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Crystallization kinetics of mica glass-ceramic in the SiO₂-Al₂O₃-MgO-K₂O-B₂O₃-F₂System

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A mica glass-ceramic in the SiO₂-Al₂O₃-MgO-K₂O-B₂O₃-F₂ glass system was prepared by a melting method. The crystallization behaviour and crystallization kinetics of a sample with glass-ceramic composition were examined. DTA and XRD analysis revealed the crystallization of phlogopite, fluorphlogopite, clinohumite and spinel phases. The activation energies for the precipitation of crystalline phases have been evaluated, and the crystallization mechanisms have been studied by applying DTA measurements performed at various heating rates. The results indicate that the growth of mica is a two-dimensional process controlled by the crystal-glass interface reaction. The average calculated values of crystallization and viscous flow for the precipitation of crystal phases from the glass matrix were measured to be 289.9 ± 8 kJ/mol and 348.7 ± 14 kJ/mol, respectively. The mica glass-ceramics exhibited excellent performance in machinability tests without cracking or deforming.

Key words: Crystallization, Glass, Mica glass-ceramic, Kinetic.

Introduction

Glass-ceramics are fine-grained polycrystalline materials that are formed when glasses of suitable compositions are heat-treated and undergo controlled crystallization to reach a lower-energy crystalline state [1, 2]. The great varieties of compositions and microstructures with specific technological properties have allowed glassceramics to be used in a wide range of applications. For glass-ceramics, the two important effects that determine their properties are their crystalline phases and microstructures, both of which can be tailored by chemical composition, heat-treatment and nucleating agents [1, 3-8]. The composition of the crystalline phases and the crystallite sizes determine the properties of the final material. Ceramic base materials are not suitable for some applications because of their brittle properties with respect to mechanical effects, such as cutting and drilling [9]. However, some modifications in chemical composition and production methods can provide better mechanical behaviour. One of the important materials that can be used to improve the machinability of ceramics is mica-based glass-ceramics. Mica-containing glass-ceramics are used as high quality electrical insulators and exhibit high resistance to thermal shock and good machinability [10]. Mica glass-ceramics based on the SiO₂-MgO-MgF₂-K₂O system are commercially produced and exhibit unique properties, such as remarkable cleavage, flexibility and elasticity, enabling excellent machinability [11]. Commercial micabased glass-ceramics are primarily of the fluorophlogopitetype [12].

The crystallization kinetics of the high temperature processes play an important role in the determination of the process parameters, such as treatment temperature and times, for the desired conditions [1, 13, 14]. Regarding the kinetic parameters, the activation energy of crystallization (Ea) and the crystal growth index (Avrami parameter: *n*) are the key parameters to evaluate the crystallization capability of the parent glass and describe the micromorphology of the crystals, respectively [1, 3, 15-18]. Because Ea is related to the energy barrier over which glassy phases transform to crystalline phase(s), it is easier for the glass to crystallise if Ea is lower [3, 18]. The crystal growth index n is a dimensionless constant related to the nucleation and growth mechanisms. Different micro-morphological crystals may be precipitated from the parent glass with different values of n [3, 19-22]. Generally, one-dimensional needles or columns, twodimensional plates and three-dimensional polyhedrons and particles are precipitated from the parent glass by bulk nucleation when the calculated values of *n* are 2, 3 and 4, respectively [1-3, 15-17, 19-22]. Differential thermal analysis (DTA) is a method used to determine crystallization and viscous flow activation energies [1, 15, 16]. Thermally activated transformations in the solid state can be investigated by isothermal or nonisothermal experiments [1, 23]. The main goal of this study was to investigate the crystallization kinetics and properties such as hardness and machinability of the

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SiO₂-Al₂O₃-MgO-K₂O-B₂O₃-F₂ glass system. In this study, the mica-glass ceramic composition including lesser fluorine compared with commercial mica glass-ceramic (MACOR) was used, the effect of decreasing in fluorine content on crystallization kinetic and other properties was investigated.

Experimental Procedure

The SiO_2 -Al₂O₃-MgO-K₂O-B₂O₃-F₂ glass was melted from reagent-grade SiO_2 , AlF₃, Al₂O₃, K₂CO₃, MgCO₃ and B₂O₃. The chemical composition of the sample is given in Table 1.

The fabricated batch was melted in an alumina crucible at 1500 °C for 2 h using an electric furnace (HERAEUS). To ensure homogeneity, the melt was poured into water. The cast was crushed, pulverised and remelted at the same temperature for 2 h to achieve homogeneity. The refined and homogenised melt was cast into a graphite mould. To remove thermal residual stress from the glass sample, it was annealed in a regulated muffle furnace at approximately 600 °C for 1 h, followed by slow cooling to room temperature. Glass-ceramic samples were prepared by applying suitable heat treatments that were planned according to the differential thermal analysis (DTA) results of the amorphous glass. Two heat treatment schedules were performed at temperatures of 850 °C for 1 h + 950 °C for 4 h and 1000 °C for 4 h in a Lenton tube furnace to promote internal crystallization, as shown in Table 2 with sample code. The crystallization temperatures were selected from the DTA curve, depending on the endothermic and exothermic reaction temperatures. A JEOL 6060 scanning electron microscopy (SEM) system was used to characterise the glass-ceramic samples. A Rigaku X-ray diffraction (XRD) system with CuK_{α} radiation ($\lambda = 1.54056$ Å) was used to analyse the phases present in the glass over a 20-range of 10-90°. DTA and differential scanning calorimetry (DSC) are widely used

Table 1.	Chemical	composition
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Starting materials Amount	Precursor constituent	Wt.%
Quartz	SiO ₂	48
Alumina (Alcoa)	Al_2O_3	18
MgCO ₃	MgO	15
K_2CO_3	K ₂ O	10
B_2O_3	B_2O_3	5
AlF ₃	F	4

 Table 2. Sample code system according to applied heat treatment procedure.

Sample code	Heat treatment procesure
GC-1	850 °C, 1 h + 950 °C, 4 h
GC-2	1000 °C, 4 h

to investigate the crystallization kinetics of glasses and glass-ceramics. DTA experiments were performed using a TA instruments Q-600 with heating rates of 10, 15 and 20 °C/min. All DTA experiments were carried out in an argon atmosphere up to a temperature of 1200 °C. Thus, the crystallization kinetics of the SiO₂-Al₂O₃-MgO-K₂O-B₂O₃-F₂ glass system were investigated.

A micro-hardness test was performed using a Future Tech FM-700 micro-hardness tester using the indentation technique. Five hardness tests were performed on polished surfaces with a load of 25 gf. The micro-hardness was calculated from the diagonal length of the indentation observed for each indentation using eq. (1) [24],

$$Hv = 1.8544 \ p/d^2,$$
 (1)

where Hv is the Vickers hardness, p is the applied load, and d is the average of the diagonal half-lengths. Machinability tests were applied to the disc shaped specimens using 5 mm diamond drills with a 200 rpm drilling rate under an uncontrolled load.

Results and Discussion

The patterns and crystal phases determined by XRD are given in Fig. 1 and Table 3, respectively. Identical phases were observed in both the GC-1 and GC-2 samples: $MgAl_2O_4$ (spinel), $Mg_9F_2(SiO_4)_4$ (clinohumite), $KMg_3(Si_3Al)O_{10}F_2$ (fluorphlogopite) and $MgSiO_3$ (protoenstatite). In addition, phlogopite (K_2Mg_6 ($Si_{.75}Al_{.25}$) $_8O_{20}$



Fig. 1. XRD patterns of the samples depending on heat treatment.

Table 3. List of the main crystal phase formations with ASTM card number.

Phase code	Crystal phase	ASTM card no
1	MgAl ₂ O ₄ (Spinel)	01-082-2424
2	Mg ₉ F ₂ (SiO ₄) ₄ (Clinohumite)	00-014-0009
3	KMg ₃ (Si ₃ Al)O ₁₀ F ₂ (Fluorphlogopite)	00-016-0344
4	MgSiO ₃ (Proto-enstatite)	00-011-0273

(OH)_{1.8}F_{2.2}) peaks were detected in the GC-1 sample. This phase is the primary structure for fluoro-silicates and can form at temperatures above 850 °C. This structure is also significant in obtaining fluorphlogopite. For instance, in the production of synthetic fluorphlogopite crystals, phlogopite is transformed into fluorphlogopite by the substitution of all of the (OH) with fluorite. Clinohumite and fluorphlogopite phases are characteristic structures for mica glass-ceramics, and these structures have a significant role in terms of machinability [10]. Although XRD results indicate that the same phases are present in both GC-1 and GC-2 samples, different phase intensities were observed depending on the heat treatment procedure. Specifically, the differences between the phase intensities of fluorphlogopite and proto-enstatite were observed depending on the heat treatment procedure. The sample sintered at 1000 °C for 4 h exhibited stronger proto-enstatite XRD peak intensities than other samples. Enstatite (Mg₂Si₂O₆) is a member of the pyroxene group and exhibits a polymorphic structure, similar to ortho-enstatite and clino-enstatite. One of these polymorphs is the proto-enstatite structure. When heated above 1000 °C at ambient pressure, ortho-enstatite transforms into proto-enstatite [25]. An increase in the proto-enstatite peak intensities indicates that these types of transformations may be possible. These formations can be observed at approximately 28 °, 30 °, 53 ° and 62 ° (2θ) . In general, the intensities of fluorphlogopite peaks increase with increasing temperature. Clinohumite [Mg₉F₂(SiO₄)₄] is another silicate mineral belonging to the humite group. This group of minerals includes norbergite, chondrodite, humite and clinohumite [26]. In general, this type of structure is observed in machinable glass-ceramics, and the presence of these phases can bring about fluorphlogopite formation. MgAl₂O₄ (spinel) is a classical refractory ceramic that is produced from MgO and Al₂O₃ powders via calcination and solid state sintering at a high temperature [27]. In this study, spinel phase formation was observed due to adequate magnesia and alumina content. At temperatures below 1000 °C, the formation of MgAl₂O₄ (spinel) due to different mechanisms has been presented in the literature [27]. The humps in the background area of the XRD patterns at 22 °-30 ° (2 θ) are due to the residual glass structure, where a larger area indicates more residual glass [28].

The hardness results are shown in Fig. 2. The hardness value as a glass was calculated to be 635.8 ± 75 HV. A decrease in hardness was observed after the glass-ceramic transformation. In general, the crystallization process causes an increase in hardness. Glass-ceramics are harder than the glasses used for their production because of the formation of hard crystalline phases. However, mica glass-ceramics have a different crystallization mechanism. Normally, crystallised ceramics have ionic and covalent bonding, are hard and rigid against mechanical stresses, and do not exhibit plastic deformation. In mica glass-ceramics, Van der Waals bonding occurring during



Fig. 2. Hardness values of the samples.



Fig. 3. Hole drilled in samples after machinability test a) GC-1 b) GC-2.

crystallization provides extraordinary properties, such as enhanced machinability, compared to traditional ceramics. Hardness and machinability were found to be highly dependent on the formation of an interconnected "house of cards" micro-structure. This microstructure is described as randomly-oriented, flexible plates that include fluorphlogopite phases. Formation of this crystallised fluorphlogopite phase, determined by XRD, provides better plastic deformation abilities compared to classical ceramic systems. The hardness values of GC-1 and GC-2 samples were determined to be 552.8 ± 81 HV and 586.6 ± 67 HV, respectively. There are decreases in hardness according to the glass samples, as reported in the literature [29, 30]. Molla and co-workers studied the wear performance of the mica-glass ceramics, where a Vickers hardness value of 6.41.2 GPa was obtained from samples of similar composition [31]. In another study by Mallik et al., a decrease in the hardness values of mica glass-ceramics via glass-ceramic transformation was reported [29].

The machined samples are shown in Fig. 3. The discshaped sample was cut by using a diamond disc cutter before the machinability test. GC-1 and GC-2 samples showed excellent machinability, and a 5 mm thick hole was successfully drilled completely. According to the results, the appropriate machining performance was



Fig. 4. SEM micrograph of GC-2 sample.



Fig. 5. SEM micrograph and EDS analysis of GC-1 sample.

obtained both two heat treatment procedure without cracking. Decreasing in fluorine content has not significant effect on machining performance of the glass-ceramics.

Figure 4 shows the SEM microstructures of GC-2 samples sintered at 1000 °C for 4 h. A classical microstructure dominated by mica plates was observed. These plates play a significant role in the machinability properties of these glass-ceramics. According to the literature, the crystallization mechanisms of machinable glass-ceramics are described as a two-step process. In the first step, phase separation and crystallization of approximately spherical mica crystals occurs; in the second step, at higher temperatures, recrystallization takes place and the typical plate-like morphology of the mica crystals is obtained [32]. These crystal structures can have different shapes, such as curved or flat, depending on the chemical composition. Commercial mica glass-ceramics, such as MACOR and DICOR, exhibit flat crystals; these structure types were also obtained in this study. Their deformation capabilities depend on this microstructure. Randomly-oriented and flexible flakes tend to either arrest fractures or cause deflection or branching of cracks; therefore, only local damage occurs as tiny polyhedra of glass are dislodged [33]. Fluoro mica crystal structures can be observed



Fig. 6. DTA curves with different heating rates.

 Table 4. Characteristic DTA peak temperatures of glass samples depending on heating rates.

Heating rate, (°C/min)	T _g (K) Glass transition temperature	T _p (K) Crystallization temperature	ΔT (K)
10	902	1239	40
15	908	1247	37
20	915	1266	35

in Fig. 4.

The EDS analysis and SEM micrograph of GC-1 are shown in Fig. 5. The SEM microstructure obtained from the polished and quenched surface shows an inhomogeneous morphology. EDS analysis indicates the presence of elemental O, F, Mg, Al, Si and K. The presence of K in EDS analysis indicates that fluorphlogopite is a pervasive phase in the microstructure. As shown in Fig. 5, the presence of more fluorine in plates than in other regions indicates that these plates make up mica crystals. In addition, these structures resemble a specific mica glass-ceramic microstructure called "house of chards". This multilayer silicate shape plays a key role in the machinability of these materials. Their controllable morphological properties provide utility in some mechanical applications thanks to good machinability.

DTA studies were performed on the prepared glass powder to determine the glass transition and crystallization temperatures with different heating rates. The variation of the crystallization peaks with different DTA heating rates can be used to calculate the activation energy for crystallization and to determine the crystallization mechanism [34]. The endothermic peak indicates the glass transition, and the exothermic peaks correspond to the crystallization reactions of the glass [35]. Figure 6 shows the DTA results for different heating rates. The glass transition temperatures (Tg) were determined to be between 902 K and 915 K, depending on the heating rate. Crystallization temperatures (Tp) were measured to be between 1239 K and 1266 K, depending on the heating rate. Both temperatures were measured using DTA curves and are given in Table 4.

The kinetics for isothermal solid-state phase transformations are described by the phenomenological Johnson-Mehl-Avrami (JMA) equation [1, 36, 37]:

$$X = 1 - [(-kt)^{n}].$$
 (2)

Eq. 3 is obtained by taking the logarithm of Eq. 2:

$$ln[-ln(1-X)] = n\ln k + n\ln t, \qquad (3)$$

where *X* is the volume fraction of crystallization after time *t*, *n* is the Avrami parameter (which depends on the growth direction number and the mechanism of nucleation and crystal growth given in Table 4) and *k* is the reaction rate constant (s⁻¹) (which depends on both the nucleation rate and the growth rate) [1, 36,37]. The equation defining *k* is given below:

$$k = V \exp\left(\frac{-Ea}{RT}\right),\tag{4}$$

where *V* is a frequency factor (s^{-1}), *Ea* is the activation energy for crystallization (J/mol), *R* is the gas constant (8.314 J/mol) and *T* is the absolute temperature (K) [1, 34].

From the value of the activation energy, the Avrami parameter can be calculated using the equation presented by Augis and Bennett for non-isothermal analysis:

$$n = \left(\frac{2,5}{\Delta T}\right) \left(\frac{Tp^2}{Ea}\right),\tag{5}$$

where ΔT is the full width of the exothermic peak at the half-maximum intensity and Tp is the crystallization peak temperature. Consequently, a sharp peak (small ΔT , large *n*) implies bulk crystallization, while a broad peak (large ΔT , small *n*) signifies surface crystallization [36]. The relationship between the crystallization mechanism and the Avrami parameters, which were calculated using Eq. (5), are given in Table 5 and Table 6, respectively.

Therefore, the reaction rate constant in Eq. (4) is no longer a constant but is a function of time, and the transformation mechanism cannot be described by the simple JMA equation (Eq. (2)). A modified form of the JMA equation that takes into account the dependence of k on t is used for non-isothermal crystallization. The value of the activation energy for the crystallization of an amorphous glassy layer was determined using a modified form of the JMA equation. It was originally applied to crystallization studies by Kissinger and modified by others [1, 36,37]. Kissinger method is proper for analyzing the crystallization kinetics of mica glass-ceramics [38]. This method is based on the dependence of the crystallization peak temperature (Tp)

Table 5. Crystallization mecnanisms depending on n values [1].

Crystallization mecnanism	Avrami parameter "n"
Surface Crystallization	1
Bulk Crystallization (one-dimensional growth)	2
Bulk Crystallization (two-dimensional growth)	3
Bulk Crystallization (three-dimensional growth)	4

Table 6. Determined "n" values and possible crystallizationmechanisms.

Heating rate, (°C/min)	n	Mechanism	ΔT (K)
10	2.751	Bulk nucleation	40
15	3.011	Bulk nucleation	37
20	3.283	Bulk nucleation	35

on the DTA or DSC heating rate (β), as follows:

$$\frac{\ln Tp^2}{\beta} = \frac{\ln Ea}{R} - \ln Va + \frac{Ea}{RTp}.$$
(6)

Likewise, Eq. (6) can also be used to predict the viscous energy, as described by Mahadevan *et al.* [39]:

$$\frac{\ln Tg^2}{\beta} = \frac{\ln Ec}{R} - \ln Vc + \frac{Ec}{RTg}.$$
(7)

Here, Ec is the corresponding activation energy for viscous flow, Tg is the glass transformation temperature, Va is the frequency factor for crystallization and Vc is the frequency factor for viscous flow. Plots of $\ln Tp^2/\beta$ versus 1/Tp and $\ln Tg^2/\beta$ versus 1/Tg, obtained at various heating rates, should be linear with slopes of Ea/R and intercepts of $[\ln(Ea/R) - \ln Va]$ and $[\ln(Ec/R - \ln Vc)]$. Plots of $\ln Tp^2/\beta$ versus 1/Tp and $\ln Tg^2/\beta$ versus 1/Tg are given in Fig. 7.

The crystallization activation energy (E_a) and the viscous flow activation energy (E_c) were calculated to be $289.9 \pm 8 \text{ kJ/mol}$ and $348.7 \pm 14 \text{ kJ/mol}$, respectively. These values are greater than those obtained from samples of similar composition in the literature. This result can be related to the use of no nucleation agents or additives, such as ZrO₂, La₂O₃, CeO₂, which cause a significant decrease in activation energy. The observation of residual glassy structures detected by XRD also correlates with this result. The n-values, which were calculated using Eq. (4), are n = 2.75 - 3.28, which indicates that the crystallization of the mica glass structures at all heating rates is caused by bulk nucleation with one and two-dimensional growth. Cheng et al. reported that fluorophlogopite-based mica glass-ceramics exhibit a crystallization activation energy of 275 ± 6 kJ/mol [40]. The result is close to the activation energy reported in this study. The system used by Cheng differs from the system in the current study by including TiO₂, Na₂O and a lower SiO₂ content. The small differences observed in



Fig. 7. Plots of ln Tp²/ β versus 1/Tp and ln Tg²/ β versus 1/Tg.

these results may stem from the nucleation agent effect of TiO_2 and the lower SiO_2 content, indicating a lower vitrification effect. In this study, the absences of any nucleative addition and the high SiO_2 content have resulted in a slightly higher crystallization activation energy. Furthermore, lesser fluorine content according to commercial MACOR glass-ceramics provided increases in crystallization activation energy and easier crystallization effect, possible.

Conclusions

In the current study, mica glass-ceramics were produced from the glass obtained from SiO₂, Al₂O₃, K₂CO₃, MgCO₃, B₂O₃ and AlF₃ powders. The investigation of the machinability and crystallization properties of this system was the main objective for this study. The significant phases for machinability, fluorphlogopite, spinel, clinohumite and proto-enstatite, were detected by XRD in both the GC-1 and GC-2 samples. In addition, the phlogopite phase was observed in the GC-1 sample. Fluorphlogopite and phlogopite phases enhance the machinability performance of this type glass-ceramic system. Apart from these phases, the presence of residual glassy structures in XRD was observed as a hump in the background area of the XRD patterns. Hardness test results showed that the glass-ceramic transformation caused a decrease in hardness. This phenomenon is natural for mica-based glass-ceramic systems due to different microstructural formation and crystallization. The produced mica glass-ceramics exhibited excellent performance in machinability tests. These tests were carried out on both GC-1 and GC-2 samples without cracking or deformation. Lesser fluorine content in the glass-ceramic composition exhibited no prominent effect on machining performance of the glass-ceramics. In SEM micrographs, classical mica glass-ceramic structures dominated by mica plates were observed, and fluoro-mica crystals were identified. Crystallization kinetics studies showed that the effective crystallization mechanism for this system is bulk crystallization according to nparameters. These parameters were calculated to be 2.75-



3.28, depending on the heating rate, which indicates bulk nucleation. The crystallization and viscous flow crystallization activation energies were measured to be 289.9 ± 8 kJ/mol and 348.7 ± 14 kJ/mol, respectively.

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