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Site-occupation of Nb atoms in ternary Ni-Ti-Nb shape memory alloy

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In this work, aberration corrected High Angle Annular Dark Field - High Resolution Scanning Transmission Electron Microscopy (HAADF-HRSTEM) combined with Precession Electron Diffraction (PED) has been used to find Nb atoms both in the matrix and the Ti_2Ni phase in a $Ti_{45.5}Ni_{45.5}Nb_9$ shape memory alloy.

The atomic model of the ordered body-centered cubic (bcc) B2 crystal structure of the austenite matrix is shown in Figure 1(a). Figure 1(b) is the atom projection of the B2 structure along the [001] zone axis. In this viewing direction every atom column is a pure column, i.e. or Ni or Ti and their columns are alternatively arranged along the <110> directions. In order to find the preferential site for the Nb solute atoms in the ternary system, Z-contrast HAADF-HRSTEM images along <001> have been obtained from the Ni-Ti-rich matrix of the reference binary $Ni_{51.7}Ti_{48.3}$ material and the as-cast $Ti_{45.5}Ni_{45.5}Nb_9$ sample. Examples of these are shown in Figure 1(c) and (d), respectively. In Figure 1(e) and (f), refined parameterized empirical models using the quantitative method explained in [1] are shown which are in close agreement with the underlying experimental data of (c) and (d), respectively. Histograms of the estimated total scattered intensities are presented in Figure 1(g) and (h) indicating the distributions of the measured scattering cross sections for the atomic columns in these images. Although it is clear that the ensembles of atom columns belonging to one of both pure Ni or Ti sub-lattices in Figure 1(c) and (e) reveal important variations in intensity (Ti atom columns in white box, Ni in black box), the respective histograms can clearly be discriminated. Contrary, for the ternary Ni-Ti-Nb, the intensity histograms of the labeled Ni and Ti+Nb columns strongly overlap as shown in Figure 1(h). The comparison of the intensity histograms of the binary and ternary matrices shown in Figure 1(g) and (h), respectively, clearly indicates that the Nb atoms are located on the Ti sites.

An alternative HAADF-HRSTEM approach is used to determine the location of the Nb atoms in the Ti_2Ni (space group is Fd m) phase. This phase has a complex face centered cubic (fcc) based crystal structure with 96 atoms of which 64 Ti atoms occupy two Wyckoff positions 48 f and 16 c, and 32 Ni atoms occupying the 32 e positions. The projection structure model for one unit cell along the [001] and [011] zone axes are displayed in Figure 2(a) and (b), respectively. In both cases all atom columns are pure columns. The purple (dark) and green (light gray) atoms represent the 48 f and 16 c Ti atoms, the silver (white centered) atoms are the 32 e Ni atoms. Figure 2(c) and (d) are HAADF-HRSTEM experimental images of one unit cell along [001] and [011], respectively. In Figure 2(e) to (j) HAADF-HRSTEM simulated images using STEMsim [2] along [001] and [011] are presented for different occupation sites for the Nb atoms. According to the STEM Energy Dispersive X-ray Spectroscopy (EDX) data of this Ti_2Ni phase, Ni has a concentration of 33.7% ± 0.8% which corresponds with the 1/3 stoichiometric ratio of Ni in the Ti_2Ni phase. In a unit cell with 96 atoms this yields 32 Ni atoms, the remaining 64 being divided over 41 Ti and 23 Nb, again following the EDX data. In Figure 2(e) and (f) all Nb substitutes on Ti f sites, in (g) and (h) all Ti c sites are replaced by Nb, the remaining Nb atoms being placed on the Ti f sites while in (i) and (j) all Nb atoms substitute on Ni e sites, with Ni atoms replacing Ti on f and c sites accordingly. Comparing the indicated intensity profiles of the experimental images with those of the three simulated cases for the [001] zone axis it is clear that Nb atoms prefer to substitute for the 48 f Ti atoms. The same conclusion can be drawn from a qualitative comparison of the [011] experimental and calculated images.

PED was used to further verify that Nb atoms prefer to substitute the 48f Ti positions. In practice, reflections were extracted from a total of 6 PED patterns with different zone axes (<110>, <112>, <113>, <116>, <123> and <255>). Since in principle there are three possible symmetry positions (f, c and e) for the Nb atoms to occupy, 3 pairs of starting structure models are created to find the occupation preference of the Nb atoms between each two positions based on the PED refinement performed with JANA2006 software. The results show that the model with all Nb atoms occupying the Ti f site gives the lowest R-value, confirming the HAADF-HRSTEM conclusions.

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2. http://www.ifp.uni-bremen.de/electron-microscopy/software/stemsim/
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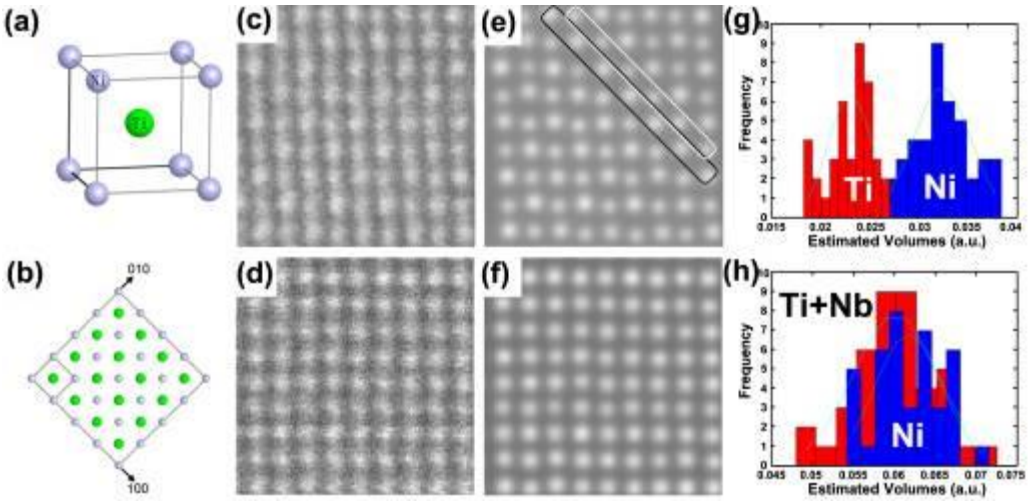

Figure 1. (a) Atomic structure model and (b) projection along [001] zone axis of binary TiNi. (c) HAADF-HRSTEM image of binary $Ti_{48.3}Ni_{51.7}$ and (d) ternary $Ti_{45.5}Ni_{45.5}Nb_9$. (e), (f) corresponding refined parameterized empirical models. (g), (h) histograms of total scattered column intensities in (e) and (f), respectively. The white and black boxes in (e) represent the Ti and Ni atom columns, respectively.

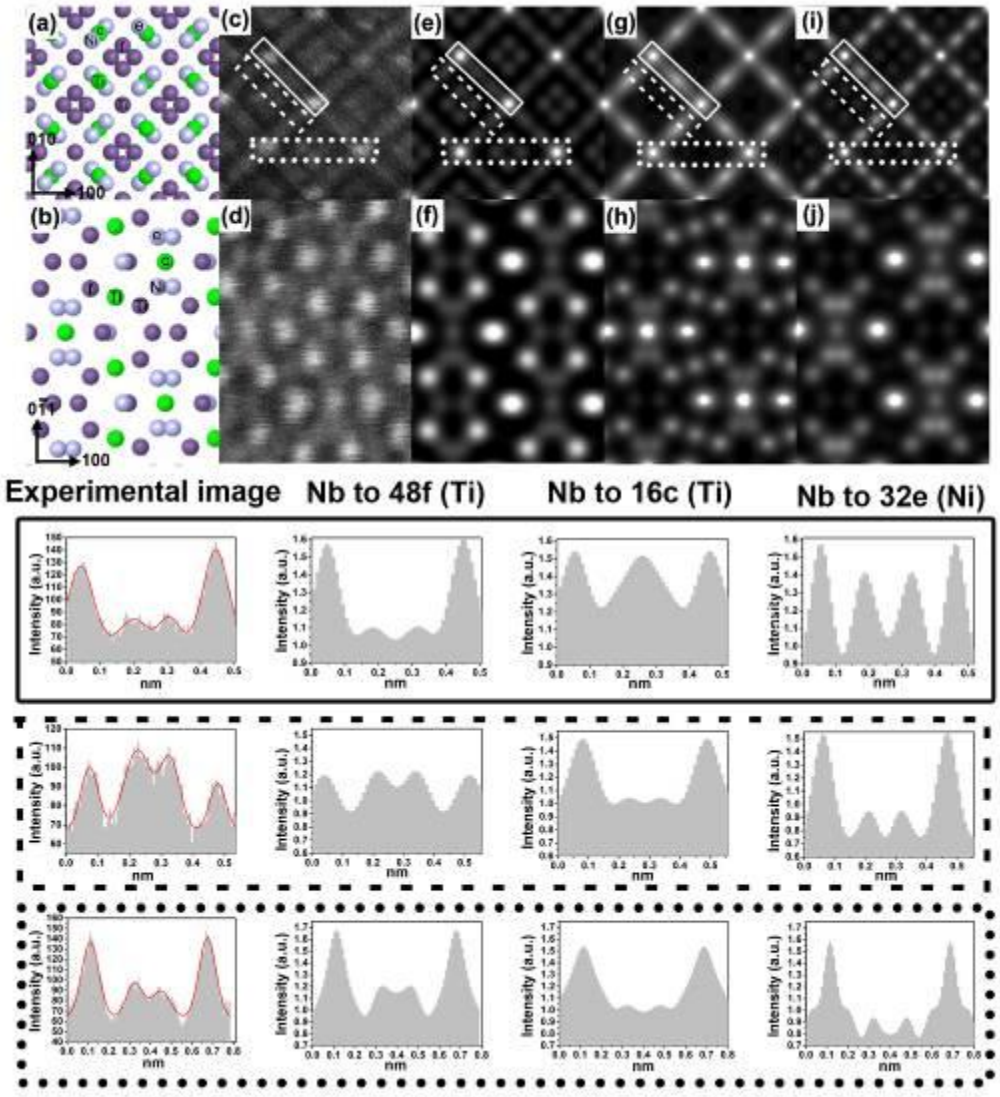

Figure 2. (a), (b) atomic projections along [001] and [011] zone axis of Ti_2Ni phase. (c), (d) corresponding experimental HAADF-HRSTEM images. (e) to (j) corresponding simulated images for different Nb occupations (48 f, 16 c and 32 e)