Chemical durability of anorthite-based low temperature co-fired ceramics

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The chemical durability of a typical low k LTCC material consisting of zinc calcium aluminoborosilicate glass and alumina filler was studied. Leaching experiments were performed by measuring weight loss of the samples in selected acid and base aqueous solutions of HCl, H2SO4 and KOH at two different temperatures of 25°C and 80°C. The leaching performance was found to depend strongly on the type of leaching solution, duration and temperature. The LTCC sample was most stable in 10 vol% KOH with a minimal weight loss of ~0.43% even after 300 min at 80°C. At the same condition, both cases of 10 vol% HCl and 10 vol% H2SO4 exhibited serious weight losses greater than 30%. It was interesting to observe that the high capability of leaching in the acid solutions originated significantly from the leaching of crystalline anorthite (CaAl2Si2O8) phase.

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1. Introduction

Low temperature co-fired ceramics (LTCC) that usually consist of glass and ceramic have been of recent choice for utilizing various electronic components and modules since they provide a unique solution for highly-integrated packages.5–7 Electroplating, which is a common method for producing highly reliable and low cost metallization of LTCC, uses various types of acid or base solutions in the continuous plating process. While physical and electrical properties are major concerns in general, unacceptable chemical leaching resistance of commercially-available LTCC materials has often been a critical issue for successful utilization of the low cost electroplating electrodes. Chemical durability of the glass/ceramic composite must depend primarily on the nature and concentration of residual glasses as well as leaching environment.5,7 This preliminary work first intends to provide an example of the chemical behavior in a typical anorthite(CaAl2Si2O8)-based LTCC material, consisting of a zinc calcium aluminoborosilicate glass and alumina filler, in acid and basic solutions under different leaching conditions including temperature and duration of leaching.

2. Experimental

A glass based on a zinc calcium aluminoborosilicate composition was prepared by the common glass melting procedure. Raw materials of CaCO3, Al2O3, B2O3, ZnO and SiO2 were properly mixed by hand shaking and soaked at 1500°C for ~2 h in a platinum crucible. The melt was quenched into water to obtain a transparent glass. The glass was then ground into powders with yttria-stabilized zirconia balls in ethanol for ~20 h, and dried on a hot plate while stirring with a magnetic bar. A fixed content of 35 wt% Al2O3 was mixed with the prepared 65 wt% glass frit by using ball-milling in ethanol for ~12 h. The glass/ceramic mixture was then tape-cast on a mylar film after making tape slurry using a commercial binder (B73225, Ferro, Vista, CA). Sintering was performed by firing the laminated tape at 850°C for 30 min with a fixed heating rate of 5°C/min.

Chemical leaching experiments were performed by measuring weight loss per exposed surface area of each sample, which was expressed in percentage relative to its original weight per surface area, after leaching in the acid and base solutions. The measurement was conducted at selected solution temperatures of 25 and 80°C over the extensive immersion period from 1 min to 300 min as also described in our previous work.8 Chemical solutions employed for leaching were the same 10 vol% - concentrated HCl, H2SO4 and KOH. Experiments were performed repeatedly through multiple trials to validate the results obtained. Phases existing in the LTCC samples after chemical leaching were identified by an X-ray diffractometer (XRD; Rigaku Co., B/Max–2500/PC, Tokyo, Japan) using Cu Kα radiation. Surface microstructure of the samples before and after leaching was examined using scanning electron microscopy (SEM; Hitachi, Ltd., S–4200, Tokyo, Japan).

3. Results and discussion

Figure 1 shows the percentage weight loss obtained for the LTCC samples as a function of exposure duration in three different chemical baths employed, i.e., 10 vol% of each HCl, H2SO4 and KOH. Although the experimental conditions employed in this study do not follow exactly the practical electro-plating process for metallization, it should be a good indicative of the leaching behavior of the typical anorthite-based LTCC materials. The leach behavior over the exposure period strongly depended on the type of solution and leaching condition. At room temperature of 25°C, the weight loss values of the samples at each exposure time were comparable in both HCl and H2SO4 solutions. At 80°C, however, the weight loss in HCl was significantly higher than the corresponding weight loss in H2SO4. At the 60 min of leaching at 80°C, for instance, the weight loss obtained for samples immersed in HCl was ~32% while it was ~16% in H2SO4. The sample exposed in KOH seemed to be very stable.
regardless of leach temperature and exposure duration as evidenced from very low weight losses less than 0.5% (Fig. 1(c)). After a leaching duration of 60 min, weight losses obtained at 80°C tended to saturate for all cases. The maximum weight losses obtained for the samples immersed in 10 vol% HCl, H₂SO₄, and KOH solutions were ~ 39, 30 and 0.43%, respectively, for the leach exposure of 300 min at 80°C.

Figure 2 shows the SEM images of the samples obtained before and after leaching at 80°C for 300 min. SEM images of the leached sample exhibited uniform crack/pore formation on surface. The pores observed for samples leached in the HCl solution were larger and more extensive in commensurate with the higher weight loss observed. Comparatively less number of pores was visible for samples leached in the H₂SO₄ solution. Relatively good surface microstructure was observed after exposure in the alkaline solution.

Figure 3 shows the XRD patterns obtained for the LTCC samples before and after leaching at 80°C for 300 min. It was found that the as-sintered sample consisted of Al₂O₃ filler and crystalline CaAl₂Si₂O₈ phase. The overall relative peak intensities of the phases became stronger after leaching, indicating that the relative content of glass decreased through the intensive leaching of the residual glass. When an LTCC consisting of glass and ceramic is exposed to an acid media, glass is likely to leach out easily from the structure. This occurs because the early stages of chemical attack involve ion exchange between H₃O⁺ ions and mobile cations in the glass from the relatively weaker glass structure. The leaching should be even more dominant in the highly-concentrated acid media used here.

As another distinguishable change, the relative peak intensity of Al₂O₃ to CaAl₂Si₂O₈ in the samples leached in HCl and H₂SO₄ became reversely larger than that of as-sintered sample. It indicates that CaAl₂Si₂O₈ is involved significantly in the acid leaching. The leaching of CaAl₂Si₂O₈ seemed to progress more intensively in HCl than in H₂SO₄ from the slightly-higher peak intensities of Al₂O₃ relative to CaAl₂Si₂O₈ in HCl. The difference in the leaching behavior between HCl and H₂SO₄ may be attributed due to the size effect of Cl⁻ vs. SO₄²⁻ and, subsequently, the leaching reactivity with glass constituents. The case of KOH
did not reveal any noticeable change except for the stronger peak intensities of the phases compared to those of the as-sintered sample. The zinc calcium aluminoborosilicate seemed to withstand effectively the aggressiveness of OH\(^-\) during the base leaching.

4. Conclusions

The chemical durability of a typical LTCC composition consisting of zinc calcium aluminoborosilicate glass and alumina filler depended largely on the type of chemical solution, temperature and immersion time. The LTCC composition was proven to have a higher potential to withstand against the base (KOH) leaching environment than the acid (HCl or H\(_2\)SO\(_4\)) one, by showing low weight losses of < 0.5% even at 80°C for up to 300 min. The cases of HCl and H\(_2\)SO\(_4\) demonstrated the extensive leach behavior strongly depending on exposure time and temperature. The massive leaching of crystalline anorthite phase in the highly-concentrated acids was another noticeable observation.

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References