INFLUENCE OF MoO_3 , ZrO_2 AND SiC ON THE CRYSTALLIZATION AND THERMO-MECHANICAL PROPERTIES OF FLUORPHLOGOPITE FUSION CAST CERAMICS

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Melts based on the K or Ba fluorphlogopite depending on their composition can behave either like conventional glasses respectively glass-ceramics upon reheating, or as fusion cast ceramics. For some specific compositions belonging to the latter group, the addition of MoO_3 , ZrO_2 and SiC has been studied. MoO_3 is selected because it is known to promote homogeneous nucleation by lowering the surface energy difference between melt and crystals. ZrO_2 and SiC are selected because they are classical nucleation catalyst in many glass-ceramic systems. It is shown that these additives substantially reduce the crystallization rates and also cause concomitant changes in the resulting ceramic microstructures and thermo-mechanical properties of fluorphlogopite fusion cast ceramics. Both effects are interpreted as a consequence of increased melt viscosity.

Keywords: fluorphlogopite, fusion cast ceramics, glass-ceramics, nucleation catalyst, surface energy.

1. INTRODUCTION

There are two techniques to produce ceramic materials starting from a homogeneous undercooled melt: fusion casting or devitrification of the already formed glass. The first technique is more general and the most practical way to produce the high refractory ceramics which are the basis of high temperature furnace construction [1, 2]. The latter process incorporates devitrification and

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DOI: 10.7546/EngSci.LV.18.03.02

uses the principles of the induced and controlled crystallization of glasses and production of glass-ceramic materials.

Fusion cast ceramics can also be made from basalts, different metallurgical slags and stoichiometric fluorphlogopite melts [3]. However, coarse crystals tend to form perpendicular to the mold interfaces and internal pits and voids are produced in castings due to difficulties in forming and control of crystallization [1, 2].

Melts based on the fluor micas, depending on their composition, can behave either like conventional glasses respectively glass-ceramics upon reheating, or as fusion cast ceramics, i.e. as materials that have been melted and then crystallized directly upon cooling or casting into a mold.

In contrast with mica glass-ceramics, F-mica fusion cast ceramics, however, tend to form coarse crystals perpendicular to the mold interfaces and internal pits and voids are produced in castings due to difficulties in forming and control of crystallization [1, 2].

Whether the crystallization process is controlled, as in the glass-ceramics, or uncontrolled as in the fusion cast ceramics and uncontrolled devitrification process, depends on the viscosity of the melt, the number and location of the crystallization centers as well as on the extent of overlapping of the nucleation and crystal growth rate curves.

The most important single factor, however, determining controlled crystallization and the largely different microstructures and properties of fusion cast ceramics as compared with glass-ceramics, is the viscosity change during crystallization. Whereas the controlled nucleation, in the glass-ceramic process, normally takes place at viscosities greater than 10^8 dPa·s (usually between 10^9 and 10^{12} dPa·s), cast ceramic materials crystallize as a rule from very fluid melts, i.e. at a viscosity normally less than 10^3 dPa·s [1, 2]. Under these conditions, grain size and microstructure cannot be controlled properly, and various stages of nucleation and crystal growth cannot be “frozen in” to permit the use of convenient methods of examination. That is why only modest efforts have been made to investigate crystallization of the fusion cast ceramics, while for glasses and glass-ceramics a large number of contributions on this subject have appeared in the world-wide ceramic literature during the past few decades [3–10]. The existing observations in this field concern as a rule either pure technological experiments, on the influence of some additives on the grain size and processes of coarsening (or refining) of fusion cast ceramic bodies, or some traditional mineralogical investigations for determination of crystal phase segregation sequence [11–18].

This is somewhat unexpected, since the fluid melt of a mica fusion cast ceramics is a very convenient medium for fundamental studies of spontaneous crystal growth of a super cooled liquid and for the observation of the influence of some additives on the “pure” crystallization of a melt. In particular in the case of phase segregation of F-mica crystals there are some possibilities for a reliable experimental verification of the action of certain glass-constituents such as: MoO_3 , V_2O_5 , WO_3 , SO_3 , As_2O_3 , etc. that promote homogeneous crystal nucleation by lowering the surface energy difference between the embryo crystals and the mother phase. These possibilities of enhancing of nucleation are well known from previous experiments [19]. These investigations, however, do not give the possibility to decide whether the action of these surfactants is a result of the inhibition of the crystal growth or of the increasing nucleation rate by lowering the surface tension at the crystal/melt interface.

On the other hand, it will be also of interest to examine the action of some “classical” catalysts for glass ceramics as ZrO_2 and SiC [20, 21] in a fusion cast ceramic medium.

Thus, the objective of this paper is to answer if MoO_3 added acts as nucleation catalyst and how zirconia and SiC influence the crystallization of a fusion cast ceramics of the F-mica type.

2. EXPERIMENTS

In the first series of experiments two fluor-mica systems are studied: I – with a potassium fluorphlogopite $\text{KMg}_3(\text{Si}_3\text{AlO}_{10})\text{F}_2$ and II – with a barium fluorphlogopite $\text{Ba}_{0.5}\text{Mg}_3\text{Si}_3\text{AlO}_{10}\text{F}_2$ as main crystalline phases segregated in the fusion cast ceramics.

Three weight per cents (%) MoO_3 , 10 and 15% ZrO_2 as well as 10% ZrO_2 introduced by ZrF_4 are additionally added to the K-fluorphlogopite batch composition (sample No 1) to give samples No: 2, 3, 5, and 4; 6% MoO_3 is added in the Ba-fluorphlogopite system (sample No 6) to give sample No 7 (see *Table 1*).

Fluorphlogopite fusion cast ceramics with two different base compositions (1 and 6) and varying in MoO_3 and ZrO_2 -contents are melted in platinum crucibles at 1500°C for 1.5 h with simultaneous stirring. Each melt is poured into a sand casting mold to give cylindrical ($d = 1.8\text{ cm}$, $h = 6 \div 8\text{ cm}$) samples as well as in water for some quantity glassy frit.

In the second series some compositions from the isomorphous line $\text{KMg}_3(\text{Si}_3\text{AlO}_{10})\text{F}_2$ - $\text{KMg}_3(\text{Si}_{3.75}\text{O}_{10})\text{F}_2$ are investigated. Five weight percentages SiC are introduced into the compositions above 100%.

TABLE 1. Chemical (oxide/batch) compositions of the two investigated samples

Components	K-fluor-phlogopite oxide comp. in [wt.%]	K-fluor-phlogopite batch comp. in [wt.%]	Ba-fluor-phlogopite oxide comp. in [wt.%]	Ba-fluor-phlogopite batch comp. in [wt.%]
SiO ₂	37.54(41.22)	32	33.89(38.62)	34.86
Al ₂ O ₃	10.35(11.54)	11	13.17(10.92)	13.10
MgO	26.34(27.65)	28	31.32(25.90)	30.50
K ₂ O	11.67(10.80)			
BaO			16.04(16.43)	
MgF ₂				2.67
K ₂ SiF ₆		29		
BaF ₂				18.87
F ⁻	14.10(8.80)		5.57(8.13)

Fig. 1. Powder diffraction dates of the K-fluor phlogopite samples as fusion cast ceramics: (a) “pure” K-fluor mica-sample No1; (b) +3 wt.% MoO₃, sample No 2; (c) +10 wt.% ZrO₂, sample No 3; (d) +10 wt.% ZrO₂ introduced like ZrF₄, sample No 4; (e) +15 wt.% ZrO₂- sample No 5; (d') +10 wt.% ZrO₂ introduced by ZrF₄, sample taken from the bottom part of the crucible

The crystalline phase content in the fusion cast ceramics and in the frits is examined by X-ray Diffraction Analysis (XRD) using one and the same sample quantity and the same sample holder, *Fig. 1*.

The reflection light micrographs are prepared by standard techniques and investigated by means of Energy Dispersive X-ray micro analysis (EDX) in a Philips CM-12 SEM with an EDAX-9800 spectrometer. Reflection light micrographs are obtained from the polished surfaces of the samples before EDX investigations.

3. RESULTS

Table 2 points out the chemical analysis of the fluorine content of the mica molten ceramics. It is seen that all samples under investigation are characterized with relatively low fluorine losses.

According to XRD analysis the main crystalline phases precipitated in the “pure” compositions (without additives: MoO_3 and ZrO_2) are: K-fluorophlogopite $[\text{KMg}_3(\text{AlSi}_3\text{O}_{10})\text{F}_2]$ and barium fluorophlogopite $[\text{Ba}_{0.5}\text{Mg}_3(\text{AlSi}_3\text{O}_{10})\text{F}_2]$ as well as some small amounts of barium magnesium aluminum fluoride $[\text{BaMg}_3(\text{Al}_2\text{Si}_2\text{O}_{10})\text{F}_2]$. In addition, very small and broad XRD-reflections from the ZrO_2 , forsterite ($2\text{MgO} \cdot \text{SiO}_2$), $\text{K}_2\text{ZrSi}_2\text{O}_7$, and KMgF_3 are detected in the K-fluorophlogopite compositions with zirconia and ZrF_4 . On the other hand, XRD peaks of MoF_3 , MoO_3 , and $\text{Ba}_2\text{MoO}_3\text{F}_4$ appear, most of which are overlapped by the main Ba-mica XRD-reflections. The XRD peak intensity I , which is proportional to the quantity of the mica crystal phase, decreases with increasing ZrO_2 and MoO_3 content. Obviously, ZrO_2 and MoO_3 in the

TABLE 2. Fluorine content of the investigated samples

Samples No	1	2	3	4	5	6	7
	Potassium – fluorophlogopite compositions					Ba-fluorophlogopite	
Compo-nents	without addi-tives	+3wt. % MoO_3	+10wt. % ZrO_2	+10wt % ZrO_2 like ZrF_4	+15wt. % ZrO_2	without addi-tives	+6wt. % MoO_3
F content [wt.%]: by synthesis	14.0	13.70	12.81	12.81	12.25	5.57	5.25
by analysis	12.10	11.94	11.68	6.27	9.35	5.35	5.39
F^- -losses [wt.%]	2.0	1.75	1.13	6.54	2.90	0.22	−0.14

fusion cast ceramics had a negative effect on the crystallization of K and Ba-fluor-mica in contrast to the case of glass-ceramic materials.

It is a little bit unexpectedly bearing in mind that the ZrO_2 and MoO_3 are perhaps one of the best known practical examples of oxide nucleation catalysts in the glass and glass-ceramic materials. It has to be noted, however, that nucleation additives (ZrO_2 and MoO_3) enhance at some extent the crystallization ability of the K-fluorophlogopite glassy frit samples as in the case of the glass-ceramic materials.

So, it has to be supposed the increase in the viscosity of the fluor-mica undercooled melt near the T_1 due to the MoO_3 addition. Because of the high temperature of crystallization (close to 1400°C) it was impossible for us to have some direct measurements of the viscosity near the melting point. Bearing in mind, however, the metal-like pouring of the melt into the casting mould, we suppose that the viscosity at T_1 of the potassium fluor-mica liquid (sample No 1 under investigation) should be of the order of 10^{-1} (dezi) dPa·s (cf. that molten metals have viscosity of the order of 10^{-2} dPa·s [22]) and that the addition of MoO_3 and especially of ZrO_2 would strongly increase it.

Figures 2–6 show reflection light images of the microstructure of compositions 1, 2, 3, 4, and 5. Mainly sheaf-like mica spherulites are present. The width of the sheaf-like spherulite crystals decreases with increasing MoO_3 and ZrO_2 content (i.e. the fern-like crystal sheaves grow thinner with the addition

Fig. 2. Reflection light micrograph of polished sample of “pure” K-fluorophlogopite composition

Fig. 3. Reflection light micrograph of polished sample of K-fluorophlogopite composition with 3% MoO_3 additive

Fig. 4. Reflection light micrograph of polished sample of K-fluorophlogopite composition with 10% ZrO_2 additive

Fig. 5. Reflection light micrograph of polished sample of K-fluor-phlogopite composition with 10% ZrO₂ additive introduced as ZrF₄

Fig. 6. Reflection light micrograph of polished sample of K-fluor-phlogopite composition with 15% ZrO₂ additive

of MoO_3 and ZrO_2) giving needle-like aggregates in some samples containing ZrO_2 . In other words the spherulite rays change from sheaves to needles with the increasing viscosity of the melt [23]. Spherical ZrO_2 crystals about $1\text{ }\mu\text{m}$ in diameter are crystallized like pearls embedded in the mica plates, *Fig. 2*.

It is worthwhile to note that the composition No 4 (the sample with ZrF_4) is characterized with relatively high content of glassy phase and has the microstructure of the glass-ceramic material (*Fig. 5*).

The barium mica compositions (samples No 6 and No 7) have a quite different microstructure (*Figs 7–8*). The highly crystalline and interlocking aggregates of needle-like Ba-mica sheet crystals give the samples higher mechanical strength compared to No 1, but a relatively lower machinability. The sheaves of mica are clearly recognizable (*Fig. 8*), whereas the spaces between the sheaves according to EDX-measurements yield a composition of a relatively lower Ba-content.

Figure 9 shows some reflection light micrographs of different mica spherulites. The microstructure of the K-fluorophlogopite with 5% SiC additive is much more finer.

The chemical composition of the K-fluorophlogopite with 5%SiC additive is shown in *Table 3*.

Fig. 7. Reflection light micrograph of polished sample of “pure” Ba-fluorophlogopite

Fig. 8. Reflection light micrograph of polished sample of Ba-fluorophlogopite with 6% MoO₃ additive

TABLE 3. Chemical composition of the K- fluorophlogopite with SiC as additive

Components	Chem. comp. wt. %
K ₂ O	11.32
MgO	26.42
Al ₂ O ₃	11.13
SiO ₂	40.67
F ₂	10.40
SiC	5.00

TABLE 4. Characteristic properties of K- fluorophlogopite with 5% SiC as additive

Properties	Value
Apparent density, g/cm ³	2.80
Mohs hardness	3
Compressive strength, MPa	72
Bending strength, MPa	21
Coeff. of thermal expansion, $\times 10^{-6} \text{ deg}^{-1}$	9.50

Fig. 9. Reflection light micrograph of polished sample of K-fluorophlogopite with 5%SiC additive

The silicon carbide is introduced into the composition as a modifier of the crystallization and for improving the physico-mechanical properties of the material (*Table 4*).

4. DISCUSSION

The influence of MoO_3 and ZrO_2 on the crystallization behavior is found to be quite different in all fusion cast ceramics investigated, compared to the case of glass-ceramic materials. In all cases the addition of these oxides decreases the crystallization rate and increases the content of the glassy phase.

It is due to two factors: (i) a relatively higher viscosity of the melt at the temperature of the fastest overall crystallization rate caused by the addition of MoO_3 and/or ZrO_2 and (ii) the redistribution of the matrix glass composition required for crystallization.

A higher viscosity results in a lower crystallization rate, a lower critical cooling rate and hence a higher content of the glassy phase [24]. The second condition, the redistribution of glass matrix, draws attention to melt compositions, which differ appreciably from those of the respective crystalline phase (in the cases considered here melts with MoO_3 and ZrO_2). This second condition is in accordance with the long-time practice of glass technologists who in formulating glass compositions often provide a multicomponent mixture of

materials; this mixture or melange aspect is undoubtedly favorable for ease of glass formation.

ZrF₄ decreases K-fluor mica formation and crystallization more substantially than ZrO₂. The final phases in the composition, which contains ZrF₄, are: mica, ZrO₂ (badellite), forsterite, K₂ZrSi₂O₇, KMgF₃, and much residual glass phase.

K₂SiF₆, as a batch constituent, considerably decreases the fluorine losses of the molten materials prepared with it, which implies that a relatively large amount of the SiF₄ does not evaporate from the melt. When the formation of the readily volatile gaseous SiF₄ occurs in the thermal decomposition of K₂SiF₆, silicon (from SiF₄) would immediately prefer the oxygen bond, forming SiO₄, thus making the liberated fluorine available for monovalent alkali metals [25].

It seems that mica crystals grown in a relatively more viscous medium (e.g. Ba-fluor-phlogopite melts, ZrO₂ and MoO₃ containing K-fluor-mica compositions) generally display a morphology more restricted in one direction (i.e. needle like) than those formed in a fluid environment of pure K-fluor-mica melt. The kinetic difficulty of transporting mica-forming species (large distance through a semi-rigid network) is responsible for the latter observation. It is worth noting that the mechanical strength in particular is generally higher for the Ba-mica systems whereas the machinability is relatively lower than in the case of K-mica compositions.

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ВЛИЯНИЕ НА MoO_3 , ZrO_2 И SiC ВЪРХУ КРИСТАЛИЗАЦИЯТА И ТЕРМО-МЕХАНИЧ- НИТЕ СВОЙСТВА НА ФЛУОРФЛОГОПИТНИ ТОПЕНО ЛЕТИ КЕРАМИКИ

ИВАН ПЕНКОВ, ВЛАДИМИР ПЕТКОВ И РАДОСЛАВ ВЪЛОВ

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Резюме. В зависимост от техния състав, стопилките на основата на К или Ва флуор слюди, при повторно нагряване, могат да се отнасят или като конвенционални стъкла, респективно, стъкло-керамики, или като топено лети керамики. За някои специфични състави, принадлежащи към последната група, е изследвано влиянието на добавки от MoO_3 , ZrO_2 и SiC . MoO_3 е избран, защото е известно, че той иницира хомогенно зародишообразуване чрез намаляване на разликите в повърхностните енергии между стопилката и кристала. ZrO_2 и SiC са избрани, защото те са класически катализатори на зародишообразуването в много стъкло-керамични ситеми. Показано е, че тези добавки съществено намаляват скоростите на кристализация и, също така, причиняват съпътстващи промени в получената керамична микроструктура и термо-механичните отнасяния на флуорфлогопитните топено лети керамики. Два-та ефекта са интерпретирани като следствие на повишения вискозитет на стопилката.

Ключови думи: флуорфлогопит, топено лети керамики, стъкло-керамики, катализатор на зародишообразуване, повърхностна енергия.

Received July 09, 2018