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Transformation behavior in NiTi-20Hf shape memory alloys – Transformation temperatures and hardness

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ABSTRACT

A series of NiTi-20Hf high-temperature shape memory alloys with varying nickel content from 50 to 51% were subjected to solution and aging heat treatments, thermal cycling, and hardness testing. Transformation temperatures for all conditions were measured and found to decrease as a function of increasing Ni content up to 50.5%. There was a gradual increase or consistent temperature for Ni contents above 50.5%, depending on the aged or homogenized condition. A similar trend was observed in the hardness values. The alloys aged at 550 °C for 3 h exhibited the highest hardness with an even greater increase at Ni contents above 50.5%.

Many applications in aeronautics, automotive, and other practices with high temperature requirements (>100 °C) can be made possible with the development of higher transition temperature NiTiHf shape memory alloys. Nickel-rich NiTi-Hf alloys have been shown to possess excellent shape memory effect and superelastic properties at a much lower cost than the precious metals containing alternatives [1,2]. These compositions can be strengthened by aging to produce fine, nanometer-size precipitates, while still generating sufficient work output and dimensional stability [3]. Of particular interest are nickel-rich NiTi-20Hf (at.%) alloys, which have been extensively investigated in recent years with batch sizes ranging from small arc melts to larger induction melts [4–6].

It is typically easier to achieve the target composition for small heats (i.e., a few grams) such as arc melts since the charge weight (before melting) and the button weight (after melting) can be matched to confirm no loss of alloying material and low oxygen pickup during the controlled-melting process. However, it is more challenging to consistently produce identical material compositions when dealing with larger heats (e.g. >20 kg), for example, using vacuum induction melting (VIM) or induction skull melting (ISM), especially in this Ni-rich version where only 0.1 at.% nickel variation can yield large temperature shifts [7]. As a result, the target and actual compositions can vary, and some measurement technique is required to pinpoint the differences. Conventional methods for determining these elemental compositions in shape memory alloys (SMAs) have been energy dispersive X-ray spectroscopy (EDS), inductively coupled plasma optical emission spectrometry (ICP/OES), X-ray fluorescence (XRF), or an atom probe. Although some of these methods can be accurate to parts per million ranges for low-level constituents, for major constituents, the accuracy can be as low as ±2% of the measured value. Other methods that can provide an accuracy of at least 0.1 at.% require some sort of calibration with standards for each measurement. Thus, it is still impractical to decipher the small percentages required to classify the alloy. In fact, this matter is not unique to the NiTiHf alloys, but has persisted in the SMA industry for years and is of such importance due to the high compositional sensitivity of these alloys. As a result, SMAs are more easily categorized by transformation temperatures and not by chemical composition.

There exist various data for binary NiTi that help correlate the transformation temperatures to compositions [8,9]. However, with the current Ni-rich NiTi-20Hf alloys, studies on the effect of Ni-content for limited compositions and heat treatments [10] provide no direct correlations with the higher transition temperature range. Thus, the goal of this work is to carry out an investigation on the effect of nickel content in the range of 50–51% on the transformation behavior for the NiTi-20Hf alloys.

The $Ni_{50+X}Ti_{30-X}Hf_{20}$ (X = 0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1 at.%) alloys were arc melted in buttons of ~30 g using high purity elemental constituents. The melting was performed in a water-cooled copper crucible under an argon atmosphere using a non-consumable tungsten electrode. Each button was inverted and re-melted five times to ensure complete mixing. Buttons were then vacuum-homogenized at 1050 °C for 72 h followed by furnace cooling. Specimens were

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machined using wire electrical discharge machining (EDM) from the buttons and subjected to solutionizing or additional heat treatment from the homogenized condition to assess the effect on hardness and transformation temperatures as outlined later. For comparison, the elemental compositions were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) for metallic elements, and LECO® Nitrogen/Oxygen and Carbon/Sulfur determinators for nitrogen, oxygen, and carbon contents. Differential scanning calorimetry (DSC) analyses were conducted using a TA Instruments Q1000 with a heating/cooling rate of 10 °C/min. Each specimen was cycled 10 times between −80 and 370 °C. Hardness measurements were conducted on mechanically polished samples using a Struers DuraScan automated Vickers microhardness tester with 1 kgf applied load for 13 s.

Fig. 1 shows the ICP results of the measured composition compared to the target composition for nickel (Ni), titanium (Ti), and hafnium + zirconium (Hf + Zr). For each alloy, two measurements were performed on the same sample, in addition to a third measurement on an independent sample for select alloys. It is clear that a trend can be observed that follows the target line, but the data scatter is too large to pinpoint the correct chemistry. For instance, the target 50.2% Ni alloy, labeled "H2" in Fig. 1a, has a scatter of approximately 1 at.% Ni, which is the whole range of this study. Similarly, the target 51% Ni alloy, labeled "H10" in Fig. 1b, has a scatter of 0.7% Ti, which is again very broad. While the range of the ICP measurements can vary based on the sample matrix, levels of analytes, and the type of elements, the current ICP accuracy in Ni, Ti, and Hf + Zr elements is ±2% relative to the amount reported. Therefore, this current method is not sufficiently accurate to identify the small changes in Ni-content and the concomitant effect on the transformation temperatures. Amongst all the alloys, the measured carbon, nitrogen, and oxygen contents were very similar at an average of 0.0059, 0.0009, and 0.0207 wt%, respectively.

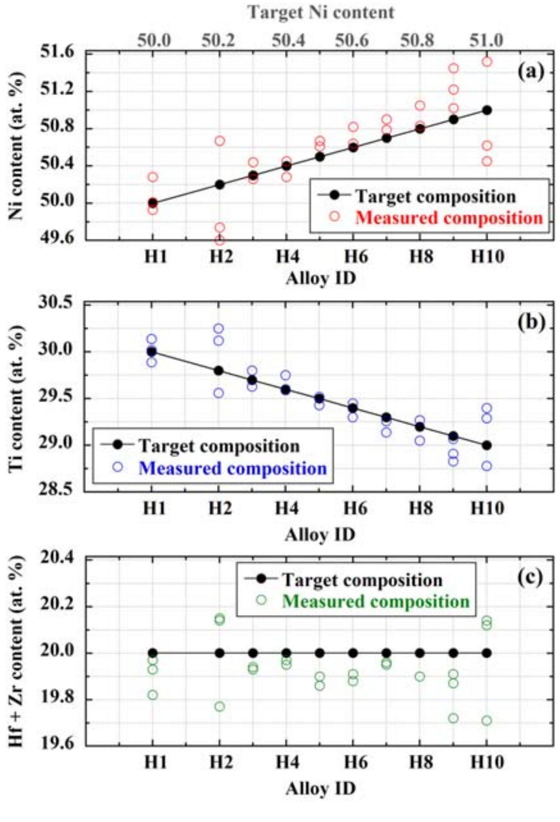

Fig. 1. Measured compositions using inductively coupled plasma atomic emission spectroscopy (ICP-AES) compared to the target compositions for (a) nickel, (b) titanium and (c) hafnium + zirconium (Hf + Zr). The labels H1 through H10 correspond to the alloys with a Ni-content of 50 through 51 at.%, respectively.

Fig. 2 shows the characteristic transformation temperatures: martensite start (M_s), martensite finish (M_f), austenite start (A_s), austenite finish (A_f) and thermal hysteresis obtained by DSC. From this point forward, it is anticipated that the target compositions match the actual compositions since the starting and ending weights were consistent. It is clearly shown that the transformation temperatures are highest at the 50% Ni content and gradually decrease as a function of increasing nickel up to the 50.5% Ni alloy for the homogenized conditions. Then, the transition temperatures slightly increase as the nickel content increases. Considering just the overall composition, the transformation temperatures are expected to drop as the Ni increases. However, keeping in mind that the homogenized alloys were furnace cooled, the slow cooling rates (~20 °C/min from 1050 to 700 °C, which reduces to ~10 °C/min at 600 °C) appeared to promote the formation of precipitates for alloys above 50.5% Ni [11]. This is confirmed by solutionizing the alloys at 1050 °C for 3 h followed by a water quench. At 50.5% Ni and below, the temperatures of the homogenized and solutionized alloys are comparable -indicating no presence of precipitates or scarce precipitation nuclei with no effect on the temperatures. For higher Ni-content, it is clear that the temperatures deviate largely where, as expected, the transformation temperatures of the solutionized conditions continue dropping, but the homogenized conditions generally increase. This trend is mainly attributed to the high driving force for precipitation in the alloys with nickel above 50.5 at.%. It is noted that no phase transformation was observed in the solutionized 50.9 and 51% Ni alloys down to the instrument's cold limit of −150 °C.

Three additional aging heat treatments after homogenization were considered to evaluate the effect of precipitates on the transformation temperatures. It is known from prior work [4] that aging at 550 °C for 3 h (peak aged condition) promotes nucleation of precipitates known as the H-phase. In this work, the same aging parameters were adopted in addition to 400 °C (underage) and 650 °C (overage) conditions for 3 h followed by air cooling. The 400 °C aging is shown to not affect the overall transformation temperatures as all alloys matched the homogenized case. It could be resolved that this aging (or lack thereof) has a slight effect on the alloys with Ni-content above 50.5%. However, the changes are very minimal at approximately +5 °C in some alloys. Going to the higher aging temperature of 550 °C, the transition temperatures are affected more and shown to increase considerably between 50.2 and 50.7% alloys, with smaller changes recorded for alloys above 50.7%. The increase in temperature was attributed to the formation and/or growth of the H-phase, which makes the matrix enriched with Ti as the Ni was depleted [12]. For the alloys above 50.7%, it was established that precipitates had already formed during the homogenization step, and this added aging promoted more growth, but with less impact on temperatures.

Finally, the 650 °C aging condition proved to have a different effect where the transformation temperatures increased in the 50.2Ni to 50.6%Ni alloys, but decreased in alloys above 50.7% Ni. In these higher Ni alloys, precipitates already present from homogenization begin to diminish, as the solvus temperature is approached. This results in more Ni going back to the matrix manifested as lower transformation temperatures.

The thermal hysteresis as a function of Ni-content for each heat treatment is shown in Fig. 2e. The hysteresis, defined here as austenite finish minus martensite start (A_f–M_s), provides an indication of transformation reversibility and ultimately stability, although the current data is generated under no-load conditions. It is shown that the hysteresis starts at ~40 °C at 50% Ni, goes down to approximately 30 °C at 50.5% Ni, followed by a severe increase to as high as 70 °C in the 51% Ni alloy. For the lower Ni-content alloys (<50.5%), the hysteresis is smaller in all aging conditions commensurate with favored transformation paths and possibly small size and fractions of precipitates. Higher Ni-content coupled with the higher propensity for greater precipitates type and size, impede the transformation path and the reversibility is further hindered resulting in a wider hysteresis. The same trend is