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Microstructural Design of Phlogopite Glass-Ceramics[1]

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Abstract—Fluorophlogopite glass-ceramics in the MgO–Al_2O_3–SiO_2 glass systems were crystallized by two stages thermal treatments. Obtained glass-ceramics were characterized by DTA, X-ray diffraction and scanning electron microscopy. The heat treated samples at 705°C/3 h + 1000°C/15 min showed 2570.32 ± 98 MPa microhardness. The effect of heat treatment and preparation methods on microhardness and microstructure were studied. The microstructure of samples showed phlogopite and forsterite phases and solved or soft edge in the semi-rod like crystals was recorded which can explain the small value of microhardness. The various microhardness were determined in the range between 1591.61 to 9610 ± 147 MPa.

Keywords: phlogopite glass-ceramic, microhardness, microstructure

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INTRODUCTION

Fluorophlogopite glass-ceramic, is the trademark for machineable glass-ceramic [1]. Recently, this material is favorable due to high use temperature, non-flammable, excellent electrical and thermal insulator and dimensionally stable. Fluorophlogopite glass-ceramic can be fabricated by melt-casting and sintering methods [2]. The comparison of the glass–ceramics specications, prepared by melt-casting and sintering methods displayed that, due to the surface crystallization of glass, the later method would be preferred from the viewpoint of crystallization and machinability [3]. But the complete densication of compacted glass powder is a problem, which should be considered, in the pressureless sintering method [4]. Also, high sintering temperature, caused by unwanted phases weakens the machinability of sample [5]. By introducing the effective disk-like crystals and forming a connected structure of crystals, the microhardness will be improved [6, 7].

According to Lee reports phase separation in as casted fluorophlogopite glass melt was a precursor to the crystallization of chondrodite which finally formed the fluorophlogopite plaths like crystals. The two-steps heat-treating of melted fluorophlogopite in his work, did not show the similar microstructure as commercial fluorophlogopite, mainly, consists of early-formed fluorophlogopite. Some fully-formed fluorophlogopite has stacking faults in their crystal system [8].

Other attempts were focused on the TiO_2 effects [9]. They revealed that by heat treating TiO_2 was separated at $T \geq 900°C$ and mica in the fine spherical particles became plate-like. Particularly, a large amount of fine TiO_2 particles surrounded the mica uniformly, which was very effective in the deterrence of disintegration.

In this work, the common fluorophlogopite type composition, which has TiO_2 as a catalyst was prepared. In order to reach the microstructure with lowest microhardness and subsequently high machinability, the details of the two-steps heat treating regarding to heat-treating rate, samples size, casted and sintered form and related microstructures have been studied. This type of microstructure in phlogopite has not been studied before, the reported microhardness of published papers pointed to <5 GPa.

EXPERIMENTAL TECHNIQUE

The glass composition was prepared according to Table 1. The raw materials of glass were, K_2CO_3 (Merck Art No. 7734, Germany), $MgCO_3$ (Merck Art No. 5828, Germany), Al_2O_3 (Merck Art No. 5550, Germany), MgF_2 (Merck Art No 7783-40-6, Germany), TiO_2 (CAS Number 13463-67-7, UK) and pure optical grade silica (Azandarian Mining Company, Iran), were melted in an electric furnace in a platinum crucible at the temperature range of 1400 to 1450°C for 1–2 h. The resulting melt was quenched in cold distilled water. The fluorine loss was 50 % according to wet chemical analysis. The obtained frit was ground in an agate mortar then sieved to give ne

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Table 1. The nominal composition of studied glass in wt %

Oxides	SiO_2	Al_2O_3	B_2O_3	K_2O	MgO	TiO_2	F^-
wt %	35	14	12	6	21	5	14

(<45 μm) frits. The obtained fine frit was applyed for subsequent use in DTA analysis. DTA analysis (Netzsch 320, Germany) which was utilized to determine the crystallization temperature of glass, was performed using 6 mg of glass powders in an alumina crucible in air at a heating rate of 10°C/min. Alumina was used as an inert reference material. The frit was mixed with 2.5 wt % polyvinyl alcohol as a binder and pressed into 79 × 30 × 5 mm bars at a pressure of 100 MPa using a laboratory uniaxial hydraulic press (home made). In order to make the casted bulk form samples, the glass melts were poured into a graphite mold. Diameter of mold was 35 mm and height was 50 mm. The resulted ingot was cut in to small disk for thermal treatment. The samples were annealed at 550°C for 1–2 h. Then the glass was cooled with 20°C/h rate. The crystallizations steps were carried out in a programmable vertical tubular furnace. The heat treatments were performed at 650, 705, 760, 950 and 1100°C for 1 h, with 20°C/min heating rate. Some sample (30 × 50 mm) heat treated at 10°C/min to avoid possible temperature gradient.

The relative densities were measured by dividing the Archimedes bulk density to powder form of samples.

The thermal expansions measurements were conducted in a dilatometer (model Nietzsche-E402, Germany) using a silica probe. The heating rate was kept at 10°C/min for all measurements. The rod shape sample was (20 × 5 mm) with flat ends. The samples were kept in a quartz holder with a constant load of 5 g for all measurement. The thermal expansion coefficient (TEC) was measured in the temperature range of 30–800°C. Alumina was used as material for correction of holder expansion.

The microhardness of the samples was measured by indentation technique using Vickers indenter (model MVK-H21). The measurement was done by applying a 100 g load for 15 s. It was taken the average of 10 measurements. Before measurements, the sample surface was polished with 3 μm alumina powder to get good reflective surface. Machinability was assayed by measuring the time required to drill holes with 6 mm depth using a 2.5 mm carbide masonry bit in a drill press operating at 790 rpm applying a load of 10 N [5].

Scanning electron microscopy (SEM) (JEOL JXA-840) was used in order to observe the microstructure and EDX analysis. Samples were mounted onto the sample holder, coated with gold, and then studied with SEM.

Crystalline phase identification was performed on powder made from ground sintered pellets, using X-ray diffraction (Philips Power Diffractometer 1710) with Ni-filtered CuK_α-radiation and the relevant JCPDS cards (Joint Committee on Powder Diffraction, 1972).

RESULTS AND DISCUSSION

After DTA and dilatometry tests (Figs. 1a, 1b respectively), four characteristic temperatures, i. e. T_g = 578°C, T_{p1} = 820°C, T_{p2} = 906°C, T_d = 677°C were detected which followed by heat treating.

Figure 2 shows the XRD patterns of samples heat-treated at DTA peaks. According to this figure when the sample heated at 820°C the main phase was MgF_2. At 906°C phlogopite evidently appeared, and forsterite crystalized at 916°C The result obtained in our work is in agreement with others studies [10]. It is believed that the MgF_2 has an important effect on the formation of phlogopite phase. The fluorine loss of

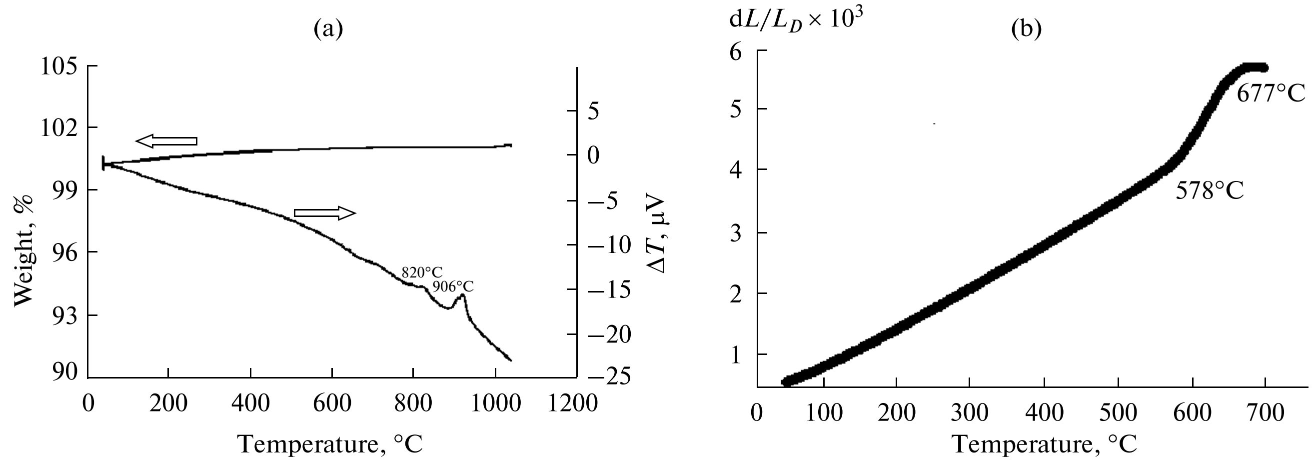

Fig. 1. (a) DTA trace of studied phlogopite; (b) dilatometer result of studied fluorophlogopite type glass T_g = 578°C, T_g = 677°C.

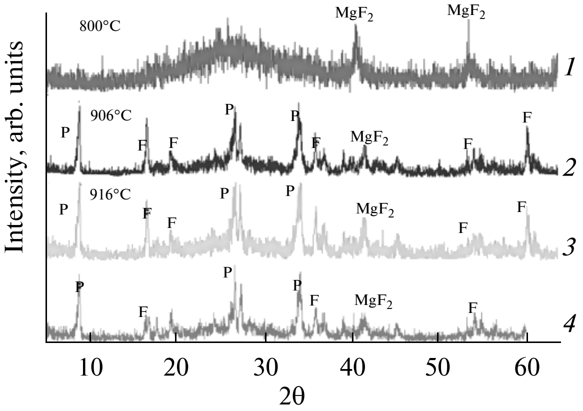

Fig. 2. The XRD results of heat treated samples at 800°C, 906°C, 916°C and 650–916°C by 10°C/min at 2 h. F—forsterite, P—phologopite.

glass composition can be resulted in magnesium and silicon rich phase corresponds to forsterite formation which has been reported before [11].

The nucleation temperature range was between T_g and T_d, which 650°C was considered as nucleation temperature. Then nucleation was followed by growth at 916°C. Heat treating at 650°C/3 h + 916°C/3 h were completed and the resulted microstructure was presented in Fig. 3.

In Fig. 3, the cubic and some needle like crystals were distinguished, but the sample was not machinable practically. Apparently, the needle like crystals cannot satisfy the machinability. Since TiO_2 has a barrier role in growth of crystals [9, 12], then the growth temperature at 1000°C, for (15 min) was performed. It was shown that, forsterite formation in this type of glass-ceramic at higher temperatures caused to high microhardness [13, 14], degraded the machinability, then the heating duration was decreased.

Figure 4a represents the micrograph of heat-treated sample, at 760°C/1 h + 1000°C/15 min, with 20°C/min heating rate. The house of cards and plate like crystals with sharp edges and considerable porosities among crystals are obvious. The flattened crystals are indicated to the forsterite as proved by [15]. The same arranges of crystals are seen in sample (Fig. 4c) which was heat treated at 705°C/3 h + 1000°C/15 min, but the sharpness of plate like crystals and porosity were decreased.

The densities of samples at different nucleation temperatures and induction time are presented in Fig. 5. As it can be seen, although the density of sample at 760°C/6 h + 1000°C 15 min was 95% of theoretical density, but the microhardness of this sample was not desired (Table 2).

On the other hand, the more porosities in Figs. 4a, 4c can be a sign of excess grain growth. The long crystals by different TEC and densities produce mismatch with the residual glass and caused to porosities formation.

Although the elongated crystals are wanted to deflect the crack growth, but due to the porosities, the machinability of this system was degraded.

On the base of microhardness and microstructure relation, the microhardness of glass-ceramics was compared in Table 2. Apparently, according to microhardness and machinability, relation, the resulted microhardness are above 2 GPa, and the found structures are not machinable However, in Fig. 4d, the edges of crystals, were not dissolved and distinguished sharply, but Fig. 4b shows some solved and soft edge in the case of semi-rod like crystals. This phenomenon, may explain the small value of latter sample's microhardness [16]. It is well known that, in these glass-ceramics, machinability arises due to the cleavable nature of mica crystals, which also deflect propagating cracks along the glass-crystal interface. A crack is blunted or localized within an interlocked crystal area. It can be concluded that, the energy absorbed in indentation (test) was increased with growing rounded edges phlogopite crystals or it can be said that the sharp edges of crystals caused to stress which

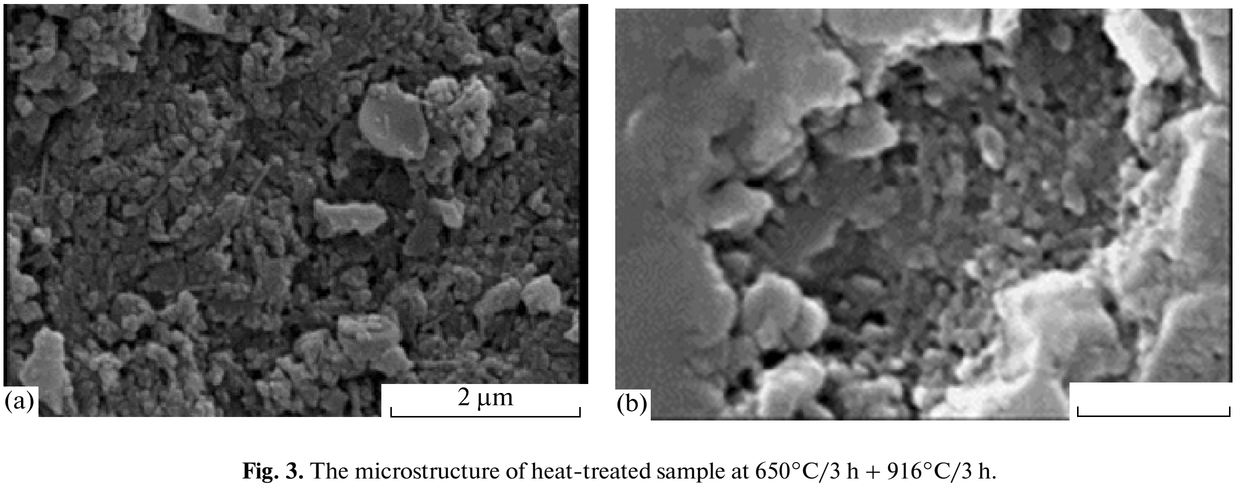

Fig. 3. The microstructure of heat-treated sample at 650°C/3 h + 916°C/3 h.

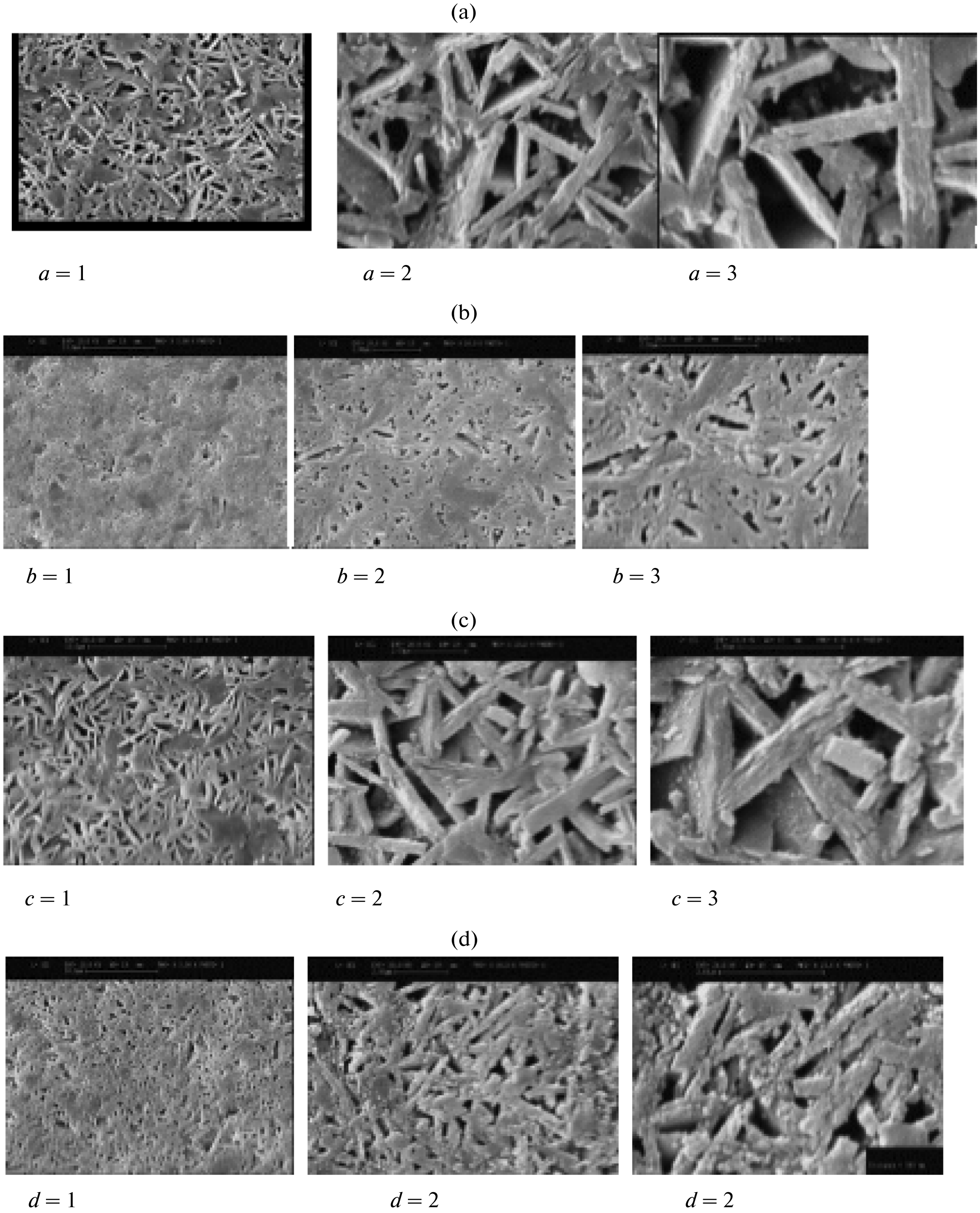

Fig. 4. The SEM micrograph of sample: a—760°C/1 h + 1000°C/15 min, b—760°C/3 h + 1000°C/15 min, c—705°C/3 h + 1000°C/15 min, d—705°C/6 h + 1000°C/15 min.
Magnification × (1) 2000, (2) 5000, (3) 10000.

decreased the machinability. Evidently, the sample, heat-treated at 705°C/6 h + 1000°C/15 min has lowest hardness (2570.32 MPa). Therefore, the high nucleation time in the heat treatment procedure, caused to high densities of nucleated phases, but the morphologies of these crystals will grow in a round edges shape. By long growth induction time, the machinibality of the samples was degraded inherently. The increase of hardness attributed to the decomposition of phlogopite [11] and forsterite formation.

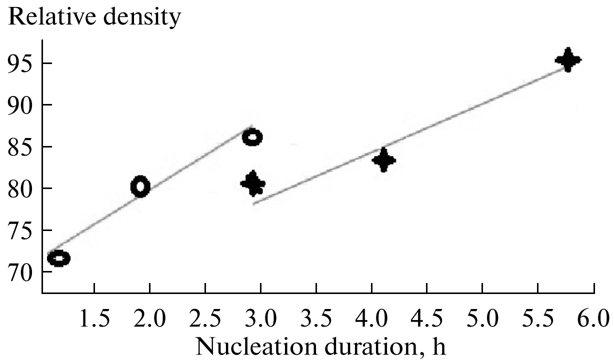

Fig. 5. The relative density of nucleated-growth samples to commercial glass as a function of nucleation step duration.

The high heating rate of 20°C/min for crystallization, has been mentioned in experimental procedure, would not practical for commercial samples. Therefore, the heating rate of large samples (30 × 50 mm) was changed to 10°C/min and the resulted microstructure presented. The microhardness of large sample at 705°C/6 h + 1000°C/15 min with 10°C/min heating rate was 4089.37 MPa. This value of microhardness is considerably higher than the microhardness of small size sample.

Apparently, the low heating rate in large glass-ceramics caused to the undesirable microstructures, which is related to forsterite (5 GPa) [17]. It can be concluded that, since the phlogopite crystals act as an insulator, the heat diffusion or absorption will be problematic in large samples, which need further analysis.

CONCLUSION

This attempt was to reach the desire fluorophlogopite in density and machinability points of view.

The nucleation and growth temperatures of casted phlogopite glass-ceramics were studied using DTA analysis. Two nucleation temperatures were taken at 705 and 760°C followed by growth at 1000°C. The optimum nucleation temperature was elected by comparing the SEM, Micro hardness and machinability results. The samples with low porosity and low microhardness were objective.

It was shown that, the high temperature and long period of heat treating, caused to forsterite formation, although this phase formation, will caused to high

Table 2. The microhardness of two-steps heat treated glass-ceramics at different conditions

Sample code	Nucleation + growth temperature (20 °C/min heating rate)	Microhardness, MPa
1	650°C/1 h + 916°C/1 h	4187 ± 9
2	760°C/1 h + 1000°C/15 min	3775.5 ± 11
3	705°C/6 h +1000°C/15 min	2569 ± 8
4	760°C/1 h + 1000°C/1 h	4001.7 ± 20
5	800°C/8 h + 1000°C/15 min	5177.2 ± 9
6	800°C/1 h + 1000°C/15 min	3922.2 ± 22
7	800°C/20 min + 1000°C/15 min	3432.8 ± 13
8	800°C/1 h	5795 ± 8
9	800°C/1 h + 1000°C/15 min	6746 ± 9
10	800°C/10 min + 1000°C/15 min	6109 ± 11
11	760°C/3 h + 1000°C/4 h	3451 ± 12
12	760°C/3 h + 1000°C/1 h	3814.1 ± 10
13	760°C/3 h + 1000°C/15 min	3638.6 ± 17
14	760°C/3 h + 1000°C/3 h	3785.6 ± 3
15	760°C/3 h + 1000°C/5 h	3687.8 ± 9
16	760°C/6 h + 1000°C/2 h	3481.0 ± 11

density product, but the hardness of system will be increased.

Effect of growth induction time on phlogopite morphologies was studied. Some solved or soft edge in semi-rod like crystals was recorded, which can explain the small value of microhardness. Sample at 705°C/6 h + 1000°C/15 min has 2569 ± 8 MPa hardness.

The microhardness of large and small size sample were evaluated. It was shown that due to insulator nature of phlogopite crystals some temperature gradients caused to unwanted phases like forsterite in large size sample.

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