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Shape memory characteristics of $Ti_{49.5}Ni_{25}Pd_{25}Sc_{0.5}$ high-temperature shape memory alloy after severe plastic deformation

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Abstract

A $Ti_{49.5}Ni_{25}Pd_{25}Sc_{0.5}$ high-temperature shape memory alloy is thermomechanically processed to obtain enhanced shape-memory characteristics: in particular, dimensional stability upon repeated thermal cycles under constant loads. This is accomplished using severe plastic deformation via equal channel angular extrusion (ECAE) and post-processing annealing heat treatments. The results of the thermomechanical experiments reveal that the processed materials display enhanced shape memory response, exhibiting higher recoverable transformation and reduced irrecoverable strain levels upon thermal cycling compared with the unprocessed material. This improvement is attributed to the increased strength and resistance of the material against defect generation upon phase transformation as a result of the microstructural refinement due to the ECAE process, as supported by the electron microscopy observations.

Keywords: Martensitic transformation; High-temperature shape memory alloys; Equal channel angular extrusion; Severe plastic deformation; Dimensional stability

1. Introduction

TiNi shape memory alloys (SMA) have revolutionized several areas of engineering and medicine with numerous practical applications within the last two decades. Today, 40 years after its discovery, the number of prospective applications exploiting the shape memory effect is still increasing. Some of these applications are based on the use of SMA as solid-state actuators. This has naturally led to a growing interest in high-temperature SMA (HTSMA) capable of actuation at elevated temperatures [1]. However, commercial TiNi alloys have relatively low transformation temperatures, limiting their use below 373 K (100 °C) [2]. SMA actuators with higher transformation temperatures are needed, especially in aviation and space applications and in the automotive and oil industries, where a high energy density and compactness are sought after.

Attempts at alloying TiNi with Pd, Pt, Au, Hf and Zr have successfully increased the transformation temperatures of the base alloy [3–10]. But very recently, additions of Pd and Pt have attracted extra attention compared with other alloying elements, since many favorable attributes of binary TiNi, such as high work output, ductility and workability, can be maintained to a reasonable extent in these ternary alloys [11–15]. In terms of transformation temperatures, TiNiPd alloys are capable of martensitic transformations up to 773 K (500 °C). However, as with any material exposed to high temperatures, HTSMA also suffer from thermally driven mechanisms such as recovery, recrystallization and creep, in addition to transformation-induced plasticity. These problems contribute to the deterioration of shape memory behavior, especially at high temperatures, significantly affecting the dimensional stability of the material in operation. Some of the proposed

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solutions to these problems are: (a) solid-solution hardening by quaternary alloying [11]; (b) thermomechanical processing, including cold working followed by post-deformation heat treatments [16–19]; and (c) precipitation hardening. All these possibilities are geared towards increasing the critical stress for slip and strengthening the material against the formation of additional defects, so that any strain generated within the material during phase transformations would be reversibly accommodated, while minimizing inelastic deformation processes.

Although there is a substantial amount of work covering the effects of thermomechanical processing on the shape memory behavior of TiNi [17,20–25], data are quite limited for the TiNiPd system. Golberg et al. [5,26,27] studied the effects of cold rolling with different reductions and subsequent annealing at various temperatures on the shape memory behavior of $Ti_{50}Ni_xPd_{50-x}$ ($x = 10$, 15, 20). They recorded 100% recovery at a total strain of 5.3% for $Ti_{50}Ni_{20}Pd_{30}$, which was cold rolled down to a 24–25% thickness reduction and subsequently annealed at 673 K (400 °C) for 1 h [26,27]. The recovered strain level was more than twice that of the solutionized material, which was only ~2%. They also demonstrated a partial superelastic effect at $A_f + 10$ K in the same processed material for the first time for this alloy system. However, the strain recovery in this case was under an unbiased or stress-free condition.

Tian and Wu [28] investigated the mechanical properties of off-stoichiometric, cold-rolled and annealed $Ti_{50.6}Ni_{19.4}Pd_{30}$. They recorded unbiased, full recovery of up to 7.2% strain and up to 95% recovery at 11% applied strain after deformation at room temperature and subsequent heating above the A_f temperature. Wu and Tian [29] recorded a 7% recoverable superelastic strain in $Ti_{51}Ni_{19}Pd_{30}$ at 513 K (240 °C) after the sample was trained with multiple superelastic cycles. However, the relatively large strain values recorded in both of these studies are considered to be a result of erroneous strain measurements. An elastic strain of ~5% was reported for the superelastic loading of $Ti_{51}Ni_{19}Pd_{30}$, corresponding to an elastic modulus of 12 GPa for the austenite phase. However, a more realistic austenite modulus of ~65 GPa and elastic strain of <1% at a testing temperature of 582 K (309 °C) ($A_f + 50$ K) has been observed for a similar $Ti_{50.5}Ni_{19.5}Pd_{30}$ alloy [14,30].

Improvements in the shape memory properties of a $Ti_{50.5}Ni_{24.5}Pd_{25}$ alloy after 0.5 at.% Sc addition have previously been shown [11]. Sc was initially chosen as an alloying addition based on the results of atomistic simulations of quaternary additions to TiNiPd, similar to previous work by Bozzolo et al. for ternary additions to NiTi [31] and PdTi and PtTi [32]. Scandium was expected to have a wide range of solubility in TiNiPd, have a positive influence on the bond strength through an increase in the formation energy of the alloy, and increase the lattice strain, making it a potent solid solution strengthener. The present work aims to improve further the shape memory properties of $Ti_{49.5}Ni_{25}Pd_{25}Sc_{0.5}$ HTSMA through thermomechanical processing, using equal channel angular extrusion (ECAE) and post-ECAE annealing heat treatments.

ECAE is a severe plastic deformation (SPD) process where the sample is pressed through a die with two channels of equal cross section intersecting at an angle of usually 90° [33]. Large amounts of strain can be imposed on the sample without a change in its cross section, unlike traditional metal forming processes such as rolling, forging and conventional area-reduction extrusion. Since the cross section of the sample does not change after a single-pass extrusion, the extruded sample can be reinserted into the die and reprocessed to achieve even more plastic strain. For instance, it is possible with a four-pass ECAE operation to obtain an equivalent strain level of 99% thickness reduction in cold-rolling [34]. ECAE processing followed by recovery and annealing can be used to obtain materials with sub-micron grain size, which exhibit superior physical and mechanical properties [35,36]. There is a considerable amount of work on the SPD of TiNi SMA showing the effectiveness of ECAE in improving shape memory behavior [16–18,22,37–42]. The processed materials display better dimensional stability under cyclic loading, owing to increased resistance to slip and other defect-forming mechanisms. An alternative SPD method used to enhance the shape memory properties of TiNi SMA is high-pressure torsion (HPT), where nanocrystalline structures can be obtained after proper annealing of the processed samples [23,39,43,44]. The advantages of ECAE over HPT are that there is no sample size limitation with ECAE, and it is possible to apply large uniform strains on bulk samples. In addition, better control of the final texture and microstructure of the product can be achieved through different extrusion routes using ECAE [33].

In the present study, ECAE is used to refine the microstructure of a $Ti_{49.5}Ni_{25}Pd_{25}Sc_{0.5}$ HTSMA to improve its shape memory characteristics, especially the dimensional stability during thermal cycling under stress, which is of paramount importance for actuator applications. Post-ECAE annealing heat treatments are also performed to partially recover the deformed microstructure and further improve the shape memory characteristics.

2. Experimental procedures

The nominal composition of the alloy used in this study was $Ti_{49.5}Ni_{25}Pd_{25}Sc_{0.5}$ (at.%). The alloy was processed by induction melting of high-purity elemental constituents (99.98 wt.% Ni, 99.95 wt.% Ti, 99.995 wt.% Pd and 99.95 wt.% Sc) using a graphite crucible and subsequently casting into a thick-walled copper mold to produce a cylindrical ingot 25.4 mm in diameter and 102 mm long. The ingot was homogenized in a vacuum furnace at 1323 K (1050 °C) for 72 h and allowed to furnace cool. Following the homogenization process, the ingot was placed into a mild steel extrusion can and extruded at 1173 K (900 °C) with an area reduction ratio of 7:1. The extrusion can was used to prevent oxidation during the extrusion process