ESRF	**Experiment title: Microstructures induced by martensitic transformations in Fe and Ti under extreme conditions**	**Experiment number**: HC-4360
Beamline: ID15B	**Date of experiment**: from: 08 June 2021 to: 12 June 2021	**Date of report**: 28/02/2022
Shifts: 12	**Local contact(s)**: Gaston Garbarino, Tomasz Poreba	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Agnès Dewaele*, CEA DAM Ile de France DPTA/SPMC Bruyères-le-Châtel FR - 91297 ARPAJON

Robin Freville*, CEA DAM Ile de France DPTA/SPMC Bruyères-le-Châtel FR - 91297 ARPAJON

Report:

-Objective & expected results-

We planned to characterize the microstructures induced by archetypical martensitic transformations under extremes conditions in Fe (α–γ–ε), Ti (α–ω) and Sn (β–γ), in samples which were initially single crystalline. This aims at an understanding of the mesoscale mechanisms of these transformations.

-Results and conclusions of the study-

Three diamond anvils cells (DAC), shortly described in **Table 1**, have been bought to ESRF. Starting sample were thin foils ($e = 12\ \mu m$) for Iron, heat treated to grow high quality single crystals which were characterized by MEB-EBSD prior to DAC loading, and powder grains with diameter varying from 4 to 8 µm for Titanium and Tin (they were found to be single crystals in a test experiment).

We used Neon as pressure transmitting medium and $SrB_4O_7:Sm^{2+}$ was placed in the experimental chamber as a pressure gauge [1].

Experiments were carried out at the ID15B beamline, with an X-ray beam focused to a 3x3 µm FWHM spot on the sample with KB mirrors, and cleaned with a pinhole. A vacuum resistive heater was provided by ESRF to perform the first run. Pressure was measured on-line using the luminescence of the gauge. XRD data were collected using a MAR555 detector with a sample to detector distance calibrated with a reference silicon sample; multi-exposures with $\pm 25°$ rotation of the DAC and 0.5° step were performed, so that we can perform single/multi-crystals analysis of XRD data. Results for the three runs are summarized below.

Run name	Diamond culet diameter (µm)	Sample	Pressure range (GPa)	Temperature (K)
FeFoil1	500	Fe in Ne	6->15	300->815
FeFoil2	400	Fe in Ne	6->17	Room T
SnTi	400	Sn {3} and Ti {3} in Ne	0->20	Room T

Table 1: Conditions of the 3 runs. Numbers between brackets indicate the number of samples in the DAC.

1. Run FeFoil1: Growth of large ε-Fe single crystals

In previous runs, we proved the possibility of synthesizing ε-Fe single crystals of good quality using α–>γ–>ε transitions instead of α–>ε transition [HC-2783,HC-2180,HC-3402]. One difficulty to use these single crystals for fine measurements (such as IXS) is their small size (<20 µm). We tried to increase it by multiple crossing of

the α–γ transition line, as this procedure is described in the literature. We performed two $\alpha - \gamma$ cycles and then increased the pressure in the stability domain of ε-Fe (see **Figure 1**). Unfortunately, this did not produce the large crystals we were expecting. The single crystal XRD data collected during this run will complete the database from runs HC-2783,HC-2180,HC-3402 to measure conditions, orientation relations and twinning deformation for α–γ and γ–ε transitions [2].

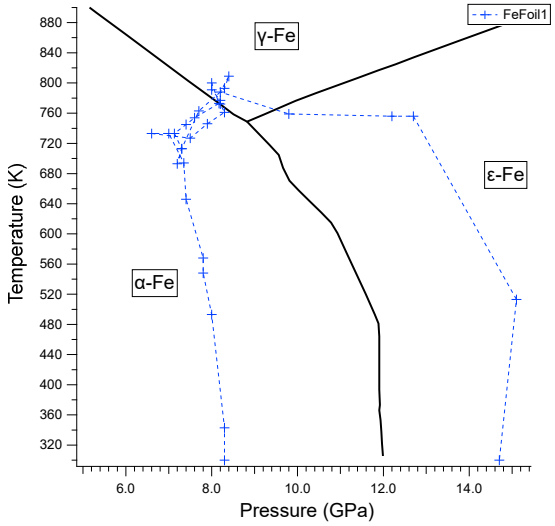

Figure 1: P-T path followed during run FeFoil1 (blue dashed lines), plotted in Fe phase diagram from [2].

2. *Run FeFoil2: deformation and twinning during the α–ε transition in Iron.*

A martensitic transformation produces large elastic stresses that is released with twinning and/or dislocation generation; the plasticity mechanism, which is favoured by the system, has a large impact on the microstructure formed by the transformation. In previous works, we have evidenced that dislocation generation is a major phenomenon in α-Fe<->ε-Fe transitions [3,4]. Recent MEB-EBSD *ex-situ* experiments performed in our laboratory suggest that twinning also occurs, mostly in ε-Fe but also in α-Fe. The aim of FeFoil2 run was to detect when twinning is occurring using *in-situ* XRD data. EBSD maps of the sample before and after α–>ε–>α cycle are presented in **Figure 2**.

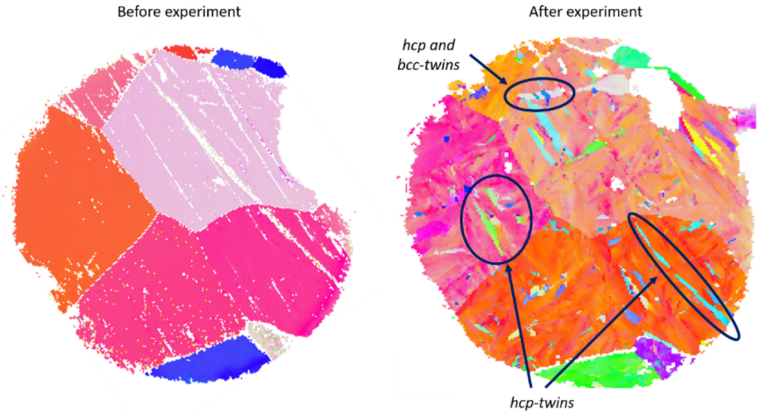

Figure 2: EBSD map of FeFoil2 sample (120 µm diameter) collected before and after $\alpha - \varepsilon - \alpha$ cycle. Overall, the orientation of single crystals is the same (the tone difference is due to a different color scale); color variation within a grain indicates high dislocation densities. Twins produced in hcp (ε) and bcc (α) phases are indicated.

XRD mapping of the sample (100 points) was performed at different pressure steps during direct/reverse transitions. Due to the small size of twin variant, we did not find yet its XRD signal; analysis is in progress.

3. *Run SnTi: transition mechanisms in Titanium and Tin*

In Titanium, α (hcp) to ω (hexagonal) phase transition induces an unusual grain enlargement, not understood yet [5]. The β-Sn to bct-Sn transition is reported under different conditions under static/dynamic compression/release [6], raising questions on its mechanism. As both transition occur in a similar and limited pressure range, we decided to study both metals in the same DAC, with 3 samples of each metal loaded in the pressure chamber.

One unexpected output of the experiment is the large effect of sample microstructure on the transition conditions. Titanium α →ω transition onset depends on the starting crystal quality: from 8 GPa for an undeformed crystal to 16 GPa for a deformed crystal (see **Figure 4**). For tin, similar observation with a direct transition between 11 GPa and 12 GPa depending on the crystallinity of the starting crystal. Then, transitions are sharp in pressure for each sample.

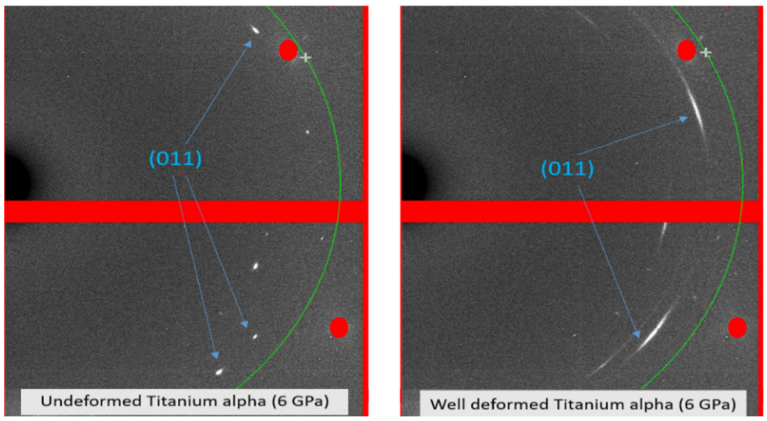

Figure 4: Image plate presenting two types of α-Ti samples at the beginning of the run.

Orientations relations between parent and child phases predicted from crystallography considerations could be observed for some crystals, but not all: Silcock [7] orientation relations for α–>ω Ti transition, and Katzke et al. [8] for β–γ Sn transition. Twinning occurred during these transformations. The single crystal analysis is still in progress. Our experience with Fe suggests that higher statistics is needed to have a better understanding of the transition mechanism; we thus need more data to corroborate these first results.

-Justification and comments about the use of beam time-

After alignment of the beamline and calibration by the local contact on the first day, the beam time was used to stabilize P-T conditions in the DAC and collect data for the three cells. The experiment went smoothly; we appreciated the very small spot size of the beamline and the fast and sensitive detector and the accurate sample holder motors.

Data analysis takes time because new methods/programs need to be established/written to treat the new h5 data format.

-References-

[1] F. Datchi, F. et al. Improved calibration of the $SrB_4O_7:Sm^{2+}$ optical pressure gauge: Advantages at very high pressures and high temperatures *J. Appl. Phys.*, 1997, *81*, 3333

[2] A. Dewaele et al., Iron under conditions close to the α–γ–ε triple point, Appl. Phys. Lett. 112, 201906, 2018

[3] A. Dewaele et al. Mechanism of the $\alpha - \varepsilon$ phase transformation in Iron. Phys. Rev. B 91 (2015)

[4] E. Boulard et al. Following the phase transitions of iron in 3D with X-ray tomography and diffraction under extreme conditions. Acta Mat., 2020, 192, pp. 30-39.

[5] D. Popov et al., Real time study of grain enlargement in Zr under room-T compression accros the α to ω phase transition, Sci. Rep. 9, 15712, 2019

[6] R. Briggs et al., Observation of the shock-induced β-sn to b.c.t-Sn transition using time-resolved X-ray diffraction, J. Synchrotron Rad. 26, 96, 2019

[7] J. M. Silcock, Acta Metall. 6, 481 (1958); sometimes attributed to A. Rabinkin, M. Talianker, and O. Botstein, Acta Metall. 29, 691 (1981).

[8] H. Katzke et al., Theory of the high-pressure structural phase transitions in Si, Ge, Sn, and Pb, Physical Review B 73, 134105, 2006