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High-Temperature functional behavior of Single Crystal Ni_{51.2}Ti_{23.4}Hf_{25.4} Shape Memory Alloy

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Abstract

In this work the functional behavior of the new Ni_{51.2}Ti_{23.4}Hf_{25.4} high temperature shape memory alloy is investigated along three crystal orientations in compression and compared with the polycrystal behavior. Transformation temperatures were measured following specific aging treatments with the aim to optimize the shape memory and pseudoelastic behaviors. Two aging treatments were then selected in order to **maximize/fulfill** the **optimum** pseudoelastic behavior (500°C/4h), and the **maximum** transformation temperatures (550°C/10h), without compromising the alloy functionality. High temperature **X**-ray diffraction was utilized to determine the crystal orientations in the austenite phase for the single crystal specimens, **and the texture for the polycrystal specimen**. The martensite structure was found to be the B19 orthorhombic, in contrast with monoclinic structure for lower Hf contents. Digital image correlation was successively **implemented** **used** during isobaric strain-temperature experiments on the single crystal and polycrystal specimens. Large strain heterogeneities were found for the single crystals which pair with **X-ray** diffraction data that show un-transformed austenite below the martensite finish temperature. This reveals the heterogeneity of the austenite-to-martensite transformation for the present NiTiHf alloy which explains the divergence between the theoretical and experimental transformations **s** strains. In addition, using digital image correlation it is possible to capture the local strain fields associated with fully transformed specimen regions. The transformation strains calculated locally are in close agreement with the theoretical transformation strains calculated

1 with lattice deformation theory for the cubic austenite to the orthorhombic martensite phase
2 transformation.

3 **Keywords**

4 Shape memory alloy; Single crystals; Transformation strain; Digital image correlation; X-ray
5 diffraction.

1

2 Introduction

3 NiTi-based shape memory alloys have become one of the most promising multi-functional
 4 materials since the addition of a ternary element enables to increase the transformation
 5 temperatures (TTs) above 100°C, the strength and the stability of the binary NiTi alloy. Among
 6 several potential ternary elements (Hf, Zr, Pd, Pt and Au), the addition of Hf guarantees high TTs
 7 (>200°C) with lower prices compared to the other alloying elements [1, 2]. In the last years, a
 8 growing number of works have been published on NiTiHf alloys mainly focused on the effect of
 9 the composition, precipitation strengthening, mechanical and functional characterization of the
 10 polycrystal and texturized materials [3-5]. A comprehensive knowledge of the basic mechanical
 11 behavior has been achieved for Hf additions up to 20 at. %, while less interest has been devoted
 12 to higher Hf compositions (>25 at. %). Few works have been published on Hf alloying >25 at. %
 13 (herein called Hf-rich NiTiHf alloys) on physical metallurgy [2, 6-8]. In particular, no works have
 14 been published on the single crystal behavior. Since the potential high temperature applications
 15 of Hf-rich NiTiHf alloys, we investigate the mechanical and functional behaviors of the new
 16 $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ composition along three different crystallographic orientations: [0 1 1], [1 1 1] and
 17 [3 4 14] with the aim to provide deeper insight into the mechanical behavior of Hf-rich NiTiHf
 18 alloys.

19 NiTiHf alloys are nowadays one of the most studied shape memory alloys (SMAs). since
 20 the possibility to shifting of the transformations temperatures to >200°C allows extending the
 21 usage of SMAs for many industrial applications (actuation, vibration damping, etc.). The
 22 possibility to use NiTiHf alloys as shape memory and pseudoelastic materials is accomplished by
 23 a proper selection of the composition and the successive heat treatments or, alternatively,
 24 specific processes. The selection of the composition is the major concern and there is still the
 25 need to investigate the optimum balance between the Ni and Hf contents depending on the
 26 specific requirements. Several works show that the martensite peak temperature (M_{PT}) remains
 27 constant for Ni-lean (<50 at. %) $\text{Ni}_x\text{Ti}_{90-x}\text{Hf}_{10}$ alloys at around 100°C [1], while Hf additions lower

1 than 10 at. % do not lead to important changes in TTs [1, 2, 9]. The disadvantages of Ni-lean
 2 NiTiHf alloys are the poor mechanical properties in terms of ductility, cyclic stability and
 3 pseudoelasticity [5]. In order to overcome these drawbacks, the material community focused the
 4 attention to Ni-rich (>50 at. %) NiTiHf alloys. Nevertheless the TTs display an abrupt decrease
 5 with Ni content between (50 - 51) at. %, the addition of the ternary element (Hf), followed by a
 6 proper aging treatment or process, provides benefits to the TTs and the mechanical properties.
 7 Depending on the desired material performances, Ni content can be increased up to 51 at. % in
 8 order to optimize the shape memory and pseudoelastic behaviors, while. Besides, Hf content can
 9 be varied from between (10% to - 30) at. % based on the desired operational temperatures. One
 10 of the most successful studied NiTiHf compositions are the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ [10-16] and the
 11 $\text{Ni}_{50.6}\text{Ti}_{29.4}\text{Hf}_{20}$ [17-20] which show perfect pseudoelasticity at temperatures near 250°C. In the
 12 present work the new $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ composition was selected in order to have good shape
 13 memory and pseudoelastic properties given by the high Ni content (Ni=51.2 at. %), along with
 14 high operational temperatures near 300°C given by the high hafnium content (Hf=25.4 at. %).

15 Since NiTiHf alloys are still on relatively early stages of development, most of the research
 16 has been focused on the polycrystalline form of the material. Previous experimental and
 17 theoretical studies on NiTi single crystals [21-23], and more recent works on NiTiHfPd [24-26] and
 18 NiTiHf [15, 27, 28] single crystals have shown that the orientation strongly influences the
 19 maximum transformation strains of NiTi-based alloys. This derives from the selective activation of
 20 martensite variants upon loading along a specific transformation shear direction and habit plane.
 21 The transformation strain is also influenced by the crystal structures of the transforming phases.
 22 For NiTiHf alloys with Hf<20 at. % the phase transformation is accomplished by the
 23 transformation from the cubic B2 lattice to the monoclinic B19' martensite phase. For this phase
 24 transformation different works have been published in the last decade covering both the
 25 experimental characterization and the theoretical calculations [11, 13, 28-37]. For the
 26 $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ alloy, Stebner and co. calculated the transformation strains in compression to be
 27 approx. 8.5% for $[011]_{\text{B2}}$ and 6% for the $[111]_{\text{B2}}$ crystal orientations [27]. Less clear is the large
 28 difference between the measured strains (<3%) and the theoretical values. Another observation is

1 **that** the phase transformation for Hf-rich NiTiHf alloys **that** is considered to occur from the cubic
 2 B2 lattice to the orthorhombic B19 lattice [4]. In this work, evidence of the orthorhombic lattice for
 3 the martensite phase is provided using X-ray diffraction. This result enables to provide the correct
 4 basis for the theoretical calculations of the transformations strains. Understanding the austenite
 5 B2 to martensite B19 phase transformations is of fundamental importance in order to optimize the
 6 Hf-rich NiTiHf alloys for future high temperature applications.

7 Based on the choice of the NiTiHf composition, a proper aging treatment (temperature and
 8 time) fulfills its shape memory and pseudoelastic behaviors [3-5, 9-12, 16, 18-20, 27, 33, 38-40].
 9 Aging affects the mechanical and functional behavior as the martensite morphology is strongly
 10 affected by the precipitate geometry (size and inter-particle distance), and by the precipitate
 11 coherency with the matrix [41, 42]. Adopting the proper aging treatment, the precipitates formed
 12 during aging strengthen the matrix and **also** provide thermal stability. Moreover, precipitation
 13 changes the basic chemical composition of the matrix. Yang and co. [43] provided the structural
 14 characterization of the H-phase formed in Ni-high NiTiHf alloys with Hf content ranging between
 15 (15 – 20) **at.** % following precipitation hardening. Successively, it was experimentally shown that
 16 this H-phase is slightly richer in Ni compared to the matrix with the consequence that the TTs are
 17 increased due to the depletion of Ni from the matrix [20, 39]. Considering the importance of
 18 precipitation, we also provide a comprehensive study of the effects of the aging treatments on the
 19 TTs.

20 Isobaric and isothermal experiments were conducted using strain measurements obtained
 21 via Digital Image Correlation (DIC) technique [44]. DIC strain measurements enable to capture
 22 the local **martensitic** transformation region in both shape memory and pseudoelastic experiments,
 23 providing a straightforward measurement of the transformation strains [45-47]. Both the
 24 isothermal and isobaric experiments were conducted measuring the real time local strain fields on
 25 small surface areas of the specimens (typically 4mm x 3mm with a resolution of 2 μ m/px). The
 26 main advantage of this technique is that the strain data are not averaged over a large specimen
 27 length as, for example, with an extensometer. DIC strain measurements enable to capture the
 28 regions where the heterogeneous nucleation and growth of the martensite develops, neglecting

the regions of the specimen where the transformation is not active. Such strain measurements are thus fundamental in providing a straightforward comparison with the theoretical calculations which assume the ideal transformation of the entire crystal from austenite to martensite (LTD).

In summary, in this work we present the mechanical and functional characterization of the new $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy focusing on three crystal orientations: [0 1 1], [1 1 1] and [3 4 14]. Differential scanning calorimetry (DSC) was used to characterize the change of TTs with aging time and temperature. After proper selection of the heat treatments, isobaric and isothermal experiments were conducted using in-situ and ex-situ high-resolution DIC strain fields. Based on the local strain measurements and the X-ray diffraction data we discuss the well-known discrepancy between theoretical transformation strains with experimentally observed ones for NiTiHf alloys. A comparison of the single crystal behavior is also made with polycrystal behavior. The work points to gain further insight into the new $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy promoting further research efforts for making Hf-rich NiTiHf alloys suitable for industrial applications.

1 Experimental Techniques

2 Polycrystal specimens with a composition of $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ at. % were manufactured using
 3 plasma arc melting. Successively, single crystals were grown using the Bridgman technique in a
 4 He atmosphere from the same polycrystal ingots. Compression specimens were sectioned into
 5 3.8 mm x 3.8 mm x 8 mm using electro-discharged machining with the loading axis along the [0 1
 6 1]_{B2}, [3 4 14]_{B2}, and [1 1 1]_{B2} crystallographic directions. The specimens were successively
 7 homogenized at a temperature of 1050°C for 20h under vacuum and successively slowly cooled
 8 inside the furnace to room temperature. The specimens were then solution-treated at 900°C for
 9 1h in air followed by water quench. The chemical composition was checked by means of an ICP-
 10 MS PerkinElmer on two solution-treated polycrystal specimens to be Ni=51.35%, Ti=23.65% and
 11 Hf=25.01%, and on two single crystal samples to be Ni=51.25%, Ti=23.35% and Hf=25.4% by
 12 means of an ICP-MS PerkinElmer instrument providing both close measurements to the average
 13 atomistic percentages Ni=51.25%, Ti=23.35% and Hf=25.4%. One of the single crystal
 14 compression specimens was successively sectioned into small samples with average weight of
 15 60mg suited for differential scanning calorimetry (DSC) technique. The samples were aged at
 16 temperatures ranging from 500°C to 650°C, and aging times between 2h and 10h. The samples
 17 were then polished using SiC paper in order to remove the thin oxide layer following solution-
 18 treatment and aging. DSC was implemented by means of a Perkin Elmer Pyris 1 differential
 19 scanning calorimeter with a heating/cooling rate of 60°C/min. The heat flow data were recorded
 20 from room temperature to 450°C. The heat flow data were used to determine the TTs variations
 21 following the specific heat treatments. More specifically, in the following we indicate the TTs using
 22 the Austenite peak temperature (A_{PT}) and the Martensite peak temperature (M_{PT}) obtained from
 23 the DSC curves.

24 Phase analysis and crystal orientation were determined by a Philips Xpert 2 X-ray
 25 diffractometer using a Philips Xpert 2 equipped with high temperature set-up. The One 7mm x
 26 22mm x 1.5mm polycrystal $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ specimen was sectioned into 7mm x 22mm x 1.5mm by
 27 means of using electro-discharged machining. The specimen was homogenized (1050°C/20h in
 28 vacuum) and solution-treated (900°C/1h followed by water quench). The crystal structure in

1 austenite phase was determined at room temperature. Following the 600°C/4h aging the same
 2 specimen was analyzed at room temperature for martensite structure characterization. The
 3 crystallographic orientations for the single crystal specimens were ~~instead~~ determined in austenite
 4 phase by means of X-ray diffraction conducted at 300°C.

5 Isobaric and isothermal experiments were conducted using a MTS servo hydraulic load
 6 frame. Cooling of the compression grips was achieved with a customized copper coil surrounding
 7 the grips ~~and isolated with a polymer~~. Liquid nitrogen was used as the coolant in order to
 8 increment the cooling rate below 60°C. A Lepel induction generator and a customized induction
 9 coil were used to heat the compression grips. The induction coil was properly designed in order to
 10 allow the temperature measurements using a Micro-epsilon infrared temperature sensor with a
 11 laser pointing the center of ~~one vertical side of~~ the compression specimens. The images suited for
 12 DIC strain measurements were captured on the opposite specimen surface by means of a IMI
 13 model IMB-202 FT CCD camera (1600 x 1200 pixels) with a Navitar optical lens. All the sides of
 14 the compression specimens were initially polished with SiC paper (P400) in order to remove any
 15 residual surface modification following EDM cutting and any residual oxides derived by the heat
 16 treatments. The specimen surface for DIC strain measurements was further polished with SiC
 17 paper up to P1500. ~~while the~~ The specimen surface selected for temperature measurements was
 18 ~~painted covered~~ with black paint. The speckle pattern for DIC strain measurements was
 19 ~~deposited obtained~~ using black paint and an Iwata Micron B airbrush. Real time (*in-situ*) strain
 20 measurements were then obtained for a specimen region of approx. 3 mm x 4 mm with a
 21 resolution of 2.5µm/px. For both isobaric and isothermal experiments the specimens were initially
 22 heated up to 350°C for 20 min in the fully austenitic region in order to stabilize the DIC speckle
 23 pattern at high temperatures. Once the speckle stabilization was reached, one image on the
 24 undeformed specimen (reference image) was captured. For isobaric experiments the reference
 25 image was captured at the maximum temperature and at zero load. The second (deformed)
 26 image was captured after applying the ~~constant isobaric~~ load at the same initial maximum
 27 temperature. Successive deformed images were captured every 5°C from 350°C to room
 28 temperature at constant load. For isothermal experiments the reference image was captured at

1 zero load on the undeformed specimen. The images of the deformed specimens were captured
2 every 2 seconds during isothermal loading and unloading.

1

2 Results

3 Transformation temperatures

4 The main DSC curves obtained after the main heat treatments adopted in this work on the
 5 $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ single crystal are reported in Figure 1a. Following homogenization at 1050°C for
 6 20h the slow cooling into the furnace produces the largest TTs measured for the present
 7 $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy, $M_{PT}=224^\circ\text{C}$ and $A_{PT}=285^\circ\text{C}$. Solution-treatment at 900°C for 1h shifts back
 8 the $A_{PT}=104^\circ\text{C}$; while the martensite peak for the solution-treated case was not detected. As
 9 shown in our previous publication [47], and in other works for similar NiTiHf compositions [13, 16],
 10 aging temperatures below 500°C are not investigated since the TTs decrease of TTs after
 11 formation of ultra-fine precipitates rich of Hf. Several aging treatments (Figure 1b) have shown to
 12 move the TTs in between the solution-treated and homogenized treatment TTs. Sixteen
 13 combinations of aging time and temperatures are reported in Figure 1b. As a general guideline,
 14 increasing the aging temperature (from 500°C to 650°C) and the aging time (from 2h to 10h),
 15 leads to higher TTs. Further increments of the aging temperature (up to 700°C) results in the
 16 saturation of the maximum TTs, eventually in the decrease of the TTs for aging temperatures
 17 >700°C being close to the solution-treatment temperature.

18 For the functional behavior of the SMAs is also relevant to analyze the A_{PT} - M_{PT} peak-to-
 19 peak distance depending on the aging treatment. since the minimum A_{PT} - M_{PT} is expected to
 20 optimize the functional behavior of shape memory alloys [48]. Figure 1b shows that longer aging
 21 times slowly increase the A_{PT} - M_{PT} (approx. from 60°C to 67°C), and higher aging temperatures
 22 also increase the A_{PT} - M_{PT} , in particular for small aging times (at 4h approx. from 55°C to 72°C).
 23 From all the aging treatments analyzed with DSC, we selected the most promising ones (see
 24 Figure 1a): the 500°C/4h which minimizes the A_{PT} - $M_{PT}=55^\circ\text{C}$, the 550°C/10h aging was also
 25 selected in order to investigate leads to shape memory and pseudoelasticity at higher
 26 temperatures. Higher aging temperatures (600°C and 650°C) has have not been considered
 27 since the detrimental effects on the pseudoelastic and shape memory behaviors generated by of

the precipitates ~~formed generated with these~~ at these temperatures aging treatments. Figure 1a shows that adopting 500°C/4h and 550°C/10h aging treatments, we mainly covered the potential TTs ranging from the solution-treated case to the homogenized. Moreover, we also study ~~analyzing also~~ the effect of the aging time (4h versus 10h), other than the aging temperature (500°C versus 600550°C). For the 500°C/4h we measured the austenite start temperature as $A_S=109^\circ\text{C}$, the austenite finish temperature as $A_F=225^\circ\text{C}$, the martensite start temperature as $M_S=161^\circ\text{C}$, and the martensite finish temperature as $M_F=39^\circ\text{C}$. For the 550°C/10h we measured $A_S=159^\circ\text{C}$, $A_F=289^\circ\text{C}$, $M_S=221^\circ\text{C}$ and $M_F=86^\circ\text{C}$.

Material characterization

The X-ray diffraction pattern for the polycrystalline $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy is shown in Figure 2. For the solution-treated condition (black line), the alloy is in fully B2 austenite state at room temperature. Peaks from B2 phase clearly appear following diffraction reflections from $(001)_{B2}$, $(011)_{B2}$, $(002)_{B2}$, and $(012)_{B2}$ planes. Following 600°C/4h aging, two B2 peaks disappear, respectively the ones from $(011)_{B2}$ and $(012)_{B2}$ planes, while two new peaks appear which correspond to the diffraction reflections from the $(002)_{B19}$, and $(012)_{B19}$ planes of the orthorhombic B19 martensite phase. The peaks corresponding to the diffraction reflections of the B2 austenite from the $(001)_{B2}$ and $(002)_{B2}$ planes are still evident in the aged specimen even if the intensity of these two peaks is much lower than in the solution-treated case. This indicates that the austenite to martensite transformation is not fully completed. In Figure 2 are also reported the atomistic structures utilized for indexing the diffraction patterns. The characteristics of the martensitic orthorhombic unit cell were obtained from [49], $a=3.02\text{\AA}$, $b=4.20\text{\AA}$ and $c= a=4.69\text{\AA}$. The structure of the austenite is the $L2_1$ composed by eight B2 unit cells with the experimentally calculated lattice constant $a_0(B2)=3.083\text{\AA}$ at RT.

Isobaric behavior

The summary of the isobaric experiments conducted on the three crystal orientations ~~are is~~ reported ~~in the temperature-strain curves~~ in Figure 3. Strains were calculated using DIC technique, and a schematic of the strain measurements is reported in the top of Figure 3. The strains reported ~~in all the strain fields~~ refer to the axial strain component in the direction of the

load. In the strain-temperature and stress-strain curves the black lines always refer to the axial strains averaged over the entire DIC region which is approximately 3.6mm x 2.7mm (bulk strain). The blue lines refer to the localized strains which are averaged over a smaller region (approximately 1mm x 0.5mm) where the largest localized strains develop (local strain). The images for correlation were captured every 5°C, and the transformation strains were calculated as follows (schematic in the top of Figure 3). Two lines were obtained with a linear regression using the points in the fully austenite and fully martensite regions, so respectively at temperatures $>A_F$ and $<M_F$. A third line was obtained using the data in the region of transformation, so approximately in between A_S and A_F . The intersection between the two lines and the third one gives ~~two points that in the strain axis the distance represents~~ the transformation strains. The procedure was adopted for both the ~~averaged strains over the DIC region, and for the localized~~ bulk and local strains. The transformation strains were calculated for the strain-temperature curves that show saturation of the transformation strains. For example, for the [1 1 1] orientation, the transformation strain calculated for the curve at -800MPa and -1100MPa were the same as all the possible martensite variants were already activated at -800MPa. Further loading at -1100MPa ~~provides some leads to~~ irrecoverable strains which ~~can be are~~ detrimental for the correct measurement of the transformation strains. This is particularly noticeable for the [0 1 1] orientation comparing the strain-temperature curves for the -800MPa and -1100MPa stresses. The largest transformation strains were measured for the [0 1 1] orientated single crystal as ~~averaged bulk strain~~, and ~~locally local strain~~. Lower transformation strains were measured for the other two crystal orientations: for the [1 1 1] orientation and , for the [3 4 14] orientation and . In Figure 3 is also reported the isobaric behavior of the polycrystal specimen. In this case the transformation strain for the bulk material is relatively low, , while locally the transformation strains were measured to be .

Nevertheless the single crystal form of the specimen, non-homogeneous deformations are observed on the DIC strain fields which indicate the heterogeneity of the austenite-to-martensite phase transformation. Figure 4a shows the DIC strain fields measured for the [0 1 1] orientation for the isobaric experiment conducted at a constant stress of -800MPa. In the stereographic

triangle reported in the top-left of Figure 4a we show the inverse pole figure obtained by means of X-ray diffraction at 300°C. The inverse pole figure describes the distribution of the crystal orientations in the load direction of the specimen. Along the strain-temperature data we reported the most interesting strain fields measured using DIC. The inset marked 1 shows the strain field after isothermal loading at 280°C from 0MPa to -800MPa. The average compressive axial strain is 0.8%, and no strain localizations are observed indicating that at 280°C the yield stress is higher than 800MPa. During cooling (from strain field 1 to strain field 6), at the temperature of 210°C, the local strains (blue curve) diverge from the averaged strains (black curve) indicating the initial initiation of local phase transformation. From strain field 2 (210°C) to strain field 6 (50°C), the phase transformation develops mainly in the central part of the DIC area. The local region showing the largest strain localization was used to calculate the local strain-temperature curve. From strain field 6 to strain field 11, (280°C after unloading) no residual strains remain on the DIC region indicating the complete reversible austenite-martensite phase transformation. The same experimental procedure was adopted for the polycrystal specimen loaded at a constant compressive stress of -1100MPa (Figure 4b). The comparison between the [011] crystal with the polycrystal was reported at different stress levels since we aim to compare the local strain fields at the stress level showing the maximum transformation strains, avoiding the occurrence of high irreversibility. According to the pole figure reported in the top-left of Figure 4b, the polycrystal specimen shows an almost random orientation distribution of the grains along the load direction of the specimen, with a small preference for the [011], [001] and [111] orientations. Three temperature-strain curves were reported for the case of the polycrystal specimen.

The localized strain-temperature curve marked with blue color refers to the region marked in the inset 6 (local ϵ_1). This region for of the polycrystal indicates that the average local strains refer to a group of approximately 4 grains (the average grain size is approximately 200 μ m). As the polycrystal shows a preference for one of the three [001], [011], and [111] grain orientations, this group of grains reasonably has possesses a local preferential [011] texture evidenced by as the large strain localization. As also indicated in Figure 3, the transformation strain displayed by this region is 2.80%, which is lower than the maximum (local) measured for the [011] single

crystal (4.04%), but higher than the bulk transformation strain of the [011] crystal (2.41%). This is an important observation as suggests that with the adopted DIC image resolution we cannot capture the strain heterogeneity at the sub-grain level for the polycrystal specimen. This suggests that the local transformation strains calculated for the polycrystal specimen (2.80%, blue curve in Figure 4b) represent the bulk average transformation strains over approximately 4 grains giving a transformation strain of 2.80% which agrees with the bulk [011] single crystal transformation strain reported in Figure 4a as 2.41%. In Figure 4b we also provide an additional temperature-strain curve in green color calculated averaging the local axial strains for a group of grains (local ϵ_2) showing negligible transformation strains. The temperature-strain curve clearly indicates that this group of grains does not show undergo phase transformation. This can be explained by two different observations. As previously reported, the austenite-to-martensite phase transformation (at zero stress) is not completed as shown in the diffraction pattern in Figure 2. Nevertheless under stress the nucleation of martensite is energetically favored, this is not sufficient to guarantee that all the grains transform from the austenite phase to the martensite one. This observation is also supported by the DIC strain fields reported for the [011] single crystal (Figure 4a) which clearly show that not all the single crystal specimen undergoes to a uniform austenite-to-martensite phase transformation. A second factor can be the simultaneous occurrence of a group of grain orientations having low transformation strains (the inverse pole figure shows local [001] texture) along with low local stresses rising from elastic and plastic grain orientation anisotropy.

21 *Isothermal behavior*

22 In order to investigate the isothermal mechanical behavior of the $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy the [0 1 1] orientation was selected as the orientation showing the largest transformation strains (Figure 3). 23 Two different aging treatments were selected: the 500°C/4h optimizes the pseudoelastic behavior 24 for similar compositions [47], while the 550°C/10h was selected in order to maximizes the 25 temperature showing pseudoelasticity. Higher aging temperatures already have already shown to 26 be detrimental for the pseudoelasticity [47]. 27

Perfect shape memory behavior was observed for temperatures lower than 170°C for the 500°C/4h aging (Figure 5). Pseudoelasticity was observed at temperatures higher than 180°C. In particular, following the 500°C/4h aging, since the austenite finish temperature is $A_F=220^\circ\text{C}$, and the martensite start temperature is $M_S=160^\circ\text{C}$, it is important to heat the specimen at $T>A_F$ in order to complete the transformation in austenite and successively slowly cool the specimen at the desired experimental temperature. As expected from DSC results (Figure 1a), the 550°C/10h aging provides higher transformation temperatures, in particular pseudoelasticity was found starting from 240°C (Figure 5). Comparing the stress-strain responses for the two agings, it is evident how the 550°C/10h aging deteriorates the pseudoelastic behavior.

The stress-strain behavior was further investigated using local strain measurements. Figure 6a and 6b show the optimum pseudoelastic stress-strain curves for the selected aging treatments for the [0 1 1] crystal orientation. Comparing the stress-strain responses for the two agings, it is evident how the 550°C/10h aging deteriorates the pseudoelastic behavior. The stress hysteresis for the 500°C/4h aged specimen is much lower than the hysteresis for the 550°C/10h aged specimen. Moreover, for the 550°C/10h aged specimen, irrecoverable plastic strain remains upon unloading. For the 500°C/4h aging, the temperature showing the optimum pseudoelastic behavior was found to be 200°C (Figure 6a), which is below the A_F temperature (220°C). DIC strain fields enable to capture the nucleation of phase transformation through the local strain measurements (blue line) for a region of the specimen where high local strains were measured (see blue box in inset marked 5). As observed during the isobaric experiments, the phase transformation is heterogeneous and the transformation strains determined from the averaged axial strains and for the local axial strains are strongly affected. The transformation strain measured for the averaged axial strain was 2.45%, while locally is 3.86%. This reveals the importance of DIC strain measurement in order to properly estimate the maximum transformation strains. Similarly, for the 550°C/10h aging (Figure 6b), DIC strain measurements provide interesting characteristics on the heterogeneous deformation following this aging. While the average axial strain measurements provide almost the same transformation strain (2.43%), the local strain measurements indicate that for the 550°C/10h aging the maximum transformation strains are lower (3.19% versus

- 1 3.86%). The decrease of the transformation strains for the 550°C/10h aging is attributed to the
- 2 increase of the volume fraction of precipitates that do not undergo phase transformation.

1

2 *Thermodynamics*

3 Calculation of the entropy for shape memory alloys reveals interesting aspects of the
 4 thermodynamics of the phase transformation associated with transformation strains and
 5 transformation temperatures. The Clausius-Clapeyron (CC) equation is written as follow

$$6 \quad \frac{d\sigma^T}{dT} = \frac{-\Delta s}{\varepsilon^T} = \frac{-h\rho}{T\varepsilon^T} \quad (1)$$

7 The term $d\sigma^T / dT$ indicates the CC slope of the temperature-critical stress in the martensite-
 8 stress induced temperature range (the slope indicated in Figure 7), ε^T is the transformation strain
 9 (which is orientation dependent), the variation of enthalpy Δh from austenite to martensite
 10 phases is determined from the DSC curves reported in Figure 1a. The equilibrium temperature
 11 $T = T_0 = 1/2(M_s + A_f)$ is chosen according the Tong and Wayman proposal [50]. Figure 67
 12 summarizes the orientation-dependence of the critical stress with temperature. From e Equation 1
 13 it follows indicates that the CC slope depends on the crystal orientation. In Figure 7 is shown the
 14 critical stress dependence on the temperature calculated from the isothermal stress-strain curves
 15 (Figure 4) for the [1 1 1] and [0 1 1] orientations. For the [1 1 1] orientation we measured an
 16 average CC slope of 10.3 MPa/°C, while for the [0 1 1] orientation we measured 7.2 MPa/°C. The
 17 aging does not affect the CC slope, while it influences the equilibrium temperature T_0 (see
 18 equation 1). The change in enthalpy Δh is not influenced by the crystal orientation (table 1),
 19 while it depends on the aging treatment adopted. The transformation strains predicted using the
 20 CC equations agrees with the experimental ones obtained during isobaric experiments (table 1
 21 and Figure 3).

22 *Theoretical transformation strains*

23 The maximum transformation strains determined from isobaric strain-temperature experiments
 24 are reported in the stereographic triangle in Figure 8. The theoretical transformation strains were
 25 calculated via lattice deformation theory (LDT) for the cubic B2 to orthorhombic B19 lattices

1 transformation. LDT considers the fully transformation from the austenite crystal to the martensite
2 crystal neglecting twinning. A close agreement was found for the $[0\ 1\ 1]$ and $[3\ 4\ 14]$ orientations,
3 while the transformation strains for the $[1\ 1\ 1]$ orientation are lower than the strains predicted with
4 LTD. Nevertheless for the $[1\ 1\ 1]$ orientation the strains are lower than predicted, we notice the
5 trend is well predicted.

1

2 Discussion

3 One of the most intriguing questions regarding NiTiHf shape memory studies is the difference
 4 between the theoretical predicted transformation strains with the ~~experimentally~~ strains measured
 5 ~~experimentally~~ for the polycrystal and, in particular, for single crystals [15, 24, 25, 27, 28, 51]. In
 6 order to address this question, in the present work, single crystals ~~and polycrystals~~ of the new
 7 $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy were studied using DIC technique. We combined strain measurements via
 8 DIC and microstructural characterization via X-ray diffraction in order to provide a straightforward
 9 ~~tool for a better~~ comparison between the experimental strains and the strains predicted by LDT.
 10 We focused on the orientation dependence of NiTiHf alloys for high(Hf) content (>25 at. %),
 11 where the cubic austenite to orthorhombic martensite phase transformation occurs.

12 *Single crystal transformation strains*

13 The transformation strains were determined from the isobaric experiments to be , and (Figure 3).
 14 These values have shown to be consistent with the theoretical transformation strains determined
 15 with LDT according ~~the phase transformation from the~~ cubic austenite B2 to the orthorhombic
 16 martensite B19 ~~phase transformation~~ (Figure 8). Nevertheless the single crystal form of the
 17 specimens, DIC strain fields (isobaric experiment in Figure 4, and isothermal experiments in
 18 Figure 6a and 6b) show that the austenite-martensite phase transformation ~~front~~ does not ~~occur~~
 19 ~~propagate~~ homogeneously over the DIC region. For example, in Figure 6a the pseudoelastic
 20 behavior of the specimen shows an average transformation strain of 2.45%, while locally we
 21 measured transformation strains up to 3.86%. ~~One possible reason for the heterogeneous phase~~
 22 ~~transformation can be deducted from x-ray diffraction pattern (Figure 2).~~ According to the ~~xXray~~
 23 diffraction data (Figure 2), peaks from B2 austenite are still present at RT nevertheless the
 24 martensite finish temperature is 110°C for the 600°C/4h aging treatment. ~~XRD results and DIC~~
 25 ~~strain measurements suggest that indicates the presence of non-transformed austenite. Regions~~
 26 ~~of non-transformed austenite might indicate that~~ some locations of the specimens are less
 27 favorable to martensitic transformation even under an applied stress (Figure 6a and 6b). The

ideal crystal transformation from austenite phase to the martensite phase is then not completely realized leading to the **typical** underestimation of the transformation strains using classical strain measurement **techniques**, e.g. extensometers.

Single crystal versus polycrystal transformation strains

In order to compare the transformation strains for the polycrystal and **the** single crystals, **specimens** it is necessary to elucidate the meaning of bulk strains and local strains **obtained measured** with DIC **for the polycrystal specimen compared to the single crystals ones**. As previously discussed, the transformation strains obtained averaging the axial strains over the DIC region for the single crystals-**specimens** (approximately 3mm x 4mm) represent the average behavior for the selected orientation (bulk strain). Such measurement **technique** considers both the transformed and untransformed regions of the specimen **providing and it an underestimation underestimates** **of** the effective transformation strain. Using local strain measurements, we provided the correct estimation of the transformation strains considering only the specimen region that completely undergoes the austenite-martensite phase transformation (approximately a region of 1mm x 0.75mm). **For the polycrystal specimen the bulk transformation strain is calculated over a DIC region which considers multiple grains with different crystal orientations. As for the single crystal specimen the DIC region is approximately 3mm x 4m, while the grain size is approximately 200 μ m. The local strain measurements are calculated over a local region that includes a limited number of grains (on the order of 4) which displays the largest localized transformation strains. As reported in the inverse pole figure obtained for the polycrystal specimen (Figure 4), we observe random grain orientations for the polycrystal specimen. This indicates that the local transformation strains measured for the polycrystal case (2.80%) are in agreement with the results obtained for the [011] crystal orientation bulk strains (2.41%). In this comparison, the local transformation strains measured for the polycrystal cannot reach the local transformation strains of the [011] orientation only because of a limitation on the DIC resolution which, with the adopted experimental set-up, cannot capture sub-grain strain heterogeneities.**

The polycrystal is formed by an aggregate of different grains having the orientation distribution as represented in the inverse pole figure of Figure 4b. Moreover, the average grain size is 200 μm . From the inverse pole figure of the polycrystal is evident that the orientation distribution of the polycrystal contains multiple grain orientations, including those close to the (011) pole. According to the theoretical calculations (Figure 8), the grains with an orientation close to (011) show the largest transformation strain. The strain maps provided for the polycrystal experiment (Figure 4b) show regions of the specimen with high local transformation strains (the maximum measured as 2.80%). These local transformation strains are averaged over a region of the specimen that contains approximately 4 grains. It is reasonable to assume that the largest local transformation strains measured in the polycrystal correspond to group of grains oriented along the 011 pole. Moreover, the local transformation strains measured for the polycrystal case (2.80%) are in agreement with the results obtained for the [011] crystal orientation bulk strains (2.41%). In this comparison, the local transformation strains measured for the polycrystal cannot reach the local transformation strains of the [011] orientation only because of a limitation on the DIC resolution which, with the adopted experimental set-up, cannot capture sub-grain strain heterogeneities.

It is also interesting to note that the bulk transformation strain for the polycrystal case (1.38%) is lower compared to any of the bulk single crystal transformation strains. DIC strain fields show that different regions of the polycrystal specimen do not undergo phase transformation during the cooling/heating thermal cycle (Figure 4). Un-complete austenite-martensite phase transformation was then observed also in the polycrystal specimen; and this explains the low bulk transformation strains measured for the polycrystal. This observation is of fundamental importance in explaining the discrepancy of—between the experimental transformation strains measured with classical techniques (for example the extensometer) and with the ones calculated theoretically transformation strains. Besides, in the polycrystal case, the incomplete austenite-martensite transformation is also made difficult due to the presence of the grain boundaries and a non homogeneous precipitate distribution which can further inhibit the volume fraction of the transformed phase.

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4 *Transformation temperatures*

5 Compared to similar NiTiHf alloys, the present $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ composition shows very high
 6 transformation temperatures. As a comparison, the $\text{Ni}_{50.3}\text{Ti}_{29.7}\text{Hf}_{20}$ composition shows $A_F=210^\circ\text{C}$
 7 for the specimen aged $600^\circ\text{C}/3\text{h}$ [5], while the present composition shows $A_F=380^\circ\text{C}$ for the
 8 homogenized specimen, and $A_F=300^\circ\text{C}$ for the specimen aged $600^\circ\text{C}/4\text{h}$. The drawback of
 9 utilizing these heat treatments for further TTs increments is the decrease of the shape memory
 10 and pseudoelastic properties. Larger precipitate size and inter-particle distances are obtained
 11 with high aging temperatures ($>550^\circ\text{C}$), and long aging times ($>4\text{h}$). The change in precipitate
 12 geometry and distribution which lowers the strength of the matrix favoring the irrecoverable
 13 plastic deformations. In the present work, we optimized the TTs and the shape memory and
 14 pseudoelastic behavior of the $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ by an aging $500^\circ\text{C}/4\text{h}$. This aging results in a
 15 perfect pseudoelastic behavior at temperatures higher than 200°C . We also show that with the
 16 $550^\circ\text{C}/10\text{h}$ aging the pseudoelastic behavior was found at temperatures higher than 250°C with a
 17 decrease of the transformation strain, 3.19% versus 3.86%. The transformation strain values
 18 reported and compared in Figure 8 were calculated for the samples aged at $500^\circ\text{C}/4\text{h}$. As
 19 reported by several authors for similar compositions, fine precipitates are observed for this aging
 20 treatment [5]. As the measured local transformation strains are close to the theoretical ones, we
 21 conclude that the precipitates do not provide a strong barrier to the austenite–martensite phase
 22 transformation.

23 *Pseudoelasticity*

24 Pseudoelasticity was found at temperatures higher than $T_{SE}>180^\circ\text{C}$ for the [011] orientation aged
 25 at $500^\circ\text{C}/4\text{h}$, and $T_{SE}>250^\circ\text{C}$ for the $550^\circ\text{C}/10\text{h}$ aging treatment. Short aging times provide fine
 26 and coherent precipitates which strengthen the matrix and allow the martensite to develop

1 resulting in a non-obstructed martensite growth. On the other side, longer aging treatments are
 2 detrimental for the transformation strains as the increment of the precipitate dimension size and
 3 loss of coherency obstacle to the growth of the martensite. This results in a reduction of thus
 4 reducing the transformation strains. Since longer aging treatments enable to deplete Ni from the
 5 matrix, it is possible to further increase the TTs with even longer aging times resulting, on the
 6 other side, on the loss of precipitate coherency with the B2 austenite. The resulted loss of
 7 pseudoelasticity can be seen comparing the stress-strain curves in Figure 6a (500°C/4h) and
 8 Figure 6b (550°C/10h).

9 *Thermodynamics*

10 Enthalpy variations were derived from DSC curves and the Clausius-Clapeyron equation (1) was
 11 used to verify the transformation strains. A close agreement was found for the [011] and [111]
 12 orientations (Table 1). The slopes of the yield stress-temperature curves in the pseudoelastic
 13 window found for the [111] and [011] orientations, 10.3 and 7.3 MPa/°C respectively, are
 14 consistent with the results already published previously for similar NiTi and NiTiHf alloys. For the
 15 aging treatments adopted in this study (500°C/4h versus 550°C/10h), negligible influence on the
 16 CC slope was found.

1

2 **Conclusions**

3 In this work we present the functional behavior of the new $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy for three crystal
4 orientation [0 1 1], [1 1 1] and [3 4 14], along with a comparison with the polycrystal behavior. The
5 work supports the following conclusions:

- 6 - The transformation strains determined from isobaric experiments for the three single
7 crystal orientations are , and . These values are in agreement with the theoretical values
8 estimated using LDT calculations based on the B2 cubic austenite to the B19
9 orthorhombic martensite phase transformation.
- 10 - X-ray diffraction performed on aged specimen shows peaks from the orthorhombic phase
11 and from the cubic phase in martensite state confirming the incomplete austenite-to-
12 martensite phase transformation; non uniform phase transformation was also found in the
13 single crystal specimens during isothermal and isobaric experiments; this was revealed by
14 large strain heterogeneities measured using the DIC technique.
- 15 - The bulk transformation strain for the polycrystal specimen is lower than any of the single
16 crystal orientations tested in this work. On the other side, local strain measurements show
17 that high local transformation strains arise for well-favored local [011] texturized group of
18 grains. In perspective, this suggests that the [011] texturized polycrystal maximizes the
19 transformation strains.
- 20 - The new $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy shows high TTs ($>250^{\circ}\text{C}$) along with high strength
21 ($>1000\text{MPa}$) making it suitable for high temperature actuator applications.

22

1

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24

Figure 1a has been modified according Reviewer's suggestion in [Question 3](#).

ONE-COLUMN FIGURE

Figure 1a. DSC curves for the most important heat treatments studied in this work. Homogenization produces the highest TTs, while solution treatment shifts back the TTs as the precipitates formed during homogenization dissolve. Based on the adopted combination of aging temperature and time the TTs are moved shift in between the homogenized and solution-treated cases.

ONE-COLUMN FIGURE

Figure 1b. Influence of the aging time and temperature on the austenite peak temperature (A_{PT}) and peak-to-peak ($A_{PT} - M_{PT}$) temperature.

TWO-COLUMNS FIGURE

Figure 2. (a) X-ray diffraction results showing the peaks from for the austenite B2 structure for the polycrystal solution-treated specimen (black curve), and the peaks from for the martensite B19 structure for the polycrystal aged specimen (blue curve); (001) and (002) peaks of the untransformed B2 austenite are still present in the aged condition; (b) crystal structures for the B2 austenite and for the orthorhombic B19 martensite.

TWO-COLUMNS FIGURE

Ni_{51.2}Ti_{23.4}Hf_{25.4} - Aged 500°C/4h

Figure 3. Influence of the crystal orientation on the isobaric strain-temperature behavior for the $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy aged at $500^\circ\text{C}/4\text{h}$. The black dots indicate the strain measurements obtained averaging the axial strains over the specimen width ($3.6\text{ mm} \times 2.7\text{ mm}$, bulk ϵ), while with blue color are indicated the local strain measurements (local ϵ). The maximum bulk and local transformation strains are reported for each crystal orientation and for the polycrystal.

Figure 1a has been modified according Reviewer's suggestion in [Question 9](#).

TWO-COLUMNS FIGURE

Figure 4. (a) DIC strain fields for the isobaric experiment along the $[011]$ orientation at -800 MPa. At the lowest experimental temperature (50°C) the strains are non homogeneous indicating the heterogeneity of the phase transformation. (b) Temperature-strain behavior for the polycrystal

case at -1100 MPa. The bulk strain is compared with a region where high local strains were measured (local ϵ_1), and with a region where low local strains were measured (local ϵ_2).

TWO-COLUMNS FIGURE

Figure 5. Comparison between the isothermal stress-strain curves for the [011] orientation for the specimens aged at 500°C/4hr and 550°C/10hr. The 500°C/4hr aging determines the best pseudoelastic behavior for the investigated $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$ alloy.

TWO-COLUMNS FIGURE

Figure 6a. Isothermal stress-strain curves for the [011] orientation for the specimen aged at $500^\circ\text{C}/4\text{hr}$ and tested at 200°C in fully austenite.

TWO-COLUMNS FIGURE

Figure 6b. Isothermal stress-strain curves for the [011] orientation for the specimen aged at 550°C/10hr and tested at 250°C in fully austenite.

ONE-COLUMN FIGURE

Figure 7. Yield stress function of temperature for the 500°C/4hr and the 550°C/10h aging treatments for the [111] and [011] crystal orientations.

ONE-COLUMN FIGURE

Figure 8. Maximum transformation strains obtained from isobaric experiments using local DIC strain measurements. The results are compared with the maximum theoretical transformation strains calculated using LDT.

Table(s)

Aging	Orientation	Enthalpy _{A→M} [J/g]	T ₀ =1/2 (M _S +A _F) (K)	(dσ ^T /dT) _{exp} (MPa/K)	(ε _{transf}) _{exp} (%)	(ε _{transf}) _{C-C} (%)
500°C /4h	[011]	12.786	466.15	6.9	4.04	3.72
550°C /10h		17.087	582.15	7.5	3.92	3.66
500°C /4h	[111]	12.786	466.15	10.4	2.58	2.47
550°C /10h		17.087	582.15	10.2	2.55	2.69

Table 1. Transformation strains estimated from the Clausius-Clapeyron equation for the Ni_{51.2}Ti_{23.4}Hf_{25.4} [011] and [111] orientations studied in this work.

New High temperature Shape Memory Alloy $\text{Ni}_{51.2}\text{Ti}_{23.4}\text{Hf}_{25.4}$

Axial Strain
in Single Crystals

Cubic B2 Austenite

Orthorhombic B19 Martensite