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Kinetic Study on the Hexacelsian–Celsian Phase Transformation

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The hexacelsian–celsian transformation from grains of $\frac{1}{4}$ in. (0.635 cm) size is slow and erratic. This is because the rate of heterogeneous nucleation in such grains is low and is influenced by contamination present in the furnace. When the grain size is reduced to a − 200 mesh powder, heterogeneous nucleation becomes a dominant factor and the transformation is accelerated. The transformation has three stages: the first is controlled by the rate of crystal growth, the second is controlled by the rates of nucleation and crystal growth, and the third is controlled by the rate of nucleation.

The activation energy of crystal growth in the first stage of transformation is 20.1 kcal mole^{-1} $\pm$ 20%. This suggests that the hexacelsian–celsian transformation does not involve Si–O and Al–O bond openings, since this would be expected to involve an activation energy of at least 60 kcal mole^{-1}.

1. Introduction

A lengthy debate on the hexacelsian–celsian transformation was recently concluded [1]. It was found that 1590° C is the equilibrium temperature of these phases. Celsian is stable below this temperature and metastable above it, and hexacelsian ceases to be metastable and becomes stable above 1590° C up to the melting point. The importance of hexacelsian and celsian in glass-ceramic applications [2] invites an investigation of the chief parameters that control the hexacelsian–celsian transformation below 1590° C.

In the present work an attempt is made to study the effects of nucleation and crystal growth rates on the rate of hexacelsian–celsian phase transformation as a function of deviations from the equilibrium temperature. The effects of crystal size and powder mixture on the rate of transformation are investigated as well.

2. Experimental Techniques

2.1. Material Preparation

A melt of the $BaAl_2Si_2O_8$ stoichiometric composition was prepared by melting Morgan Sand ($SiO_2 = 99.8\%$), T-61 aluminium oxide ($Al_2O_3 = 99.7\%$), and $BaCO_3$ (reagent) at 1800° C for 4 h in a 80% Pt-20% Rh crucible. The crucible was then rapidly transferred to 1400° C, kept overnight and then removed to room temperature. At 1400° C, characteristically, hexacelsian crystallised at the top and periphery of the open crucible and celsian crystallised at the centre and bottom of the crucible. The two polymorphs were separated by hand picking.

The separated crystals were then further divided into three groups for the heat-treatment: (a) crystals of hexacelsian were broken by a hammer into sizes of approximately $\frac{1}{4}$ in.; (b) the hexacelsian crystals were ground by a tungsten carbide Spex mill jar into −200 mesh; (c) both hexacelsian and celsian crystals that had been ground separately by a tungsten carbide Spex mill into −200 mesh were then blended into a mixture of 95% hexacelsian powder plus 5% celsian powder.

2.2. Heat-Treatment

The hexacelsian crystals and powders were heated at various temperatures between 950 and 1400° C. The crystals were placed on platinum foil which rested on alumina brick in a furnace, and each week a single crystal was removed from the furnace. Similarly, the powders were placed as a dry thin layer approximately $\frac{1}{32}$ in. (0.8 mm) thick on platinum foil which sat on an alumina brick. At various times the platinum foil carrying the powder was

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removed from the furnace. A portion of the thin layer (partially sintered already) was taken as a sample and the foil with the rest of the material was rapidly returned to the furnace.

Prior to and during the experiment, temperature control tests were carried out by two methods: (a) individual heat-treatments on samples were performed at various temperatures for certain durations of time with the time of heating being progressively increased at each heat-treatment; (b) various samples were heated during the experiment for a given time after being removed from the furnace a different number of times, and for different durations, before returning to the furnace. The results of these tests indicated that the removal of the material from the furnace several times during the experiment did not introduce significant errors to the experiment, and results at time intervals of hours were reliable.

The heat-treatments of the powders were carried out in a furnace heated by Super Kanthal heating elements. In this furnace, readings of temperature were within 3° C error and the return of the furnace temperature to its normal level after a rapid opening and closing of the door (twice for each sampling) was rapid (about 2 min).

2.3. Analytical Procedure

For the kinetic study of the hexacelsian–celsian phase transformation, accurate quantitative results of hexacelsian/celsian ratios were necessary. Hexacelsian has a sheet-like structure and a perfect 0001 cleavage. Accordingly, it shows a high tendency toward preferred orientation when examined by X-ray diffraction. For this reason, the X-ray diffraction method was not used.

It was observed, however, that the intensity of a strong infra-red absorption peak at about 8.2 μm produced by the hexacelsian structure [3] was sensitive to small changes in the celsian/hexacelsian weight ratio. Hoover (in preparation) proposed a quantitative method by which the fraction of hexacelsian could be accurately determined (with an error of $\pm 5\%$) for each sample by measuring the intensity of the 8.2 μm absorption peak of the hexacelsian. This method was used in the present study for the quantitative investigation. A best-fit curve of the fraction of hexacelsian as a function of the heat-treatment has an even smaller error over most of the range. The transformation of the powder hexacelsian and the powder mixture of 95% hexacelsian and 5% celsian during the first hour of reaction is too rapid to enable accurate measurements of the results, with the method employed in the present experiment. A more carefully designed experiment that would enable measurements at 1 min time intervals is likely to supply important information on the first stage (see below) of the phase transformation. Such information may also alter somewhat the extrapolation of the powder mixture curves at zero time (fig. 3), since this extrapolation is based on a short heat-treatment, of 3 h. The extrapolation of the hexacelsian powder curves at zero time (figs. 2 and 4) on the other hand, should not be significantly altered since it is based on results obtained during 8 h of heat-treatment. However, the limited scattering of the results about the respective lines in fig. 4, introduces an estimated error of $\pm 20\%$ into the activation energy figure obtained.

3. Results

3.1. Heat-Treatment of $\frac{1}{4}$ in. Size Crystals

Hexacelsian grains of $\frac{1}{4}$ in. size were heated at various temperatures for long times (up to three months). Several types of furnaces used included furnaces employing Globar SiC heating elements, nichrome-wound furnaces, and an alumina tube furnace with platinum-rhodium winding. During the heat-treatments temperature was recorded for the Globar and Super-Kanthal furnaces (see below), and was repeatedly checked for the other two. The results were highly inconsistent when heat-treatments were carried out in different furnaces. For instance, one heat-treatment at 950° C in a furnace employing Globar heating elements showed a progressive transformation of hexacelsian to celsian. Scattering of results was, however, considerable (fig. 1). On the other hand, a heat-treatment at still higher temperature, 1000° C, in a nichrome-wound furnace for 56 days showed no significant phase transformation (fig. 1), whereas heating the hexacelsian crystals at 1100° C in a tube furnace, produced a linear phase transformation from 21 to 63 days of heating. An induction period of three weeks apparently had taken place before the continuous transformation began (fig. 1).

3.2. Heat-Treatment of Hexacelsian Powder

Hexacelsian powder was heat-treated at various temperatures (in a furnace heated by Super-Kanthal heating elements). Results showed a

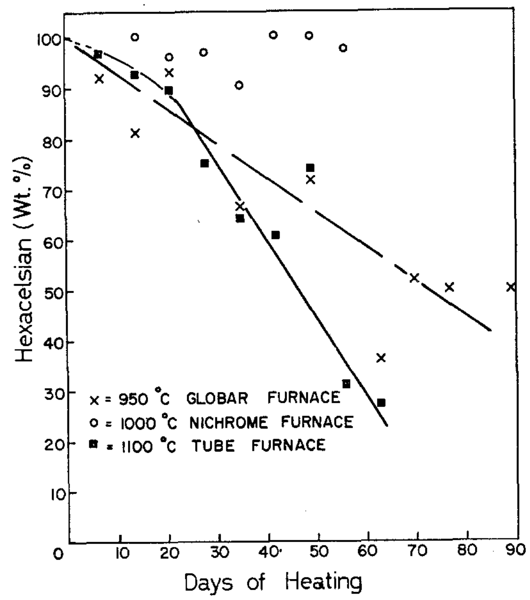

Figure 1 Hexacelsian–celsian phase transformation. The starting materials are hexacelsian crystals of $\frac{1}{4}$ in. size.

rapid transformation and a clear trend of change in the rate of phase transformation with temperature (fig. 2). There is a wide gap between 1050 and 1100° C. The curve produced at 1050° C shows a considerably lower rate of transformation than at higher temperatures. At higher temperatures (from 1100 to 1250° C), the curves have similar shapes with a gradual increase of transformation rate with temperature. At 1300° C, after about 40% of the reaction, the rate of transformation slows down, more than at lower temperatures, and the curve for the 1300° C treatment crosses curves for lower temperature treatments. Apart from the curve of 1050° C, the other curves cross the ordinate (at zero time) at various concentrations of hexacelsian. This indicates that prior to the transformations described by the various curves, an initial transformation occurs almost instantaneously. As may be expected, the extent of the initial transformation is enlarged with the temperature increase. It is noticeable that the scattering of experimental results is very low at the early part of the reaction and increases somewhat towards the end.

3.3. Heat-Treatments of Powder Mixtures of 95% Hexacelsian and 5% Celsian

The phase transformation in the powder mixture was generally more rapid than in the hexagonal powder (figs. 3 and 2, respectively). At 1000° C owing to kinetic reasons the transformation is slow. An induction period of several hours is observed before the transformation really starts. At 1100° C the transformation is already very rapid (the fastest transformation observed in this study). At 1100° C and higher temperatures, the characteristic feature is curve-crossing. With the temperature increase the transformation rate is faster at the beginning and slower at a late stage of the reaction.

The curves for the 1100 and 1200° C treatments cut the ordinate at 95% hexacelsian, whereas the curves for the 1300 and 1400° C treatments cut it at lower concentrations of hexacelsian.

4. Discussion

4.1. Nucleation Crystal Growth and Phase Transformation

The rate of phase transformation is a function of two factors – the rate of nucleation of the new phase and the rate of crystal growth of the nuclei.

There are two types of nucleation. One is homogeneous nucleation, which is determined by statistical fluctuation in a crystal that has a homogeneous composition and structure. The nuclei may be formed in any part of the crystal. (Such nucleation rarely occurs because heterogeneities in composition and structure are invariably present so that homogeneous nucleation is unlikely.) The other is heterogeneous nucleation, which occurs at contacts of surfaces due to crystal imperfections, impurities, twinning and other discontinuities. Such contacts reduce the surface energy of the new nuclei and stabilise them. Most, or perhaps all, transformations are initiated by heterogeneous nucleation.

Since the number of nucleus sites at a surface of a large crystal is relatively small, the rate of nucleation is low, erratic and largely dependent on external effects. The inconsistent results obtained for the heat-treatment of $\frac{1}{4}$ in. crystals reported above must have been related to some contamination present in the furnaces (either due to evaporation of material from the furnace walls or from the heating elements, or from chemicals that had been previously used in these furnaces). This contamination had a dominant effect on the nucleation and rate of phase transformation.

The number of nucleus sites is increased very considerably when the crystals are ground into powder, owing to the increase of lattice defects

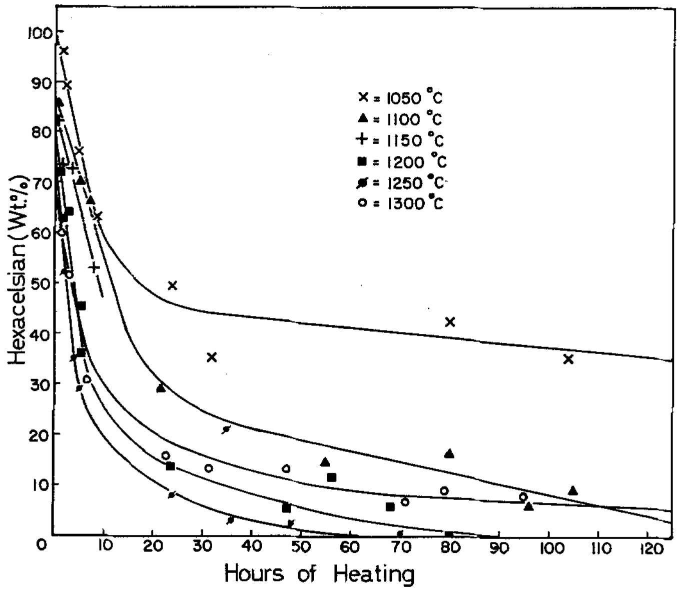

Figure 2 Hexacelsian–celsian phase transformation. The starting material is – 200 mesh hexacelsian powder.

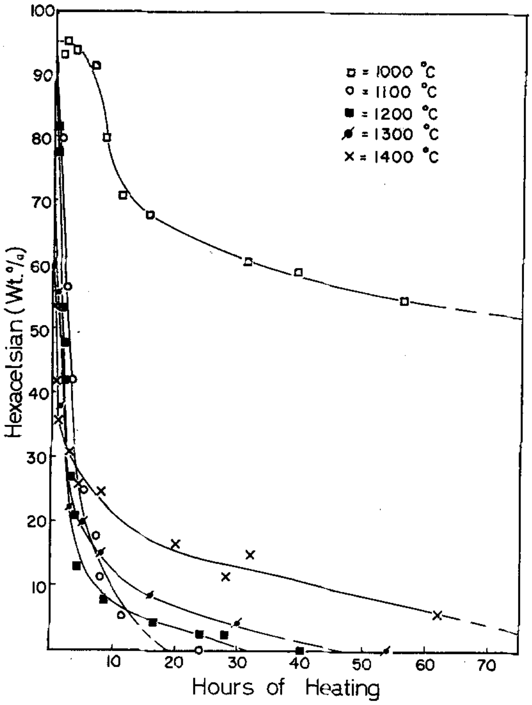

Figure 3 Hexacelsian–celsian phase transformation. The starting material is – 200 mesh powder of a 95% hexacelsian and 5% celsian mixture.

caused by the physical abrasion, more interface contacts, and possibly some contamination as well. There is an increase in the rate of heterogeneous nucleation, and its dependence on temperature becomes more consistent.

Fig. 3 indicates that in the powder mixture of 95% hexacelsian and 5% celsian, heterogeneous nucleation was more effective by providing better conditions for nucleus stabilization at the fine grain contacts. Phase transformation became faster than in the 100% hexagonal powder, and scattering of experimental results was lower.

Fig. 2 seems to indicate that there are three stages of the phase transformation: (a) at the beginning, nucleation sites are in abundance and the transformation is very rapid. It is solely controlled by the rate of crystal growth (note the curve-crossing of the ordinate). (b) The second stage of the reaction can be described by a straight line. At this stage the concentration of nucleation sites is lower than in the first stage, and embryos consumed by the transformation are replaced by new ones which are generated. This stage is controlled by the rates of nucleation and crystal growth. Since the reaction is still in an early stage, nucleation is fairly rapid, and so is phase transformation. (c) At the third stage the nuclei are used up or enveloped by the growing crystals. The rate of nucleation, which is the controlling factor, is low, and phase transformation is slow.

The rates of nucleation and crystal growth are dependent on the undercooling temperature.

Undercooling is defined as the difference in temperature between the hexacelsian–celsian transformation point and the measured temperature. The rate of nucleation is at a maximum at a greater degree of undercooling than that in which the maximum of the rate of crystal growth is obtained. This explains why at 1300° C there is a curve-crossing in fig. 2 and why the curve-crossing is a characteristic feature in fig. 3. At the higher temperature the initial transformation rate is high because many heterogeneities are present, but, the rate slows down because the rate of production of further nuclei is low. At lower temperatures the growth rate is lower so that the initial rate of transformation is lower. At this temperature however, further nuclei are created at a higher rate than at the higher temperature with the result that the observed transformation rate does not fall off so rapidly with time.

In the three starting materials investigated in the present study, the mechanisms of nucleation and crystal growth were different, as can be seen in figs. 1-3. Among the different variables, grain size was the most important, as had been observed before [5].

Fig. 3 indicates that in the powder mixture of 95% hexacelsian and 5% celsian, phase transformation became faster than in the 100% hexacelsian powder (fig. 2), and scattering of experimental results was lower. Also, in the powder mixture the maximum rate of transformation occurred at a lower temperature (1100° C) than in the hexacelsian powder (1250° C). These differences are attributed to different grain boundaries and other structural singularities which are present in the two powders, which contribute to dissimilarities in the rates of nucleation.

The sluggish hexacelsian–celsian transformation reported by Sorrell [6] and others seems to suggest that this transformation is analogous to other sluggish transformations in feldspars, namely Al/Si ordering. Accordingly, celsian would have an ordered structure [7] and the high temperature modification hexacelsian would be a disordered crystal.

A qualitative study of the present results indicates, on the other hand, that the sluggishness of reaction observed in large grains is mainly due to lack of nucleation (with the increase of grain size, diffusion rate also has an important effect on the phase transformation). When adequate nucleation is supplied, the transformation becomes very rapid, suggesting that the transformation does not involve diffusion that requires an opening of Si-O and Al-O bonds; but, as Ito observed [8], the hexacelsian and celsian have such a close structural relationship that one may easily be derived from the other. In other words, relatively minor re-arrangement of the tetrahedra, which involves some displacement of the barium cations, may be sufficient.

4.2. Activation Energy

The above suggestion is supported by quantitative data. It is assumed that at the first stage of the transformation from the pure powder (fig. 4) the availability of nucleation at the various temperatures is the same, and the transformation is solely controlled by the rate of crystal growth. The rate is temperature-dependent, and the extent of transformation at the first stage (as shown by the various intercepts on the ordinate) may be expressed according to an Arrhenius equation as follows:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

where k is the rate of crystal growth, T is the absolute temperature, E is the activation energy, and R is the gas constant.

Integrating, the above equation becomes

$$\ln k = -\frac{E}{RT} + \ln A\,,$$

where $\ln A$ is the constant of integration. It follows that a plot of the logarithm of k against the reciprocal of the absolute temperature should

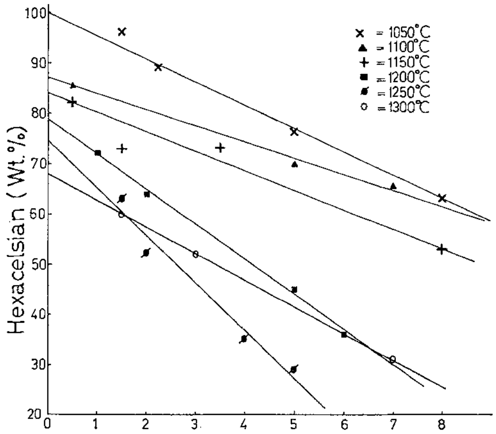

Figure 4 An expanded scale of a part of fig. 2. Hexacelsian–celsian phase transformation.

be a straight line, the slope of which would give the activation energy of the reaction.

The intercepts on the ordinate of fig. 2 for 1100, 1150, 1200, 1250, and 1300° C were 12.9, 16.0, 21.2, 25.5, and 32.0. respectively. The plot in fig. 5 produces a straight line with a slope of 4.4×10^3. The activation energy is, therefore,

$4.4 \times 10^3 \times R \times 2.303 = 20.1$ kcal mole^{-1}. This activation energy is much lower than 60 kcal mole^{-1}, which is the energy required for the ordering of albite [9] and involves Si-O and Al-O bond opening.

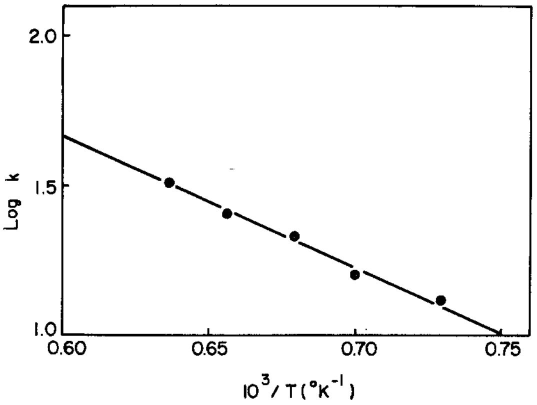

Figure 5 Arrhenius plot of log *k* (rate of crystal growth) against T^{-1}.

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