Structure of Jadeite Sintered with Spodumene Addition

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Jadeite powder was sintered with α-spodumene (Li$_2$O·Al$_2$O$_3$·4SiO$_2$) powder, at 5 mass%, under ordinary pressure at 1173 K for 3 hours. Structural characterization of the product was performed by using powder X-ray diffractometry (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). A complex structure was observed in the grains, where crystals and glasses formed in a network pattern. The results showed that the presence of spodumene improved the sintering and densification of jadeite powder.

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1. Introduction

Jadeite (NaAlSi$_3$O$_8$) is one of the minerals used for ornamental purposes, and it has a pyroxene structure. Most of the achievements in pyroxene research have been summarized by Deer et al. and Prewitt. By combination of Jadeite and other pyroxene mineral, investigations of pyroxenes in a diopside (CaMgSi$_2$O$_6$)-jadeite system under high-pressure conditions have been made by transmission electron microscopy (TEM) and single-crystal X-ray structure refinement. Similar investigations were also made, performed under high-pressure conditions, because jadeite becomes unstable at elevated temperatures and decomposes into nepheline above 1073 K under ordinary pressure. Therefore, a few published reports have dealt with the thermal reactivity of jadeite under ordinary pressure.

Jadeite has a higher value of toughness than that of diamond. In this work, we tried to sinter a jadeite powder under ordinary pressure with the exception of synthesizing a new ceramic. We selected α-Spodumene as a sintering aid, which is also one of a pyroxene mineral and the combination is an original in our experiment. This phase undergoes an irreversible phase change above 1173 K, forming the more open tetragonal polymorph, β-spodumene. It is commonly used for making glasses and ceramics that are hard, smooth and thermal-shock resistant.

In the present paper, the effect of the addition of spodumene on sintering and the densification of jadeite powder are discussed. The obtained product was characterized by powder X-ray diffractometry (XRD), scanning electron microscopy (SEM) and a high-resolution transmission electron microscopy (HRTEM) equipped with energy-dispersive spectroscopy (EDS).

2. Experimental Procedure

Starting materials were a white-colored jadeite rock yield from Myanmar and a synthetic α-spodumene powder that is commercially available (Kinsei Kogyo, Japan). Chemical compositions of the jadeite rock by fluorescence X-ray analysis are given in Table 1. The jadeite rock was crushed into agate mortar and then mixed with spodumene powder at 5 mass%. The mixture was pressed into pellets and then heated at 1123 K or 1173 K for 3 hours.

Density of the product was measured by Archimedes method. Phase composition was determined by a powder X-ray diffractometery (XRD) apparatus (RINT 2000, Rigakudeni, Japan). The product was buried in a resin, and the surface of the resin was polished. The surface of the specimen was characterized by scanning electron microscopy (SEM) (JEM-5410 JEOL, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS). A TEM foil was prepared by the standard technique used for preparing the thin foils of ceramics. This involved cutting, grinding, dimpling, Ar-ion thinning, and carbon coating to minimize the electric charge under the irradiated electron beam. Microstructural characterization of the thin specimen was performed with a transmission electron microscope (TEM) (JEOL-3000F), which makes it possible to provide electron probes with a full width at half maximum (FWHM) of around 0.5 nm, and also with sufficiently high current for a point analysis by EDS.

3. Results and discussion

Figure 1 shows XRD patterns of non-doped jadeite fired at 1123 K in (a), 5 mass% spodumene-doped jadeite at 1123 K in (b), and 5 mass% spodumene-doped jadeite at 1173 K in (c). At 1123 K, some of the jadeite decomposed to nepheline (NaAlSi$_3$O$_8$), as seen in (a), which has a CaF$_2$O$_2$-type structure. When 5 mass% spodumene powder was added in the jadeite powder, however, no decomposition into nepheline was found at 1123 K in (b). At 1173 K, we obtained denser composite from spodumene-doped jadeite powder. The bulk densities of these products were 1.47, 1.77, and 1.79 g/cm$^3$ in (a), (b) and (c), respectively. The values of the density increased by addition of spodumene. The intensity of the background rose in the XRD pattern in (c), indicating that an amorphous material might be formed in the jadeite composite. This assumption was verified in microscopic images of the specimen.

The surface of the composite was polished and then observed by SEM. Figure 2 (a) and (b) show back-scattered electron (BSE) images of the surface structure of the 5 mass% spodumene doped jadeite fired at 1173 K. Some pores between the grains were found in (a). Dark and bright contrasts were

| Table 1. Chemical Compositions of Jadeite Rock yield from Myanmar |
|-----------------|---|---|---|---|---|---|---|
| element        | Na | Al | Si | Ca | Fe | Mg | K |
| mass%          | 14.3 | 26.0 | 59.3 | 0.23 | 0.10 | 0.06 | 0.01 |
found in the enlarged BSE image in (b), and they formed a complex structure like a network pattern. From the results of XRD analysis and SEM observation, it was considered that a glassy phase was formed in the composite. Then, the composite was etched with a 2.5% HF solution for 90 sec, and the surface was also observed in Fig. 2(c). The glass material in the grain was etched out and the area was observed with a dark contrast in the network pattern of (c). These findings indicated that the specimen was composed of the crystalline- and glassy-phases, in which the chemical composition of the glassy phase was different from that of crystalline.

Figure 3 shows a low-magnification TEM image of the thin film of the 5 mass% spodumene doped jadeite fired at 1173 K. The numbers in the TEM image corresponded to the analytical measurement points by the selected area diffraction (SAD) method. Dark and bright contrasts were found in the TEM image. The SAD patterns showed that the dark and bright areas with a 1–3 μm size were composed of crystalline phase and amorphous phase, respectively. The orientation of the crystalline phases was different with each other.

Figure 4 shows a high-resolution TEM (HRTEM) image of the crystalline phase in the 5 mass% spodumene doped jadeite fired at 1173 K. The inset is a corresponding SAD pattern, which was taken along the [001] zone axis of jadeite with a monoclinic structure \( a = 0.973 \), \( b = 0.861 \), \( c = 0.524 \), and \( \beta = 104.48^\circ \). The lattice image was observed with a repeat distance of (110) spacing of the jadeite structure in the TEM image. In general, non-doped jadeite crystal is not damaged so easily during TEM observation. In the present case, however, the crystalline phase easily changed to an amorphous state by a thermal-electron beam, which indicated that the structure of jadeite in the crystalline phase changed by addition of spodumene. Therefore, we took this HRTEM image carefully.

The chemical compositions of the crystalline- and amorphous-phases were analyzed by EDS equipped with a TEM device. Figure 5 shows the EDS spectrum obtained from the crystalline phase in (a) and amorphous phase in (b). A difference in the content of Na was found between the EDS spectra obtained from the crystal and amorphous phases. Li cannot be detected with an energy-dispersive spectroscopy. It was considered that the amorphous phase was formed by a reaction of spodumene (LiAlSi₂O₆) and jadeite (NaAlSi₂O₆); according-
Na content in the amorphous phase was lower than that of the crystalline phase of jadeite. This was supported by the results of BSE images, as shown in Fig. 2. Spodumene has been used as a liquid-phase-sintering aid for the densification of alumina, mullite, and aluminum titanate ceramics. In this case, this reaction might also occur during the liquid-phase-sintering process. The surface of the jadeite grain might have dissolved and reacted with the liquid phase of the spodumene during the liquid-phase-sintering process. Using spodumene provided material containing a mix of crystalline- and glassy-phases. As a result, spodumene acted effectively for the densification of the jadeite powder as a sintering aid under ordinary pressure.

4. Conclusions

Spodumene was used as an additive for the densification of jadeite powder under ordinary pressure. Microscope images of the spodumene-jadeite composite revealed that glass phases and crystalline phases were formed in a network pattern. The glassy phase was formed by a reaction between jadeite and spodumene during the liquid-phase-sintering process. As a result, the densification was achieved by forming a combination of crystalline- and glassy-phase in the ceramics.

References