ROBL-CRG	**Experiment title:** ***In-situ* XRD during thermal cycling of Ni-Ti Shape Memory Alloy**	**Experiment number**: **20_02_626**
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Shifts: 9	**Local contact(s)**: Dr. Norbert Schell	*Received at ESRF:*

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Report

Aim

The aim of the experiment was to analyse the structural evolution during *in-situ* annealing of Nickel-Titanium (Ni-Ti) SMA subjected to thermal/mechanical treatments.

Experimental Methodology

The material in study was Ti-rich (Ti 51 at%) NiTi SMA extracted from a 2 mm thick plate, in strain annealed conditions and supplied by Memory-Metalle GmbH, Germany. The samples were analyzed in the following conditions: (i) as-received (AR), (ii) heat treated at 500ºC (HT), (iii) heat treated at 500ºC followed by 10% thickness reduction by cold rolling (HT + CW10%) and (iv) heat treated at 500ºC followed by 40% thickness reduction by cold rolling (HT + CW40%). The heat treatment (HT) was performed by holding the specimen at 500ºC for 30 minutes and subsequently quenching in water at room temperature. The samples were subjected to chemical etching (10% vol HF + 45% vol HNO_3 + 45% vol H_2O) in order to remove the oxide layer as well as the layer deformed during the cutting operation.

XRD analysis was performed at ROBL/BM20 of ESRF for the *in-situ* high temperature $\theta/2\theta$ scans and texture analysis. *In-situ* XRD analysis during annealing has been carried out using x-rays of wavelength 1.54 Å and a vacuum furnace with a hemispherical Be-dome evacuated to a pressure less than $2x10^{-6}$ mbar. The furnace was installed on the ϕ circle (azimuthal orientation) of the six-circle goniometer. The pole figures have been determined for $-85º < \phi < +5º$ and $0º < \chi < +54º$. The rolling direction (RD) is aligned with $\phi = -55º$. The structural evolution during annealing up to 800ºC was observed by *in-situ* XRD.

Results

All the samples are in the martensitic state, at room temperature before *in-situ* high temperature analysis (scan 1 in Fig. 1a-d). The structural evolution while heating (Fig. 1 for the scans up to 400ºC, where the recrystallisation is completed, and Fig. 2 for the full range of temperatures) and cooling (Fig. 3) was followed by *in-situ* XRD. For the HT+CW10% and HT+CW40% samples, overlapping of the martensite peaks are observed. The XRD scans in $\theta/2\theta$ mode (Figs 1 and 2) show a clear variation in peaks corresponding to the structural evolution. In Figs 1c-d, for HT+CW10% and HT+CW40%, it is seen that the full transformation to austenite occurs only when the sample is heated above 100ºC. The recrystallisation temperature is close to 350ºC, which is in agreement with other results [1-4]. At higher temperatures (above 600ºC) a significant structural evolution takes place, illustrated by the increased austenitic peak intensity in both HT and HT+CW40% samples (Figs 2b and c), and the growth of Ti_2Ni precipitates. The structural evolution during cooling (Fig. 3) shows B2→B19' in the AR sample (after heating up to 800ºC) and B2→R→B19' in the

HT+CW10% sample (after heating up to 400ºC). These results are in agreement with previous results [3-6], where the R-Phase formation is gradually suppressed with increasing annealing temperatures, leading to one step transformation as it is detected by DSC analysis.

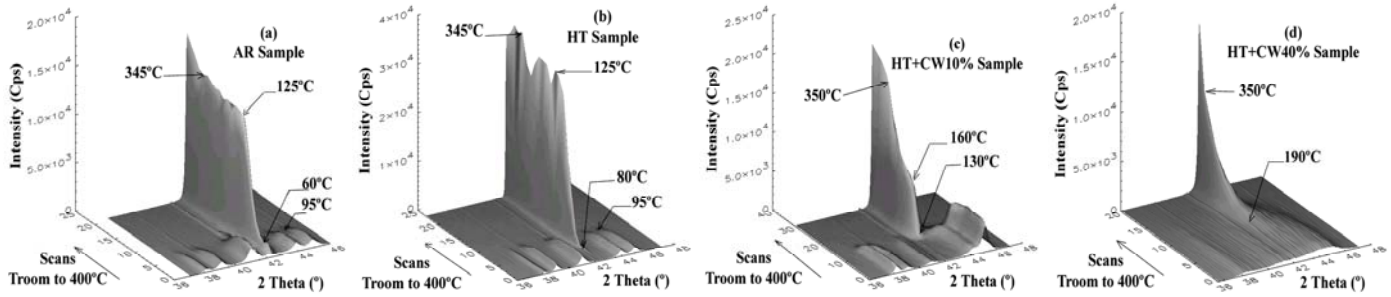

Fig. 1: *XRD spectra during the in-situ high temperature analysis for AR, HT, HT+CW10% and HT+CW40% samples while heating up to 400ºC.*

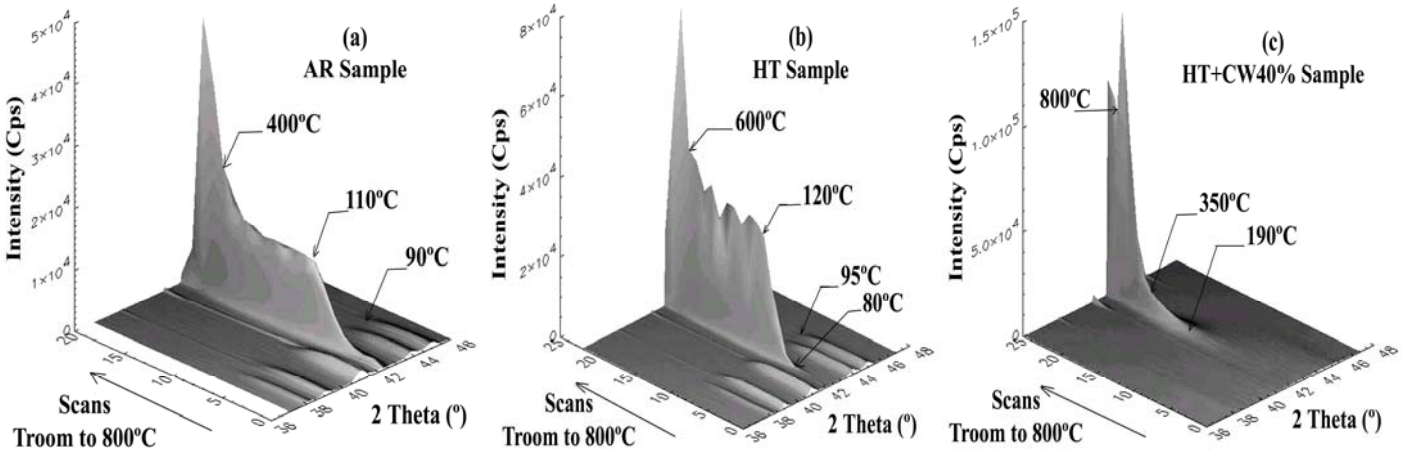

Fig. 2: *XRD spectra evolution during the in-situ high temperature analysis for AR, HT and HT+CW40% samples while heating up to 800ºC.*

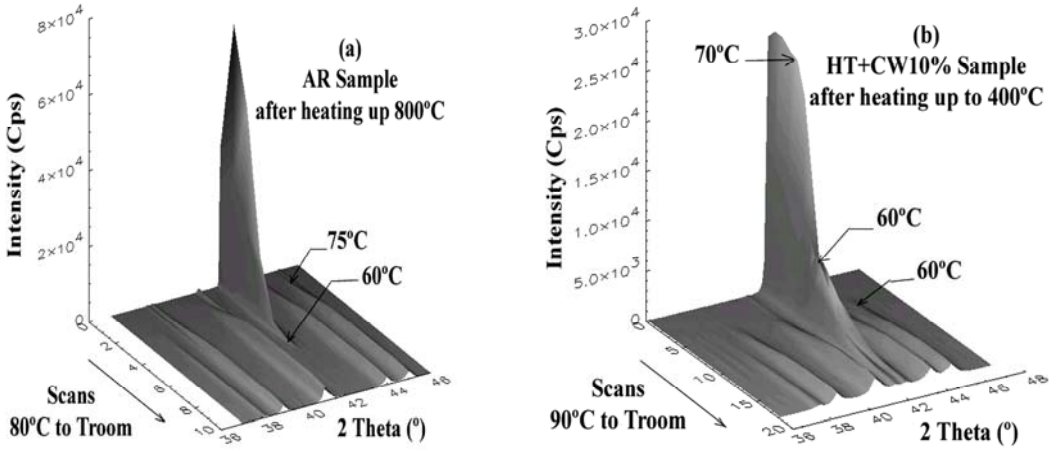

Fig. 3: *XRD spectra evolution during the in-situ high temperature analysis for AR and HT+CW10% samples after heating up to 800ºC and 400ºC, respectivily.*

The texture evolution during the *in-situ* high temperature XRD analysis of the HT and HT+CW40% samples is shown in Figs 4 and 5, respectively.

Annealing up to 350ºC (Figs 4a-c), gives no significant modifications in the {111}<110> austenite texture components of AR and HT samples; recrystallisation in HT+CW40% sample is completed at 350ºC (Fig. 1d) [2-4]. Between 400º and 500ºC (Figs 4d-f and 5a), there are texture evolutions in the direction of {110}<110> austenite texture components [2-4, 7-9]. Above 600ºC, anomalous grain growth of austenite is starting to occur.

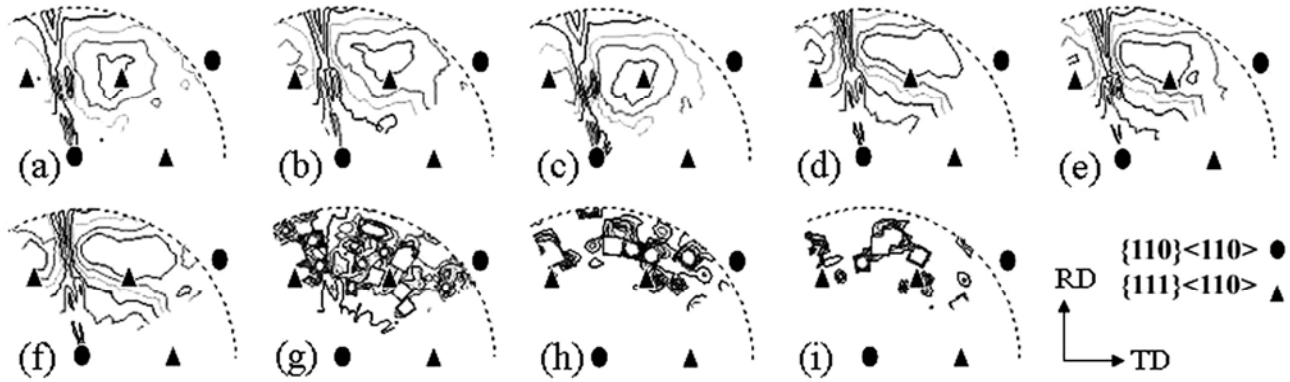

Fig. 4: *Austenite (110) Pole Figures – HT sample – (a) 250ºC, (b) 300ºC, (c) 350ºC, (d) 400ºC, (e) 450ºC, (f) 500ºC, (g) 600ºC, (h) 700ºC and (i) 800ºC during the in-situ high temperature XRD.*

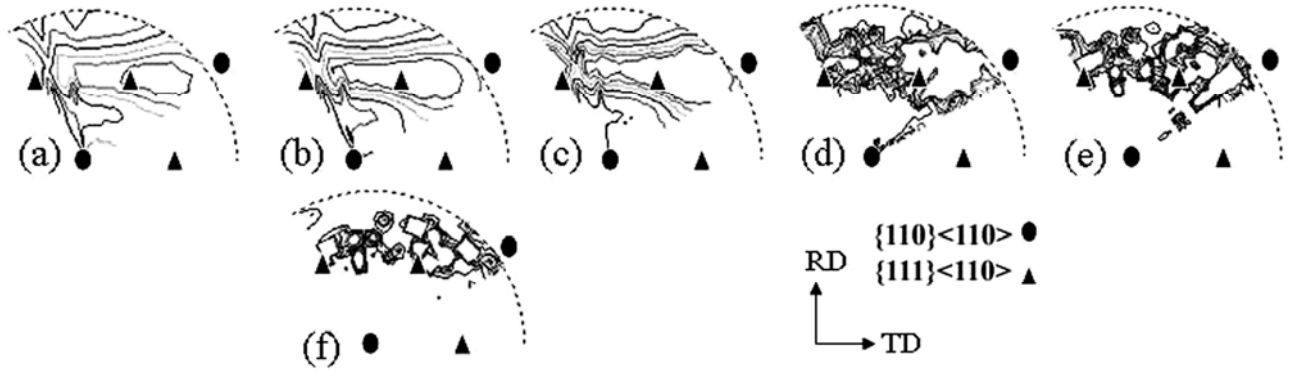

Fig. 5: *Austenite (110) Pole Figures – HT+CW40% sample – (a) 400ºC, (b) 450ºC, (c) 500ºC, (d) 600ºC, (e) 700ºC and (f) 800ºC during the in-situ high temperature XRD.*

Conclusions:

(1) The thermal / mechanical treatments significantly affect the structural evolution in the Ti-rich NiTi SMA.
(2) High annealing temperature develops {110}<110> austenite texture component in Ti-rich NiTi SMA.
(3) Above 500ºC, precipitation of Ti_2Ni takes place, and above 600ºC a tendency for anomalous grain growth appears.

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