ranging from 37.6 to 49.8 at.% were prepared by magnetron co-sputtering system using pure Fe, Zr and Ti targets. Through XRD and TEM analyses, the amorphous phase was confirmed for each coating. The glass transition temperature (T_g) and crystallization temperature (T_x) of TFMG increased with increasing Fe content and reached 963 K and 989 K, respectively, when Fe content was 49.8 at.%. The supercooled liquid region was around 26.3 to 51.6 °C, which was shown to be unrelated to Fe concentration. The hardness, elastic modulus, and H/E ratio of TFMGs increased with increasing Fe concentration. Based on the HRC-DB test, adequate adhesion quality was obtained for all TFMGs. The corrosion resistance of TFMGs also increased with increasing Fe content and spontaneous passivation behavior was discovered due to the large content of Zr and Ti valve metals. Nevertheless, the corrosion resistance of Fe–Zr–Ti TFMGs was strongly influenced by surface defects. A series of high hardness Fe–Zr–Ti thin film metallic glasses with good adhesion property and adequate corrosion resistance was reported in this study.

1. Introduction

The research and development of amorphous bulk metallic glass (BMG) materials have been highlighted by researchers and industries due to their unique properties, such as high hardness, good wear and corrosion resistance [1,2] for the last few decades. Among a number of BMG alloy systems, the Fe-based BMGs have attracted great interest since 1995 [3] due to their high mechanical properties, excellent wear resistance, good corrosion resistance, and relatively cheap material cost [3–7]. For example, rather high hardness and elastic modulus, around Hv900 and 150 GPa and Hv1200–1300 and 170 GPa, were reported for Fe-P and Fe-B BMGs, respectively [1]. The micro hardness for $Fe_{40}Ni_{38}Mo_4B_{18}$ and $Fe_{77}Cr_2B_{16}Si_5$ BMG ribbons are Hv885 and Hv858, respectively [8]. On the other hand, the hardness and elastic modulus for $Fe_{74}Ni_4Mo_3B_{17}Si_2$ and $Fe_{77}Cr_2B_{16}Si_5$ BMG are Hv990 and higher than 60 GPa, Hv860 and 58 GPa, respectively [9]. Extremely high elastic moduli of approximately 180–200 GPa and microhardness of approximately 13 GPa have been reported [10]. Meanwhile, excellent anti-corrosion behavior of $Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$ BMG [11] and $Fe_{71.4-x}C_{7.1}Si_{4.4}B_{6.5}P_{8.6}Cr_xAl_{2.0}$ BMG [12]was investigated and showed that the addition of Cr played a critical role for the enhancement of corrosion resistance for Fe-based BMGs. In addition, an excellent anti-corrosion Fe-based $Fe_{41}Ce_{15}Co_7Mo_{14}C_{12}B_9Y_2$ BMG with large glass forming ability has been developed recently [13].

The brittleness of Fe-based BMGs below the glass transition temperature (Tg) restricts their applications in industries [14]. The Fe-based metallic glass coatings fabricated by thermal spraying process [15–17] or by sputtering [18,19], however, provide applicable routes to overcome its brittle problem. High hardness and excellent corrosion resistance have also been reported for the thermal sprayed Fe-based coatings [19–22].

In this work, the newly developed Fe–Zr–Ti thin film metallic glasses with different Fe contents were prepared by magnetron co-sputtering system using pure Fe, Zr and Ti targets. Reasons for selection of Zr and Ti elements are due to their biocompatibility and frequent use as main constituents of TFMG and BMG materials. The aim of this study is to increase the understanding of the new Fe–Zr–Ti thin film metallic glass

* Corresponding author at: #84 Gungjuan Rd., Taishan, New Taipei City 24301, Taiwan.
E-mail address: jefflee@mail.mcut.edu.tw (J.-W. Lee).

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Table 1
The deposition parameter for Fe–Zr–Ti TFMGs.

Sample no.	FF300	FF350	FF400	FF450	FF500
Background pressure (Pa)			1.73×10^{-4}		
Working pressure (Pa)			0.4		
Deposition time (hr)			1.5		
Input argon gas (sccm)			60		
Zr target power (W)			600		
Ti target power (W)			800		
Fe target power (W)	300	350	400	450	500
Substrate RF bias voltage (V)			−100		
Rotation (rpm)			10		

material and provide greater knowledge of the mechanical and anticorrosion properties for further potential applications. The influence of Fe concentration on the amorphous state, mechanical properties and corrosion resistance of Fe–Zr–Ti thin film metallic glasses was further discussed.

2. Experimental procedure

In this work, the iron-based Fe–Zr–Ti thin film metallic glasses (TFMGs) were fabricated on p-type (100) Si wafers, polished and hardened AISI 420 stainless steel discs and Al 1050 plates by a magnetron co-sputtering system without any substrate heating. The magnetron co-sputtering system was reported in a previous work [23]. The substrates were cleaned ultrasonically in a bath of acetone, ethanol and de-ionized (D.I.) water progressively, each for 10 min. The deposition was carried out using pure Fe, Zr, and Ti targets with 6 in. in diameter. Thin film compositions can be adjusted by tailoring the power of pulsed direct current (DC) power supply for Fe target. A radio frequency (RF) and pulsed direct current (DC) power supply were connected to Ti and Zr targets, respectively. The 20 kHz frequency and 5 μs power pulse reverse time were selected for the pulse DC power supply. The substrates were rotated in a speed of 20 rpm to maintain the uniformity of chemical composition of coating. The detailed sputtering parameters and designation for each coating are presented in Table 1.

The cross-sectional morphologies of TFMGs were examined with a field emission scanning electron microscope (FE-SEM, JSM-6701, JEOL, Japan) and by transmission electron microscopy (TEM, JEOL, JSM-2100, Japan). The chemical composition of TFMGs was analyzed with a field emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Japan). The phases of thin films were explored by a grazing incidence X-ray diffractometer (GIXRD, PANalytical, X'pert, Holland) with an incidence angle of 1°. Cu Kα radiation generated at 30 kV and 40 mA from a Cu target was used. The surface topography and roughness of thin films were investigated by atomic force microscopy (AFM, DI 3100, Bruker, USA). The thermal behavior of thin film was determined by using a differential scanning calorimeter (DSC, NETZSCH DSC 404F3, Germany) in Ar at a heating rate of 40 K/min. The temperature resolution of DSC is 0.1 °C. A calibration of the DSC was held by heating the empty crucible to deduct the background signal. The DSC film sample was delaminated from the glass without the aid of any chemical solutions.

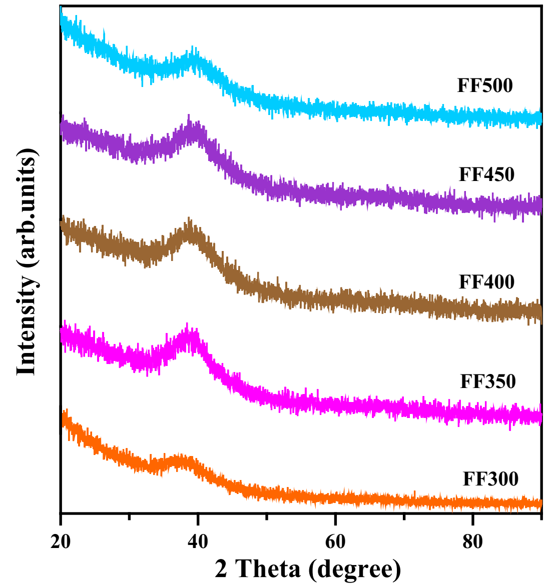

Fig. 1. The X-ray diffraction patterns for the Fe–Zr–Ti TFMGs.

The nanoindentation hardness, H, and elastic modulus, E, of thin films were investigated by means of a nanoindenter (TI-900, TriboIndenter, Hysitron, USA) by using a Berkovich 142.3° diamond probe at different loads to achieve a fixed indentation depth of 100 nm. The loading rates were between 3.3 and 6.0 μN/s. Eight indentation tests were performed for each coating. The hardness and elastic modulus of each indent were determined on the basis of the Oliver and Pharr method [24]. The elastic modulus, E, was expressed as follows:

$$\frac{1}{Er} = \frac{1-\nu^2}{E} + \frac{1-\nu_i{}^2}{E_i} \quad (1)$$

Table 2
The chemical compositions, thermal behavior, coating thickness and mechanical properties for Fe–Zr–Ti TFMGs.

Designation		Sample no.				
		FF300	FF350	FF400	FF450	FF500
Chemical composition (at.%)	Zr	38.0 ± 0.3	35.2 ± 0.2	32.4 ± 0.1	30.8 ± 0.6	29.8 ± 0.4
	Ti	21.2 ± 0.3	20.2 ± 0.2	19.4 ± 0.3	18.1 ± 0.4	17.3 ± 0.3
	Fe	37.6 ± 0.2	42.4 ± 0.1	45.5 ± 0.3	47.7 ± 0.2	49.8 ± 0.6
	O	3.2 ± 0.1	2.2 ± 0.0	2.8 ± 0.1	3.4 ± 0.3	3.1 ± 0.2
Composition ratio of Fe/(Fe + Zr + Ti)		0.39	0.43	0.47	0.49	0.51
Glass transition temperature, T_g (°C)		574.8	638.9	653.7	665.4	689.9
Crystallization temperature, T_x (°C)		626.4	665.2	686.6	704.4	716.2
Supercooled liquid region, ΔT (°C)		51.6	26.3	32.9	39	26.3
Surface roughness, R_a (nm)		0.21 ± 0.02	0.19 ± 0.01	0.21 ± 0.01	0.15 ± 0.01	0.18 ± 0.01
Thickness (μm)		2.069	2.297	2.431	2.481	2.563
Deposition rate (nm/min)		22.99	25.52	27.01	27.57	28.48
Hardness (GPa)		7.3 ± 0.2	8.0 ± 0.2	8.3 ± 0.1	9.0 ± 0.2	9.3 ± 0.2
Elastic modulus (GPa)		102 ± 1	109 ± 1	111 ± 1	122 ± 3	124 ± 2
H/E		0.072	0.074	0.075	0.074	0.075
Critical load, Lc (N)		17	38	15	>50	15
HRC-DB adhesion quality		HF2	HF2	HF3	HF3	HF2

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