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Combined effects of work hardening and precipitation strengthening on the cyclic stability of TiNiPdCu-based high-temperature shape memory alloys

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Abstract

The combined effects of work hardening and precipitation strengthening were employed to improve the cyclic stability of TiNiPdCu-based high-temperature shape memory alloys. Annealing after cold deformation resulted in the formation of nano-scale TiPdCu and Ti_2Pd precipitates, stable at high temperatures in $Ti_{50}Ni_{25-x}Pd_{25}Cu_x$ alloys. The nano-scale precipitates were also observed to retard recovery/recrystallization processes at higher temperatures. It was found that the combined effects of work hardening and precipitation strengthening remarkably enhanced the high-temperature stability of the $Ti_{50}Ni_{20}Pd_{25}Cu_5$ alloy and increased its maximum working temperature range while keeping the transformation temperatures and recovery strains at sufficiently high levels. Precipitation strengthening helped to greatly improve the high-temperature cyclic stability of the alloy. Creep tests at 673 K under 500 MPa confirmed that the better high-temperature cyclic stability of the precipitate-containing alloy was mainly due to its higher creep resistance.

Keywords: High-temperature shape memory alloys; Nano-scale precipitates; Thermomechanical treatment; Hysteresis

1. Introduction

High-temperature usage of shape memory alloys requires some additional characteristics to perform the desired functions successfully compared with their low-temperature counterparts. At high temperatures these materials face a serious threat from thermally driven mechanisms, i.e. dimensional instability due to creep deformation, recovery and recrystallization processes and transformation induced plasticity [1–9]. TiNiPd-based high-temperature shape memory alloys offer an attractive set of properties which make them worthy of study, especially for the high-temperature functional applications, i.e. high transformation temperatures, small hysteresis and adequate workability. These alloys are capable of significant strain recovery under stress-free as well as constrained conditions upon heating [10–16]. Similar to all other metallic materials, the performance of TiNiPd-based alloys is significantly affected when they are used at high temperatures. Also, resistance to permanent deformation is dependent upon compatibility between the cubic B2 and orthorhombic B19 phases in these alloys. Compatibility between the two phases is strongly dependent upon the Pd content of the alloy. $Ti_{50}Ni_{39}Pd_{11}$ alloy has been reported to exhibit very low hysteresis because of the excellent phase compatibility between the two transforming phases. Although the transformation temperatures

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can be increased by increasing the Pd content, the hysteresis is also increased because of a loss of compatibility and, as a result, the resistance to permanent deformation decreases, especially during thermal cycling under load at higher temperatures [17,18]. The situation further deteriorates if the load is increased [19]. Moreover, the susceptibility to permanent deformation increases as the maximum temperature to which the alloy is thermally cycled is increased, because of creep or viscoplastic deformation [1–6]. This actually imposes a limit on the maximum reverse transformation temperature range of TiNiPd-based alloys.

Several techniques have been used to improve the dimensional stability of these alloys, including precipitation hardening, thermo-mechanical treatment, aging, training and quaternary element addition [3,20–27]. Atli et al. reported improved high-temperature functional characteristics of TiNiPd alloys by the quaternary addition of 0.5 at.% Sc. According to their claim micro-alloying of Sc improves the dimensional stability of TiNiPd alloys through a solid solution strengthening mechanism [20]. Improvements in the shape memory characteristics due to Cu addition have been previously reported for $Ti_{50}Ni_{25-x}Pd_{25}Cu_x$ alloys. Replacement of Ni with Cu causes an increase in the lattice parameters of orthorhombic B19 martensite and improves the strength through solid solution strengthening [3]. Goldburg et al. reported the beneficial effects of different percentages of cold deformation and subsequent annealing at various temperatures on the shape memory characteristics of $Ti_{50}Ni_xPd_{50-x}$ alloys ($x = 10$, 15, 20). They reported 100% recovery of a 5.3% total strain in a thermo-mechanically treated $Ti_{50}Ni_{20}Pd_{30}$ alloy [21]. Shimizu et al. reported an improvement in the shape memory characteristics of Ti-rich TiNiPd alloys due to the formation of fine Ti_2Ni type precipitates [22]. Kocker et al. reported significant improvement in the cyclic stability of a $Ti_{50.3}Ni_{33.7}Pd_{16}$ alloy due to microstructural refinement down to the 100 nm scale achieved by a severe plastic deformation process [23]. Although the strengthening mechanism, i.e. work hardening or grain refinement after severe plastic deformation, proved to be effective in improving the cyclic stability of TiNiPd-based alloys, this stability is still questionable when higher working temperatures are involved, at which recovery and recrystallization softening mechanisms and creep or viscoplastic deformation mechanisms could become real problems. It is also well known that if the amount of work hardening is increased, in order to increase the strength of metallic materials, recovery and recrystallization are also accelerated, nullifying the work hardening effects at higher working temperatures [28,29].

Only a small number of studies have been reported which explain the high-temperature shape memory response and creep behavior of TiNiPd-based high-temperature shape memory alloys [1–3]. In our previous research it was found that in a $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloy very high densities of nano-scale precipitates of TiPdCu and Ti_2Pd were preferentially formed at heterogeneous nucleation sites provided by deformation-induced defects as a result of spinodal type decomposition [30]. It was also observed that the alloying addition of Cu played an important role in precipitation of the nano-scale precipitates. These precipitates were found to be stable at temperatures >773 K. In the present research a systematic study of the effect of Cu content on the precipitation behavior and transformation temperatures of TiNiPdCu alloys was conducted. A combination of work hardening and precipitation strengthening was also employed to improve the high-temperature cyclic stability and increase the effective working range of TiNiPd-based alloys. Another important purpose of the introduction of nano-scale precipitates in the cold deformed microstructure was to investigate the resistance of these precipitates to softening mechanisms, i.e. recovery and recrystallization, which actually nullify the strain hardening effects.

2. Experimental procedures

$Ti_{50}Ni_{25-x}Pd_{25}Cu_x$ alloys ($x = 0$, 3, 5, 7.5, 10) were prepared using the argon arc melting method. Hereafter, the alloys are referred to according to their Cu contents (at.%), i.e. 0Cu, 3Cu, 5Cu 7.5Cu and 10Cu. The ingots were melted six times and flipped over after each melting in order to maximize the homogeneity. The ingots were sealed under vacuum in a quartz tube and homogenized at 1223 K for 7.2 ks. The homogenized ingots were sliced into 1 mm thick plates and these plates were cold rolled up to 40%. Specimens for X-ray diffraction (XRD), differential scanning calorimetry (DSC), shape memory testing and microstructural observations were cut using an electro-discharge machine. Thermomechanical treatments were done by annealing the 40% cold rolled samples at various temperatures between 673 and 973 K in Ar filled quartz tubes for 3.6 ks. Solution treatment of some samples was carried out at 1173 K for 3.6 ks in Ar filled quartz tubes for comparison purposes. All the heat treatments were followed by water cooling without crushing the quartz tubes. Phase constitutions at 298 K were determined by XRD analysis using a Cu Kα source. Transformation temperatures were determined by DSC using a heating and cooling rate of 10 K min^{-1}. Microstructural investigations of some selected alloys were carried out by transmission electron microscopy (TEM) (JEOL 2010F). TEM specimens were prepared at 233 K by twin jet electro-polishing using an electrolyte consisting of 85 vol.% methanol (CH_3OH) and 15 vol.% sulfuric acid (H_2SO_4). Shape memory behavior was characterized by thermal cycling under various constant tensile stress levels. Constant stress thermal cycles were conducted after initial loading in the austenite state at various stress levels within the range 50–600 MPa in order to investigate the shape memory behavior. Thermal cycles at a stress of 500 MPa within the temperature range 300–673 K were carried out to assess the high-temperature training response of the alloys. Creep tests at a constant stress of 500 MPa and at 673 K temperature were also