Martensitic transformation in freestanding and supported Cu–Al–Ni thin films obtained at low deposition temperatures

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ABSTRACT

In order to use the shape memory alloy Cu-Al-Ni in micro-actuators, freestanding thin films with martensitic transformation are required. Here we show that freestanding Cu-Al-Ni thin films with $L2_1$ structure, martensitic transformation and shape memory effect can be obtained using iron as a sacrificial layer. The Cu-Al-Ni films with best performance are obtained at deposition temperatures between 533 K and 563 K. The Fe layer can afterwards be removed selectively by electrochemical etching.

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1. Introduction

Low dimensional systems based on shape memory alloys (SMA) have potential applications for micro-scale sensors and actuators [1]. Copper based alloys are particularly useful for applications in cases in which biocompatibility is not required and low-cost devices can be designed for specific purposes. Cu–Al–Ni SMA have some particular characteristics such as high thermal stability [2], broad range of martensitic transformation temperature M_s (70–470 K), and high mechanical performance in polycrystalline and sub-micrometric systems [3,4].

Freestanding thin films are required for micro-actuators based on SMA. Films are usually grown by sputter deposition and they can be deposited at either room temperature or high temperatures [5]. Films obtained at room temperature usually need a post-sputtering annealing process [5]. Films obtained at high temperatures are usually difficult to release from the substrate. However, this can be done by using a sacrificial buffer layer that is removed selectively after film growth [6,7].

For some alloys such as Cu-Al-Ni, the thermal stability for β-phase restricts the range of deposition temperatures in which films with austenitic phase can be obtained [8,9]. In bulk β-phase Cu-Al-Ni, the thermal annealing at temperatures above 573 K produces precipitation of stable phases [9]. Austenitic phase in bulk and films is recovered above 1000 K [10].

A novel approach to obtain freestanding Cu-Al-Ni thin films by using a sacrificial Fe layer is presented here. Deposition temperatures between 533 K and 563 K produce polycrystalline Cu-Al-Ni thin films with metastable austenitic β-phase with $L2_1$ structure. The freestanding films can be manipulated and they present martensitic transformation. In addition, the films show shape memory.

2. Material and methods

Films with thickness of $\approx$ 2 μm were grown on c-cut Al_2O_3 by DC magnetron sputtering from a $Cu_{69}Al_{21}Ni_{10}$ target ($M_s \approx$ 250 K) with an applied power of 50 W under Ar atmosphere at a pressure of 10 mTorr. Cu-Al-Ni films were deposited at different temperatures of substrate (T_D): 503 K, 533 K, 563 K and 593 K. Previously, a 0.1 μm thick Fe buffer layer (deposited at 720 K) was introduced as a sacrificial layer to help release the Cu-Al-Ni films later on. Similar results were obtained for films with the Fe buffer layer deposited at temperatures of 573 K. After deposition, the films were pulled out from the substrate by electrochemical etching of Fe using a 0.05 M H_3BO_3 solution at -0.05 V vs. Ag / AgCl electrode (usually by 24 h). Wherever used, the notation [T_DX] indicates a 2 μm thick Cu-Al-Ni film with deposition temperature X. It is important to mention that the inclusion of a sacrificial buffer layer is necessary to release the films from the substrate because there is a chemical reaction at the Cu-Al-Ni / substrates interface when the substrate temperature is above self-heating ($\approx$ 420 K).

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The microstructure of the films was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD data were obtained using a Panalytical Empyrean equipment. TEM results were obtained using a Tecnai F20 microscope operated at 200 kV. Side-view (cross-section) TEM specimens were obtained by a focused ion beam (FIB, FEI Helios 600) system. The martensitic transformation was characterized by electrical transport using conventional four probe geometry. The shape memory effect was confirmed through mechanical deformation.

3. Results and discussion

Fig. 1a shows a XRD for [T_D533K]. β-phase is found in all the films with T_D between 503 K and 593 K. No texture was observed for the β-phase reflections. The iron buffer layer is textured with planes (110) parallel to the plane of the films. The rocking curve along the $(110)_{Fe}$ reflection was $\approx$ 2.1°. [T_D503K] thin films displayed suppressed martensitic transformation and reduced M_s. [T_D593K] thin films displayed wider hysteresis transformation than [T_D533K] and [T_D563K]. This can be attributed to the presence of nanometric γ_2 (Cu_9Al_4) precipitates (which is largely increased for higher T_D). Hence, we focused on the martensitic transformation in [T_D563K], which is representative of films obtained at T_D between 533 K and 563 K. The chemical composition in [T_D563K]

(obtained by SEM-EDS) is $Cu_{72}Al_{21}Ni_7$. The root-mean-square (rms) surface roughness for [T_D563K] measured by AFM in a 10 μm² area, is 15 nm and 12 nm for supported and freestanding samples, respectively.

Fig. 1b shows the normalized resistance (R/R^{270K}) vs. temperature curves for [T_D563K] supported and freestanding films. Both samples show martensitic transformation at around 200 K with no significant differences observed. The disparity in the temperature dependence of R/R^{270K} can be attributed to the conductivity of the Fe buffer layer. The variation in M_s in comparison with the bulk target ($M_s \approx$ 250 K) can be attributed to slight changes in the chemical composition [10] and to the increment in the hysteresis ($\Delta h \approx$ 44 K) due to microstructural effects [11]. In addition, the transformation in the film is not abrupt (finishes below 150 K), which can be associated with the presence of small grains and chemical gradients [10].

Fig. 2a shows a bright field plan-view TEM image for [T_D563K]. The image displays a polycrystalline structure with nanosized grains. Fig. 2b shows the selected area electron diffraction (SAED) pattern obtained from Fig. 2a, which corresponds to the L2$_1$ structure of the β phase. By analyzing different TEM plan-view images, the mean grain size (D) and the distribution width (σ) were obtained. Fig. 2c shows the grain size histograms and the corresponding fitting with a log-normal function with D = 159 nm (σ = 6 nm). Similar grain size histograms were obtained for samples with T_D between 503 K and 593 K (not shown). A small increment in D from 105 nm to 165 nm is observed when the temperature is increased. These grain sizes are smaller than that obtained by annealing of Cu-Al-Ni films grown without any intentional heating of the substrate. These films initially display $D \approx$ 20 nm and the grain size is increased to $D \approx$ 200 nm after annealing at temperatures above 1000 K [10].

Fig. 2d shows a TEM cross-section dark field image for [T_D533K]. Columnar grains along the growth direction (n) are observed. The dark field image was obtained from the 022 ring in the diffraction pattern. The SAED pattern corresponds to the L2$_1$ structure and exhibits quite uniform rings in agreement with the polycrystalline nature of the film (Fig. 2e). No regions that can be associated to γ_2 phase (precipitates) were identified. The columnar structure present in the film is typically observed in metallic films obtained by sputtering at low deposition temperatures.

The driving force for the transformation is given by the chemical free energy ($\Delta G^{chem} = \Delta H - T\Delta S$; being ΔH the enthalpy and ΔS the entropy). Interfacial energies and size effects increase the barrier for the transformation. The interfacial energies depend on grain boundary attained by martensite plates (γ_{gb}), the interfaces between austenite and martensite plates (γ_{am}), and the twin interfaces within martensite plates (γ_{tw}) [12]. The chemical driving force ΔG^{chem} generated by undercooling around T_0 is related to the $\Delta S^{L21 \to 18 R}$ and it can be estimated as $\partial \Delta G / \partial T = -\Delta S$. The $\Delta S^{L21 \to 18 R}$ in bulk Cu-Al-Ni is $\approx -2 \times 10^5$ J K^{-1} m^{-3} [13]. The value for the energy barrier for the film is approximately $(\Delta h/2)^{film} \approx$ 22 K, being E$^{T\text{-}film}$ $\approx 4.4 \times 10^4$ J m^{-3}.

In polycrystalline SMA the nucleation and growth of the martensite plates are controlled by austenite grain boundaries. The martensite plate thickness (h_{plate}) decreases as D is reduced [14]. A domain of parallel plates is usually observed in grains smaller than 10 μm. Bulk Cu-Al-Ni shows $h_{plate} \approx$ 0.36 D [14]. Assuming spherical grains, the total area A_{tw}^t can be calculated by the expression:

$$A_{tw}^t(D, N) = \frac{\pi}{2}D^2\left(\frac{N^2-1}{3N}\right)$$

(1)

where N is the number of interfaces ($D/h_{plate} \approx$ 26). Subsequently, A_{tw}^t depends only on D. The total interface energy per unit volume
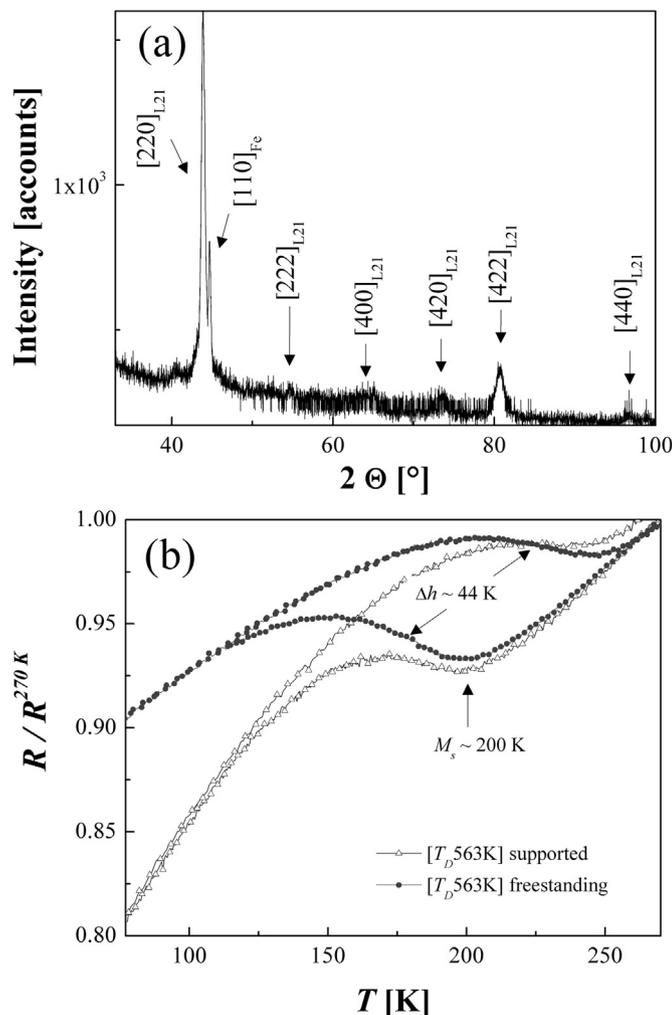

Fig. 1. (a) X-ray diffraction patterns at room temperature of supported [T_D533 K]. The film was slightly tilted to reduce the Al_2O_3 (006) reflection. (b) Normalized resistance (R/R^{270K}) versus temperature for the supported and freestanding [T_D563K] film.
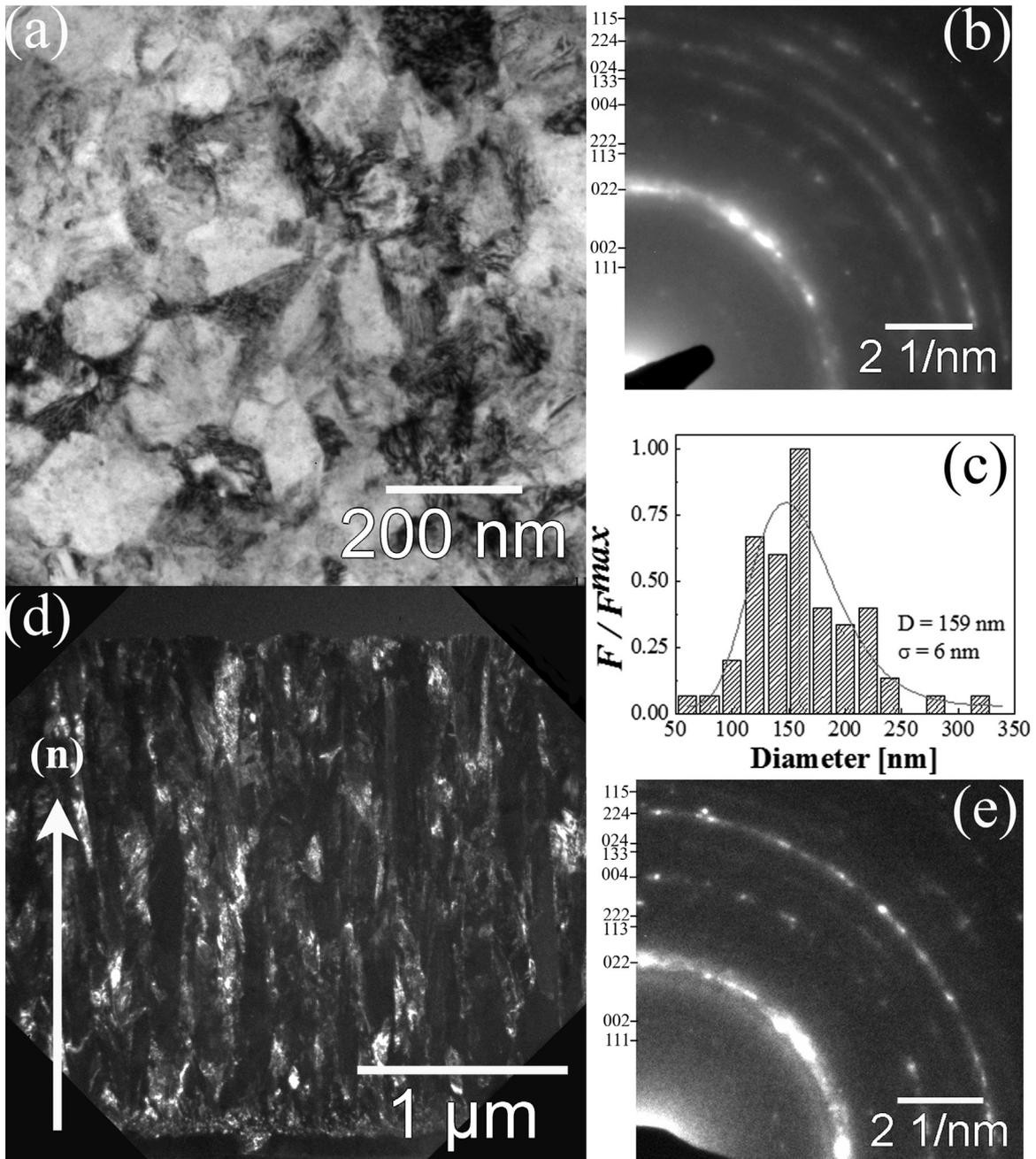
Fig. 2. (a) Bright field TEM image of [T_D563K] in plan-view orientation. (b) Corresponding SAED pattern to image (a) with identification of L2$_1$ reflections. (c) Grain size distribution from plan view images in [T_D563K]. (d) Cross-section dark field TEM image was obtained from the 022 ring in the diffraction pattern in [T_D533 K]. The normal (n) to the substrate surface is parallel to the growing direction. (e) Corresponding SAED pattern to image (d) with identification of L2$_1$ reflections.

is given by:

$$E^{tw} = \gamma_{tw} \frac{A_{tw}^t}{V(D)} = \left(\frac{N^2 - 1}{N} \right) \frac{\gamma_{tw}}{D} \qquad (2)$$

where $V(D)$ is the volume of a spherical grain. Values between 0.02–0.07 J m^{-2} have been reported in Cu-Al-Ni [12,15]. Using these values E$^{tw} \approx 3.7 \times 10^4 - 1.2 \times 10^5$ J m^{-3} is obtained, which corresponds to the same order as the barrier observed for [T_D563K]. This indicates that the observed Δh in the film is in agreement with bulk samples with sub-micrometric grain size, which could be mainly ascribed to the existence of an energy barrier related to the twin interface energy [14].

Finally, the presence of shape memory was verified. A film was fixed to a copper wire using silver paint. An initially flat film was mechanically deformed at liquid nitrogen temperature, as can be observed in Fig. 3a. The film was heated as it was removed from the liquid nitrogen vapor source. Although a shape-recovery process began (Fig. 3b) and continued as temperature was increased up to room temperature (Fig. 3c), no complete recovery was obtained. This is most probably due to some permanent plastic deformation induced during the mechanical deformation of the martensite at low temperatures.

4. Conclusions

Summarizing, freestanding Cu-Al-Ni thin films can be obtained at low deposition temperatures, which can be associated with metastable growth of β phase with L2$_1$ structure. The freestanding
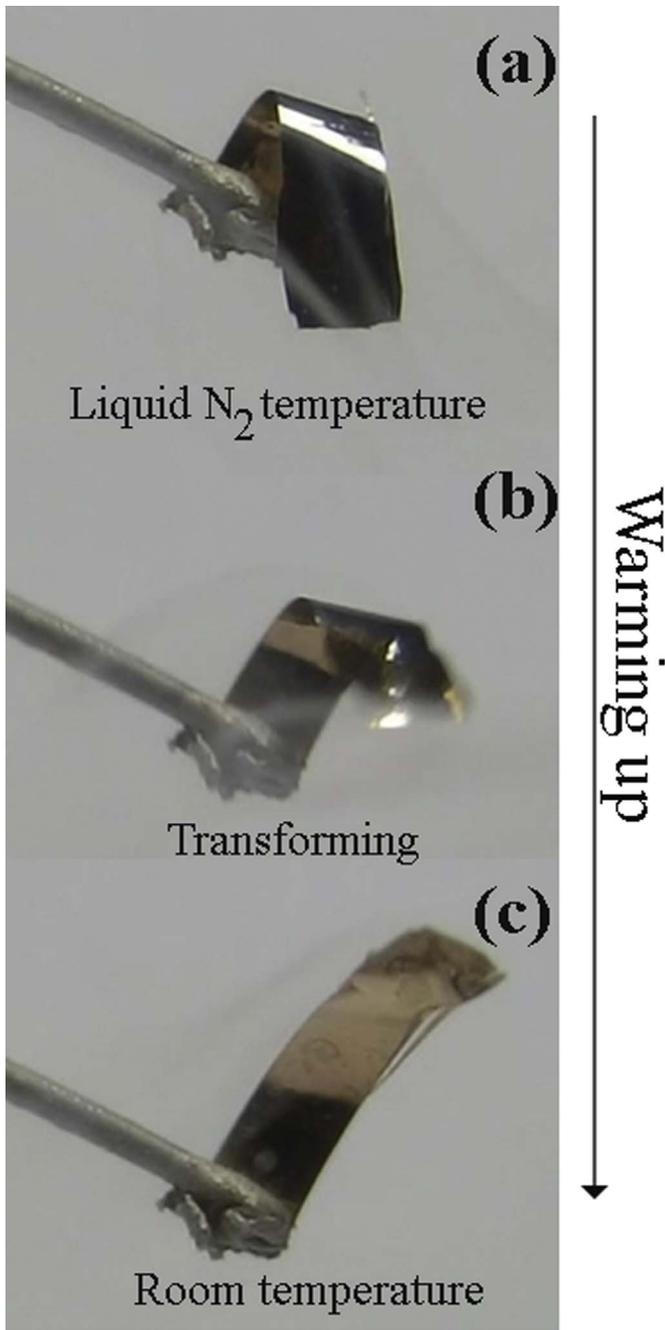
Fig. 3. The shape memory effect in the freestanding [T_D563K] film. (a) A flat film was mechanically deformed at liquid nitrogen temperature. (b) The shape start to be recovery at intermediate temperatures. (c) The initial flat shape is largely re-covered at room temperature. The film is ≈ 1 mm wide and ≈ 5 mm long.

films present martensitic transformation and shape memory effects. The feasibility of obtaining freestanding or partially supported (dissolving partially the Fe buffer layer) Cu-Al-Ni thin films at low deposition temperatures enhances their application in thermomechanical micro-actuators.

Acknowledgments

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