SCIENCE FOR CERAMIC PRODUCTION

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SINTERING OF CALCIUM CARBONATE IN THE PRESENCE OF LITHIUM CARBONATE ADDITIVE

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It is shown that calcium carbonate can be sintered in the liquid phase at a low temperature (620 – 650°C). The sintering temperature is decreased by introducing lithium carbonate. It is established that the degree of crushing of the calcium carbonate for sintering is an important factor.

Calcium carbonate can be sintered by several methods. Articles are manufactured from $CaCO_3$ by the method of hot isostatic molding with creation of the requisite atmosphere and by liquid-phase sintering of calcium carbonate in the presence of additives, for example, Fe_2O_3 at a temperature of 1300 – 1600°C or Li_2CO_3 at a temperature of 620°C [1 – 3].

In our experiments we studied the possibility of preparing sintered calcium carbonate by recrystallization in liquid-phase sintering with an additive of lithium carbonate at a very low temperature. The use of the additive was caused by the necessity of liquid-phase sintering, where in order to melt the calcite congruently we should have a CO_2 pressure of 102.5 MPa at a temperature of 1339°C [4].

Sintering of calcium carbonate depends on many factors, i.e., the polymorphic form of $CaCO_3$, the degree of purity of the initial raw material, the amount of the additive for promoting sintering, the firing conditions (heating rate, firing temperature and time).

Under conventional pressure and temperature, anhydrous calcium carbonate can have two forms, i.e., a stable form with rhombohedral crystals with a density of 2.71 g/cm^3 (calcite) and a metastable form with orthorhombic crystals with a density of 2.94 g/cm^3 (aragonite) [5, 6]. Aragonite is transformed into calcite when heated in air at 450 – 490°C. The transformation of calcite into aragonite is possible as a result of crushing at ambient temperature. Since aragonite is a metastable form, it is characterized by two endothermic effects [7] (397 – 417°C and 810 – 910°C) one of which is below the firing temperature and hence can affect sintering of calcium carbonate; it is necessary to crush the calcite so that aragonite would not be formed.

Crushing of calcium carbonate promotes its sintering and thermal decomposition of calcite into CaO and CO_2. The decomposition of calcium carbonate begins at different temperatures, which is obviously connected with the size of the initial crystals and the presence of impurities. The effect of the degree of crushing of calcite (with 99.5% $CaCO_3$) on its thermodynamic and kinetic properties is considered in [8] under the assumption that the specific surface area of calcite crystals can substantially influence the decomposition process. The initial rates of the reactions at a temperature of 574°C were 1.10×10^{-3} sec^{-1} for specimens with a specific surface area of 4 m^2/g and 1.48×10^{-3} sec^{-1} for specimens with a specific surface area of 25 m^2/g. The activation energy of decomposition decreased as a function of the specific surface area. It varied from 140.6 kJ/mole for crystals 10 μm long to 182 kJ/mole for crystals 0.03 μm in diameter in the same temperature range. The variation of the activation energy with the grain size is explained in [8] by the presence of two successive decomposition stages, namely,

$$CaCO_3 \rightarrow [CO_2(ads.), CaO]; \quad (1)$$

$$[CO_2(ads.), CaO] \rightarrow CaO + CO_2. \quad (2)$$

Reaction (2) occurs more rapidly due to the higher reactivity of the phase interface. In the case of large crystals it occurs more slowly than reaction (1) and is determined by the structure of the specimen, whereas in decomposition of the finest crystals, the activation energy is lower. The data from differential thermal analysis made it possible to determine the effect of the specific surface area on the thermodynamics of decomposition of calcite. As a result of a study conducted for a mixture of coarse (5 μm) and fine (0.07 μm) crystals in one-

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to-one ratio, we established the presence of two endothermic peaks (at 642 and 666°C).

The rate of the reaction of decomposition of calcium carbonate depends on the rate of diffusion of CO_2 through a layer of active CaO with a constant thickness [9]. The active CaO is represented by calcium and oxygen groups still positioned in the initial site occupied by them in the $CaCO_3$ lattice. Due to withdrawal of CO_2 from this lattice, the metastable structure should be very porous and active. Since CaO is highly reactive, it is probable that emission of CO_2 occurs in a series of adsorption-desorption processes, each of which is equivalent to a chemical reaction. The active CaO is transformed into a form recrystallized into its conventional lattice. Thus, the rate of decomposition depends on the number of active CaO groups on the $CaCO_3$ – CaO interface.

When calcium carbonate is crushed, a layer of CaO is formed on the surface of the crystals, and its thickness is greater the smaller the crystal. In wet milling CaO reacts with water with the formation of $Ca(OH)_2$ that decomposes into CaO and H_2O at 577°C. Thus, the finer the crystals, the more $Ca(OH)_2$ is formed during wet milling and the greater the loss of mass in firing at a temperature of about 650°C, which is confirmed by our experimental data.

The effect of impurities on the kinetics of decomposition of calcite is considered in [10]. It is assumed here that the difference in the activation energies of decomposition of calcite with 98.2% $CaCO_3$ (110.5 kJ/mole) and 99.5% $CaCO_3$ (193.8 kJ/mole) is caused by the impurities contained in the calcite.

Lithium carbonate is used in [10] as a sintering-promoting additive. Its introduction in the ceramic mixtures in production of faience, porcelain, refractories and glaze makes it possible to decrease substantially the firing temperature and obtain articles of higher quality, with lower TCLE and elevated thermal stability [11].

Lithium carbonate promotes both decarbonization and recarbonization of calcium carbonate [12, 13], which creates the possibility of using lithium carbonate as a low-melting additive in liquid-phase sintering of calcium carbonate in appropriate conditions.

Lithium carbonate is a very good catalyst for the carbonization reaction. It is known that the reaction between CaO and CO_2 is limited by slow diffusion of CO_2 through the layer of $CaCO_3$ formed on the CaO particles in the carbonization process. The degree of carbonization of CaO always increases in the presence of Li_2CO_3 [13].

Lithium carbonate and calcium carbonate form an eutectic (43% $CaCO_3$ and 57% Li_2CO_3) that melts at 662°C [13]. The temperature corresponding to the maximum on the DTA curve and coinciding with the maximum carbonization rate is 10 – 30°C lower than the melting point of the eutectic depending on the heating rate.

Thus, the effect of Li_2CO_3 on the reaction rate depends substantially on the quantitative ratio of Li_2CO_3 and $CaCO_3$ and the firing temperature. The reaction rates and size of the crystals in the final product can differ, namely:

at the melting point of the eutectic $CaCO_3$, the protective coating formed on CaO dissolves and reprecipitates in the form of larger $CaCO_3$ crystals, and the reaction occurs on the surface of CaO at a high rate;

with a large enough amount of Li_2CO_3, the liquid phase is not saturated with $CaCO_3$, its content increases in the course of the reaction, and the liquid phase itself acts as a protective coating;

below the eutectic temperature the added Li_2CO_3 promotes a decrease in the grain size of the polycrystalline $CaCO_3$ surface layer, and the acceleration of the reaction seems to be caused by the diffusion of CO_2 over the increased number of intergrain boundaries.

Consequently, in order to sinter calcium carbonate with lithium carbonate additive, we should choose a temperature somewhat lower than the melting point of the eutectic (< 662°C), determine the optimum heating rate and the amount of the additive (not high) for creating a liquid phase through which the calcite should recrystallize.

Since on one hand the temperature of the beginning of decomposition of calcium carbonate exceeds 600°C [2], and on the other hand the liquid phase promoting sintering appears at a temperature of at least 600°C [14], we should create a firing atmosphere that would impede decomposition of the calcium carbonate. The protective atmosphere can be CO_2. In sintering in a CO_2 atmosphere, calcium carbonate with no lithium carbonate additive begins to decompose at 920°C; with the additive, it decomposes at 860°C [3]. When sintering calcium carbonate with 1% lithium carbonate at 620°C in a CO_2 atmosphere, the mean grain size of the final product is 12 μm; in sintering in air it is 4 μm. However, sintering of calcium carbonate in air is more effective than sintering in a CO_2 atmosphere.

Thus, special attention in sintering calcium carbonate should be devoted to the preparation of the initial powder. It should be totally composed of calcium carbonate, i.e., should not contain even insignificant amounts of CaO or $Ca(OH)_2$ formed due to excess milling of the calcium carbonate. In the presence of CaO or $Ca(OH)_2$ sintering should be conducted in an atmosphere of CO_2.

The optimum firing temperature lies within 620 – 650°C. Lithium carbonate should be used for promoting sintering in the amount of 1 – 2%.

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