Involution domains in Nickel-Titanium

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Abstract

The near equiatomic NiTi alloy is the most successful shape memory alloy by a large margin. It is widely used in biomedical devices and is the focus of nearly half of all research on metallic materials. Yet, despite having a repeatable pseudoelastic effect and excellent shape-memory, NiTi is very far from satisfying any of the conditions of compatibility that currently characterize the most reversible phase transforming materials. Thus, the scientific reasons underlying its vast success present an enigma. We are led by a systematic theoretical study of transformation mechanisms to previously unrecognized kinds of twin-like defects that we term *involution domains*, and we observe them in NiTi in the scanning-tunneling electron microscope. Involution domains lead to an additional 216 compatible interfaces between phases in NiTi, and we theorize that this feature contributes importantly to its reliability. They are expected to arise in other transformations and to alter the conventional interpretation of the mechanism of the martensitic transformation.
The near equiatomic NiTi alloy is a key element in a vast array of current medical devices, including stents, guidewires, embolic filters, dental arch wires, bone implants and microforceps. NiTi alloys also are essential to emerging designs of brain stents and devices for deep brain stimulation. These medical applications depend critically on the ability of the NiTi alloy to pass reversibly back and forth through its big first order phase transformation without failure.

Many authors have presented ideas on the reasons for the success of NiTi. The desirable role of precipitates in slightly Ni rich NiTi is widely accepted [1, 2]. These strengthen the high-temperature austenite phase, and mitigate against dislocation motion during transformation. A limited amount of prior plastic deformation has a similar effect [1]. In this article we present an alternative hypothesis for the reliability of NiTi based on the observation that it allows for a plethora of non-standard and previously unrecognized interfaces between phases.

Recently, conditions of compatibility between phases and the elimination of stressed transition layers between phases have been shown to profoundly influence the functional degradation, reversibility and hysteresis of a variety of phase-transforming materials [2–6]. Currently, the most highly reversible alloys measured by the absence of degradation of properties under cycling satisfy such conditions of “supercompatibility” [materials today]. However, the near equiatomic NiTi alloys are in fact very far from satisfying any known conditions of supercompatibility. We show in this article, however, that NiTi satisfies a certain nongeneric involution relation, leading to many additional nonstandard compatible interfaces. An involution is a mapping \( f \) of a domain to itself that, when applied twice, gives the identity: \( f(f(x)) = x \).

To explain the origins of this involution and its implications for microstructure, we revisit accepted ideas of the crystal structure of NiTi. Following a period of debate in the 1960s [1, 2, 7–13], the B19′ crystal structure of the martensite phase of NiTi and the associated transformation mechanism and pathway – which atom goes where – are now well accepted. B19′ is monoclinic having \( \text{P2}_1/\text{m} \) symmetry and its unit cell contains 4 atoms [12]. This phase is deformed from B2 phase of \( \text{Pm}\overline{3m} \) symmetry by a basal shear on the \((110)_\text{B2} \) plane along \([001]_\text{B2} \) direction [9] which yields a Bain-like strain [11, 13, 14] illustrated in Figure 1 a to b. During the homogeneous deformation, the 4-atom unit cell of the B2 sublattice having basis of \([001], [1\overline{1}0] \) and \([110] \) (marked by the cell A in Figure 1a) becomes the 4-atom unit cell of the product phase B19′ (marked by the unit cell \( A′ \) in Figure 1b). This 4-atom unit cell is widely accepted as the primitive unit cell of the B19′ phase, but shuffling of atoms within this unit cell (consistent with this periodicity) occurs whose exact form is less well-accepted and not shown in Fig. 1. The sequence of all \((h\overline{h}0)\text{B2} \) layers does not shear, so the axis \([1\overline{1}0]_\text{B2} \) simultaneously becomes the monoclinic 2-fold axis \((010)_{19′} \) for the accepted B19′ phase. This is known as Bain correspondence [11, 14].

Since this transformation mechanism was established, a variety of theoretical and algorithmic methods [15–17] have emerged for the interpretation of experimental data in materials science, especially for phase transformations [18–20]. One such method is an algorithm (StrucTrans[21]) for determining the lattice correspondence with the smallest strain, among all
FIG. 1: (a) The (110)\textsubscript{B2} projection of B2 lattice corresponding to the (010)\textsubscript{B19'} projection of deformed lattice by (b) accepted mechanism and (c) new mechanism respectively. Here we only plot the atom positions under the homogeneous deformation given by \( \mathbf{U}_B \) and \( \mathbf{U}_N \).

correspondences that map a sublattice of the parent phase to the lattice of the product phase. The strain here is determined from the lattice correspondence by the Cauchy-Born rule \[22, 23\]. This is a rigorous algorithm that is mathematically guaranteed to converge in a finite number of steps to the linear transformation between these lattices with the smallest strain. In this letter we report a new transformation mechanism – a new transformation strain and a new B19' lattice parameters – discovered by this algorithm. More importantly, we reveal the existence of a new crystal defect – involution domain – derived from the new transformation mechanism.

Is the Bain transformation described above the most likely mechanism based on a smallest strain criterion for deforming the B2 lattice with the unit cell \( \Lambda \) (Fig. 1a) to the monoclinic B19' lattice (Fig. 1b) with the unit cell \( \Lambda' \)? The StrucTrans algorithm addresses exactly this question by searching for the lattice correspondence that minimizes the transformation strain defined by \( (1/3)\sqrt{\sum_{i=1}^{3} \epsilon_i^2} \) where \( \epsilon_1, \epsilon_2, \epsilon_3 \) are the principal strains. The result indeed confirms that the Bain correspondence (or a symmetry related correspondence) gives the smallest strain, and there are no near competitors.

However, by testing other sublattices using the StrucTrans we noticed a peculiar feature of the B2 to B19' transformation in NiTi which is reflected in the similarity of the purple and green cells in Fig. 1b and c. For this sublattice of B19' having a relatively small unit cell, there exists a transformation strain smaller than or close to the Bain strain, depending on precisely which lattice parameters one chooses. In this case, it is possible that the crystal may undergo a new transformation that deforms the sublattice C (green cell in Fig.1a), then shuffles the atoms inside the sublattice unit cell to finally achieve a stable new B19' structure. Of course, these two processes - homogeneous deformation of the cell and atomic shuffling within the cell - would typically occur simultaneously. Importantly, the unit cell in principle does not have to be the primitive one of the undeformed or the deformed structure.

A concrete example based on the reported lattice parameters \textit{i.e.} Pm\bar{3}m, \textit{a}_0 = 3.015\text{Å} \[9\] for B2 and P2\textsubscript{1}/m, \textit{a} = 2.898Å, \textit{b} = 4.108Å, \textit{c} = 4.646Å and \( \beta = 97.78^\circ \)[12] for B19' is the following. The new transformation deforms a 16-atom sublattice of B2 marked as the green cell C in Fig.
1a to the monoclinic sublattice \( C' \) in Fig. 1c subject to transformation strain 0.047 ± 0.001. On the other hand, the Bain mechanism has the strain 0.0474 ± 0.0005. The deformed sublattice unit cell \( B' \) in Fig. 1b is isometric to the sublattice unit cell \( C' \) in Fig. 1c.

The key difference between this new and the Bain mechanisms is that the transformation stretch tensors are different. Considering the unit cells \( A, A' \) and \( A'' \) in Fig. 1, there are two transformation stretch tensors, denoted \( U_B \) and \( U_N \) given by Eqn. S5 and Eqn. S6 in Supplementary Information. They deform the 4-atom unit cell \( A \) of \( B2 \) to \( A' \) and \( A'' \) respectively. Since \( A'' \not= A' \), \( U_N \not= U_B \). Nor is \( U_N \) a variant of \( U_B \), because \( U_N \not= QU_BQ^T \) for all \( Q \) in the point group of austenite [24]. However, one must not be mistaken by the illusion that \( U_N \) is just an arbitrary minor perturbation of \( U_B \). In fact they are related through a strong crystallographic restriction: the 16-atom sublattice \( B' \) of accepted \( B19' \) has the same periodicity as the 16-atom sublattice \( C' \) of the new \( B19' \), as depicted in Fig. 1b and 1c. By this geometrical restriction, the lattice parameters describing \( A' \) and \( A'' \) must satisfy the equations below

\[
\begin{align*}
4\hat{a}^2 &= a^2 + c^2 - 2ac \cos \beta \quad \text{(C1)} \\
4\hat{c}^2 &= 9a^2 + c^2 + 6ac \cos \beta \quad \text{(C2)} \\
4\hat{a}\hat{c} \cos \hat{\beta} &= -3a^2 + c^2 + 2ac \cos \beta. \quad \text{(C3)}
\end{align*}
\]

Here \( \hat{a}, \hat{b}, \hat{c} \) and \( \hat{\beta} \) are the lattice parameters of the \( A'' \) lattice, deformed from \( A \) by the new mechanism, as noted in Fig.1c.

For any monclinic lattice with lattice parameters \((a, b, c, \beta)\), the relations (C1) to (C3) give a set of new monoclinic lattice parameters\((\hat{a}, \hat{b}, \hat{c}, \hat{\beta})\). Also, (C1) to (C3) is an exact involution on \( a, c, \beta \) space. (One can also add \( b \) since it stays the same.) Under mild conditions, involutions have fixed points and that is the case here: there is a two-dimensional surface in \( a, c, \beta \)-space where (C1) to (C3) satisfies \( \hat{a} = a, \hat{c} = c \) and \( \hat{\beta} = \beta \). A miracle of NiTi is that its lattice parameters lie extremely close to this surface. For example if we substitute the reported \( a = 2.898, c = 4.646 \) and \( \beta = 97.78^\circ \) [12] as the lattice parameters of \( A' \) deformed by accepted mechanism, the values of \( \hat{a}, \hat{c} \) and \( \hat{\beta} \) are 2.8995\( \hat{\AA} \), 4.6431\( \hat{\AA} \), and 97.743\( ^\circ \), which are extremely close to \( a, c, \beta \). The most accurate way of determination of lattice parameters of crystalline solids is X-ray diffraction. The accuracy of the structural parameters depends on the quality of samples, X-ray source and the geometrical factors of the X-ray facility. The best achievable accuracy for solving the monoclinic structure is about 0.0001 \( \AA \)[12], which is not enough to distinguish the new \( B19' \) structure from the accepted one, especially for the monoclinic angle. DFT calculations show that the energy difference between the new and the accepted \( B19' \) is negligible compare to the difference between accepted \( B19' \) and \( B2 \). (See Supplementary Information). These observations motivated us to seek experimental signatures of the new mechanism, e.g. the direct observation of atomic structure in real space.

In general, the lattice parameters of the involution lattice are quite different from those of the reference one. As an example, a typical \( \beta \)-phase alloy CuAlZn [25] has monoclinic structural parameters \( a = 4.553\hat{\AA}, b = 5.452\hat{\AA}, c = 4.33\hat{\AA} \) (e.g., for the non-modulated case) and \( \beta = 87.5^\circ \).
After the involution transformation (C1) to (C3), $\tilde{a} = 3.0724\text{Å}$, $\tilde{c} = 7.2539\text{Å}$ and $\tilde{\beta} = 117.904^\circ$.

There is a huge lattice mismatch between these two lattices and the involution lattice is highly incompatible with the reference one. More importantly, the transformation strain of the involution lattice from the parent $\beta$-phase is much bigger than the accepted transformation strain of this alloy. It is physically unrealistic to have such a transformation, nor the resulting structure.

Interestingly, in the case of NiTi, since the transformation strains are close, the accepted and its involution lattices may form compatible interfaces through certain irrational plane. Due to the nature of involution, the two domains are alternated just like the twin structure. (See Supplementary Information for a justification). This new kind of martensitic interface differs from conventional twinning planes since the atomic structures, i.e. the atom positions in unit cell, across the interface are not related by a mirror symmetry. We called this new family of twin-like microstructure the involution domains. Given the stretch tensors delivered by the StrucTrans algorithm [21], we theoretically solved the compatibility equation [26] and determined the normal of the interface between the lattices deformed by new and accepted mechanisms. It is close to one of the compound twin interfaces for the accepted mechanism, but irrational. This involution domain satisfies the equations of the crystallographic theory of martensite [26, 27] with the twin-like ratio of 1 : 1. The Supplementary Information provides the detailed calculation.

The search for this involution twin between lattices deformed by the accepted and new mechanisms in NiTi was carried out at the National Center of Electron Microscopy, Lawrence Berkeley National Lab. The morphology of the interface as well as the atomic structures were studied using the aberration-corrected scanning transmission electron microscopy, which provides direct information of atomic positions in real space under certain conditions. We used a near equi-atomic NiTi specimen, which was synthesized and heat treated to reduce the internal stress in bulk martensite at room temperature (See Methods). The electron transparent foil cut from the bulk martensite was finally thinned by electrolytic polishing to minimize the surface deformation (See Methods for sample preparation). The austenite and martensite start/finish temperatures of the specimen were $88^\circ\text{C}/118^\circ\text{C}$ and $78^\circ\text{C}/40^\circ\text{C}$ associated with a structural transformation from B2 to B19’. The R-phase transformation was not observed (See the evidence in Supplementary Information).

We looked for regions where self-accommodated twins [11] were not present. To observe the predicted twin-like interface, we tilted the foil so that the e-beam was aligned with the [010]$_{B19'}$ direction, as in the theoretical pictures of Figure 1. Within an area of about $100 \times 100\text{nm}^2$ shown in Fig. 2a, we observed a series of laminated structures distinct from the usual Type I and Type II twin structures. To reveal the morphology of these interfaces, a higher magnification micrograph (Fig. 2b) was taken. Consistent with the results of the crystallographic theory quoted above, the twin-like bands are of equal width and the planar interface between them is straight and sharp, without an elastic transition layer, which suggests that these interfaces are compatible. The atomic columns in the zone of [010]$_{B19'}$ are directly seen from the drift-corrected high
resolution STEM image in Figure 2c. Clearly, the atomic structures across the interface are not mirror-related.

Fig. 3a shows the enlarged view of the boxed region M1 and M2 in Fig. 2c. Its Fourier transform reveals that the lattices across the interface have quite similar periodicities. Using a Bragg peak filter (Methods), the interface is resolved between the blue and orange lattices. First, this interface is not a conventional twin wall. The irrational morphology of the sharp interface shown in Fig. 3a clearly rules out the possibility of Type I and Compound twins. It is not the Type II twin interface either, because all possible Type II twins that can form compatible austenite/martensite interfaces should have the twinning volume ratio 0.27: 0.73 [11]. All three types of twins require that the crystal structure satisfies the mirror relation across the twin

FIG. 2: STEM images of the martensitic microstructure in NiTi. a. Morphology of the laminate at low magnification. b. New/accepted involution domains in the same area at a higher magnification. c. The high resolution STEM image in the same area showing the atomic structures near the interface in the zone of [010]B19'.
boundary. In contrast, the involution domain well explains the irrationality, asymmetry and 1:1 volume twinning volume ratio for the morphology of domain boundary in Fig. 3a. Second, the interface is not a generic boundary between such two lattices that one is slightly deformed from another by an arbitrary small strain. Because an arbitrary shear deformation does not necessary form a sequential parallel domains with almost 1:1 volume ratio. However, the nature of the involution property of the conditions (C1)-(C3) spontaneously guarantees the morphology observed in STEM image of Fig. 2.

To compare this observed interface with theory, we measured the lattice parameters of B2 and B19’ for this TEM foil (Table I) at the Advanced Light Source, Beamline 12.3.2, Lawrence Berkeley National Lab (See Methods for the structural determination). Using the measured lattice parameters of B19’, the conditions (C1)-(C3) give the lattice parameters \( \tilde{a}, \tilde{c}, \tilde{\beta} \) by the new transformation mechanism, listed as the calculated B19’ in Table I. As expected, the two sets of lattice parameters are quite close, consistent with the transformation strains predicted by the StrucTrans algorithm. Solving the equations of compatibility [26] between the two strains, the interface is computed as \( n = (1, 1, -0.015) \) written in orthogonal B2 basis. The deformed lattices across the predicted interface by the new and accepted mechanisms with proper atomic shuffles are plotted in Figure 3b. The calculated irrational interface and the atomic arrangements agree well with the experimental observations, which support our conjecture for the existence of the new transformation mechanism and the involution domains.

A widely accepted idea in the study of martensitic phase transformations is that the number of variants, and the number of compatible interfaces between them, play a key role in reversibility of the transformation, which is usually characterized as the degradation of recover-

FIG. 3: Atomic structure of involution domains observed in NiTi. a. STEM image of the atomic positions, where both lattices are color coded by Bragg filtering from the peaks shown in the image Fourier Transform inset in the upper right corner. b. Calculated involution domain interface with proper atomic shuffles by the mechanics theory of compatibility [26].
TABLE I: Lattice parameters of the B19' structure (4-atom primitive unit cell) and the B2 austenite structure of the NiTi used for STEM.

|         | \(a(\text{Å})\)       | \(b(\text{Å})\)       | \(c(\text{Å})\)       | \(\beta(°)\)       |
|---------|------------------------|------------------------|------------------------|---------------------|
| B2      | \(3.0179 \pm 0.0005\)  | \(3.0179 \pm 0.0005\)  | \(3.0179 \pm 0.0005\)  | \(90°\)             |
| measured B19' | \(2.8785 \pm 0.0004\) | \(4.1106 \pm 0.0002\) | \(4.6189 \pm 0.0001\)  | \(97.171 \pm 0.006\) |
| calculated B19' | \(2.8696 \pm 0.0003\) | \(4.1106 \pm 0.0002\) | \(4.6354 \pm 0.0007\)  | \(97.39 \pm 0.01\)  |

able superelastic strain. In addition, the number and types of interface between the variants of martensite and the parent phase are also relevant. Thus, for example, the reversible shape memory effect has not documented in any alloy that undergoes a tetragonal-to-orthorhombic transformation (only 2 variants) or any alloy that does not satisfy the conditions of the crystallographic theory of martensite [28] (some martensitic steels). In recent years this accepted idea has been extended to encompass special non-generic relations between lattice parameters at which unstressed interfaces between austenite and martensite become possible (“\(\lambda_2 = 1\)” [4]), or many such interfaces become possible (“cofactor conditions” [5, 6]). Currently, the alloys exhibiting the greatest resistance to the functional fatigue satisfy the latter. NiTi is not anywhere near to satisfying these conditions. Thus, aside from ancillary considerations such as its early-accepted biocompatibility, good strength and corrosion resistance [29], the success of its broad use of superelasticity is a puzzle. Certainly, a large body of work has gone into optimizing its synthesis and processing, by the development of synthesis routes that yield exceptionally clean material without oxides, nitrides, etc., and also heat treatments that optimize the types, shapes, and sizes of precipitates that mitigate against fatigue mechanisms [1]. In this letter we offer an additional reason for its success: it has in fact two monoclinic martensitic phases and 24 variants (instead of the accepted 12), which offers an additional 216 compatible interfaces among new and accepted variants. Furthermore, we theorized and demonstrated the involution domains, which should be considered as a new type of defect responsible for the theory of martensitic microstructure and plasticity. Detailed study of the involution domains will be discussed in our forthcoming theoretical paper. As it is based on sublattice correspondences, the StrucTrans algorithm [21] enables high throughput screening of the involution domains in a wide range of materials.

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