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Shape memory effect in sputtered Ti-Ni thin films

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Abstract

The microstructure and electrical transport properties of Ti–Ni granular films have been investigated with X-ray diffraction and DC resistivity measurements, respectively. Samples with the eutectoid composition ($\sim 50 \text{ at}\%$ Ni) were grown by RF magnetron sputtering on a heated sample holder. These films comprised Ti₂Ni, TiNi₃ and TiNi granular phases, their relative proportions and microstructures critically depending on the substrate temperature. A majoritary metastable TiNi phase was obtained in samples grown at temperatures above 600°, as inferred from the discussion of the X-ray diffraction plots. These crystalline films showed the hysteretic behaviour of the electrical resistance which is attributed to the characteristic shape memory effect of such a binary alloy. Besides, the DC resistivity measurements are accomplished in Joule-heated samples by which efficiently modify their microgranular structure from amorphous to crystalline, or even stabilize the TiNi phase after a flash annealing. \bigcirc 2004 Elsevier B.V. All rights reserved.

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Amongst the shape-memory alloys (SMA), the equiatomic TiNi compound is the most widely studied owing to several reasons: its resistance to large deformations and, consequently, a great shape-restoring force, its compatibility with biological purposes and its promising application as a micro-actuator in electro-mechanical systems [1]. Besides, this martensite alloy is the precursor of several ternary SMA alloys with ferromagnetic elements, e.g. Ti–Ni–(Co,Fe). Although easy to fabricate, the TiNi phase is metastable at RT and needs to be stabilized following a quenching process [2]. Afterwards, the obtained alloy can reversibly mutate from its high-temperature crystallographic structure to its low-temperature one, i.e. from the ClCs (B2,

austenite) to the monoclinic phase (B19', martensite), directly or via the intermediate rhombohedrical (Rphase) [3,4]. This transition is responsible for the shape memory effect in the TiNi compound [5-7]. Relevant features of this called martensitic transition, e.g. the start and finish temperatures, the sharpness or the amplitude, have been found to critically depend on the alloy composition and its fabrication procedure [3,8]. Additionally, the application of the SMA properties to the micro-electromechanical systems has led the recent research to the fabrication of TiNi thin films by different methods [5,8]. Thus, a thorough knowledge of the influence of the TiNi growing parameters in its microgranular structure is required both for these technical purposes and for investigating the ferromagnetism in the thermoelastic martensites.

The main aim of our work has been to investigate the correlation of several growing parameters into the crystalline structure and the electrical transport of

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sputtered TiNi thin films. Besides, we have shown that the Joule heating effectively modifies their granular structure, similar to a high-temperature annealing.

 $Ti_{100-x}Ni_x$ thin films were grown on glass substrates using RF magnetron sputtering system. The substrates could be heated from RT up to 650 °C. The substratetarget distance was fixed at about 4 cm. Prior to deposition, the background pressure was about $6 \times$ 10^{-7} mbar. Deposition was carried out without any bias voltage in Ar gas atmosphere $(3 \times 10^{-3} \text{ mbar})$. The sample composition could be fixed by symmetrically attaching small Ni pieces on the Ti sputtering target $(x \sim 50 \text{ along this work})$. RF power and time of deposition were adjusted to give an average thickness of around 0.8 µm for all samples. The composition of the alloys was determined by energy dispersive X-ray microanalysis (Philips XL-30 scanning electron microscope). The microstructure of the multilayers was studied using high angle X-ray diffraction (Philips X'pert-MPD system) equipped with a CuKa radiation tube. Electrical resistivity was measured from 8 to 300 K using an ⁴He closed cycle refrigerator with a conventional four-point DC method ("punctual" pressure contacts). A home made experimental setup allowed us to sharply heat the TiNi films by applying current pulses in vacuum (flash annealing by Joule heating).

According to the Ti-Ni phase diagram, the TiNi compound is only stable above $T_e \sim 630 \,^{\circ}$ C [2]. Hence, the as-deposited TiNi thin films are amorphous and a later annealing above T_e is required to obtain that metastable phase [3,5]. An alternative method avoiding such high-temperature treatment is the growing of TiNi thin films on heated substrates during the deposition. Substrate temperatures, T_s , in the range of 300–450 °C, are reported to be adequate to obtain TiNi films with a good shape memory effect [8]. We have firstly investigated the influence of T_s in the microgranular structure of the TiNi thin films by means of X-ray diffraction. The $\theta - 2\theta$ plots for TiNi samples grown at different RF powers and T_s are shown in the Fig. 1. As expected, the measured spectra for the samples deposited at RT are characteristic of an amorphous matrix containing TiNi tiny nanocrystallites. This microstructure evolves to crystalline thin films for T_s well over 550 °C (middle and upper plots in Fig. 1). In the case of 30 W TiNi samples, the diffraction peaks can be tentatively indexed to diverse Ti-Ni phases, e.g. the metastable Ti₃Ni₄ and Ti₂Ni₃ precipitates or the very similar Ti₂Ni and $Ti_4Ni_2O_x$. However, for thin films grown at 100 W, the main reflection corresponds to the austenite TiNi. That would indicate that sputtered grains at higher RF powers are quenched from temperatures well above $T_{\rm e}$, thus avoiding the occurrence of those mentioned odd phases. From our results, the value $T_s = 550 \,^{\circ}\text{C}$ seems to be the threshold to grow crystalline TiNi films, agreeing with F. Ciabatarri et al. [5]. This deposition



Fig. 1. $\theta - 2\theta$ diffraction spectra of selected TiNi thin films. Growth conditions (RF power, T_s): (lower plot) 100 W, RT; (middle plot) 30 W, 550 °C; (upper plot) 100 W, 550 °C. The inset shows the same measurement for a crystalline TiFe thin film sputtered at $T_s = 420$ °C.

temperature points to the best experimental condition to obtain a majority shape memory alloy in the sample, displaying the least number of structural defects. For comparison, we have included a diffraction plot of a TiFe thin film grown at $T_s = 420$ °C, where the crystallization seems to be already accomplished (see the inset of Fig. 1). In spite of the similarity between both compounds, such a smaller threshold value is due to the stability of the TiFe alloy down to RT.

In turn, those structural transformations bring about dramatic changes into the electrical transport properties. The thermal dependence of ρ_n (normalized DC resistivity to 320 K) from 8 to 320 K is plotted in Fig. 2 for TiNi films grown at 100 W and different T_s . On the one hand, the progressive crystallization of the samples induces an evident diminishing of the intrinsic defects. That yields $\rho_{\rm n}$ to change from the classical semiconducting behaviour (amorphous alloys) to the metallic regime (crystalline alloys). On the other hand, the normalized DC resistivity of the TiNi thin films deposited at $T_s > 550^\circ$ clearly displays a hysteresis cycle roughly bounded in the interval 150-300 K. This unusual phenomenon is due to the predominance of the TiNi austenite phase in the corresponding thin film deposited at $T_s > 550^\circ$ (as seen in Fig. 1) and its later martensitic transformation. Related with that assertion, we have intentionally included in Fig. 2 the ρ_n graphs of two TiNi films grown at the same high temperature. Their dissimilar hysteresis cycles are due to the slight differences in the ratio of the TiNi phase over the other spurious intermetallics, greater in the sample of the lower plot. This fact has been observed in their respective X-ray diffraction characterization (not shown here). In spite of their same growing conditions, thermal gradients on the



Fig. 2. Thermal dependence of ρ_n for the TiNi thin films grown at room temperature (upper plot) and $T_s = 550 \,^{\circ}\text{C}$ (medium and lower plots).

substrate holder can slightly differentiate the local quenching rate occurring in each sample.

As the temperature is lowered, the TiNi austenite grains first evolve to the R-phase and then to their stable phase, the martensite, retaining internal stresses which are responsible for the mentioned hysteresis. Evidences of the existence of that R-phase even at RT can be obtained after noticing the progressive splitting of the (110) B2 diffraction peak (see the upper plot in Fig. 1). As observed in our results, ρ_n returns later to its original value on reversing the sense of the transition. The reason is both the elimination of internal deformations in the sample and the recovery of its "memorized" shape (SMA). All of these effects induced by the referred crystallographic transition show up visibly in ρ_n once the structural disorder has been noticeably diminished, correlating with the X-ray diffraction results for the TiNi samples grown at high T_s (upper plot in Fig. 1).

As an alternative method to the in situ annealing, the Joule heating was employed in some TiNi thin films previously deposited at RT. Then, these amorphous samples were sharply heated with pulses of electrical current, *I*. For instance, the thermal dependence of ρ_n in those samples after applying I = 0.6 A during 1 min is shown in Fig. 3. At first glance, it seems clear that these flash annealings efficiently modify their microgranular structure as it progressively turns the behaviour of ρ_n from semiconducting into metallic. More interesting seems to be the appearance of a small hysteresis cycle similar to the one shown in Fig. 2 (medium plot). In the



Fig. 3. Thermal dependence of ρ_n for a TiNi thin film after being flash annealed (Joule heating, I = 0.6 A during 1 min). The inset shows its diffraction spectrum which clearly reveals a crystalline microstructure.

light of these results, Joule heating allowed us to crystallize the TiNi thin film and to quench the austenite to room temperature. That would confirm the capability of that simple method to stabilize the TiNi phase responsible for the shape memory effect. The comparatively small hysteresis cycle obtained by this method could be due to the percolative character of this annealing.

In summary, we have grown crystalline TiNi thin films by means of RF sputtering on a heated substrate in situ. That has enabled us to investigate the effects of some deposition parameters such as the RF power and the substrate temperature into the TiNi microstructure and its electrical transport. The thermal dependence of ρ_n of those TiNi films showed a hysteresis cycle characteristic of the shape memory alloys. Besides, we have confirmed Joule heating as a simple and promising tool to generate and stabilize the austenite phase in the TiNi samples.

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