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Formation of nanoscaled precipitates and their effects on the high-temperature shape-memory characteristics of a $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloy

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Abstract

The effects of thermomechanical treatment on the microstructure and high-temperature shape-memory characteristics of a TiNiPdCu alloy were investigated. An unexpected precipitation behavior was identified in a $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloy. Very high densities of nanoscale precipitates of TiPdCu and Ti_2Pd types were found to be formed in the thermomechanically treated $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloy. A spinodal type of decomposition process was expected to be the cause of the observed precipitation behavior. It was noticed that the preferential diffusion of Cu atoms towards the heterogeneous nucleation sites promoted the precipitation of TiPdCu-type precipitates, which in turn promoted the precipitation of fine Ti_2Pd-type precipitates. These precipitates greatly increased the resistance against the transformation-induced plasticity and creep deformation, especially at high stresses and high temperatures, mainly because of the high-temperature stability of these precipitates. High densities of these nanoscaled precipitates caused an anomalous increase in hardness and retarded the martensitic transformation. It was expected that the current research results could be highly beneficial for the development of high-temperature shape-memory alloys stable at temperatures >773 K, while keeping the benefits of ease of fabrication.

Keywords: TiNiPd; High-temperature shape-memory alloys; Precipitation strengthening; Thermomechanical treatment; Cold deformation

1. Introduction

High-temperature shape-memory actuators for power generation, space exploration applications and automotive applications have attracted much research interest recently [1–5]. Binary TiNi shape-memory alloys (SMA) do not fulfill the requirement of high transformation temperatures [6]. Some ternary alloys such as TiNiPt, TiNiAu, TiNiZr, TiNiPd and TiNiHf have been reported to exhibit high transformation temperatures [7–10]. TiNiPd, TiNiPt and TiNiAu alloys are well known to exhibit shape-memory effect at high temperatures along with a small hysteresis. The transformation temperature range in these alloys can be altered between 373 and 1073 K by changing the amount of ternary alloying elements [7,11]. The relatively less costly TiNiHf and TiNiZr alloys also exhibit high transformation temperatures, but their thermal hysteresis is much larger (~45 K), which makes them unattractive for the actuator type of applications. Moreover, the addition of Hf or Zr causes drastic deterioration in the ductility, which makes them difficult to process [12–14]. In TiNi-based ternary high-temperature shape memory alloys, Pd is considered a better choice as a third alloying element because it offers an attractive combination of high transformation temperatures, small hysteresis, adequate workability and a relatively lower cost compared with Au and Pt [15–19].

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At high temperatures, the functional performance of TiNiPd alloys is seriously degraded because of the transformation-induced plasticity and creep, which become much easier at higher temperatures [20–22]. It has been reported earlier that a $Ti_{50}Ni_{39}Pd_{11}$ alloy exhibits very small hysteresis because of the excellent phase compatibility condition. If the Pd content is increased in order to increase the transformation temperatures, the hysteresis is also increased because of the loss of compatibility between the B2 parent phase and B19 martensite phase and, as a result, the resistance against the permanent deformation becomes worse, especially during thermal cycling under load. This situation further deteriorates if the load level is increased [3,23]. Also, the permanent deformation increases as the maximum temperature, to which the alloy is thermally cycled, increases. This actually puts a limit on the maximum reverse transformation temperature of TiNiPd-based alloys. Therefore, the main focus of the recent research in the area of TiNiPd alloys has been directed to improving the resistance against permanent deformation at high temperatures. These alloys have been researched quite extensively in the recent past, and a number of efforts have been exhausted to further improve their performance, especially for their use at high temperatures, i.e. quaternary alloying addition, thermomechanical treatment and annealing after severe plastic deformation [24–28].

Precipitation hardening has been reported as an effective way to significantly improve the shape-memory properties of TiNi-based binary alloys [29–35]. Different types of precipitates and precipitation mechanisms have also been reported in TiPd- and TiNiPd-based high-temperature shape memory alloys. Shimizu et al. [36] claimed that the improvement in the shape-memory characteristics of Ti-rich TiNiPd alloys was due to the formation of fine Ti_2Ni-type precipitates. Matsuda et al. [37] reported the precipitation mechanism of different morphologies of Ti_2Pd precipitates formed in the B2 parent phase and B19 martensite phase in Ti-rich TiPd alloys. Delville and Schryvers [38] reported a new mode of precipitation in a B19 martensitic $Ti_{50}Ni_{30}Pd_{20}$ high-temperature shape memory alloys, which described a mechanism of combined precipitation of $Ti_2Ni(Pd)$ and $Ti_2Pd(Ni)$ precipitates. Lin et al. [39] reported the precipitation of Ti-rich Ti_2Pd- and Cu-rich $Ti(Cu, Pd)_2$-type precipitates in a $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloy aged within the temperature range of 723–923 K for 21.6 ks. They reported the effect of these precipitates on the transformation temperatures, but did not explain the precipitation mechanism of these precipitates in an equiatomic composition of $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$.

The present research results revealed the thermally activated preferential precipitation of Cu-rich TiPdCu-type precipitates at the heterogeneous nucleation sites in a $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloy when it was annealed at various temperatures after cold deformation. It was noticed that a very strong relationship existed between the pre-heat-treatment condition and the precipitation behavior. It was observed that cold deformation induced a high density of defects, i.e. point defects or dislocations, which promoted the precipitation of very high densities of nanoscaled Cu-rich TiPdCu-type and Ti-rich Ti_2Pd-type precipitates as a result of a spinodal type of decomposition. The evolution of these precipitates with respect to the annealing temperatures is also discussed in the current study. This precipitation behavior was not observed in a ternary $Ti_{50}Ni_{25}Pd_{25}$ alloy. At the end, a possible mechanism of the combined precipitation of nanoscaled TiPdCu- and Ti_2Pd-type precipitates in the $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloy was proposed. Based on the current study, it was expected that, if properly controlled, these precipitates could be highly beneficial to expand the high-temperature functional range beyond 773 K and to improve the dimensional stability of the TiNiPd-based alloys, especially in severe working environments at high temperatures and high stresses.

2. Experimental procedure

$Ti_{50}Ni_{25}Pd_{25}$ and $Ti_{50}Ni_{15}Pd_{25}Cu_{10}$ alloys were prepared using the Ar-arc melting method. Hereafter, the alloys are referred to as 0Cu and 10Cu according to their Cu content. The ingots were melted six times and flipped over after each melting. Then they were sealed in vacuum in a quartz tube and homogenized at 1223 K for 7.2 ks. The homogenized alloys were cold-rolled up to 40%. The cold-rolled samples were annealed at various temperatures within the temperature range 623–973 K for 3.6 ks. Hereafter, these samples are called annealed samples. Solution treatment of some samples was done at 1173 K for 3.6 ks. Some solution-treated samples were aged at 773 K for 3.6 ks for comparison purposes. Hereafter, these samples are called aged samples. All the heat treatments were done in Ar-filled quartz tubes followed by water cooling without crushing the tubes.

Specimens for hardness testing, X-ray diffraction (XRD), differential scanning calorimetry (DSC) and microstructural observations were cut using an electro discharge machine. Microhardness tests were performed at 298 K on an Akashi HM102 hardness tester using a 50 g load. 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}. The shape-memory behavior was characterized by thermal cycling under various constant tensile stress levels. The dimensions of the specimen were 8 mm in gauge length, 1 mm wide and 80 μm thick. During each cycle, the tensile samples were first heated up to a temperature well above A_f^σ, and then a predefined stress was applied. The stressed sample was then cooled to a temperature well below M_f^σ (where M_f^σ and A_f^σ are the forward and reverse martensitic transformation finish temperatures under the applied stress σ) and then heated again to a temperature above A_f^σ; this completed one cycle under a predefined stress level. At this point, the next level of stress was applied, and the thermal cycle repeated again until the end of the cycling experiment. Compositional and microstructural investigations were done by electron probe microanalysis (EPMA) using a JEOL JXA 8530F instrument and by transmission electron