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Transformation of tridymite to cristobalite below 1470° C in silica refractories

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Because silica refractory has good volume stability and creep properties at high temperature, it has been used in several furnaces. However, silica has three polymorphs (quartz, tridymite and cristobalite) and each polymorph has an α–β type transformation. It is known that cristobalite is the stable phase of silica between 1470° C and the melting point of silica refractories. However, sometimes cristobalite was found in silica refractories used in the stable temperature region of tridymite. Therefore, the cause and mechanism of this tridymite-to-cristobalite transformation below 1470° C was studied. Although the transformation temperature of tridymite to cristobalite was also 1470° C in the sample used in this research, it decreased on addition of Al_2O_3. The apparent activation energy of the tridymite-to-cristobalite transformation was found to be 787 kJ mol^{-1} above 1470° C and 176 kJ mol^{-1} below 1470° C with Al_2O_3 by measuring the transformation rate. It was also observed using EPMA that the tridymite included CaO; however, CaO and Al_2O_3 were located on the outside of the cristobalite which was produced below 1470° C. Therefore, it is supposed that the liquid phase was produced by the penetration of Al_2O_3, and impurities in the tridymite crystal diffused outside and then silica was precipitated as cristobalite.

1. Introduction

Silica refractory has good volume stability and creep properties at high temperature, and therefore has been used in electric furnaces, hot blast stoves, coke ovens and glass melting furnaces. However, silica has three polymorphs (quartz, tridymite and cristobalite) and each polymorph has an α–β type transformation (quartz: 573° C, tridymite: 117° C, 163° C, cristobalite: 200 to 275° C) [1]. It is generally known that quartz is stable up to 867° C, that tridymite is the stable polymorph from 867 to 1470° C, and that cristobalite is the stable phase of silica between 1470° C and the melting point in silica refractories [2]. The transformation of quartz to tridymite or cristobalite in these polymorphs has been studied for the manufacture of silica refractories; however, the transformation of tridymite to cristobalite has been little researched.

Cristobalite is often found to appear in the surface layer of silica refractories used in hot blast stoves [3]. In the present research, it was ascertained that this transformation was caused by impurities and cristobalite also appeared at a temperature in the stable region of tridymite (below 1470° C). The aim of this paper was to determine the cause and mechanism of the tridymite-to-cristobalite transformation below 1470° C by investigating the effect of additives, measuring the transformation rate and observing the microstructure in silica refractories.

2. Experimental procedure

Silica refractory which had been used below 1470° C for about 4 years in a hot blast stove was examined for chemical composition: the mineral composition by X-ray diffraction and the microstructure by microscopy and electron probe microanalysis (EPMA).

Silica refractory powder, crushed to < 147 μm, was heat-treated in order to investigate the transformation behaviour. The sample on a platinum plate was heated in the electric furnace using an SiC heater at each temperature. The heated sample was identified by X-ray diffraction and the ratio of tridymite to cristobalite was determined from the calibration curve (Fig. 1) which was obtained by measuring the peak height of tridymite (d = 0.4328 nm) [4] and cristobalite (d = 0.405 nm) [5] of samples mixed with tridymite and cristobalite in each ratio by X-ray diffraction.

3. Results and discussion

The results of chemical and mineral composition analysis of the original and used silica refractories are given in Table I. Tridymite and cristobalite, except

TABLE I Chemical and mineral composition of silica refractories (wt %)

	Original	Surface layer	Inner layer
SiO_2	95.6	93.8	94.9
Al_2O_3	0.8	1.6	1.0
Fe_2O_3	0.9	0.7	0.8
K_2O	0.2	0.3	0.1
CaO	1.6	2.2	2.0
Tridymite	72	0	100
Cristobalite	28	100	0

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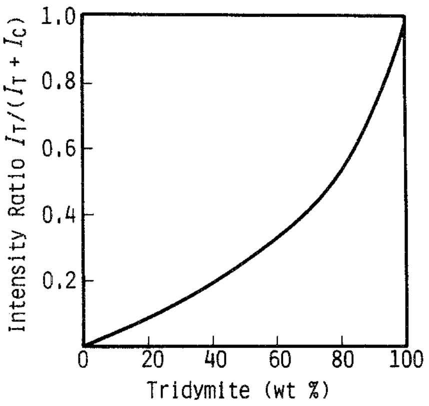

Figure 1 Calibration curve of tridymite by X-ray diffraction. I_T = intensity of tridymite, I_c = intensity of cristobalite.

quartz, were included in the original silica refractory. However, it was observed that the surface layer (10 to 15 mm thick) was white and the inner layer was brown on the cut surface of the used silica refractory. The mineral component was cristobalite in the surface layer and tridymite in the inner layer. The microstructure of the boundary area of each layer seen by polarization microscopy is shown in Fig. 2. Wedge-shaped crystals (tridymite) are seen in the inner layer and scale-shaped crystals (cristobalite) in the surface layer. Therefore, it was confirmed that cristobalite was present in silica refractory below 1470° C, which was the stable region of tridymite.

As it is thought that the surface layer is influenced by the penetration of impurities, the effect of impurities on the transformation of tridymite to cristobalite below 1470° C was investigated. Each original silica refractory (shown in Table I) together with 1 wt % Na_2O, K_2O, BeO, MgO, CaO, FeO, Al_2O_3, Fe_2O_3, ZrO_2 was heat treated at 1400° C for 72 h and the degree of transformation between tridymite and cristobalite was analysed by X-ray diffraction (target: cobalt). As seen in Fig. 3, only the sample containing Al_2O_3 transformed to cristobalite; the other samples were induced to transform to tridymite compared to the sample with no impurity added. As a result of this experiment, it is concluded that the transformation of tridymite to cristobalite below 1470° C is caused by Al_2O_3 and there is no relationship between this transformation and the ionic radius or atomic charge number of additives.

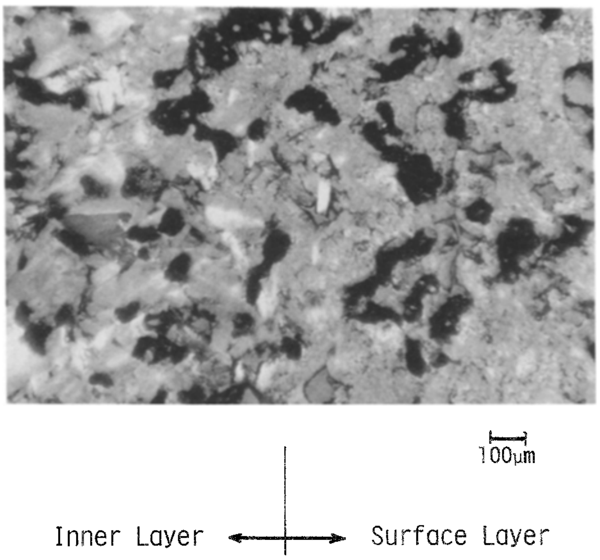

Figure 2 Microstructure of the boundary area in used silica refractories by polarization microscopy.

The effect of Al_2O_3 on the transformation of silica was investigated quantitatively. Unused samples which were mixed with different amounts of Al_2O_3 chemical powder were heat-treated at each temperature for 72 h. X-ray diffraction was used to determine if the heat-treated samples had transformed to tridymite or cristobalite. The results are shown in Fig. 4. In the SiO_2–Al_2O_3 system phase diagram given by Muan and Osborn [6], the tridymite–cristobalite transformation temperature is constant for a SiO_2-rich composition. Silica refractory also includes CaO, so that the transformation temperature of tridymite to cristobalite is also 1470° C in the SiO_2–Al_2O_3–CaO system phase diagram [7]. However, although the transformation temperature between tridymite and cristobalite in the original silica refractory is 1470° C, it gradually decreases with increasing Al_2O_3 addition and becomes constant over 4 wt % Al_2O_3. Therefore, it is thought that the appearance of cristobalite causes the cristobalite region below 1470° C in Fig. 4.

The transformation of tridymite to cristobalite above 1470° C is a fundamental phenomenon; therefore, it is supposed that the transformation mechanism with Al_2O_3 below 1470° C is different from that above 1470° C. Therefore the transformation rate of tridymite to cristobalite was measured. Tridymite

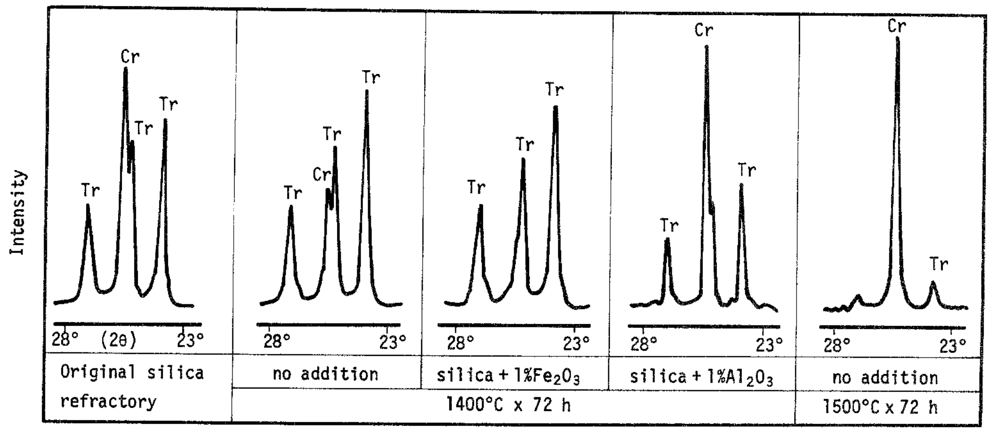

Figure 3 X-ray diffraction patterns of heat-treated samples. Tr = tridymite, Cr = cristobalite.

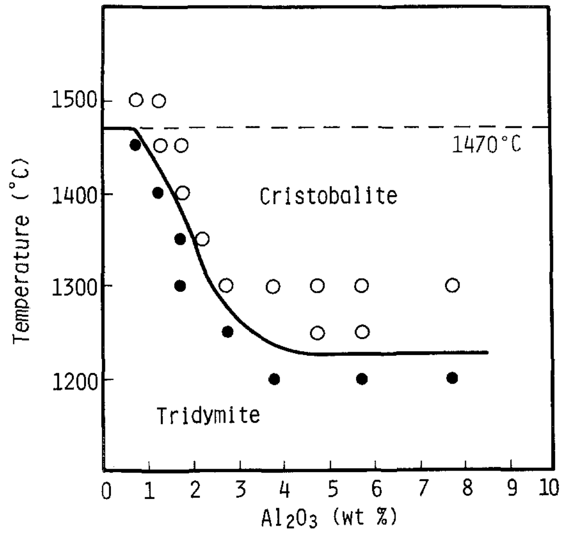

Figure 4 Effect of Al_2O_3 on the transformation temperature of tridymite to cristobalite in silica refractory. (○) transformation to cristobalite, (●) transformation to tridymite.

powders with 4 wt % Al_2O_3 were heat-treated at 1300, 1350 and 1400° C. In addition, tridymite powders with no additive were heat-treated at 1500, 1550 and 1600° C. The results are shown in Fig. 5. The transformation proceeded rapidly at first and then it gradually slowed. The higher the heating temperature, the faster the transformation proceeded.

The transformation rate of silica is described by the following equation as a popular relationship for the reaction rate

$$\frac{dC}{dt} = A\,e^{-Q/RT} \tag{1}$$

$$\ln\frac{dC}{dt} = \ln A - \frac{Q}{RT} \tag{2}$$

where C is concentration, t the time, A a constant, Q the activation energy, R the gas constant and T the absolute temperature. The transformation rate of tridymite to cristobalite given by Arrhenius plots is shown in Fig. 6. The rate was described by the reciprocal of the time at which 50 wt % cristobalite was produced. The apparent activation energy above 1470° C is found to be 787 kJ mol^{-1} and that below 1470° C is 176 kJ mol^{-1} by calculation from the gradient of lines in Fig. 6. This indicates that the transformation mechanism of tridymite to cristobalite above 1470 and below 1470° C are obviously different. It is generally stated that the transformation between tridymite, cristobalite and quartz is of a reconstructive type. The destructive energy of the Si–O bond is 465 to 1268 kJ mol^{-1} [8] and it is related to the apparent activation energy of the transformation of tridymite to cristobalite above 1470° C. On the other hand, as the apparent activation energy of the transformation of tridymite to cristobalite below 1470° C is too low, it is thought that it is a different transformation mechanism from that above 1470° C.

It is known that Al_2O_3 produces liquid phase easily in SiO_2. Because CaO is added as a stabilizer when the silica refractory is manufactured, the eutectic point in the phase diagram of the CaO–Al_2O_3–SiO_2 system [7] is low (1170° C) and it becomes easier to produce the liquid phase. It is seen that an amorphous phase (transition phase) exists in the transformation process from quartz to cristobalite [9, 10]. Therefore, as the amorphous phase is seen by microscopy, it is considered that the liquid phase is present as the amorphous state.

These results suggest that it is necessary to determine the distribution of CaO and Al_2O_3 in silica refractory. Therefore, the tridymite layer and the cristobalite layer in used silica refractory below 1470° C were observed by EPMA. Specimens were polished and deposited with vaporized gold.

The results of EPMA analysis of the tridymite crystal are given in Fig. 7. Calcium as a stabilizer was detected in the tridymite crystal and aluminium as an impurity existed to a small extent with the calcium. The results for cristobalite crystal are shown in Fig. 8. Calcium and aluminium were detected on the outside of the cristobalite crystal. Furthermore, pure silicon without calcium was detected in the round-shaped cristobalite crystal by spot analysis. Thus it is indicated that calcium is transferred to the outside of the crystal.

The phase transformation mechanism from tridymite to cristobalite by the penetration of Al_2O_3 below 1470° C was also considered. At first, the tridymite crystal includes Ca^{2+} because CaO is added in the manufacturing stage of silica refractory. When Al_2O_3 penetrates around the SiO_2 crystal, the liquid phase is produced and changes to the amorphous state. Ca^{2+} in SiO_2 crystal is transferred to produce the CaO–Al_2O_3 or the CaO–Al_2O_3–SiO_2 amorphous phase and the saturated SiO_2 precipitates in the pure state crystal, which is cristobalite. Studies on the crystal state of pure SiO_2 have been reported. Silica has three polymorphs (quartz, tridymite and cristobalite) in the silica refractory which includes impurities. On the

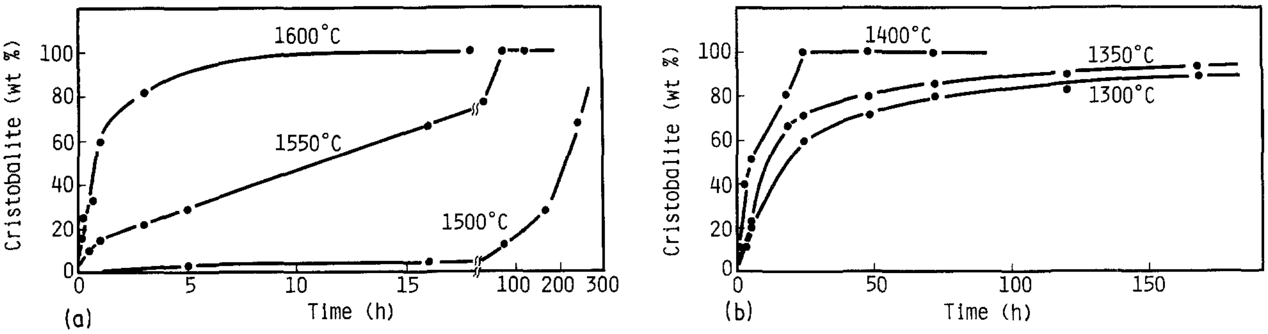

Figure 5 Transformation curves from tridymite to cristobalite; (a) no addition; (b) addition of 4 wt % Al_2O_3.

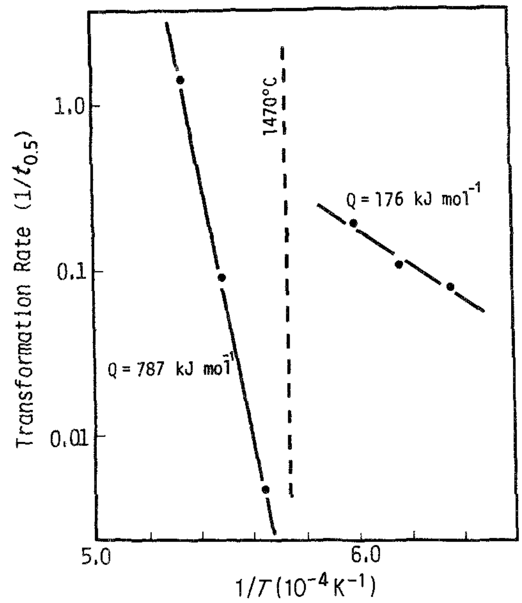

Figure 6 Arrhenius plots of the transformation of tridymite to crystobalite.

other hand, the tridymite phase is not stable in pure SiO_2 as shown in Fig. 9 [11]. Therefore, it is thought that impurity in the tridymite crystal diffuses out of the crystal and SiO_2 becomes pure and precipitates as cristobalite. The transformation on removal of a component has been reported by Flörke [12]. In this case, when the tridymite sample was charged by the voltage, impurities in the sample were transferred to the cathode side and cristobalite appeared on the anode side. These results show that the appearance of cristobalite is influenced by impurity.

From transformation temperature curve in Fig. 3 for the silica refractory with 1.6 wt % CaO, it was concluded that the transformation temperature approached 1470° C with increasing CaO content in the silica refractory as shown in Fig. 10. These results indicate that after the reaction between CaO and Al_2O_3, excess CaO remained in the silica crystal and the stable area of tridymite below 1470° C was thus extended.

4. Conclusions

The appearance of cristobalite even in the stable temperature region of tridymite, below 1470° C, was studied and the following results were obtained.

1. The appearance of cristobalite in the stable temperature region of tridymite is caused by penetration of Al_2O_3. This transformation temperature decreases from 1470° C with increasing addition of Al_2O_3.
2. The apparent activation energy of the transformation of tridymite to cristobalite was measured by the transformation rate. The energy above 1470° C is 787 kJ mol^{-1}, which relates to the binding energy of SiO_2, and that below 1470° C is 176 kJ mol^{-1}. These results show that each transformation occurs by a different mechanism.
3. It was observed by EPMA that the tridymite included CaO; however, CaO and Al_2O_3 were located in the outside of cristobalite which was produced below 1470° C.
4. It is supposed in the transformation of tridymite to cristobalite below 1470° C that the liquid phase was produced by the penetration of Al_2O_3 and then CaO in the tridymite crystal diffused out of the crystal, therefore silica became pure and precipitated as crystobalite.

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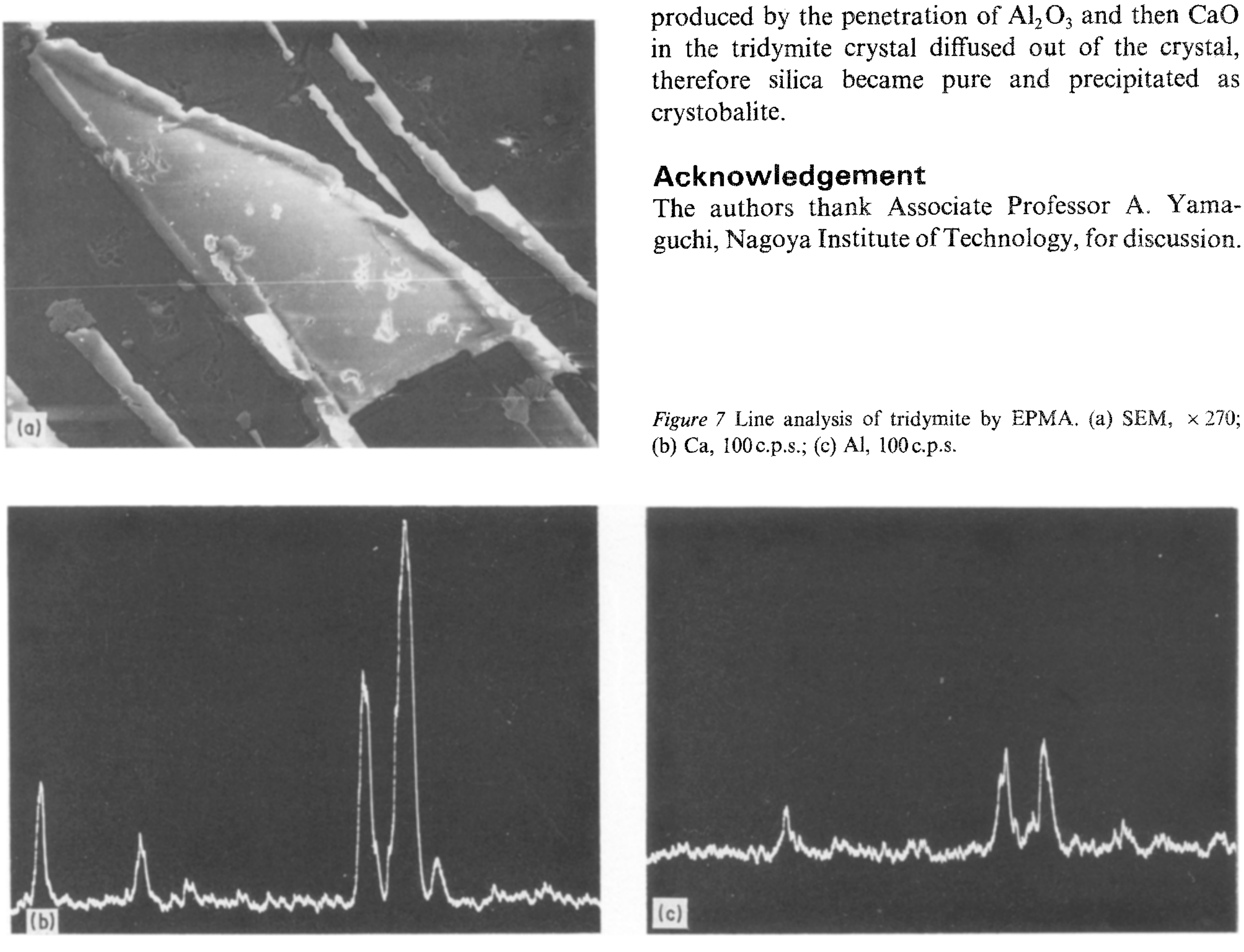

Figure 7 Line analysis of tridymite by EPMA. (a) SEM, × 270; (b) Ca, 100 c.p.s.; (c) Al, 100 c.p.s.

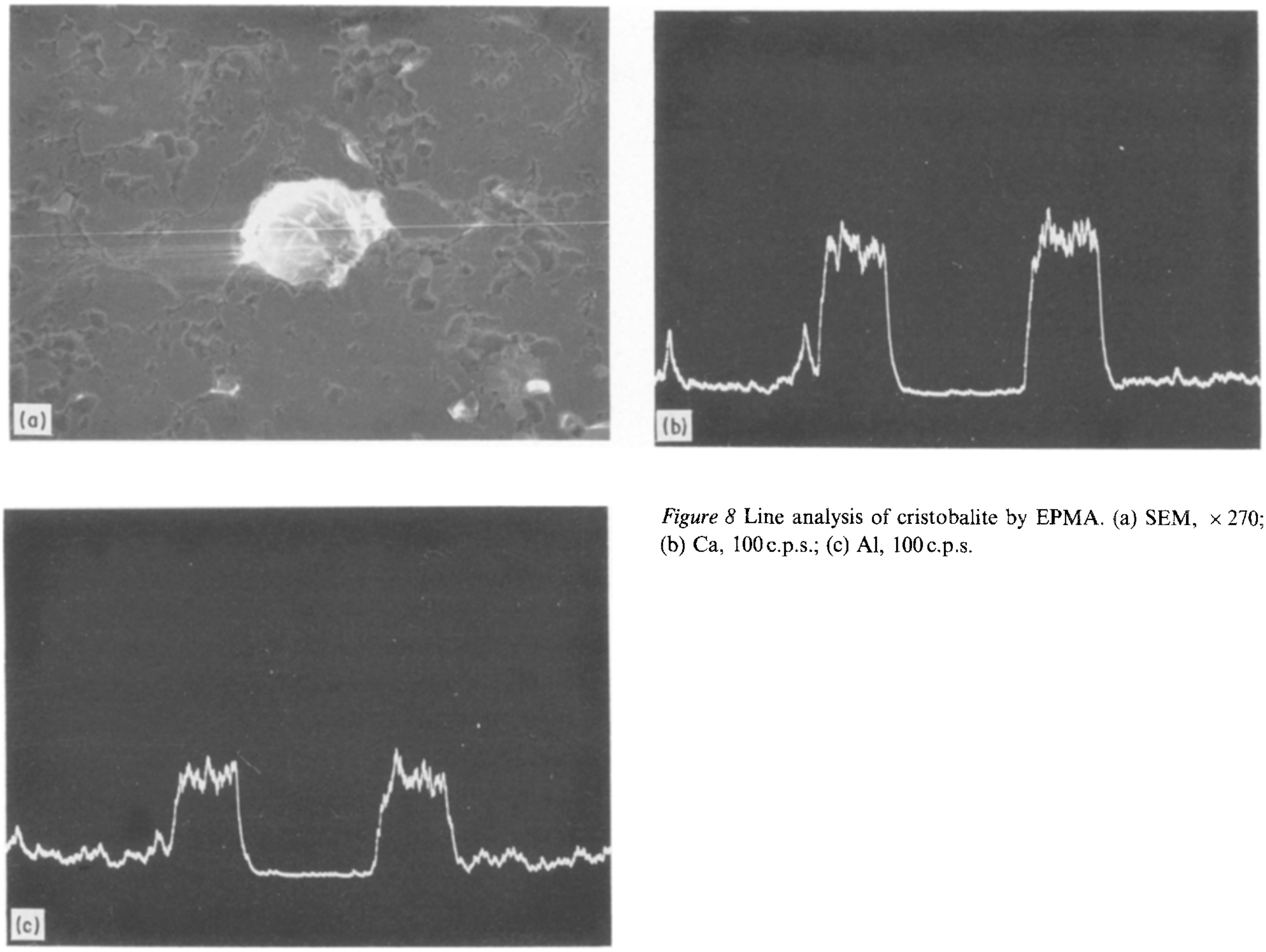

Figure 8 Line analysis of cristobalite by EPMA. (a) SEM, × 270; (b) Ca, 100 c.p.s.; (c) Al, 100 c.p.s.

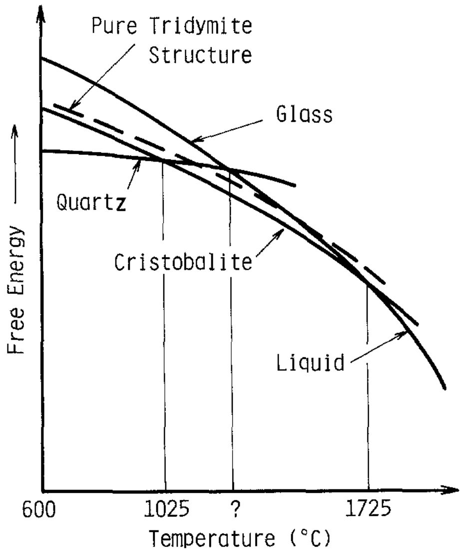

Figure 9 Free energy of modification of silica [12].

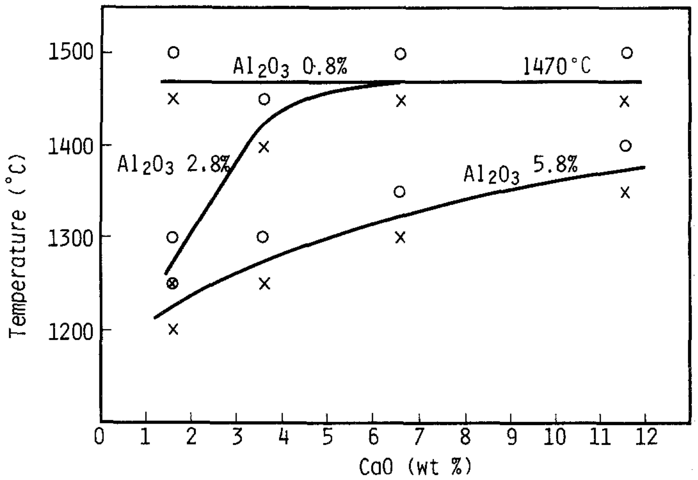

Figure 10 Effect of CaO on the transformation temperature of tridymite to cristobalite in silica refractory. (○) Transformation to cristobalite, (×) transformation to tridymite.

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