Electron microscopy study of Nb-rich nanoprecipitates in Ni–Ti–Nb and their influence on the martensitic transformation

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In order to adjust the transformation temperatures and the resulting hysteresis of NiTi shape memory alloys for use in a larger variety of applications, extensive research has been carried out to find suitable ternary or quaternary alloying elements [1–3]. For example, from earlier work it was found that Nb additions to Ni–Ti will notably increase the hysteresis to 150 °C after martensitic deformation, which is useful for thermal couplings, since the coupling parts can then be expanded and stored at ambient temperature [4–7]. Heating to above the stabilized Af temperature restores the original shape, leading to a clamping force.

While a microscopic explanation for the mechanism of hysteresis increase in Ni–Ti–Nb SMAs is still not available, the most popular hypothesis is that plastic irreversible deformation of the Nb-rich precipitates hampers the shape recovery, while elastic strain energy stored in the precipitates will shift the transformation starting temperatures [5,8,9]. Although this hypothesis has been proposed in several papers, there is no detailed documentation of the microstructure of the Nb-rich precipitates or their microstructural changes, if any, during the martensitic transformation (MT). Moreover, often no distinction is made between Nb-rich regions in the eutectic and nanoprecipitates in the matrix [10]. The purpose of the present work is to further clarify the composition and microstructural aspects of Nb-rich nano-

precipitates formed by annealing at 900 °C and their possible interaction with the MT in Ni–Ti–Nb.

The material used in this study is a commercial (Ni–Ti)8.4 at.% Nb alloy rod, 9 mm in diameter, which has been hot extruded and quenched from 900 °C. The transformation temperatures were measured by differential scanning calorimetry (DSC) on a TAQ2000 instrument. Transmission electron microscopy (TEM) samples were prepared by lift-out focused ion beam (FIB) thinning in an FEI-Nova-Nanolab-200 SEM/FIB instrument or ion milling in a Gatan Duo-Mill 600 instrument to avoid preferential thinning when electropolishing.

The SEM observations were carried out in a JEOL-5510 microscope. The slice-and-view was performed on the SEM/FIB instrument. The three-dimensional (3-D) reconstruction was performed in Matlab® and Amira®. For the TEM characterizations, a Phillips CM20 and a FEG TECNAI F20-ST were used, the latter being equipped with a scanning transmission electron microscopy (STEM) unit and an energy-dispersive Si(Li) X-ray spectrometer (EDX). Electron energy loss spectroscopy (EELS) measurements were done with a Gatan GIF2000 post-column spectrometer attached to a JEOL-3000FX transmission electron microscope.

Figure 1 shows an SEM image in which the Ni–Ti– rich austenitic phase formed during cooling through the solid–liquid dual phase region is revealed as the darker matrix labeled C. Upon full solidification, the remaining liquid produces an eutectic phase, revealed as...
Figure 1. SEM image showing white Nb-rich (nano)particles in the eutectic and matrix (inset).

From the SEM inset shown in Figure 1 nanoprecipitates can be recognized in the matrix. Due to overlapping with the matrix, no statistically analyzed composition for these nanosized precipitates is obtained from the SEM. However, STEM-EDX of the precipitates located on the thinned edge of TEM samples yields almost pure Nb, with only small amounts of Ti and Ni for these nanoprecipitates. Moreover, the Ti/Ni ratio calculated from STEM-EELS data using EELSMODEL [16] reveals no composition gradient in the matrix close to the nanoprecipitates (see Suppl. Data Fig. SD1), indicating a well-developed precipitation process.

Table 1. Average composition of the matrix, large Nb precipitates in the eutectic and Nb-rich nanosized precipitates obtained from 20, 20 and 5 measurements by STEM-EDX, respectively, including standard errors.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Ni</th>
<th>Nb</th>
<th>Ti/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>44.12 ± 0.11</td>
<td>52.43 ± 0.09</td>
<td>3.45 ± 0.07</td>
<td>0.840 ± 0.003</td>
</tr>
<tr>
<td>Large Nb-rich particles in the eutectic area</td>
<td>10.49 ± 0.30</td>
<td>1.45 ± 0.80</td>
<td>88.08 ± 0.10</td>
<td>9.5 ± 1.2</td>
</tr>
<tr>
<td>Nanosized precipitates in the matrix</td>
<td>4.40 ± 0.26</td>
<td>3.06 ± 0.24</td>
<td>92.89 ± 0.66</td>
<td>1.48 ± 0.18</td>
</tr>
</tbody>
</table>

(mean ± SD), their total volume fraction of 1.8% remains rather low. Such a dense distribution, however, implies little space or matrix between these precipitates, which might affect the growth of martensite plates [17]. The matrix volume available for martensitic transformation is measured based on minimum distances between the precipitate images in all 2-D slices, yielding a mean matrix distance transform [18] of 277 ± 200 nm (see Suppl. Data Fig. SD2). The corresponding histogram of the filling fraction (FF) obtained via a so-called water penetration transform averaged over four different directions yields a mean FF of 81 ± 11% (see Suppl. Data Fig. SD3) [18]. This FF represents the amount of matrix that will be transformed into martensite when a plate enters the 2-D slice on one edge and following a pre-defined cone shape. An FF of 81% indicates that the precipitates will indeed hamper the growth of the martensite plates to some extent. Since both DT and FF measures are still based on 2-D data, they certainly yield an overestimate of the matrix space since the effects of possible precipitates existing in the neighboring slices are not taken into account.

Figure 2. 3-D reconstruction of the distribution of the Nb-rich nanoprecipitates in the matrix. The box size is 4.955 × 5.955 × 6 μm³.
which is chosen as the reference frame. The matrix has a color between blue and green, corresponding to \(-10\%\) lattice strain when compared with the reference, perfectly confirming the known difference in lattice parameter.

However, unlike the results from the GPA analysis for Ni\(_4\)Ti\(_3\) precipitates in an Ni–Ti matrix [22], there is no strain gradient in the matrix (and also not in the precipitate), which results in a sharp separation between the precipitate and the matrix. In the Ni\(_4\)Ti\(_3\) precipitate case, the lattice mismatch between the precipitate and the matrix is only about \(3\%\), allowing the matrix to contract to accommodate the lattice mismatch, yielding a coherent interface as long as the precipitate remains relatively small, i.e. below 300 nm diameter [22,23]. However, for the Nb-rich nanoprecipitates, the lattice mismatch of \(10\%\) is too large for a lattice accommodation via elastic strain. Indeed, as seen in the zoom of Figure 3d, the inverse fast Fourier transform (FFT) clearly reveals periodic interface mismatch dislocations (see also Suppl. Data Fig. SD4). Such lattice mismatch dislocations between the small precipitate and the B2 matrix occur, on average, every \(10/11\) \{110\} planes for the precipitate and matrix, respectively, which is consistent with the lattice parameter difference of \(10\%\), thereby fully accommodating all lattice mismatch between both structures. Essentially the same conclusion was obtained earlier for the accommodation of the strain at the large flat interfaces in the lamellar eutectic in Ti\(_{40}\)Ni\(_{40}\)Nb\(_{20}\) [19].

Microstructure changes observed during in situ cooling are presented in Figure 4. No martensite plates were seen to nucleate from the Nb-rich nanoprecipitates, in contrast to the R-phase and B19\(^*\) martensite, which are known to nucleate at Ni\(_4\)Ti\(_3\) precipitates as a result of an induced elastic strain field [22-24] and the surrounding composition gradient [25,26]. This is consistent with the absence of an elastic strain field and composition gradient around the Nb-rich precipitates as seen above. Figure 4a and b are sequential images taken upon cooling, which reveal a microtwinned martensite plate growing from the thicker austenite part (left) and hitting an Nb-rich nanoprecipitate. The difference in temperature between \(-145^\circ\)C for Figure 4a and \(-165^\circ\)C for Figure 4b and the burst-like nature of the process in between both instances indicate that the small precipitate hampers the continued growth of the incoming martensite plate (the difference in absolute measured temperatures between the in situ TEM and DSC experiments are probably due to thin foil effects in the TEM sample, often resulting in a lowering of transformation temperatures).

Figure 4c is an enlargement of the contact area between the incoming needle-shaped martensite and the small precipitate at the lowest temperature obtained. The interaction is seen to result in a strain field around the precipitate and induces the nucleation of another martensite variant in another direction (already initiated in Fig. 4b). This stop-and-go process is expected to be part of the reason for the measured increased hysteresis of this ternary alloy when compared to binary NiTi as it smears out the martensitic transformation process and thus lowers the \(M_p\) when compared to a system without precipitates [5,15]. Moreover, such a mechanism thus implies the need for an extra driving force to overcome the extra threshold energy, which can partly explain the lowering of the transformation temperatures when compared to binary NiTi [12,15]. Upon heating, the situation is less clear, but the series of images shown in Supplementary Data Figure SD5, selected from a video sequence, indicates that a line-up of nanoprecipitates can pin the martensite/austenite interface, thus stabilizing the martensite and increasing the \(A_p\). The lowering of the \(M_p\) and the increase in the \(A_p\) due to the existence of the Nb-rich nanoprecipitates thus constitute the main ingredients of the larger hysteresis.

Earlier work on Cu–Zn–Al by Roqueta et al. [27–29] revealed an increase in hysteresis by the introduction of nanoscale \(\gamma\) precipitates in a bcc austenite matrix. The density of these precipitates is of the order of \(10^{23}\) m\(^{-3}\), which is only slightly higher than in the present case. The main difference is that in the Cu–Zn–Al case the lattice mismatch with the \(\gamma\) precipitates was only about \(1\%\), so that no lattice mismatch dislocations were introduced at the interface when the precipitates remained at the nanoscale. As a result, the martensite...
plates could easily surround the precipitates, with the hysteresis increase being explained by the energy needed to reshape the precipitate to fit into the volume of the original shape in the martensite lattice. After several cycles of stress or temperature of the induced transformation, dislocations start to develop around the precipitate to fit into the volume of the matrix. This implies that no conclusions can be drawn on any stored energy contributions; more details about Nb-rich precipitates become plastically deformed during the martensitic transformation of the matrix. This implies that no conclusions can be drawn on any stored energy contributions; more details about Nb-rich precipitates being surrounded by martensite or after the passage of the transformation are required. The solute Nb in the Ni–Ti matrix is also expected to affect the transformation temperatures. Indeed, changing the composition of the binary alloy or adding a third element is known to potentially change the Ms by a large amount, e.g. nearly 200° per 1 at.% at the Ni-rich side for the binary system [31]. However, due to the intrinsic nature of this contribution, which works via the electronic structure of the material, the effect on the different transformation temperatures, \(M_s - M_f - A_s - A_t\), involved in defining the hysteresis is expected to be the same or at least very similar, so the net effect on the hysteresis is expected to be negligible. Only the increase in point defects might have some influence on the hysteresis [32]. In the present case, due to the expected preference of Nb for the Ti sublattice in the matrix, the Ni/Ti ratio of the matrix increases, resulting in a decrease in the Ms as in the binary system [12]. When Nb-rich nanoprecipitates are formed by annealing, the Nb content of the matrix decreases, i.e. the Ni/Ti ratio decreases again, and the Ms is expected to increase slightly when compared with a sample rapidly quenched from the melt and having the maximum Nb solubility in the matrix. Since some Nb remains in the matrix, the Ms will not reach the binary value. The net effect is that in an annealed sample containing a large amount of Nb-rich nanoprecipitates the transformation temperatures will be lower than in the corresponding binary alloy due to the remaining Nb solubility in the matrix.

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