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DOES THE RECONSTRUCTIVE MECHANISM OF PHASE TRANSFORMATIONS EXIST?

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Introduction

Original Application to Transformations in Inorganic Compounds

The concept of the reconstructive transformation (hereinafter RT) was introduced by Sosman (1) in 1934 and, in a better known paper, by Buerger (2) in 1951 in the context of ceramic crystal structures. Fig. 1 (2) provides a useful illustration of this context. Part (a) of this Figure is a network structure such as can provide the matrix in the quartz↔tridymite, red↔green manganous sulfide and yellow↔red mercuric iodide (3) phase transformations. A displacive transformation is illustrated by the conversion of the structure of Fig. 1(c) to that of either Fig. 1(b) or 1(d). This transformation involves a systematic distortion of the network structure in which all first nearest neighbor/coordination shell bonds are preserved but other (2nd, etc.) nearest neighbor/coordination shell bonds are distorted. On the other hand, transformation of the structure of Fig. 1(a) to that of Fig. 1(c) is termed a RT. This terminology is employed because "The higher coordination can be changed while the first coordination contacts of a structure are retained, by a process radically different from that described above. The entire network can be unlinked, then relinked again to form a new and different network, yet one having first coordination identical with that of the first structure." "Since such a transformation consists of the disintegration of the original structure into small bits, followed by a reassembly of the bits to form a new pattern, it is appropriately called a reconstructive transformation." Later in the same article, Buerger extended the designation of RT to cases in which the environment experienced by first nearest neighbors is also changed, e.g., when the aragonite structure of $CaCO_3$ is replaced by that of calcite.

Buerger (2) also distinguished between displacive and reconstructive transformations on the basis of transformation kinetics, with the former being rapid and the latter very much slower. However, in a discussion to this paper Egli et al. (4) properly criticized this additional criterion, pointing out that the kinetics of nucleation and of growth must be separately considered, and noting as a counter-example that once the transformation in mercuric iodide is nucleated, the growth process proceeds very rapidly. Since high velocity growth has long been abandoned as a criterion for martensitic transformations in metallic alloys, e.g., ref. (5), we shall not consider transformation kinetics further in this discussion.

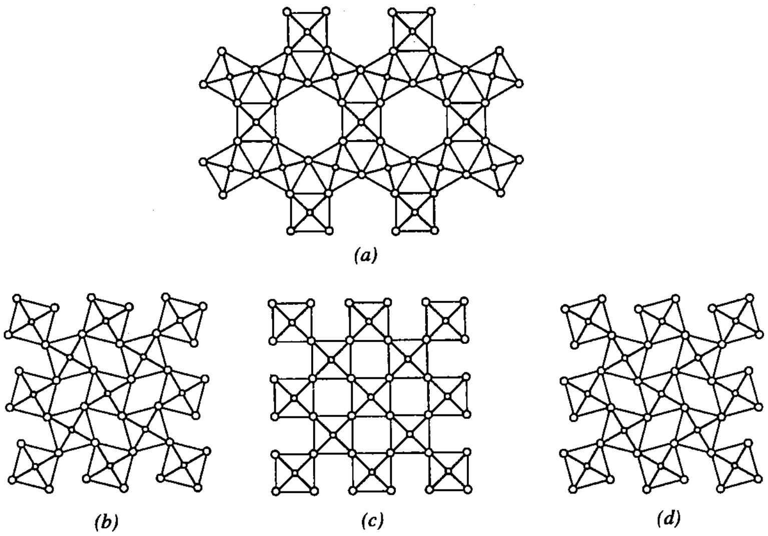

Figure 1. Transformations in network structures. Buerger (2).

Recent Applications to Transformations in Metallic Alloys

Although appearance of the term “reconstructive transformation” in the literature on phase transformations in metallic alloys is comparatively recent, it was undoubtedly presaged by the famous 1953 observation by Ko (6) that grain boundary ferrite allotriomorphs do not yield a pronounced relief effect at a free surface. When the phenomenological theory of martensite crystallography was introduced shortly afterwards (7,8), the surface relief accompanying formation of a martensite plate growing into contact with a free surface was quantified as an invariant plane strain (IPS). Christian (9) noted that “In a transformation where there is no correspondence of equivalent lattice sites [in the matrix and product phases], the volume change may still produce visible surface changes”. He characterized these as “surface rumpling”, and urged care in distinguishing between such effects, resulting from plastic deformation, and the shape change attending the phase transformation. This well known paper, and another important review published a few years later in which such transformations were described as “civilian” (10), in turn presaged a series of review papers appearing more than a generation later (11–14) in which the concept of the RT was formally introduced to transformations in metallic alloys and utilized in enlarging upon the distinctions made earlier between RT and displacive transformations.

These considerations by Christian et al. may be summarized as follows. A RT is characterized by an incoherent, i.e., disordered interphase boundary separating the transformed from the untransformed regions. This boundary cannot transmit shear stresses or strains and in some formal respects as a liquid-like layer. A RT thus cannot yield a macroscopically defined shape strain, e.g., an IPS. Prerequisite to occurrence of a RT is sufficient mobility of all participating atoms in the incoherent boundary. At sufficiently high temperatures, countercurrent diffusion of vacancies and atoms between the growing precipitate and dislocations, grain boundaries and free surfaces can relieve the volume change usually associated with a RT. At temperatures too low to support enough volume diffusion for this purpose, the transformation strain energy can be relieved by development of a lenticular morphology, and concurrently, expansion or contraction of its broad faces, both by means of interfacial diffusion. In both temperature regimes, diffusion ensures the absence of an IPS.

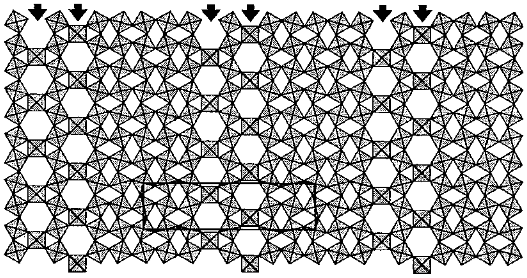

Figure 2. HTB Intergrowth (designated by arrows), extended downward for the sake of clarity, in WO_3. Hussain and Kihlborg (16).

Grain boundary allotriomorphs and intragranular idiomorphs were described as morphologies formed by RTs. The finding of King and Bell (15) that "allotriomorphic ferrite in steels is known to grow into austenite grains with which it has an orientation which is random or outside the Bain region" was cited in support of the first of these characterizations. The eutectoid decomposition product pearlite was also so described as an RT. In the most recent of these papers (14), the existence of phase transformations involving both volume diffusion and an IPS were described as "diffusional displacive".

Comparison of Predictions from the Reconstructive Transformation Mechanism with Experiment

In Inorganic Compounds

Hussain and Kihlborg (16) have made detailed HRTEM and X-ray diffraction analyses of hexagonal tungsten bronzes (HTB), M_xWO_3, "intergrown" in WO_3, where M = Tl, K, Rb or Cs and $x \geq 0.10$. When $x = 0.13$, only the HTB phase was present; at lower x's, both phases appeared. Figure 2 shows the structure model derived from the experimental studies. Comparison of the HTB structure with that of Fig. 1(a) demonstrates that they are the same. "Tunnels" of this structure are two columns wide and alternate with WO_3 slabs four octahedra thick. The WO_3 slabs have been tilted by 15° to make the two phases fit perfectly together, in the manner of the invariant line crystallography (17). (The alkali elements, not shown here, are located within the "tunnels".) Amongst the many compositions studied, the HTB phase usually occurred as two columns of tunnels, though occasionally single or triple columns were observed. The WO_3 phase, on the other hand, had widely variable widths, ranging from 5–13 columns in a single HRTEM micrograph.

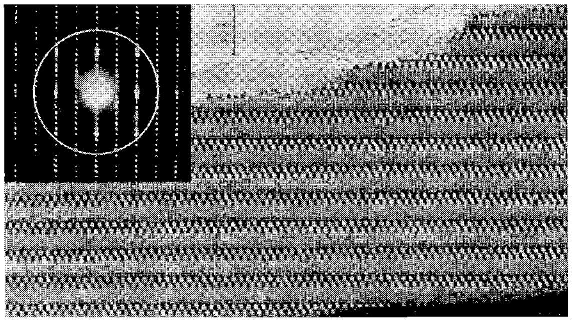

Figure 3. Lattice image of $K_{0.10}WO_3$. Hussain and Kihlborg (16).

Figure 3 shows a typical HRTEM microstructure. This is closely similar to the microstructures showing well formed alternating plates of the α and κ phases in Cu-Si (18) and of the α_2 and γ phases in Ti-Al (19) alloys. That the boundaries between the slabs of alternating structure in Fig. 3 are coherent, consistently with Fig. 2, is immediately apparent. Obviously the very fine scale of this microstructure would make examining the surface relief effect very difficult. However, comparison of Figs. 1 and 2 makes clear that, with Buergers' definition, the microstructure of Fig. 3 was formed by a RT.

Such well matched interfaces between inorganic compounds are not rare. Examples include intergrown perovskite-structured layers separated by Bi_2O_2- (20) and by NaCl- (21) structured layers as well as magnetoplumbite vs. spinel layers (22). The (fcc) $\gamma \rightarrow$ (hcp) α Al_2O_3 transformation has the familiar $\{111\}_\gamma /\!/ (0001)_\alpha$ habit plane (23) and proceeds by means of the ledge mechanism (24).

In Metallic Alloys

No information on either interphase boundary structure or surface reliefs is available on intragranular idiomorphs produced in phase transformations in which the difference in crystal structure is sufficient to cause a change in stacking sequence across the interphase boundaries. In the case of grain boundary allotriomorphs, on the other hand, studies on the (bcc) $\beta \rightarrow$(hcp) α transformation in a hypoeutectoid Ti-Cr alloy (25) and the fcc→bcc transformation in a Ni-Cr alloy (26) have demonstrated partial coherency across both the interfaces formed by rational or near-rational orientation relationships as well as those produced by decidedly irrational orientation relationships, in agreement with a prediction derived from comparison of experimental measurements of nucleation kinetics at grain faces and heterogeneous nucleation theory (27,28). IPS or tent-shaped surface reliefs have been observed only occasionally on grain boundary allotriomorphs (29-31), presumably in situations where the habit plane is nearly parallel to the grain boundary plane, or possibly where directions in these two planes are nearly parallel. However, this question has yet to be examined with a microscopy capable of observing surface reliefs produced by facets with lengths in the 10–100 nm. range (25).

The absence of IPS or related surface reliefs in association with pearlite has long been accepted (6,32). However, the view that the edges of pearlite lamellae in steel are incoherent with their austenite matrix (33) has been disproved by the experimental observation that these lamellae lengthen by means of growth ledges shared between them (34). Additionally, clear indications have been found of misfit compensating defects at the edges of both ferrite and pearlite lamellae (35). Again, the question of whether or not IPS, tent-shaped or more complex surface relief effects are present at the edges of pearlite lamellae should be studied with a high-resolution form of surface microscopy.

Discussion

The foregoing considerations lead to the conclusion that the RT mechanism is unlikely to exist in either inorganic compounds or in metallic alloys. The reason underlying this deduction derives directly from nucleation theory. Cahn and Hilliard (36) point out that nucleation will not be kinetically feasible unless the work of critical nucleus formation, ΔF^*, is less than about 60kT, where k = Boltzmann's constant and T = absolute temperature. When analyzing the measured nucleation kinetics of grain boundary ferrite allotriomorphs at austenite grain faces in Fe-C alloys, Lange et al. (27) found that ΔF^* vastly exceeds the Cahn-Hilliard upper limit whenever critical nucleus models include a portion of a spherical cap whose energy is taken to be that of a disordered austenite:ferrite boundary. Hence they were forced to resort to a pillbox model co-planar with the austenite grain face in which all interfaces, including that facing the austenite grain to which the allotriomorph was presumably irrationally lattice-oriented, are fully or partially coherent.* The same conclusion was later reached in experimental studies of the bcc→hcp massive transformation in Ti-X alloys (38) and the analogous proeutectoid α reaction in other Ti-X systems (39).

In a historical context, the notion that the transformation of the crystal structure of Fig. 1(a) to that of Fig. 1(c) requires disintegration of the former structure into small bits and reassembly of these bits into the latter structure might not have been proposed had the founders of the RT concept (1,2) been familiar with, for example, the work of Mehl and co-workers (40), showing the general prevalence (though not in all cases because of undiscovered transition lattices and of experimental and theoretical techniques yet to be invented for detailing interfacial structure) of good matching between closely packed planes of the matrix and product phases. Thus, the row of square sub-lattices in Fig. 1(c) could have been matched with the row of such sub-lattices lying in the middle of Fig. 1(a), albeit with adjustments of scale occurring elastically.

Conclusions

Insofar as the requisite experimental information is presently available, the interfacial structure prediction of the model for the mechanism of reconstructive transformation (RT) (1,2,11–14) has been shown to be incorrect in model phase transformations examined in both inorganic compounds and metallic alloys. Information on surface relief effects, which bear on the same issue, is from one point of view contradictory to the interfacial structure observations (14) and from another (41) is incomplete. Various experiments which would elucidate these points are noted or implied. The underlying objection to the RT model and the mechanism proposed for its operation is that it requires prohibitively high values of ΔF^* for nucleation, at least in metallic systems, but probably also in inorganic compounds as well.

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*Lange et al (28) were also able to model critical nuclei at grain faces which are incoherent with either of the two matrix grains forming these faces. However, observations of faceting on both faces of grain boundary allotriomorphs (26,38) indicate that the coherent pillbox model is in principle more accurate.

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