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# Transmission electron microscopy investigation of microstructures in low-hysteresis alloys with special lattice parameters

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A sharp drop in hysteresis is observed for shape memory alloys satisfying the compatibility condition between austenite and martensite, i.e. $\lambda_2 = 1$, where $\lambda_2$ is the middle eigenvalue of the transformation strain matrix. The present work investigates the evolution of microstructure by transmission electron microscopy as the composition of the $Ti_{50}Ni_{50-x}Pd_x$ system is systemically tuned to achieve the condition $\lambda_2 = 1$. Changes in morphology, twinning density and twinning modes are reported along with twinless martensite and exact austenite–martensite interfaces.

*Keywords:* Shape memory alloys (SMA); Transmission electron microscopy (TEM); Martensitic phase transformation; Hysteresis; Twinning

Reducing the hysteresis is an important improvement for the design of many shape memory devices. A small hysteresis is particularly important for applications such as actuators, sensors and other cycling parts. It would also improve the resistance of shape memory alloys (SMAs) to fracture since the dissipated work measured by the hysteresis goes mainly into the creation of defects that subsequently become the sites of crack initiation [1]. Until recently, the development of low-hysteresis alloys was largely based on trial and error. The latest developments of the general non-linear theory of martensite (GNLTM) [2–4] support the dependence of the hysteresis with $\lambda_2$, an indicator of the compatibility between the austenite and martensite phases [4]. The experimental confirmation came with the work of Cui et al. [1], who investigated the lattice parameters and the thermal hysteresis of composition-spread Ti–Ni–Cu and Ti–Ni–Pd thin-films using a high throughput, combinatorial approach. They observed in all cases a sharp drop of the hysteresis for alloys when the middle eigenvalue $\lambda_2$ of their transformation stretch tensor approaches 1. James and Zhang [4] found the same correlation for bulk alloys of Ti–Ni–Au, Ti–Ni–Pt and Ti–Ni–Pd. The drop in hysteresis is symmetric on both sides of $\lambda_2 = 1$ with an apparent singularity when $\lambda_2 = 1$. These combined results point towards a universal behavior of hysteresis as a function of $\lambda_2$. In this paper, we investigate the evolution of microstructures by transmission electron microscopy (TEM) as the composition in the $Ti_{50}Ni_{50-x}Pd_x$ system is systemically tuned to approach the condition $\lambda_2 = 1$.

Alloys were prepared from pure elements (99.98 mass% Ti, 99.995 mass% Ni, 99.95 mass% Pd) by arc melting in an argon atmosphere. Slabs 1 mm or less in thickness were cut from the ingot by electrical discharge machining and subsequently homogenized at 1100 °C during 20 ks followed by quenching in room-temperature water. Lattice parameters of both martensite and austenite were measured on a Scintag X-ray diffractometer on polycrystalline slabs previously chemically etched using an electrolyte of 85% $CH_3COOH$ and 15% $HClO_4$. Transformation temperatures and hysteresis were measured by differential scanning calorimetry on a TA Instruments Q1000 with 100 μm thick slabs, previously etched by the same method. For the TEM study, disks 3 mm in diameter were spark-cut or slurry drilled from the slabs, mechanically polished to 200 μm thickness and finally electropolished to perforation in a Tenupol 3 operated at 12 V, 0.1 A, −20 °C with an electrolyte of 80% $CH_3OH$ and 20% $H_2SO_4$. Conventional Transmission Electron Microscopy (CTEM) observations were carried out in a Phillips CM20 microscope operated at 200 kV using a side-entry type double-tilt specimen holder with angular ranges of ±45°. High

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Resolution Electron Microscopy (HREM) observations were carried out in a FEG Phillips CM30 microscope operated at 300 kV using a side-entry type double-tilt specimen holder.

The $Ti_{50}Ni_{50-x}Pd_x$ system undergoes a martensitic transformation on cooling from a cubic (B2) to an orthorhombic (B19) lattice for compositions above $x = 7$ [6,7]. This transformation gives rise to six variants of martensite, denoted 1, 2, 3, 4, 5 and 6. Each of the possible transformations can be described by its own transformation strain matrix, $U_1$–$U_6$, with $U_1$ shown as an example in Eq. (1) :

$$U_1 = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} \\ 0 & \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} \end{pmatrix} \quad \beta = \frac{a}{a_0} \quad \alpha = \frac{b}{\sqrt{2}a_0} \quad \gamma = \frac{c}{\sqrt{2}a_0} \tag{1}$$

Lattice parameters of austenite ($a_0$) and martensite ($a, b, c$) are listed in Table 1 for the different compositions studied, along with $\lambda_2$, the middle eigenvalue of any one of the six transformation strain matrices, $\theta_c$, defined as the average of the four characteristic transformation temperatures, and $H$, the thermal hysteresis. Variants are associated in pairs to form twins. The pairs 1–2, 3–4 and 5–6 have a compound twin connection, while all other pairs (e.g. 1–3) have type I/type II twin connections. Table 2 shows the twin parameters for three selected alloys calculated with the GNLTM. $K_1$ is the twinning plane and $\eta_1$ the shear direction. There are three twinning modes, {1 1 1} type I, ⟨2 1 1⟩ type II and {0 1 1} compound. Only the values of the irrational planes and directions depend on the composition. It has been shown that, in the frame of the GNLTM [4,5], type I/II twins cannot participate in the austenite–martensite interface when $\lambda_2 < 1$ and conversely compound twin cannot participate when $\lambda_2 > 1$. For this reason, the twin ratio $\lambda$, defined such that $\lambda/(1 - \lambda)$ is the volume fraction of the smaller variant participating in the austenite–martensite interface, only has meaning when these conditions are satisfied. The closer $\lambda_2$ is to 1, the smaller the twin ratio $\lambda$.

Figure 1(a)–(c) shows the evolution of morphology of the B19 martensite as the content of Pd is decreased towards the compatibility condition. The alloy with the highest Pd content, $Ti_{50}Ni_{25}Pd_{25}$, has a $\lambda_2$ of 1.0070, the largest value in the series studied. Its morphology (Fig. 1(a)) is one commonly found in SMAs with parallel lamellae of martensite internally twinned. The internal twins extend diagonally across the width of the martensite plates with rather regular spacing. Twins from alternate plates share the same orientation dependence to each other throughout the sample. The selected-area diffraction (SAD) patterns in Figure 1(d) and (e) were taken from internally twinned plates A and B (Fig. 1(a)) in two different orientations, the beam edge-on with the twinning plane. Each pattern consists of two sets of reflections which are in mirror symmetry with respect to the (1 1 1) plane. The same {1 1 1} type I twin is found throughout the sample and is considered to be the lattice invariant shear (LIS), which means that martensite is sheared along this mode to accommodate a habit plane with austenite during the phase transformation. The same morphology and LIS twinning have been reported for higher Pd content [8,9].

As the content of Pd decreases, so does $\lambda_2$. $Ti_{50}Ni_{30}Pd_{20}$ ($\lambda_2 = 1.0050$) shows some significant changes in microstructure compared to higher Pd alloys. The lamellar morphology is retained, but many plates now exhibit a lower twin ratio or even no twinning. Figure 2(a) is a bright-field micrograph taken inside a martensite plate of this alloy with an average twin ratio of 0.09, meaning that one variant is now more than 10 times larger than the other one. The smaller variant

**Table 1.** Lattice parameters of the austenite B2 phase ($a_0$) and the martensite B19 phase ($a, b, c$). The middle eigenvalue $\lambda_2$ is equal to $b/(\sqrt{2}.a_0)$. It decreases as Pd decreases for the series studied. $Ti_{50}Ni_{39}Pd_{11}$ is the closest alloy to the compatibility condition $\lambda_2 = 1$. $\theta_c$ is defined as the average of the four characteristic transformation temperatures, $\theta_c = (A_s + A_f + M_s + M_f)/4$ and the hysteresis as $H = (A_s + A_f - M_s - M_f)/2$.

| Alloys | $a_0$ | $a$ | $b$ | $c$ | $\lambda_2$ | $\theta_c$ | $H$ |
|---|---|---|---|---|---|---|---|
| $Ti_{50}Ni_{41}Pd_9$ | 3.0469 | 2.8461 | 4.3036 | 4.5827 | 0.9988 | 40 | 18 |
| $Ti_{50}Ni_{39}Pd_{11}$ | 3.0499 | 2.8304 | 4.3135 | 4.6041 | 1.0001 | 25 | 13 |
| $Ti_{50}Ni_{32}Pd_{18}$ | 3.0556 | 2.8194 | 4.3429 | 4.6281 | 1.0050 | 113 | 22 |
| $Ti_{50}Ni_{30}Pd_{20}$ | 3.0508 | 2.8202 | 4.3404 | 4.6126 | 1.0060 | 103 | 26 |
| $Ti_{50}Ni_{25}Pd_{25}$ | 3.0625 | 2.8074 | 4.3614 | 4.6667 | 1.0070 | 189 | 32 |

**Table 2.** Twinning modes and twin ratios for $Ti_{50}Ni_{50-x}Pd_x$, $x = 9, 11, 20$, calculated from the GNLTM. $K_1$ is the twinning plane and $\eta_1$ the shear direction. The twin ratio is defined as the width ratio between two martensite variants accommodating a habit plane with the austenite.

| Type of twins | $x$ | $K_1$ | $\eta_1$ | Twin ratio $\lambda$ | $\lambda_2$ |
|---|---|---|---|---|---|
| {1 1 1} type I | 9 | {1 1 1} | ⟨1 −0.21 −0.80⟩ | ø | 0.9988 |
| | 11 | | ⟨1 −0.23 −0.77⟩ | 0.003 | 1.0001 |
| | 20 | | ⟨1 −0.26 −0.74⟩ | 0.15 | 1.0060 |
| ⟨2 1 1⟩ type II | 9 | {0.59 −0.18 −1} | ⟨2 1 1⟩ | ø | 0.9988 |
| | 11 | {0.60 −0.20 −1} | | 0.004 | 1.0001 |
| | 20 | {0.63 −0.26 −1} | | 0.18 | 1.0060 |
| {0 1 1} compound | 9 | {0 1 1} | ⟨0 1 −1⟩ | 0.019 | 0.9988 |
| | 11 | | | ø | 1.0001 |
| | 20 | | | ø | 1.0060 |