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Role of severe plastic deformation on the cyclic reversibility of a $Ti_{50.3}Ni_{33.7}Pd_{16}$ high temperature shape memory alloy

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Abstract

The present work focuses on the effect of microstructural refinement on the thermo-mechanical cyclic stability of a $Ti_{50.3}Ni_{33.7}Pd_{16}$ high temperature shape memory alloy (HTSMA) which was severe plastically deformed using equal channel angular extrusion (ECAE). The grain/subgrain size of the high temperature austenite phase was refined down to about 100 nm, the lowest reported to date in HTSMAs. The increase in strength differential between the onset of transformation and the macroscopic plastic yielding after ECAE led to a notable enhancement in the cyclic stability during isobaric cooling–heating experiments. The reduction in irrecoverable strain levels was attributed to the increase in critical stress for dislocation slip due to the microstructural refinement during the ECAE process.

Keywords: TiNiPd; High temperature shape memory alloys; Severe plastic deformation; Equal channel angular extrusion; Equal channel angular pressing

1. Introduction

NiTi shape memory alloys (SMAs) have revolutionized the development and use of active materials in the last 40 years by providing large reversible shape changes, high actuation forces, and large elastic strains as a result of thermoelastic martensitic transformations. The development of SMA actuators has recently been a priority in space, automotive and power generation applications, where high operating temperatures are needed. However, the low operation temperatures (<100 °C) and relatively large transformation hysteresis of binary NiTi limit their utility in high temperature applications [1]. Luckily, the transformation temperatures of NiTi can be controlled by the addition of alloying elements. For instance, Pd addition at more than 10 at.% increases the transformation temperatures to above 100 °C [2,3].

NiTi-based ternary alloys with the addition of one of Pd, Pt, Zr, Au, or Hf have been the most studied high temperature shape memory alloys (HTSMAs) to date [2–5]. The addition of Zr and Hf could be more favorable as a third alloying element due to their low cost, however, NiTi alloys with Zr and Hf exhibit unstable shape memory properties and their thermal and stress hystereses are large [4,5]. The addition of Pt to a NiTi binary alloy would massively increase the cost. Therefore, Pd could be a better choice as a third alloying element considering the increase in transformation temperatures and the decrease in thermal hysteresis [2,6].

Dislocation plasticity that may accompany martensitic transformation is an important anticipated problem in NiTiPd HTSMAs, affecting the stability of the shape memory effect and superelasticity. A low critical stress for dislocation slip at high temperatures can easily cause the

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accommodation of transformation shear and volume change by dislocation slip, and cause dissipation of stored elastic energy during transformation. Eventually, this leads to an apparent permanent deformation, dimensional instability, and a lack of superelasticity [7,8]. Well-developed dislocation substructures, desired crystallographic texture, refined grain sizes, and coherent precipitates, all of which improve the critical stress for slip (CSS), have been reported as necessary conditions for cyclic and dimensional stability and for superelasticity in HTSMAs [9,10]. Four strategies have been proposed to achieve an increase in CSS: (1) addition of a quaternary element, (2) age hardening of the parent phase, (3) thermo-mechanical treatment and (4) severe plastic deformation (SPD) [10].

A limited number of studies have reported on the mechanical and shape memory properties of NiTiPd alloys. Cai et al. [7] showed that the shape memory behavior of TiNiPd alloys was fairly good when deformed at room temperature, however, became relatively poor with increasing deformation temperature in martensite due to a decrease in CSS. Lindquist and Wayman reported 6% unconstrained shape recovery [6]. Khachin et al. [11] showed 4% complete strain recovery, which was introduced by applying 200 MPa torsional stress in $Ni_{13}Ti_{50}Pd_{37}$. Otsuka and co-workers studied the shape memory effect in $Ti_{50}Pd_{50}$ [8]. They reported poor shape memory behavior, which could again be attributed to a low CSS possibly leading to a high density of slip upon deformation, in addition to the twinning in martensite [8]. NiTi alloys with 40–50 at.% Pd show only 0.5% shape recovery when loaded in tension [1].

Several attempts at enhancing the shape memory response of NiTiPd alloys have been reported. Yang and Mikkola [12] examined the effect of boron addition on the shape memory characteristics of a $Ni_{22.3}Ti_{50.7}Pd_{27}$ alloy and found 90% shape recovery for 2–3% applied strain under compression. Boron had no real effect on the shape memory characteristics. However, they determined an increase in ductility at room temperature and attributed this to grain refinement due to boron addition [12]. Another method to improve the shape memory characteristics of the NiTiPd alloys is to use slightly off-stoichiometric compositions and generate homogeneously distributed Ti_2Ni precipitates in a $Ni_{19.4}Ti_{50.6}Pd_{30}$ alloy [13]. 90% shape recovery was observed when a $Ni_{19.4}Ti_{50.6}Pd_{30}$ alloy was deformed to a total strain of 6% at 473 K. This was about 10% higher than that of $Ti_{50}Ni_{30}Pd_{20}$, in which precipitation was not observed. Such an increase was attributed to the hardening effect of the homogeneously distributed Ti_2Ni precipitates [13]. Moreover, certain thermo-mechanical treatments have been applied to modify the microstructure and strengthen the material via grain refinement and dislocation hardening. Golberg and co-workers reported some improvement in the shape memory properties of $Ti_{50}Ni_{30}Pd_{20}$ after cold rolling and subsequent heat treatment [14,15]. They claimed superelasticity for the first time in $Ti_{50}Ni_{30}Pd_{20}$ after annealing the alloy at 673 K and testing at 535 K [14,15]. Cai et al. [7] studied the effect of thermal cycling on the shape memory properties of $Ni_{19.4}Ti_{50.6}Pd_{30}$ and found that M_s temperature, total transformation strain, and irrecoverable strain increased with the number of cycles. The change in these parameters occurred quickly in the first 40 cycles and then tended to stabilize [7].

As an alternative to cold working, precipitation hardening and thermo-mechanical training, microstructural refinement using severe plastic deformation (SPD) should also bring about good cyclic reversibility and shape recovery in NiTiPd HTSMAs. SPD via high pressure torsion (HPT) leads to the formation of nanosized grains and amorphization in bulk binary NiTi samples, however, HPT samples are too small to investigate the shape memory properties of the alloys [16–18]. On the other hand, SPD via equal channel angular extrusion (ECAE) has several advantages over HPT, such as producing larger samples, introducing uniform deformation, and allowing some control over grain morphology and crystallographic texture. Our previous studies on ECAE of Ni-rich NiTi, equiatomic NiTi and TiNiHf HTSMAs have shown that SPD via ECAE enhances the cyclic stability and shape recovery behavior under relatively high stress levels by reducing the grain size and inducing fine dislocation substructures [10,19–22].

Most of the aforementioned studies on TiNiPd alloys demonstrated shape recovery of these alloys under stress-free conditions, and presented the isothermal mechanical properties and microstructure. Most applications, however, require shape recovery under applied stress and/or thermal cyclic stability under constant loads. Only one research group has recently reported the shape memory response of $Ni_{19.5}Ti_{50.5}Pd_{30}$ HTSMAs and corresponding work outputs during few thermal cycles under various loads, who observed irrecoverable strains at relatively high stress levels [23,24].

Thus, this work presents the first report on the SPD of a $Ti_{50.3}Ni_{33.7}Pd_{16}$ alloy produced by ECAE. We introduce the influence of ECAE on the evolution of microstructure, and cyclic reversibility and shape recovery during thermal cycling under stress. The material was ECAE processed at 425 °C following route E for four passes. The results show that the cyclic stability was dramatically enhanced after the ECAE process.

2. Experimental procedure

The $Ti_{50.3}Ni_{33.7}Pd_{16}$ alloy was prepared by vacuum induction melting. A cylindrical billet was then hot rolled at 925 °C down to 1.2 cm diameter. 10 or 12.5 cm long bars were canned in 304 stainless steel (SS) before ECAE. Both Ti (commercial purity grade 2) and 316 SS were explored as canning materials prior to using 304 SS. Ti was too soft at the processing temperature and caused the enclosed SMA billets to undergo severe shear localization during multipass ECAE. The high strain hardening of 316 SS at the extrusion temperature substantially increased the press