Electron energy-loss spectroscopy and first-principles calculation studies on a Ni–Ti shape memory alloy

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Abstract

Electron energy-loss spectroscopy (EELS) investigations and first-principles calculations were carried out on different aspects of a Ni–Ti shape memory alloy. The composition of lens-shaped precipitates is determined to be Ni 4Ti3 by model-based EELS quantification and the Ni-depleted zone in the B2 matrix surrounding those precipitates is quantified. EELS spectra show that the intensity of the normalized Ni L3 peak of both the Ni 4Ti3 precipitates and Ni-depleted zones is higher than that of matrix regions with the nominal composition, which is confirmed by first-principles simulations. The total amounts of 3d electrons, however, are the same for both elements in the different Ni–Ti structures and regions. The Young’s and bulk moduli of the B2 matrix with 51 at.% Ni and the Ni4Ti3 precipitates were evaluated and the precipitates are found to be harder than the matrix, while first-principles calculations indicate that the bulk modulus for the Ni4Ti3 precipitate is higher by 5% than that for the equiatomic NiTi B2 phase.

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1. Introduction

Ni–Ti alloys with near-equiatomic compositions can exhibit shape memory and superelastic properties resulting from an austenite–martensite phase transformation [1]. The behavior and characteristics of this transformation are strongly influenced by the presence of lens-shaped precipitates in the B2 austenite matrix as obtained by appropriate annealing procedures. The formation of these precipitates not only introduces a strain field in the surrounding matrix [2], it also affects the composition of the retained matrix since the precipitates are enriched in Ni compared with the original material with a near-equiatomic composition [3]. Some early energy dispersive X-ray (EDX) investigations in scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed a composition of Ni14Ti11 for the precipitates [4,5]. Shortly after, Tadaki et al. deduced a composition of Ni4Ti3 based on the results of electron diffraction and EDX measurements, combined with space group theory [6]. In a previous paper, we quantified the concentration gradients upon the precipitation using a relative quantification method of electron energy-loss spectroscopy (EELS) based on the assumption of a Ni4Ti3 composition for the precipitate [3]. Since the precipitation affects the elemental concentration of the matrix and the temperature of the austenite–martensite phase transformation is strongly influenced by this composition, it is important to accurately determine the composition of the precipitate as well as that of the surrounding matrix in these Ni–Ti shape memory alloys. Besides the depletion of Ni upon precipitation, the precipitates can influence the austenite–martensite phase transformation in two more aspects: (i) the nucleation of R-phase and/or martensite is affected by the strain field formed due to lattice mismatch between the precipitates.
and the matrix; (ii) the growth/propagation of the martensitic phase can be influenced by the presence of precipitates depending on the hardness of the precipitates. The magnitude of the strain field is not only dependent on the difference in crystalline lattices, it is also affected by the difference in mechanical properties between the precipitates and the matrix. However, the mechanical properties of the precipitates are unknown up to now due to their small sizes and the fact that they cannot be grown into larger grains.

Inelastic scattering in a solid is sensitive to the local electronic structure and elemental composition as well as crystallographic structure [7]. Electron energy-loss spectroscopy in a TEM gives information on the energy loss of fast incident electrons passing through the specimen. There are several ways of interaction of the incident electrons with the specimen, giving rise to various features in the energy-loss spectrum. One of the important interactions is atomic ionization, in which inner shell electrons of atoms are ejected by receiving an energy equal to the critical ionization energy, which can be uniquely defined for a specific electron shell of a specific element. The edge intensity is then related to the amount of the element present [7,8]. Additionally, the intensity fluctuation above the edge onset, termed energy-loss near-edge structure (ELNES), is dependent on the electronic structure of the bonding of the element. The study of the area of the EELS spectrum behind a given edge can yield information on the total charge around a given element, while the details of ELNES are related to the local density of states (DOS) above the Fermi level [9–12]. However, most of the inelastic collisions are interactions with valence electrons in the outer shells, yielding plasmon excitations, which result in energy losses of below 100 eV. Strong correlations between the physical and mechanical properties of materials and their volume plasmon energy, $E_P$, have been revealed for many different materials [13]. EELS in a TEM has thus been recognized as a powerful technique to probe microstructures at very high spatial resolution down to the nanometer level, allowing studies of precipitates, internal interfaces, grain boundaries and lattice defects [14,15].

In this paper, (i) the composition of the precipitates in a Ni–Ti shape memory alloy is determined by using EELS measurements and a newly developed standardless quantification technique; (ii) the electronic structure in the B2 phase and the precipitate is compared; (iii) the elastic moduli of the precipitates and matrix are evaluated by measuring the plasmon energy; and (iv) first-principles calculations on ELNES and bulk moduli are performed.

2. Experiments and calculations

A binary nickel-rich Ni–Ti alloy with nominal composition of 51 at.% Ni was used in the present study. The sample was first annealed at 950 °C for 1 h followed by water quenching, and then aged for 4 h at 500 °C in vacuum. TEM specimens were prepared by mechanical grinding to a thickness of $\frac{1}{2}$ $\mu$m followed by twin-jet electropolishing with a solution of 93% acetic acid and 7% perchloric acid at 6 °C. Fig. 1a shows the TEM image revealing the lens-shape morphology of the precipitates and Fig. 1b the electron diffraction pattern corresponding to the $[111]_{\text{B2}}$ zone axis and the $[001]_{\text{H}}$ zone axis of two variants of the precipitate, demonstrating an orientation relationship of $(111)_{\text{B2}}//(001)_{\text{H}}$ and $[321]_{\text{B2}}/[100]_{\text{H}}$ between the B2 matrix and the hexagonal parameters of the precipitates.

EELS experiments were carried out on an ultratwin Philips CM30 field emission gun TEM equipped with a GIF2000 post column energy filter. Before each TEM session, the specimen was cleaned by Ar$^+$ ion-milling to remove a possible oxide layer on the surface in order to minimize possible artifacts in ELNES analysis of Ti edges. Also, plasma cleaning was carried out to reduce contamination during the spectrum acquisition with a focused electron beam. EELS spectra were collected in diffraction mode with a camera length of 195 mm and an entrance aperture to the GIF system of 2 mm, corresponding to an

Fig. 1. (a) TEM image showing three variants of the lens-shaped precipitates, (b) electron diffraction pattern showing the orientation relationship between the B2 matrix and hexagonal precipitates. The major spots are indexed as $[111]_{\text{B2}}$ zone, the fine superspots belong to two variants of the precipitates with their $[001]_{\text{H}}$ axis parallel to the $[111]_{\text{B2}}$ zone.
effective collection semi-angle of about 3.5 mrad. This way, a spatial analysis resolution of the spot probe of 1 nm and a spectral energy resolution of 1.1 eV (FWHM of the zero-loss peak) could be obtained. When acquiring EELS spectra, zone orientations slightly off-axis from [101]B2 are chosen in order to minimize overlap between the lens-shaped precipitate and the matrix and to reduce diffraction effects. All the EELS spectra were corrected for dark current and gain variation of the CCD detector. Low-loss spectra containing the zero-loss peak were acquired both before and after the acquisitions of the core-loss spectra, in order to check the effect of contamination on the thickness of the probed positions.

The elemental concentration was quantified by using a newly developed quantification method of EELS spectra, the so-called model-based quantification EELSMODEL [16]. A model of the EELS spectrum is constructed with a Poissonian noise model describing the statistical noise in the experimental data. The maximum likelihood method (ML) is used to estimate the expectation values. The effect of multiple scattering on the core edges was taken into account by convolution with the low-loss spectrum in the new quantification method, but not removed by deconvolution, which usually enhances the statistical noise of the spectrum. The constructed model is for statistical validity using the likelihood ratio (LR) test. A confidence interval of 95% is applied in practice in order to evaluate the level of confidence of the estimates of the ML method. This means that the constructed model can be accepted if the significance level is below 5% for the LR test. The ELNES was analyzed following the route suggested by Pearson et al. [10], but using smaller energy windows for the normalization [17].

For the ELNES calculations, full-potential-linearized-augmented-plane-waves (FLAPW) calculations [18] were performed within the density functional theory (DFT) formalism using the WIEN2k code [19], with the core states being treated in a fully relativistic fashion. For the exchange and correlation energy the generalized gradient approximation (GGA) was considered using the Perdew–Burke–Ernzerhof (PBE) functional [20]. $R_K_{\text{max}} = 9$ was used and the scalar-relativistic calculations were performed for the valence band states and the 3s, 3p-states of Ni and Ti atoms. The expansion of the potential and charge density in the muffin-tin spheres was cut off at $l = 10$. Additional local orbital extensions were used to avoid linearization errors. Non-spherical contributions to the charge density and the potential within muffin-tin spheres were considered up to $l_{\text{max}} = 4$. In the interstitial region the charge density and the potential were expanded into a Fourier series with wave vectors up to $G_{\text{max}} = 14$ a.u. $^{-1}$. The Brillouin zone integration was carried out using 165 k-points in its irreducible part for B2-NiTi but less k-points (56 and 40) were used in the case of Ni$_7$Ti$_8$ and Ni$_4$Ti$_3$. The self-consistency was considered to be achieved when the total energy variation from iteration to iteration did not exceed $10^{-5}$ Ry. The experimental lattice parameter of 0.3015 nm was taken for B2 Ni–Ti and it was expanded by 2.0% in the case of the strained regions next to the precipitates. For Ni-depleted material, a B2 structure with a Ni vacancy yielding a composition of Ni$_7$Ti$_8$ was used. The positions of all atoms were relaxed. In the case of Ni$_4$Ti$_3$, we used our own TEM and DFT data for lattice parameters and atomic positions [21], which were slightly different from previous data of [22]. For each compound, the same radius of muffin-tin sphere of Ni and Ti equal to 2.3 a.u. was used. The ELNES was calculated according to the formalism described by Nelhiebel et al. [23], accounting both for orientation of the crystal and for integration over the collection angle of the experiment.

The bulk modulus of NiTi and Ni$_4$Ti$_3$ was calculated from first principles by using the WIEN2k code. We used $R_K_{\text{max}} = 8$ and the atomic sphere radii were set to 2.0 a.u. for both Ni and Ti. The Brillouin zone integration was performed using 165 (12) k-points in the irreducible part of the Brillouin zone for NiTi (Ni$_4$Ti$_3$). The influence of the composition on the bulk modulus of NiTi has been considered by constructing a $2 \times 2 \times 2$ supercell consisting of 8 body-centered-cubic (bcc) cells in which a Ti atom was replaced by a Ni atom and for which the Brillouin zone integration was performed with 35 k-points in its irreducible part. The total energies were calculated using the PBE functional and were converged up to $10^{-5}$ Ry.

3. Results

3.1. Experiment

3.1.1. Composition of a precipitate and concentration gradient in the surrounding matrix

Fig. 2 shows examples of EELS spectra from the precipitates for (a) Ni and (b) Ti together with the corresponding fitting results. For the purpose of high precision, an energy dispersion of 0.3 eV per channel was used when acquiring the EELS spectra. Since the energy difference between the L edges of Ni and Ti is about 400 eV (Ni L$_3$ 855 eV and Ti L$_3$ 456 eV), these edges had to be acquired separately on a 1 k x 1 k CCD camera with the illumination kept unchanged. The proposed fitting model consists of a power-law function for the background and a Hartree–Slater cross-section available in the Gatan DigitalMicrograph® package. The multiple scattering is involved by convolution with the low-loss spectrum. The fine structures of the white-line peaks are modeled by Lorentzian or Gaussian profiles. As seen from Fig. 2, the constructed models correspond very closely to the experimental data. The atomic ratio of Ni/Ti can be calculated according to the fitted strength of the L edges, and the results for three precipitates with different thickness are listed in Table 1. The compositional data in the table are all from quantification with a significance level less than 5%, i.e., the obtained Ni/Ti atomic ratio can be considered as true with a statistical confidence interval higher than 95%. The uncertainty given in this table is the standard deviation for three
individual measurements on each precipitate. The error bar for each probed position was not calculated, because the correlation matrix for the measurements of the two elements in question is unknown since the corresponding spectra were acquired separately. Judging from the data shown in Table 1, the precipitates in this study have a Ni/Ti atomic ratio of 1.33 ± 0.04, i.e., it perfectly confirms the composition of Ni\textsubscript{4}Ti\textsubscript{3}.

Fig. 3 shows quantification results of the Ni/Ti atomic ratio for precipitate 1 listed in Table 1 and its surrounding B2 matrix, again obtained using the model-based EELS quantification technique. The Ni/Ti ratio for the precipitate is 1.33 ± 0.02 and it is seen that there is a Ni-depleted region with a minimum ratio of 0.96 ± 0.04 and within a range of about 150 nm from the precipitate–matrix interface. An evaluation based on the size of the precipitate and the Ni-depleted region demonstrated a local balance of Ni upon the precipitation between the Ni\textsubscript{4}Ti\textsubscript{3} precipitate and the surrounding Ni-depleted region. Similar results of Ni depletion were previously obtained using relative quantification of EELS taking the 4:3 ratio of the precipitate as a reference [3]. The check of balance of Ni upon the Ni\textsubscript{4}Ti\textsubscript{3} precipitation confirms a good accuracy of the measurements and the new quantification method applied.

### 3.1.2. ELNES

The d band of Ni is almost full, which can screen successfully the unoccupied states from the core hole [24]. On the other hand, many-body effects under the influence of the core hole in the 2p state in Ti are more significant due to fewer 3d electrons [25]. In addition, the Ti L\textsubscript{2} and L\textsubscript{3} edges overlap severely in the EELS spectrum due to their small energy difference, while the energy difference in the L\textsubscript{2} and L\textsubscript{3} edges of Ni is large enough to obtain ELNES with fine features. Fig. 4a shows the ELNES of Ni from the precipitate as compared with that from the B2 phase far away from the precipitates, i.e., beyond the Ni-depleted region, and acquired with an energy dispersion of 0.1 eV per channel. For the purpose of quantitative comparison, the spectra were normalized, after background subtraction and deconvolution with the corresponding zero-loss spectra, to a window of 10 eV located between 890 eV and 900 eV, i.e., about 15 eV above the Ni L\textsubscript{2} threshold where the background model is still valid and where no strong fluctuations in the ELNES are observed. It is noted that the normalized L\textsubscript{3} peak of Ni from the precipitate is slightly higher than that from the B2 phase, a small but experimentally reproducible feature of about 2.5%. Correspondingly, the ELNES of Ti shows slightly lower L\textsubscript{3} peaks and a slight broadening of the L\textsubscript{2} peak.

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Thickness (t/\lambda)</th>
<th>Ni/Ti atomic ratio</th>
<th>Ni (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.62–0.72</td>
<td>1.33 ± 0.02</td>
<td>57.08 ± 0.51</td>
</tr>
<tr>
<td>2</td>
<td>0.52–0.58</td>
<td>1.33 ± 0.03</td>
<td>57.17 ± 0.60</td>
</tr>
<tr>
<td>3</td>
<td>0.38–0.43</td>
<td>1.34 ± 0.02</td>
<td>57.25 ± 0.43</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1.33 ± 0.04</td>
<td>57.17 ± 0.86</td>
</tr>
</tbody>
</table>

Relative thickness of the probed positions shown here was calculated in the form of t/\lambda using the log-ratio method embedded in digital micrograph, where t is the real thickness, and \lambda is the total mean-free-path of all inelastic scattering (for Ni\textsubscript{4}Ti\textsubscript{3} \lambda is roughly 100 nm [10]).

Fig. 2. Experimental EELS spectra for (a) Ni (b) Ti from the precipitates and the corresponding fitting.

Fig. 3. EELS results of Ni-depletion in the B2 matrix surrounding a precipitate. The precipitate/matrix interface is set arbitrarily as the origin of the position axis. The dotted line indicates the nominal atomic ratio of Ni\textsubscript{51}Ti\textsubscript{49} for the original material.
for the precipitate compared with the B2 phase, as seen from Fig. 4b. Since the many-body effect is small for Ni, the ELNES of Ni can be reasonably well interpreted as a fingerprint of the unoccupied DOS distribution. The above results mean that the local unoccupied DOS within a narrow energy window covering the peak maximum of L3 for Ni in the precipitate is slightly higher than that in the B2 phase. However, further analysis shows that the difference in the normalized integrated ionization cross-section of the L edges for both Ni and Ti in the two phases is less than 1.0%, i.e., within experimental error. Therefore, the change in the total unoccupied DOS for each element in the precipitate compared with the undisturbed matrix is negligible. For the reasons outlined at the beginning of this paragraph, we will in what follows always focus on the L3 edge of the Ni spectrum.

Fig. 5 shows the normalized ELNES of Ni from the Ni-depleted region and a matrix region away from the precipitate and with the nominal composition. The intensity of the first peak in the ELNES from the Ni-depleted region is again slightly higher than that from a matrix region away from the precipitate and with nominal composition. This indicates that the local unoccupied DOS of Ni in the Ni-depleted region is slightly larger than those in the region not depleted in Ni within a narrow energy range around the peak maximum of L3. Further analysis of the ELNES demonstrates that there is again no essential difference in the amount of Ni 3d electrons between the regions with slightly different Ni concentration, which is similar to the above situation when comparing the Ni4Ti3 precipitate and the unaffected Ni51Ti49 B2 matrix.

3.1.3. Young’s and bulk moduli from plasmon

The Young’s modulus is a measure of the stiffness of a given material and which gives information on the capability to resist an elastic deformation or deflection upon an applied force. Therefore, the Young’s modulus is one of the primary parameters describing mechanical properties and/or behavior of materials. On the other hand, based on a free-electron model, the bulk modulus can be related to $E_p$ [26], the position of the maximum of the plasmon in an EELS experiment. Since the Young’s and bulk moduli are related this means that it is possible to evaluate the mechanical properties of small precipitates by measuring their plasmon energy using EELS in a TEM which has a high spatial resolution down to the nanometer scale. Howe and Oleshko have established a log–log correlation for the Young’s modulus as a function of $E_p$, i.e., $Y_m = \alpha E_p^\beta$ [13]. By least-square-fitting of available data for elements of group IV, the group to which also Ni and Ti belong, $\alpha$ and $\beta$ were determined to be 0.129 and 2.32, respectively. Fig. 6 shows the plasmon spectra acquired using an energy dispersion of 0.1 eV per channel for a Ni4Ti3 precipitate and the surrounding matrix, showing the difference in plasmon energy between the two phases. From Fig. 6, the plasmon energies for the B2 phase and the Ni4Ti3 precipitate were determined to be $18.9 \pm 0.5$ eV and $21.7 \pm 0.6$ eV according to fittings with Gaussian functions, respectively. Thus the Young’s moduli of the B2 phase and the Ni4Ti3 precipitate were evaluated to be $118 \pm 4$ GPa and $163 \pm 4$ GPa, respectively, according to the above given relation. Following a similar reasoning based on the data.
from Howe and Oleshko [13], the bulk modulus for the precipitates is evaluated as 141 ± 3 GPa and that of the matrix as 106 ± 3 GPa with $a$ and $b$ in $B = aE_p$ equal to 0.234 and 2.08, respectively.

3.2. Calculations

3.2.1. ELNES

Since there are three different lattice positions for the Ni atoms in the hexagonal unit cell of the Ni$_4$Ti$_3$ precipitate, as listed in Table 2, the L-edge ELNES of the Ni atoms at different positions has to be calculated separately in the first step of ELNES calculations. An averaged result is then obtained by taking into account the relative weight of Ni atoms at each position. In order to compare the calculated spectra they have been normalized with respect to the area under the spectrum between 5 and 30 eV. Fig. 7 shows the calculated ELNES of Ni L$_3$ edge from the Ni$_4$Ti$_3$ precipitate in comparison with that of the equiatomic B2 NiTi phase, with an energy resolution of 1.2 eV, which is close to the EELS measurements, demonstrating that the maximum of the averaged result of the Ni L$_3$ edge from the Ni$_4$Ti$_3$ precipitate is higher than that from the B2 NiTi, which agrees with the experiment. Though small, the increase of ~2.5% in peak intensity is still an order of magnitude larger than the changes induced by increasing the number of k-points or changing the value of $RK_{\text{max}}$ (0.48% and 0.24%, respectively) and therefore a genuine property of the precipitate. In detail it is found that the maximum of the normalized L$_3$ peak of atoms Ni 2 and 3 from the hexagonal Ni$_4$Ti$_3$ structure is higher than that in the cubic B2 phase, while that of atom Ni 1 is slightly lower. Also the weak shoulder peak about 7 eV above the sharp L$_3$ peak is reproduced in the calculated ELNES, although the small difference of about 0.5 eV between precipitate and matrix could not be resolved in the experimental results of Fig. 4a.

Point lattice defects in NiTi alloys are vacancies appearing in the Ni sub-lattices and substitutions appearing in the Ti sub-lattices [27]. For the purpose of simplicity, a super unit cell with the atomic concentration of Ni 7Ti8 was constructed in order to simulate the Ni-depleted B2 matrix region surrounding the Ni$_4$Ti$_3$ precipitates. This was done by removing the Ni atom located at the center of a super unit cell consisting of 8 (i.e., $2 \times 2 \times 2$) unit cells of the B2 structure. The remaining 7 Ni atoms in the Ni$_7$Ti$_8$ unit cell are located at three different lattice positions in the super unit cell, as listed in Table 3. The resulting Ni L-edge ELNES as compared with an equiatomic B2 structure is shown in Fig. 8a, again with an energy resolution of 1.2 eV, from which a confirmation of the experimental spectra in Fig. 5 is seen, i.e., the normalized Ni L$_3$ peak of the Ni-depleted region is 2% higher than that of the equiatomic matrix (the procedure of calculating the ELNES for the Ni$_7$Ti$_8$ unit cell is similar to that for the precipitate). Regarding the contribution from each Ni atom, the calculations showed that the height of the normalized L$_3$ peak of atoms Ni 1 and 2 in Ni$_7$Ti$_8$ is almost the same as that in B2 NiTi, while the L$_3$ peak of Ni 3 was higher. However, a proper comparison should also take the expansion strain in the B2 matrix next to the precipitates into account [2]. In Fig. 8b, a 2.0% strained B2 lattice is com-

### Table 2

<table>
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<tr>
<th>Atoms</th>
<th>X</th>
<th>Y</th>
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<th>Occupancy</th>
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<tbody>
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<td>0</td>
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</tr>
<tr>
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</tr>
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<tr>
<td>Ti</td>
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<td>0.251</td>
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### Table 3

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<th>Atoms</th>
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<td>Ni 1</td>
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<td>Ni 2</td>
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<td>1</td>
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<tr>
<td>Ni 3</td>
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<td>1</td>
</tr>
<tr>
<td>Ni vacancy</td>
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<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.25</td>
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<td>0.25</td>
<td>1</td>
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</table>
pared with the unstrained matrix, indicating that this lattice expansion has no measurable effect on the height of the Ni L3 peak. The measured effect can thus fully be attributed to the difference in composition as a result of the Ni-depletion.

3.2.2. Bulk modulus

The calculated equilibrium lattice parameter of equiatomic NiTi is $a = 0.3018 \pm 0.0002$ nm, which agrees very well with the experimental value of 0.3015 nm [28] and the equilibrium lattice parameters of Ni4Ti3 have been calculated in a previous paper [21]: $a_R = 0.6697 \pm 0.0011$ nm, $x = 113.84^\circ \pm 0.05^\circ$ for the rhombohedral unit cell. These GGA results are in good agreement with the experimental values of $a_R = 0.6695$ nm and $x = 113.95^\circ$ [21]. In order to calculate the bulk modulus of both structures we considered a series of volume expansions and compressions up to 20% of the equilibrium volume for which the total energy was calculated. The bulk modulus was evaluated around the equilibrium volume by fitting the total energies with the Murnaghan equation of state [29]. For Ni–Ti this results in 164 ± 2 GPa where the error bar follows from the statistical uncertainty of the fitting procedure. This result is in quite good agreement with the value of 156 GPa obtained from DFT calculations performed within the local density approximation (LDA) [30] and the value of 157.8 GPa also obtained within LDA but with the bulk modulus evaluated around the experimental volume [31]. Significant differences in the calculated values of the bulk modulus (even up to 30%) [32] are not unusual and are mainly a result of the different approximations made within the DFT approach (GGA versus LDA), the functional form of the fitting function and/or the volume around which the bulk modulus is evaluated (experimental volume versus equilibrium volume) [32]. For example, optimizing the cell parameter of B2 NiTi within LDA [33] yields a lattice parameter $a = 0.2944 \pm 0.0005$ nm and a corresponding bulk modulus of (196 ± 2) GPa. This overbinding is a well-known shortcoming of LDA and results in a too-large bulk modulus, which can be corrected by evaluating the bulk modulus at the experimental volume [32] resulting in 153 GPa for Ni–Ti. The calculated bulk moduli are somewhat higher than values between 125 and 140 GPa obtained experimentally from quenched and aged equiatomic NiTi single crystals [34,35]. The difference between experimental and computed elastic moduli is not only a result of the approximations made within DFT but also of zero-point and finite-temperature effects, which are not taken into account in the calculations (and which can yield differences up to 20% for the bulk modulus) [36]. The bulk modulus of Ni4Ti3 was determined to be 172 ± 2 GPa (using GGA). In order to study the effect of the composition on the elastic properties of the B2 NiTi structure we performed a calculation of the bulk modulus for a 2×2×2 supercell in which a Ti atom was replaced by a Ni atom which corresponds to the composition Ni56Ti44 or Ni56.25Ti43.75. The equilibrium lattice parameter of the supercell is $a = 0.5975 \pm 0.004$ nm, which is shorter than twice the size of the unit cell of the equiatomic composition but the substitution of Ti by Ni does not alter the atomic positions within the unit cell. The contraction of the lattice is accompanied by a higher value of the bulk modulus, namely 168 ± 2 GPa. A linear interpolation suggests a value of 165 GPa for the 51 at.% Ni compound.

4. Discussion

The early EDX results from Nishida [4,5] and Tadaki et al. [6] showed an atomic concentration of about 56 at.% Ni for the precipitates, i.e., a Ni/Ti atomic ratio of 1.27. Tadaki et al. also deduced a space group of R3 with 14 atoms in the unit cell based on electron diffraction results and further modified the composition from Ni56Ti44 to Ni54Ti3. Recently, quantitative electron diffraction investigations and first-principles calculations were carried out to refine the positions of the atoms in a Ni54Ti3 unit cell by Tirry et al. [21]. For the composition of Ni56Ti44 they also modified the site occupancies of Ni positions, but did not obtain a better structure. Therefore, the atomic ratio of 1.33 determined by the present EELS measure-

Fig. 8. Calculated Ni L3 edges for (a) Ni7Ti8 and (b) 2.0% expanded B2 NiTi compared with undistorted equiatomic NiTi, assuming a 1.2 eV resolution.
ments is consistent with the structure with the space group of \( R3 \) with 14 atoms (6 Ti and 8 Ni) in the unit cell deduced from electron diffraction results and group theory by Tadaki et al. [6] as well as with the refined cell by Tirry et al. [21]. Although the signal-to-background ratio in EDX is much higher than that in EELS, the spatial resolution of EELS in a TEM is much higher than that of EDX.

The relatively poor spatial resolution of EDX could be the main source of the lower Ni/Ti atomic ratio for the precipitates with thicknesses less than 100 nm when measured by EDX in Refs [4–6], especially in the case of EDX measurements in a scanning electron microscope on thicker samples, as in those cases averaging with surrounding matrix with a lower Ni concentration can be expected.

EELS measurements performed before cleaning by ion milling showed that oxide was formed on the surfaces of the electropolished TEM samples. The oxide was demonstrated to be Ti-oxide by energy-filtered TEM [37], with no preference for surface of the matrix or precipitates. Quantifications of EELS spectra showed that the O/Ti atomic ratio was usually much less than 5.0% for those samples with thicknesses of \( \sim 60–70 \text{ nm} \). This means that the thickness of the Ti-oxide layer formed on the surface of the TEM samples is below 1.5 nm. Simulations of the effect of the ion milling on the metallic surface indicated that the milling probably also removed part if not all of the thin Ti-depleted surface layer beneath the oxide layer. Since no difference could be detected in the oxide layer between the precipitates and the matrix, no diminishing effect of this oxidation nor the milling treatment on the analytical results is expected.

The observation of a Ni-depleted zone surrounding the precipitates can be of importance to the martensitic transformation underlying the shape memory and superelastic behavior. Indeed, when the Ni content decreases, the martensite start temperature (Ms) increases up to the point of transformation edges. Thus there is essentially no charge transfer on the comparison between the normalized integrated ionization edges. Therefore, both the structural and compositional changes do not have a significant influence on the total amount of 3d electrons of the elements in the Ni–Ti compounds. The present results are consistent with Muller’s assumption saying that the total charge around each atom does not change upon the formation of intermetallic compounds [13]. It has been claimed that the intensity of the Ni L\(_{2,3}\) white lines could be increased upon a martensitic transformation in a Ni–Ti alloy [38] which also clearly changes the lattice structure, but that observation could also have been influenced by minor changes in composition during the in situ experiment. The present simulations indeed indicate that the major effect in the present case is that of the chemical concentration, while the lattice deformation has no visible effect under a resolution of 1.2 eV.

It is known that crystal orientation can affect the position of the plasmon peak in EELS [7,39]. In highly anisotropic material like graphite, the value of \( E_p \) can vary as much as 6.0 eV by changing the zone orientations from [100] to [001] [40]. Measurements from different zone orientations demonstrated that the position of the plasmon peak for the B2 phase did not change, which can be understood from the isotropic nature of the cubic structure. On the other hand, the plasmon peak for the precipitate was found to vary within a narrow energy range from 20.8 eV to 21.7 eV by tilting the sample. Thus the values of the Young’s modulus are deduced to be in a range of 147–163 GPa, which shows slight anisotropy along different crystallographic directions.

Comparing the experimental values for the moduli between the matrix and the precipitate it is concluded that the precipitate has substantially higher values for both Young’s and bulk moduli, which corresponds with the fact that the Ni\(_4\)Ti\(_3\) structure has a smaller atomic volume (shorter nearest neighbor distances) compared to that of B2 NiTi. The Ni\(_4\)Ti\(_3\) precipitates are indeed known to be harder or more reluctant to a displacive transformation than the matrix, i.e., they do not follow the martensitic transformation, which plays an important role in the shape memory behavior of this material. This nanosopic measurement of relative as well as absolute stiffness of a precipitate with respect to its surrounding matrix is extremely powerful, especially since the present precipitate structure cannot be formed in larger quantities and shapes since Ni\(_4\)Ti\(_3\) is a metastable phase. The difference in stiffness is to some extent confirmed by the ab initio calculations in the sense that the B2 phase indeed shows lower values for the bulk modulus, be it by only 5% whereas the experiment shows a much larger difference of about 25%. The actual reason for this discrepancy is unclear till now, but could be due to the fact that the experimental measurements are performed on precipitates under stress inside a matrix while the calculations are done for relaxed structures. Indeed, as the precipitate has a shortened c-axis per-
Young's modulus of the B2 Ni51Ti49 phase can be understood to originate from a single crystal. From literature, the elastic moduli of the B2 matrix with others from the literature are often rather different. The value of 118 ± 4 GPa for single crystals of the cubic B2 Ni–Ti phase with a Ni concentration of 41 at.% are around 190 GPa and 155 GPa, respectively, both ±10 GPa [35]. From this, the Young’s modulus of the B2 Ni51Ti49 phase can be evaluated to be 51 GPa based on the elastic theory for isotropic media:

\[ v = \frac{c_{12}}{c_{11} + c_{12}}, \quad Y_m = (1-2v)(c_{11} + 2c_{12}) \]

which means that our nano-probe measured value is substantially higher than the one found by conventional techniques. The corresponding bulk modulus \( B = (c_{11} + 2c_{12})/3 \) is around 167 GPa [35], which is in its turn substantially higher than the one measured by the present plasmon technique. The reason for the latter is the relatively high value for \( c_{12} \) as this yields \( c_{12} >> c_{11}/2 \) by which also the Poisson ratio \( v \) becomes substantially larger than 1/3, namely 0.449. The latter immediately implies that Ni–Ti strongly deviates from the average fits in Ref. [13] obtained from the pure elements, even when limited to those from group IV, as for those elements the average \( v \) is slightly below 1/3, explaining a slightly larger Young’s than bulk modulus when calculated through these fits. So in order to obtain better values for the elastic moduli from the plasmon energy for the present system, one could return to the formula underneath the fitted function \( B = 2E_p^\delta \) and fit both parameters \( x \) and \( \beta \) using the measured values for \( E_p \) and calculated ones for \( B \) for the two Ni–Ti compounds (B2 and Ni4Ti3). Doing so yields \( x = 68 \) and \( \beta = 0.3 \), values strongly deviating from those from Oleshko and Howe, as could be expected. Unfortunately, we have no additional results on other Ni–Ti compounds to improve the fit or check the validity of this approach. Also, the observed anisotropy of the precipitate is not included in this procedure.

For polycrystalline equiatomic B2 NiTi materials, the Young’s modulus was reported to be in the range 40–90 GPa [42] with a value of 65 GPa, which can be calculated from recent measurements on Ni50.5Ti49.5 [43]. However, a value of about 130 GPa was measured from an amorphous Ni50Ti50 thin film deposited on a steel substrate [44]. Since the Young’s modulus is sensitive to microstructures, the latter difference between the literature data and the present results can be expected due to different microstructures in the polycrystalline materials and their single crystal counterparts. Another factor influencing the position of the plasmon peaks is the crystal size. Theoretical calculations showed that the peak energy would increase with decreasing the particle size to below 5 nm [45]. The sizes of the precipitates investigated here, however, are much larger than 5 nm, therefore the size effect can be ignored.

5. Conclusion

The composition of precipitates in a Ni–Ti shape memory alloy was directly determined by EELS using a newly developed quantification technique EELSMODEL, which confirmed the Ni/Ti atomic ratio of 4:3. Further, depletion of Ni in the matrix upon the Ni4Ti3 precipitation was investigated, showing a Ni-depleted zone within the matrix surrounding the Ni4Ti3 precipitate with a total balance of Ni on both sides of the precipitate. Both the EELS experiments and the first-principles calculations show that the normalized L3 peak of Ni from the Ni4Ti3 precipitate and the Ni-depleted region is slightly higher by about 2–2.5% than that from the B2 phase; however, essentially no electron transfer is observed from Ni to Ti upon the formation of the precipitate. The plasmon EELS evaluation shows that the Ni4Ti3 precipitates are harder than the B2 phase but the numbers for the Young’s and bulk moduli found from empirical fits from tabulated values for the elements are not resulting in data comparable with macroscopic experiments. First-principles calculations show that the bulk modulus of Ni4Ti3 is indeed higher than that of B2 NiTi, be it by a much smaller percentage of only 5%.

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References