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

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Nb-rich nanoprecipitates in the matrix of an annealed commercial Ni–Ti–Nb alloy are investigated by scanning and transmission electron microscopy, including slice-and-view and chemical analysis. The precipitates have a diameter of around 100 nm, are faceted and have a cube-on-cube relation with the B2 matrix. In situ TEM cooling shows that the martensitic transformation is hampered by the presence of these precipitates. The latter could explain the increase in hysteresis when compared with the binary system.
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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 A_f 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 nanoprecipitates 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 a eutectic phase, revealed as

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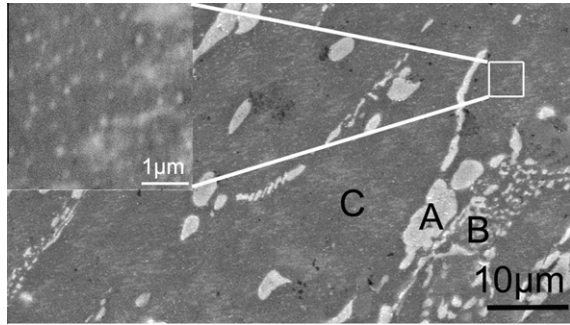* Corresponding author. E-mail: nick.schryvers@ua.ac.be

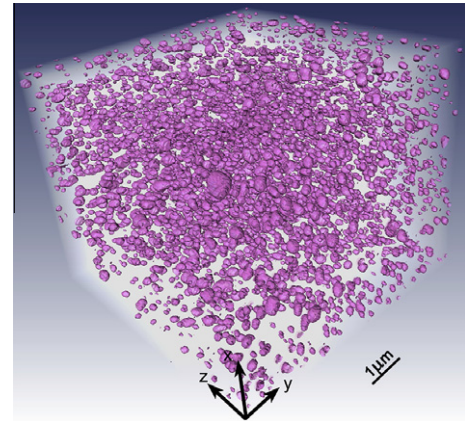**Figure 1.** SEM image showing white Nb-rich (nano)particles in the eutectic and matrix (inset).

Figure 2. 3-D reconstruction of the distribution of the Nb-rich nanoprecipitates in the matrix. The box size is $4.955 \times 5.955 \times 6 \ \mu m^3$.

a white spotty surface labeled B, which is consistent with the phase diagram reported before [11,12]. The bright areas in the eutectic regions correspond to the Nb-rich β-phase part of the eutectic phase, with the elongated texture being due to the extrusion of the rod. The STEM-EDX results are given in Table 1 and are obtained with a probe size smaller than the particle or precipitate size. The matrix is slightly Ni-rich, while the Nb-rich phase contains a substantial amount of Ti, confirming earlier results on similar compositions [12]. The former is coincident with earlier proposed modeling results showing that Nb is more likely to alloy with Ti than with Ni [13,14]. From the DSC transformation temperature peak values of $M_p = -63 \ °C$ and $A_p = 3 \ °C$ can be measured, from which an increment of the hysteresis of about 50% with respect to the 50/50 binary system, with $M_p = 2.5 \ °C$ and $A_p = 45 \ °C$, can be concluded, confirming earlier results on similar Ni–Ti–Nb alloys [15].

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.

Although most conjectures in the literature about Nb-rich regions in Ni–Ti–Nb are related to the micron-sized parts in the eutectic phase, a possible contribution of the nanoparticles seen in the inset of Figure 1 should not be overlooked. Indeed, in Figure 2 a FIB/SEM slice-and-view reconstruction of a $5 \times 6 \times 6 \ \mu m^3$ matrix box is reproduced, clearly revealing the abundance of the nanoprecipitates. In total, 5567 nanoprecipitates are counted, corresponding to a precipitate density of $3.1 \times 10^{19} \ m^{-3}$, implying a high nucleation rate. With an average diameter of $99.9 \pm 52.7 \ nm$

(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 $277 \pm 200 \ nm$ (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 $81 \pm 11\%$ (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.

From Figure 3b it is clear that the nanoprecipitates prefer a cube-on-cube orientation relationship with the matrix confirming earlier work on the lamellar eutectic in NiTi–Nb [19]. The large difference in lattice parameter of about 10% between the two unit cells (Ni–Ti matrix = $0.297 \pm 0.005 \ nm$; Nb precipitate = $0.331 \pm 0.006 \ nm$) yields a clear distinction between the two spots for each **g**-vector. The corresponding precipitate observed along the same zone axis in Figure 3a reveals {110} faceting, with some Moiré fringes due to partial overlapping with the matrix. Figure 3c shows the corresponding geometric phase analysis (GPA) evaluation [20,21]. The color map represents the strain component according to the ε_{xx} [110] direction (arrow in Fig. 3c) and shows no strain in the center of the precipitate,

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.

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