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Letter

Crystallization of amorphous NiTiCu thin films

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ABSTRACT

The effect of copper additions (1.3 at%) on the crystallization of amorphous nickel-titanium thin films was explored. Using differential scanning calorimetry (DSC), the overall activation energy and crystallization temperatures were found to be similar to pure NiTi. However, *in situ* transmission electron microscopy (TEM) showed the nucleation and growth behaviors were markedly different. NiTiCu exhibited a lower nucleation rate, suggesting a higher activation energy in comparison to NiTi. The large grains in NiTiCu microstructures are consistent with a lower growth activation energy. These data suggest copper additions create higher interfacial energies. This paper presents experimental measurements that corroborate this mechanism.

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1. Introduction

Several efforts have been made to incorporate NiTi thin films into microelectromechanical systems (MEMS), since they have large deformation and recovery forces [1–3]. Despite their superior actuation properties, the integration of shape memory alloys (SMA) in MEMS is limited, because their behavior shows an acute compositional sensitivity, i.e. a small compositional shift causes a large transformation-temperature change [4]. One method of mitigating this compositional sensitivity is through alloying [5]. Recent studies have found that substituting copper (<25 at%) for nickel in NiTi significantly reduces the compositional sensitivity [6]. Like NiTi, the as-deposited state of sputtered NiTiCu thin films is amorphous; annealing is required for crystallization. However, knowledge of the microstructural evolution of NiTiCu thin films during crystallization is limited.

Preliminary studies on the crystallization behavior of NiTiCu have been done using differential scanning calorimetry (DSC) and X-ray diffraction [7–14]. However, most studies describe only the overall crystallization process rather than determining the individual contributions of nucleation and growth. Thus, the mechanism by which the addition of copper affects the components of crystallization remains unknown. Aiming to elucidate the effect of copper on both nucleation and growth, we observed the crystallization of NiTiCu thin films using *in situ* TEM.

2. Experimental methods

Using two dc magnetron sputtering targets of NiTi (at 302 W) and Ti (at 150 W), and one rf magnetron sputtering target of Cu at 30 W at a deposition rate of 0.67 mm/s, we deposited 0.2 μm amorphous NiTiCu thin films onto silicon-nitride TEM membrane samples [15,16] and silicon wafers coated with 0.2 μm silicon-nitride. The resulting composition of $Ni_{48.3}Ti_{50.4}Cu_{1.3}$ was determined by electron microprobe analysis.

Real-time *in situ* TEM heating studies were performed in bright-field mode using a 200 kV field-emission gun. NiTiCu TEM samples were heated within the microscope on a single-tilt holder with heating controllable up to 1200 °C (and measured with a thermocouple). Using a low magnification to achieve a wide field of view and resolution of 50 nm, digital images were continuously recorded and time-stamped, giving a precise time-temperature record. Samples were heated at a rate of 50 °C/min to target temperatures of 480, 500, and 520 °C and then held constant until crystallization was complete. For comparison, we also analyzed binary NiTi samples with the same amount of Ti (50.4 at%), since copper substitutes for nickel [6]; with a thickness of 1 μm deposited on silicon wafers both NiTiCu and NiTi films were tested to 550 °C at rates of 50, 20 and 10 °C/min, using differential scanning calorimetry (DSC). The contact angles of both distilled water and formamide droplets on both amorphous and crystallized NiTi and NiTiCu thin films were measured using a contact-angle measurement system.

3. Results and discussion

The crystallization temperatures and overall activation energies of NiTi and NiTiCu films were determined by DSC. Fig. 1 shows our DSC curves of NiTi and NiTiCu thin films under different heating rates with the peak crystallization temperature, T_p, indicated. Previous research has shown a decrease in crystallization temperatures and activation energies with a significant amount of copper addition (≥10 at%) [7–14]. The peak crystallization temperatures appear to remain nearly the same after adding a small amount of copper (of

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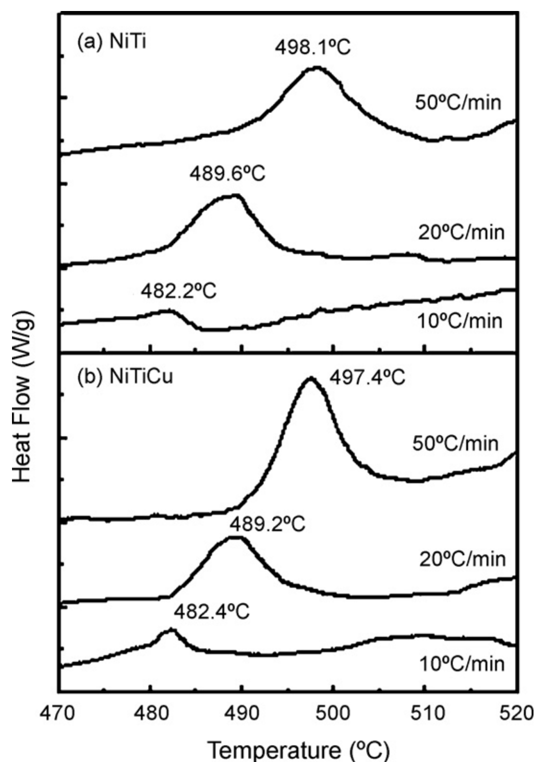

Fig. 1. DSC curves for (a) $Ni_{49.6}Ti_{50.4}$ and (b) $Ni_{48.3}Ti_{50.4}Cu_{1.3}$ thin films under different heating rates, which are used to determine the overall activation energy for crystallization using the Kissinger method [17].

1.3 at.%). Based on the results in Fig. 1, the overall activation energy, E_a, is determined by the Kissinger method [17]:

$$\ln\left(\frac{\alpha}{T_p^2}\right) = C - \frac{E_a}{RT_p} \quad (1)$$

where R is the gas constant, C is a constant, and α is the heating rate. The activation energies calculated from the slope of $\log T_p^2/\alpha$ versus $1/T_p$ approximate 474 kJ/mol for both NiTi and NiTiCu, implying that the overall crystallization behavior does not have a significant change after adding 1.3 at% copper.

However, the results obtained by *in situ* TEM observations indicate a marked difference in crystallization behaviors after copper additions. Fig. 2 depicts NiTiCu samples at various stages of crystallization (1, 30 and 100%) for isothermal anneals of 480, 500, and 520 °C. The crystallization behavior of NiTiCu differed markedly from that of NiTi: in previous work [16,18,19], we found that NiTi crystallized polymorphically with nucleation occurring rapidly and continuously, whereas the NiTiCu thin films form fewer nuclei that grow to produce a small number of crystals, which are much larger (5–8 μm) than those observed in NiTi (0.8–1.6 μm) [18,19]. Our previous work shows the duration required for NiTi to be fully crystallized at 475, 495, and 515 °C are 210, 107, and 11 s, respectively [18]; by contrast, the duration needed for NiTiCu at 480, 500, and 520 °C are 800, 280, and 31 s.

Using TEM images such as those in Fig. 2, we determined the growth rate, V_0, by analyzing the size of individual crystals as a function of time, and found that the growth rate was constant throughout the crystallization process (at a rate of 0.061 μm/s at 500 °C; compared to 0.032 μm/s for NiTi at 495 °C). We further explored the temperature dependence of the growth rate in order

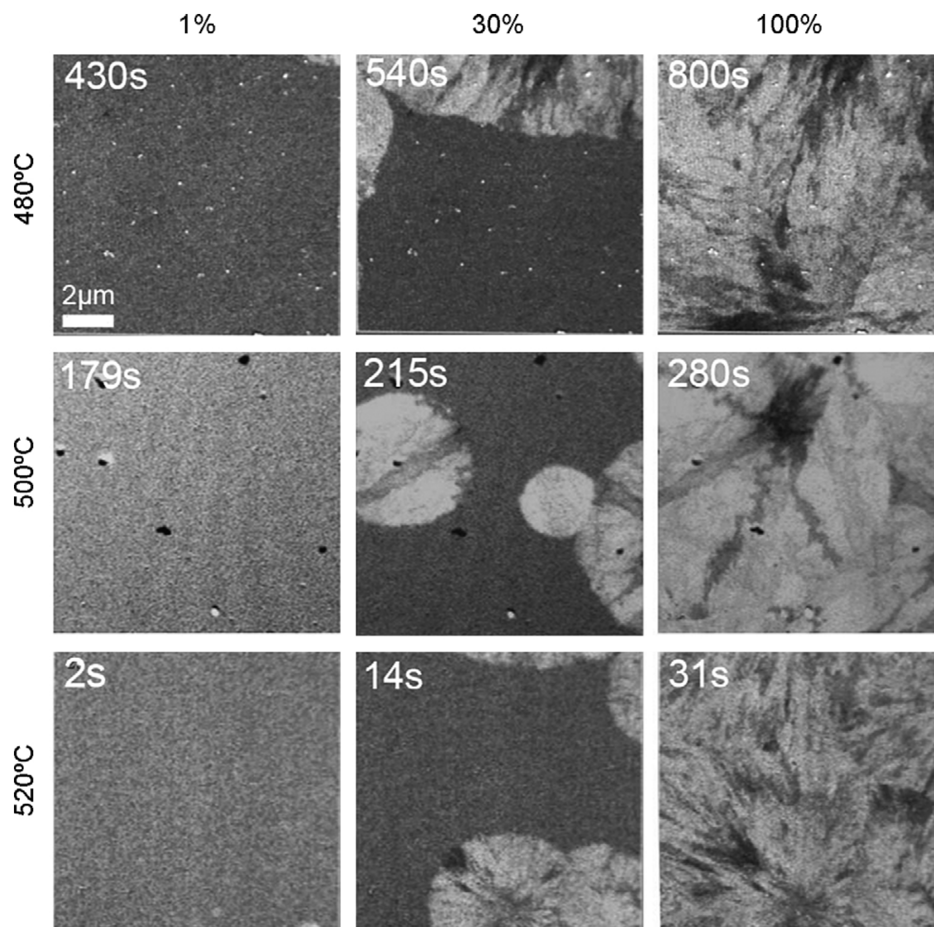

Fig. 2. Bright-field TEM images of NiTiCu thin films at 1, 30 and 100% crystallization for temperatures of 480, 500 and 520 °C. The area observed was a 10.4 μm square.

Table 1
Contact angles, surface and interfacial energies for NiTi and NiTiCu films.

Sample	Contact angle (water) (°)	Contact angle (formamide) (°)	γ^d (10^{-2} J/m^2)	γ^p (10^{-2} J/m^2)	γ (10^{-2} J/m^2)	$\gamma_{a/c}$ (10^{-3} J/m^2)
NiTi (a)	60.7 ± 1.0	46.5 ± 3.2	1.25	2.93	4.18	1.1
NiTi (c)	76.7 ± 0.5	61.4 ± 1.2	1.28	1.63	2.91	
$NiTiCu_{1.3}$ (a)	56.2 ± 1.2	37.3 ± 2.6	1.55	3.02	4.57	2.5
$NiTiCu_{1.3}$ (c)	80.2 ± 1.0	64.5 ± 2.0	1.29	1.38	2.67	

a: amorphous; c: crystalline; $\gamma_{a/c}$: interfacial energy between amorphous and crystalline phase.

to determine the activation energy of growth for NiTiCu thin films. Using the Arrhenius relationship $V_0 = V^* \exp(-E/kT)$ [20], which is valid for a small temperature region [18,19], the activation energy for growth, E, can be taken from the slope of $ln(V_0)$ versus $1/T$, and equals 283.5 kJ/mol for our NiTiCu, which is smaller than that of NiTi (404.8 kJ/mol) [18,19]. These values are consistent with our TEM observations of faster growth in NiTiCu.

Given the similar overall activation energy and the decreasing activation energy for growth, it is expected that the activation energy for nucleation increases with copper additions. For NiTi thin films, we determined the activation energy for nucleation from the nucleation rate (i.e. the number of nuclei per frame) [18,19]. The nucleation rate of NiTiCu was difficult to measure directly since nuclei were so few in number in our viewing area. Therefore, we used the incubation time ($\tau_0 = \tau^* \exp(H/kT)$ to estimate the activation energy for nucleation (H) [21]. The slope of $ln(\tau_0)$ versus $1/T$ generates the activation energy for nucleation (H), which equals 662.3 kJ/mol. By contrast, the activation energy for nucleation of NiTi is 520.6 kJ/mol [18,19], using this same method. It also agrees well with the reduced nucleation rate observed from TEM images for NiTiCu films. These data indicate that the addition of copper increases the activation energy for nucleation but decreases it for growth, even though the overall activation energy is unaffected. This work shows the individual components of nucleation and growth change; such observations are non-trivial with DSC studies on crystallization.

The lower nucleation rate for NiTiCu thin films has been attributed to a higher interfacial energy between the amorphous and crystalline phases [13]. To explore the role of interfacial energies in NiTi and NiTiCu, we determined the surface energies of the amorphous and crystallized films and estimated the interfacial energy between them using [22]:

$$\gamma_{ab} = ({\gamma_a}^{1/2} - {\gamma_b}^{1/2})^2 \tag{2}$$

where γ_a and γ_b are surface energies of phase a and b, and γ_{ab} is the interfacial energy between them. The surface energies in Eq. (2) consist of two components: a polar interaction, γ^p, and a London dispersion force, γ^d, and can be expressed as $\gamma = \gamma^p + \gamma^d$. The surface energy can be determined by measuring the contact angle (θ) of a liquid droplet (see Fig. 3) and by using the Eqs. [23,24]:

$$(1+\cos\theta)\gamma_L = 2[(\gamma_S^d \gamma_L^d)^{1/2} + (\gamma_S^p \gamma_L^p)^{1/2}] \tag{3}$$

where γ_L is the surface tension of liquid, γ_S is the surface energy of a solid sample and the superscripts d and p designate the dispersive and polar components. The surface energies of amorphous and crystallized thin films of both NiTi and NiTiCu were calculated from these contact angle measurements (in Table 1), assuming the polar and dispersive values of distilled water ($\gamma_L^W = [2.21]_{\text{disp}} + [5.07]_{\text{polar}} = 7.28 \times 10^{-2} J/m^2$) and formamide $\gamma_L^F = [3.95]_{\text{disp}} + [1.87]_{\text{polar}} = 5.82 \times 10^{-2} J/m^2$ [24] (assuming little contribution from the surface oxide) [24]. The resulting interfacial energy in NiTiCu (2.53×10^{-3} J/m^2) is found to be twice that of NiTi (1.14×10^{-3} J/m^2), which is consistent with TEM observations of a lower nucleation rate in NiTiCu, and may be one contributor that impedes nucleation in copper-containing alloys.

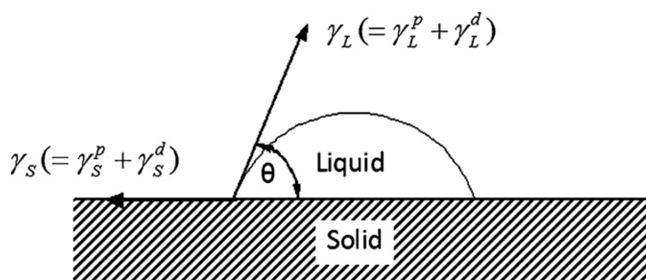

Fig. 3. A schematic drawing of a liquid droplet and its resulting contact angle, θ, surface tension of liquid, γ_L, and surface energy of a solid sample, γ_S in an equilibrium solid–liquid system.

4. Conclusions

In summary, DSC measurements of amorphous NiTiCu thin films with a small amount of copper (of 1.3 at%) exhibit crystallization temperatures and activation energies similar to those of pure NiTi films. However, *in situ* TEM observations reveal a marked difference in crystallization behavior between NiTiCu and NiTi. The crystallization of NiTiCu thin films at several temperatures showed a higher growth rate and a lower nucleation rate with concomitantly larger crystals than those observed in NiTi. By determining the temperature dependence of the growth rate and incubation time, we found that copper additions decrease the activation energy for growth but increase it for nucleation. Further, by contact angle measurements, we found that the interfacial energy between the amorphous and crystalline phases in NiTiCu is almost twice that of NiTi, which is consistent with the observed lower nucleation rate in NiTiCu thin films. These observations suggest that the interfacial energy may play a dominant role in the crystallization of copper-containing NiTi thin films. Such work in improving our scientific understanding of shape memory alloys is essential to tailoring materials for use in MEMS applications.

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