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# Effect of $TiO_2$ addition on crystallization and machinability of potassium mica and fluorapatite glass ceramics

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**Abstract** In this study, the effect of $TiO_2$ addition as a nucleating agent on the crystallization and machinability of potassium mica and fluorapatite base glass ceramics were investigated. Glass compositions were prepared and casted at predetermined temperatures. Differential thermal analysis and XRD methods were applied to characterize phase precipitation sequence and identification of phases. Disc and cylindrical shaped samples were prepared to determine microstructural and mechanical properties in terms of microhardness and machinability. FEG-SEM was used to characterize variation of microstructural constituents depending on the amount of nucleating agent. The results indicate that optimum microstructure and machinability can be obtained in machinable glass-ceramic by the addition of 1 wt% $TiO_2$ for the composition having 3:7 weight ratio of fluorapatite to potassium mica.

## Introduction

Glass-ceramic materials, which are applied to dental and bone implantation, are increasingly important in surgery due to the development of glass-ceramics. These materials are required to have high strength and be machinable in order to avoid unacceptable levels of failure in clinical practice. Apatite containing glass ceramics are greatly important for surgical implantation due to the high bioactivity, close crystallographic and chemical similarity of apatite to human bone tissue [1–5]. Machinable glass ceramics can be machined, drilled, milled or threaded like metals. The excellent machinability of mica glass-ceramics originates in the cleavage and the interlocking microstructure of mica platelet crystals [6–9]. The development of such glass ceramics is based on the controlled precipitation of mica phases from certain base glasses. Mica glass ceramics have exhibited excellent machinability and high thermal shock resistance. The precipitated crystalline phase is potassium phlogopite ($KMg_3(AlSi_3O_{10}F_2)$) which must constitute more than two-thirds of the total volume for an effective machinability [10–12]. In the production of glass-ceramics, nucleating agents such as $TiO_2$ can be used in order to induce bulk crystallization of the phases. Furthermore, the introduction of nucleating agent to the main glass can decrease the crystallization temperature and time [13, 14]. Several investigations [2, 7, 13–16] focused on the role of $TiO_2$ as a nucleating agent in mica-based glass-ceramics have showed that small addition of titania has a remarkable effect on the crystallization process. Shyu and Wu has reported a study on crystallization of $MgO–CaO–SiO_2–P_2O_5$ glass by the addition of $TiO_2$ as nucleating agent. The effects of $TiO_2$ on the nucleation of apatite in this glass-ceramic were summarized that the addition of $TiO_2$ improved both of the nucleation and growth rates of apatite by decreasing the viscosity and decreasing the surface energy between crystal and glass [2]. Taruta et al. has investigated the effect of

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$TiO_2$ on calcium-mica and fluorapatite system. They reported that, Ca-mica and fluorapatite were crystallized at lower temperatures than undoped specimen and $TiO_2$ acted as a nucleation agent of Ca-mica but impeded the crystallization of fluorapatite.

The purpose of this study is to find out the effect of $TiO_2$ addition as a nucleating agent on the crystallization behaviour, microstructural morphology and machinability of the potassium mica based glass ceramics [15].

## Experimental procedure

The compositions of the $MgO–CaO–SiO_2–P_2O_5–Al_2O_3–K_2O–F–TiO_2$ glasses are given in Table 1. The reagents (Merck) of $SiO_2$, MgO, $P_2O_5$, $Al_2O_3$, $K_2CO_3$, $CaCO_3$ and $CaF_2$ were used as starting materials of glass-ceramics having 7:3 weight ratio of potassium mica ($K_2Mg_3AlSi_3O_{10}F_2$) to fluorapatite ($Ca_{10}(PO_4)_6F_2$). $TiO_2$ was added to the compositions as nucleating agent. The raw materials were mixed for 2 h and then calcined powders were melted in a sealed platinium crucible at 1,400 °C for 1 h and then quenched into the water.

Differential thermal analysis (DTA) measurements were performed for each glass powders under nitrogen atmosphere. The DTA scan rate was 10 °C/min and glass powders were heated up to 1,000 °C.

The developed crystalline phases were identified by X-ray diffraction (XRD) in the $2\theta$ range 5–90° using a Philips PW 1820 diffractometer, employing CuK$\alpha$ radiation. In order to determine microstructural and mechanical properties of the glass-ceramics, disc and cylindrical shaped samples were prepared by using casting method. The melted glass was poured into the preheated graphite moulds and the as-cast glasses were immediately put in a furnace in order to release thermal stresses. After that, controlled heat treatment process was applied for glass-ceramic production. The microstructures of the glass-ceramics were examined by the field emission gun scanning electron microscope (SEM) type JEOL JSM-7000F (Japan) after coating with gold and etching in HF for 45 s. Microhardness tests were applied to the polished cylindrical samples under constant load of 1,000 g with 12 s indentation time. Furthermore, machinability tests were applied to the disc shaped specimens using 5 mm diamond drills with 710 rpm drilling rate under water cooling and uncontrolled load. The experimental procedure is summarized in Fig. 1. The glass compositions with no additive, 1 and 2 wt% $TiO_2$ additions have designated as T0, T1 and T2, respectively.

## Results and discussion

### DTA analysis

DTA curves of the T0, T1 and T2 glasses are shown in Fig. 2. According to the results, all compositions showed double endothermic peaks indicating the formation of phase separation. The glass transition and crystallization temperatures of the glasses are listed in Table 2. According to the DTA curves, $TiO_2$ addition decreased the glass transition temperature of the glasses, and further decrease of $T_g$ was observed when $TiO_2$ content increased. This could be attributed reducing of the number of bridging bonds in the silica-

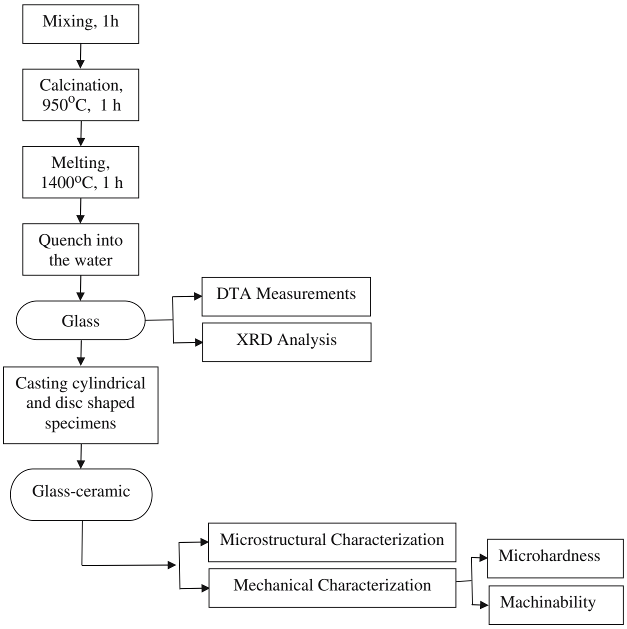

**Fig. 1** Flow chart of the experimental studies

**Table 1** Compositions of glasses (in wt%)

| Glass | Components (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | MgO | CaO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $K_2O$ | $CaF_2$ | $TiO_2$ |
| T0 | 20.09 | 5.68 | 8.47 | 29.92 | 12.67 | 7.89 | 15.28 | – |
| T1 | 19.90 | 5.63 | 8.40 | 29.63 | 12.55 | 7.76 | 15.13 | 1.00 |
| T2 | 19.69 | 5.58 | 8.31 | 29.33 | 12.43 | 7.67 | 14.99 | 2.00 |

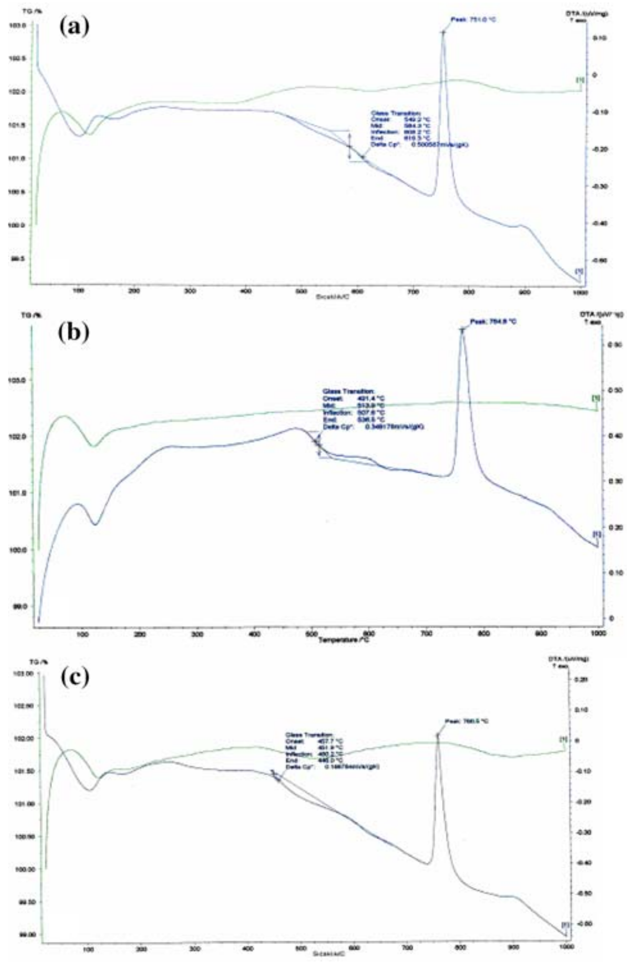

**Fig. 2** DTA curves for (**a**) no additive glass; (**b**) glass with 1 wt% $TiO_2$ addition; (**c**) glass with 2 wt% $TiO_2$ addition

based network and leading to a decrease of the viscosity and glass transition temperature [16]. On the other hand, addition of $TiO_2$ did not have a significant effect on the crystallization temperatures of the T1 and T2 glasses (Fig. 2).

## XRD analysis

The glasses were subjected to heat treatment according to the DTA results and X-ray diffraction analyses were applied to characterize phase precipitation sequence and identification of phases. The XRD patterns and the crystallization sequences of the identified phases by XRD are shown in Fig. 3 and Table 3, respectively. Heat treatment procedures were performed according to the evaluation of DTA results and XRD analysis. In case of composition without additive, nucleation occurred at 590 °C for 1 h and crystallization process took place at 755 °C for 15 min and 2 h when compositions do not contain any nucleating agent. It was observed that amorphous phase exists after heat treatment at 590 °C. In addition, some fluorapatite peaks appeared at 590 °C as a result of the surface crystallization of fluorapatite. When the T0 specimen was heated at 755 °C, potassium mica (JCPDS, 16-0352) and fluorapatite (JCPDS, 15-876) appear in XRD patterns (Fig. 3a). According to the results, it

**Table 2** Glass transition ($T_g$) and crystallization temperatures ($T_c$) of glasses

| | Glass | | |
|---|---|---|---|
| | T0 | T1 | T2 |
| $T_g$ (°C) | 584 | 514 | 452 |
| $T_c$ (°C) | 751 | 765 | 761 |

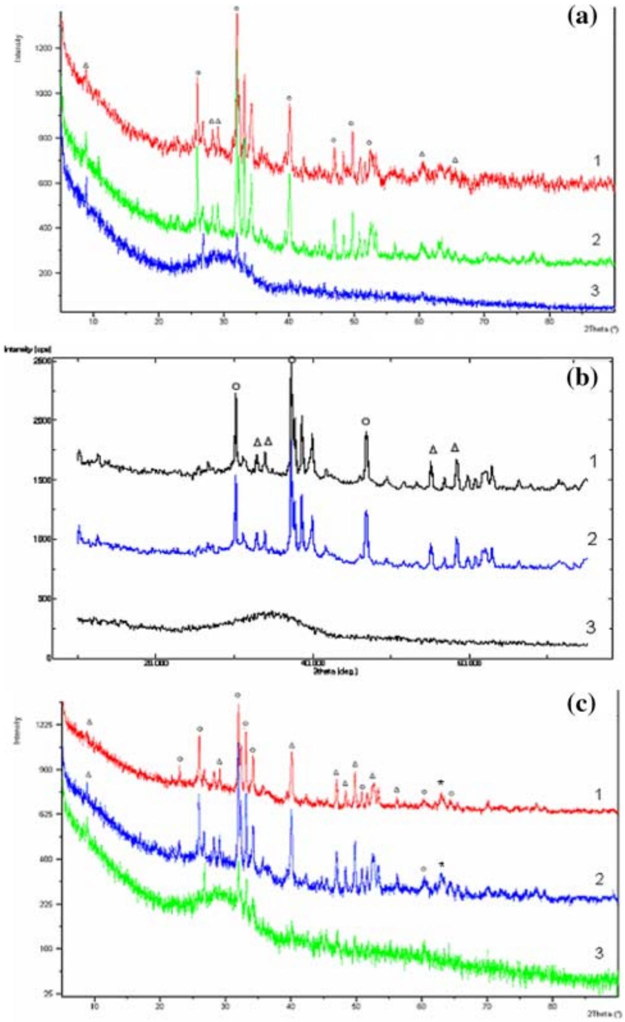

**Fig. 3** XRD results for (**a**) no additive specimen (1) 590 °C/1 h + 755 °C/2 h, (2) 590 °C/1 h + 755 °C/15 min, (3) 590 °C/1 h; (**b**) T1 specimen (1) 520 °C/1 h + 770 °C/2 h, (2) 520 °C/1 h + 770 °C/15 min, (3) 520 °C/1 h; (**c**) T2 specimen (1) 460 °C/1 h + 765 °C/2 h, (2) 460 °C/1 h + 765 °C/15 min, (3) 460 °C/1 h. Δ, K-Mica, ○, fluorapatite, *diopsite

**Table 3** Crystalline phases of samples at various heat treatment conditions

| Glass Type | Treatment | Crystalline phases |
|---|---|---|
| T0 | 590 °C/1 h | Glass |
| | 590 °C/1 h + 755 °C/15 min | Potassium mica, fluorapatite |
| | 590 °C/1 h + 755°C/2 h | Potassium mica, fluorapatite |
| T1 | 520 °C/1 h | Glass |
| | 520 °C/1 h + 770 °C/15 min | Potassium mica, fluorapatite |
| | 520 °C/1 h + 770 °C/2 h | Potassium mica, fluorapatite |
| T2 | 460 °C/1 h | Glass |
| | 460 °C/1 h + 765 °C/15 min | Potassium mica, fluorapatite |
| | 460 °C/1 h + 765 °C/2 h | Potassium mica, fluorapatite, diopsite |

was observed that, potassium mica and fluorapatite were crystallized simultaneously at 755 °C. For T1 glasses, the XRD results of glasses nucleated at 520 °C for 1 h showed an amorphous structure (Fig. 3b, curve 3). The T1 glasses were heated at 520 °C for 1 h and then crystallized at 770 °C for 15 min and 2 h. It was observed that, the sample was amorphous after heat treatment at 520 °C for 1 h and potassium mica and fluorapatite were crystallized simultaneously at 770 °C. As a result of XRD analysis at nucleation temperature (460 °C) for T2 glasses, fluorapatite peaks at low intensities were also observed (Fig. 3c, curve 3). This indicated that surface crystallization at the nucleation temperature for this composition. From XRD results of T2 glasses, as a result of crystallization heat treatments at 765 °C for 15 min and 2 h, crystallization of diopside (JCPDS, 82-0599) was observed.

## Microstructural characterization

Glass ceramics with having 3:7 weight ratio of fluorapatite ($Ca_5(PO_4)_3F$) to potassium mica ($K_2Mg_3AlSi_3O_{10}F_2$) were prepared by applying controlled heat treatment according to the DTA and XRD results. The cylindrical shaped samples were prepared and selected contolled heat treatments were applied for microstructural characterization. The controlled heat treatment programme is given in Table 4.

**Table 4** Controlled heat treatment programme

| | Glass type | | |
|---|---|---|---|
| | T0 | T1 | T2 |
| Nucleation temperature (°C) | 600 | 520 | 460 |
| | 610 | 530 | 470 |
| Crystallization temperature (°C) | 770 | 770 | 770 |

The microstructural characterization of glass-ceramics was carried out by using JEOL JSM-7000F field emission gun electron microscope (Figs. 4 and 5). The microstructure of T0 glass ceramics heated at 610 °C for 1 h and 770 °C for 4 h was shown in Fig. 4a. In this micrograph, average size of mica crystals with 4 µm having an interlocking microstructure. On the other hand microstructure of T1 glass-ceramics did not show such an interlocking microstructure. In the microstructures of T1 and T2, fluorapatite phases surrounded the mica crystals instead of interlocking microstructure. For T1 sample, the size of the mica crystals was approximately 7 µm. In the specimens containing 2 wt% $TiO_2$, crystallized at 770 °C, mica crystals with size of 5 µm were surrounded with fluorapatite.

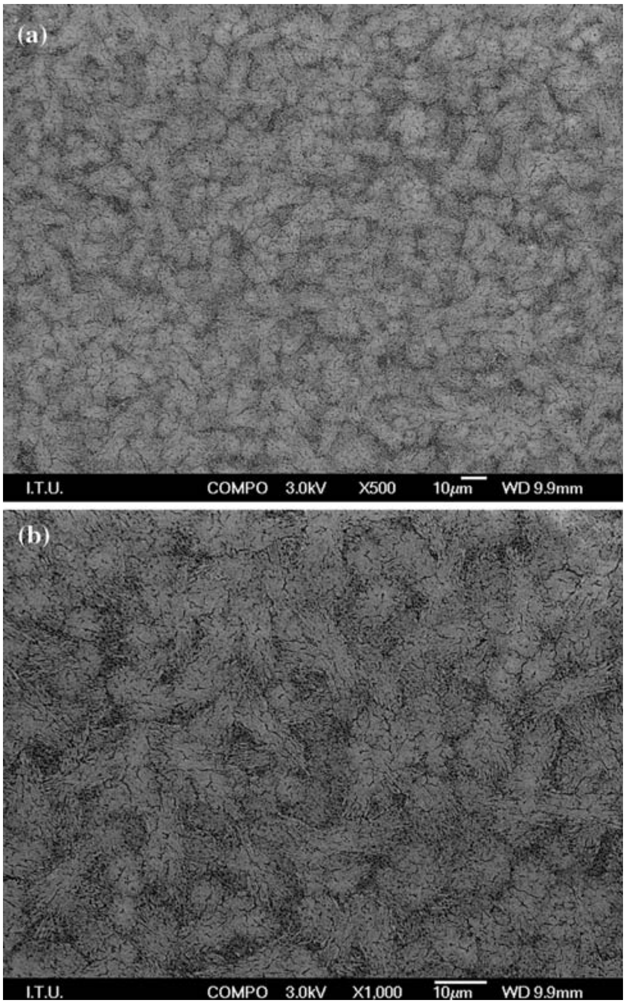

**Fig. 4** SEM micrographs of no additive (T0) specimen, nucleated at 610 °C for 1 h and crystallized at 770 °C for 4 h, (**a**) ×500 magnification; (**b**) ×1,000 magnification

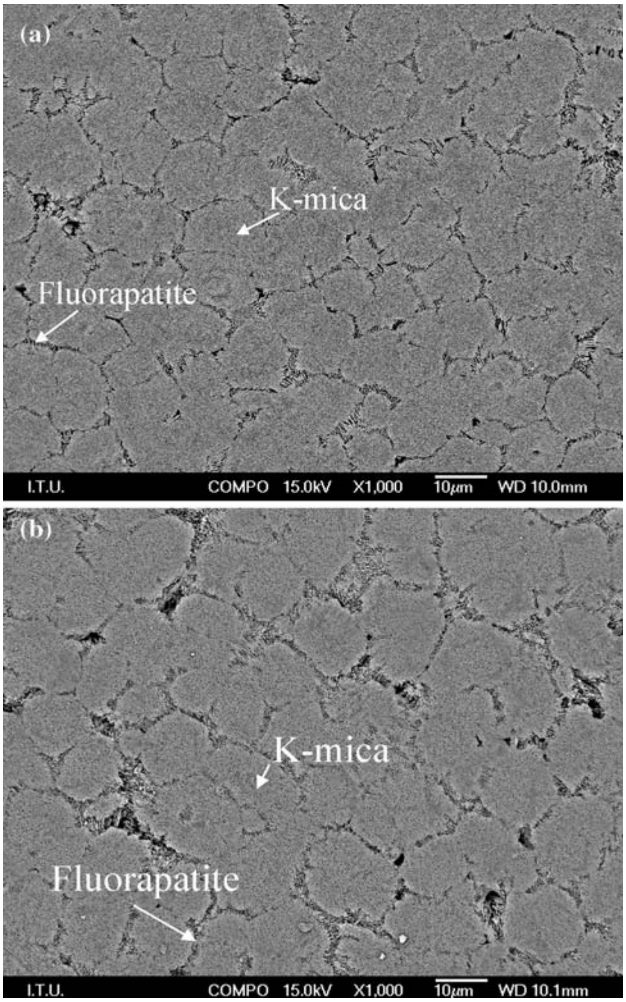

**Fig. 5** SEM micrographs of (**a**) T1 specimen nucleated at 530 °C for 1 h and crystallized at 770 °C for 3 h; (**b**) T2 specimen nucleated at 470 °C for 1 h and crystallized at 770 °C for 4 h

## Mechanical characterization

Microhardness of the samples is a key parameter for machinability of the glass ceramics. The overall Vickers hardness results are given in Figs. 6–8 and Table 5.

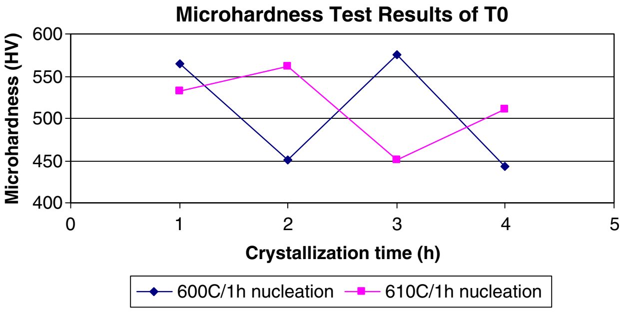

**Fig. 6** Microhardness test results of T0 glass ceramics nucleated at 600, 610 °C for 1 h and crystallized at 770 °C for 4 h

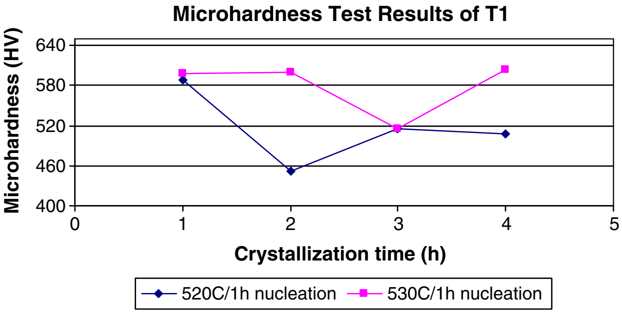

**Fig. 7** Microhardness test results of T1 glass ceramics nucleated at 520, 530 °C for 1 h and crystallized at 770 °C for 4 h

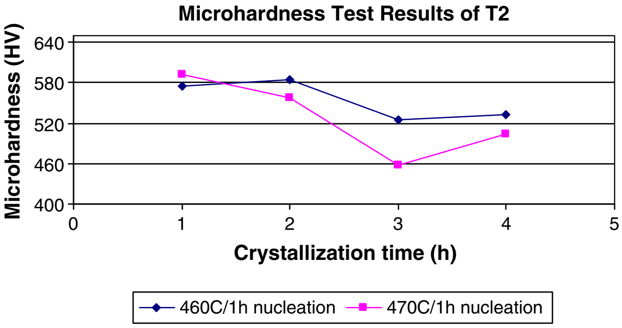

**Fig. 8** Microhardness test results of T2 glass ceramics nucleated at 460, 470 °C for 1 h and crystallized at 770 °C for 4 h

According to the microhardness test results, the proper controlled heat treatment process for machinability of T0 glass ceramics was determined as nucleated at 610 °C for 1 h and crystallized at 770 °C for 4 h. The change in microhardness value depending on the nucleation and crystallization temperatures is given in

**Table 5** Microhardness (HV) values of T0, T1 and T2 glass-ceramics

| | Heat treatment programme | Average microhardness |
|---|---|---|
| T0 | 600 °C/1 h + 820 °C/1 h | 565.20 |
| | 600 °C/1 h + 820 °C/2 h | 451.42 |
| | 600 °C/1 h + 820 °C/3 h | 575.55 |
| | 600 °C/1 h + 820 °C/4 h | 443.71 |
| | 610 °C/1 h + 820 °C/1 h | 531.68 |
| | 610 °C/1 h + 820 °C/2 h | 561.16 |
| | 610 °C/1 h + 820 °C/3 h | 450.09 |
| | 610 °C/1 h + 820 °C/4 h | 511.28 |
| T1 | 520 °C/1 h + 770 °C/1 h | 588.19 |
| | 520 °C/1 h + 770 °C/2 h | 451.42 |
| | 520 °C/1 h + 770 °C/3 h | 516.02 |
| | 520 °C/1 h + 770 °C/4 h | 507.91 |
| | 530 °C/1 h + 770 °C/1 h | 598.37 |
| | 530 °C/1 h + 770 °C/2 h | 599.58 |
| | 530 °C/1 h + 770 °C/3 h | 514.59 |
| | 530 °C/1 h + 770 °C/4 h | 604.71 |

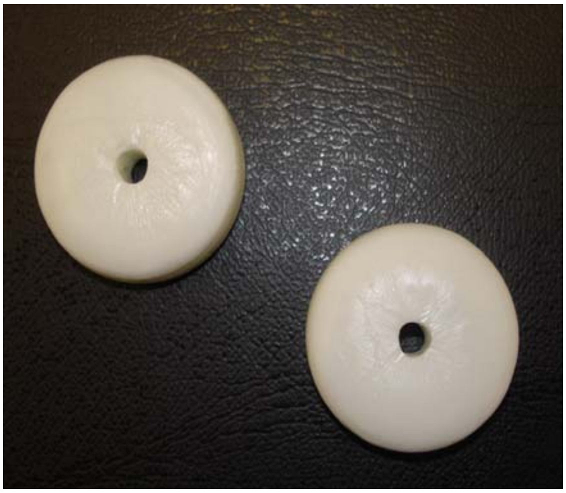

**Fig. 9** Hole drilled in samples after machinability test

Fig. 6. For T1 composition, the proper nucleation and crystallization heat treatment process was determined as nucleation at 520 °C for 1 h and crystallized at 770 °C for 3 and 4 h. In addition, nucleation at 530 °C for 1 h and crystallized at 770 °C for 3 h was selected another proper controlled heat treatment process. Disc shaped specimen of T2 was heated at 470 °C for 1 h for nucleation and crystallized at 770 °C for 4 h.

The machinability of heat treated disc shaped specimens of each composition was tested and compared with each other. The drilling tests were applied using a 5 mm diamond drill operating at 700 rpm with cutting fluid (water) under uncontrolled load.

The disc shaped sample of T0 glass ceramic that nucleated at 610 °C for 1 h and crystallized at 770 °C for 4 h showed excellent machinability and a 10 mm thick hole was drilled successfully without cracking in 3.5 min. The disc shaped samples of T1 glass ceramics that nucleated at 520 °C for 1 h and crystallized at 770 °C for 3 and 4 h showed excellent machinability and completely a 10 mm thick hole was drilled without cracking in 4.5 and 7 min, respectively. Also, the sample heat treated at 530 °C for 1 h and crystallized at 770 °C for 3 h had excellent machinability and drilled in 3.5 min. For T2 glass ceramics, disc shaped samples that heat treated at 470 °C for 1 h and 770 °C for 4 h showed excellent machinability and drilled a 10 mm thick hole in 3.5 min. According to the results, it was observed that, the drilling time of the samples show variation according to the microstructure and mechanical properties of the glass-ceramics. The machined samples are shown in Fig. 9.

## Conclusion

Although the addition of $TiO_2$ as a nucleating agent decreases the glass transition temperature of the glasses, it does not have any significant effect on the crystallization temperature of the glasses. Addition of $TiO_2$ has an effect on the microstructural morphology as well. It is observed that, the glass-ceramic specimen without additive has an interlocking microstructure whereas the glass-ceramics containing 1 and 2 wt% $TiO_2$ have larger mica crystals that surrounded by fluorapatite. All three glass ceramics have excellent machinability but the lowest crystallization time can be obtained by using 1 wt% addition of $TiO_2$. It can be concluded that, the optimum nucleation agent addition for glass ceramics with having 3:7 weight ratio of fluorapatite ($Ca_5(PO_4)_3F$) to potassium mica ($K_2Mg_3AlSi_3O_{10}F_2$) is addition of 1 wt% $TiO_2$.

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