Dedicated TEM on domain boundaries from phase transformations and crystal growth

Dominique Schryvers\textsuperscript{a,*}, Sandra Van Aert\textsuperscript{a}, Rémi Delville\textsuperscript{a}, Hosni Idrissi\textsuperscript{a}, Stuart Turner\textsuperscript{a} and Ekhard K.H. Salje\textsuperscript{b}

\textsuperscript{a}EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium; \textsuperscript{b}Department of Earth Sciences, Cambridge University, Downing Street, Cambridge CB2 3EQ, UK

(Final version received 14 May 2012)

Investigating domain boundaries and their effects on the behaviour of materials automatically implies the need for detailed knowledge on the structural aspects of the atomic configurations at these interfaces. Not only in view of nearest neighbour interactions but also at a larger scale, often surpassing the unit cell, the boundaries can contain structural elements that do not exist in the bulk. In the present contribution, a number of special boundaries resulting from phase transformations or crystal growth and those recently investigated by advanced transmission electron microscopy techniques in different systems will be reviewed. These include macrotwins between microtwinned martensite plates in Ni–Al, austenite-single variant martensite habit planes in low hysteresis Ni–Ti–Pd, nanotwins in non-textured nanostructured Pd and ferroelastic domain boundaries in CaTiO$_3$. In all discussed cases these boundaries play an essential role in the properties of the respective materials.

Keywords: interface; habit plane; twin; martensite; transmission electron microscopy; nanostructure

1. Introduction

The present manuscript reviews a few examples from different fields in materials science in which advanced transmission electron microscopy (TEM) has unraveled the details of boundary structures that play an essential role in the macroscopic properties of the respective materials. In three of the four cases the boundaries result from a symmetry lowering phase transformation, such as martensitic transformations, in one case they are due to the need for energy minimization during crystal growth. For first-order displacive martensitic transformations elastic energies at habit planes and interacting martensite plates resulting from imperfect matching at the atomic scale between both sides of the interface will affect the height of the energy barriers to overcome and thus the related macroscopic properties such as hysteresis, superelasticity etc. In ferroelectric systems, local displacements or elasticity at the atomic scale can induce changes in the electric components so that the boundaries behave in a different way than the matrix. Similarly, twin boundaries can act as obstacles to dislocation motion as well as sources for...
dislocation storage and multiplication thus strongly affecting the mechanical behaviour of nanostructured materials.

2. Results

2.1. Crossing macrotwins in Ni–Al martensite

In the first example atomic details of particular microscopic configurations resulting from the cubic-to-tetragonal martensitic transformation in Ni$_{65}$Al$_{35}$ are presented. At this composition, the transformation occurs at around 250°C [1]. The ideal orientation relationships between, e.g., twin and habit planes have been predicted before by the conventional crystallographic theories and have in some cases already been documented for this transformation [1–3]. However, the actual atomic configurations at the interfaces reveal remarkable features that indicate a higher level of complexity than what classic theoretical discussions take into account. Unfortunately, the high speed and small hysteresis of the transformation usually result in completely transformed samples at room temperature and major difficulties for in situ temperature work, the latter also being hampered by thin foil effects in TEM samples. As a result, the actual dynamic origin of a given structure usually cannot be followed directly and has to be inferred from its final configuration. In Figure 1 an example of a macrotwin interface involving two families of periodic microtwin plates is shown in low and high magnification, the latter revealing atomic resolution up to the interface. In this case, two out of the three possible deformation variants of the martensite are involved, which implies that the microtwins in the two plates involved originate from two perpendicular $(110)_i$ families of planes in the austenite [4]. From the analysis of the observed angles between the microtwins it could be concluded that the two plates on either side of the interface have nucleated and grown separately to coalescence and merge forming the interface with the layer of crossing or

![Figure 1.](attachment://image1.png)

Figure 1. (a) Low magnification image of a macrotwin boundary revealing crossing type configurations. (b) $(110)$ martensite HRTEM image revealing the atomic configurations at a crossing type macrotwin boundary with of angle $<90^\circ$. The arrows indicate the direction of curvature for the small penetrating microtwin tips. The power spectra are incorporated in order to measure relative deformations and orientations.
penetrating microtwin tips, including bending of the microtwins. In cases where the microtwin configurations are less periodic, the penetration is less systematic and a more staircase-like interface is observed [4]. Without going into the details of the theoretical analysis and the differences between the different configurations originating from combinations of various plates and variants, it is clear that these structural features observed at the plate interfaces are strongly different from the bulk. From the observation of bend microtwins and small lattice deformations, an increased strain energy storage at these domain boundaries can be inferred. This will affect the resistance against detwinning playing a role in the superelasticity and possibly also increase the hysteresis of the reversible martensitic phase transformation, which is the basis for the shape memory behaviour of these materials.

2.2. Matching austenite-martensite habit plane in Ni–Ti–Pd

Whereas the first example focused on an interface between two variant plates of the product phase of a transformation, resulting from the lowering in symmetry during that transformation, in the second example we stick to martensitic transformations but now focus on the interface between the parent and the product phase, the so-called habit plane. In an attempt to reduce the hysteresis, Cui et al. [5] developed a series of ternary and quaternary alloys based on the geometric non-linear crystallographic theory of martensite (GNLTM) by Ball and James [6]. By matching the lattice parameters of the parent and product phases in such a way that the middle eigenvalue $\lambda_2$ of the transformation matrix is as close as possible to 1, it can be shown that the martensite will appear as a single untwinned variant and the hysteresis of the transformation drops to zero. A typical example of the former feature is shown in the mosaic in Figure 2 of TEM BF pictures of a Ti$_{50}$Ni$_{40.5}$Pd$_{9.5}$ ($\lambda_2 = 0.9993$) sample and matched together to render a full view of the plate which is too large to be properly observed in full detail in a single image. The plate is more than 30 $\mu$m wide, which is unusually large and does not contain a periodic microtwin laminate structure, as do samples from the same series but with different composition and thus different value for $\lambda_2$ [7]. It does, however, contain a few single fine martensite twin platelets. Most of these find their origin in the Ti$_2$Pd precipitates (round white structures) observed inside the plate or at the edges of the plate [8]. This overall structure is unique to the alloys satisfying the compatibility condition.

Figure 2. Mosaic of BF pictures matched together to show the full extend a very large martensite plate in Ti$_{50}$Ni$_{40.5}$Pd$_{9.5}$ containing single fine martensite platelets but no microtwin laminates.
Figure 3(a) shows a high-resolution micrograph of the second feature, a habit plane between a single variant of martensite and austenite in Ti50Ni40Pd10 (or ‘exact austenite-martensite interface’). The slightly rotated \( \frac{5}{4}\) (001)\( _{\text{B19}} \) crystallographic planes of the martensite (upper part) join the (01-1)\( _{\text{B2}} \) planes of the austenite (lower part) at the interface oriented parallel to the (75-5)\( _{\text{B2}} \) plane. When calculating the geometric lattice spacing mismatch between the B2 and B19 projected along the trace of this plane, one finds only a small mismatch of 0.36\%. In other words, the lattice planes join very well at the interface with very little distortions and no misfit defects were detected, as can indeed be confirmed from the magnification in Figure 3(b). Furthermore, the even grey scale in the geometrical phase analysis (GPA) [9] images clearly shows that no strain field is produced in the matrix nearby the interface as seen from the displacement and rotation maps in Figure 3(c) and (d), respectively. This observation confirms a low energy boundary configuration for this \( \lambda_2 = 0.9998 \approx 1 \) case supporting the experimental measurement of a low hysteresis related to the atomic structure of the habit plane.

2.3. Nanotwins in nanostructured Pd

In the next case the defect arrangement at a twin interface in a Pd nanostructured alloy is presented. In this case neither the twin boundary nor the defects arise due to a phase transition, but they do play an essential role in the mechanical properties of the material. During growth of the Pd film by sputtering or electron beam evaporation, increasing internal strains at grain boundaries between non-textured grains will be released by the formation of twins and the reorientation of the grain boundary involved, despite the high stacking fault energy of Pd [10]. For slow growing films, this yields perfect coherent twin
boundaries, extending from one grain boundary to the next crossing the nanograins. When the films are subjected to moderate or large strains, up to 6%, dislocations are created at the grain boundaries which will cross the nanograins and interact with the twin interfaces leaving multiple glissile Shockley partial dislocations (SPD) with Burgers vector in the twin plane and a few sessile Frank dislocations with Burgers vector pointing out off the twin boundary, as seen in Figure 4 [11]. The plastic deformation is not carried by grain boundary mediated processes but the coherent twin boundaries offer multiple barriers to dislocation motion as well as sources for dislocation storage and multiplication, via two major types of lattice dislocation/twin boundary interactions: the creation of sessile Frank dislocations and the transmission of the lattice dislocations. All these mechanisms involve SPDs left along the twin boundary. The twin boundaries progressively become incoherent and thus more resistant to dislocation penetration. The combination of nanograins free of twins and those containing one or more twins partially explains the unexpected high ductility and strain hardening behaviour of nanobeams produced from this material [12].

2.4. Ferroelastic domain boundaries in CaTiO₃

The examples presented so far are two cases in which conventional high resolution TEM can still play a useful role in understanding the material’s behaviour. More and more, however, interest shifts to better quantification such as the determination of exact atom positions and atom shifts with respect to a reference lattice such as the matrix. With the help of novel imaging techniques and statistical quantification tools, precisions up to the picometer range have recently been obtained by advanced TEM. In the following example a single twin boundary in CaTiO₃ has been imaged using aberration-corrected TEM in combination with exit wave reconstruction [13]. A FEI Titan³ 50-80 operated at 300kV has been used in this study providing direct structural imaging at a sub-Å resolution level. Further improvement of the resolution up to the information limit of the microscope can be achieved by reconstructing the so-called exit wave, which is the complex electron wave when leaving the specimen. Here the through-focal series reconstruction method was used in which the exit wave is reconstructed from a set of images taken at different defocus values [13]. The present observations relate to a (110) type twin boundary formed in the orthorhombic \textit{Pnma} CaTiO₃ phase after cooling from the cubic high temperature phase.
and imaged along its [001] zone-axis in order to maximize the visibility of any expected atomic displacements. This twin is seen as the horizontal line indicated in the reconstructed amplitude and phase images of Figure 5(a) and (b), respectively, also showing the positions of the Ca and Ti atoms. From careful analysis using statistical parameter estimation of the images we find, in the \(x\)-direction (i.e., perpendicular to the twin wall), systematic deviations for Ti of 3.1 pm in the second closest layers and pointing toward the twin wall. A larger displacement is measured in the \(y\)-direction (i.e., parallel to the twin wall) in the layers adjacent to the twin wall. The averaged displacement in these layers is 6.1 pm. In all layers further away from the twin wall as well as for Ca, no systematic deviations in \(x\)- or \(y\)-direction are observed. The significant shifts are schematically shown in Figure 5(g) and (h) [15].

Using atomic-scale numerical simulations Goncalves-Ferreira et al. [14] found large displacements of Ti with much smaller values for Ca. They also showed that the main Ti displacements occur parallel to the twin wall, with only a small component perpendicular to the wall. The thickness of the domain wall is ca. 2 octahedra, which is the same length scale as in the present experiments. The displacement pattern can be seen as a
combination of ferroelectric and anti-ferroelectric/ferrielectric components. The ferroelectric component is the smaller one and has both parallel as well as perpendicular effect on the wall. It is the only component that we can observe in our experiment because the anticipated larger anti-ferroelectric movement of Ti atoms displaces pairs of Ti in an antiparallel fashion at the wall. Averaging over the wall along the viewing direction thus yields no resulting displacement that would be visible in the electron microscope. Nevertheless, these simulations [14] show a very strong coupling between the ferroelectric and antiferroelectric movement so that our observations imply that antiferroelectricity concurs with ferroelectricity in the domain walls. In other words, ferroelectricity is not enhanced by the twin boundaries, it is generated at these boundaries! This means that ferroelectricity is indeed confined to twin boundaries in a paraelectric matrix. In addition, we can now observe such localized effects experimentally. Moreover, the density of these defects can be controlled by slow cooling through the cubic-to-orthorhombic transformation temperature while their position can be changed by external stress applied using a micromanipulator. Devices can thus be imagined where each domain wall acts as a memory element, which can be switched electrically. The pixel density is then as high as the domain wall density and can surpass all known ferroelectric devices known so far. Recent developments in electron microscopy have advanced our resolution to the point that we can now measure small atomic displacements inside domain boundaries, which opens the door for using such domain boundaries as active elements in such device applications.

3. Conclusions

From the above examples it is clear that TEM is an essential tool in understanding the atomic scale building blocks that distinguish domain boundaries of various types from their surrounding matrix. Conventional techniques including regular high resolution TEM allowed visualizing the local crystallographic arrangements and crystal defects while newer instruments containing aberration correction lens systems and aided by statistical quantification methods yield picometer precision. Using the conventional approaches one can focus on qualitative or semi-quantitative observations to relate the interface structure to the macroscopic properties of a material while the aberration corrected instruments allow for quantitative details on atomic positions which can be used as input for numeric simulations to guide the development of improved functional materials.

Acknowledgments

The authors acknowledge financial support from the Fund for Scientific Research-Flanders (References G.0064.10N and G.0465.05) and the Flemish Hercules 3 programme for large infrastructure. S.T. gratefully acknowledges financial support from the Fund for Scientific Research Flanders (FWO) for a postdoctoral grant. The authors also thank MULTIMAT ‘Multi-scale modeling and characterization for phase transformations in advanced materials’, a Marie Curie Research Training Network (MRTN-CT-2004-505226). The support of the ‘Fonds Belge pour la Recherche dans l’Industrie et l’Agriculture (FRIA)’ for M.S.C. and of the Belgian Science Policy through the IAP 6/24 project is gratefully acknowledged. R. James (Univ. of Minnesota, USA) is acknowledged for providing the TiNiPd material and the group of T. Pardoen (UCL, Belgium) for the Pd nanobeams.
References


