Lattice deformations in quasi-dynamic strain glass visualised and quantified by aberration corrected electron microscopy

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Advanced transmission electron microscopy and statistical parameter estimated quantification procedures were applied to study the room temperature quasi-dynamical strain glass state in Ni–Ti alloys. Nanosized strain pockets are visualised and the displacements of the atom columns are quantified. A comparison is made with conventional high-resolution transmission electron microscopy images of point defect induced strains in Ni–Al alloys.

1 Introduction Martensitic transformations have attracted a lot of attention for decades, since they play a key role in superelasticity (SE) and shape memory (SM) behaviour, which enable a wide range of applications as actuators, coupling joints, medical implants, etc. [1]. In recent years, a new glass state was observed in some martensitic and ferroelastic systems, including the widely used Ni–Ti [2–5], Ni–Ti–Fe [6–8], Ti–Pd–Cr [9, 10], and Ni–Co–Mn–Ga [11]. The strain glass state, considered to be a conjugate state to the martensite and ferroelastic state, has features of all glass behaviours such as dynamic freezing, ergodicity breaking and existence of local strain [8, 12]. The strain glass behaviour is achieved by doping sufficient point defects (excess solute atoms or alloying elements) into materials to suppress the long-range martensitic transformations. These randomly distributed point defects decrease the thermo-dynamic driving force for the formation of martensite and create random local stress fields that favour local strain order [13]. As a result, the martensitic transformation is prohibited, but local strains still exist and reveal a strain glass transition into a structurally disordered state below a particular freezing temperature, with the lattice strain being the order parameter. X-ray diffraction (XRD) investigations show there is no average structure change or macroscopic symmetry change during the strain glass transition [5]. Several transmission electron microscopy (TEM) investigations have been carried out in order to reveal the details of the strains, however, so far these have only revealed the existence of nanodomains or diffuse superlattice scattering in electron diffraction patterns, without providing true structural detail at the atomic level [3, 4, 6–8].
Due to the inherent random-like nature of glassy systems, direct visualisation of the actual atomic configurations is indeed not trivial. Ultimately, only a true atomic resolution tomographic experiment of such a system will be able to provide the three-dimensional (3D) configurations of atoms, their local displacements and initiating point defects. Although important steps towards the quantification of 3D atomic resolution have been made in recent years [14], for bulk structures with a glassy and quasi-dynamic type of deformation we are still limited to two-dimensional information. In the present paper the results of a dedicated transmission electron microscopy (TEM) study aimed at quantifying the quasi-dynamic glassy deformations in two different Ni-Ti alloys are reported. These results are placed in perspective with earlier data on pre-martensite in Ni–Al.

2 Materials and methods Ni–Ti bulk samples homogenised for at least 2 h at 1000 °C and water quenched were obtained from S. Kustov. TEM disks were electro-polished to perforation in a Tenupol 3 operating at 12 V, 0.1 A, −20 °C with an electrolyte of 80% CH3OH and 20% H2SO4 [15, 16]. Sub-A resolution images have been obtained using an FEI Titan 50–80 monochromated and Cs-corrected TEM operating at 300 kV. In situ cooling was performed in an FEI Tecnai G2 instrument.

3 Results and discussion Tweed and other features precursing displacive phase transformations have received a lot of attention over the years, both experimentally as well as theoretically. Due to the sensitive nature of the many parameters playing a role in these phenomena, obtaining accurate quantitative data at the atomic level has not been obvious. For example, when interpreting conventional TEM images such as the original cross-hatched tweed patterns in, e.g., Ni-Al [17], care needs to be taken about the actual imaging conditions. Indeed, the observed length scale of the modulations is not only related to the underlying strain or disorder pattern but also to the actual orientation of the sample in the used two-beam bright- or dark-field procedure [17–19]. Since the strain in the matrix is expected to degrade away from any stress or disorder locus, a streak of diffuse intensity rather than a sharp reflection nearby affected diffraction spots in reciprocal space is observed. For each particular orientation of observation the Ewald sphere cuts this streak at a particular distance from the basic reflection resulting in one particular magnitude for the imaged modulation periodicity [18]. As a result, only average numbers such as the position of an intensity peak on the \( \langle 110 \rangle _{B2} \) diffuse intensity streak in electron diffraction patterns or the shift of the dip in the \([110]T_A2\) phonon branch with composition or temperature are available. Ultimately, atomic resolution images obtained along well-chosen crystallographic directions need to be used to directly reveal the local strains underlying the tweed pattern.

A classic high-resolution (HR)TEM image for a Ni62.5Al37.5 B2 austenite matrix splat-cooled with a cooling rate of approx. \( 9 \times 10^5 \) K s\(^{-1} \) is shown in Fig. 1a revealing the atomic lattice strained in the precursor condition occurring in a temperature regime above the bcc (B2) to fct (L10) martensitic transformation [20]. Although the overall symmetry of the corresponding selected area diffraction pattern (SAED) is perfectly square, the image clearly does not reveal a homogeneous microstructure, but instead pockets with a diameter of around 2–3 nm, each with a slightly different image resolution can be recognised. Rows of strong dots aligned along the indicated \( \langle 100 \rangle \) direction correspond with one of the sublattices of the ordered B2 structure (e.g., at A), while rows of dots of equal intensity along one of the \( \langle 110 \rangle \) directions reveal the projected basic bcc lattice (e.g., at B). Since large steps in sample thickness are improbable at such a small scale such local image differences are seen as a signature of local distortions or disorientations. A clearer signature of lattice deformations is seen in the regions indicated by arrows where the lattice is...
tilted or strained resulting in line contrast instead of atom column imaging. Moreover, when looking along a grazing incidence, all resolved lines are seen to be distorted yielding a wave-like pattern again indicating local strains. These strains result in the diffuse streaks in the \( \{110\} \) directions observed in the inset SAED pattern.

In Fig. 1b a HRTEM image of the same system but water quenched in a conventional way reveals extra modulations with an average periodicity of 6.5 \( \{110\}_{B2} \) lattice planes and a correlation length of 5–10 nm. This periodicity perfectly fits with the position of the intensity peak along the \( \{110\} \) diffuse streaks observed in corresponding electron diffraction patterns, as shown by arrowheads in the inset, as well as in elastic phonon scattering experiments [21, 22].

The observed contrast, also referred to as microtweed, can moreover be explained by assuming transverse \( \{110\}_{B2}\{110\}_{B2} \) displacements of the atoms [21]. Already in the 1980s it was proposed that these lattice modulations are induced by atomic scale point defects such as vacancies or anti-site atoms in the centre of the modulated domain. Such point defects are omnipresent in these off-stoichiometric systems and induce a strain field, which couples with the anisotropy of the lattice yielding so-called embryo’s for the ensuing martensitic nucleation [23–27].

Such point defects are omnipresent in these off-stoichiometric systems and induce a strain field, which couples with the anisotropy of the lattice yielding so-called embryo’s for the ensuing martensitic nucleation [23–27]. Such an embryo was also referred to as an inhomogeneously strained domain (ISD) [21]. However, no direct observations of the central defects have been performed as yet, but models including defects as disorder in the austenite confirm the possibility of such a coupling [27, 28].

Although the observed lattice displacements are of the same transversal type as those occurring during the ensuing displacive martensitic transformation and also accommodate the same wavelength as the long-period martensite structure 14M (or 7R) [29], their maximum amplitude within the ISDs only reaches about 10% of those producing the full martensite and fade out farther away from the central defect [21]. In other words, no full-grown product phase nuclei are observed in the tweed structure precursing the first-order transformation, as had been suggested in some earlier theoretical models [30]. The omnipresence of the observed \( \{110\}_{B2}\{110\}_{B2} \) modulations indicates that the ISDs cover the entire lattice and that no undistorted lattice remains. Although these observations provided a certain understanding of the structural details of these precursor features, the utilised instrumentation at the time did not allow to measuring the individual displacements with sufficient precision.

The appearance of a defect-induced precursor state in the form of either a tweed-like pattern as discussed above or nanocluster configurations is quite common in martensitic systems such as Ni–Al [21, 22, 32], Co–Ni–Ga [33] or Ni–Ti–Fe [34]. More recently the interest has shifted to similar features as those described above but in the case of the isotropic near-equiatomic Ni–Ti [16, 17, 28]. In this system, for a concentration above 51.3 at% Ni the martensite is found to be suppressed due to the large number of point defects, locally straining the lattice in small nanopockets thereby prohibiting the martensite to form [3, 5, 13].

In Fig. 2a, a room temperature Cs-corrected [001] HRTEM image of Ni\(_{51.7}\)Ti\(_{48.3}\) austenite is shown. According to the phase diagram of Zhang et al. [13] this system exists in the so-called unfrozen or quasi-dynamical disordered local strain state at room temperature. This is a non-frozen precursor state to the strain glass, i.e. occurring above the true strain glass freezing transition temperature. Still, despite the expected quasi-dynamical character of the precursor state, the image clearly reveals a large number of locally distorted nanoscale regions as highlighted by white circles, one being zoomed as inset. From the image the size of the...
domains can be estimated as to be around 3 nm in diameter, which is close to the size of the domains observed in splat-cooled Ni–Al but about half the size of the smallest ISDs found in microtweed of water-quenched anisotropic Ni–Al. The corresponding FFT inset in Fig. 2a shows the ordered B2 reflections as well as some diffuse intensity enhancement at $1/2\{110\}$ indicating a B19 or B19’ martensite precursor modulation. No sign of Ni$_4$Ti$_3$ nanoprecipitation or R-phase formation was found, as seen from the lack of corresponding reflections in the FFT [35]. Upon in situ cooling in a conventional microscope these precursors did not transform into complete martensite plates, confirming the strain glass phase diagram [3, 5, 13], but so far also no increment in domain size or local strain could be determined. The fact that such strained domains can be observed in the quasi-dynamic, i.e. unfrozen, state is probably similar to the observation of the modulated pre-martensite domains in Ni–Al, even without complete softening of the corresponding phonon branch and could possibly be related to a thin foil effect lowering the frequency of the quasi-dynamic state or to a hysteresis effect after the cooling during electropolishing (or a combination of those).

In Fig. 2b a similar image is shown but now from the Ni$_{50.8}$Ti$_{49.2}$ system, i.e. at a concentration which, according to the phase diagram of Zhang et al. [13], should not reveal any quasi-dynamic or static strain glass. From this image no obvious deformed regions can indeed be recognised confirming the link between an increased number of point defects and strain glass features. Since both TEM samples have been prepared in the same way, the latter also indicates that the observation of such deformed regions is not induced by an extrinsic thin foil effect. As mentioned above, the latter could shift the stability range, but without the intrinsic nature of sufficient point defects it would not induce the glassy state.

In an attempt to quantify the above qualitative observations, both images were subjected to a statistical parameter estimation quantification procedure. In general, the aim of such a statistical parameter estimation approach is to estimate unknown physical quantities or parameters on the basis of experimental observations such as HRTEM images. Usually, these observations are not the quantities to be measured themselves but are related to certain quantities of interest. This relation is often known in the form of a mathematical function, which might be derived from physical laws and the quantities to be determined are the parameters of this function. Parameter estimation is the computation of numerical values for the parameters from the available observations. For example, if electron microscopy images are recorded of a specific object, this function describes the electron–object interaction, the transfer of the electrons through the microscope, and the image detection. The parameters are the atom positions and atom types. The parameter estimation problem then turns into computing the atom positions and atom types from the observations. Therefore, the parameterised mathematical function is fitted to the observations using a criterion of goodness of fit, which quantifies the similarity between this function and the observations. Despite the fundamental limitation of noise in the observations, the precision of the position estimates of projected atom columns that can be obtained from HRTEM images is orders of magnitude better than the resolution of the electron microscope, especially for Cs-corrected microscopes that minimise delocalisation problems typical for non-corrected field emission gun (FEG) instruments [36–38]. A general overview of statistical parameter estimation theory was given by van den Bos [39] while den Dekker et al. [40] have provided a summary of this theory with a focus on electron microscopy.

Figure 3a shows a zoom of a visibly strained part of the image in Fig. 2a of Ni$_{51.7}$Ti$_{48.3}$, while in Fig. 3b the corresponding model function estimated in the least squares sense is given. The latter figure can be regarded as an optimal reconstruction of the original image. From these, interatomic distances as well as displacements from the perfect cubic lattice positions and their corresponding SDs have been computed. As seen from Fig. 4, these SDs, being a measure of the precision, range from 3 to 10 pm, which is one to two orders of magnitude better than the resolution of the microscope (10 pm) and implies that all displacements above 10 pm are larger than the statistical uncertainty. As an example, the schematic in Fig. 3c reveals relative displacements of the atom columns (one column = one pixel) w.r.t. a reference lattice and showing pockets of large and small distortions. Although only few clear distorted regions could be visually identified in the original image in Fig. 2a (white circles), the map in Fig. 3c indicates that most atom columns reveal an averaged displacement above 10 pm. A similar observation can be made by mapping the orientation distribution of the displacement vectors.

In this respect it should further be noted that the 2–3 nm domain size of the distorted regions is about five to ten times smaller than the expected foil thickness of an electropolished TEM sample suitable for quantitative HRTEM. Moreover, in Fig. 2a some undistorted regions can still be observed. Although the actual image can be affected by the focusing conditions this indicates that in this case some undistorted matrix still exists above and/or below the distorted regions. As a result of this overlapping the obtained measures of atomic displacements in the following paragraphs should thus be considered as a lower bound and actual displacement values can be slightly higher due to the masking of surrounding undistorted matrix.

In Fig. 4 the mean interplanar spacing between a series of 15 subsequent (110) planes in the Ni$_{51.7}$Ti$_{48.3}$ case is shown. The average for each plane was obtained over all interatomic spacings measured between two subsequent (110) planes in Fig. 3. Such a typical set of 15 (110) planes is highlighted by a horizontal bar with 15 dashes in Fig. 3b. One case of an average measure of interatomic distances between planes 4 and 5 is also shown as vertical lines and will result in the measure of plane 5 in Fig. 4. The total average value of all these (110) interplanar spacings equals 0.212 nm and perfectly matches the ideal B2 cubic structure with a lattice...
parameter of 0.30121 nm confirming the average austenite structure as concluded from macroscopic measurements [5]. Figure 5a and b shows the distribution of the displacements of atom columns from the perfect nearby cubic lattice positions. From these it is clear that the average amount as

Figure 3 (a) Zoom of a distorted region in Ni$_{51.7}$Ti$_{48.3}$ together with the corresponding model function in (b). (c) Schematic indicating the displacements of the atoms w.r.t. the perfect bcc lattice (each pixel corresponds with one atom column).

Figure 4 Mean (110) interplanar spacing in Ni$_{51.7}$Ti$_{48.3}$. Each point is the average over all interatomic spacings measured between two subsequent (110) planes, as indicated in Fig. 3b. The horizontal line is the total average value of 0.212 nm corresponding with the respective B2 interplanar spacing.

Figure 5 Distributions of the displacements of atom columns from the perfect nearby cubic lattice positions for (a) Ni$_{51.7}$Ti$_{48.3}$ and (b) Ni$_{50.8}$Ti$_{49.2}$. 
well as the spread in displacement is larger for the Ni_{51.7}Ti_{48.3} case (Fig. 5a; resp. 28 pm; 16 pm) than for the Ni_{50.8}Ti_{49.2} one (Fig. 5b; resp. 19 pm; 12 pm), again confirming the effect of an increment in number of point defects on the strain glass character.

Not only structure analyses but also chemical analyses may benefit from statistical parameter estimation. Recently, progress has been made in the quantitative evaluation of high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images [41]. It is generally known that these images show Z-contrast meaning that the intensity scales with the atomic number. One of the advantages is therefore the possibility to visually distinguish between chemically different atomic column types. However, if the difference in atomic number of distinct atomic column types is small or if the signal-to-noise ratio is poor, direct interpretation of HAADF-STEM images remains inadequate. In order to extract quantitative chemical information on a local scale, the total intensity of the scattered electrons for the individual atomic columns can be quantified using statistical parameter estimation. The thus estimated intensities can then be used as a performance criterion to identify point defects such as vacancies or antisite atoms, which are expected to be at the core of the strained regions.

4 Conclusions Advanced transmission electron microscopy and statistical parameter estimated quantification were applied to study the point defects induced quasi-dynamic strain glass state in Ni–Ti. Nanostrained regions are observed in Ni_{51.7}Ti_{48.3} while interatomic distances as well as displacements from the perfect cubic lattice positions and their corresponding SDs have been measured with high precision. The link between an increased number of point defects and precursor or strain glass features is demonstrated. A comparison is made with the conventional high-resolution transmission electron microscopy study of the nanostrains in non-stoichiometric Ni–Al alloys.

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