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Correlation between $MgSiO_3$ phases and mechanical durability of steatite ceramics

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Abstract

The steatite ceramics are mostly used in electrotechnics. Although distinguished by their mechanical and electrical properties they are unstable. The desirable, high temperature protoenstatite phase inverses into magnesium metasilicate low-temperature form—clinoenstatite, even upon standing. In this work the steatite polymorphism was studied in relation with steatite mechanical properties and microstructure. It was find out that the stabilization of protoenstatite in steatite body is achievable by the development of small crystals, yet it is still not resistant to action of water what put in question its potential application as dental material.

Keywords: Sintering; X-ray methods; Strength; $MgSiO_3$; Steatite

1. Introduction

The four polymorphic forms of $MgSiO_3$: enstatite, protoenstatite, clinoenstatite and high temperature clinoenstatite are distinguished at present.[1–5] The character of $MgSiO_3$ polymorphism is complicated and changes from one form to another depend on temperature, pressure, dopants, internal stresses in grains, grain sizes.[6,7]

Choudhury and Chaplot[8] found that orthoenstatite to protoenstatite transition is temperature driven while the orthoenstatite to clinoenstatite transition is pressure driven.

The kinetics of phase transition (by nucleation and growth process) describes the Avrami equation. It enables to evaluate the reaction rate constant at each temperature:

$$x = 1 - \exp\left\lfloor -(kt)^n \right\rfloor$$

where x is the volume fraction transformed after time t, k is the reaction rate constant, and n is the Avrami parameter which characterize the type of the rate controlling process.[9–11] Rearranging gives:

$$-\ln(1 - x) = (kt)^n.$$

Purified, grinded and calcinated at the appropriate temperature, talc, upon heating, through the several stages reactions, changes to magnesium metasilicate high temperature form, protoenstatite.

To get the steatite ceramics the mixture of talc, glass forming components and plasticizers is wet or dry mixing for homogenizing and sintered at 1380–1410 °C. During sintering the glassy phase grows soft, wetting and imbedding the few micrometer large grains of protoenstatite. Presently the two basic steatites are processed. They differ in glass phase which can be feldspar or barium one. The latter is more suitable for electrotechnics.[12] The steatite glass ceramics are distinguished by mechanical and electrical properties. The highly pressed talc has been used in electrotechnics for over 100 years. The most recent report issued[13] see the steatite potential application as dental material. However steatite is very susceptible for deterioration. The bloom of the bright powdering spots on steatite body is the first sign of its worsening in quality and humidity rapidly accelerates this process.[14]

Talc is a shell silicate structure with triclinic elementary cell. Upon heating, in dehydroxylated talc grains form micropores (500 Å large) which disappear as the temperature increase. This process is accompanied by production of free silica (quartz). Both, the micropores and the quartz grains

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are undesirable constituents of steatite. Another undesirable phenomenon taking place in steatite is that the high temperature protoenstatite phase inverses into magnesium metasilicate low-temperature form—clinoenstatite. The destructive effect of proto- to clinoenstatite inversion is caused by the 2.8% difference in volumes of their elementary cells.[1] The intrinsic stresses resulted from the volume changes lead to the loss of mechanical strength.[1,15]

Therefore the steatite improvement seems possible by either protoenstatite form stabilization to room temperature or by reinforcing the ceramics with glass matrix. In up to now studies problem is solved by doping steatite with aluminum oxide[15] or antimony oxide.[16] Others[1,17] reach the protoenstatite stabilization by substituting of magnesium ions by manganium ones.

In this work the steatite polymorphism was studied in relation with steatite mechanical properties and microstructure. For this purpose the changes of steatite bending strength with period of time of steatite conditioning at room temperature were determined simultaneously with the measurements of the amounts of protoenstatite and clinoenstatite crystallites in examined samples. The mechanism of magnesium silicate phase transformation with temperature was studied in relation with crystallite sizes.

Microstructure observations were performed to display the reasons of steatite ceramic deterioration.

2. Experiment

The starting material for these studies was Chinese talc. The details on its composition are given in Table 1.

The barium steatite samples for this study were prepared by wet milling of the mixture of 90 wt.% of talk and 10 wt.% of barium carbonate for 24 h in ball mill. After drying 10 wt.% of binder agent (water solution of paraffin oil and spent sulfite liquor) was added and the mixture was formed into samples by cold pressing at 100 MPa and sintered at 1380 °C.

The specimens for testing of mechanical properties were shaped in rods 80 mm long and 10 mm in diameter. Before testing they were seasoned in exsiccator. The three point bending test was performed, on a universal testing machine INSTRON.

The specimens for XRD measurements of $MgSiO_3$ polymorphism were 15 mm × 20 mm × 5 mm large.

For microstructure measurements the steatite samples were polished with chromium oxide and rinsed with waterless ethanol. The crystal phases were identified by X-ray diffractometer DRON 2, using Fe-filtered Co-radiation. The quantities of proto-and clinoenstatite were computed for selected (2 2 1) reflections. The interplanar distances d of proto- and clinoenstatite were 2.762 and 2.967 Å, respectively. The specimens for magnesium metasilicate polymorphism measurements were made of talc calcinated at 1460 °C for 1 h.

To set the point of protoenstatite to clinoenstatite inversion, clinoenstatite samples were heated in the XRD high temperature attachment up to 1060–1400 °C and cooled. In that manner clinoenstatite forms in $MgSiO_3$ by inversion (during cooling) of pre-existing protoenstatite.[3] If at the completion of a run no change of form was detected, the temperature was lowered and the specimen was held at the new temperature. After the run involving the crystalline form inversion the sample was cooled with furnace to room temperature, in order to determine the crystallite size (from Scherrer equation corrected for instrumental and spectral line broadening and $K\alpha_1\alpha_2$ doublet[19]).

Table 1
Composition of Chinese talc (wt.%)

SiO_2	MgO	Al_2O_3	$Fe_2O_3 + TiO_2$	CaO	$NaO + K_2O$	H_2O
58.65	33.55	0.47	0.40	0.047	0.05	5.0

3. Results

3.1. Polymorphism of magnesium metasilicate

The data on crystal phase occurrence in talc under the conditions of heat treatment were gathered within the temperature range of 1250–1450 °C. The scheme of magnesium silicate polymorphism based upon these data is presented in Fig. 1. As can be seen the process of protoenstatite crystallization starts at temperatures above 1250 °C and fully develops at 1420 °C. At 1460 °C protoenstatite formation is complete. Protoenstatite crystallites formed at 1460 °C (and higher temperatures) are unstable and they all inverse to clinoenstatite crystallites after cooling.

To get the point of protoenstatite to clinoenstatite inversion the talc sample was heated to 1450 °C and the XRD data were taken at elevated temperatures as sample was steeply cooled. As can be seen in Fig. 2 no protoenstatite →

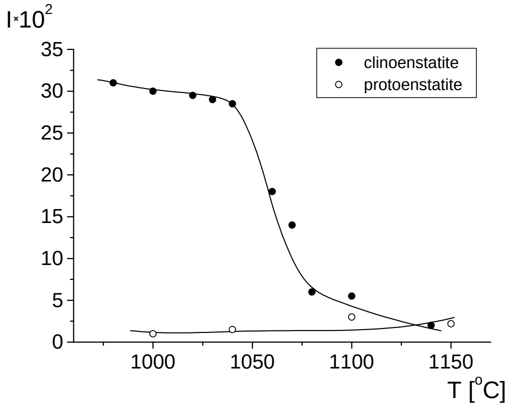

Fig. 1. Scheme of polymorphism of magnesium metasilicate in dependence on temperature of talc calcinations.

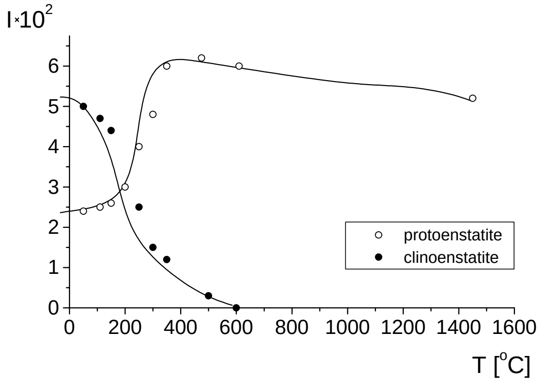

Fig. 2. Protoenstatite → clinoenstatite transition in precalcined and then cooled talc body.

clinoenstatite transition was detected until temperature of XRD run was lowered to 600 °C. In re-heated sample clinoenstatite → protoenstatite transformation takes place at 1060 °C (Fig. 3). In comparison to protoenstatite → clinoenstatite, the clinoenstatite → protoenstatite inversion occurs in the narrow range of temperatures. The increase of protoenstatite phase is not adequate to the decrease of clinoenstatite, what indicates diffusion controlled mechanism of transformation. Clinoenstatite crystal structure disintegrates due to the break of Mg–O bonds. Protoenstatite regeneration takes place at much higher temperatures.

To get the strict temperature of protoenstatite → clinoenstatite inversion the clinoenstatite was heated in XRD attachment up 1060 °C and the XRD data were taken at this and at temperatures further elevated up to 1400 °C. The specimen was held at the temperature of the particular run for 10 min and cooled. Then the sizes of clinoenstatite crystallites were measured. The results are shown in Fig. 4.

The smallest clinoenstatite crystallites reappeared during cooling of magnesium metasilicate sample heated to 1060 °C, i.e. to the temperature at which the inversion of preexisting clinoenstatite to protoenstatite nearly starts. Although this temperature is sufficient for decay of clinoenstatite crystals, it is too low for formation of protoenstatite ones. The clinoenstatite crystals reappeared at 850 °C and crystallite sizes were small.

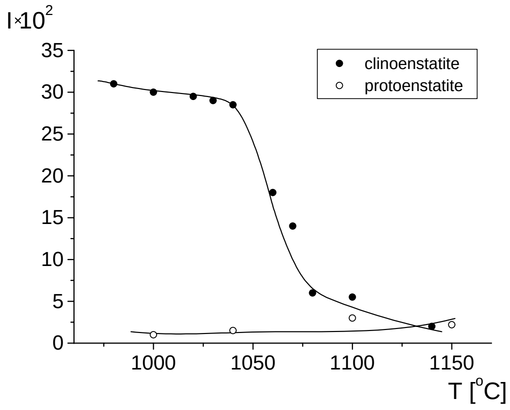

Fig. 3. Clinoenstatite → protoenstatite transition in precalcined, cooled and then reheated talc body.

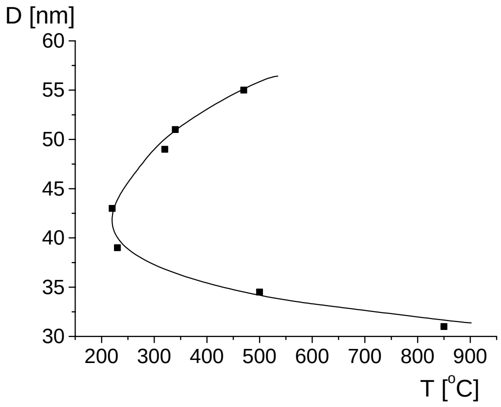

Fig. 4. Clinoenstatite crystallite sizes in dependence on temperature of protoenstatite → clinoenstatite inversion.

The small well crystallized protoenstatite grains appeared in sample heated to 1350 °C. The temperature of protoenstatite to clinoenstatite inversion was 250 °C and it is the lowest one. The clinoenstatite crystals for this temperature were 40 nm large. The further increase of heating temperature leads to the increase of the inversion temperature.

3.2. Kinetics of phase transition in barium steatite ceramics

Under the name of barium steatite is understood the enstatite material in which the glass forming component is barium silicate. The barium steatite samples compounding and preparation is described in clause 2. The samples behavior in normal conditions ($t = 23\,^{\circ}\mathrm{C}$, $P = 0.1\,\mathrm{MPa}$) was monitored at up to 800 h of test duration.

To get the kinetics of phase transition firstly the reaction rate constant at each temperature (Table 2) was computed from the equation:

$$x = 1 - \exp\left\lfloor -(kt)^n \right\rfloor$$

Table 2
Values of reaction rate constant $k = 1/\tau$ (1/h), the Avrami parameter n and the activation energy E for clinoenstatite and protoenstatite

k at particular T			
T (°C)	k (1/h)	T (°C)	k (1/h)
Clinoenstatite ($n = 1.1$)		Protoenstatite ($n = 0.7$)	
1400	0.0047	1300	0.0242
1420	0.0581	1320	0.0492
1440	0.1519	1340	0.1562
1450	1.3303	1360	0.4969
		1390	0.9078
		1420	2.6768
		1450	2.6768
		1460	1.2136
$E = 25 \pm 4$ kJ/mol		$E = 39 \pm 2$ kJ/mol	

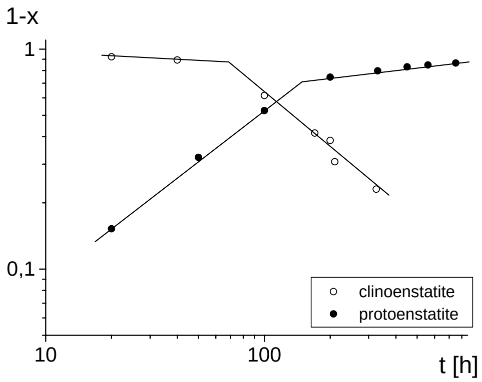

Fig. 5. The $(1-x)$ results obtained at various temperatures and plotted vs. time in a double logarithmic scale.

Then the curves of $(1-x)$ values (as $-\ln(1-x) = (kt)^n$) versus the time were plotted on a double logarithmic scale. The results are shown in Fig. 5. The Avrami parameter for clinoenstatite was found to be 1.1, what suggests one-dimensional growth with the interface rather than a diffusion-controlled transformation mechanism.[12–14] From the temperature dependence of k, the apparent activation energy for this reaction was evaluated to be 25 ± 4 kJ/mol.[11] From the temperature dependence of k for protoenstatite, the apparent activation energy for this reaction was evaluated to be 39 ± 2 kJ/mol (for increasing part) and 12 ± 1 kJ/mol (for decreasing part).

These values are consistent with a mechanism involving the transformation. Concluding, from the foregoing observations and literature data,[1,2,6,15–18] the following scheme of magnesium silicate polymorphism is proposed (Fig. 6):

The talc transformation commences at 850 °C (Fig. 6a, area shaded with lines) with formation of small, stable protoenstatite grains.

The further increase of heating temperature brings about the better crystallization and the growth of crystal sizes. During cooling the large protoenstatite crystallites inverse to clinoenstatite ones (broken line in Fig. 6a).

Prolonged, high-temperature heating causes the further growth of sizes of protoenstatite crystallites. All the large protoenstatite crystals inverse to clinoenstatite ones during cooling.

Clinoenstatite crystallites formed during cooling, when reheated, broke at 1060 °C and crystallizes in protoenstatite form at higher heating temperatures (Fig. 6b) and the temperature of proto- to clinoenstatite inversion depends on temperature of heating.

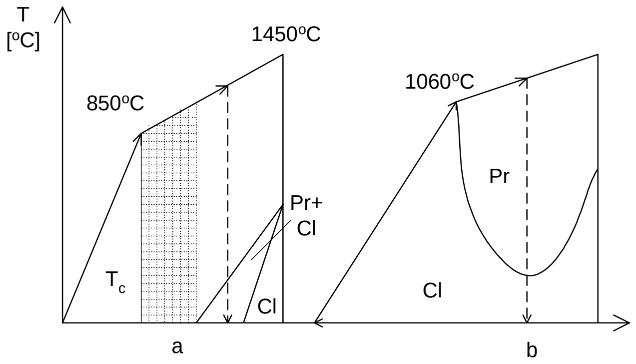

Fig. 6. Diagram of polymorphism of magnesium metasilicate derived from talc: Tc-talc, Pr-protoenstatite, Cl-clinoenstatite.

This model of magnesium metasilicate polymorphism is supportive to Foster's[3] and in contrast with Lindeman[20] suggestion that clinoenstatite phase is stable in the whole range of temperatures. As it was resolved, the clinoenstatite can form only by inversion, during cooling, from pre-existing protoenstatite.

3.3. *The protoenstatite → clinoenstatite transition effect upon mechanical strength of barium steatite*

The barium steatite for study of mechanical endurance were prepared, conditioned and monitored as above. The contents of protoenstatite and clinoenstatite crystallites in the samples and the samples flexural strength measured at predetermined time intervals are combined in one presentation in Fig. 7.

As can be seen after 250 h of conditioning the bending strength of specimens was twice less than at the beginning. Then the drop of steatite mechanical strength was less steeply, as the proto- to clinoenstatite inversion proceeded more sluggishly after that time.

In Fig. 8 the microstructure of the polished sample of steatite, after 700 h of aging in normal conditions, is presented. In steatite body, as natural process, developed the cracks and discontinuity of the glassy intergranular phase (due to fragmentation of large grains of protoenstatite). The glassy bonds remain stable only in case of small protoenstatite grains.[21]

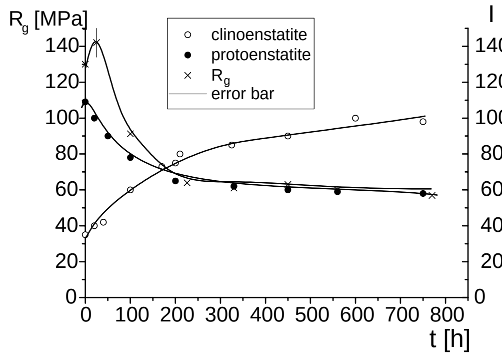

Fig. 7. Changes of both bending strength and protoenstatite and clinoenstatite contents with the period of time of steatite conditioning (at room temperature).

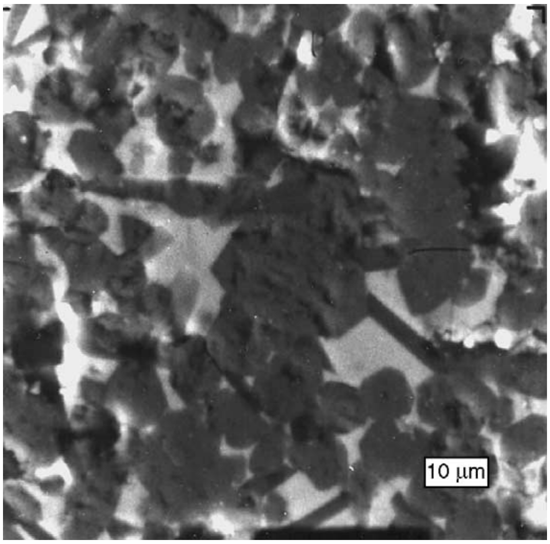

Fig. 8. Microstructure of steatite after 700 h of natural aging, visible cracks and discontinuity of the glassy intergranular phase.

In the frame of this experiment the samples of barium steatite ceramics with the small protoenstatite grains (regarded as relatively stable) were subjected to the action of boiling water. In that conditions they appeared to had been pulverized in 30 min.

4. Conclusions

Crystallites developed in steatite ceramics during sintering are the protoenstatite. The size of crystallites depends on temperature. During cooling protoenstatite crystallites invert to clinoenstatite ones, what is the cause of steatite ceramics deterioration and the loss on steatite mechanical endurance is strictly correlated with the degree of proto- to clinoenstatite inversion.

There is much greater tendency for large protoenstatite to invert to clinoenstatite than for small ones. The temperature 1350 °C was find optimal for formation small, well crystallized protoenstatite crystals. This is also the temperature for which the temperature of proto- to clino- inversion is the lowest and it is 250 °C.

The process of steatite deterioration considerably accelerates in the presence of water what put in doubt its application as dental material (considered as promising in the most resent report on the issue).

The stabilization of protoenstatite in steatite body is achievable by both the development of small crystals of protoenstatite and by incorporating an interstitial glassy phase into body of ceramic. Anyway the system is still metastable.

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