

CERIC EXPERIMENTAL REPORT

Proposal number: 20227134

Title: Martensitic and austenitic local structures in a bcc Ti-Zr-Hf-Co-Ni-Cu-Pd related high entropy shape-memory alloy

Proposer: Andrea FANTIN

Usages and assigned hours:

* LISA: LISA@ESRF (hours:144)

Achievements: ---

_____ do not change anything above this line

Objectives (adapted from proposal 20227134)

- In general, the idea is to clarify relationship between mechanical properties, specimen composition and structure at the atomic scale of a novel High Entropy Alloy family in the of *fcc*, *bcc* and *hcp* structures. The data collected so far on *fcc*-based high entropy alloys [1-5], on a tetragonal-based alloy [published recently in ref. 6] *hcp*-based alloy [ESRF proposal MA4814], and on a *bcc*-based alloy [CERIC proposal 20217113] will be complemented with the work outlined in this report. This broad comparison is still under development at the time of writing the report.
- A more specific purpose is to investigate at the local scale the phase transition between austenite (s.g. *Pm-3m*) and martensite (s.g. *P2₁/m*) structure observed in all alloys shown in Table 1 [7-9]. Local structures will be determined by EXAFS, with particular focus on local lattice distortions and short-range chemical ordering. This Ti-Ni based system is especially suited for an X-ray experiment as Ti, Co/Ni/Cu, Hf, Zr and Pd are well separated in the periodic table, allowing a good discrimination between most of the alloying elements. The bond distances between selected elements will be the first solid outcome of this work. This allows to discuss which element is the most active upon martensitic-austenitic phase transition, if any. The obtained bond lengths will be compared e.g. to those assuming tabulated metallic radii, and to the average distances obtained by X-ray diffraction [7]. The successful outcome of the project complemented by other undergoing analysis (XRD, Transmission Electron Microscopy, Pair Distribution Function and corresponding simulations, ref. 5) will represent one of the first systematic and quantitative approach to the structure-property relationships in HEAs, with the final technological goal of understanding alloy strengthening as a function of its components.

1) Report

Due to a problem to the heating device, it was not possible to collect measurements at high-temperature except at one edge and only on one specimen (Ti K-edge, at 500 K), out of which we report the results and comparisons in the following Figures. A proposal “continuation” will be submitted where only the high-temperature measurements will be requested in order to complete the dataset.

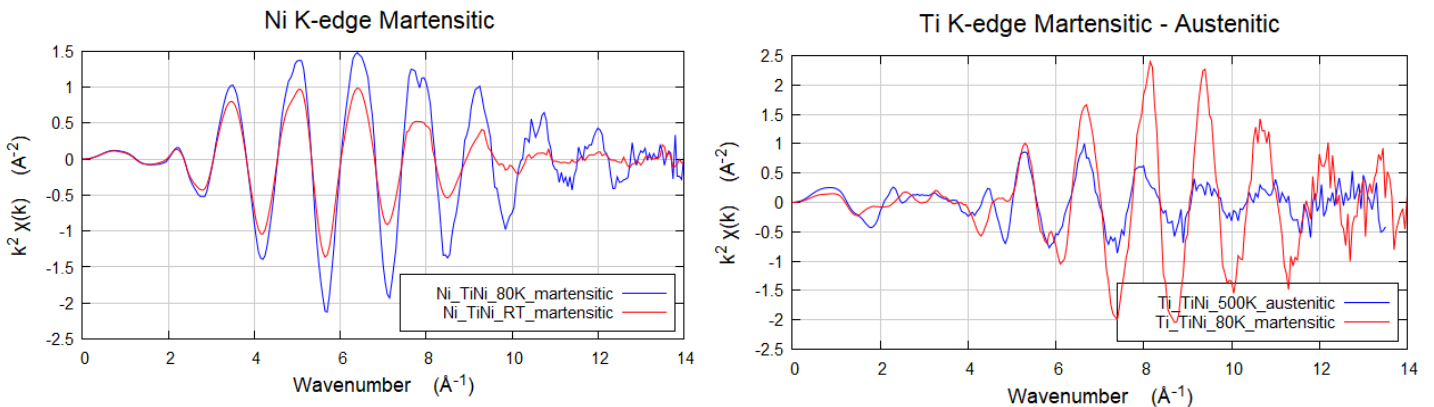


Figure 1. (left) Ni-K edge for the binary alloy TiNi measured at room temperature (initial test measurements) at 80K. (right) Ti-K edge measured at 80K and the only measurements taken at 500K.

In Figure 1 (left), the Ni K-edge is shown for the binary TiNi shape-memory alloy, measured at 80K and at RT. The structure at 80K is fully martensitic belonging to space group, *P2₁/m*. This follows the Martensitic phase finish temperature (M_f) reported to be $M_f = 339$ K for this alloy [7,8], below which only a martensitic phase appears. On the other hand, the austenitic phase finish temperature (A_f) is $A_f = 383.2$ K [7,8], above which a fully austenitic phase (*Pm-3m* space group) appears, crystallizing in a *bcc* structure with Ti and Ni on different sublattices. This is what can be seen at the Ti-K edge at 80K and at 500K in Figure 1 (right). Despite the much larger thermal disorder at 500K, especially in the low *k*-region, differences arise. A list of distances from CIF files at room temperature are reported in Table 1.

Table 1. Room temperature martensitic and austenitic bond length distances from CIF files, together with the number of neighbors which correspond to those distances.

	Martensitic (RT) <i>monoclinic</i>			Austenitic (RT) <i>bcc</i>		
Ti K-edge (from CIF)	Ni1	1x	2.5304(27)	Ti1	1x	2.6480(1)
	Ni1	1x	2.5305(27)	Ti1	3x	2.6481(1)
	Ni1	1x	2.5423(47)	Ti1	3x	2.6482(1)
	Ni1	1x	2.6015(42)	Ti1	1x	2.6483(1)
	Ni1	1x	2.6050(26)	Ni1	3x	3.0577(2)
	Ni1	1x	2.6051(26)	Ni1	3x	3.0579(2)
	Ni1	1x	2.6061(43)			
	Ti1	2x	2.8943(58)			
	Ti1	2x	2.9476(43)			
Ni K-edge (from CIF)	Ti1	1x	2.5305(27)	Ni1	1x	2.6480(1)
	Ti1	1x	2.5306(27)	Ni1	3x	2.6481(1)
	Ti1	1x	2.5423(47)	Ni1	3x	2.6482(1)
	Ti1	1x	2.6015(42)	Ni1	1x	2.6483(1)
	Ti1	1x	2.6050(26)	Ti1	3x	3.0577(2)
	Ti1	1x	2.6051(26)	Ti1	3x	3.0579(2)
	Ti1	1x	2.6061(43)			
	Ni1	1x	2.6339(14)			
	Ni1	1x	2.6340(14)			
	Ni1	2x	2.8943(25)			

In Figure 2 the XANES region is reported at the Ti and Cr-K edge (plotted as a function of $E-E_0$) where it is evident, as XANES is sensitive to local coordination, the change from monoclinic (red curve) to cubic (green curve) above the martensitic-austenitic transformation temperature. For comparison, the bcc Cr foil signal is superimposed, and it can be noticed how the Ti in TiNi at 500K resembles the Cr signal until around 25 eV above the edge, suggesting that indeed that the transformation into the austenitic phase happened as expected.

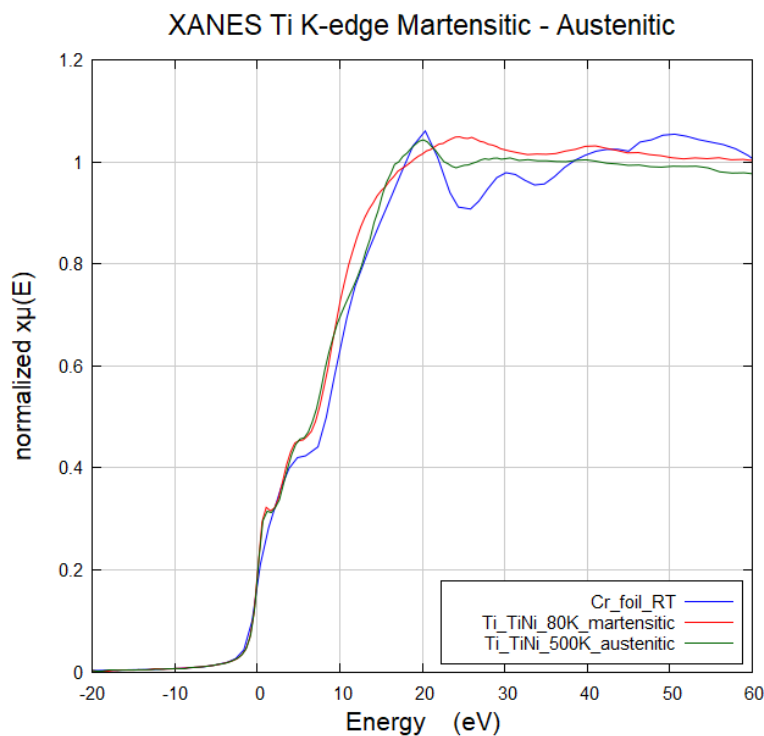


Figure 2. XANES comparison of Ti-K edge of both 80K and 500K measurements, in addition to a bcc Cr-foil measured at RT. Data is plotted as a function of $E-E_0$ (eV) in order to be able to compare the different edges.

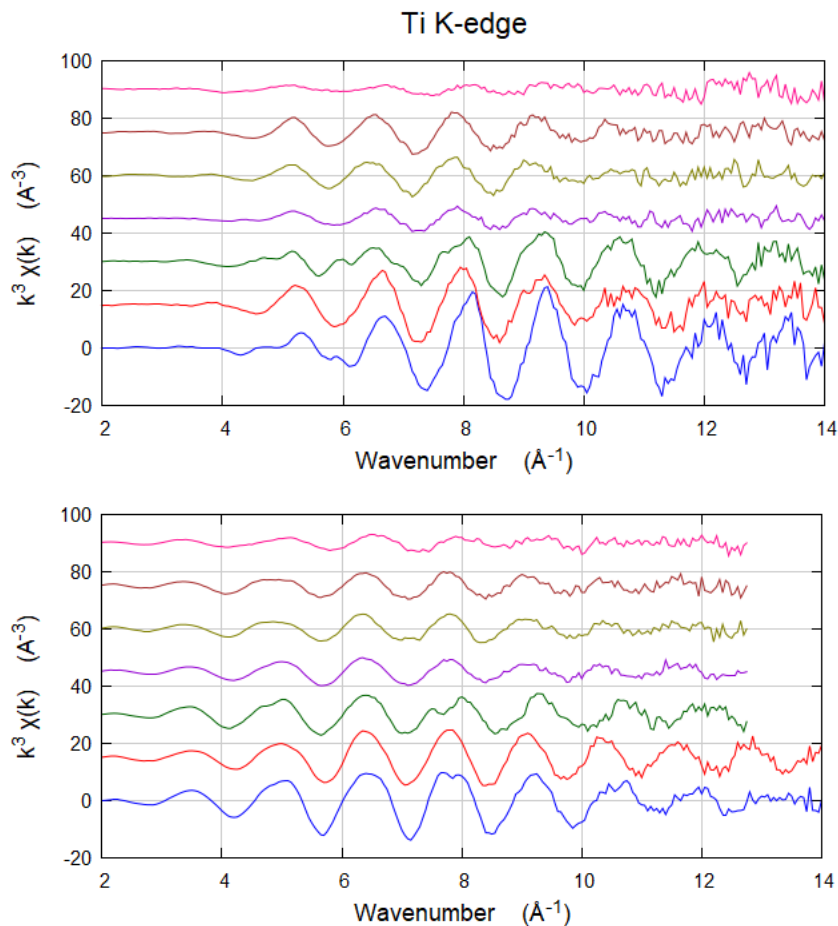
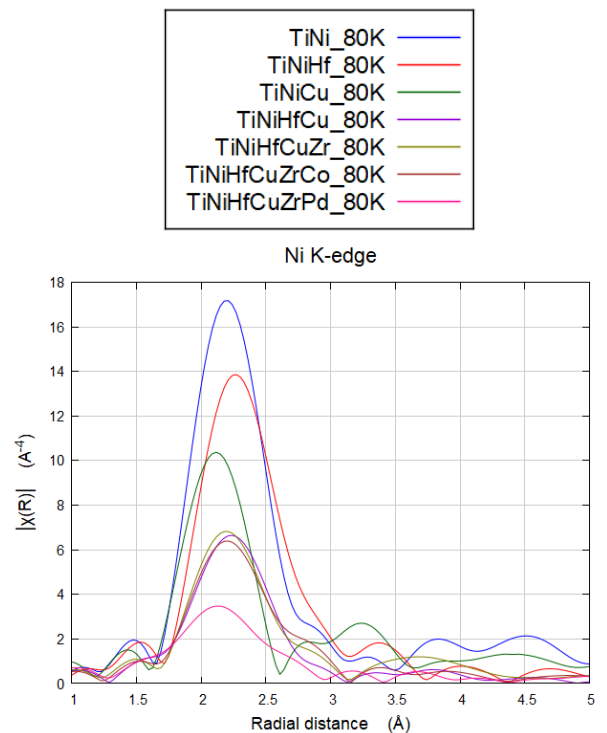


Figure 3. EXAFS k-space region of Ti-K edge and Ni-K edge measured at $T=80\text{K}$ for a series of binary to senary shape-memory high entropy alloys. Some spectra are cut (below) because of the presence of Cu-K edge at a wavenumber of ca. $k=12.6 \text{ \AA}^{-1}$. On the right the Fourier Transform in R-space of Ni-K edges is presented.



In Figure 3 the EXAFS k-space region is shown for low temperature acquisitions of all specimens (binary to senary) at Ti and Ni-K edges. It is obvious that increasing the number of elements generates more (local) distortions into the structure, in turn reducing the EXAFS oscillation amplitudes. This effect depends both to the number and type of elements. Notice how adding Hf to the binary TiNi has less effect into the 1st shell amplitude compared to Cu addition to TiNi. No difference is observed between the quaternary TiNiHfCu the quinary TiNiHfCuZr and the senary TiNiHfCuZrCo, which is probably due to the similarity, in terms of metallic radius and/or scattering power, between the added elements and the existing ones in the alloy (e.g. Zr with Hf, or Co with Ni and Cu). On the other hand, when a different element like Pd (late 3d metals Ni, Co, Cu and refractory metals Ti, Zr, Hf) is added into the alloy, even further increase of static disorder is observed. This is probably because Pd behaves differently or has different properties than the other alloying elements. To cite one, Pd has a tabulated radius of 1.37 Å, which is exactly in between the smaller 3d late metals (1.24-1.28 Å), and the larger refractory metals (1.47-1.60 Å). This specific behavior of Pd should be further investigated with accurate EXAFS refinements.

2) References

IMPORTANT: include the references to your work performed at CERIC-ERIC or CERIC's Partner Facilities if relevant for this proposal

- [1] Fantin et al. Acta Materialia 193, 329-337 (2020)
- [2] Kasatnikov S., Fantin et al., J. All. Comp. 857, 157597 (2021).
- [3] Fantin et al. Mat. Chem. and Phys. 276, 125432 (2022)
- [4] Andreoli A.F., Fantin et al., Acta Materialia, Under review (2023)
- [5] Fantin et al., Small Science (2023), accepted
- [6] Joubert, J-M., Kalchev Y., Fantin et al., Acta Materialia 259, 119277 (2023)
- [7] C. Hinte et al., Shap. Mem. Superelasticity, 2020, 6, 181-190
- [8] Piorunek et al., Intermetallics Volume 122, July 2020, 106792
- [9] Sitnikov et al., Adv. Mat. Tech., 2017, 4, 15-21;