Acta Materialia 109 (2016) 353–363

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Group theory description of transformation pathway degeneracy in structural phase transformations

Yipeng Gao [a], Rongpei Shi [a], Jian-Feng Nie [b], Suliman A. Dregia [a], Yunzhi Wang [a, *]

[a] Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43210, USA
[b] Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia

ARTICLE INFO

Article history:
Received 11 November 2015
Received in revised form
8 January 2016
Accepted 10 January 2016
Available online xxx

Keywords:
Structural phase transformation
Crystal symmetry
Pathway degeneracy
Group theory
Deformation variant

ABSTRACT

Pathway degeneracy of structure transformations with symmetry breaking underpins the functionalities of a broad class of smart materials – the ferroics. Despite of its significance, there has been a lack of rigorous theoretical description of pathway degeneracy, leading to several case-dependent treatments which are not generally correct. In this work, we incorporate lattice correspondence into group theory to define and determine pathway degeneracy during structural transformations. In particular we show that a stabilizer can be determined by taking into account either the deformation relationship (under a given lattice correspondence) or the orientation relationship, through which deformation variant is defined rigorously and distinguished clearly from orientation variant. Such a definition provides a theoretical foundation for investigating the formation of domain and defect structures arising from symmetry breaking during structural phase transformations.

1. Introduction

From the crystallographic point of view, symmetry breaking during structural transformations provides a natural means of achieving self-organized polydomain structures. These domains can switch from one to another by external fields such as stress, electrical and magnetic fields, offering special "smart" properties such as piezoelectricity, electro- and magneto-striction, superelasticity, shape-memory, and transformation toughening [1–5] to name a few. The symmetry breaking attending a phase transformation is understood on the basis of group theory [6–8], and the concept of orientation variants (i.e., the number of crystallographically equivalent domains of the low symmetry phase) has been established since 1970s [9,10]. Such a group theory description of coexisting phases that are related by observed orientation relationships (ORs) has profound influences on the development of advanced geometrical theories of structures of hetero-phase interfaces such as the Coincidence Site Lattice theory [11] and the O-lattice theory [12]. However, such a group theory description applies to any two coexisting crystals, even if they were joined artificially without a transformation (e.g., epitaxial growth of one crystal on top of the other during vapor deposition). It is the number of crystallographically equivalent transformation pathways (TPs) for the structure change (i.e., the TP degeneracy or *deformation variant*) that determines the reversibility of the transformation and the formation of various defect structures such as domain walls, twin boundaries and dislocations [13]. In order to describe TP degeneracy during a structural phase transformation, the fact that the two crystal structures are related by a deformation under a given correspondence before and after the transformation should be taken as an additional physical constraint besides the crystal structure information.

To illustrate the difference between orientation degeneracy and TP degeneracy at the intuitive level, we consider the relations between a square unit cell and a rectangular unit cell of two different lattices with a common origin. If the rectangle is oriented such that its long edge is parallel to an edge of the square, then two equivalent orientation variants are dictated by the symmetry and given OR. Likewise, if the long edge of the rectangle is made parallel to a diagonal of the square, there would be two equivalent variants of this OR. But in any other OR there would be four equivalent orientation variants of the rectangle relative to the square. An OR is defined whenever two crystals coexist, with or without contact. Now suppose a rectangle is made by stretching a square along one of its edges, i.e., with edge-to-edge correspondence. Clearly, there are two equivalent deformation pathways that satisfy the

* Corresponding author.
E-mail address: wang.363@osu.edu (Y. Wang).

http://dx.doi.org/10.1016/j.actamat.2016.01.027
1359-6454/

prescribed correspondence, leading to the so-called correspondence variant defined in martensitic transformation crystallography [2,14]. Moreover, the number of correspondence variants is independent of any rotation of the rectangle relative to the square, i.e., it is independent of the OR for a fixed lattice correspondence (LC) [15–18]. It has been recognized [19] that the symmetry of the transformation strain, which includes the information of LC rather than OR, should be considered in the study of pathway degeneracy during martensitic transformations.

Thus the types of symmetry breaking and degeneracy are determined by the types of relationships between two crystals that one is considering, e.g., OR or LC. The former is characterized by rigid-body rotation and translation, leading respectively to crystallographically equivalent orientation variants and anti-phase domain variants, both of which have been well addressed in the literature [6,9]. The latter is characterized by a uniform lattice distortion and an internal atomic shuffle, which can also be described through the matching and splitting of Wyckoff position [7,20–22]. Despite of its importance, several key issues in determining the latter degeneracy (referred to as TP degeneracy in this study) have not been realized and well-addressed in the literature, including: (1) besides the information of the symmetry groups of individual crystals involved during the transformation, a relationship connecting the two crystals of the parent and product phases is necessary and critical, which could be a piece of information characterizing the transformation pathway (e.g., LC); (2) the two symmetry groups of individual crystals cannot be used directly in Lagrange's Theorem [8], because it is not guaranteed that there is a group–subgroup relationship between them; instead, a stabilizer (or intersection group) has to be determined first, which is strictly a subgroup of the symmetry group of the parent phase and satisfies the requirement of Lagrange's Theorem; (3) the effects of shuffle on TP degeneracy should be included within the framework of group theory. Overlook of the above issues may lead to case-dependent treatments which are not generally correct. For example, to exclude the effect of orientation dependence, one popular way to determine TP degeneracy is by using proper symmetry operations only, which is workable in some shape memory alloy systems [15]. However, such a treatment is limited not only because the degeneracy caused by breaking of mirror symmetry cannot be captured, but also it fails when dealing with reconstructive martensitic transformations [13]. One classical counter-example is the face-centered cubic (FCC) to body-centered cubic (BCC) transformation through the Bain path in pure iron. The point group of both FCC and BCC lattices are $\mathbf{m\bar{3}m}$, leading to only one pathway according to this treatment, which is definitely contradict to the three equivalent Bain pathways intuitively well-known in the literature [16–19,23].

TP degeneracy plays a critical role in formulating theoretical descriptions of structural phase transformations, as has been demonstrated in the phenomenological theory of martensitic crystallography (PTMC) [16–18] and Landau theory of phase transformations [24]. Because of the lack of rigorous group theory description of the TP degeneracy, however, orientation degeneracy determined by the group theory formulation [9] using a particular OR as the constraint has been used frequently in literature as the TP degeneracy [25,26]. As has been discussed above, however, the TP degeneracy should be determined by the constraint of LC and be *independent of* OR. Consider again the classical FCC to BCC transformation in steels. If the Kurdyumov–Sachs and Nishiyama–Wasserman ORs commonly observed in the experiments are used, then the number of orientation variants will be 24 and 12, respectively. Only when the Baker–Nutting OR or Bain OR (not Bain LC) is used, the number of orientation degeneracy equals the number of TP degeneracy, which is 3. Note that the Baker-Nutting OR has not been observed in experiments. Another well-known example is the BCC to hexagonal-close-packed (HCP) structural transformation in Ti-based and Zr-based alloys. Depending on the experimentally observed ORs, including the Burgers, Potter, Pistch–Schrader and Rong–Dunlp [27], the number of orientation variants can be systematically obtained through group theory [9]. However, the TP degeneracy for the Burgers path has yet been determined rigorously, because of the difficulty caused by the internal atomic shuffle during the transformation.

In this work, we formulate a group theory framework to define and determine TP degeneracy during structural transformations that involve a lattice deformation. Through a change of basis, a stabilizer can be determined by either LC or OR, leading to rigorous definitions of TP degeneracy and orientation degeneracy within a general framework. Such a definition of TP degeneracy is critical in formulating Landau free energy dictated by the symmetry of Hamiltonian and investigating deformation mechanisms that governs microstructural evolution and materials properties during structural transformations. Several examples are presented, through which not only the standardized mathematical procedure to determine the degeneracies but also the symmetry related features in terms of microstructures are described in great details.

2. Mathematical formulations of orientation variant and deformation variant

We consider an $\alpha \rightarrow \beta$ phase transformation, where the two crystals have point groups $\mathbf{H}^{\alpha}$ and $\mathbf{H}^{\beta}$, respectively. Individual operations in the two groups, $\mathbf{h}^{\alpha} \in \mathbf{H}^{\alpha}$ and $\mathbf{h}^{\beta} \in \mathbf{H}^{\beta}$, can be represented in matrices in particular coordinates. Symmetry dictated degeneracy during the transformation is given by the following relation [9,10]:

$$N_{\alpha \rightarrow \beta} = \frac{|\mathbf{H}^{\alpha}|}{|\mathbf{J}^{\alpha/\beta}|} \tag{1}$$

where $|\mathbf{H}^{\alpha}|$ is the order of the group of the parent phase, and $\mathbf{J}^{\alpha/\beta}$ is known as the stabilizer subgroup, it consists of symmetry operations that are preserved during the transformation. Eq. (1) follows from the coset decomposition of a group ($\mathbf{H}^{\alpha}$) in terms of its subgroup ($\mathbf{J}^{\alpha/\beta}$), and the quotient (called the index of $\mathbf{J}^{\alpha/\beta}$ in $\mathbf{H}^{\alpha}$) is guaranteed to be an integer by Lagrange's Theorem [8]. In some particular phase transformations (e.g., ferroic phase transitions) $\mathbf{J}^{\alpha/\beta} = \mathbf{H}^{\beta}$, which allows Eq. (1) to be expressed as the ratio of the orders of the groups of the two phases (i.e., $|\mathbf{H}^{\alpha}|/|\mathbf{H}^{\beta}|$). However, such an expression not only obscures the fact that using $\mathbf{H}^{\beta}$ in the denominator is only conditionally correct, but also overlooks the dependence of the degeneracy on a critical link (e.g., OR or LC) between the two groups. As pointed out by Cahn and Kalonji [9], the orientation degeneracy should depend on the stabilizer (or intersection group) dictated by the OR between two crystals, and parallel conclusion could also be expected for TP degeneracy. In general, the stabilizer is a subgroup of both $\mathbf{H}^{\alpha}$ and $\mathbf{H}^{\beta}$, and it consists of operations that are common to the two groups, not belonging to either group exclusively [9,10].

Considering the α crystal defined in the B_{α} basis, $\mathbf{H}^{\alpha}$ can be represented in B_{α} as $\mathbf{H}^{\alpha}_{\alpha}$ (similarly, $\mathbf{H}^{\beta}$ are represented in B_{β} as $\mathbf{H}^{\beta}_{\beta}$).$B_{\alpha} = \{\mathbf{a}_i^{\alpha}\}$ and $B_{\beta} = \{\mathbf{a}_i^{\beta}\}$, with $i = 1,2,3$. In order to calculate their intersection group, $\mathbf{H}^{\alpha}$ and $\mathbf{H}^{\beta}$ should be represented in the same basis, and an operator $\widehat{\mathbf{T}}$, can be used to link B_{α} and B_{β} without loss of generality. The superscript used here indicates the crystal lattice (α or β) that the vector (or operation) belongs to. Under the action of a point operation $\mathbf{h}^{\alpha}$, the α crystal will be self-coincident, but every vector will be transformed to a new position