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# **Analysis of Ti-Ni-Hf shape memory alloys by combinatorial nanocalorimetry**

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## **Abstract**

The martensitic transformation in Ti-Ni-Hf thin films with ultra-fine grain structure has been analyzed as a function of composition using a high-throughput array of nanocalorimeters. The martensite-austenite transformation temperature is significantly lower than in bulk Ti-Ni-Hf, but increases linearly with Hf content at a rate comparable to bulk Ti-Ni-Hf. The response to high-temperature cycling ( $22^{\circ}\text{C} < T < 850^{\circ}\text{C}$ ) changes with Ni concentration. For  $\text{Ni} \leq 47$  at%, the transformation temperature increases during high-temperature cycling because precipitation of  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  enriches the surrounding matrix in Hf; for  $\text{Ni} \geq 47.7$  at%, precipitation of the same phase gradually suppresses the transformation. Low-temperature cycling ( $22^{\circ}\text{C} < T < 450^{\circ}\text{C}$ ) causes the transformation temperature to initially decrease and then stabilize. Relaxation of internal stresses by dislocations generated during thermal cycling is suggested as the active mechanism. Thermal cycling stability of the films is improved compared to previous studies on bulk Ti-Ni-Hf. This is attributed to the very small grain size ( $18 \pm 5$  nm) of the samples. Alloys with superior thermal cycling stability are identified and the ability to control the transformation temperature through multiple thermal cycling is demonstrated.

**Keywords:** Thin film, Calorimetry, Martensitic transformation, Thermal cycling, High-temperature shape memory alloy.

## 1. Introduction

Many titanium-nickel based alloys display shape memory behavior as a result of a thermoelastic martensitic transformation between a high-temperature cubic phase (austenite) and a low-temperature monoclinic phase (martensite). The shape memory behavior, along with good biocompatibility and corrosion resistance, makes these materials suitable for biomedical and aerospace applications. When fabricated in thin-film form, these alloys can also be used as actuators in micro-electro-mechanical systems (MEMS) [1-6]. TiNi binary thin films are used mainly in low-temperature applications because of their low transformation temperatures ( $< 100^{\circ}\text{C}$ ) [7]. In order to use shape memory-based micro actuators at elevated temperatures, thin films with higher transformation temperatures need to be developed. Ti-Ni-Hf alloys are promising candidates for this purpose, as they demonstrate both high transformation temperatures ( $> 100^{\circ}\text{C}$ ) and low cost compared to the Ti-Ni-Pd and Ti-Ni-Pt systems [8-11]. A number of studies have reported on the characterization of relatively thick Ti-Ni-Hf coatings prepared through magnetron sputtering and laser ablation [8, 12-14], but the number of studies on submicron films is very limited [15].

Combinatorial materials synthesis and high-throughput screening accelerate materials discovery, development and optimization [16-19]. The combinatorial approach is now widely used to synthesize and explore various types of polymeric [20], inorganic [21] and hybrid materials [22]. This approach has been reported for Ti-Ni-Cu [23-25], Ti-Ni-Pd [26], Ni-Mn-Ga [18], Ni-Mn-Al [27, 28] and Ti-Ni-Zr [29-31] shape memory thin films. In these studies, composition spreads were characterized using high-throughput screening methods, resulting in the discovery of

various shape memory materials with promising shape memory characteristics. In shape memory alloys (SMAs), exploring phase transformation characteristics such as transformation temperatures is important because they dictate the usable temperature range of the material [32-34]. Calorimetry is one of the most established methods to study phase transformations in SMAs. Using calorimetry, transformation temperatures, enthalpies and heat capacities can be measured over a wide range of temperatures [33-40]. Calorimetric techniques are typically employed for bulk samples where the sample mass is in the milligrams range; they are generally not sensitive enough to measure small quantities of materials in the range of micro or nano grams as required for thin films [41, 42]. Furthermore, analysis of SMA materials with a spread of compositions using conventional calorimetry takes a long time. Here we characterize the transformation behavior of a Ti-Ni-Hf composition spread through use of a parallel nano-scanning calorimeter (PnSC), a powerful device developed for calorimetric analysis of nanoscale to microscale quantities of materials using a high-throughput methodology [30, 31, 43]. The PnSC is a silicon-based micromachined instrument that allows high-throughput measurement of enthalpy-related materials properties in thin-film samples. Besides the nanoJoule sensitivity, the main advantages of this device are its capability to characterize transformations in a range of compositions over a wide temperature range, its very fast measurement times, and the capability to heat treat and thermally cycle samples in-situ [30].

The paper is organized as follows. First, a brief description of the PnSC device is provided; the synthesis of the Ti-Ni-Hf sample library is described and the calorimetric measurement technique is explained. Next, the dependence of the martensite transformation temperature on the composition is discussed, and the results obtained from nanocalorimetry and traditional

calorimetry are compared. In the final section of the paper, the effects of high and low-temperature cycling on the martensitic transformation are evaluated.

## **2. Experimental Methods**

### **2.1. Physical Description of the Parallel nano-Scanning Calorimeter**

The PnSC device consists of a  $5 \times 5$  array of micromachined calorimetric cells supported by a square Si frame with an edge dimension of 55 mm (Fig. 1) [30]. Each calorimetric cell consists of a thin-film resistance thermometer sandwiched between two electrically insulating silicon nitride layers that form a membrane. The membrane has a thickness of 200 nm and in-plane dimensions of  $2.5 \text{ mm} \times 5 \text{ mm}$ . The resistance thermometer consists of tungsten strip approximately  $800 \text{ }\mu\text{m}$  wide and 125 nm thick patterned for a four-point measurement scheme. The resistance thermometer is also used as a resistive heater during the experiments (Fig. 1b). The horizontal metal lines at the extremes of the heater in Fig. 1b are the voltage probes. The segment of the heating element between the voltage probes is the resistance thermometer and constitutes the sensing area of the cell. Each cell has four electrical leads that are connected to the contact pads at the edges of the Si substrate through a  $\sim 1 \text{ }\mu\text{m}$  patterned copper film (Fig. 1a). For this study, a single PnSC device was fabricated using standard silicon micromachining techniques, as detailed in Ref. [30].

## 2.2. Ti-Ni-Hf Sample Synthesis and Structural Analysis Methods

Ti-Ni-Hf samples were deposited onto the sensing areas of a PnSC device through a micromachined shadow mask by co-sputtering pure Ni, Ti and Hf (Fig. 2). The deposition was performed at ambient temperature in a sputter system (ATC 1800, AJA International) equipped with three confocal sputter guns with adjustable inclination. The sputter guns were tilted toward substrate holder so that the chimneys were close to touching (Fig. 2). This positioned the guns directly under the device and reduced secondary shadowing from the openings in the shadow mask. For the same reason, the working distance was set to approximately 120 mm, the maximum value allowed by the sputtering system. The deposition was performed at an Ar working gas pressure of 3 mTorr in a vacuum chamber with a base pressure in the  $10^{-8}$  Torr range. The DC power applied to the Ni, Ti and Hf targets ( $\text{\O} 50.8$  mm) was 70, 180, and 30 W, respectively. The deposition lasted 30 minutes and resulted in a uniform sample thickness of approximately 300 nm. During the deposition process, the PnSC device and attached shadow mask were held stationary to produce a composition gradient across the array of nanocalorimeters (Fig. 2). Finally, the samples were capped with approximately 30 nm of  $\text{SiN}_x$  using a plasma-enhanced chemical vapor deposition process (PECVD, Surface Technology Systems). Chemical composition measurements were performed on reference samples, deposited under identical conditions, using wavelength dispersive X-ray spectroscopy (WDS) in a JEOL JXA 8200 scanning electron microscope using the standard spectra of pure nickel, titanium and hafnium. Table 1 provides the compositions of all samples on the PnSC device. A 4800 nm film of a specific Ti-Ni-Hf alloy was also deposited on a rotating (3 rpm)  $\text{Si}_3\text{Ni}_4$ -coated Si substrate using the same sputtering conditions. The as-deposited film was removed from the substrate and

used for traditional DSC measurements. The composition of this film was uniform across the substrate because of the substrate rotation and similar to cell R on the PnSC device (Table 1).

The crystal structure of the samples was examined by X-ray diffraction (XRD) using a Bruker D8 system with Cu K $\alpha$  radiation and a Vantec2000 2D area detector. Transmission electron microscopy (TEM) operating in high-resolution mode was conducted using a JEOL 2010 instrument at a voltage of 200 kV.

### 2.3. Calorimetry Measurement Method

Nanocalorimetry measurements were performed by applying a direct current pulse ( $I$ ) through the W heater, resulting in a temperature rise of the sensor by Joule heating. During this process, the current  $I$  through the sensor and the voltage  $V$  across it were recorded as a function of time. The resistance of the thermometer ( $R = V/I$ ) and the power dissipated in it ( $P = VI$ ) can be obtained directly from the measurements. The temperature of the sample is then determined from  $R$  using Eqn. (1),

$$T(R) = \frac{1}{\alpha} \left( \frac{R}{R(T_0)} - 1 \right) + T_0, \quad (1)$$

where  $\alpha$  is the temperature coefficient of resistance and  $R(T_0)$  is the resistance of the thermometer at ambient temperature  $T_0$ . The value of  $\alpha$  was determined to be  $1.56 \times 10^{-3} \text{ K}^{-1}$  by calibrating the device to a thermocouple in an oven. All nanocalorimetry measurements were



performed by heating the sensors from an ambient temperature of 22°C at a rate of approximately  $10^4$  K/sec. The sampling rate for the measurement was 100 KHz, which corresponds to a temperature resolution of 0.1 K. All calorimetric measurements were performed inside a vacuum chamber to minimize thermal losses.

A detailed description and analysis of calorimetry measurements using the PnSC device is given in Ref. [30]. Briefly, the primary equation governing the thermal behavior of a sensor with sample is represented by the following expression,

$$\frac{P}{T'} = \frac{dH}{dT} + \frac{Q}{T'}, \quad (2)$$

where  $P$  is the total power dissipated in the resistance thermometer of the sensor,  $T'$  is the heating rate,  $dH/dT$  is the change in enthalpy with temperature, and  $Q$  is the heat loss to the ambient. The left hand side of the equation can be calculated directly from the measured quantities and is defined as the calorimetric signal. The heat loss term in the right hand side of the equation is typically very small because the fast heating rate makes the measurements very nearly adiabatic. The contribution of the heat loss can be eliminated from the signal by comparing measurements on a sensor with sample to a reference measurement performed at the same heating rate.

In this study, both the sample and the reference measurements were made using the same sensor in a scheme where calorimetric measurements on non-transforming phases were used as reference measurements for transforming phases. Specifically, the as-deposited amorphous

samples were fully crystallized in one heating cycle to approximately 850°C, resulting from a current pulse of 86 mA lasting 65 ms. Subsequent cycles to 850°C showed no indication of further crystallization; two of these cycles were used to ensure that the microstructure was stable before performing low-temperature cycles. The average of ten additional high-temperature cycles then served as a reference measurement for the crystallization process. Low-temperature cycling to 450°C was used to investigate the martensite-austenite phase transformation. One hundred of these low-temperature cycles were performed before and after the ten additional high-temperature cycles. The reference for low-temperature measurements was established by averaging 100 low-temperature cycles of each as-deposited amorphous sample. This reference measurement approach very nearly eliminated the contributions to the calorimetric signals from both heat loss and calorimeter addendum. An advantage of using a sensor plus sample as its own reference, as opposed to a bare reference sensor, is that its mass is exactly the same. Consequently, any deviation between calorimetric signals must be related to a change in the enthalpy of the sample. The difference in calorimetric signals between sample and reference, i.e., the differential calorimetric signal, was used to calculate transformation temperatures and latent heats throughout this study.

Differential scanning calorimetry (DSC) using a Q200 from TA instrument was employed to study the transformation behavior of the freestanding Ti-Ni-Hf film. The DSC measurement was performed under an N<sub>2</sub> atmosphere (50 ml.min<sup>-1</sup>) at heating and cooling rates of 10 K/min. The mass of the sample was 7.4 mg and an empty aluminum pan was used as a reference. The as-deposited film was first crystallized by heating the sample to 540°C, followed by cooling to -10°C before equilibrating at room temperature. To analyze the martensitic transformation, the

crystallized sample was heated to 540°C, followed by cooling to -10°C; this cycle was repeated two times.

### **3. Results and discussion**

#### **3.1 Crystallization of the Ti-Ni-Hf sample library**

All as-deposited Ti-Ni-Hf samples were determined to be amorphous by X-ray diffraction. Figure 3a shows the heating curves of a sensor with a sample in the as-deposited state and of the same sensor with the sample in the crystalline state. The slight step in the temperature response of the as-deposited film is due to the exothermic crystallization reaction, which creates a sharp rise in the heating rate of the sample between 35 and 45 ms (Fig. 3b). The corresponding crystallization peak is readily observed in the calorimetric signal for the as-deposited sample (Fig. 3c) and is clearly absent in the curve for the crystallized sample (reference sample). Figure 3c also shows that radiation losses become significant at high temperatures causing a decrease in the overall heating rate. This heat loss is eliminated by taking the difference of the two sample and reference signals, although a small radiation correction is needed to completely eliminate it as explained in reference [29]. Figure 3d shows the differential calorimetric signal as a function of temperature – the exothermic crystallization peak and a glass transition right before crystallization are clearly visible. The crystallization peak temperature ( $658 \pm 2^\circ\text{C}$ ) is significantly higher than previously reported values ( $505 \pm 11^\circ\text{C}$ ) for Ti-Ni-Hf films with thicknesses in the micron range [13]. It is also much higher than the crystallization temperature we obtained for the freestanding Ti-Ni-Hf film using traditional calorimetry ( $501 \pm 2^\circ\text{C}$ ). This

temperature shift is caused by the kinetics of the crystallization reaction and the very different heating rates used in the measurements (approximately  $2.9 \times 10^4$  K/s at the peak of crystallization for nanocalorimetry versus 0.167 K/s for the traditional DSC measurement). The rise in crystallization temperature can be used in a Kissinger analysis to estimate the activation energy of the crystallization process, leading to a value of approximately 450 kJ/mol, comparable to previous measurements for Ni-Ti-Hf thin films of 487-519 kJ/mol [12].

Figure 4a shows a typical TEM micrograph of a sample crystallized using the PnSC. The crystallization process results in a very small ( $18 \pm 5$  nm) grain size. The insert in Fig. 4a shows the fine twin structure of the martensite that is observed in some of the grains. The grain size in this sample is much smaller than for the freestanding film crystallized using traditional calorimetry ( $197 \pm 32$  nm) (Fig. 4b). The small grains formed at grain boundaries of the freestanding film are  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  precipitates, which have the  $\text{Ti}_2\text{Ni}$  base structure [44].

### **3.2 The martensite-austenite transformation**

A typical low-temperature response of a cell with a sample in the crystalline state, and that of the same cell with the sample in the amorphous state (reference sample) are shown in Fig. 5a. The martensite-austenite (M-A) transformation is not immediately obvious in the temperature history of the crystalline sample, but can be clearly discerned in the heating rate trace and the calorimetric signal (Fig. 5b and c). The calorimetric signal of the amorphous sample increases faster than that of the crystalline film at temperatures above the M-A transformation (Fig. 5c), demonstrating that the specific heat capacity of the amorphous sample has a greater temperature

dependence than the crystalline sample. The differential calorimetric signal is shown in Fig. 5d. The enthalpy of transformation ( $H_{M-A}$ ) is obtained as the area between the transformation peak and a linear baseline fitted to the differential calorimetric signal outside the transformation region. The peak transformation temperature,  $A_p$ , is the temperature at which the differential calorimetric signal is farthest from the baseline. The differential calorimetric signal is plotted versus temperature for all the cells, resulting in a transformation library (Fig. 6). A majority of the cells show a M-A transformation except for a few samples in the Ni-rich region of the library.

The specific enthalpy of transformation ( $h_{M-A}$ ) is calculated by normalizing  $H_{M-A}$  with respect to sample mass. Assuming that the transforming samples have the martensite structure (B19') at room temperature, the mass of each sample can be estimated from the following expression,

$$m_s = 4V_s \left( \frac{f_{Ni}M_{Ni} + f_{Ti}M_{Ti} + f_{Hf}M_{Hf}}{N_A V_{UC}} \right), \quad (3)$$

considering that the martensite unit cell contains four atoms [45]. In this expression,  $V_s$  is the measured sample volume,  $f$  represents the atomic fractions of Ni, Ti, or Hf obtained from the measured chemical composition,  $M$  denotes the molar mass, and  $N_A$  is Avogadro's number.  $V_{UC}$  is the volume of the martensite unit cell for each sample estimated from the crystal structure information for the  $Ni_{50}Hf_xTi_{50-x}$  and  $Ni_{(100-x)/2}Ti_{(100-x)/2}Hf_x$  systems [45]. The values of  $h_{M-A}$  calculated using this method are reported in Table 2 along with the measured  $A_p$  values.

The dependence of  $A_P$  on Hf and Ni content can be found in Fig. 7.  $A_P$  increases with increasing the Hf content, reproducing the trend previously reported for *bulk* samples by Abujudom and Sanjabi [11, 13] (Fig. 7). The Ni content, by contrast, does not seem to affect the transformation temperature (Fig. 7), which has also been observed for bulk samples [11]. It is evident from the figure that the  $A_P$  values of the 300 nm thin films are lower than for 2  $\mu\text{m}$  films [13] or bulk samples [11]. This size effect is attributed to the microstructure of the samples, i.e., the fine grain structure and even finer twin structure (Fig. 4a). For TiNi, it was shown that the excess twin-boundary energy associated with a fine twin structure decreases the stability of the martensite and lowers the transformation temperature [46]. This effect has also been observed in fine-grained Ni-Ti-Zr [30].

The transition between transforming and non-transforming samples takes place at a Ni concentration between 49.3 and 49.8 at%. This transition is likely related to the dependence of the transformation temperature on Ni content reported for binary Ti-Ni alloys [47]. Once the Ni content exceeds 50 at% in a binary Ti-Ni alloy, an increase by 1 at% Ni decreases the transformation temperature by as much as 100°C [33]. This behavior is also observed in  $\text{Hf}_{10}\text{Ti}_{90-x}\text{Ni}_x$  alloys, where  $A_P$  is significantly reduced by the addition of Ni above 50 at% [11], suggesting that at least some of the Ni-rich cells (Cells B-E and H-J) may demonstrate a M-A transformation below ambient temperature.

In contrast to the transformation temperatures, the  $h_{\text{M-A}}$  values do not show any obvious correlation with chemical composition (Table 2). The majority of samples transform with a specific enthalpy ranging from 3.8–15.4 J/g, which is less than the reported bulk value of 25.3

J/g [48]. A comparable range of  $h_{M-A}$  (4.9-14.9 J/g) has been also reported for Ti-Ni-Hf films with micro-scale thickness [13, 14]. Cell G ( $\text{Ti}_{36.1}\text{Ni}_{49.3}\text{Hf}_{14.6}$ ) demonstrates a reduced specific enthalpy of transformation, which is most likely due to the formation of the R-phase instead of the B19' martensite phase. XRD analysis indeed confirms the presence of R-phase in this sample (not shown). The R-phase has a reduced lattice distortion relative to the austenite phase, which decreases the entropy of transformation, and hence the latent heat [49]. It is also possible that the martensite volume fraction in this sample is reduced because of the low transformation temperature and insufficient undercooling. The maximum value of  $h_{M-A}$  ( $15.4 \pm 0.5$  J/g) belongs to cell S ( $\text{Ti}_{36.7}\text{Ni}_{45.4}\text{Hf}_{17.9}$ ), where the martensite phase transforms to austenite in a two-stage process; the first stage is attributed to the martensite  $\rightarrow$  R-phase and the second one is for the R-phase  $\rightarrow$  austenite transformation. In binary NiTi, the R-phase has been shown to stabilize with reduced length scale [50] and increased Ni content [51]. The R-phase transformation has been reported in  $\text{Ni}_{50}\text{Ti}_{50-x}\text{Hf}_x$  thin films, where the Hf content is less than 16 at% [13]. A second report observed the R-phase at Hf compositions of less than 3 at% in the  $\text{Ti}_{51-x}\text{Ni}_{49}\text{Hf}_x$  and  $\text{Ti}_{52.5-x}\text{Ni}_{47.5}\text{Hf}_x$  systems [15]. These reports combined with the results of this work show that the R-phase can be observed over a wide range of Hf compositions (1-16 at%), depending on processing conditions.

Figure 8 compares the martensite-austenite transformation curves of samples crystallized by fast scanning on the PnSC device or slow heating in a conventional DSC. The transformation peak is significantly wider for the PnSC measurement. This observation is not caused by temperature non-uniformity in the PnSC device. Indeed, thermal modeling and calibration experiments show that the temperature distribution along the W sensor is highly uniform in the temperature range

of 22 to 450°C [30, 43], indicating that the broadening of the peak is a real material effect. We attribute the broadening of the transformation peak to the small grain size and the heterogeneous microstructure of the PnSC samples. As mentioned earlier, the grain sizes of PnSC samples are significantly smaller than for samples crystallized using traditional means. The relative widths of the grain size distributions (i.e. the standard deviation divided by the average value) of PnSC samples (~28 %) are also larger than for traditional samples (~16%). It has been reported that the energy barrier to form martensite in TiNi increases significantly when the grain size decreases below 50 nm, due to grain boundary constraints and the interfacial energy of the refined twin variants [46]. Given that the PnSC samples have a wide distribution of very small grains and that these grains transform at different temperatures, it is not surprising that the transformation peak is much broader than for samples with larger grains. This interpretation is supported by recently reported results on the broadening of the martensite transformation in NiTi due to a size distribution of nanoscale grains [52].

### **3.3 Effects of thermal cycling on transformation behavior**

Understanding the thermal stability of SMA materials is important because of practical considerations. Typically, shape memory phases are intermetallic compounds that exist over a narrow composition range in a materials system with many intermetallic phases. Precipitation of secondary phases at elevated temperature alters the composition and the stress state of the shape memory phase; both of these factors affect the shape memory characteristics. SMAs also exhibit thermal fatigue, where repeated cycling through the martensite-austenite phase transformation results in reduced transformation temperatures, enthalpies and useable work capacity. Thermal



fatigue is a dislocation-mediated phenomenon. It is of particular concern for high-temperature SMAs where dislocation activity may be enhanced because of the higher transformation temperatures.

In this section, the PnSC technique is used to study the effect of thermal cycling on the transformation behavior of the Ti-Ni-Hf alloy. Two types of thermal cycles were applied to the samples: 1) samples were heated to 450°C and then cooled to ambient temperature (low-temperature or LT cycling), and 2) samples were heated to 850°C before cooling (high-temperature or HT cycling).

### **3.3.2 Low-temperature cycling**

Figure 9 shows the variation of the differential calorimetric signal as a function of the number of low-temperature thermal cycles for cell L ( $\text{Ti}_{38.1}\text{Ni}_{47.0}\text{Hf}_{14.9}$ ). In the figure, the transformation peak shifts toward lower temperatures with increasing number of cycles. This behavior is observed for all transforming samples as illustrated in Fig. 10. The value of  $A_P$  decreases fast initially, but then stabilizes after a certain number of cycles. The reduction in  $A_P$  is attributed to plastic deformation caused by the crystallographic incompatibility between the austenite and martensite phases at the phase boundary [53, 54]. This mismatch results in large stresses that lead to the formation of dislocations. These dislocations, in turn, can relax residual stresses caused by crystallization and precipitation. Since the residual stresses can be relaxed more easily by the self-accommodating twin structure of the martensite, and the elimination of these stresses removes this bias, the net result is to make the austenite relatively more stable, thus reducing the

transformation temperature. It is difficult to discern a clear correlation between the change in  $A_P$  temperature and the composition of the samples. The average reduction in transformation temperature of Ti-Ni-Hf thin films in this study ( $7.9 \pm 4.0^\circ\text{C}$  for 100 cycles) (Fig. 10) is significantly less than the reported bulk values ( $28 \pm 13^\circ\text{C}$ ) [9, 55, 56].

Thermal fatigue is undesirable from a practical standpoint. It has been shown that thermal cycling stability can be improved by various methods. Reducing the lattice mismatch, and hence the driving force to generate dislocations, can improve thermal cycling stability [57, 58]. Limiting the activity of dislocations by creating barriers within the crystal structure, for example grain boundaries or precipitates, will also improve stability [59]. Finally, a fine grain structure and martensite twin structure will reduce the volume of material exposed to the large elastic stresses caused by the lattice mismatch. This decreases the elastic energy available to create dislocations, thus reducing the likelihood of dislocation formation. The improved thermal cycling stability of the samples in this study compared to previous results for *bulk* materials can be attributed to their nanoscale grain structure, which reduces the elastic energy available to nucleate dislocations and creates boundaries to dislocation motion. This finding is supported by recent reports that demonstrate improved thermal cycling stability in Ni-Ti-Hf thin films due to Laves phase precipitates acting as barriers to dislocation motion [15], and improved thermal cycling stability in nanocrystalline Ni-Ti-Zr [60]. Among the samples in this study, the  $\text{Ti}_{39.6}\text{Ni}_{46.1}\text{Hf}_{14.3}$  and  $\text{Ti}_{42.3}\text{Ni}_{42.5}\text{Hf}_{15.2}$  alloys demonstrate superior thermal cycling stability – approximately  $2^\circ\text{C}$  for 100 cycles (Fig. 10). This extraordinary stability suggests a high degree of crystallographic compatibility between the austenitic and martensitic phases for these samples [57, 58], although the nanoscale grain size and multiple phases make it difficult to confirm this by x-ray diffraction because of broad and overlapping diffraction peaks. Very recent work has

shown that the optimal composition for minimizing the lattice mismatch between the austenite and martensite occurs around 3 at% Hf [15] and that the lattice compatibility decreases with increasing Hf content. It is then not surprising that the samples with the best thermal cycling stability occur at the lower end of the Hf composition range investigated in this study.

For Ti-Ni-Hf thin films, the martensite twin structure has been observed in grain sizes ranging from 9 to 27 nm (e.g. Fig. 4a). Previous observations of nanocrystalline TiNi binary systems have reported martensite only in grains larger than 50 nm [46, 50]. These observations suggest that the Ti-Ni-Hf system is an attractive materials system for control of thermal cycling stability by grain refinement, since martensite can be formed at smaller grain sizes than in the Ti-Ni system. Indeed, improved thermal cycling stability due to grain refinement has also been reported for bulk Ti-Ni-Hf after severe plastic deformation (SPD) [61, 62].

### 3.3.1 High-temperature cycling

A total of twelve HT cycles were applied to each transforming cell. Depending on the Ni concentration, two distinct trends were observed during cycling:

(a) For  $\text{Ni} \leq 47$  at%, the M-A transformation peak shifts toward higher temperatures with increasing number of cycles (Fig. 11). The evolution of  $A_P$  with cycle number is illustrated in Fig. 12 for all samples demonstrating this behavior. It is evident from the figure that  $A_P$  increases by 30-51°C over twelve cycles. TEM analysis of cell X ( $\text{Ti}_{38.1}\text{Ni}_{43.3}\text{Hf}_{18.6}$ ) shows that the microstructure consists of finely twinned martensite grains and  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  precipitates with a  $\text{Ti}_2\text{Ni}$  base structure [44] (Fig. 13a and b). Precipitation of  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  with HT cycling

increases the Hf content of the matrix and leads to a higher transformation temperature. A similar mechanism has also been observed in Ni-Ti-Zr thin films [60].

(b) For  $\text{Ni} \geq 47.7$  at%, the behavior with HT cycling is significantly different. Figure 14 demonstrates the transformation curve of cell N ( $\text{Ti}_{35.1}\text{Ni}_{47.7}\text{Hf}_{17.2}$ ) as a function of the number of HT cycles. In this case, the martensite-austenite transformation is gradually suppressed with thermal cycling. Initially a single-stage transformation is observed. As thermal cycling continues, two peaks develop, indicative of a two-stage phase transformation. With further cycling, the transformation disappears altogether. Cells O, F and G also demonstrate this behavior when subjected to HT cycles. TEM analysis of cell N after the calorimetric measurements shows that this cell consists of austenite (B2),  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  precipitates, and some R-phase (Fig. 13 c and d). Evidently, precipitation of  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  with HT cycling enriches the austenite in Ni. Consequently, the sample starts to behave more like the Ni-rich samples of Ti-Ni-Hf transformation library (non-transforming samples) (Fig. 6). This evolution is indeed observed: the transformation temperature shifts down and the martensitic transformation is suppressed due to the lack of sufficient undercooling.

The effect of HT cycling on the thermal stability of Ti-Ni-Hf thin films is explored. For this purpose, seven cells were subjected to 100 low-temperature cycles after the HT heat treatments. All the cells show a similar trend, which is illustrated in Fig. 15 using cell L as a representative example. Evidently HT cycling reduces the thermal stability of Ti-Ni-Hf thin films. The average  $A_P$  reduction after high-temperature cycling ( $15.3^\circ\text{C}$  for 100 cycles) is significantly larger than before HT cycling ( $7.8^\circ\text{C}$  for 100 cycles). We attribute this increase in thermal fatigue to the

continued precipitation of  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  during the HT heat treatments. Precipitation of  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  has several effects. Precipitation of  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  enriches the matrix in Hf, which apart from a rise in transformation temperature also leads to a decrease of the compatibility between the austenite and martensite phases. As mentioned earlier, such a decrease makes the alloy more sensitive to thermal fatigue. It has indeed been reported in the literature that increasing the Hf content in Ti-Ni-Hf materials increases the thermal hysteresis, and increasing the hysteresis degrades the thermal cycling stability [15]. Precipitation also enhances the internal stresses in the austenite, which in turn leads to greater dissipation during transformation and to more pronounced thermal fatigue [60]. Finally, precipitation can create obstacles to dislocation motion, which would reduce thermal fatigue. This last effect is not significant in this case, presumably because the grain size is so small that the additional obstacles created by precipitation have little effect on dislocation motion.

### **3.3.3 Control of transformation temperature aided by multiple thermal cycling**

The transformation temperatures are important characteristics of a shape memory alloy, since they dictate the specific applications of the alloy [32, 33]. Adjusting the chemical composition is one method to control these temperatures. Transformation temperatures are, however, sensitive to slight changes in chemical composition and this makes reliable temperature control difficult [33]. An alternative method for controlling the transformation temperatures consists of a thermal treatment such as aging in which the transformation temperatures vary due to the formation of second phases as described previously. The results obtained from LT and HT cycling experiments demonstrate the capability to change  $A_P$  using a combination of these two

treatments. Figure 16 shows a possible treatment that includes two series of LT heat treatments and two series of HT heat treatments. The results show that  $A_P$  of this sample can be precisely controlled between 207 and 260°C through the application of appropriate heat treatments protocols.

## 7. Conclusions

In summary, parallel nano-scanning calorimetry was used to study the martensitic transformation and thermal cycling behavior of Ti-Ni-Hf shape memory thin films as a function of composition. The experimental results lead to the following conclusions:

- 1) The Ti-Ni-Hf alloy compositions with Ni contents below 49.3 at% exhibit a martensite-austenite transformation. The transformation temperature increases linearly with increasing Hf content in the range 14-20 at% at a rate comparable to that observed for bulk materials, but with reduced  $A_P$  temperature. The decrease in transformation temperature is caused by the fine nanoscale structure of the thin-film samples.
- 2) The martensite-austenite transformation peak in the PnSC is significantly broader than the peak observed in bulk calorimetry. The peak broadening is attributed to the very small grain size and the grain size distribution of the PnSC samples. The large variation in the energy barrier for the martensitic transformation at very small grain size translates into a wide range of transformation temperatures.

3) Low-temperature cycling ( $22^{\circ}\text{C} < T < 450^{\circ}\text{C}$ ) results in a decrease and stabilization of the transformation temperature. Relaxation of residual stresses during thermal cycling is suggested as the active mechanism. The PnSC samples demonstrate improved thermal cycling stability (averaging  $7.9^{\circ}\text{C}$  for 100 cycles) compared to bulk Ti-Ni-Hf materials. This observation is attributed to the nanoscale grain structure in the PnSC samples, which reduces the elastic energy available to nucleate dislocations and which creates obstacles to dislocation motion. Alloys with compositions  $\text{Ti}_{39.6}\text{Ni}_{46.1}\text{Hf}_{14.3}$  and  $\text{Ti}_{42.3}\text{Ni}_{42.5}\text{Hf}_{15.2}$  have superior thermal cycling stability.

4) The response of the Ti-Ni-Hf thin films to high-temperature cycling ( $22^{\circ}\text{C} < T < 850^{\circ}\text{C}$ ) changes with Ni concentration. For  $\text{Ni} \leq 47\%$ , the transformation temperature increases during high-temperature cycling due to precipitation of  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$  and the resulting enrichment of Hf in the surrounding matrix. For  $\text{Ni} \geq 47.7\%$ , the transformation is gradually suppressed; the transformation temperature decreases and the reverse transformation is suppressed due to insufficient undercooling.

5) Thermal cycling stability is reduced after high-temperature cycling. High-temperature heat treatments precipitate  $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ , which increases the internal stresses in the SMA and enriches the austenite with Hf. The internal stresses and the reduced compatibility between austenite and martensite at greater Hf concentrations both lead to more pronounced thermal fatigue.

6) The ability of PnSC to precisely control of the transformation temperature through multiple thermal cycles is demonstrated. In this manner, the  $A_P$  of  $\text{Ti}_{38.1}\text{Ni}_{43.3}\text{Hf}_{18.6}$  alloy was controlled

precisely between 207 and 260°C through the application of appropriate heat treatments protocols.



## References

- [1] Benard WL, Kahn H, Heuer AH, Huff MA. *J Microelectromech Syst* 1998;7:245.
- [2] Johnson AD. *J Micromech Microeng* 1991;1:34.
- [3] Kohl M, Dittmann D, Quandt E, Winzek B, Miyazaki S, Allen DM. *Mater Sci Eng A* 1999;273-275:784.
- [4] Krulevitch P, Lee AP, Ramsey PB, Trevino JC, Hamilton J, Northrup MA. *J Microelectromech Syst* 1996;5:270.
- [5] Makino E, Mitsuya T, Shibata T. *Sens Actuators A* 2001;88:256.
- [6] Mineta T, Kida N, Nomura S, Makino E, Sugawara T, Toh S, Shibata T. *Sens Actuators A* 2008;143:14.
- [7] Fu Y, Du H, Huang W, Zhang S, Hu M. *Sens Actuators A* 2004;112:395.
- [8] Sanjabi S, Cao YZ, Sadrnezhaad SK, Barber ZH. *J Vac Sci Technol A* 2005;23:1425.
- [9] Meng XL, Cai W, Chen F, Zhao LC. *Scripta Mater* 2006;54:1599.
- [10] Grummon DS. *J Met* 2003;55:24.
- [11] Abujudom DN, Thoma PE, Kao M-Y, Angst DR. US Patent 5114504. Johnson Service Company, Milwaukee (WI), 1992.
- [12] Tong Y, Liu Y, Miao J. *Thin Solid Films* 2008;516:5393.
- [13] Sanjabi S, Cao YZ, Barber ZH. *Sens Actuators A* 2005;121:543.
- [14] Gu HD, You L, Leung KM, Chung CY, Chan KS, Lai JKL. *Appl Surf Sci* 1998;127-129:579.
- [15] König D, Zarnetta R, Savan A, Brunken H, Ludwig A. *Acta Mater* 2011;59:3267.
- [16] Zhao JC. *Prog Mater Sci* 2006;51:557.
- [17] Xiang XD. *Annu Rev Mater Sci* 1999;29:149.
- [18] Takeuchi I, Famodu OO, Read JC, Aronova MA, Chang KS, Craciunescu C, Lofland SE, Wuttig M, Wellstood FC, Knauss L, Orozco A. *Nat Mater* 2003;2:180.
- [19] Rajan K. *Annu Rev Mater Res* 2008;38:299.
- [20] De Gans BJ, Wijnans S, Woutes D, Schubert US. *J Comb Chem* 2005;7:952.
- [21] Sakurai J, Hata S, Yamauchi R, Shimokohbe A. *Appl Surf Sci* 2007;254:720.
- [22] Chisholm BJ, Berry M, Bahr J, He J, Li J, Balbyshev S, Bierwagen GP. *J Coat Technol Res* 2010;7:23.

- [23] Zarnetta R, König D, Zamponi C, Aghajani A, Frenzel J, Eggeler G, Ludwig A. *Acta Mater* 2009;57:4169.
- [24] Cui J, Chu YS, Famodu OO, Furuya Y, Hattrick-Simpers J, James RD, Ludwig A, Thienhaus S, Wuttig M, Zhang Z, Takeuchi I. *Nat Mater* 2006;5:286.
- [25] Borgia C, Olliges S, Dietiker M, Pigozzi G, Spolenak R. *Thin Solid Films* 2010;518:1897.
- [26] Zarnetta R, Savan A, Thienhaus S, Ludwig A. *Appl Surf Sci* 2007;254:743.
- [27] Famodu OO, Hattrick-Simpers J, Aronova M, Chang KS, Murakami M, Wuttig M, Okazaki T, Furuya Y, Knauss LA, Bendersky LA, Biancaniello FS, Takeuchi I. *Mater Trans* 2004;45:173.
- [28] Dwivedi A, Wyrobek TJ, Warren OL, Hattrick-Simpers J, Famodu OO, Takeuchi I. *J Appl Phys* 2008;104:073501.
- [29] McCluskey PJ, Vlassak JJ. *Scripta Mater* 2010;64:264.
- [30] McCluskey PJ, Vlassak JJ. *J Mater Res* 2010;25:2086.
- [31] McCluskey PJ, Vlassak JJ. *MRS Proc*; 2006. 0924-Z08-14 doi:10.1557/PROC-0924-Z08-14.
- [32] Zarinejad M, Liu Y. *Adv Funct Mater* 2008;18:2789.
- [33] Otsuka K, Ren X. *Prog Mater Sci* 2005;50:511.
- [34] Motemani Y, Nili-Ahmadabadi M, Tan MJ, Bornapour M, Rayagan S. *J Alloy Compd* 2009;469:164.
- [35] Wang ZG, Zu XT, Fu YQ. *Mater Sci Eng A* 2005;390:400.
- [36] Otsuka K, Wayman CM. *Shape Memory Materials*, 1<sup>st</sup> ed. Cambridge: Cambridge University Press; 1998.
- [37] Li Y, Cui L, Zheng Y, Yang D. *Mater Lett* 2001;51:73.
- [38] Dlouhy A, Khalil-Allafi J, Eggeler G. *Philos Mag* 2003;83:339.
- [39] Beyer J, Besselink PA, Aartsen AJ. *Thermochim Acta* 1985;85:187.
- [40] Firstov GS, Van Humbeeck J, Koval YN. *Scripta Mater* 2004;50:243.
- [41] Olson EA, Efremov MY, Zhang M, Zhang Z, Allen LH. *J Microelectromech Syst* 2003;12:355.
- [42] Allen LH, Lai SL. *Microscale Thermophys Eng* 1998;2:11.
- [43] McCluskey PJ, Vlassak JJ. *Thin Solid Films* 2010;518:7093.

- [44] Yurko GA, Barton JW, Parr JG. *Acta Crystallogr* 1959;12:909.
- [45] Zarinejad M, Liu Y, White TJ. *Intermetallics* 2008;16:876.
- [46] Waitz T, Antretter T, Fischer FD, Simha NK, Karnthaler HP. *J Mech Phys Solids* 2007;55:419.
- [47] Gyobu A, Kawamura Y, Horikawa H, Saburi T. *Mater Trans* 1996;37:697.
- [48] Meng XL, Cai W, Zheng YF, Rao YB, Zhao LC. *Mater Lett* 2003;57:4206.
- [49] Ren X, Miura N, Zhang J, Otsuka K, Tanaka K, Koiwa M, Suzuki T, Chumlyakov YI, Asai M. *Mater Sci Eng A* 2001;312:196.
- [50] Waitz T, Kazykhanov V, Karnthaler HP. *Acta Mater* 2004;52:137.
- [51] Gyobu A, Kawamura Y, Saburi T, Horikawa H. *Nippon Kinzoku Gakkaishi* 1999;63:201.
- [52] Peterlechner M, Waitz T, Gammer C, Antretter. *Int J Mater Res* 2011;102:634.
- [53] Wagner MFX, Dey SR, Gugel H, Frenzel J, Somsen C, Eggeler G. *Intermetallics* 2010;18:1172.
- [54] Miyazaki S, Igo Y, Otsuka K. *Acta Metall* 1986;34:2045.
- [55] Besseghini S, Villa E, Tuissi A. *Mater Sci Eng A* 1999;273-275:390.
- [56] Meng XL, Tong YX, Lau KT, Cai W, Zhou LM, Zhao LC. *Mater Lett* 2002;57:452.
- [57] Zarnetta R, Takahashi R, Young ML, Savan A, Furuya Y, Thienhaus S, Maaß B, Rahim M, Frenzel J, Brunken H, Chu YS, Srivastava V, James RD, Takeuchi I, Eggeler G, Ludwig A. *Adv Funct Mater* 2010;20:1917.
- [58] James RD, Zhang Z. A way to search for multiferroic materials with “unlikely” combinations of physical properties, In: Planes A, Mañosa L, Saxena A (Eds.). *Magnetism and Structure in Functional Materials*. Berlin: Springer Berlin Heidelberg; 2005.
- [59] Gall K, Maier HJ. *Acta Mater* 2002;50:4643.
- [60] McCluskey PJ, Zhao C, Kfir O, Vlassak JJ. *Acta Mater* 2011;59:5116.
- [61] Kockar B, Karaman I, Kim JI, Chumlyakov Y. *Scripta Mater* 2006;54:2203.
- [62] Atli KC, Karaman I, Noebe RD, Garg A, Chumlyakov YI, Kireeva IV. *Acta Mater* 2011;59:4747.

## Tables

Table 1: Calorimetric cell labeling with corresponding chemical composition (at%). The Ti, Ni, and Hf uncertainties are approximately 0.3, 0.4 and 0.1 at% respectively.

Table 2: Martensite-austenite transformation characteristics for compositions demonstrating a transformation in the calorimetric signal.

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