Microstructures and orientation relationships in the dry-state aragonite–calcite and calcite–lime phase transformations

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Abstract

The aragonite-calcite and calcite-lime transformations are observed in situ in the high voltage transmission electron microscope. Above 400°C aragonite single crystals begin to transform into calcite through heterogeneous nucleation on dislocations, twin boundaries, and modulated microstructures. Subsequent growth is generally topotactic with (100)_A ~ (1120)_C, (010)_A ~ (1104)_C, (011)_A ~ (0001)_C, and [001]_A ~ [rr:fl] in the aragonite-calcite transition. Above 500°C calcite decomposes into lime and CO₂. This reaction is also topotactic with (001)_L ~ (1104)_C, and (111)_L ~ (0001)_C. Movement of partial dislocations and propagation of stacking faults are not observed during the transformations. In situ observations therefore support a heterogeneous nucleation and interface-controlled growth mechanism rather than a martensitic mechanism for the aragonite-calcite transformation under the conditions of the experiment. Decomposition may proceed initially by loss of CO₂ from a relatively rigid framework.

Introduction

The aragonite–calcite polymorphic phase transformation and the decomposition reaction, calcite to lime plus CO₂, have been extensively studied and widely debated (see below). Although X-ray diffraction and optical microscopy provide information on the topotaxy and bulk kinetics of the transformations, details of the mechanisms have not been resolved. In situ heating experiments in the high voltage transmission electron microscope, however, yield information on both the orientation relationships and the microstructures involved as the transformations proceed.

Aragonite, the high-pressure polymorph of CaCO₃, is metastable at low temperatures and atmospheric pressure. It transforms into calcite upon heating above 400°C. At higher temperatures and prolonged heating time calcite decomposes into lime (CaO) plus CO₂. The three mineral structures have similarities when viewed along [0001] and [1210] in calcite, [001] and [100] in aragonite, and [111] and [101] in lime respectively (Fig. 1). Lime is cubic and has the NaCl structure, and calcite is the rhombohedral derivative of it with CO₃ groups substituting for oxygen. Aragonite corresponds to the hexagonal close-packed analog. Crystallographic orientation relationships between calcite and aragonite have been documented by several studies (e.g., Brown et al., 1962; Dasgupta, 1964).

The correspondence between crystallographic planes and directions in the transformation suggests that an oriented martensitic mechanism is possible, as in fcc-hcp transformations in metal alloys (e.g., Barrett and Massalski, 1980, p. 486–495). Gillet and Madon (1982) proposed a martensitic mechanism involving the movement of partial dislocations in the basal plane, dragging stacking faults between them (with additional atomic shuffles) and producing the requisite change in stacking between aragonite and calcite structures. Carlson and Rosenfeld (1981) and Carlson (1982, 1983) argue that heterogeneous nucleation and interface-controlled growth on preferred planes and directions is a more likely mechanism. Both proposals suffer from an inability to resolve the transformation in progress at the scale of the appropriate microstructures.

Burrage and Pitkethly (1969) have performed an in situ experiment using beam-heating in a 100 keV transmission electron microscope, but the technique employed is qualitative, since temperatures can not be accurately recorded, and radiation damage during beam heating can destroy the specimen. High voltages (1500 keV) reduce the effects of ionization damage, and with a heating stage the temperature at the surface of the sample can be accurately measured. The high voltage transmission electron microscope (HVEM), equipped with a heating stage, provides a dynamic, high resolution laboratory for in situ analysis of changing diffraction conditions and contrast effects of microstructures involved in the aragonite-calcite and calcite-lime transformations.

Materials and methods

Aragonite single crystals from Eugui, Spain, occurring in hydrothermal veins, have been cut normal to [001] and [100]. Thin sections are ion-thinned, carbon coated, and placed in a folding nickel grid, which immobilizes the specimen with a locking hinge. Grids are placed in a Swann side-entry, double-tilt heating stage. Analysis is performed in the Kratos 1500 keV instrument at the...
When the temperature is slowly raised to 400°C, there is little noticeable effect on the sample. Above 400°C the thin foil begins to shift and buckle (Fig. 2), requiring minor adjustments in tilt to maintain a desired orientation. The aragonite-calcite transformation involves a 7–10% in-
crease in volume, which accounts for the observed shifting and buckling. The aragonite single crystal may fracture before transformation is complete (Fig. 2). By raising the temperature slowly (less than 5°C per minute) and allowing the sample to equilibrate at each step, motion and misorientation are minimized.

Transformation at macroscopic rates (in the order of minutes) requires heating above 500°C. The appearance of
noncommensurate reflections in the aragonite SAD pattern signals the onset of transformation to calcite.

Brightfield images reveal microstructural controls on the aragonite-calcite transformation. Calcite nucleates preferentially at the thin edge of the sample (Fig. 3a) and at defects, such as the intersection of a twin boundary and a dislocation (Fig. 4a). Growth proceeds through movement of oriented grain boundaries, which sweep across the thin foil until aragonite is consumed by calcite (Fig. 3a–d). The transformation interface maintains its sharp, linear appearance during migration (Fig. 4b).

A modulated microstructure appears in some lamellar domains of the aragonite (Fig. 4c). Although the structural nature of the modulations has not been determined, upon heating they slowly homogenize and disappear. An irregular boundary migrates through the modulated structure with calcite precipitating behind the boundary (Fig. 5a–c). White spots superimposed on both aragonite and calcite appear to be centers of incipient radiation damage and possible amorphization (Fig. 5b, c). Disintegration of the modulated microstructure is most rapid in relatively homogeneous regions between lamellar twins and individual septa of the modulated structure (Fig. 4d). Calcite precipi-
Fig. 5. (a–c) Irregular transformation (homogenization) boundary migrates through the modulated microstructure in aragonite. Calcite precipitates behind the boundary. White spots appear to be incipient radiation damage or amorphization.

tating behind the homogenization boundary is relatively defect-free. At no time are partial dislocations or stacking faults observed propagating at the transformation interface.

Orientation relations are best documented in diffraction patterns. An aragonite (100) SAD (Fig. 6a) transforms into a calcite (1120) SAD (Fig. 6b). The stereographic projection illustrates the coincidences of planes and directions between aragonite and calcite (Fig. 6c). In this case, \((100)_A = (1120)_C, (010)_A \sim (\bar{T}104)_C, (011)_A = (0001)_C\), and \([001]_A \sim [\bar{T}_2; f_1]_C\). These observations correct a previously reported orientation relation in which \((001)_A \sim (\bar{T}012)_C\) (Wenk and McTigue, 1983).

Rings in the SAD pattern indicate contemporaneous development of polycrystalline lime through decomposition of calcite above 500°C (Fig. 7). Heterogeneous density of intensity in the lime rings suggest preferred orientation of lime crystallites with respect to the calcite precursor. If centers of heterogeneous intensity in the rings are indexed as if they formed a single crystal pattern, an orientation
relationship is recorded between calcite and lime with (0112)C ~ (111)L and (1015)C ~ (110)L (Fig. 8a, b). If this orientation is then rotated in stereographic projection into a (1120) orientation for calcite, the coincident planes are (1120)C = (110)L, (1104)C ~ (001)L, and (0001)C = (111)L (Fig. 8c).

Discussion

Observation of the dry-state aragonite-calcite transformation in the TEM reveals topotaxy among low-index crystallographic planes and directions. The coincidence of (100)A with (1120)C and (010)A with (1104)C are predicted based on structural similarities (Fig. 1). This is consistent with the observations of Brown et al. (1962) on metamorphic aragonite. Dasgupta (1964), however, documents the coincidence of [001]A with [0001]C, [100]A with [1010]C, and [110]A with [0110]C in an X-ray diffraction experiment using aragonite single crystals. Frisia-Bruni and Wenk (1984) note the coincidence of (010)A with (1120)C in sedimentary carbonates where replacement occurred through dissolution-reprecipitation. Hiragi et al. (1966) report (001)A = (0001)C, (100)A = (1210)C, and (010)A = (1014)C.

The discrepancies between observed orientation relationships are difficult to rationalize on a purely crystallographic basis. Physical conditions governing nucleation and growth, such as temperature, pressure, and the presence or absence and composition of a fluid phase, may dictate that different kinetic mechanisms may operate which may favor different orientation relations. In the dry-state heating of an aragonite single crystal, for example, a calcite nucleus may grow through coordinated atomic jumps across a high energy interface. In such a transformation the minimum jump distance, hence the minimum strain energy, will occur...
between planes and directions in which the two phases are most structurally similar. In this case, orientation relationships are predictable. In the presence of a fluid phase, however, a complicated mechanism involving dissolution, hydration, diffusion, adsorption, and growth, each with its own characteristic rate, is more appropriate.

In this case, orientation relations may depend more on the original orientation and surface perfection of the aragonite substrate and the relative growth rates in crystallographic directions in calcite controlled by diffusion through the fluid phase.

Consistent topotactic relationships observed in the dry-state aragonite-calcite transformation suggest that the mechanism involves minor atomic displacements between the structures rather than long-range diffusion. A coincidence of both \((100)_A = (1210)_C\) and \((001)_A = (0001)_C\) as reported by Hiragi et al. (1966) is unlikely. Although the calcium sublattice appears to be similar between the structures, carbonate groups are displaced by both a e trans-
Fig. S. (a) SAD of calcite in a \(<\{\overline{2}31\}\) orientation with lime rings developing. (b) Pervasive decomposition. Heterogeneous intensity distribution in the rings can be indexed as a single crystal pattern with \([012]_c \sim [110]_c\) and \([015]_c \sim [110]_c\). (c) Stereographic projection of orientation relations among aragonite, calcite, and lime. Calcite-lime orientation relationship obtained by rotating a calcite \(<\{\overline{2}31\}\) into a \(<110\rangle\) with equal angular rotations for lime, yielding a \(<110\rangle\) lime orientation.

The observed transformation mechanism may depend on the presence of planar defects in the aragonite precursor. A martensitic transformation, with different orientation relationships, may be possible in more structurally homogeneous samples, in which the density of possible nucleation sites is low. The characterization of microstructures in phases both prior to and following transformation is a critical step in eliciting the transformation mechanism.

The origin of the modulated microstructure is not known. Ordering of solute species, such as Mg,

\[\text{Mg}^{2+}\], within the aragonite structure is possible, creating domains with slightly different structures. Streaking does not appear in the SAD patterns, however. EDX microanalysis has not
been carried out on these domains, although this could help to determine the nature of the modulations.

The decomposition reaction calcite-to-lime plus CO₂ exhibits preferred orientation with respect to calcite, as evidenced by SAD patterns and darkfield images. The transformation mechanism may be the driving off of CO₂ molecules from a relatively rigid cation framework, collapsing the structure slightly and creating porosity but preserving an orientation relationship in which (110)ₗ = (1120)ₖ, (TT1)ₗ ∼ (0001)ₖ, and (001)ₗ ∼ (104)ₖ.

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**References**


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