Phenomenological Analysis of Martensitic Transformation in Dicalcium Silicate

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ケイ酸カルシウムにおけるマルテンサイト変態の現象論的解析

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Matrix algebra analysis of martensitic transformations has been employed for the determination of habit planes and shape deformations of Ca_2SiO_4 upon β- to -α'_L transformation during heating. The cell parameters of both the parent β and product α'_L-phases at the transformation temperature (710°C) have been found from extrapolation of the regression of their cell-parameter variations. The analysis indicates that one of the principal distortions ($=c_{\alpha'L}/3b_\beta$) of the lattice deformation is equal to unity, and the other principal distortions are larger and smaller than unity. This satisfies the requirement for the formation of completely coherent interfaces between the two phases, which are almost parallel to either $(100)_\beta$ or $(001)_\beta$. Because the transformation involves a very small volumetric expansion of 0.3%, the strain accommodation would be almost completed. Both the complete coherency at the interphase boundaries and the effective strain accommodation probably lead to the thermoelasticity of the transformation, in accord with a previous study for doped Ca_2SiO_4.

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1. Introduction

With Ca_2SiO_4 (C_2S) solid solution, the phenomenological crystallographic theory of martensitic transformations[1] has been applied to the phase transformation from orthorhombic α'_L to monoclinic β.[2] The calculation was based on the orientation relationship between the two phases, $(100)_{\alpha'L} \| (100)_\beta$ and $[001]_{\alpha'L} \| [010]_\beta$, and their cell parameters at the transformation temperature. Because the accuracy of the latter is essential to the reliability of the calculation results, they were determined for the crystals in which the two phases coexist. By virtue of the constraint represented by the equation $3b_\beta = c_{\alpha'L}$, one of the three principal distortions of the lattice deformation was equal to unity. The other two principal distortions satisfied the requirement for the formation of coherent interphase boundaries between the two phases. The coherency as well as the effective strain accommodation have strongly suggested the thermoelasticity of the transformation. The predictions were in good agreement with the actual experimentally determined shape deformation.[3]

The thermoelasticity of C_2S solid solutions has been confirmed based on the growth and shrinkage behavior of the martensite plates during cooling and heating.[3] The thermal hysteresis (A_s–M_s) was negative, where A_s and M_s are the starting temperatures of the reverse (β- to -α'_L) and forward transformations, respectively.[3)-5] Because of the athermal nature of the transformation, the amount of transformation remains unchanged when the temperature is kept constant. Thus, the α'_L- and β-phases coexist within the temperature intervals between M_s and M_f during cooling and between A_s and A_f during heating, where M_f and A_f are the finishing temperatures of the forward and reverse transformations, respectively. These transformation temperatures have been successfully determined by high-temperature X-ray diffractometry (HT-XRD) and high-temperature optical microscopy.[3)-5]

With pure C_2S, the thermoelasticity of the $\alpha'_L \leftrightarrow \beta$ martensitic transformations is still uncertain. Recently, Remy et al.[6] have determined the temperature dependence of the cell parameters by HT-XRD. This has enabled us to determine the cell parameters of both the α'_L- and β-phases at the transformation temperature. In the present study, the phenomenological crystallographic theory has been applied to the β- to -α'_L reverse transformation of pure C_2S during heating. The complete coherency with the lattices at the habit planes as well as the very small volume change strongly suggest the thermoelasticity of the transformations.

2. Results and discussion

2.1 Cell parameters at the transformation temperature

Remy et al.[6] detected the occurrence of the β- to -α'_L transformation during the heating process between 711°C and 732°C, and the completion at 759°C. These are consistent with the previously determined transformation temperatures of 710°C for A_s and 740°C for A_f.[4] Thus, we determined the A_s to be 710°C in the present study. The cell parameters of both phases at that temperature (**Table 1**) were found from extrapolation of the regression of their cell-parameter variations (**Fig. 1**). According to the lattice correspondence between the two phases, a_β becomes $a_{\alpha'L}$, b_β becomes $1/3c_{\alpha'L}$, and c_β becomes $b_{\alpha'L}$.[7),8] The β- to -α'_L transformation is accompanied by the very small volumetric expansion of 0.3%, in accord with previous studies.[6),8)-10]

2.2 Principal distortions and habit planes

We assume that, upon β- to -α'_L transformation, the β-phase lattice is homogeneously distorted into the α'_L-phase lattice. The magnitudes and directions of the principal distortions (λ_i) are therefore given by the eigenvalues and eigenvectors of the following equation:[11]

$$|(\mathrm{MC'O})(\mathrm{O^*GO})(\mathrm{OCM}) - \lambda_i^2(\mathrm{M^*GM})| = 0 \quad (1)$$

The matrix (OCM), representing the lattice correspondence between the monoclinic β-phase (M) and the orthorhombic α'_L phase (O), is given by

$$(\mathrm{OCM}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1/3 & 0 \end{bmatrix} \quad (2)$$

The metrics (O*GO) and (M*GM) are determined, respec-

Table 1. Cell Parameters of β and α'_L Phases at 710℃

Phase	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å^3)
β	5.548	6.814	9.414	93.63	355.2
α'_L	5.566	9.381	20.46 (= 6.820 × 3)	———	1068.6 (= 356.2 × 3)

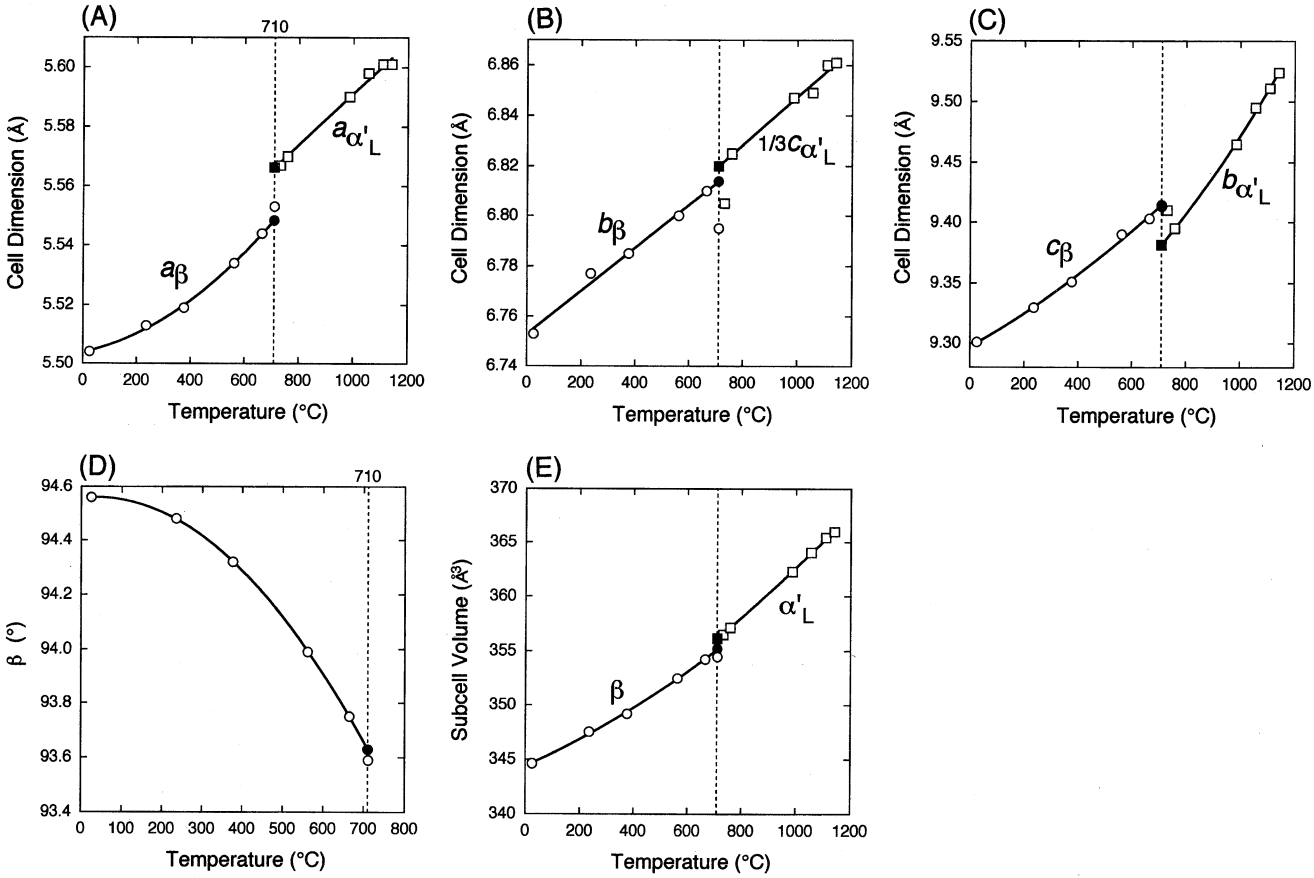

Fig. 1. Determination of cell parameters for the (●) β- and (■) α'_L- phases at the transformation starting temperature of 710℃ during heating. The variation in cell parameters with temperature for the (○) β- and (□) α'_L-phases is given by Remy et al.[6] (A) a_β and $a_{\alpha'L}$, (B) b_β and $1/3c_{\alpha'L}$, (C) c_β and $b_{\alpha'L}$, (D) angle β and (E) subcell volume. The settings of the axes differ from those given in the original article. Because the two phases coexisted at 711 and 732℃, the cell parameters at these temperatures are excluded from those used for the regression.

tively, from the cell parameters of the α'_L- and β-phases.[2] The matrix (MC′O) is the transpose of (OCM). In the orthonormal basis parallel to the principal axes, the lattice distortion matrix (B) takes the simple form of a diagonal matrix, consisting of the three eigenvalues (λ_1, λ_2 and λ_3).

Equation (1) was solved using the matrix (2) to determine the magnitudes and directions of the principal distortions (Table 2). One of the principal distortions, λ_2 ($=c_{\alpha'L}/3b_\beta$), is, within the limits of measurement error, equal to unity. The other principal distortions, λ_1 and λ_3, are respectively larger and smaller than unity. Accordingly, the present lattice deformation satisfies the general requirement for the invariant plane deformation.[12] The subsequent rigid body rotation (R) then ensures the complete coherency with the lattices at the habit planes, which separate the two phases. Because the shape deformation, represented by RB, is equivalent to the invariant plane deformation, we have

$$RB = I + m\mathbf{d}\mathbf{p}' \quad (3)$$

where I is the identify matrix, m is the magnitude of displacement, d is the unit vector parallel to the displacement and p′ is the unit row vector parallel to the habit plane normal.[13] Equation (3) was solved to determine the two types of shape deformations P_1 and P_2 (Table 3), which produce the habit planes almost parallel to $(100)_\beta$ and $(001)_\beta$, respectively (Fig. 2).

2.3 Twinning structures of the β-phase and shape deformations

The polysynthetic twinning, frequently on $(100)_\beta$ and

Table 2. Principal Distortions of β- to -α'_L Lattice Deformation

λ_1	λ_2	λ_3
$\lvert\lambda_1\rvert = 1.033$	$\lvert\lambda_2\rvert = 1.001\ (\approx 1)$	$\lvert\lambda_3\rvert = 0.970$
$0.764\mathbf{i} + 0.645\mathbf{k}$	$\mathbf{j}$	$-0.645\mathbf{i} + 0.764\mathbf{k}$

i, **j** and **k** are the unit vectors in the orthonormal basis defined by **i** || a_β*, **j** || b_β and **k** || c_β.

Table 3. Direction and Magnitude of Shape Deformation

Type	Habit Plane Normal (p')	Displacement: Direction (d)	Displacement: Magnitude (m)	Shape Deformation Matrix (RB)
P_1	$\begin{bmatrix} 0.9985 \\ 0 \\ -0.0551 \end{bmatrix}$	[0.0823, 0, 0.9966]	0.0638	$\begin{bmatrix} 1.0052 & 0 & -0.0003 \\ 0 & 1 & 0 \\ 0.0635 & 0 & 0.9965 \end{bmatrix}$
P_2	$\begin{bmatrix} 0.1140 \\ 0 \\ 0.9935 \end{bmatrix}$	[0.9962, 0, -0.0869]	0.0638	$\begin{bmatrix} 1.0072 & 0 & 0.0632 \\ 0 & 1 & 0 \\ -0.0006 & 0 & 0.9945 \end{bmatrix}$

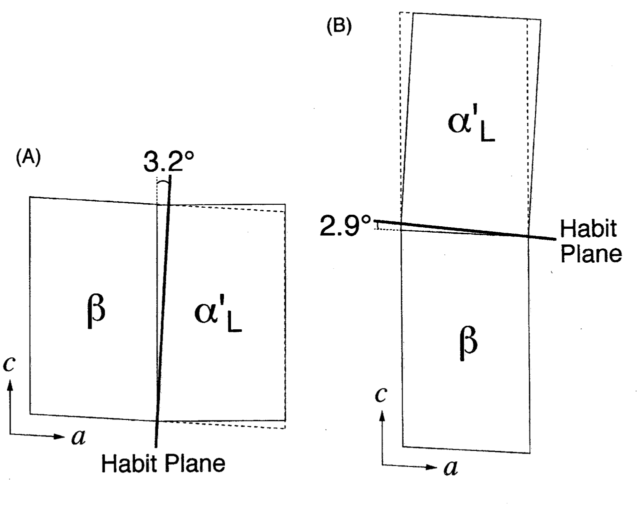

Fig. 2. Schematic of invariant plane deformations (A) P_1 and (B) P_2 in Table 3. The habit planes separating the α'_L- and β- phases are almost parallel to $(100)_\beta$ in (A) and $(001)_\beta$ in (B). The interface boundaries between the two phases are completely coherent.

rarely on $(001)_\beta$,[8] is peculiar to the β-phase. These internally twinned structures come about by having alternate regions in the parent α'_L-phase undergo the lattice deformation along different contraction axes.[2] With the $(100)_\beta$ twinning, the relative volume of the variants (denoted by 1 and 2) is almost identical, which effectively reduced the elastic stresses in both the parent and the product phases.[2]

Upon reverse (β- to -α'_L) transformation of the $(100)_\beta$ twinned crystal, both variants 1 and 2 undergo the same lattice deformation P_1 (Table 3). The resulting α'_L-phase lattices originated from the variants 1 and 2 require additional rigid body rotations around the b_β-axis at angles of $+0.02°$ and $-0.02°$, respectively, to ensure that they coherently fit on $(100)_{\alpha'L}$. The displacement vector of the whole twinned crystal is along the a_β*-axis with a magnitude of 0.005 (Fig. 3).

In a manner similar to that above, the transformation of the $(001)_\beta$ twinned crystal is achieved by the deformation P_2 (Table 3), followed by the additional rigid body rotations around the b_β-axis at angles of $+0.01°$ and $-0.01°$ for the variants 1 and 2, respectively. Assuming the same frequency of the variants, the whole displacement occurs along the c_β*-axis with a magnitude of -0.001. Because the displacement magnitude is very small, the transformation of the $(001)_\beta$ twinned crystal would make an insignificant contribution to the actual shape deformation.

2.4 Thermoelasticity

The prediction indicates the complete coherency with the lattices across the habit planes. This would actually be realized because the β- to -α'_L transformation is accompanied by the very small volume change. The strain accommodation would therefore be elastically and almost completely achieved without dislocation generation at the interface boundaries. The coherency at the interface boundaries as well as the effective reduction in the elastic stress would lead to the thermoelasticity of C_2S. This is consistent with the previous study for phosphorus-bearing C_2S.[2]

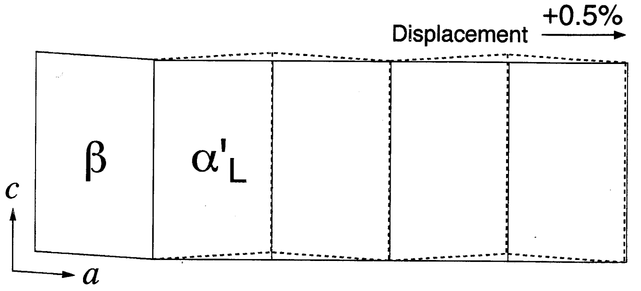

Fig. 3. Schematic of overall displacement upon β- to -α'_L transformation. The β-phase, exclusively twinned on (100), undergoes the lattice deformation P_1 with the displacement along the a_β*-axis.

3. Conclusions

(1) The β- to -α'_L lattice deformation meets the general requirement of the invariant plane deformation. This ensures the complete coherency with the lattices across the habit planes, which are almost parallel to either $(100)_\beta$ or $(001)_\beta$.

(2) The transformation is accompanied by the very small volumetric expansion of 0.3%, suggesting that the strain accommodation would be almost completed.

(3) Both the coherency with the lattices at the transformation front and the effective strain accommodation probably cause the thermoelasticity of the martensitic transformation in C_2S.

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