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Preparation and Microstructure of Machinable Al_2O_3/Mica Composite by Ball Milling and Hot-Press Sintering

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Abstract: A machinable α-Al_2O_3/mica composite was prepared by hot-press sintering. In this experiment, a mica-contained glass ceramic in the MgO-Al_2O_3-SiO_2-F glassy system was employed and the base glass powders were obtained by traditional melting-quenched method. Then, α-Al_2O_3 milling swarf was introduced by medium α-alumina milling ball to the glass powders. The test results indicate that the composites consist of mica crystal and mullite crystal, which are precipitated in the base glass. The α-Al_2O_3 shows an irregular polygon, which is inlayed in the base material. With the decrease of size of the base glass powders, the boundaries of composites among the sintered powders gradually vanish. The mica crystals in the composite also show an interlocking characteristic, which is a prerequisite of mica-contained glass ceramics with good machinability. Under different pressures, the tendency of preferred orientation is decreased with the reduction in grain size of glass powders, and the microstructure is proved to be consistent, significantly decreasing the composite's hardness. Therefore, the machinability of the composite is improved.

Keywords: alumia/mica composites; ball milling; glass ceramic; sintering.

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1 Introduction

Sintering is a processing method in which powders are heated to form a solid mass of material, and is widely used in ceramic, glass ceramics, fire-resistant materials, and composites [1–3]. The sintering of glass ceramics, first presented by Frenkel [4], has the advantage of obtaining higher crystal contents in a shorter time and at lower temperature compared with the traditional method of glass ceramic production. Some proper compositions can be added via the sintering method to control and adjust the performance of composites.

In a glass ceramics system, mica-contained glass ceramic in the MgO-Al_2O_3-SiO_2-F glassy system has gained increasing attention owing to its good machinablity [5–11]. However, most studies have focused on which strength is improved for the mica-contained glassy system [5–9], because the mica crystal has the flake structure that tends to decrease the strength of the glass ceramic. The addition of a second rigid and the formation of composites are known to improve the mechanical properties of a material by several mechanisms, and these have also been utilized in the production of mica-contained glass ceramics in recent years. Cordierite/mica compositions were obtained at low temperatures by adding mica-composition glass powders to the conventional magnesia, alumina and silica powders, which are the raw materials of the formed cordierite [11]. Their results indicated that the addition of the mica-composition glass proved to be very effective in the formation and sintering of materials. In addition, the resulting material showed relatively high bending strength and higher Vickers hardness than those of mica-contained glass ceramics. Yekta et al. [10] reported that when PbO and P_2O_5 are added to the base glass, mica crystal changed from plate shape to globular shape to improve the material's performance. Alizadeh et al. [6] added the diopside-based glass to the mica-based glass ceramic, which changed the mica morphology from spherical to a plate-like shape. Mechanical strength and microhardness of glass-ceramics have also been increased with the complex of diopside due to the formation and

increase of potassium-calcium mica solid solution, instead of a less hard pure potassium one.

Uno et al. [12] demonstrated that the strength of materials could reach to 500 MPa by adding ZrO_2 to obtain dispersed nano-ZrO_2/mica composite. In a spodumene-fluorophlogopite glass ceramic, El-Meliegy [9] fabricated fluorophlogopite as the primary mineral phase, which produced a porcelain product with good machinability and the simultaneous crystallization of beta-spodumene solid solution as a compound phase, thus reducing the overall coefficient of thermal expansion and improving hardness. Tian et al. [13] prepared composites of a machinable mica/mulllite ($Al_6Si_2O_{13}$) glass-ceramics by adjusting the additive composition and controlling the thermal treatment schedules. The mica crystals grew through epitaxial processes on the mullite crystals and, finally, the homogeneously distributed mica/mullite composites formed in the non-isothermal treatment. However, this composite should be carefully prepared and depends on strict composition and technology. Recently, Xie et al. [14] reported the fabrication of a composite with less strict composition, in which α-alumina (or milling swarfs) is produced from the medium α-alumina ball, and introduced into the base materials. A small amount of fine α-alumina addition, which was evenly mixed with the base materials, also played a role of crystal seeding.

In this study, the mica-composition glass powder was mixed with the α-alumina, which was introduced by ball milling, to fabricate machinable alumina/mica composites by hot-press sintering. The crystallization and sintering of the powder mixtures and some properties of the obtained alumina/mica composites were also investigated.

2 Materials and methods

The chemical composition (mass fraction) of base glass is 37.9% SiO_2, 17.6% Al_2O_3, 14.5% MgO, 17.6% F, 9.1% K_2O, 2.6% ZrO_2, and 0.7% Fe_2O_3. All the test materials were pure chemical agents and purchased from Sinopharm, Shanghai, China. During the experiment, the base materials were accurately weighed and filled in the α-alumina crucible after being mixed homogeneously. Then, they were heated into 1430°C and melted when the holding time reached 1 h. This melting liquid glass was poured into cooling water. As a result, the base glass particles were obtained after drying. The glass particles were placed in the high pure α-Al_2O_3 tank (the milling ball was highly pure α-Al_2O_3 supplied by Advanced Ceramic Centre, Dalian Jiaotong University, China) and ground in a planetary mill (ND7-2L, Nanjing, China). The rotational speed of ball milling was 150 r/min, and the time of ball milling was about 5 to 20 h. After ball milling, the particle distribution of glass powders was tested by Laser Particle Size Analyzer (LPSA, Winner2000s, Jinan, China).

Some adequate powders were filled into the graphite jip and were heat treated in a hot-press sintering furnace (ZR50B-8T, China). After a holding time of 1 h, the pressure was unloaded at a temperature of 670°C and pressure of 40 MPa. Then, the temperature was heated to temperature 950°C (holding time 1 h), so that the glass ceramics were obtained. These samples of glass ceramics were cut into strip specimens along the directions of the vertical pressure and parallel pressure; the crystal orientation along the different directions was analyzed using X-ray Diffraction of Rigaku D/Max-2400 (Rigaku, Japan). The microstructure was observed by scanning electron microscopy of JCXA-733 JEOL, Japan. These samples were pre-erased, polished, and corroded by 5% HF solution (5 min) prior to observation. The element composition of some special test spots was analyzed using an energy dispersive spectrometer (JCXA-733 JEOL, Japan). The measurement of microhardness of specimens was conducted by microhardness tester (HV1000A, China) with load force of 4.9 N and load time 10 s.

3 Results and discussion

3.1 XRD analysis of composites

The grain size of glass particles by 20 h ball milling is D_{50}=0.94 μm. The XRD patterns before and after 20 h are

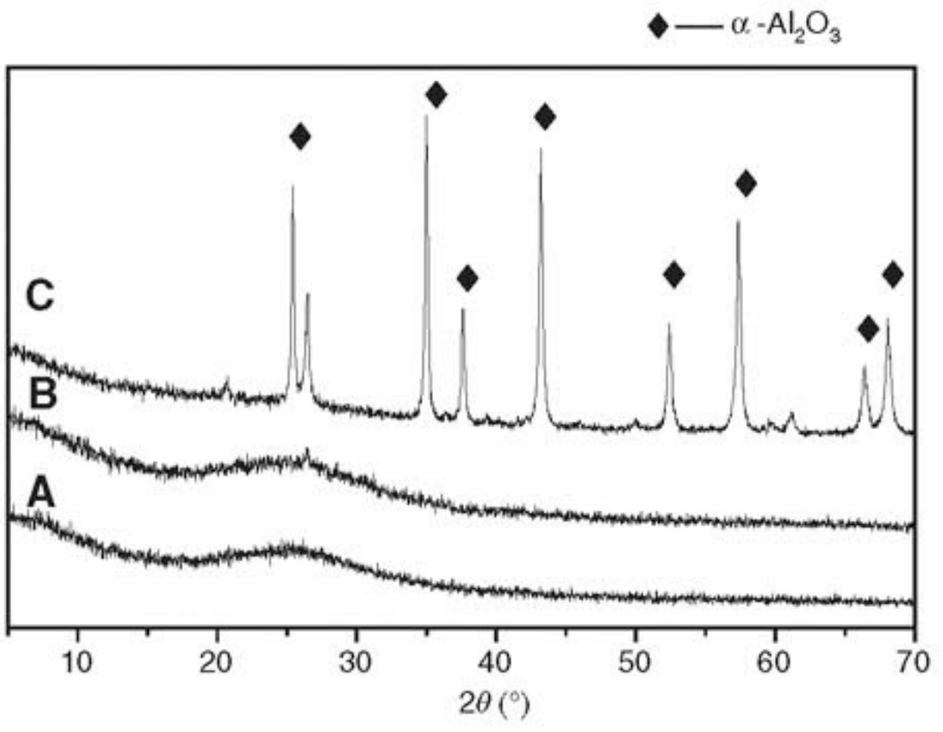

Figure 1: XRD patterns of glass samples with or without ball milling. (A) Before ball milling, (B) milling with PU balls, and (C) milling with alumina balls.

shown in Figure 1. According to this pattern, there is no obvious diffraction peak before ball milling (Figure 1A). At this time, glass samples show a typical amorphous characteristic. However, after 20 h by ball milling treatment, the typical diffraction peak can be observed. These diffraction peaks might be α-Al_2O_3 crystal (Figure 1C), indicating that some composition of α-Al_2O_3 might have gone into the glass powder. To further verify this phenomenon, the same ball milling process was carried out using a resin milling ball. Some new powders were also tested using XRD. The test result can be seen in Figure 1B. The XRD pattern produced when using the resin milling ball is similar to that of the glass powder produced without using the milling ball. Both show a typical amorphous characteristic, suggesting that the α-Al_2O_3 crystal in the glass powder is led through the alumina milling ball.

The XRD results of the glass sample produced via hot-press devitrification in D_{50}=0.94 μm are shown in Figure 2. In this sample, some new crystals must have existed except for α-Al_2O_3 crystal, although the intensities of diffraction peaks are low (Figure 2A and B). From the XRD results of the samples with larger sizes, in which the intensities of diffraction peaks are higher, it can be concluded that the devitrification phases are mica crystal and mullite crystal (Figure 2C–F). In the vertical and parallel orientation, there is no obvious change for the diffraction peak intensity of α-Al_2O_3 and mica crystals. The diffraction peak intensity for the same crystal is also nearly similar.

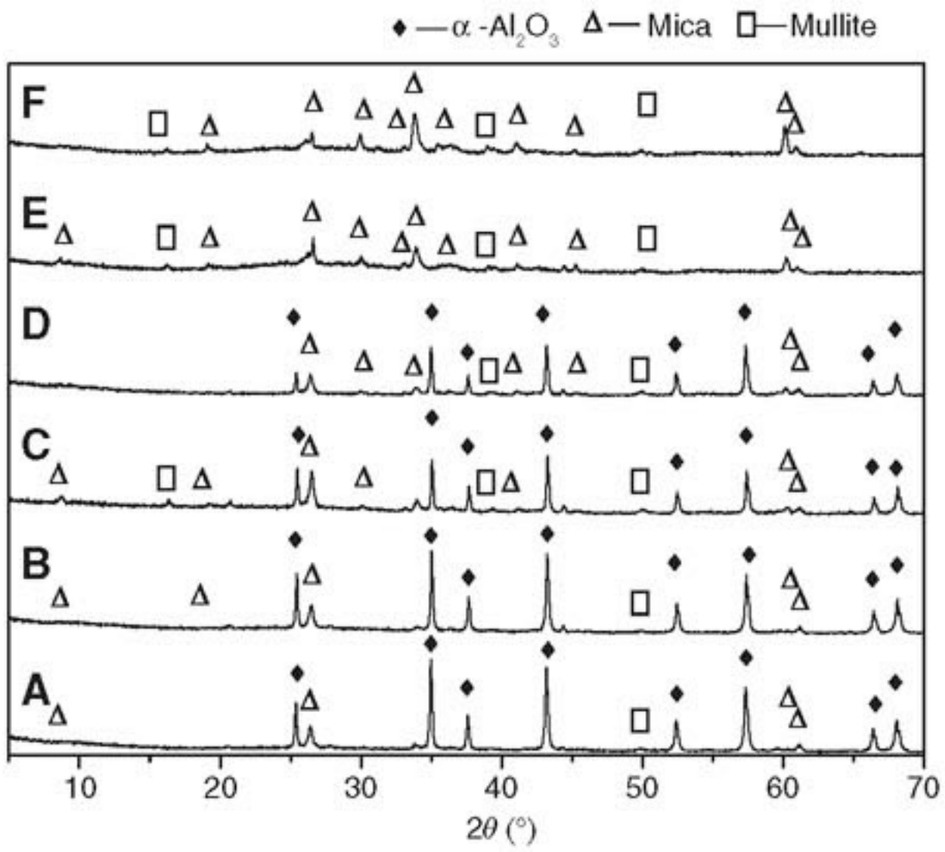

Figure 2: The XRD patterns of different samples varied with average grain size.
(A) D_{50}=0.94 μm, parallel to the press axis; (B) D_{50}=0.94 μm, perpendicular to the press axis; (C) D_{50}=1.29 μm, parallel to the press axis; (D) D_{50}=1.29 μm, perpendicular to the press axis; (E) average D=100 μm, parallel to the press axis; (F) average D=100 μm, perpendicular to the press axis.

This indicates that the precipitations of crystal in the different directions are not affected by the pressure, and the orientation and distribution of the precipitated crystals tend to be uniform. This is different from several investigation results [15, 16], in which the preferred precipitation of crystals seemed to be formed by the hot pressed processes.

In order to verify this phenomenon, the same hot-press treatment was carried out on the glass samples with different grain sizes. Compared with that of glass powder of D_{50}=0.94 μm, diffraction intensities of mica and mullite crystals are higher and the diffraction intensity of α-Al_2O_3 is lower in the samples with the grain size of D_{50}=1.29 μm (Figure 2C and D). There are some differences to the same crystal in various pressure directions. In the orientation of parallel pressure, the diffraction intensity of the (003) crystal plane (2θ=26.64°) for the mica cryatal is higher; however, the diffraction peak intensities of the (130) crystal plane (2θ=33.90°) and (060) crystal plane (2θ=60.23°) are lower, than that in the orientation of vertical pressure (Figure 2C and D), indicating that mica crystal shows the preferred growth. However, in the different pressure directions, there are no obvious differences observed for the α-Al_2O_3 crystal.

In order to observe the effects of the powder sizes of glass on the orientated growth of crystals, the sample of sintered glass (without ball milling) with average grain size of 100 μm was prepared. The XRD results (Figure 2E and F) show that there are no the diffraction peaks of α-Al_2O_3 crystal observed, which also indicate that α-Al_2O_3 crystal observed in Figure 2A–D should be produced by the milling ball. The precipitation of crystals is mainly composed of mica phases and little mullite phases in the samples. Mica crystal shows the same characteristic of diffraction peaks with those in the samples of glass grain sizes D_{50}=1.29 μm, that is, the diffraction intensity of (003) is higher and those of (130) and (060) are lower in the direction of parallel pressure than that in the direction of vertical pressure. However, compared with the sintered glass sample of grain size D_{50}=1.29 μm, the diffraction peaks intensity of precipitation crystals is lower, indicating that the increase of grain size is unfavorable to precipitate these crystals. As a result, the grain size decrease of glass powders can accelerate the precipitation, and decrease the tendency of the preferred orientation of mica crystals.

3.2 SEM analysis of composites

Figure 3 shows the SEM images and EDS results of the sintered glass powders for average grain size 0.94 μm in the

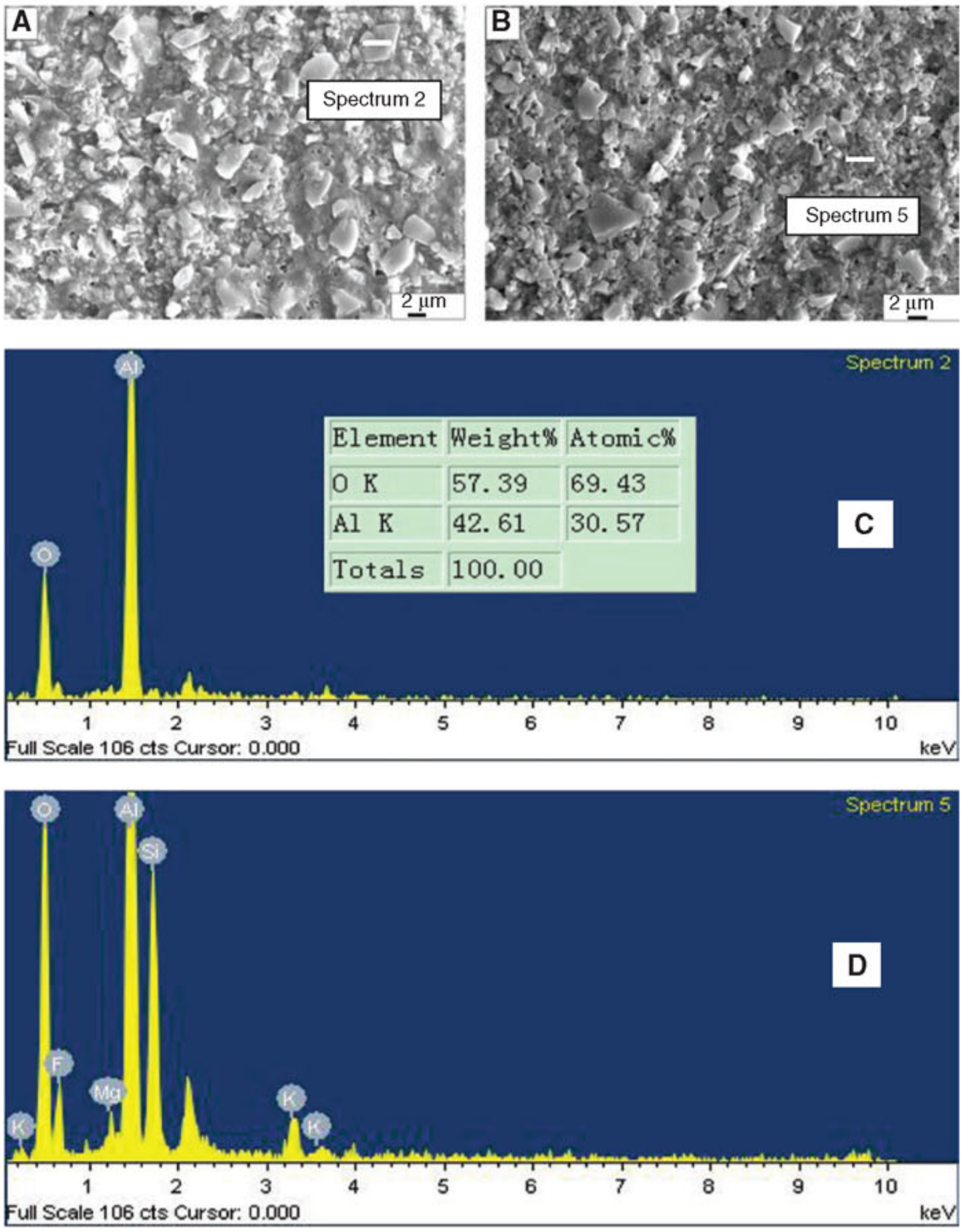

Figure 3: SEM micrographs and the analysis of energy distribution spectrum of sample with D_{50}=0.94 µm.
(A) Parallel to the press axis, (B) perpendicular to the press axis, (C) the EDS result of the bulk-like crystal, (D) the EDS result of the flake-shape crystals.

different pressure directions. In the vertical and parallel press orientation, some random polygonized crystal can be observed. These crystals embedded in the base glass are about 0.2–4.6 µm. EDS results show that this phase is α-Al_2O_3 (Figure 3C) [14]. Moreover, in glass-based materials, some fine flaky crystals sized 0.2–0.5 µm are precipitated, and this crystal phase has similar composition with that of mica crystal by EDS (Figure 3D). Therefore, the flaky crystal should be mica crystal. There are closed sintered holes after the materials are sintered, but the void size (about 0.2 µm) is small (Figure 3A and B). There is no obvious boundary among glass powders, which induces the interlocked distribution of mica crystal. As a result, the material obtained has good machinablity. Moreover, in the different press orientations, the microstructures of sintered samples show no obvious difference. The average hardness values of samples are also close to one another, which are 2.12 GPa and 2.13 GPa, respectively, in the directions of parallel and vertical pressure. These also indicate that the precipitation of crystal has no preferred orientation. This is also consistent with XRD results. In addition, the addition of α-Al_2O_3 does not change the crystallizing characteristics of glass ceramic, and does not greatly improve the hardness of the glass ceramic [9]. Thus, the machinablity of glass ceramic fabricated is less influenced. This is different from other mica-contained glass ceramic composites, which always sacrifice the machinability of the produced glass ceramics [11, 17].

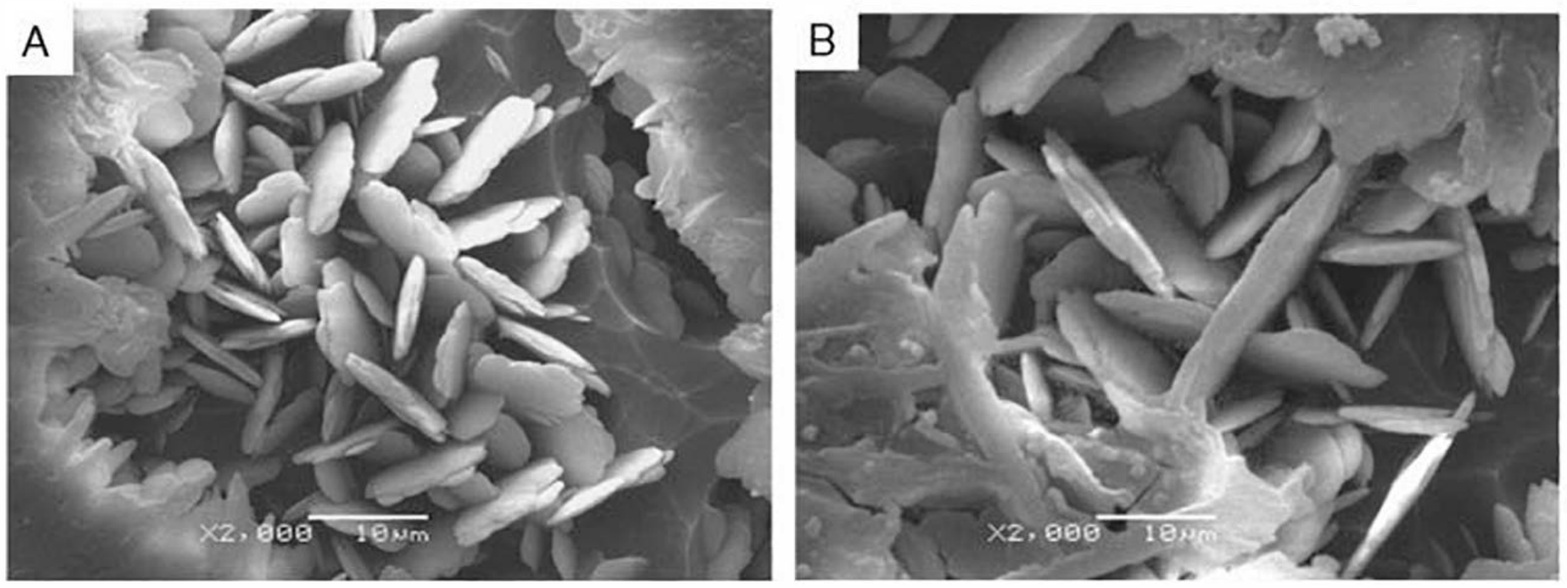

Figure 4: SEM micrographs of sample with average grain size of 100 μm.
(A) Parallel to the press axis and (B) perpendicular to the press axis.

SEM images of glass powder sintered with the average grain size of 100 μm are shown in Figure 4. According to the images, the precipitation of coarse flake crystal shows a certain preferred orientation in the different pressure orientation. There are obvious boundaries among glass powders. In the parallel and vertical pressure orientation, the hardness values of the samples are 4.16 GPa and 4.06 GPa, respectively, suggesting that there is a certain preferred orientation. Therefore, the grain sizes of glass powders have a great effect on the sintered form and microstructure of the precipitation crystal. With the decreased grain size of the glass powder, the increase of surface energy can accelerate the precipitation of glass. The boundaries of glass powders vanish and the microstructure tends to be consistent, which is the result of decreasing hardness and improving the machinability of the composites.

4 Conclusions

In the MgO-Al_2O_3-SiO_2-F glass system studied, α-Al_2O_3 was introduced into the glass powders by milling ball, and an Al_2O_3/mica glass-ceramic composite was obtained by hot-press sintering. The samples consisted of α-Al_2O_3 crystal introduced by the medium α-alumina balls, mica crystal, and little mullite crystal precipitated in the glass powders. The α-Al_2O_3 showed an un-regular polygon, being inlayed in base materials, and the flake mica crystal was precipitated homogeneously in the glass matrix. The decreased grain size of the sintered glass powders can accelerate the precipitation of glass crystal and induces the formation of the homogeneous and uniform microstructures, which decrease the tendency of preferred orientation of the precipitated crystals.

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