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Microstructure and flexural strength of anorthite-diopside mixed phase

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Low Temperature Co-fired Ceramics (LTCC) are widely used in electronic devices due to their ease of layering and outstanding applicability to RF technologies. These LTCC parts are manufactured by thick film process. However, unlike electronic devices of the past, modern portable electronic devices now require high strength materials, and LTCCs, which have a mixed glass and crystal phase, are relatively low strength materials. Thus their strength has been enhanced with crystallized glass induced by low temperature sintering. The most commonly used crystal phase is anorthite, but there is a comparative lack of research on other crystal phases or mixed phases and their strengths. Thus this study observed and compared the physical properties of mixed phases of synthesized anorthite and diopside at varying proportions. The two crystal phases were synthesized at the respective temperatures of 1300 °C and 1250 °C and as there was almost no change in the phases caused by the sintering process, mixed phases of varying proportions could be produced. The flexural strength of the sintered mixed phases increased along with the amount of anorthite but decreased for 100% anorthite. The decrease in flexural strength was judged to be caused by the presence of glass phase. This was tested by comparing the flexural strength and microstructure of sintered anorthite having varying Al₂O₃ content. This enabled us to confirm indirectly that the glassy phase was the cause of decreased flexural strength.

Key word: LTCC, Anorthite, Diopside, Strength, Sintering.

Introduction

LTCC (low temperature co-fired ceramic) is a material and a processing technology used to sinter low resistance Cu and Ag electrodes and ceramic boards simultaneously. LTCC is widely used in electronic devices and circuit boards due to its ease of layering compared to PCB and outstanding RF properties [1, 2]. However, the increased portability of electric devices has created the need for higher strength in electronic parts and as ceramic based materials are more brittle than materials such as PCB, they are less resistant to physical impact [3, 4]. Portable electronic devices also contain a higher density of vias and wires due to their reduced size and the maximum integration of components [5, 6]. The vias and wires act as faults in ceramic parts, further weakening their resistance to physical impact. Hence, the strength of ceramic materials is highly affected by any microstructures and faults within the sintered ceramic [7].

Anorthite glass, which has come into widespread usage as an LTCC material, is a type of crystalized glass composite made of Ca-Al-Si-O elements. Al_2O_3 reacts with glass in the sintering process to form anorthite crystal phases, enhancing its strength through both liquid phase sintering and crystallization. This makes it difficult to confirm the exact sintering mechanism taking place [8, 9]. Moreover, the effect of LTCC materials' composition and crystal phases on physical properties such as strength has not been clearly explained as yet. There is a similar lack of research looking at the effects of anorthite and diopside phase volume ratio, and corresponding changes in sintering behavior and microstructure on material strength.

In this study an experiment was conducted to measure the strength of synthesized anorthite and diopside crystal phases. The reactions between these two phases when mixed and sintered together, as well as changes in strength and microstructure according to the volume ratios used in the mixture, were observed as well. Through this investigation we aimed to explain the effect of crystal phase distribution within LTCCs on their material strength.

Experimental Method

Ingredients used in the synthesis of the crystal phases were CaCO₃ (99%, High Purity Chemical Co. Ltd., Japan), Al₂O₃ (99.9%, High Purity Chemical Co. Ltd., Japan), MgO (99.9%, High Purity Chemical Co. Ltd., Japan) and SiO₂ (99.9%, High Purity Chemical Co. Ltd., Japan). Anorthite was synthesized using CaCO₃, Al₂O₃ and SiO₂ powders, while diopside was

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synthesized using MgO, CaCO₃, and SiO₂ powders stoichiometrically mixed. Wet mixing was conducted for 24 hours at 100 °C using an ethanol solvent in a ball mill. The mixed powders were placed in an aluminum crucible and heated to 1000 °C-1300 °C at a rate of 5 °C/min for anorthite, and 1000 °C-1250 °C at a rate of 5 °C/min for diopside, and both were maintained at the high temperature for 2 hours before cooling. The synthesized anorthite and diopside were put through a wet mixing process using ethanol as a solvent, combined at volume ratios of 2: 8, 4: 6, 6: 4 and 8: 2, and then dried for 24 hours at 100 °C. The anorthitediopside mix powders thus obtained were granulated using a small amount of PVA 10 wt% solution and then formed into pellets using a pressurized moulder. The pellets were heated to 600 °C at a rate of 5 °C/min and the temperature was maintained for 2 hours to burn out the added bonding agent. Then they were heated to the sintering temperature at a rate of 5 °C/min, maintained for 2 hours and cooled.

The anorthite and diopside powders synthesized at different calcination temperatures were put through phase analysis via X-Ray Diffraction (M03XHF22, MAC Science Co. Ltd., Japan) (XRD hereafter), their microstructures were observed via FE-SEM (JSM 6700F, Jeol, Japan) and the strength of each material was tested using a Universal Testing Machine (4202, Instron, U.S.A.) (UTM hereafter) in 3 point flexural strength tests.

Outcome and Discussion

Fig. 1 shows the results of XRD phase analysis of synthesized anorthite powders according to synthesis temperature. Line a) shows Al₂SiO₅, CaSiO₃, CaAl₂SiO₆ peaks without anorthite peaking when the temperature was maintained at 1000 °C for two hours. Similar results were seen for 2 hours at 1100 °C without a clear change in intensity. However, main anorthite phase peaks were observed at 1200 °C and finally line d) shows only



Fig. 1. X-ray diffraction patterns of synthesized anorthite powders with synthesis temperature; (a) 1000 °C, (b) 1100 °C (c) 1200 °C and (d) 1300 °C.



Fig. 2. X-ray diffraction patterns of synthesized diopside powder with synthesis temperature; (a) 1000 °C, (b) 1100 °C (c) 1200 °C and (d) 1250 °C.



Fig. 3. X-ray diffraction patterns of sintered anorthite-diopside (1 : 1 volume fraction) mixed phase.

anorthite peaks without other phases at 1300 °C.

Fig. 2 shows the results of XRD phase analysis of diopside powder mixed according to stoichiometric ratio and synthesized at varying temperatures. Line a) shows peaks of the raw materials with almost no diopside when heated at 1000 °C for 2 hours while line b) shows diopside beginning to appear and fewer raw material peaks at 1100 °C. When the synthesis temperature was raised to 1250 °C in line d), we can observe a pure diopside phase without other materials.

Then an experiment was conducted to produce a sintered mixture using anorthite powder synthesized according to the conditions in Fig. 1, condition d) at 1300 °C, and diopside powder synthesized according to Fig. 2 condition d) at 1250 °C. Fig. 3 shows the results of XRD phase analysis on a 1:1 mixture of sintered Anorthite-Diopside. Seeing that there are no secondary phases other than anorthite and diopside, we can deduce that there was no reaction between the two. This result concurs with the experiment conducted by Kim *et al.* (2009) which showed that no new secondary

Microstructure and flexural strength of anorthite-diopside mixed phase



Fig. 4. SEM image of sintered anorthite-diopside mixed-phase with composition volume ratio(Anorthite:Diopside); (a) 0: 10, (b) 2: 8, (c) 4: 6, (d) 6: 4, (e) 8: 2, (f) 10: 0.



Fig. 5. Flexural strength test of sintered anorthite-diopside mixedphase with composition volume ratio.

phases were formed by the combination of anorthite glass and diopsite glass [10]. Also a comparison of phase intensity showed that the mixture has a similar intensity to the mixed ratio of respective phase intensities, showing that the phase ratio remained about the same as well.

Fig. 4 shows changes in the microstructure depending on the ratios of anorthite and diopside by volume. Pictures (a) to (e) all show sufficient density and the absence of grain growth in the sintering process regardless of mix ratios. On the other hand, mixed phases from pictures (b) to (e) show microstructures typical of solid phase sintering, but 100% anorthite left behind residual glassy phases, as shown in picture (f).



Fig. 6. SEM image of sintered anorthite $(CaAl_2Si_2O_8)$ with $X(Al_2O_3)$ contents; (a) X = 0.05, (b) X = 0.1 (c) X = 0.3 and (d) X = 0.6.



Fig. 7. X-ray diffraction patterns of synthesized anorthite $(CaAl_2Si_2O_8)$ with powders with $X(Al_2O_3)$ contents; (a) X = 0.05, (b) X = 0.1 (c) X = 0.3 and (d) X = 0.6.

Fig. 5. shows the results of flexural strength tests on anorthite-diopside mixed phases by mix ratios. Pure diopside phase has a relatively low value of 138 Mpa. Flexural strength increases along with the ratio of anorthite in the mixture. However, pure anorthite has a low flexural strength of 114 Mpa. An earlier study had shown that strength decreases as glassy phases increased in the microstructure of anorthite [11]. As picture (f) in Fig. 4 shows, glassy phases have been formed in the microstructure with 100% anorthite, and this can be seen to have caused the drop in flexural strength, concurring with the earlier study.

Anorthite is a phase formed at high temperatures [12]. In a ternary system diagram, the melting point rises along with the amount of Al_2O_3 , probably due to the decrease in liquid phases. Thus, if the amount of Al_2O_3 goes above the stoichiometric amount, it would lead to a decrease in liquid phases and a corresponding decrease in glassy phases after sintering. Fig. 6 shows SEM pictures of anorthite with added Al_2O_3 arranged



Fig. 8. Flexural strength test of sintered anorthite (CaAl_2Si_2O_8) with Al_2O_3 contents.

according to Al_2O_3 content. In comparison to picture (f) in Fig. 4, one can see the reduction in liquid phases and clearer grain boundaries as Al_2O_3 content increases. This shows indirectly that adding Al_2O_3 to anorthite reduces liquid phases by increasing the melting point.

Fig. 7 shows the results of XRD analysis on anorthite showing changes depending on Al_2O_3 content. When the Al_2O_3 content, x, was at 0.05 and 0.1, the XRD analysis shows a pure anorthite phase. But when x was 0.3, both anorthite and Al_2O_3 peaks begin to be observed. Al_2O_3 peak intensity increased when x was 0.6. This was interpreted to be Al_2O_3 being extracted as the amount went beyond the upper limit of Al_2O_3 engagement in anorthite.

Fig. 8 shows the results of flexural strength tests on sintered anorthite with varying amounts of Al₂O₃ content. As the microstructure in Fig.4 picture (f) showed, a sintered material with high liquid phase content displayed low flexural strength value, but the value increased to above 200 MPa with an increase in Al₂O₃ content. A pure anorthite phase with Al₂O₃ content, x, of 0.1 had a flexural strength value of 159 Mpa, 45 MPa more than when x was 0.05. When the Al_2O_3 content, x, increased to 0.6 the flexural strength rose to 209 Mpa, concurring with the XRD analysis results in Fig. 7 showing that the extracted Al₂O₃ had an effect on material strength. This concurs with the finding reported by Kim et al. (2005) that an increase in Al₂O₃ content and the resulting Al₂O₃ phases helped prevent cracks from spreading, working to enhance material strength [13].

Conclusions

In order to test the strength of anorthite-diopside mixed phases according to their mix ratios, we synthesized anorthite at 1300 °C and diopside at 1250 °C to obtain their respective crystal phases. No secondary phases other than their respective phases were found when they sintered. Observing the resulting microstructures of anorthite-diopside mixed phases according to their mix ratios, we saw increases in liquid phases corresponding to increases in anorthite ratios. Three point flexural tests based on mix ratios showed increased strength corresponding to increased anorthite content but the 100% anorthite crystal phase displayed drastically reduced flexural strength performance. A study of its microstructure showed excess amounts of glassy phases in the 100% sintered anorthite which was thought to be the cause. This theory was confirmed by testing the impact of increased Al₂O₃ content in anorthite phases which showed decreased liquid phases and increased strength as a result.

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