ROBL-CRG	**Experiment title:** ***In-situ* XRD and Electrical Resistivity Study of the Phase Transformations in Ni-Ti Shape Memory Alloys (SMA)**	**Experiment number:** **20_02_679**
Beamline: BM 20	**Date of experiment:** from: 23.01.2009 to: 27.01.2009	**Date of report:** 28.02.2009
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REPORT:

In situ XRD has been used by the authors to study the structural changes during (i) the crystallization of Ni-Ti thin films [1], (ii) the growth of Ni-Ti thin films by sputtering [2-11], and (ii) the transformation characteristics of bulk N-Ti subject to thermomechanical treatments [12-16]. The phase transformations of Ni-Ti SMA can also be investigated by measuring some physical properties such as electrical resistivity (ER) as a function of temperature. During cooling of Ni-Ti SMA from B2-phase, the resistivity value decreases linearly with the temperature down to R_s , where R-phase self-accommodated (by twinning) starts to be formed. Twinning in an alloy matrix results in electron scattering, which in turn leads to the increase of the ER [17]. Additional cooling below R_f promotes the continuous increase of rhombohedral distortion angle of the R-phase. It is assumed that this rhombohedral distortion is the reason for a further increase of ER (between R_f and M_s). Below M_s, this distortion is relaxed by the R-phase transforming to monoclinic B19’ martensite, giving a gradual decrease of ER.

EXPERIMENTAL

A new chamber, based on the Be dome furnace, enables heating and cooling between -100 and 150°C. The chamber was mounted on the Phi-circle of the 6-circle goniometer of ROBL beamline. The sample is contacted with 4 springs at the corners for resistivity measurements. This mounting makes possible the access in nearly all scattering directions; at least, there is no restriction for GIXRD and θ/2θ scans even for angles up to 2θ = 60°. The temperature was measured with a Shell-TC (below the sample). The chamber can be flushed with nitrogen or helium, or evacuated. Two samples were tested: one Ni-Ti thin films deposited on TiN buffer layers and another one deposited on Si(100) oxidized. In both cases the transformation sequence during cooling will be B2 => R-phase and R-phase => B19’.

The following samples (S23 and S32) from previous campaigns have been studied for in situ XRD characterization simultaneously with ER measurement.

sample	***Power applied to the 2nd magnetron (W)***				***Substrate***			
	NiTi	*Ti*	*Hf*	*Cu*	Si oxidized	Si (100)	MgO (100)	MgO (111)
S23	40	20			X			

Sample	***TiN deposition: ratio Ar/N$_2$***	***Substrate bias (V)***		***Deposition (min.)***						***Annealing (min.)***	
		TiN deposition	*Ni-Ti deposition*	***TiN (on top of Si wafer)***	***NiTi 1st layer***	***TiN 1st inter-mediate***	***NiTi 2nd layer***	***TiN 2nd inter-mediate***	***NiTi 3rd layer***	***TiN (on top of Si wafer)***	***After last deposition of NiTi***
S32	10/2.5	-30	0	15	120	-	-	-	-	28	60

RESULTS AND DISCUSSION

Only results for the sample S23 are shown. Results for S32 are still being processed.

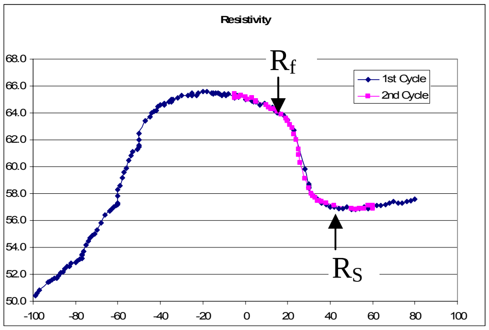

Fig. 1 – Electrical resistivity measurements during 2 consecutive cooling cycles showing the good reproducibility of the results (sample 23).

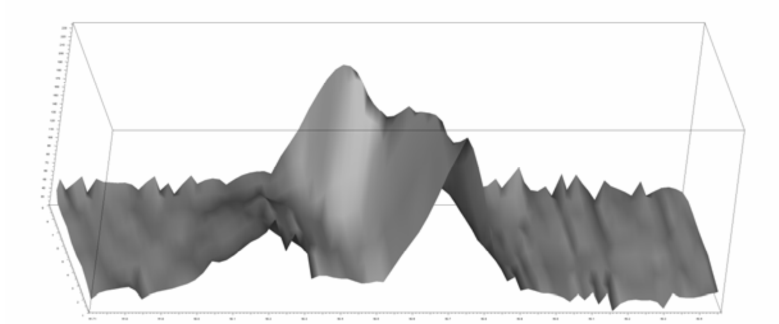

Fig. 2 – In situ XRD during cooling, showing the splitting of the B2 (110) peak, giving the (211) and (300) of the R-phase (back to forth in the 3-D plot) for the sample 23.

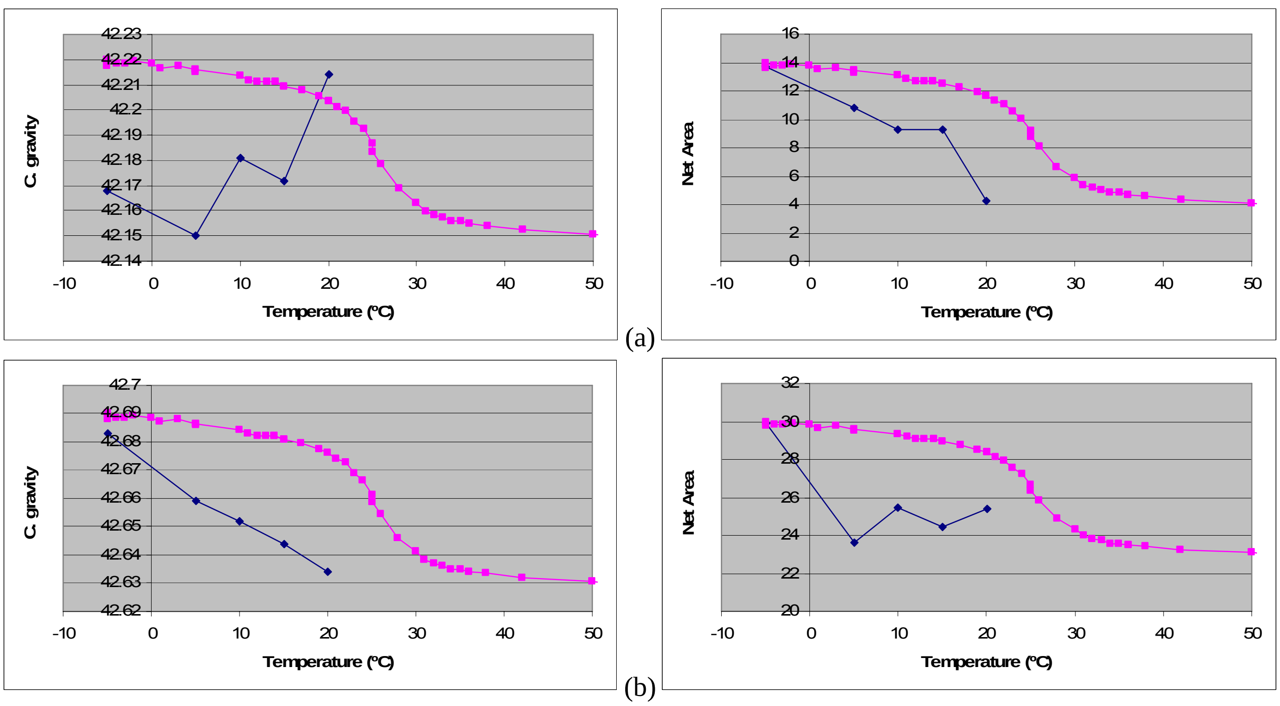

Fig. 3 – Variation of the peak position and net area for (a) (211) and (b) (300) of the R-phase represented in blue. In cyan it is represented the variation of the electrical resistivity (in an arbitrary scale) as a function of the temperature for the sample 23.

CONCLUSIONS

- The simultaneous measurement of the electrical resistivity and XRD during thermal cycles allows establishing a direct correlation between features of electrical resistivity variation and structural changes.

- It is usually assumed in the published literature [1] that, during cooling, the B2 to R-phase transformation shows a significant electrical resistivity increase associated to (i) formation of R-phase from R_s to R_f, followed by (ii) increasing rhombohedral distortion (with no further R-phase formation). Data presented in left-hand graphs of Fig. 3 (a) and (b) confirm that the rhombohedral distortion is notorious (variation of the peak position of (211) and (300) from R-phase) when cooling below the temperature usually identified as R_f. But data presented in right-hand graphs of Fig. 3 (a) and (b) show that the net areas of both R-phase peaks (211) and (300) are still increasing during the last step of the electrical resisitivity increase. These results suggest that, besides a significant rhombohedral distortion below R_f, there is still new R-phase formation.

Reference

[1] V. Novák, P. Šittner, G.N. Dayananda, F.M. Braz-Fernandes, K. K. Mahesh. *Materials Science and Engineering A* 481–482 (2008) 127–133.