Effect of Additives on the Pressureless Sintering of Calcite

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Effect of additives on the sintering of calcite under the atmospheric pressure was studied. Calcite could be sintered at about 793 K by adding a small amount of lithium fluoride. The microstructure of the sintered calcite was consistent with that of ceramics fabricated by liquid-phase sintering.

Key-words: Calcite, Sintering, Liquid phase sintering, Microstructure

1. Introduction

Carbonate minerals such as calcite and dolomite are widely used as a raw material of ceramics. They are decomposed on heating into alkali earth metal oxides and CO$_2$ which is discharged in the atmosphere. Recently, the relation between the increase of CO$_2$ content in the atmosphere and air temperature on the earth has been discussed. If a sintering process of carbonates is established, the process will contribute, at least in some extent, to slow down the increase of CO$_2$ content in the atmosphere. However, few reports have been published about sintering of carbonate. Fujikawa et al.\cite{1} have succeeded to prepare sintered calcite by using HIP. Yamasaki et al.\cite{2} applied a hydrothermal hot pressing technique for the fabrication of sintered calcite and showed that the compressive strength of the material reached to about 700 kg/cm$^{-2}$. Komatsu and Yamamoto\cite{3} reviewed processes of man made coral, in which they described the optimum temperature for the fabrication of man made coral by the hot press method being in the range 600 to 650$^\circ$C.

The purpose of this study is to find additives for sintering under the atmospheric pressure.

2. Experimental

Starting material was a chemical reagent of calcium carbonate with 99% in purity, which was identified to be calcite by the X-ray powder diffraction method. Ionic compounds with low melting points were employed as additives to promote sintering of the starting material. They were lithium fluoride (LiF), lithium phosphate (Li$_3$PO$_4$), sodium chloride (NaCl), and sodium carbonate (Na$_2$CO$_3$). The starting material and 5 and 10 mass% of those additives were mixed in ethanol and those mixtures were pressed into pellets of 10 mm in diameter and 5 mm in height by a uniaxial press at 3 to 4 MPa.

Those pellets were heated in an electric furnace at temperatures ranging from about 673 to 973 K for 24h. Durability was tested for the heated specimens by soaking in water for 24h at the room temperature. Phases of the specimens were determined by the X-ray powder diffraction method and the microstructure was observed by scanning electron microscopy (SEM).

Vickers hardness of the specimens was measured and degree of sintering was estimated by these values.

The mixtures of calcite and additives were examined by DTA using Rigaku TAS 200 at the heating rate of 10 K/min.

3. Results and discussion

Most of the specimens were porous looked like a chalk and could be broken easily by hand. Some of the specimens containing LiF, however, looked dense bodies and were provided for the measurement of Vickers hardness. Table 1 shows the results of the soaking test. Specimens containing LiF, and Na$_2$CO$_3$ remained unchanged after the test. However, most of the specimens of no additives and those containing 10 mass% of NaCl were broken into powders. This result indicates that the additives positively influence in the sintering of calcite.

The specimens containing LiF heated at temperatures below 797 K looked compact bodies and possessed smooth surfaces. However bubblelike bulges appeared when the specimen of a similar composition was heated at 973 K. Since the decomposition temperature of calcite is 793 K in the atmospheric condition,\cite{4} these bulges are considered to be caused by the decomposition.

Figure 1 shows changes in Vickers hardness of the specimens with firing temperatures. The values of Vickers hardness increased linearly as higher firing temperature and reached to 2.80 GPa in the specimen heated at 795 K. This increase suggests that sintering of calcite occurs below the decomposition temperature.
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Microstructure of the calcite powder used as the starting material and the specimen containing 5 mass% of LiF sintered at 798 K are shown in Figs. 2 and 3, respectively. As shown in Fig. 2, the starting material is consisted of small rhombohedral crystals with sharp edges and those crystals are less than 10 μm in size. The rhombohedral crystals changed their shapes into polyhedral and grew up more than 10 μm by the firing. The polyhedral shape is similar to that generally observed in other ceramics, e.g., sintered alumina.

A sharp endothermic peak appeared at about 843 K on the DTA curve of the mixing powder of calcite and 5 mass% of LiF. The binary phase diagram LiF-CaCO₃ has not been published. The endothermic peak is, however, considered to be caused by the formation of a liquid phase. The liquid phase should contribute to promote the sintering of calcite.

From the results, the optimum temperature of the sintering of calcite was deduced to be about 793 K, which was as high as the decomposition temperature of calcite. Four pieces of the specimens containing 5 mass% of LiF were prepared by firing at the optimum temperature. The averaged value of shrinkage and that of bulk density of those specimens were 19% and 2.24 m·kg/m³, respectively. The bulk density reached to 83% of the ideal density of calcite.

4. Conclusions

Effect of additives on sintering of calcite under the atmospheric pressure was studied. It was found that additives, especially LiF, promoted the sintering of calcite below its decomposition temperature. Microstructure of the sintered calcite was similar to that usually observed in the materials formed by the liquid-phase sintering. It was suggested that the sintering occurred under the presence of a liquid phase.

References