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Effects of nanoprecipitation on the shape memory and material properties of an Ni-rich NiTiHf high temperature shape memory alloy

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Abstract

Shape memory properties of a $Ni_{50.3}Ti_{29.7}Hf_{20}$ (at.%) polycrystalline alloy were characterized after selected heat treatments. The effects of heat treatment temperature and time on the transformation temperatures (TTs) and temperature hysteresis were determined by differential scanning calorimetry. Thermal cycling under constant compressive stress was carried out to reveal the changes in transformation strain, temperature hysteresis, and TT as a function of stress. Isothermal stress cycling experiments were conducted to reveal the critical stresses, transformation strain, and stress hysteresis as a function of temperature. The crystal structure and lattice parameters of the transforming phases were determined by X-ray diffraction at selected temperatures. Precipitate characteristics and martensite morphology were revealed by transmission electron microscopy. Precipitation was found to alter the martensite morphology and significantly improve the shape memory properties of the Ni-rich NiTiHf alloy. For the peak aged condition shape memory strains of up to 3.6%, the lowest hysteresis, and a fully reversible superelastic response were observed at temperatures up to 240 °C. In general, the nickel-rich NiTiHf polycrystalline alloy exhibited a higher work output (≈16.5 J cm^{-3}) than other NiTi-based high temperature alloys.

Keywords: Shape memory alloys; Phase transformations; High temperature; NiTiHf; Mechanical tests

1. Introduction

Shape memory alloys (SMA) are an extraordinary group of materials that can produce very high recoverable shape changes, stresses, and work outputs as a result of a reversible martensitic phase transformation. Due to their remarkable properties, which can be used for a variety of applications, such as actuation, vibration damping, and noise reduction, SMAs have permeated into the mainstream of many industries, particularly in the biomedical, automotive, energy, and aerospace fields [1–4].

NiTi is the most explored and also the most widely utilized SMA due to its good dimensional stability, superior shape memory properties, corrosion resistance, biocompatibility, ductility, and high work output capability. However, it can only operate below 100 °C due to its low martensitic transformation temperature [5]. This limitation in conventional NiTi alloys has resulted in the development of "high temperature shape memory alloys" (HTSMAs), designed to operate at temperatures above 100 °C. Recently the aerospace, automotive, oil, and many other industries have become interested in compact, lightweight, high force and high strain HTSMAs, since SMAs intrinsically possess higher energy densities than most conventional actuators. Furthermore, they are robust,

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frictionless, do not require extraneous systems, such as hydraulic or pneumatic lines, and are easier to inspect and maintain [5,6].

Large additions of ternary elements (⩾15 at.%) have been added to NiTi alloys to increase the transformation temperatures (TTs), while attempting to maintain the good mechanical and functional properties of the base alloy. The addition of Hf, Zr, Pd, Pt, and Au are known to increase the TTs, but they also decrease ductility and make processing more difficult [6–8]. Among the potential HTSMA systems NiTiHf seems to be the most promising for a wide range of applications in the critical 100–250 °C temperature range, primarily due to the low cost of Hf. It has also been reported that Hf has a greater influence on the TTs than Pd and Au at an equivalent concentration [5,8,9].

It is well known that the TTs of NiTi-based SMAs are highly composition dependent [6,10], including NiTiHf alloys [11,12]. The TTs of NiTiHf alloys do not increase much up to 10 at.% Hf, but at concentrations higher than 10 at.% the TTs increase linearly with Hf content and by 30 at.% Hf reach 525 °C [9,11]. However, NiTiHf alloys exhibit poor mechanical and functional properties, including a large temperature hysteresis (>50 °C), low strength, a low transformation strain (when compared with NiTi), a lack of cyclic stability due to the high stresses required for reorientation of martensite and detwinning, and a low resistance to slip, leading to plastic deformation of both the martensite and austenite phases at relatively low stresses [9].

Among the most common methods employed to improve the shape memory and mechanical properties of SMAs are thermo-mechanical processing, precipitate hardening, solid solution hardening, and grain refinement of polycrystalline alloys [1,6,9,11,13–17]. In general, cold working improves the shape memory behavior by increasing the stress required for slip, resulting in higher values of recoverable strain ε_{rec} [6]. Goldberg et al. [16,17] reported that the shape memory properties of a $Ti_{50}Ni_{20}Pd_{30}$ HTSMA improved remarkably after thermo-mechanical processing, which consisted of cold rolling up to a 25% reduction in thickness and subsequent annealing at 400 °C for 1 h. This treatment increased the yield strength of the martensite phase from ≈200 to 400 MPa at 170 °C. ε_{rec} also significantly improved, as a 5.3% applied strain was fully recovered (under stress-free conditions) when the samples were heated above the austenite finish temperature (A_f) in comparison with the mere 2.5% strain recovered for the solution-treated alloy after tensile deformation at 170 °C. In addition, a type of linear superelastic behavior was reported for the first time in a NiTiPd alloy due to the thermo-mechanical treatment (cold working followed by annealing).

Previously Meng et al. [13] examined the tensile properties of (Ti + Hf)-rich NiTiHf alloys and did not observe a stress plateau at room temperature but rather observed continuous yielding with high work hardening, which can be attributed to the high resistance to martensite reorientation and the low stress needed for plastic deformation. To increase the resistance to dislocation slip Kockar et al. [9] employed severe plastic deformation of (Ti + Hf)-rich NiTiHf alloys and reported an increase in the recoverable strain and a decrease in the irrecoverable strain levels during isobaric thermal cycling experiments. They also found that thermal cyclic stability improved and thermal hysteresis decreased. However, the large thermal hysteresis prevented the observation of a reversible superelastic response [9].

Unfortunately, the majority of prospective HTSMA systems are ordered intermetallics with limited ductility at low and intermediate temperatures, making it difficult and expensive to apply thermo-mechanical processing techniques to increase the material strength. Thus precipitate hardening becomes a more viable method for increasing the strength of difficult to work alloys. The precipitates act as obstacles in the path of dislocations, which must then either cut through the precipitate or bypass it to proceed. Of course, the strengthening ability of the precipitates depends on the size, volume fraction, interparticle spacing, and coherency of the second phase. Until recently most HTSMA research was focused on (Ti + Hf)-rich NiTiHf alloys due to the low TTs of Ni-rich materials. Meng et al. [10] revealed that it was possible to form $(Ti,Hf)_3Ni_4$ precipitates in Ni-rich NiTiHf alloys and in the process restore the TTs to a higher temperature. They also reported that these coherent precipitates increased the matrix strength and enhanced the thermal stability of the alloy [10,18]. Since those original studies by Meng et al. much more thorough and detailed analyses have been performed on the structure of the precipitate phase in Ni-rich NiTiHf alloys [19,20]. The results of these comprehensive studies indicate that the precipitate is not the $(Ti, Hf)_3Ni_4$ phase as originally reported [10], but is rather a new and much more complicated structure referred to as the H-phase.

Recently the shape memory and superelastic behaviors of a Ni-rich NiTi–20Hf alloy were studied by Bigelow et al. [21], who reported high TTs, near perfect dimensional stability without training, and a maximum work output of 18.7 J cm^{-3} in isobaric thermal cycling experiments. In addition, they observed near perfect superelastic behavior at up to 3% applied strain at high temperatures (180–220 °C). A follow-up in situ neutron diffraction study of the same alloy by Benafan et al. [22] indicated that the near perfect dimensional stability was a result of the exceptional microstructural stability exhibited by the alloy and could be attributed to the second phase. While Bigelow et al. [21] examined the preliminary superelastic response of the NiTi–20Hf alloy in tension, Coughlin et al. [23] performed a more thorough study of the superelastic response of this alloy in compression as a function of aging condition over a temperature range of about 150–290 °C. In addition, Evirgen et al. studied the effect of aging on the martensitic transformation behavior of an Ni-rich NiTi–15Hf HTSMA [24]. They reported a decrease in the TTs after short-term aging at 450 and 500 °C due to the extremely small inter-