The Effect of Zirconia Addition on Crystallization Behaviour and Machinability of Potassium Mica and Fluorapatite Glass-Ceramics

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ABSTRACT

Machinable bioactive glass-ceramics containing microcrystalline phases of mica and apatite can be considered as new materials for bone implants and substitutes in human body. Such a glass-ceramic has a better machinability than others due to the large amount of layered mica phase which is oriented randomly and distributed uniformly in glass matrix. Consequently, it is easier to process mica-based glass-ceramics into surgical parts with different complex shapes by using normal clinical machining methods. The purpose of this study is to investigate the crystallization behavior and mechanical properties of machinable glass ceramics having 3:7 weight ratio of fluorapatite ($Ca_5(PO_4)_3F$) to potassium mica ($K_2Mg_3AlSi_3O_{10}F_2$) as a function of zirconia addition, as nucleating agent. Glass compositions were prepared and casted at proper temperatures. Differential thermal analysis (DTA) 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. FE-SEM was used to characterize variation of microstructural constituents depending on the amount of nucleating agent.

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1. INTRODUCTION

The glass ceramics containing mica phase have been widely used in orthopedic and dental applications, especially in the replacement of natural bone and dental restorations /1-2/. These materials have higher mechanical strength, toughness, refractory properties and lower thermal expansion coefficient than glasses. Main advantages of glass ceramics are; their resistance to the chemical effects and wear resistance at high temperatures when compared with metals, and as implants, their lower density than metals /1-3/. Mica containing glass ceramics provide machinability, so they can be machined, drilled, cut or scratched by using normal metalworking tools. The excellent machinability of mica based glass ceramics results from the cleavage of interlocking layers of mica crystals precipitated in the glass matrix. The precipitated mica phase must constitute more than two-thirds of the total volume for an effective machinability /4-7/. For a material to be machinable and bioactive, it should contain both mica and apatite crystals. Apatite crystals provide biocompatibility and bioactivity of the glass ceramics.

In the production of glass ceramics, nucleating agents such as ZrO_2, TiO_2 or P_2O_5 can be used in order to induce bulk crystallization of the phases. Also these additions may decrease the crystallization time and temperature of the phases /8/.

Table 1
Compositions of the Z0, Z1 and Z2 glasses

Components (wt%)	Z0 (wt%)	Z1 (wt%)	Z2 (wt%)
SiO_2	29.93	29.63	29.33
MgO	20.10	19.90	19.70
CaO	5.69	5.63	5.58
K_2O	7.89	7.76	7.67
Al_2O_3	8.48	8.40	8.31
CaF_2	15.29	15.14	14.99
P_2O_5	12.68	12.55	12.43
ZrO_2	-	1.00	2.00

2. MATERIALS AND METHODS

The compositions of the SiO_2-MgO-P_2O_5-CaO-Al_2O_3-K_2O-F-ZrO_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 mass ratios of potassium mica ($KMg_3(AlSi_3O_{10}F_2)$) and fluorapatite ($Ca_{10}(PO_4)_6F_2$) and ZrO_2 was added as nucleating agent.

Initially, raw materials were mixed for 2 hours and then calcined at 1223 K. Calcined powders were melted in a sealed platinum crucible at 1673 K and then quenched into water. The glass granules were subjected to the differential thermal analysis (DTA). The DTA scan rate was selected as 10 K/min and glass powders were heated up to 1273 K. According to DTA results, heat treatment programme was determined as nucleation and crystal growth and applied to the glass compositions. Characterization of crystals precipitated from glass phase after heat treatment was carried out by using X-ray diffraction (XRD) analysis method. Rigaku Miniflex diffractometer was used by employing CuK_α radiation and in the 2θ range from 4° to 80°. Disc and cylindrical shaped samples were prepared by using casting method in order to determine microstructural and mechanical properties of the glass ceramics, the melted glass was poured into the preheated graphite moulds and the as-cast glasses were immediately put into in a furnace for annealing. After that, controlled heat treatment programme was applied for glass ceramic production. The glass ceramic samples after polishing and etching in 5% HF solution for 20-30 s, were coated with a thin film platinum and subjected to microscopic examination. Microhardness tests were applied to the polished samples under constant load of 1000 g with 12 s indentation time. Machinability tests were applied to the disc shaped specimens by using 3.5 mm diamond drills with 710 rpm drilling rate under water cooling and uncontrolled load. The glass compositions with no additive, 1, and 2 mass % ZrO_2 additions have designated as Z0, Z1 and Z2, respectively.

3. RESULTS AND DISCUSSION

3.1. DTA results

DTA curves of the Z0, Z1 and Z2 glasses are shown in **Figure 1**. According to DTA results, all glass compositions showed double endothermic peaks indicating the formation of phase separation. The glass transition (T_g) and crystallization temperatures (T_c) of the glasses are listed in **Table 2**.

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

	Glass		
	Z0	Z1	Z2
T_g (°C)	582	582	582
T_c (°C)	738	736	734

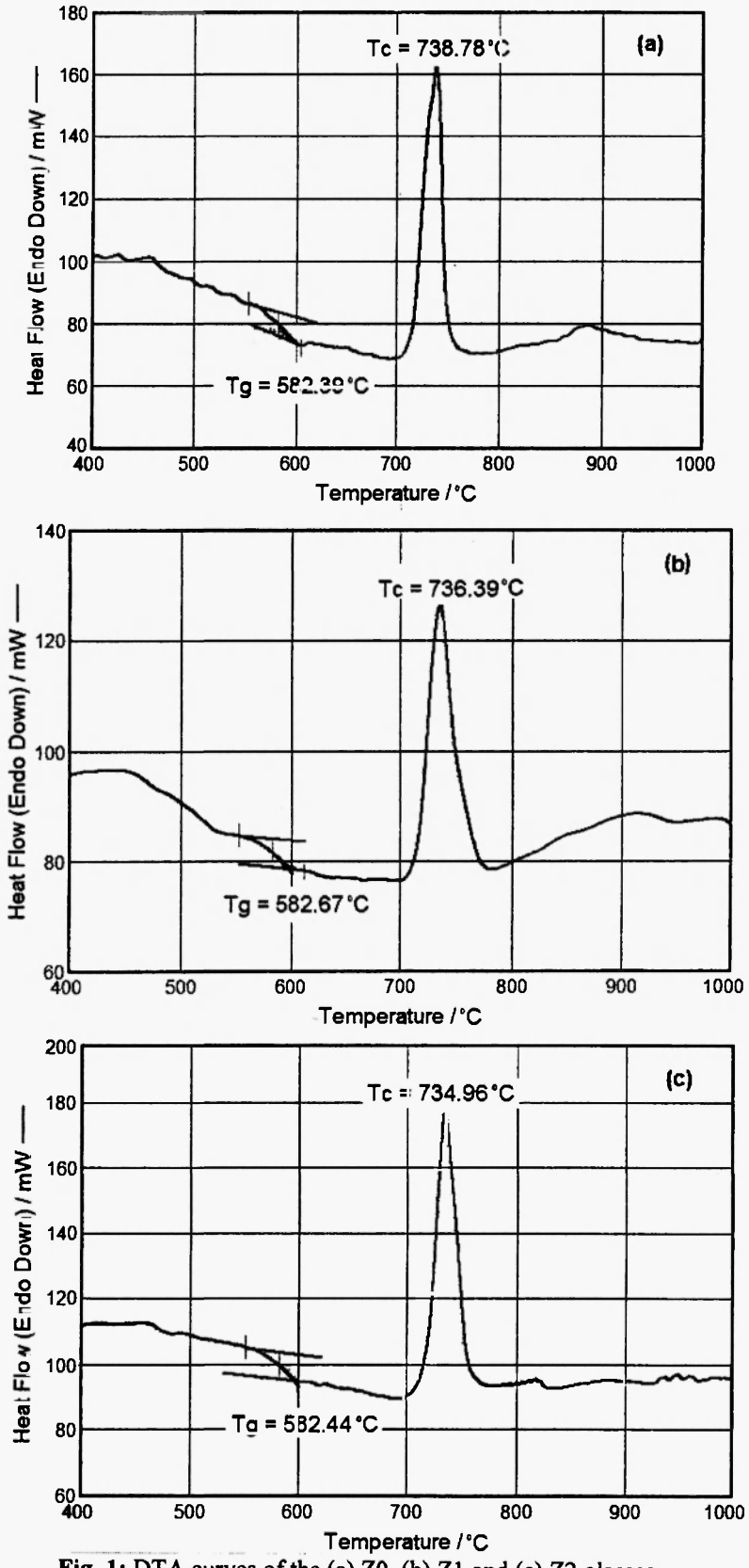

Fig. 1: DTA curves of the (a) Z0, (b) Z1 and (c) Z2 glasses.

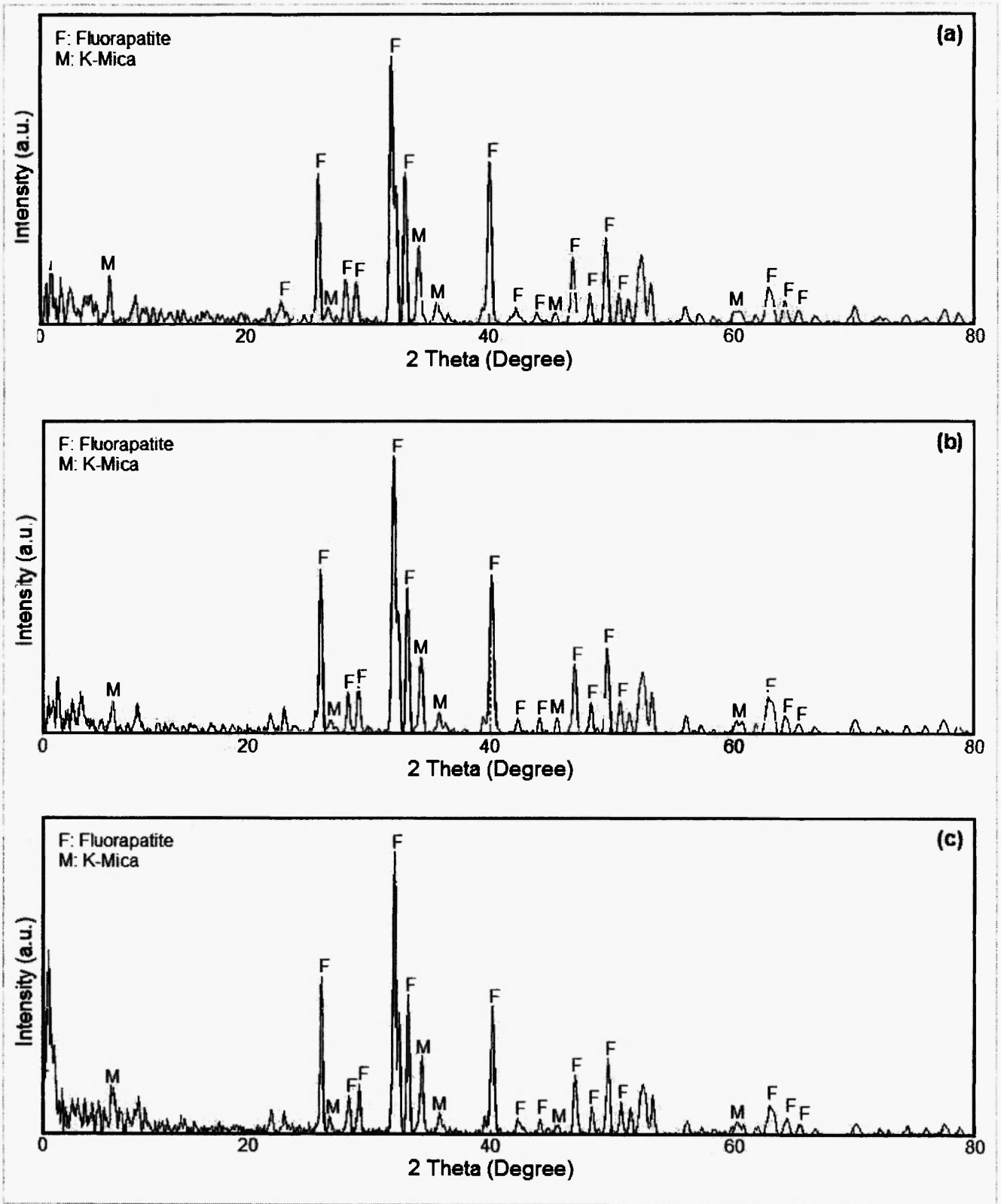

Fig. 2: XRD results for (a) no additive (Z0) specimen heat treated at 873K/1h and 1028K/1h, (b) Z1 specimen heat treated at 873K/1h and 1033K/1h, (c) Z2 specimen heat treated at 878K/1h and 1028K/900s.

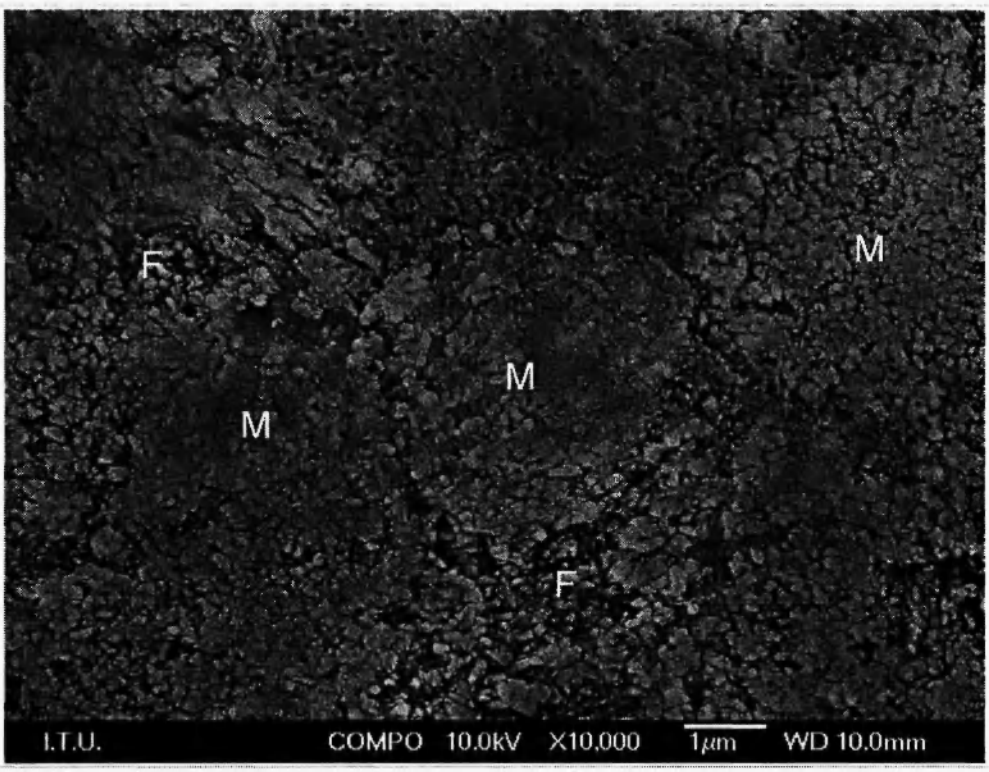

Fig. 3: SEM micrographs of no additive (Z0) glass ceramics nucleated at 873K for 1 h and crystallized at 1028K for 4 h.

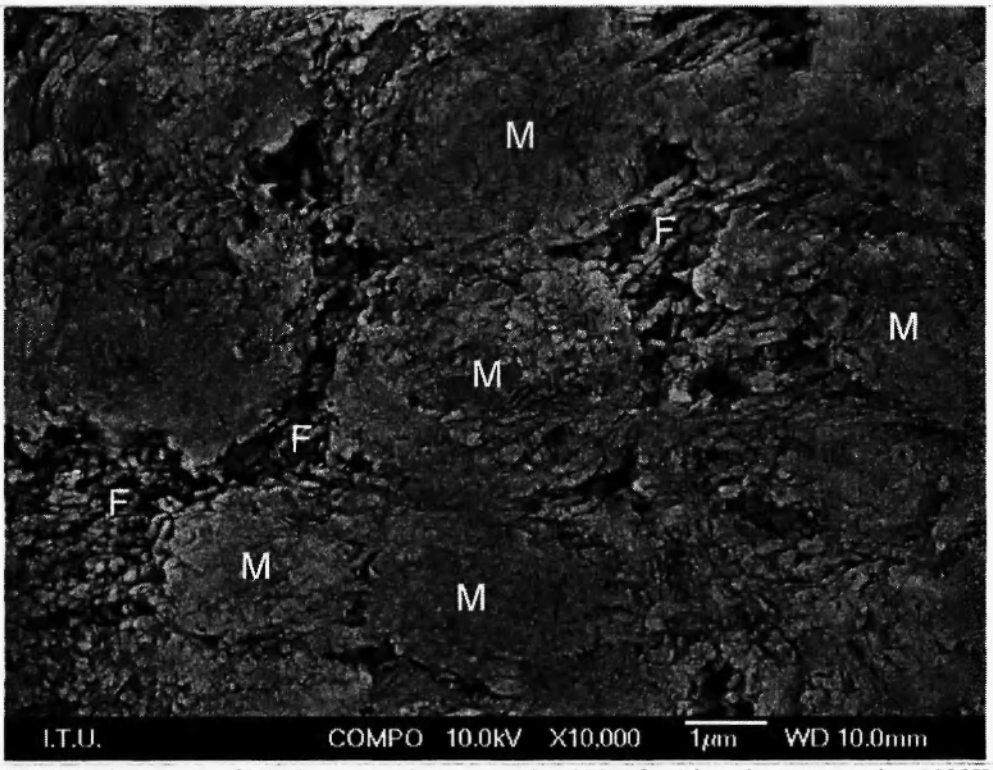

Fig. 4: SEM micrograph of Z1 glass ceramic nucleated at 873K for 1 h and crystallized at 1033K for 4 h.

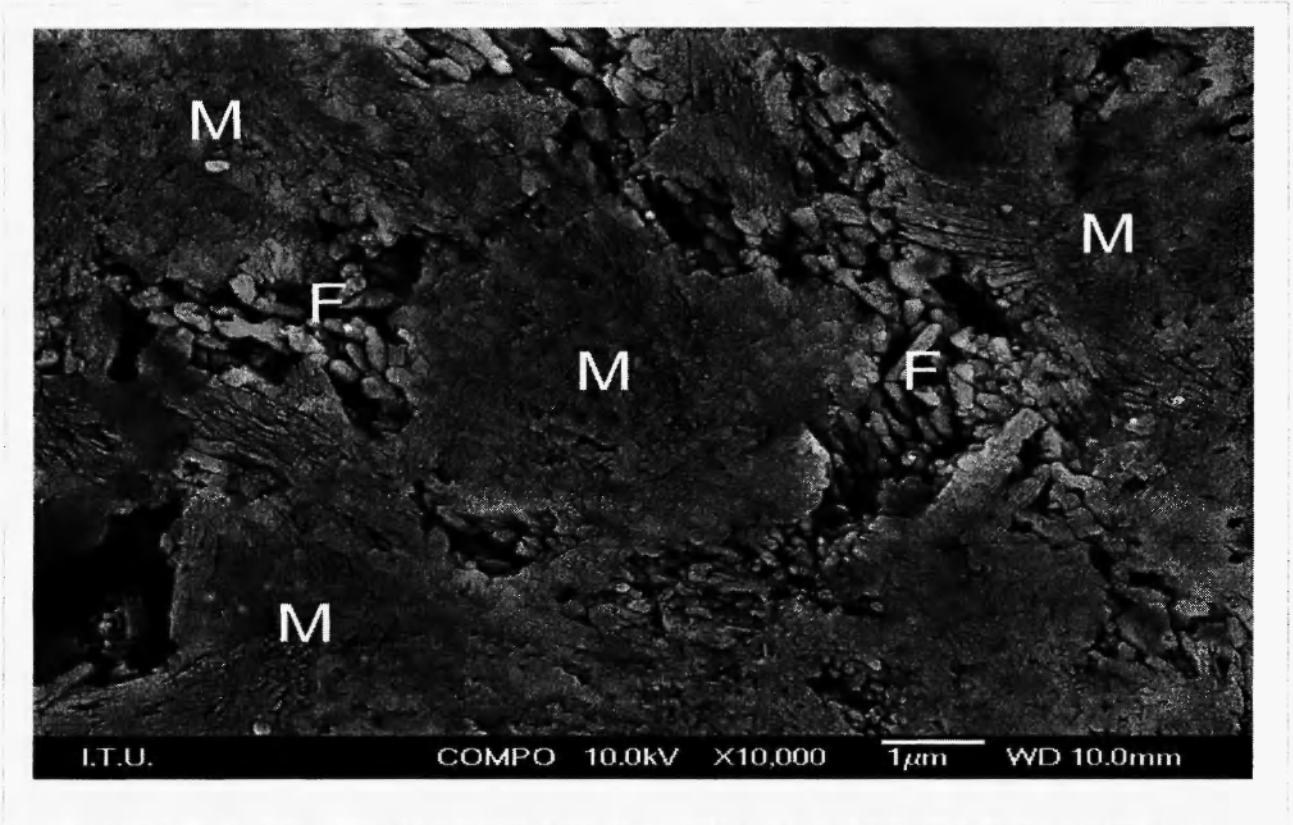

Fig. 5: SEM micrographs of Z2 glass ceramic nucleated at 878K for 1 h and crystallized at 1028K for 4 h.

According to the overall DTA results, ZrO_2 addition does not have a significant effect on glass transition temperature of the compositions.

3.2. XRD analysis

The phase constitutions of the Z0, Z1 and Z2 glass ceramics heat treated at different temperatures are shown in **Figure 2**. XRD diagram of the specimen which was heat treated for 1 hour at nucleation temperature (873K) and 1 hour at the crystallization temperature (1028K) of Z0 composition is given in **Figure 2.a**. Crystallization sequence of Z0 glass ceramic consists of a single step where precipitation of fluorapatite (JCPDS 15-0876) and potassium mica (JCPDS 16-0352) were maintained at the same time. The Z1 glasses were nucleated at 873 K for 1 hour and crystallized at 1033 K for 1 hour. According to XRD results, it was observed that, potassium mica and fluorapatite were crystallized simultaneously at 1033 K (**Figure 2.b**). When the Z2 specimen was nucleated at 878K for 1 hour and crystallized at 1028K for 900s, potassium mica and fluorapatite crystals appeared in XRD patterns (**Figure 2.c**).

3.3. Microstructural characterization

The cylindrical shaped samples were prepared and selected controlled heat treatment programme was applied for microstructural investigations. The microstructural characterization of Z0, Z1 and Z2 glass ceramics were carried out by using JEOL JSM-7000F field emission scanning electron microscope. The micrograph of Z0 glass ceramic nucleated at 873K for 1 h and crystallized at 1028K for 4 h are shown in **Figure 3**. In this micrograph, average size of mica crystals with 3-4 μm were surrounded by fluorapatite phase.

In the specimens containing 1 mass % ZrO_2, nucleated at 873K for 1 h and crystallized at 1033K for

4 h, it was observed that mica crystals with size of 3 μm were surrounded by fluorapatite (**Figure 4**).

For Z2 glass ceramics, nucleation and crystallization heat treatment was selected as 878K for 1 h and 1028K for 4 h, respectively. According to micrographs, fluorapatite phases surrounded the mica crystals. For Z2 sample, the size of mica crystals was approximately 3-4 μm (**Figure 5**).

3.4. Machinability testing

Disc shaped specimen of Z0, Z1 and Z2 glass ceramics were prepared for the machinability tests. The drilling tests were applied using 3.5 mm diamond drill operating at 710 rpm with cutting fluid (water) under uncontrolled load. The disc shaped sample Z0 glass ceramic that nucleated at 873K for 1 h and crystallized at 1028K for 4 h showed excellent machinability and completely 9 mm thick hole was drilled successfully in 540s. Z1 glass ceramic, nucleated at 873K for 1 h and crystallized at 1033K for 4 h, was drilled without cracking in 300s. Also, Z2 glass ceramic sample heat treated at 878K 1 h and 1028K for 4 h showed excellent machinability and drilled in 480s.

4. CONCLUSION

All three glass ceramics have excellent machinability but the lowest crystallization temperature can be obtained by using 2 mass % addition of ZrO_2. It can be concluded that, the optimum nucleation agent addition for glass ceramics with having 3:7 mass ratio of fluorapatite ($Ca_5(PO_4)_3F$) to potassium mica ($K_2Mg_3AlSi_3O_{10}F_2$) is addition of 2 mass % ZrO_2. At the end of the experimental studies, it can not be observed any significant effect on glass transition and crystallization temperatures of Z0, Z1 and Z2 glasses.

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