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Transformation kinetics from hexacelsian to celsian for powders having uniform particle size

Yuichi Kobayashi *

Department of Applied Chemistry, Aichi Institute of Technology 1247 Yachigusa, Yakusa, Toyota, Aichi 470-0392 Japan

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Abstract

Transformation kinetics from hexagonal to monoclinic form of celsian, which is an attractive material as a matrix of fiber-reinforced ceramics, were studied. Rate constants for nucleation and crystal growth were determined by isothermal transformation using classified powders having different ranges of particle size. Kinetics could be successfully analyzed by a modified first order equation. The activation energies for nucleation and growth were evaluated separately to be 407 and 228 kJ/mol from the temperature dependencies of the rate constants. The difference in the activation energies affected the change in shape of sigmoidal isotherms, and sluggishness of this phase transformation was attributed to a small value of the crystal growth rate.

Keywords: A. Powders: solid state reaction; B. X-ray methods; D. Silicate; Phase transformation

1. Introduction

Monoclinic celsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$, hereafter referred to as celsian) is an attractive material as a matrix for fiber-reinforced ceramics (FRC) and also as a substrate material for high-frequency electric circuit board, because it has low thermal expansion, high melting point, low dielectric constant and low dielectric loss. Many researches reported the applicability of sintered celsian for FRC, which were prepared by sintering and crystallization of melt-derived glass powders or sol–gel powders [1]. However, the complexity and high-cost performance of these preparation processes have limited the practical application of celsian ceramics as industrial utilization.

One of the difficulties for application of celsian ceramics that has been pointed out is the metastable pseudo-hexagonal celsian crystal (hereafter referred to as hexacelsian), which shows high thermal expansion coefficient, appears in the beginning of heat treatment of powders that are prepared using glass-melting and sol–gel processes [2]. Hexacelsian once formed sluggishly transforms into monoclinic form [3], so that some additives, such as Li_2O, etc., for acceleration of the transformation from hexacelsian to celsian has been necessary to prepare celsian ceramics [1,4,5].

The object of this work is to study the transformation kinetics from hexacelsian to celsian in order to understand this sluggish transformation. Rate constant of nucleation and crystal growth were determined by isothermal transformation using the powders having different ranges of particle size, and their activation energies were evaluated from the temperature dependences of respective rate constants, separately.

2. Experimental procedure

2.1. Sample preparation

$BaCO_3$ (reagent grade) and New Zealand kaolin (hereafter referred to as NZ kaolin) were used as starting materials. NZ kaolin was elutriated into the particle size below 1 μm by sedimentation in aqueous suspension. Chemical composition of elutriated NZ kaolin is shown in Table 1, revealing that it has a molar ratio SiO_2/Al_2O_3 of 2.01 and almost ideal composition of kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$). It contains virtually few alkaline and alkaline-earth elements. $BaCO_3$ was

* Corresponding author. Tel.: +81-565-48-8121; Fax: +81-565-48-0076.

E-mail address: kobayasi@ac.aitech.ac.jp (Y. Kobayashi).

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Table 1
Chemical composition of elutriated New Zealand kaolin

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	IG.loss	Total mass%
NZ Kaolin	45.49	38.49	0.27	0.07	0.01	0.17	0.01	0.01	15.37	99.89

ball-milled into a mean particle size of 1.5 μm in order to achieve sufficent thermal reaction with NZ kaolin.

Mixture in the composition of $BaO{\cdot}Al_2O_3{\cdot}2SiO_2$ was calcined at 1300°C for 5 h in air. After ball-milling the calcined aggregates, further heating was carried out at 1400°C for 40 h. Single phase of hexacelsian and celsian were obtained by the former heat treatment and the latter, respectively. Crystal constituents except celsian or hexacelsian are not detected by X-ray diffraction experiments.

About 100 g of hexacelsian powders were ball-milled and classified into particle size ranges of 2.0–4.0, 4.0–6.0, 6.0–8.0 and 8.0–10 μm by sedimentation in aqueous suspension. Sample names are designated as H-3, H-5, H-7 and H-9, depending on the mean particle size in μm.

2.2. Isothermal heat treatments

Isothermal heat treatments of hexacelsian powders were carried out in a PID controlled electrical furnace at a constant temperature between 1300 and 1400°C, with an accuracy better than ±1°C, for various periods up to 80 h. Powdered specimens of about 0.2 g were poured in a small alumina crucible and then the crucible was quickly introduced in the furnace kept at the pre-set temperature and quenched after the prescribed heating periods.

2.3. Measurements

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RAD-rX powder diffractometer equipped with a crystal monochromator, employing Cu K_α radiation. X-ray diffraction intensities of 131 peak for celsian and that of 102 peak for hexacelsian were determined as a mean value from three independent measurements on a sample, and the fraction transformed from hexacelsian to celsian was determined using calibration curve of intensity ratio between these two peaks versus weight percentage of celsian. The correlation coefficient from linear regression analysis was 0.9998, indicating a high degree of accuracy in the fraction transformed.

3. Results and discussion

3.1. Isothermal transformation

Isothermal transformation curves (fraction transformed α vs. heating time) at temperatures from 1300 to 1400°C are shown on H-3 in Fig. 1. All the transformation curves are sigmoidal and transformation rate increases with the increase in heat treatment temperature. Sigmoidal characteristics suggest that the transformation from hexacelsian to celsian occurs in nucleation and crystal growth mechanism. In Fig. 2, fraction transformed α is plotted against reduced time ($t/t_{0.5}$) at each temperature, where $t_{0.5}$ is a time when α reaches to a half. An accelerating interval increases with

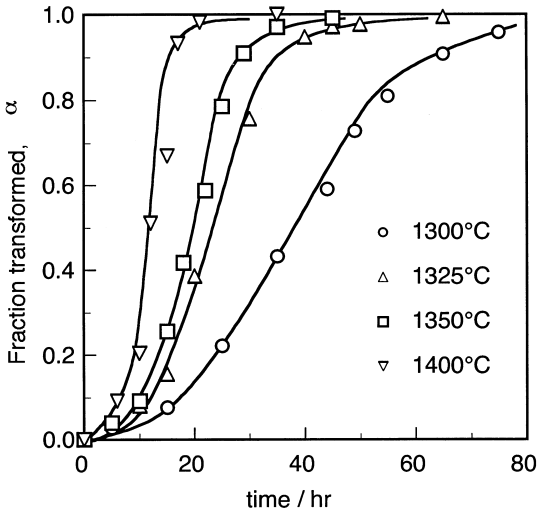

Fig. 1. Transformation isotherms of H-3 at various heat treatment temperatures.

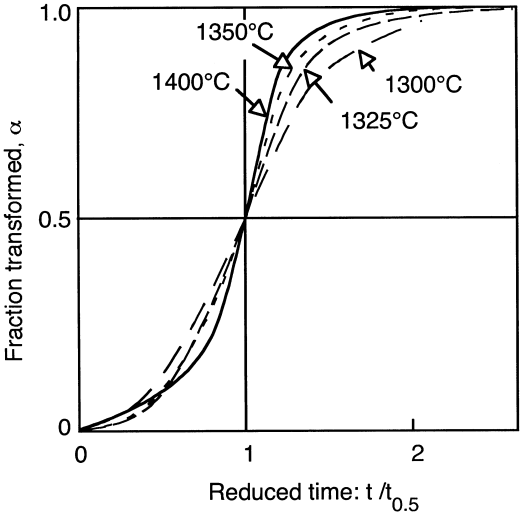

Fig. 2. Fraction transformed against reduced time $t/t_{0.5}$. Redrawn from Fig. 1.

the increase in temperature. These results indicate that the transformation mechanism is gradually altered with the change in heat treatment temperature.

Isothermal transformation curves of H-3, H-5, H-7 and H-9 at 1350°C are compared with each other in Fig. 3. Transformation rate increases a little with an increase in mean particle size of hexacelsian. In Fig. 4, fraction transformed α is plotted against reduced time ($t/t_{0.5}$). All the isotherms are overlapped with each other and give a master curve. From a comparison with Fig. 2, effect of particle size seems to be less pronounced than that of heat treatment temperature.

3.2. Application of JMA equation

Many kinetic models [6] have been proposed for the analysis of solid state reactions, such as phase transformation, crystallization, decomposition, etc. However, rigorous models with some parameters that allow the change in mechanism with heat treatment temperature and particle size of starting materials are very few. One of the typical reaction equations is JMA equation (also called Avrami–Erofe'ev equation) and represented as follows [6],

$$\ln\ \ln\frac{1}{1-\alpha} = n\ln k + n\ln t \tag{1}$$

where α is fraction transformed, t heat treatment time, k rate constant, and n a parameter which is related with the mechanism of nucleation and growth of the transformed crystal. In Fig. 5, the data of Fig. 1 are replotted according to JMA equation. The linearity of the relations for each temperature is not satisfactory, but the slope of the straight part of lines alters with heat treatment temperatures. Since a JMA equation was derived from an assumption of homogeneous nucleation and growth processes in a bulk material, its application to the transformation of powders with a minute particle size seems to be inadequate because the growth area is limited within a particle.

3.3. Application of modified first order equation

The present author developed a modified first order equation [7] for the decomposition reaction of β-Al_2TiO_5 to α-Al_2O_3 and TiO_2. The equation is derived on the basis of an assumption that nucleation rate is proportional to the number of sites where nuclei can be generated, where a time "τ" is introduced in order to express an average of time in which the transformation initiates and then completes within a particle.

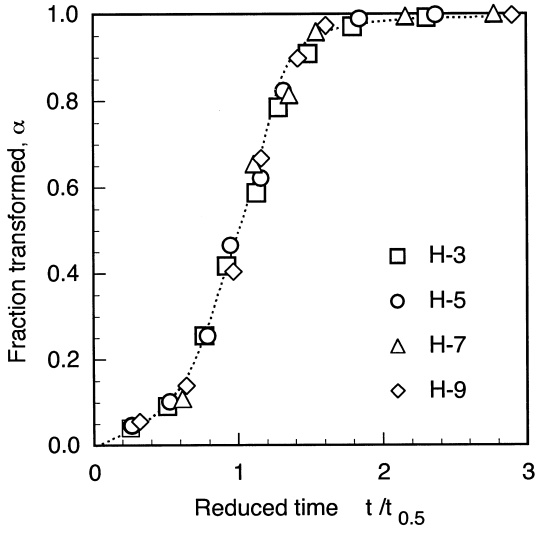

Fig. 4. Fraction transformed against reduced time $t/t_{0.5}$. Redrawn from Fig. 3.

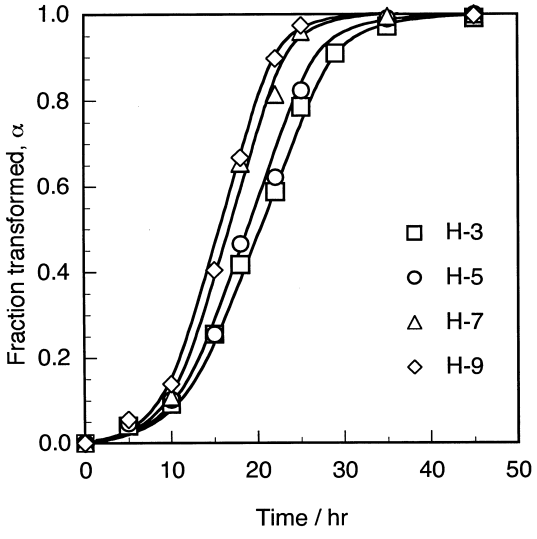

Fig. 3. Effect of particle size on the transformation of H-3, H-5, H-7 and H-9 at 1350°C.

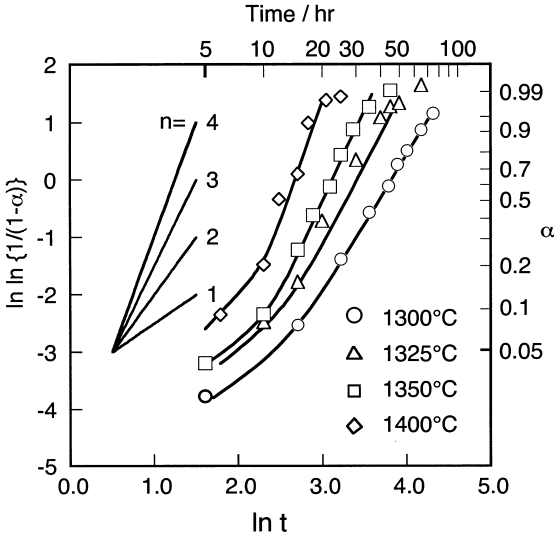

Fig. 5. JMA plot for the data of Fig. 1.

The relation between fraction transformed α and time t is expressed as follows: for the accelerating period ($t \leqslant \tau$),

$$\alpha = \frac{1}{k\tau}\{kt - (1 - e^{-kt})\} \tag{2}$$

and for the decelerating period ($t \geqslant \tau$),

$$\ln(1-\alpha) = \ln\left\{\frac{1}{k\tau}(e^{k\tau} - 1)\right\} - kt. \tag{3}$$

In Fig. 6, the relations expressed with Eqs. (2) and (3) are illustrated for different values of τ. When τ is zero, the curve coincides with the first order equation, because no accelerating period exists. With increasing τ from 0 to 2.5, accelerating period expands in the early stage of the reaction, so that the shape of the transformation isotherm becomes sigmoidal. Inflection point (indicated as circles in Fig. 6) represents a time τ. Eq. (3) indicates that the straight line would be obtained by plotting $\ln(1-\alpha)$ against time t in a long treatment time, and that the slope of the straight portion corresponds to the nucleation rate constant k. After calculating a value of k, $\tau(= 1/G)$ can be estimated from the Eqs. (2) and (3). Here, the reciprocal of τ, G, may be defined as a mean value of rate constant for the growth of the transformed crystal.

In Figs. 7 and 8, the present results shown in Figs. 1 and 3 are replotted according to Eq. (3), respectively. For all cases, a linear relationship is obtained in a side of long period of transformation. All the numerical values of k, τ and G calculated on the samples with different particle size and on the sample H-3 at different heat treatment temperature are shown in Table 2. The two values, τ_2 and τ_3 [estimated from Eq. (2) and (3)], give a fairly good agreement with each other. This result reveals that the modified first order equations can be effectively adopted for the phase transformation from hexacelsian to celsian. The values of growth rate constant G are much smaller than nucleation rate constant k. Therefore, a small value of G (namely a large value of τ) is considered to be the major cause for sluggish phase transformation from hexacelsian to celsian.

Nucleation rate constant k is defined as a formation probability of nuclei per unit time and per a particle in the modified first order equation, so that particle size naturally affects the value of k, because the nucleation of most phase transformation takes place heterogeneously at the boundaries, surfaces and/or structural imperfections. An effect of particle size of hexacelsian on k is shown in Fig. 9. Nucleation rate constant k increases linearly with the increase in particle size. Although the detailed mechanism is not known, surface area of a grain would affects the probability of nucleation.

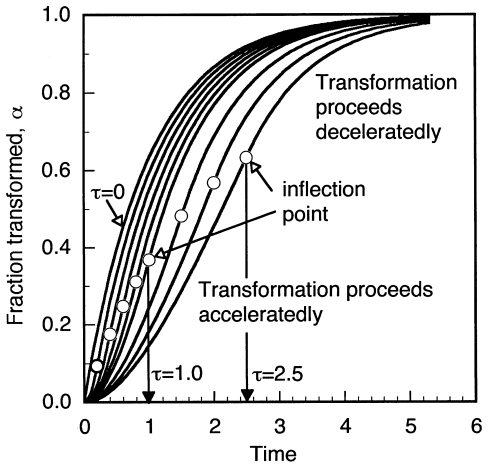

Fig. 6. Schematic illustrations of phase transformation according to the modified first order Eqs. (2) and (3). Inflection point indicates a time τ.

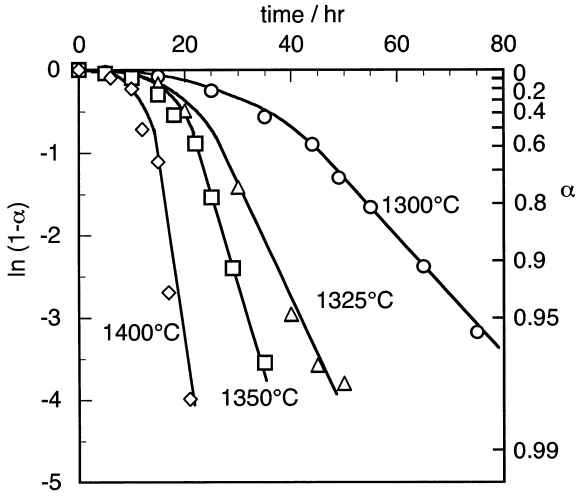

Fig. 7. Relation between $\ln(1-\alpha)$ and time for transformation of H-3.

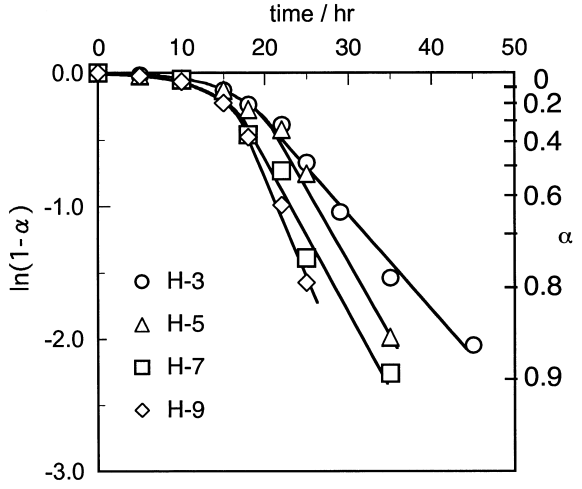

Fig. 8. Relation between $\ln(1-\alpha)$ and time for transformation of H-3, H-5, H-7 and H-9 at 1350°C.

Table 2
Parameters calculated from Eqs. (2) and (3) for phase transformation from hexacelsian to celsian in powders

Sample	Temperature	k(hr^{-1})	τ (hr)			
			Eq. [2]	Eq. [3]	$G(=1/\tau_2)$	$G(=1/\tau_3)$
M-3	1300°C	0.0693	52.7	49.1	0.0189	0.0204
M-3	1325°C	0.128	33.0	26.9	0.0303	0.0370
M-3	1350°C	0.200	30.3	25.4	0.033	0.0394
M-3	1400°C	0.457	19.2	16.4	0.052	0.0610
M-5	1350°C	0.279	32	25.7	0.031	0.0389
M-7	1350°C	0.506	24	23.6	0.42	0.0424
M-9	1350°C	0.540	25	23.0	0.040	0.0435

If only one nucleus of celsian crystal forms in one particle of hexacelsian, τ should be proportional to the particle size of hexacelsian crystals. In the present case, however, τ is almost independent on a particle size (Fig. 9). This result suggests a possibility that multiple nuclei form in case for large particles and the number of nuclei increases with the surface area of the particle. This multiple nucleation mechanism can be used successfully to explain the dependency of k on a particle size without any discrepancy between the dependency of τ and k.

3.4. Activation energy for transformation

Arrhenius plots of nucleation constant k and growth rate constant G are shown in Fig. 10. Straight lines are obtained in both cases. The activation energy for nucleation E_n is 407 kJ/mol, about twice as large as that for growth E_g 228kJ/mol. This relationship ($E_n \geqslant E_g$) is analogous to the decomposition reaction of β-Al_2TiO_5 to α-Al_2O_3 and TiO_2 [7]. The difference between these activation energies affected the change in shape of isotherms with the heat treatment temperature as indicated in Fig. 2.

These two activation energies are far larger than the value of 84 kJ/mol which has been reported for the same transformatoin of hexacelsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) to celsian before [3], where the rate constants were calculated only from the intercept of asymptotic lines at the beginning of transformation. The basis of the definition of the rate constants was extremely vague. On the other hand, Bansal and Drummond [8] reported the activation energy of 527 kJ/mol for the phase transformation from hexacelsian to celsian in $SrAl_2Si_2O_8$, using hexacelsian polycrystals which were synthesized by heat treatment of stoichiometric glass via melt or sol–gel routes. Furthermore, Lee et al. [2] reported that the activation energy for the crystallization of hexacelsian crystals from celsian stoichiometric glass ($BaAl_2Si_2O_8$) is about 544 to 627 kJ/mol.

Kingery enunciated [9] that the activation energy for a nucleation is a total value of the activation energies for the formation of an embryo in critical size and for transport across the interface. If the latter corresponds to the energy for the crystal growth process E_g, the activation energy for nucleation E_n should be larger

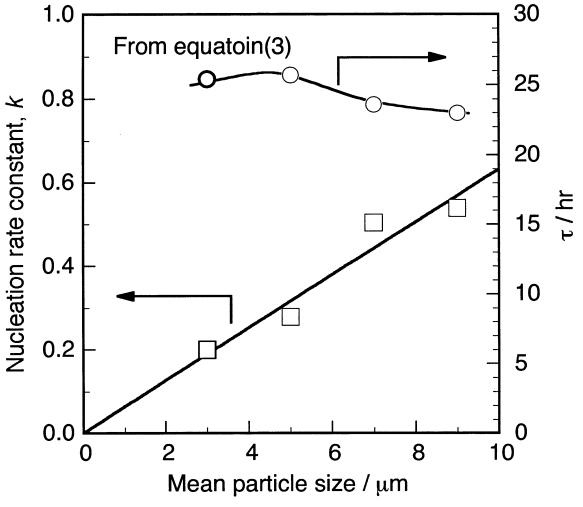

Fig. 9. Effect of particle size of hexacelsian powders on the rate constant k and τ for the transformation at 1350°C.

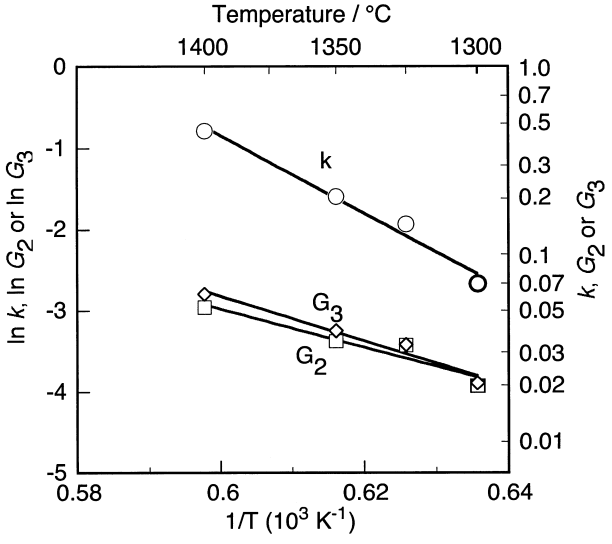

Fig. 10. Arrhenius plot of nucleation rate constant k and growth rate constant $G(=1/\tau)$.

than that for crystal growth E_g. In the present study, the relationship of $E_n > E_g$ is actually confirmed, just as the case for the decomposition of β-Al_2TiO_5 to α-Al_2O_3 and TiO_2 [7].

4. Conclusions

Transformation isotherms of hexacelsian to celsian were sigmoidal and the shape altered with the heat treatment temperature. The straight line was obtained by plotting ln(1-α) against time (α = fraction transformed) in a long period of transformation. Rate constant of nucleation k and that of growth G ($= 1/\tau$) could be estimated using a modified first order equation. The activation energies for nucleation and growth are evaluated separately to be 407 and 228 kJ/mol, respectively. It was concluded that the difference of the activation energies affected the change in shape of isotherms and also the sluggishness of phase transformation was attributed to a small value of G, namely a large value of τ.

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