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Development of Machinable Glass-Ceramics Produced from Vermiculite

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In this study, machinable glass-ceramics were produced from vermiculite and K_2CO_3, SiO_2, Al_2O_3 and MgF_2 as additives by melting process. The starting materials were mixed together and milled in a mill with alumina ball for 2 h. The mixed powders were melted by aluminum crucible at 1500 °C. The melted glass was cast into graphite mold, and then it was exposed to crystallization heat treatment for glass-ceramic transformation. The glass-ceramic samples were characterized with X-ray diffraction analysis, scanning electron microscopy, mechanical tests such as hardness, fracture toughness and machinability test. The results indicate that machinability properties can be obtained from vermiculite based glass-ceramic with some additives.

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1. Introduction

Glass-ceramics which are polycrystalline materials were obtained by controlled crystallization heat treatment process from suitable glass. This process usually involves two stages, namely a nucleation stage and a crystallization stage. Glass-ceramics can be obtained from various sources, such as pure oxides, natural rocks, and industrial wastes (blast furnace, arc furnace, cupola furnace, flying ashes etc.). Vermiculite is a member of clay minerals, produced by the decompositions of micas and occurs as large crystals of mica-like habits [1]. Vermiculite was sporadically used for cordierite synthesis [2]. Silva Jr et al. used vermiculite to synthesize glass-ceramic [3]. Mica containing glass-ceramics is an important group of glass-ceramics because of their high machinability, which results in an increased versatility of the products and numerous possibilities of industrial application. It is clear that very high machinable precision in these materials can be achieved using regular high-speed tools [4]. Many researchers studied the system related SiO_2–Al_2O_3–MgO–K_2O–F glasses and Baik et al. defined that both microhardness and machinability increases with increased ratio of mica crystals [5–8].

In this study we tested machinability property of vermiculite based glass-ceramic with some additives like SiO_2, K_2Co_3 and Al_2O_3 for make easy to produce suitable glass and also fluorine source to obtain machinability.

2. Materials and equipment

In Table I the chemical composition of the vermiculite used in this study were given. It was provided from Organik Madencilik company in the Yıldızeli region of Sıvas, Turkey. SiO_2, K_2CO_3, Al_2O_3, and MgF_2 was added to vermiculite for obtaining both glassy and machinability properties. The starting powders were mixed by using an alumina ball mill at 250 rpm for 60 min in an alumina media. The mixture was sieved to a particle size fraction of 75 μm and then melted in the alumina crucible at 1500 °C for 1 h, and cast into the graphite mold. The bulk glass sample obtained from casting process were exposed to differential thermal analysis (DTA-TA Instrument Q600) for 1 h at heating rate of 10 °C/min for crystallization temperatures determination. Rigaku D-max 2200-type diffractometer with Cu K_α radiation was used to analyze X-ray diffraction (XRD). The microstructural examinations was conducted by using scanning electron microscopy (SEM-JEOL 6060). Energy-dispersive spectrometer (EDS) was used to provide elemental analysis. Hardness and fracture toughness values were performed with a Future-Tech FM 700 microindentation hardness tester. The indentation tests were carried out on polished cross-sectional coatings with loads of 100 g and 300 g for the hardness and fracture toughness measurements, respectively.

TABLE I

Chemical composition [wt%] of the vermiculite. l.o.i. — loss of ignition.

SiO_2	Al_2O	TiO_2	Fe_2O	Ca	Mg	K_2O	l.o.i.
39.49	17.06	2.78	11.98	2.58	18.91	5.67	1.53

3. Results and discussion

Figure 1 shows the phase analysis of the glass and glass-ceramic which was made from vermiculite and some additions. Before the crystallization procedure, there is not any crystalline peak in the XRD

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result. Fluorophlogopite $KMg_3(AlSi_3O_{10}F_2)$, phlogopite $KMg_3(AlSi_3O_{10}OHF)$, diopside $CaMgSi_2O_6$ and forsterite Mg_3SiO_4 in the glass-ceramic system after the crystallization. These phases are known for machinable glass-ceramics [9]. Mica structures include Mg^{2+}, Al^{3+}, Si^{4+}, F^- ions and a large alkali ion such as K^+ and Na^+, apart from these, some different components like Fe^{2+} and OH^- can be in these. Mica structures strongly exhibit excellent machinability due to their sheet structure; it provides different mechanical behavior depending on directions. While mica crystals have cleavage planes perpendicular to the *c*-axis regarding to weak bonding of alkali layers, fracture propagation across the basal plane of mica is more difficult [10]. There are different approaches about diopside phase crystallization; some of these theories are that precipitated mica crystals have a role as nucleating site of diopside phase regarding mica crystals are crystallized in lower temperatures than densification temperature of sintered glass-ceramic or Fe_2O_3 has similar nucleating site effect for diopside crystallization [9–11]. It is possible that diopside crystals occur on Fe_2O_3structures in the current study, Fe_2O_3 in vermiculite composition can cause this.

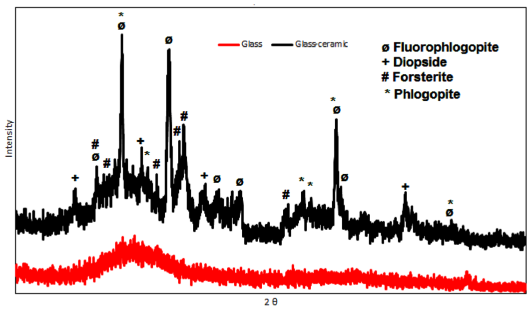

Fig. 1. XRD pattern of base glass and glass-ceramic.

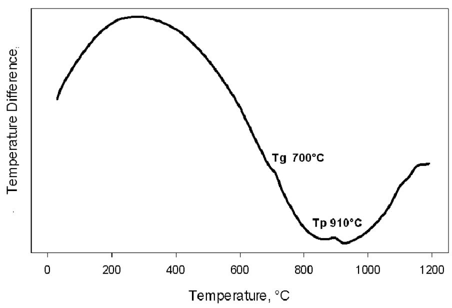

Fig. 2. DTA analysis of the vermiculite base glass.

Figure 2 explains DTA analysis of the vermiculite base glass, two strong peaks were determined on the results. One of them is endothermic at 700 °C and the other one is an exothermic at 910 °C, approximately. The first endothermic peak a 700 °C is glass transition temperature and the exothermic peak at 910 °C corresponds to crystallization temperature for the vermiculite base glass. The literature has reported that fluorophlogopite phase crystallizes from 800 °C to upper temperatures depending on composition [12, 13]. Diopside is major phase for CMAS glass-ceramic systems [14], its effective crystallization bands are from 900 °C to 1000 °C [15–17], depending on composition, it can crystallize at lower temperatures. The crystallization temperatures detected in DTA have good agreement with these temperatures.

Figure 3 shows SEM image of the vermiculite based glass-ceramic material. When mica crystals exhibit igneous and rod-like structures, diopside phases are seen as fibrous crystals in machinable glass-ceramic systems [9, 18]. Apart from these, another structure for mica crystals is plate-like structure. In this study, it has been identified the crystals overlapping as plate-like structures.

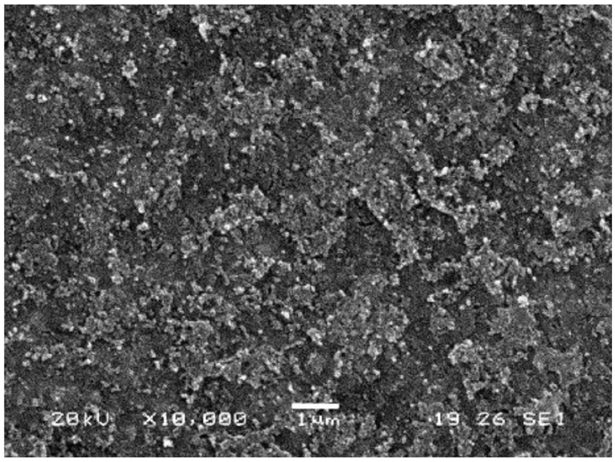

Fig. 3. SEM images of the glass-ceramic.

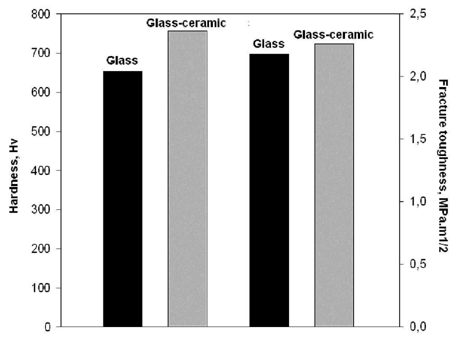

Fig. 4. Hardness and fracture toughness results of the glass and glass-ceramic.

Figure 4 shows hardness and fracture toughness results of the glass and glass-ceramic. The results indicated that both hardness and fracture toughness increased with glass-ceramic transformation. It is natural that crystallization causes increase in mechanical resistance [19]. The results have similarity with machinable glass-ceramic systems [12].

SEM image and EDS analysis obtained from whole surface of this image were given in Fig. 5. In Fig. 5a, average size of mica crystals with 5–10 μm having an interlocking microstructure can be seen. Also in Fig. 5b strong fluor signal observed in EDS analysis approves presence of mica crystals, homogeneously. Other elemental signals have good agreement with XRD results, but Fe signal is remarkable. Detected phases by XRD do not include Fe, it is possible that Fe in vermiculite composition exists in the glass structure.

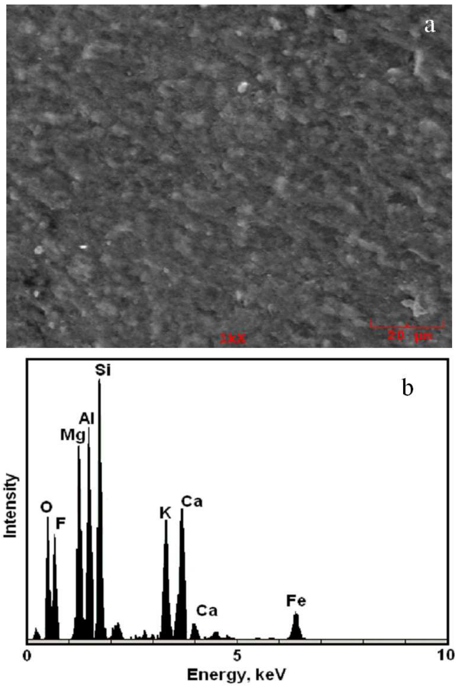

Fig. 5. SEM image (a) and EDS analysis (b) of the glass-ceramic.

4. Conclusion

Fluorophlogopite, phlogopite, diopside, and forsterite phases were determined by XRD. Except for forsterite, all phases provide machinability and crystallize at 910 °C successfully. The EDS analysis has good agreement with XRD results. The drilling test results showed that glass-ceramic specimen was drilled. As a result, vermiculite can be used for machinable glass-ceramic production with some additions.

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