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Surface & Coatings Technology 201 (2007) 5843-5849

www.elsevier.com/locate/surfcoat

Effect of composition on surface relief morphology in TiNiCu thin films

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Received 30 March 2006; accepted in revised form 22 October 2006 Available online 4 December 2006

Abstract

TiNiCu films were deposited on a (100) type Si substrates by co-sputtering of TiNi and Cu targets at room temperature, and then post-annealed at 450 °C for crystallization. Significant surface relief due to martensitic transformation occurred on the film surface after cooling, and variations in surface relief morphology (the size and density of martensite crystals) have been quantified with atomic force microscopy. Energy dispersive X-ray analysis showed that the surface relief morphological difference in the TiNiCu films is due to the change in composition. It was proposed that the crystallization of the amorphous thin film during annealing behaved differently with chemical composition, which in turn induced fluctuations in phase transformation temperatures at various regions, as confirmed by differential scanning calorimeter measurements. © 2006 Elsevier B.V. All rights reserved.

Keywords: Crystallization; Martensitic transformation; Surface relief; Shape memory alloys

1. Introduction

Phase transformation in shape memory alloy (SMA) thin films is accompanied by significant changes in mechanical, physical, chemical, electrical and optical properties, such as yield stress, elastic modulus, hardness, damping, shape recovery, electrical resistivity, thermal conductivity, thermal expansion coefficient and surface roughness [1,2]. These changes can be exploited in the design and fabrication of microsensors and microactuators [3,4]. Significant surface relief caused by the martensitic transformation is commonly observed in TiNi bulk materials, and more recently this has also been seen in sputtered TiNi thin films [5,6]. During martensitic transformation, the atomic displacement introduces stacking faults that lead to relief on the surface of the SMA. A flat surface in austenite becomes rough upon cooling into twinned martensite without macroscopic shape change, and vice versa. This interesting phenomenon might be used for optical applications and devices [1,6].

TiNi films deposited at low temperature are usually amorphous and do not show shape memory effect (SME). Post annealing is necessary to realize a transition from amorphous status to crystalline thin films. Kinetics of crystallization behaviour of amorphous shape memory thin films is critical for microstructural control and the fabrication of microelectromechanical actuators. The nucleation and growth behaviour of crystals inside an amorphous TiNi thin film have been recently investigated by using transmission electron microscopy (TEM) [7,8]. Structural evolution and phase transformation in sputtered TiNiCu thin films as a function of compositional change have been systematically investigated by Chang and Grummon [9,10]. Moreover, crystallization temperature for amorphous TiNi thin films has been found to vary with composition, processing technique, stress and annealing temperatures [11-14]. Recently, chemical evolution in NiTiCu thin film along film growth direction using molecular beam epitaxy (MBE) has also been reported [15]. Although martensitic transformation in thin films can be characterized by examining the surface relief morphology evolution, a systematic study of crystallization of amorphous thin film (for example, the thermodynamic database for various alloy systems and the time-temperature-transformation plot) is not available. In particular, the nucleation and growth of martensite plates in the TiNi-based amorphous thin films as a function of temperature and composition have not been reported systematically.

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 $^{0257\}text{-}8972/\$$ - see front matter M 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.surfcoat.2006.10.033



Fig. 1. Schematic illustration of the sputtering configuration for preparing TiNiCu thin films.

In this study, we focus on the compositional impact on the crystallization behaviour in a TiNiCu thin film. The addition of copper replacing Ni in fabricating SMA device is to enhance the damping capability with low hardness [12,16]. Copper is also effective in decreasing the transformation temperature hysteresis and increasing strength difference between parent and martensite phases for a better recovery strain required [17,18]. Most previous studies on the crystallization in TiNi thin films were performed with various samples with defined chemical compositions. To minimize the effect of temperature variation during post-deposition annealing, one single piece of sample with concentration variation in different area was employed in this study. A detailed surface relief analysis in TiNiCu films after crystallization using atomic force microscopy (AFM) was performed; the variations in relief morphology and martensitic transformation temperatures were interpreted in the light of compositional effect.

2. Experimental

Films of TiNiCu were deposited on standard 4-inch (100)type silicon wafers without intentional substrate heating by magnetron sputtering of a Ti(55 at.%)Ni(45 at.%) target (3-inch diameter, RF, 400 W) and a pure Cu target (3-inch diameter, DC, 2 W). The deposition configuration is shown schematically in Fig. 1. The different areas, chosen for analysis on one of the 4inch wafers, are marked in Fig. 1. The substrate-to-target distance was 100 mm, and argon pressure was 0.8 mTorr. The resulting film had a thickness of 3.5 µm after deposition for 4 h. The Si substrate holder was rotating during deposition to gain a homogeneous chemical distribution in the radial direction. The films were then annealed in vacuum $(1 \times 10^{-7} \text{ Torr})$ at a temperature of 450 °C for 1 h for crystallization. Surface morphology of the films was characterized using optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Film composition was determined using energy dispersive X-ray microanalysis (EDX) attached to the SEM. Film crystalline structure was defined using X-ray diffraction (XRD). Martensitic transformation temperatures



Fig. 2. AFM measurement of various areas around area 1 in Fig. 1 (a. between sample edge and area 1; b. center of area 1; and c. between area 1 and 2). *Z*-range is 300 nm for all AFM images except separately stated.

were measured using a differential scanning calorimeter (DSC) at a heating/cooling rate of 10 K/min.

3. Results and discussions

As-deposited films showed featureless surfaces, which were smooth, shiny and reflective to the naked eye. XRD analysis indicates that the film is amorphous. The average surface roughness, R_a , from AFM, was about 2.3 nm over a scanning area of 100 µm × 100 µm.

Annealing the amorphous film at 450 °C for 1 h changed the surface morphology dramatically, with variations in both morphology and size of martensite/austenite crystals across the wafer surface. Circular crystals with diameter of around 30 µm were observed in a featureless matrix at the edge of the wafer (region between the sample edge and area 1 in Fig. 1), as shown in Fig. 2a. The crystals become coarser with an average diameter of about 35 µm but are still isolated in the center of area 1, as shown in Fig. 2b. The region in between area 1 and 2 is featured with very coarse crystals (bigger than 40 µm and some of the adjacent crystals coalesce) co-existed with fine crystals of around 10 µm, as shown in Fig. 2c. Those crystals close to the sample edge (Fig. 2a and b) are proven to be a mixture of austenite and martensite (with both austenite and martensite peaks, as shown in Fig. 3) and randomly distributed in the amorphous matrix (Fig. 4).

There is an obvious increase in density and size of the crystals located at the areas half way between the edge and center of the sample (area 2 in Fig. 1). The crystals are of $40-60 \mu m$ and some adjacent ones coalesce and form a larger crystal, as shown in Fig. 5. Those crystals are proven to be martensite (Fig. 3) with characteristic twined structure. Further into the center of the wafer (area 3), the martensite plates impinge and connect with each other forming a dense and continuous martensite plate network, as shown in Fig. 6. XRD results reveal that those crystals are martensite with strong martensitic phase peaks (Fig. 3). Similar to area 3, for the other wafer surface areas (areas 4 to 6 in Fig. 1), there is few amorphous matrix observed and almost entire film surface is



Fig. 3. XRD analysis of TiNiCu film showing crystalline structures at the different positions on the Si wafer.



Fig. 4. Optical micrograph of TiNiCu thin film showing crystals are randomly distributed in area 1.

covered with significant relief morphology (interweaving martensite plates). Optical observation and AFM measurements reveal significant roughening due to formation of crystals from amorphous matrix during crystallization, and martensite crystals dominate the sample wafer after cooling. Surface roughness in a selected area can be derived from AFM measurements. The surface roughness over a scanning area of $100 \,\mu\text{m} \times 100 \,\mu\text{m}$ varies with areas or positions, and is plotted in Fig. 7. It can be seen from Fig. 7 that the roughness increases steady with distance from the wafer edge to the center, roughness reaches maximum (about 35 nm) at the center of area 3 in Fig. 1, and does not vary too much from area of 3 to 6. Further AFM analysis of the isolated crystals in the area 1



Fig. 5. Typical AFM micrograph of the region in the center of area 2.



Fig. 6. Typical AFM micrograph of the region in the center of area 3.

shows that the surface roughness is around 30 nm, this value is close to the calculated roughness in martensite plates in areas 2 and 3. One can therefore conclude that the change in roughness with position in the sample is predominantly due to the density and distribution of crystals. Figs. 2–6 provide a clear picture of variation in surface relief in the TiNiCu films, i.e. the size and distribution of martensite plates vary with position.

In-situ AFM measurement was carried out on one single martensite crystal (in area 2) during heating (using a hot stage). As shown in Fig. 8, the twinned structure within this martensite crystal disappears and the surface becomes smooth (with a roughness of less than 5 nm) upon heating to around 80 °C. The measured surface roughness of this crystal as a function of



Fig. 7. Surface roughness (RMS) of a scanning area of 100 μm by 100 μm measured by AFM varies with position of the thin film deposited on the 4" Si wafer.



Fig. 8. Morphological change of one martensite crystal measured with AFM (a. 25 $^{\circ}$ C and b. 100 $^{\circ}$ C). Z-range is 200 nm for both images.

temperature during heating is plotted in Fig. 9. The surface roughness decreases monotonously with temperature and becomes constant after heating to 70 °C. After cooling to room temperature, the martensite plate structure reappears with identical surface morphology before heating. The surface becomes slightly opaque and cloudy with naked eyes. In-situ XRD analysis on both areas 2 and 3 showed that martensite peaks disappear gradually during heating and austenite peak becomes dominant at a high temperature. This process is completely reversible during cooling. These results demonstrate that the surface relief and its variation along with the different regions are caused by the martensitic transformation.

The variation in size and distribution of crystals at different regions as shown in Figs. 2-6 is unlikely due to the temperature variation across the wafer during annealing. The annealing lasted for 1 h and the samples were also rotated during crystallization



Fig. 9. Surface roughness (RMS, measured by AFM) of a single martensite crystal as a function of temperature during heating.

process. The probable reason is minor variation in chemical composition during sputtering and the influence of residual stress. Co-sputtering from two targets easily causes the non-uniformity of film composition [1]. Based on EDX analysis, the compositional change with positions of the TiNiCu thin film on the Si wafer is plotted in Fig. 10, and results confirmed that along the radial direction of the substrate holder. Ti content varies by about 1 at.% and Ni by about 2% crossover the edge and center of Si wafer. It can be seen from Fig. 10 that majority compositional change on the thin film is concentrated on the areas 1 and 2 (as marked in Fig. 1). Although there are still confusions in the published data, it is expected that slight off-stoichiometrical composition of equal-atomic NiTi can cause an obvious decrease in phase transformation temperatures [17-20]. Fig. 11 shows DSC results of the freestanding films peeled off from the Si wafer obtained from areas 1, 2 and 3. A one-stage transformation between martensite and austenite was observed during both



Fig. 10. Compositional change with distance of TiNiCu thin film from the sample edge to the center.



Fig. 11. DSC results of TiNiCu films showing phase transformation behaviors differently at various areas of the thin film.

heating and cooling for all three samples, but the transformation temperatures gradually increase from area 1 to area 3. The martensite start temperatures for films in areas 1, 2 and 3 are 27 °C, 38 °C and 55 °C, respectively. The martensite finish temperatures for areas 1, 2 and 3 are about -10 °C, 13 °C and 39 °C respectively. Thus, crystals at areas 1 and 2 at room temperature upon cooling is a mixture of martensite and austenite and the component portion of martensite at area 2 is higher than area 1, which is also confirmed by the XRD data (Fig. 3). Assuming a uniform thickness and same quantity of the thin film used in DSC tests, the area between endothermic and exothermic curves in DSC measurement corresponds to the mass of phase that experiences phase transition. Fig. 11 shows that this area decreases in the order of area positions of 3, 2 and 1 on the sample. Amorphous matrix does not contribute to the change of heat flow during DSC measurement. Area 3 is featured with fully crystallized martensite plates (Figs. 3 and 6) and therefore has largest energy dissipation during cooling. In contrast, area 1 has lowest content of crystals (Figs. 2 and 4) and has the smallest energy dissipation during cooling, and the low content of crystals also causes the fuzzy boundaries of endothermic and exothermic curves in DSC measurement (Fig. 11). From Fig. 11, the phase transformation peak intensities decrease dramatically from area 3 to 1 due to the weak phase transformation performance for films with Ti contents deviating away from 50 at.% [21]. Over the remaining areas of film-coated wafer (areas 4, 5 and 6), the Ti content is close to 50.6 at.% (the composition for area 3), and thus the surface relief morphology is similar to that shown in Fig. 6.

The nucleation and kinetics in an amorphous TiNi thin film has been well studied and the kinetics data derived from quantitative TEM analysis fit well into the Johnson–Mehl– Avrami–Kolmogorov (JMAK) model [7,8]. In another comparative study, crystallization of Ti-rich sample exhibits a complicated non-steady-state nucleation and sluggish growth accompanying with precipitation reactions, in contrast to a polymorphic crystallization of an equiatomic TiNi thin film [13]. However, few reports are available on the compositional effect in crystallization of TiNiCu thin films. Normally, the relationship between the rate of crystal growth and temperature in solidification or crystallization follows Arrhenius relationship:

$$K = A \cdot \exp(-E_{q}/RT) \tag{1}$$

where K is the growth rate, A is a constant, E_q is the Gibbs energy of activation, R is the gas constant and T is temperature (in the unit of K). A similar equation applies for the nucleation of crystals from amorphous matrix. Temperature and activation energy play critical roles in the kinetics of both nucleation and crystal growth. Due to the lack of thermodynamics data for amorphous-crystallization transition in ternary system of Ti-Ni-Cu, it is hard to find the exact transition temperature for each constitutional composition. However, one can estimate that the variation in constitutional composition would change the chemical bonding in the alloy system (i.e. the Gibbs free energy). The stability of phase is determined by the Gibbs free energy, thus the change in chemical composition alters amorphous-crystallization transition temperatures, and also the activation energy for nucleation and growth rate at a constant annealing temperature.

It has been proposed that the addition of Cu to replace Ni will decrease the stability of amorphous NiTiCu thin film, the activation energy for glass transition for Ti_{49.96}Ni_{40.09}Cu_{9.95} and Ti_{49,93}Ni_{50,07} is 388 and 416 kJ/mol, respectively. This is due to the weak chemical bonding of Ni-Cu and Ti-Cu compared to the Ti-Ni bonding, Ti-Ni has largest negative enthalpy of mixing [12,22,23]. It is also suggested that the crystallization onset temperature T_X increases with the composition approaches the eutectic composition and T_X is the lowest for an intermetallic phase (e.g. NiTi or Ti₂Ni in Ni-Ti binary system) [12]. Since Cu concentration in this thin film varies little, it is reasonable to assume that the larger the difference from equiatomic composition the higher the T_X . EDX analysis revealed the compositional difference for the thin film at various areas (Fig. 10). Compare area 3 (with composition of $Ti_{50.9}Ni_{47.6}Cu_{1.5}$) and area 1 (Ti_{51.6}Ni_{46.4}Cu_{2.0}), area 3 has a concentration more close to the equiatomic composition, thus has lower T_X . The lower the T_X the lower the activation energy for crystallization (Eq. (1)), and more likely the fully crystallized martensite plates can be obtained after annealing (Fig. 6). It is this compositional difference that causes the size and distribution of crystals after post-annealing crystallization process and also the differences in the phase transformation temperatures of the resulting martensite crystals.

As can be seen from the above discussion, more work on thermodynamics calculation and experiment of amorphous– crystal transition in TiNi-based thin film facilitates physical understanding of various phenomena associated with this group of materials. A quantitative analysis on stress field before and after crystallization and martensitic phase transformation is necessary for a better understanding of stress on crystallization process. Work in this direction is in progress.

4. Conclusion

In summary, significant surface relief occurs on a TiNiCu film surface due to the formation of martensite plates after crystallization and subsequent cooling to room temperature. The surface relief morphology of the sample was quantified with AFM. It has been found that the edge of the sample is featured with randomly scattered crystals with diameter of about 30 μ m and the crystals consist of co-existent martensite and austenite, as defined by XRD. The size and density of the crystals increases toward the center area of the sample. Fully interweaved martensite plates were found in the center of the sample, and they are martensite.

The significant surface relief morphology difference of the sample is due to the compositional variation during fabrication. It has been interpreted in a way that the change in chemical composition causes the variation in activation energy during post-deposition annealing process. Center area with a composition close to NiTi intermetallic has lowest activation energy for crystallization and therefore the crystals can nucleate and grow faster than other areas. The edge area has a composition away from equiatomic and therefore has higher activation energy, which results in partially crystallized crystals.

DSC measurements of different area of the sample shows the phase transformation temperature difference, this is in good agreement with literature and further proves the compositional variation in this sample. It can be seen from the current study that a significant difference of crystallization and martensitic transformation of thin film is possible with small change in composition. For optimal design and fabrication of SMA thin film devices, a further investigation of chemical composition and processing technique on crystallization of thin film is required. A thermodynamic database for different alloy systems will facilitate the industrialization of those thin film materials.

Acknowledgements

This project is partly supported by the U.S. Department of Energy under Grant No. DE-FG03-02ER45988. We thank Dr. Forrest Stevens, Washington State University, for the help with AFM work and valuable discussions.

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