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Fabrication and characterizations of thin film metallic glasses: Antibacterial property and durability study for medical application

Jinn P. Chu [a],*, Tz-Yah Liu [a], Chia-Lin Li [a], Chen-Hao Wang [a], Jason S.C. Jang [b], Ming-Jen Chen [c], Shih-Hsin Chang [c], Wen-Chien Huang [c]

[a] Dept. of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan
[b] Dept. of Mechanical Engineering, National Taiwan Central University, Jhongli 32001, Taiwan
[c] Mackay Memorial Hospital, Taipei 10449, Taiwan

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ABSTRACT

Metallic glasses with the disordered atomic structure have unique properties of high strength, high toughness, good corrosion and abrasion resistances. These materials are thus potentially useful for medical application. In this work, we evaluate the antibacterial property and durability of materials sputter-coated with Zr-based ($Zr_{53}Cu_{33}Al_9Ta_5$) and Cu-based ($Cu_{48}Zr_{42}Ti_4Al_6$) thin film metallic glasses (TFMGs). Good adhesive coating of Zr-based TFMG on the dermatome gives rise to blade sharpness improvement of ~27%, substantial surface roughness reduction of ~66% and smoother incised wound on the pig skin. As compared to 48.8° on the bare Si wafer, the water contact angles of 119.5° and 106.6° for Zr- and Cu-based TFMGs, respectively, reveal the hydrophobic characteristic of the coated surfaces. The bacterial adhesion of *Escherichia coli* and *Staphylococcus aureus* to both Zr- and Cu-based TFMGs is hindered to different extents.

1. Introduction

As a distinct group of materials, bulk metallic glasses (BMGs) have being widely studied in recent years because of their unusual characteristics of physical, chemical and mechanical properties resulting from the disordered atomic structure. The excellent features include high strength, high toughness, low thermal shrinkage, good corrosion and abrasion resistances [1–3]. For instance, together with the superior elastic limit of ~2%, the typical yield strength of 2 GPa is about 2–3 times higher than those of conventional crystalline stainless steel and titanium alloy [4]. Hence, taking these distinctive properties into account, it is reasonable to consider BMGs as candidate materials for medical application such as implantation and surgical instruments. Biodegradable implantation studies show an excellent performance of biocompatibility for Mg- [5,6] and Ca-based [7] BMGs. Recent studies reported that Zr- [8] and Ti-based [9] BMGs had a better bone-cells-affixing and biocompatibility than titanium implants applied as the dental material [10]. When coated with the Zr-based thin film metallic glass (TFMG) [11], a study reported the good antibacterial activity against the most common nosocomial infection pathogens such as *Escherichia coli* (*E. coli*), *Staphylococcus aureus* (*S. aureus*), *Pseudomonas aeruginosa*, *Acinetobacter baumannii* and *Candida albicans* over a 24-hour period. Also, the good hydrophobic property of TFMG with a water contact angle of approximately 88° superior to 46° of 304 stainless steel is believed to play a role in preventing the formation of bio-film on the coated surface. Further, Shao and Zhao [12] used a strong correlation between surface condition and bacterial adhesion to confirm the surface as one of the important factors influencing antibacterial properties.

In addition to the surface effects, metal ions released from the coated surfaces are found effective for antibacterial properties. These ions include Ag and Cu ions reported in silver [13–15] and Cu-bearing [16–19] surfaces, respectively. Since TFMGs generally have the smooth surface, Cu-bearing TFMG systems may be potentially useful to be coated on medical devices. However, studies and application of TFMGs in the biomedical field are still limited, as compared to the plentiful literatures of BMGs in other fields. The present study is thus directed toward the feasibility evaluations of the use of TFMG for improvements of (1) antibacterial property and (2) durability on coated materials. Through the surface modification by coating with TFMGs, Si wafers are subject to antibacterial examinations of bacteria *E. coli* and *S. aureus*. The single-crystal Si wafer is selected because of the simplicity in crystal structure and composition, while the use of commercial medical materials such as 316L stainless steel may yield a complexity for identifying antibacterial mechanisms due to their crystal grains and multicomponent compositions. Hence, the results obtained in the present study would be useful to design further experiments on real surgical instruments (such as stainless steel) in our future works. For the durability study, dermatome is chosen to evaluate the blade sharpness after coating with TFMG, because dermatome is one of the typical surgical grafting instruments. The surgery quality and wound healing are

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* Corresponding author.
E-mail address: jpchu@mail.ntust.edu.tw (J.P. Chu).

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known to be affected by the blade condition such as sharpness. The sharper the blade the smoother the wound surface will be for wound healing.

2. Experimental procedure

RF magnetron sputtering with the base pressure of 6.7×10^{-5} Pa and working pressure of 0.4 Pa at sputtering power of 100 W was used to deposit 200 nm-thick Zr-based and Cu-based TFMGs on 3×3 cm^2 p-type (100) silicon wafers. For the dermatome substrate, 200 nm-thick Zr-based TFMG was deposited with a −100 V substrate bias. Surface roughness was measured using tapping-mode atomic force microscopy (AFM, Bruker Icon) and coherence correlation interferometer (CCI, Taylor Hobson CCI 6000). Crystallographic analysis was performed using X-ray diffractometer (XRD, Bruker D8 Discover SSS) with Cu Kα radiation ($\lambda = 1.5406$ Å), accelerating voltage of 40 kV and emission current of 200 mA. The sample was scanned continuously between 20° and 80° with a glancing angle of 0.5° at a step size of 0.05° and a step time of 1 s. A dual-beam focused ion beam (FIB, FEI Quanta 3D FEG) equipped with scanning electron microscope (SEM) mode operated at an accelerating voltage of 20 kV was employed for the topographic analysis. Thermal properties were measured using a differential scanning calorimeter (DSC, Netzsch 404 F3) with a heating rate of 40 K/min in Ar to validate the amorphous characteristics such as glass-transition (T_g) and crystallization (T_x) temperatures. The electron probe microanalyzer (EPMA) was used to confirm the composition of TFMG. For the surface wettability evaluation, the apparent contact angle of 1 μl deionized water on the surface was measured. The blade sharpness index (BSI) value of dermatome was measured by a device, which is originally designed by Jang et al. [20]. BSI represents the measure of external work done by the loading required to initiate a cut or crack inside styrene-butadiene rubber [21,22]. The lower the value the better the sharpness will be for dermatome.

To further evaluate the dermatome, the animal study was conducted according to the protocol approved by the Faculty of Mackay Memorial Hospital Commission for animal experiment. The split thickness skin graft surgery was performed on the skin of the middle back of 6-month-old minipig using the dermatome. After adequate anesthesia, the whole back of the minipig was shaved and prepared with antiseptic solution (10% povidone iodine) and then sterilely draped with the minipig in prone position. In the experiment, partial thickness of skin graft (~380 μm in thickness) was harvested from the pig with a standardized size of 30 cm × 2 cm by using the dermatome. The skin samples were dehydrated in 15% sucrose for one night, followed by the final dehydration overnight in 30% sucrose. To prepare specimen matrix for cryostat sectioning, the dehydrated skin samples were then embedded in optimum cutting temperature compound (Tissue-Tek, USA). Embedded tissues were sectioned in 10 μm thickness, fixed with methanol, and evaluated after H & E stain.

Antibacterial evaluation of thin films was achieved using the bacteria *E. coli* (ATCC 25922) and *S. aureus* (ATCC 25923). Prior to the evaluation, all equipment were sterilized using an autoclave (Tomin TM-320). The culturing solution containing bacteria was diluted to 10^5 CFU/ml (CFU: colony forming unit) in a sterile normal saline (0.9 wt.% NaCl) and 10 ml of the solution was applied to the surface of the specimens, which had been placed horizontally within a sterilized petri dish. The bacteria on the specimens were incubated at 37 °C for 24 h, then 300 μl of which was dropped into Mueller–Hinton agar. Finally, the quantity of surviving bacteria (CFU/ml) was determined based on the number of colonies formed on the medium following incubation for 24 h at 37 °C. The antibacterial rates (ARs) were used according to the Japanese Industrial Standard (JIS Z 2801:2000) [23]. The AR value is equal to $(N_0 - N_i)/N_0$, where N_0 and N_i are the numbers of viable bacteria on a reference bare sample and TFMG-coated sample after testing, respectively.

3. Results and discussion

3.1. Thermal properties, crystallography and compositions of TFMG

Typical DSC results in Fig. 1(a) reveal important thermal properties of $T_g = 468$ °C and $T_x = 520$ °C for Zr-based TFMG; $T_g = 460$ °C and $T_x = 506$ °C for Cu-based TFMG. Fig. 1(b) shows typical XRD patterns of Zr- and Cu-based TFMGs. XRD results reveal a broad peak at approximately 30 to 50° in both TFMGs, clearly indicating the amorphous characteristics. Hence, both DSC and XRD results confirm the amorphous state of TFMGs used in this study. Compositions of TFMGs, determined by EPMA, are as follows (in atomic percentage): $Zr_{53}Cu_{33}Al_9Ta_5$ for Zr-based TFMG and $Cu_{48}Zr_{42}Ti_4Al_6$ for Cu-based TFMG.

3.2. Smoothness and durability of coated dermatomes

SEM micrographs of dermatomes after the BSI test are presented in Fig. 2. Severe damage is observed along the edge/tip of the bare dermatome with many chips with some edge areas curved inward. In contrast, the dermatome coated with TFMG (Fig. 3) remains almost intact with only some minor peeling after BSI test. Thus, the surface condition appears to be maintained in the coated dermatomes after BSI test. Fig. 4

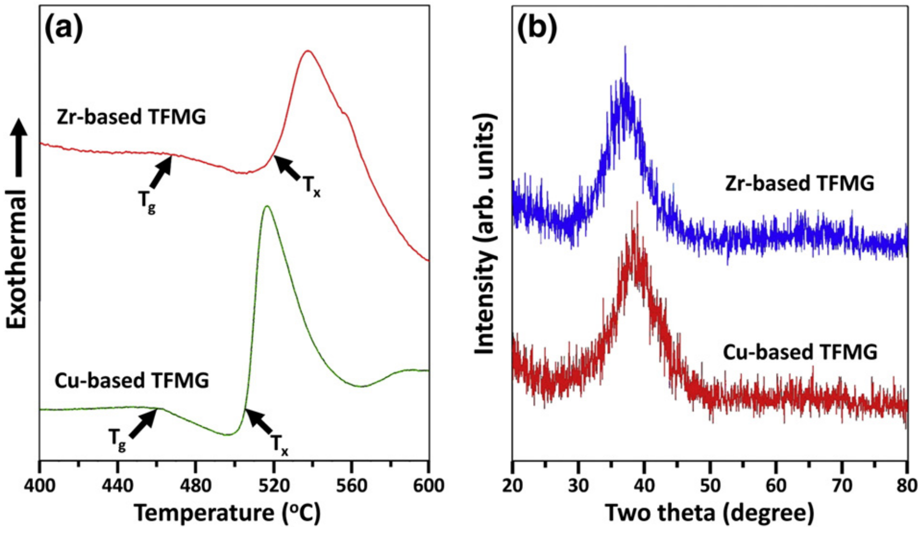

Fig. 1. (a) DSC curves and (b) XRD patterns confirming the amorphous state of TFMGs used in this study.