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Crystallization kinetics of machinable glass ceramics produced from volcanic basalt rock

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A B S T R A C T

This study investigates the utilization of basalt in manufacturing machinable glass ceramics. As the fluorine and potassium phases, MgF_2 and K_2O added into basalt are responsible for the machinability of glass ceramics. Three different compositions containing 80%, 85%, and 90% basalt, with K_2O and MgF_2 as the remainder, were mixed and melted in an alumina crucible at 1500 °C. Glass samples were obtained by casting the melt into a graphite mould. Glass ceramics were prepared through subsequent crystallization heat treatment of the obtained glass. Compositional and mechanical characterizations were carried out via XRD-SEM and hardness/fracture toughness and machinability tests respectively. The effect of change in the obtained phases with basalt composition on the machinability of glass ceramics was investigated. Furthermore, crystallization kinetics of the glasses were investigated by differential thermal analysis (DTA) using the Kissinger kinetic model with several different heating rates. This study reports that basalt can be utilized in the production of machinable glass ceramics only if the basalt ratio is justified. The results showed that good machining performance was observed in low-basalt content conditions (B80), When the basalt content increased (B85 and B90), the machining capability decreased markedly. Furthermore, the crystallization activation energies decreased with increase in basalt content.

1. Introduction

Glass ceramic materials are crystalline materials produced by controlled heat treatment of appropriate glasses. The crystalline phases depending on the glass system type and residual glass structure make up these materials. Although glass ceramic materials having high hardness and toughness compared to glasses can be used for some applications that are important in terms of mechanical behaviour, they are still inadequate for use in machining and drilling applications. Fluorine has been utilized in glass ceramic systems to improve the aforementioned properties, which has been commercialized under the name of fluormica and used in dental bio-implant applications. These materials are known to have favourable combinations of thermal, mechanical and biomedical properties due to their laminated structure, which enables them to be cut and drilled [1]. The unique microstructure of an interlocking plate provides the desirable machinability, and deformation occurs along with the interfaces between layers while being machined. These laminar structures provide excellent machinability and preserve the body against cracking and mechanical damages [2]. Commercial mica glass ceramics are produced from pure oxides along with certain compositions. For instance, a commercial machinable glass ceramic MACOR® consists of 46% SiO_2, 17% MgO, 16% Al_2O_3, 10% K_2O 7% B_2O_3 and 4% F. A literature analysis on machinable glass ceramics reveals that studies were more focused on the effect of additives on the mechanical, thermal and machining behaviours of these commercial systems.

Basalt is a grey to black, fine-grained volcanic rock that is formed by magmatic movement and subsequent sudden cooling of magma in atmospheric conditions. As it occupies approximately 2.5 million square kilometres on earth, it is cheap and readily available. Basalt, containing SiO_2 and Al_2O_3 as the major oxides with approximately 40–55% and 10–20% respectively, consists of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and other oxides such as K_2O and TiO_2. It can be used for glass ceramic production via its high silica content. Basalt-based glass ceramics exhibit good abrasion, wear and chemical resistance. They can be used when the transport of material causes mechanical or chemical abrasion as well as mineral wool for heat, noise and fire insulation [3]. Basalt-based glass ceramic products are commercial materials, and diverse glass ceramic phases can be produced from basalt because it has many different oxides. Some modifications and additions in basalt composition provide different glass ceramic phases and systems formation. In terms of machinable glass ceramic phases, basalt has similar elements compared to these phases. For example, Phlogopite is one of the major phases for machinable glass ceramics. Its chemical formula consists of

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K, Mg, Al, F and Si elements; except for F, the other oxides are in the basalt composition [4, 5, 6].

In the study, the possibility of using basalt for machinable glass ceramic material production was investigated. Basalt, which is used for glass ceramic production, includes high amounts of SiO_2 and earth alkaline metal oxides such as CaO and MgO. Diopside is one of the major crystalline phases from studies of basalt-based glass ceramic systems, and there are investigations on the machining capability of glass ceramics containing the Diopside phase. In terms of chemical composition, basaltic rocks can be used for machinable glass ceramic production. As the phases that impart machinability to glass ceramics are mica-based phases, we modified the basalt composition by additives including fluorine to obtain the required phases. Thus, mica phase crystallization effects on basalt crystallization were observed, and the formation of mica and other phases that provide machinable properties and transformations among these phases depending on compositions were investigated in the current study.

2. Experimental procedure

Basalt rocks obtained from Central Anatolia Konya region of Turkey were used in this study. Basalts crushed by a jaw crusher were milled by a ring miller and then sieved to obtain the particulate size of −75 μm, and the obtained powders were characterized by using Perkin-Elmer 2300 atomic absorption spectroscopy. The chemical composition of the basalt powder is given in Table 1. MgF_2 and K_2O were mixed with basalt to provide mica phase formation. The compositions, sample codes, and heat treatment procedures can be seen in Table 2. Mixtures were melted in an alumina crucible at 1500 °C for 2 h and cast into a graphite mould. Bulk glass samples obtained from the casting process were exposed to differential thermal analysis (DTA-TA Instrument Q-600) at heating rate of 10–20 °C/min to examine thermal properties and crystallization kinetics. X-ray diffraction analysis (XRD) was conducted by using a Rigaku D-max 2200-type diffractometer with Cu–Kα radiation, which has a wavelength of 1.54056 Å to analyse the phases present in the samples over a 2θ range of 5°–90°. The microstructural examinations by using scanning electron microscopy (SEM-Jeol 6060) were performed on polished and etched surfaces; a solution of 5 vol% HF was used for the etching process for 1–2 min. An energy-dispersive spectrometer (EDS) was employed for elemental analysis. Hardness and fracture toughness values were obtained from the indentation technique by using a Future Tech FM-700 micro hardness tester. These tests were carried out on polished surfaces with loads of 100 gf and 300 gf for the hardness and fracture toughness measurements, respectively. The hardness was calculated from the diagonal length of the indentation optically determined for each indentation, using the following Eq. (1) [7]:

$$Hv = 1.8544x\frac{P}{d^2} \tag{1}$$

where Hv is the Vickers hardness, P is the applied load (kg), and a is the average of the diagonal half lengths (mm). The fracture toughness was calculated using the Evans–Charles Eq. [8]:

$$K\iota c = 0.0824x\left(\frac{P}{c^{\frac{3}{2}}}\right) \tag{2}$$

where K_{IC} is the fracture toughness, P is the load, and C is half of the crack length. Eq. 3 was used to convert Hv into GPa [2],

Table 1
Chemical analyses of the basaltic used.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	L.O.I*
wt%	45.88	18.2	9.95	9.28	6.62	1.64	4.76	1.04	2.63

* Lost on ignition.

Table 2
Glass compositions and codes of the studied glasses.

Sample codes	Basalt	MgF_2 (wt %)	K_2O (wt %)	Heating Procedure	
				Temperature (°C)/ Time (h)	Heating rate
B80	80	15	5	660/1 760/1 860/1 975/1	10 °C/min.
B85	85	10	5	680/1 820/1	
B90	90	5	5	750/1 830/1	

$$Hv(GPa) = \frac{9.81}{1000}xHv \tag{3}$$

The machinability parameter m is a significant value for machinable glass ceramic characterization. The equation of machinability parameter calculation is given below as Eq. 4 [9, 10]

$$m = 0.643 - 0.122Hv \tag{4}$$

where m is the machinability parameter and Hv is the hardness in GPa. Furthermore, machinability tests were applied to the disc shaped specimens using a 5-mm diamond drill with a 440-rpm drilling rate under a load of 20 N for 1 min. The samples were subjected to the drilling test to characterize the drilling depths; a deeper drilling trail characterizes good machinability compared to others.

3. Results and discussion

3.1. XRD analysis results of the glass ceramic samples

The XRD patterns of glass ceramic samples depending on the basalt content and crystallization temperature can be seen in Fig. 1. Thermal behaviours and phases developed were given in Table 3. Phlogopite ($KMg_3AlSi_3O_{10}OHF$-01-073-1657), Fluorphlogopite ($KMg_3(Si_3Al)O_{10}F_2$-01-076-0816), Sanidine ($KAlSi_3O_8$-01-074-0700), Augite ($Ca(Mg,Fe)Si_2O_6$-00-024-0203) and Diopside ($Ca(Mg,Al)(Si,Al)_2O_6$-00-041-1370) phases were determined depending on the crystallization temperature and the compositions. The XRD pattern of B80 sample heated at 660 °C exhibits strong mica phases such as Phlogopite, and Fluorphlogopite; these phases crystallize above 700 °C [11, 12]. The mica structures can exhibit different formulas. Depending on their composition, they can be defined using the A-R-T-X general formula. The atomic substitutions are expressed relative to phlogopite composition as follows: A = K = Na, Ca, Ba, Rb, Cs / R = Mg = Fe^{2+}, Fe^{3+}, Al, Mn, Li, Ti / T = ($AlSi_3$) / X = OH = F [13]. Iron ion can behave differently in glass ceramic systems. Octahedral (R) cation: Fe═Mg substitution occurs; thus, annite type mica crystals form. The strong XRD peaks of these phases were observed in B80 and B85 samples heated at 660 °C and 680 °C. Fe_2O_3 is a nucleating agent for glass ceramic systems, and it is known that some phases crystallize at a lower temperature due to Fe_2O_3 in basalt compared with the conditions that do not contain any nucleating effect. It has been reported that iron plays an important role in the crystallization of $MgO-Al_2O_3-SiO_2$ glass ceramic systems, and it has been presented that the substitution of Mg^{2+} by Fe^{3+} forms the vacant site of Mg^{2+} cations [14].

The characteristic mica phase peaks at approximately 9°, 19°, 27°, 34°, and 60° show low intensities for the B80 sample heat treated at 660 °C, 760 °C and 860 °C. The mica phases have a better crystallization condition at these temperatures for the B80 sample owing to the high fluorine and low basalt contents. When the temperature reached 975 °C, crystallization of the characteristic basalt-based glass ceramic phases Augite and Diopside occurred. However, because of the low basalt and