An in-situ grazing incidence x-ray diffraction study of the crystallisation of Ni-Ti thin films

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1. Introduction

The shape memory effect (SMA) relies on martensitic transformations which are macroscopically due to a pseudo-shearing deformation, resulting from a deformation mode similar to slip or twinning in ordinary metals and alloys under stress. However, since martensitic thermoelastic transformations are reversible, the deformation behaviour of alloys that undergo this type of transformations is remarkably different from that of ordinary metals and alloys in which the deformation, by slip or by twinning, is not recoverable [1]. The martensitic transformation starts (in cooling) at a certain temperature $M_s$, and is completed when a lower temperature $M_f$ is reached. When this martensite is deformed (below $M_f$) it undergoes a strain, which, within certain values, is completely recoverable upon heating. The shape recovery begins at a temperature $A_s$ (where the martensite $\rightarrow$ austenite transformation starts), and is completed at a higher temperature $A_f$ (where the transformation martensite $\rightarrow$ austenite is finished). The $M_s$, $M_f$, $A_s$ and $A_f$ temperatures are characteristic of the alloy system, and recoverable strains typically range from 2% to 10%. The martensite in shape memory alloys (SMA’s) may also be isothermally induced above the Ms temperature by the application of a stress [2]. The NiTi system is the most popular of the SMA’s because of the considerable work per unit mass it can produce during recovery (work output $\sim$1 Joule/g), because of the value of the transformation temperature (near room temperature, i.e. from $-100^\circ$C to $+100^\circ$C) and because of its good oxidation resistance.

The thin films of SMA’s can be electrically driven using joule heating, and they demonstrate fast cooling rates because of their large surface-to-volume ratio. The control of film composition and properties has proven difficult in sputter-deposited films, and further study of deposition techniques is needed [3].

It is known that NiTi alloys need to be composed of around 50 at% Ni - 50 at% Ti to have shape memory, with any slight change in alloy composition causing a significant deterioration in this property. Although a number of techniques have been tried for depositing NiTi SMA thin films, from the practical point of view, only the sputter deposition has succeeded so far. Historically, the first attempt at the formation of NiTi SMA thin films was vacuum evaporation. However, this method has failed to form NiTi alloy thin films with good shape memory properties. This is because conventional vacuum evaporation of NiTi binary alloy entails the potential problem of the evaporation rates of each component not being the same due to differences in vapour pressure. A flash evaporation method has been proposed to solve this problem providing an alternative to sputtering deposition [4], and the thermo-mechanical properties have been studied [5–8] in order to optimise their application as microactuators [8–10] and microsensors [11].
At CENIMAT, work has been performed on the optimisation of the flash evaporation and sputter deposition techniques, aiming to obtain improved thin films with higher performances [12].

The as deposited films are amorphous; a crystallisation process is necessary in order to induce the shape memory effect, see Fig. 1. A deeper understanding of this crystallisation is needed in order to obtain materials presenting different transformation temperature ranges, for different applications. It is also aimed at obtaining the lowest crystallisation temperature, because this will allow the use of flexible (polymeric) substrates. Thus, before starting to test the feasibility of microsystems construction based on these thin films, it is intended to optimise the crystallisation conditions by studying at a finer dimensional scale the structural changes that are induced and their correlation with the localized chemical composition changes associated with the precipitation of different intermetallic phases of the Ni-Ti system, e.g. Ni₃Ti and NiTi₂ (Fig. 2). The strong dependency of the temperature $T_o$ for the austenite–martensite thermodynamic equilibrium (and, as a consequence, $M_s/M_f$ and $A_s/A_f$) on composition (Fig. 3), gives a high sensitivity of SMA properties to a variation in composition, especially in Ni rich alloys.

![High temperature in-situ XRD of a sputtered Ni-Ti film.](image)

**Fig. 1:** High temperature in-situ XRD of a sputtered Ni-Ti film.

![Ni-Ti phase diagram](image)

**Fig. 2:** Ni-Ti phase diagram [13].

![$T_o$ versus Ni content](image)

**Fig. 3:** $T_o$ versus Ni content ($T_o$ can be expressed as $(M_s+A_s)/2$) [13].

In this article we present the results of the optimisation of the sputter deposition technique, as well as the heat treating procedure leading to the crystallisation of the thin
films. The crystallisation sequence was studied by using grazing incidence x-ray diffraction (GIXRD) at the materials research station of ROBL at ESRF [14].

2. Experimental method

2.1 Thin films production

The NiTi thin films were deposited on Si(100) wafers using sputtering rf technique with the parameters given in Table 1. The chemical composition of the target material was 44 wt% Ni – 56 wt% Ti, i.e. 49 at% Ni – 51 at%Ti.

Table 1: Parameters used for sputtering deposition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>S 8</th>
<th>S 11</th>
<th>S 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance target-substrate (mm)</td>
<td>70</td>
<td>90</td>
<td>186</td>
</tr>
<tr>
<td>Initial pressure (mbar)</td>
<td>4.4×10^{-6}</td>
<td>8.5×10^{-6}</td>
<td>4.8×10^{-5}</td>
</tr>
<tr>
<td>Argon pressure (×10^{-3} mbar)</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Deposition pressure (×10^{-2} mbar)</td>
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<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Argon flow rate (sccm)</td>
<td>10</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>R.f. power (W)</td>
<td>150</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

2.2 GIXRD in-situ annealing

Samples of 10x10 mm² were cut to be analysed. The annealing of the films took place under vacuum (pressures ranging from 5.7×10^{-6} mbar to 1.4×10^{-5} mbar). A half-spherical Be-dome furnace was used to study the kinetics of the crystallisation of the thin films using GIXRD under grazing incidence of 1° and with a wavelength of 1.54 Å. The six-circle goniometer itself allows equally well full horizontal as well as vertical scattering geometries. A closed Eulerian cradle (χ circle with beam direction as rotation axis) is fitted to the θ circle (incidence angle on sample), and with an identical rotation axis the 2θ circle (vertical scattering angle) is independently mounted. A fourth φ rotation allows an azimuthal sample orientation (surface normal as rotation axis). All four circles described rest on two other horizontal circles, ω and 2ω, with the same vertical rotation axis. The inner circles φ and χ are used for the orientation of the furnace, i.e. the sample orientation (as the sample is fixed inside the furnace). The two scattering planes are realized with the θ/2θ circles for the vertical as well as the ω/2ω circles for the horizontal plane. The half-spherical Be-dome furnace was installed on the φ circle inside the Eulerian cradle, thus allowing full 2π access in the horizontal, as well as in the vertical planes. These two geometries are accessible without change of the experimental configuration.

Samples of 0.3–1 µm thick NiTi thin films deposited on Si(100) wafers with different sputtering conditions were studied. The temperature range covered for the crystallisation studies was from room temperature (RT) to 525°C.
3. Results

The samples S8 (Fig. 4) and S11 (Fig. 5) – distance target-substrate during sputtering 70 and 90 mm, respectively – showed, after annealing, the presence of the austenite phase (B2) of the Ni-Ti system and the intermetallic Ni₃Ti, as well as the presence of silicides. The sample S12 (Fig. 6) – distance target-substrate 186 mm – only shows the presence of the Ni-rich solid solution of Ti and TiO₂. Both S8 and S11 are not crystallised at 325°C, but they show a significant degree of crystallisation at 365°C. Increasing the temperature up to 445°C or 525°C, improves the degree of crystallisation.

**Fig. 4:** GIXRD spectra of sample S8 at room temperature and different annealing temperatures (* B2, + Ni₃Ti, # Ni₂Si, x Si).

**Fig. 5:** GIXRD spectra of sample S11 at room temperature and different annealing temperatures (* B2, + Ni₃Ti, # Ti₅Si₃, x Si).
A stress state determination by GIXRD was performed on sample S8 at room temperature, after annealing at 445°C. The results in Fig. 7 show that the residual stress state is very low.

4. Discussion

The experiments performed at ROBL allowed us to obtain a very clear definition of the peaks associated with the intermetallics, i.e. Ni₅Ti, that are present in minor quantities in our samples. The experimental results show that:

- The greater distance target-substrate (186 mm) used for sample S12 led to a significant Ti depletion on the sputtered thin film. During annealing, a further depletion of Ti by oxide formation led to the appearance of the Ni solid solution (Ti solute). This type of result is consistent with oxidation studies previously reported [15].
- The films S8 and S11 with the smaller target-substrate distances showed the formation of the B2 phase, the crystallisation temperature being comprised between 325°C and 365°C. The presence of Ni₃Ti intermetallic shows that the sputtered thin film is slightly enriched in Ni.
- The residual stress state of the S8 film after annealing appears to be very low.

Acknowledgements

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References