Microstructural dependence on middle eigenvalue in Ti–Ni–Au

H. Shi\textsuperscript{a,}* R. Delville\textsuperscript{a,c} V. Srivastava\textsuperscript{b,d} R.D. James\textsuperscript{b} D. Schryvers\textsuperscript{a}

\textsuperscript{a} EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
\textsuperscript{b} Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455, USA
\textsuperscript{c} SCK-CEN, Boeretang 200, B-2400 Mol, Belgium
\textsuperscript{d} GE Global Research, 1 Research Cir, Schenectady, NY 12309, USA

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The microstructure of various compounds of the Ti–Ni–Au alloy system is investigated by transmission electron microscopy in relation with changing lattice parameters improving the compatibility conditions between austenite and martensite expressed by the $\lambda_2 = 1$ equation based on the Geometrically NonLinear Theory of Martensite (GNLTM). Although local differences in microstructure are observed, when increasing the gold content compound twins are replaced by Type I twins, while twinned lamellar structures are replaced by untwinned plates and self-accommodating structures when $\lambda_2 = 1$ is approached, all confirming the predictions of the GNLTM.

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1. Introduction

TiNi-based shape memory alloys (SMAs) have been widely studied for their unique thermo-mechanical properties arising from the energy-dissipating martensitic transformation. The application of certain shape memory devices, such as actuators, sensors and other cycling parts, is, however, often limited by a relatively large hysteresis, which can lead to poor fatigue properties. It also decreases their resistance to fracture since the work dissipated during the hysteresis causes the creation of defects, which can become sites of crack initiation \cite{1}. Therefore, reducing hysteresis is a particularly important aspect in the process of alloy improvement for many SMA applications. In order to minimize the thermo-mechanical hysteresis by increasing the austenite–martensite lattice compatibility, extensive research has been carried out to find a suitable ternary element for the TiNiX system. It was found that adding certain noble elements such as Pd, Pt and Au can dramatically decrease the SMAs' hysteresis at certain precise concentrations \cite{1,2,3,4}.

Some years ago, a new application of the Geometrically NonLinear Theory of Martensite (GNLTM) concerning hysteresis reduction was proposed by James and Zhang \cite{5,6}. It was found that for a particular combination of austenite and martensite lattice parameters the hysteresis can be greatly reduced as a result of a perfect match between parent and product phases, which lowers the energy barrier resulting from the mismatch strain existing between austenite and classically twinned martensite \cite{2}. In particular, the middle eigenvalue $\lambda_2$ of the transformation strain matrix is an indicator of this compatibility, so when $\lambda_2$ equals 1 a low hysteresis is expected. Tuning this eigenvalue $\lambda_2$ can be done by adding ternary and quaternary elements to the binary Ni–Ti alloy. Cui et al. have already experimentally confirmed this theory by investigating the lattice parameters and the thermal hysteresis of composition-spread Ti–Ni–Cu and Ti–Ni–Pd thin-films \cite{1}. They observed in all cases a sharp drop of the hysteresis for alloys when $\lambda_2$ approaches 1. This was further confirmed by Zhang et al., who found the same correlation for bulk alloys of Ti–Ni–Au, Ti–Ni–Pt and Ti–Ni–Pd \cite{2} and by Zarnetta et al. for the quaternary Ti–Ni–Cu–Pd system in which an increased fatigue life was observed \cite{7}. Also other systems such as the Ni$_{50}$Co$_{20}$Mn$_{20}$Sn$_{10}$ Heusler alloy reveal particular features such as minimal thermal hysteresis, high magnetization, low magnetic anisotropy and relatively high transformation temperature when approaching the $\lambda_2 = 1$ condition \cite{8}.

According to the same theory, the perfect match of austenite and martensite structures at the habit plane translates into the occurrence of large plates of single martensite variants for the product phase instead of the classic multiply twinned martensite plates. Under general conditions, Ti–Ni martensite plates consist of lamellar twinning with the tapering tips of two variants forming an intermediate layer close to the habit plane \cite{9} whereas $\lambda_2 = 1$ systems form single variant martensite–austenite interfaces.
The type of twinning also follows from the GNLTM theory and is found to be Type I or II for $\varphi_2 > 1$ and compound for $\varphi_2 < 1$. These structural predictions have led to a transmission electron microcopy (TEM) microstructural investigation of the Ti–Ni–Pt system around the composition where the hysteresis is greatly reduced. It was confirmed that the decrease of hysteresis is indeed accompanied by significant changes in the microstructure [3,4,10]. In order to prove the universality of these findings, we have extended these investigations to other systems, such as Ti–Ni–Au or Ti–Ni–Pt. The addition of Pt in the latter, however, greatly reduces the quality of electropolished samples which are necessary for a study looking for large scale effects, so the focus of the present TEM work is on the microstructure of the Ti50Ni50.3Au system, where $x$ is systematically tuned to approach and cross the $\varphi_2 = 1$ condition. The set of alloys originates from the samples used by Zhang et al. [2,11].

2. Experimental

The Ti50Ni50.3Au alloy (x = 10, 13, 15 and 18) bulk alloys used in this study were prepared by arc melting pure elements (99.98 mass% Ti, 99.95 mass% Ni, 99.95 mass% Au) in an argon atmosphere. The ingots were cut into slabs of about 1 mm in thickness by EDM (Electrical Discharge Machining) subsequently followed by homogenization at 900°C during 20 ks followed by water quenching. TEM samples of 3 mm disks in diameter were spark-cut from the slabs, mechanically polished to a 150–200 μm thickness and finally electropolished to perforation in a Tenupol 3 system with an electrolyte of 80% CH3OH and 20% H2SO4 operating at +15 V, 0.12 A, –20°C. Extra care had to be taken to minimize Au nanoparticle redeposition on the thin foil by reducing the starting thickness of the sample and tuning the pump flow rate, the voltage and current of the instrument. TEM observations were carried out in a Philips CM20 microscope operated at 200 kV using a side-entry type double-tilt specimen holder with angular ranges of +45° to –45°.

Precise average lattice parameters of both martensite and austenite at the transition temperature were measured with a Scintag X-ray diffractometer (XRD) equipped with a temperature-controlled stage on polycrystalline slabs chemically etched using an electrolyte of 85% CH3OH and 15% HClO4 [2]. Local lattice parameters of austenite were measured using SAED (select area electron diffraction) as internal reference. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q1000 using 100 μm thick slabs, etched by the same method. Transformation temperatures were measured from these DSC curves and compared with the more precise determination using in situ XRD.

3. Results and discussion

The Ti50Ni50.3Au system undergoes a martensitic transformation from a cubic (B2) to an orthorhombic (B19) lattice except for compositions with a small amount of Au (x < 10) in which case the monoclinic B19’ is formed, as in binary Ti–Ni. Table 1 shows averaged XRD lattice parameters of both B2 austenite (a0) and B19 martensite (a, b, c) for four different compositions of the Ti50Ni50.3Au alloy along with the corresponding $\varphi_2$ and H, the thermal hysteresis defined as ((A + A f) – (M s + M f))/2 (with A/M = A f/M f the respective start/finish temperatures). The austenite/martensite transformations are of the first order (a, b, c) and (A), $\varphi_2$ and H denote the middle eigenvalue of the transformation matrix and the thermal hysteresis (degrees), the latter determined from DSC.

<table>
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<tr>
<th>Alloys</th>
<th>$a_0$</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\varphi_2$</th>
<th>H</th>
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<td>4.6073</td>
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<td>4</td>
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<td>4.4005</td>
<td>4.6323</td>
<td>1.0079</td>
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</tbody>
</table>

Table 1

Fig. 2(a) shows B19’ martensite with compound twins with (010)$_{B19}$ twin plane and (100)$_{B19}$ shear direction observed in the Ti50Ni50.3Au10 alloy. Fig. 2(b) and (c) are selected area electron diffraction (SAED) patterns corresponding to the encircled zones 1 and 2 in Fig. 2(a) revealed twinned and untwinned martensite, respectively. The $\beta$ angle indicated in Fig. 2(c) equals 84.3°, which confirms the monoclinic structure of B19’ which is only observed in the Ti50Ni50.3Au10 alloy and not in the investigated alloys with higher Au content. The existence of twinned and non-twinning B19’ areas could be due to local concentration differences and their influence on the lattice parameters or to local strain fields.

Some samples of the Ti50Ni50.3Au10 also contain the orthorhombic B19 martensite with compound twins, which, in view of the results with the higher Au content samples, may again indicate small and local concentration differences in the alloy. Fig. 2(d) shows a bright field (BF) TEM micrograph of lamella of such twins with the corresponding diffraction patterns obtained from the encircled region in two different zone axes [311] and [011], as shown in Fig. 2(e) and (f), respectively. The black dots visible on Fig. 2(d) (and also somewhat in Fig. 2(a)) are due to Au nano-deposition in the process of sample preparation by electropolishing, although thinning conditions have been adjusted to minimize this deposition. As a comparison with Fig. 2(c), the $\beta$ angle indicated in Fig. 2(f) is 90°, which confirms the orthorhombic B19. 3.2. Ti50Ni57Au13

A large B19 martensite plate of several microns wide but without twins is observed in the Ti50Ni57Au13 alloy, as seen in Fig. 3(a). In order to ensure no twins exist in this plate, diffraction patterns taken from the region inside the circle in the BF image and along different zone axes [100], [2 1 0] and [3 1 0] are presented in Fig. 3(b), (c) and (d), respectively. The arrows point at a self-accommodating triangle formed by different B19 variants [12,13]. Even when phase compatibility is achieved in the Ti50Ni57Au13, due to the $\varphi_2 \approx 1$, there still exists shape change and volume change between the austenite and martensite. In order to accommodate this shape/volume change, self-accommodation of martensite plates is necessary and plays an important role in the final morphology of the microstructure. Fig. 3(e) shows a typical triangle self-accommodating
Unlike the traditional SAG in NiTi as seen in Fig. 3 of [13], internal twins are not observed in the present SAG. This is another consequence of the phase compatibility. According to the three-dimensional model of the self-accommo-
dating variants [12] as represented in the inset of Fig. 3(e), the three martensite plates can be labeled as variants 2, 4 and 6 of the model. Fig. 3(f), (g) and (h) are corresponding SAED patterns from variants 2, 4 and 6. Experimentally, variants 4 and 6 are observed to meet along a (1 1 1) Type I twin interface in [0 1 1] zone orientation with the electron beam slightly tilted from the above [1 0 0] direction.

In order to check the assumption of local concentration varia-
tions affecting the observed structural features through the changes in lattice parameter, precise lattice parameters of 4 differ-

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**Fig. 1.** DSC curves of (a) Ti50Ni37Au13 and (b) Ti50Ni35Au15. The transformation temperatures $A_s$, $A_f$, $M_s$ and $M_f$ and thermal hysteresis $H=(A_s + A_f - (M_s + M_f))/2$ are measured by crossover from the tangent line of the peak and the extrapolated background. The lower hysteresis for the Au13 sample as well as the difference in peak width between both samples is clear.

**Fig. 2.** Illustration of B19 and B19 martensite with compound twins in Ti50Ni40Au10. (a) BF image of twinned and untwinned B19’ martensite, (b) and (c) are SAED from the encircled regions 1 and 2 in (a) along [1 1 0], respectively. (d) BF image of twinned B19 martensite, (e) and (f) SAED from the encircled region in (a) along [3 1 1] and [0 1 1] zones, respectively, the former confirming the twinning, the second the orthorhombic character.
ent austenite regions in this sample were measured by SAED, using the 111 diffraction ring of the omnipresent Au particles as an internal reference. Taking into account the dependence of the lattice parameter on the size of the particles [14], here between 5 and 20 nm, the austenite lattice parameters found in 3 of the 4 regions equals 3.08 ± 0.01 Å (which corresponds with the averaged XRD result of this sample), while one region yields a lattice parameter of 3.05 ± 0.01 Å. This confirms local variations in lattice parameter, which appear to be unavoidable in these types of systems and can lead to local differences in transformation temperatures and martensite microstructures, such as the observation of Type I twins in this Ti50Ni37Au13 sample. In other words, in the region showing the Type I twins, the gold content is expected to be slightly higher than 13 at.%. Although the presented TEM images and SAED measures should not be considered to provide proper statistical data on the concentration variations, such a compositional inhomogeneity could be one of the reasons for the (slight) width of the DSC peaks as seen in Fig. 1. Unfortunately, the accuracy and precision of any spectroscopic tool available is not sufficient to detect these extremely small differences.

3.3. Ti50Ni32Au15

In Ti50Ni32Au15 pockets of lamellar twins inside a larger untwinned plate of B19 martensite are observed as shown in Fig. 4(a). The corresponding diffraction pattern with zone axis [011] in Fig. 4(b) clearly reveals the (1 1 1) Type I twinning. The observation of (1 1 1) Type I twins in Ti50Ni32Au15 is consistent with the theory by James et al. when following the lattice parameter data in Table 1 showing 1.2 > 1 for this compound. The variation between twinned and untwinned areas can again be related to local variations in concentration. As the DSC curves in Fig. 1 illustrate, the width of the transformation peaks in Ti50Ni32Au15 is larger than in Ti50Ni37Au13-which could indicate a higher degree of compositional inhomogeneity in the former.

3.4. Ti50Ni32Au18

As shown in Fig. 5(a), B19 martensite is found in Ti50Ni32Au18 (circle 2) together with some retained austenite (circle 1), as seen from the corresponding SAED patterns in Fig. 5(c) and (b), respectively. The fact that austenite is observed although Mf is above room temperature is possibly due to a thin foil effect, locally reducing the transformation temperature, although again composition inhomogeneities can play an enforcing role. (1 1 1) Type I twins are shown in Fig. 5(d). Fig. 5(e), (f) and (g) are SAED patterns from the encircled zones 1, 2 and 3, respectively. Region 2 represents one of the three variants of B19 martensite, while regions 1 and 3 are the \{1 1 1\}B19 Type I twins.

The changes in microstructure with composition of the Ti50Ni50-xPdx system are shown in Fig. 1 of Ref. [3]. Twinless martensite plates exist in Ti50Ni50Pd13, with \( \lambda_2 = 1.0001 \) while lamellar twins-within-twins appear when Pd increases up to 25 at.% and \( \lambda_2 \) becomes 1.0079. As shown in Fig. 5, the Ti–Ni–Au system does not show lamellar Type I twins in Ti50Ni32Au18 where \( \lambda_2 = 1.0070 \). However, lamellar twins were reported in this ternary system for a Au content of 40 at.% [15]. In other words, a much larger content of Au than Pd is needed to provide the lamellar Type I twins for Ti50Ni50-xAu_x. Since Pd atoms are larger than Au ones, with the same content of ternary additions to binary NiTi, the change of lattice parameters for Ti50Ni50-xPdx system is larger than Ti50Ni50-xAu_x. This may explain why the microstructures in the Ti50Ni50-xPdx system vary more drastically than in the Ti50Ni50-xAu system along with changing \( \lambda_2 \) value and opens the possibility to easier fine tuning of the microstructure and thermo-mechanical behaviour.

As for the composition inhomogeneities, similar microstructural variations were also observed in the Ti50Ni50-xPdx system [16] and are related with the fact that these structures are not line
compounds but cover relatively large stability regions in the respective phase diagrams, allowing for small local deviations of the nominal composition without much difference in free energy. The differences in concentration are inferred based on the observation of local changes in lattice parameter of the austenite by comparison with the internal reference of the Au particles. The latter is essential, since even convergent beam ED could not resolve the small differences in lattice parameter in the Ti50Ni50Pdx system [16]. Although this approach is appropriate, the expected differences in Au content are relatively small and could not be confirmed by spectroscopic means, due to the limited accuracy and precision of such techniques for individual local measurements. Moreover, the present TEM observations provide only a very limited view on the entire bulk sample, so extrapolations to the bulk level should be handled with care. Nevertheless, the respective peak broadenings in the different DSC curves could give some indication of the concentration spread in each of the samples.

4. Conclusions

The microstructural predictions of the GNLTM are confirmed by the observation of large twinless B19 martensite plates and SAGs in Ti50Ni37Au13 when k2 is close to 1. Also the change from compound to Type I twins when increasing the Au content and shifting k2 from smaller to larger than 1 confirms the predictions of the GNLTM. Although the above trends are clear, local microstructure changes may arise from local concentration inhomogeneities in the sample, which is suggested from the local lattice parameter deviations as measured through the Au particles remaining from the electropolishing and used as reference. Such concentration inhomogeneities could further induce some peak broadening in the DSC curves.

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