ESRF	**Experiment title:** In-situ phase evolution of sputtered reactive multilayers	**Experiment number**: **MA-1637**
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Report:

OBJECTIVE

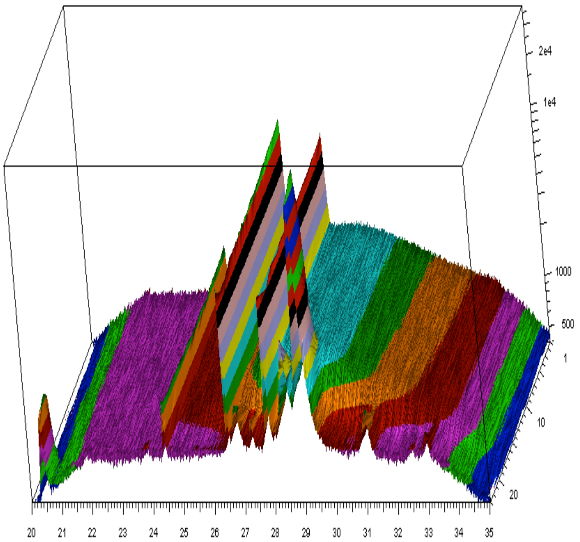
In situ X-ray diffraction (XRD) using synchrotron radiation has proven extremely effective in analysing phase formation sequence in multilayer films. So far, special attention has been paid to the Ni-Al and Ti-Al systems [1,2]. Therefore, the objective of this work is to use synchrotron radiation for real-time investigation of the phase evolution during heat treatment of magnetron sputtered Ni/Ti multilayer thin films.

EXPERIMENTAL PROCEDURE

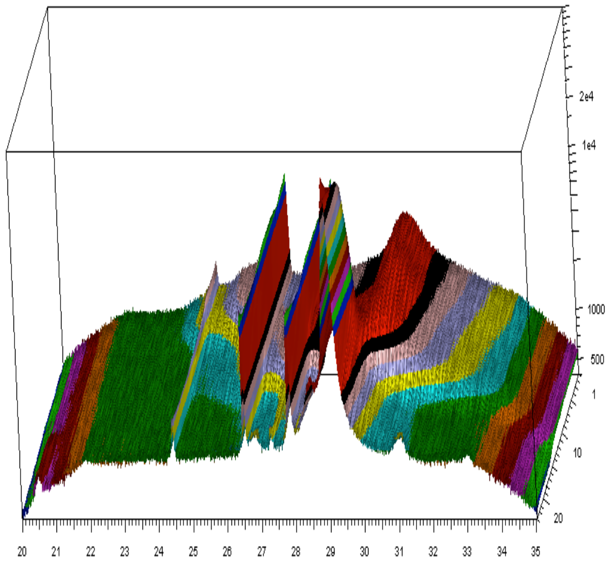
Ni/Ti multilayer thin films with equiatomic chemical composition were prepared by d.c. magnetron sputtering. Ni and Ti alternated nanolayers were deposited onto NiTi and Ti-6Al-4V substrates at 0.35 Pa argon pressure from pure Ni and Ti targets operating simultaneously. Ni/Ti films 2-2.5 μm thick with 4, 12 and 25 nm modulation period (bilayer thickness) were produced by varying the substrates' rotation speed. For the *in situ* XRD experiments using synchrotron radiation, the Ni/Ti multilayer thin films were placed in a furnace equipped with kapton windows, which was mounted on a six-circle goniometer. The incident X-ray beam was monochromatized to 11.5 keV ($\lambda = 0.1078$ nm). Two thermal cycles were adopted: i) temperature increase from 50 to 600ºC with steps of 25ºC (θ-2θ scans $20 < 2\theta < 35º$ each 25ºC step); ii) fast heating while recording scans centred at $2\theta = 30º \pm 1.9º$ each 0.5 s. At the beginning/end of the thermal cycles wider ($20 < 2\theta < 54º$) scans were acquired.

EXPERIMENTAL RESULTS

After deposition, Ni and Ti layers present a quasi-amorphous structure, in particular for the short period multilayers. During heating, the Ni and Ti of the multilayer thin films react to form the B2-NiTi austenitic phase. The reaction of the Ni/Ti multilayers to produce B2-NiTi occurs in a short delay of time and within a narrow temperature range. The XRD data enables the identification of the reaction initiation and the structural evolution sequence. Although the start of the B2-NiTi formation is much more clear using Ti-Al-V substrates and particularly for larger periods, all the other situations are easily identified. Figure 1 shows the XRD data obtained, as 3D plots, where the X axis represents the 2θ angle ($20º < 2\theta < 35º$), the Y-axis is the scan number (temperature progressing from back to front of the graph) and the intensity is represented in $\log_{10}$ scale (Z-axis). In addition to the austenitic phase, $NiTi_2$ precipitates were detected for higher temperatures (figure 2). The diffusion of Ti from the substrates could favour the precipitation of $NiTi_2$.



Nº	Sample Temperature (°C)	
	Λ 4 nm	Λ 25 nm
1	27	52
3	50	94
5	83	143
7	122	195
9	163	244
11	205	256
13	250	287
15	293	328
17	337	368
19	382	413
21	444	465
23	500	526



(a) Λ = 4 nm (b) Λ = 25 nm

Fig. 1 – 3D superposition of XRD patterns during heating up to 600 ºC. (Ti-6Al-4V substrate)

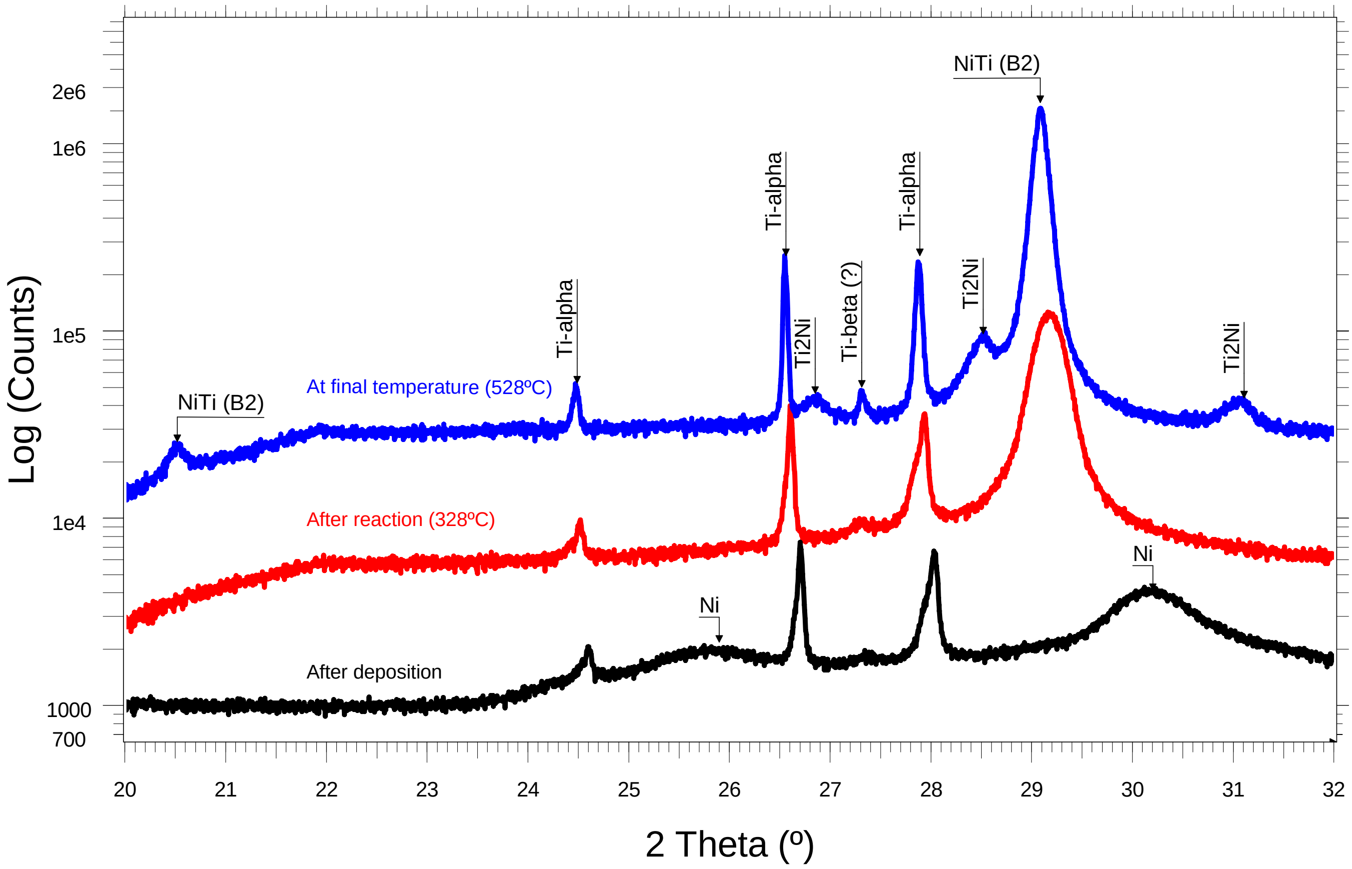


Fig. 2 – XRD patterns of the Ni/Ti multilayer with 25 nm period after deposition, after reaction and at final temperature.

The X-ray synchrotron experiments allowed the reaction temperature of the different Ni/Ti multilayer thin films to be established. This temperature is close to 320, 350 and 385ºC for modulation periods of 25, 12 and 4 nm, respectively. After cooling to room-temperature, besides B2-NiTi (major phase) and $NiTi_2$, it was possible to detect the presence of R-phase.

References

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[2] G. Lucadamo, K. Barmak, C. Lavoie, C. Cabral, Jr., C. Michaelsen, J. Appl. Phys. 91 (2002) 9575.