The effect of the composition on the crystallization behavior of sintered glass-ceramics from blast furnace slag

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Glass-ceramics manufacturing has been considered as a very effective method for recycling and utilizing different types of industrial wastes. The purpose of this paper was to investigate the crystallization process of sintered glass-ceramics prepared from vitrified mixtures which were composed on blast furnace slag (68–80 %$_{mass}$), kaolin, Al_2O_3 and TiO_2. First the parent glasses were prepared. Then the glass-ceramics were obtained by one-step heat treating at 1000 °C from pressed glass powders. The crystallization behavior was studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystalline phases were identified to be melilite, anorthite and pyroxene. The ratio between crystalline phases depends on chemical composition of the parent glasses. The examined microstructures were in accordance with the surface mechanism for crystal nucleation. The enhanced nucleation activity of fine glass powders caused crystallization, which led to good mechanical properties of glass-ceramics.

Key words: blast furnace slag, glass-ceramics, crystallization, structure.

INTRODUCTION

Although the exploitation of industrial wastes is not a new problem, it is still very actual and relevant one. Large part of solid wastes is formed by slags as by-products of metallurgical industry. The issue of slag application is still not resolved, not only for the metallurgical slags produced annually, but also for the large quantities of slags accumulated over the decades. One of the alternative options is to use slags as a raw material for the production of glass-ceramics [1–10] known as "slagsitall" and "slagceram". Glass-ceramics manufacturing is a well established process [3]. The glass-ceramic is a fine-grained crystalline material obtained by controlled crystallization of glass. There are two main production techniques. The first one usually involves a two-step thermal treatment of nucleation and crystal growth performed on monolithic glass. In most cases so-called nucleation agents are added to the base composition of the glass-ceramic. These nucleation agents aid and control the crystallization process. The second approach is based on the viscous flow sintering of fine glass powders, with concurrent crystallization, known as "sinter-crystallization". The use of sinter-crystallization technology gives many advantages. The high specific surface of fine powders enhances the surface nucleation and thus crystallization may occur without the use of any nucleating agent. This technology gives the possibility to obtain materials with diverse and complicated shapes and good mechanical properties [10]. Glass-ceramics with not frequently encountered crystal phases [11], or processed with rapid heating [12], have been successfully prepared.

Although there are many studies of glass-ceramics obtained from metallurgical slag [1–10], some of the problems remain unresolved. Even slags ensuing from one type of production process have specific composition, depending on the type of ores used. For example, blast furnace slags are usually considered with regard to the systems $CaO–Al_2O_3–SiO_2$ or $CaO–Al_2O_3–MgO–SiO_2$. In addition to these major components sometimes they also include BaO, MnO, FeO, K_2O, Na_2O and other components [13], i.e., the actual processes take place in a far more complex multi-component system. Another typical problem in the production of glass-ceramic materials based on metallurgical slag is the non-uniform (variable) chemical composition of slags. On the other hand, the phase composition and microstructure of slag glass-ceramics, and respectively their

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Table 1. Composition of the batches

Sample, №	1	2	3	4	5	6	7
Materials, % $_{mass}$							
Blast furnace slag	73.6	67.8	68.2	74.3	80.2	79.9	74.0
Kaolin	20.7	24.8	20.5	12.0	7.9	12.2	16.4
Al_2O_3	–	1.7	5.7	8.0	6.2	2.2	3.9
TiO_2	5.7	5.7	5.7	5.7	5.7	5.7	5.7

properties, are dependent on the slag composition and the used additive agents. The purpose of this study is to determine the effects of the change in the chemical composition on the phase composition and microstructure of glass-ceramics. This was the reason to select seven batch compositions with different proportions of the main oxides CaO, Al_2O_3 and SiO_2. Blast furnace slag from Kremikovtsi plant, as a main component and inexpensive additives (kaoline, Al_2O_3 and TiO_2) were used for the synthesis of glass ceramics materials via sinter-crystallization technology. The choice of particular compositions and additives was based on our previous experimental data [14–16], which showed that glass-ceramics with good mechanical properties can be obtained from such compositions.

MATERIALS AND METHODS

Synthesis of glass ceramics

The investigations performed have shown the blast furnace slag to be suitable for the production of melilite containing glass ceramics material without substantially changing the chemical composition of slag. Blast furnace slag, kaolinite, Al_2O_3 and TiO_2 were used for the synthesis of glass ceramics

Table 2. Chemical composition of the used blast furnace slag

Oxides	Content,% $_{mass}$
SiO_2	35.16
Al_2O_3	9.29
FeO	0.97
MgO	5.15
MnO	2.61
BaO	3.24
CaO	40.46
Na_2O	0.28
K_2O	0.97
S^2	1.17
Fe	0.70

materials by sintering of the samples obtained by semidry pressing. In the experiments, TiO_2 was chosen as nucleating agent. TiO_2 is the most common nucleating agent in the glass-ceramics. TiO_2 is soluble in wide range of molten glasses. But during cooling or subsequent reheating large number of submicroscopic particles are precipitated and these assist the development of major crystalline phases [17]. Data is also available for the role played by TiO_2, which is usually considered to induce amorphous separation and volume crystallization during ceramming. The heat treatment of amorphous glasses leading to nucleation would cause a disruption of silica network which followed phase separation. The phase separation followed the generation of crystal [18]. Taking into account our previous studies [14–16] the compositions were chosen in the upper boundary region of the crystallization field of gehlenite in the $CaO-Al_2O_3-SiO_2$ system. The batches for the seven experimental compositions are given in Table 1.

The chemical composition of the used blast furnace slag from Kremikovtsi is reported in Table 2.

The synthesis of the seven experimental samples was carried out under identical conditions. First the parent glasses were prepared. The batches were melted in a laboratory box furnace at 1450–1470 °C for 60–90 minutes. The melt were fritted and the resulting frit was ground in a porcelain ball mill to a grain size below 0.1 mm. A 3% aqueous polyvinyl alcohol solution was added. Then the mixture was homogenized, granulated and pressed with an automatic press (pressure 300 kg/cm²). Cylindrical briquettes (with a diameter 30 mm and a height of 14 mm) were obtained. The sintering and crystallization proceeded in a muffle furnace at 1000 °C, with retention time of 3 hours. Thus glass-ceramics were obtained from pressed glass powders by one-step heat treatment. The obtained glass ceramic samples are presented in Fig. 1. They were labeled as № 1, 2, 3, 4, 5, 6 and 7. According our previous studies [14–16] data on some of the properties of glass-ceramics, such as: density 2.88–3.00 g/cm³; water absorption 0.01–0.05 %; Vikers microhardness 5.5–8.3 GPa, chemical resistance in NaOH 35% w/w aqueous solution above 99.9%, temperature of the onset of

Fig. 1. Glass-ceramics samples

Experimental methods

The X-ray diffraction (XRD) was performed using a D2 Phaser (Bruker) X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å). The measurements were carried out on powder samples in the 5º to 70º 2θ (30kV, 10 mA, step 0.05 º/sec). The crystalline phases were identified using the International Centre for Diffraction Data (ICDD) database. PowderCell 2.4 software [19] was applied to determining the unit cell parameters on the basis of experimental X-ray data.

The microstructure of the glass ceramic materials was investigated by SEM. Microscope JEOL JSM 5510 is used. The samples were coated with gold in an auto fine coater JEOL JFC-12200.

RESULTS AND DISCUSSION

deformation ~1150 °C, thermal stability ~700 °C, linear thermal expansion coefficient (x10^{-7}/°C) ~90, agrees with literature data for similar materials [3] and proves to be promising and feasible.

XRD data is given in Fig. 2. Three main crystal phases in varying proportions were present in the samples: melilite, anorthite and pyroxene. Experimental XRD data were compared with
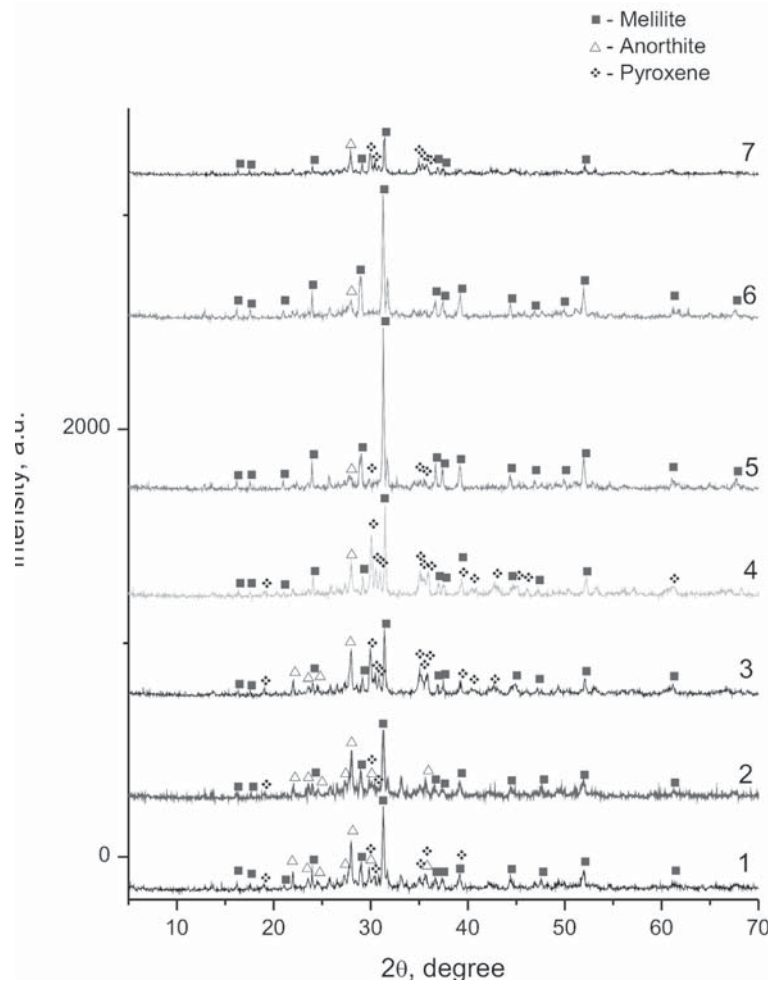

Fig. 2. XRD patterns of glass-ceramics samples

Table 3. Phase composition of glass-ceramics – crystalline phases identified in glass-ceramics

Sample № Crystalline phases	1	2	3	4	5	6	7
Melilite, vol.%	32	33	20	26	60	66	25
Anorthite, vol.%	51	55	40	23	25	34	33
Pyroxene, vol.%	17	12	40	51	15	–	42

Powder diffraction file cards № 35-0755, 41-1486 and 31-0249. The phase compositions of the glass-ceramic samples determined through the XRD analysis are presented in Table 3. The quantitative phase analysis of the samples was performed with the PowderCell 2.4 software. The amorphous mass (glass) quantity was not taken into consideration. No amorphous hallo is visible in Fig. 2. but SEM analysis clearly indicates the presence of glass.
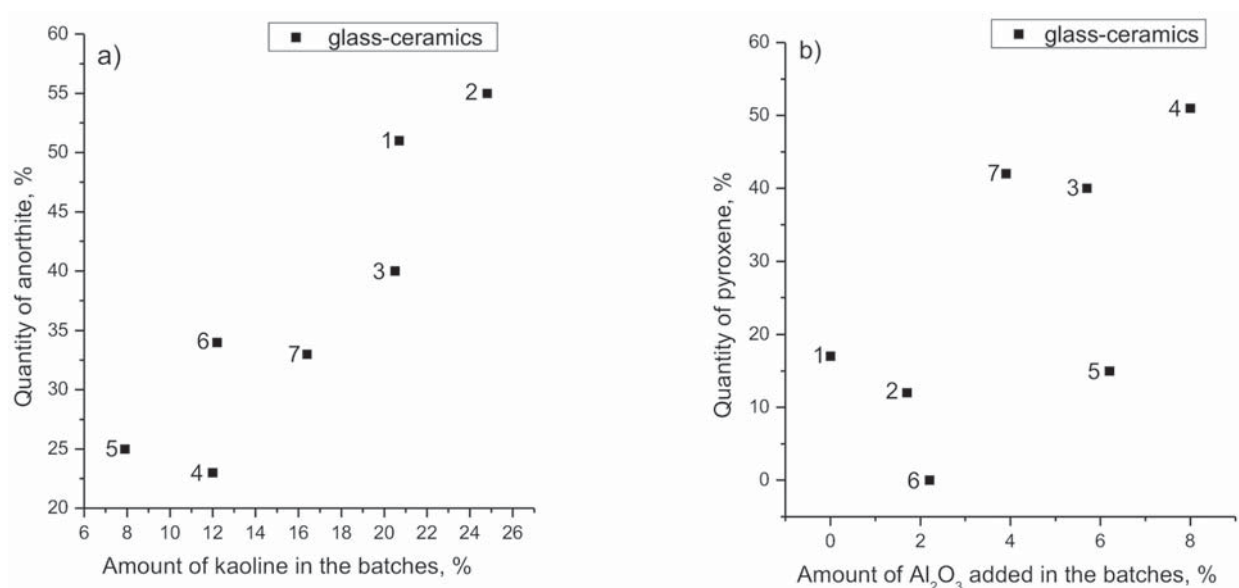
XRD data show maximum intensity of the diffraction peak (211) of melilite in all X-ray diffraction patterns. However, melilite was the predominant crystal phase only in samples 5 and 6. These were the compositions with the highest CaO content (e.g. highest blast furnace slag content), and it is logical that the compositions that are the closest to the gehlenite stoichiometry show the highest melilite content.

The phase content of samples 1 and 2 was nearly identical, with anorthite accounting for slightly more than 50% of the crystalline phases. These were the compositions containing the smallest quantity of blast-furnace slag and the largest quantity of kaolin,

i.e., relatively less CaO and more SiO_2. Composition 2, in which the largest amount of anorthite was observed, corresponds to the minimum content of CaO and the maximum content of SiO_2.

Compositions 3, 4 and 7 are characterized by a more significant participation of pyroxene in the phase content: 40–50% of the crystalline phases. Their chemical composition differs by the relatively high content of Al_2O_3, composition 4 having the highest Al_2O_3 content and the highest pyroxene content. Judging by the intensity of the diffraction peaks of the crystalline phases when compared with other samples, composition 7 exhibited the lowest degree of crystallization and the lowest content of the melilite phase.

The observed dependencies are presented graphically in Fig. 3 and 4. Fig. 3 shows the dependencies of phase composition of the glass-ceramics on the amount of additives while Fig. 4 illustrates the effect of chemical composition. The calcium, silicon and aluminum contents in parent glasses are presented in oxide form. Note that the dependence between the content of anorthite and SiO_2 (Fig. 4a) is more

Fig. 3. Dependence of phase composition of the glass-ceramics on the amount of additives
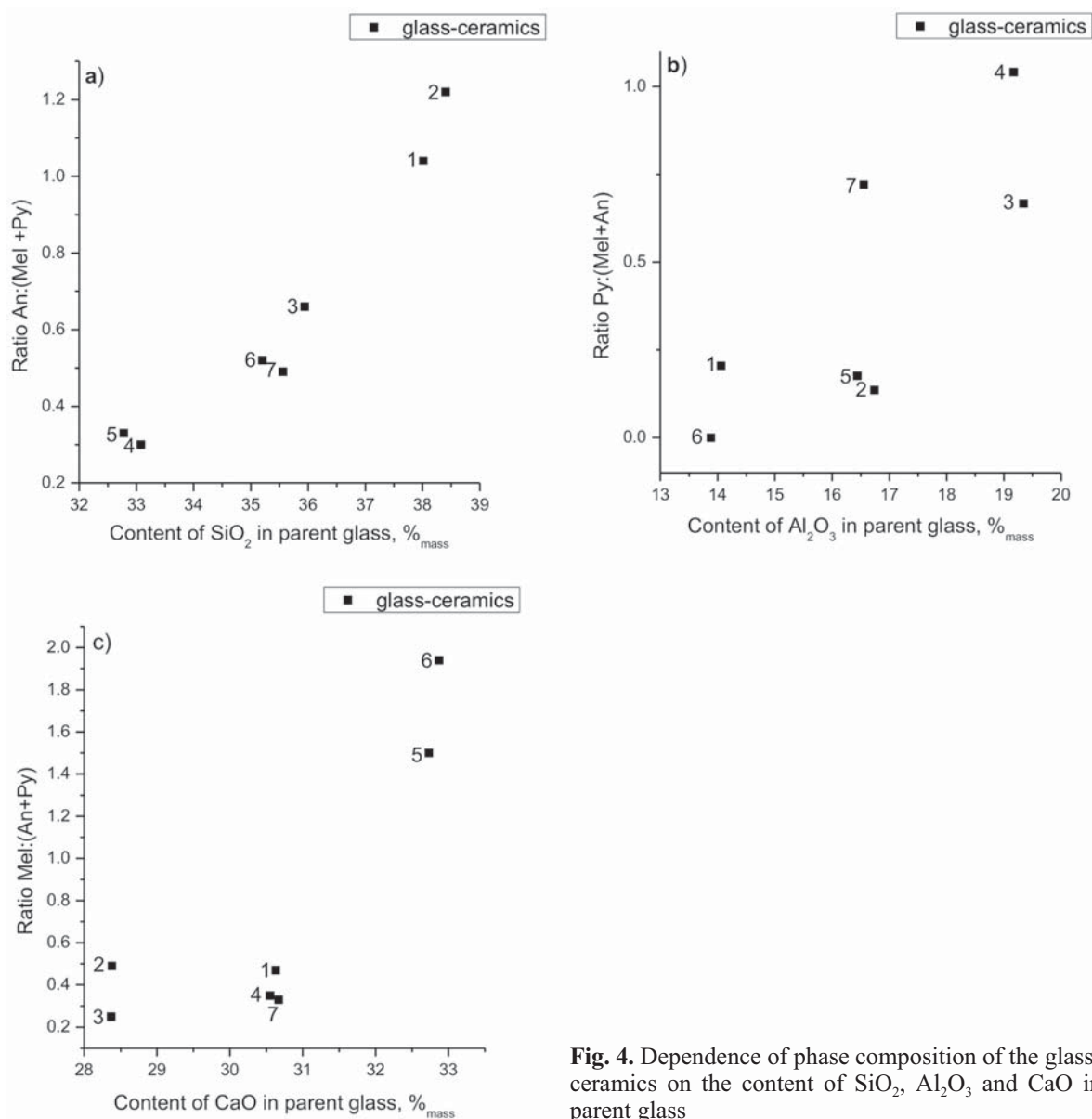
Fig. 4. Dependence of phase composition of the glass-ceramics on the content of SiO_2, Al_2O_3 and CaO in parent glass

clearly expressed than the dependency between melilite and CaO content (Fig. 4c). The replacement of SiO_2 with Al_2O_3 leads to an increase of pyroxene for compositions with the same content of CaO: 1, 7 and 4, 6 and 5, 2 and 3 (Fig. 4b).

It is known that the three crystalline phases identified in glass-ceramics can form solid solutions. Melilites, usually regarded as solid solutions between gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$), may include a number of isomorphic impurities: Ba, Na, Mn, Fe and others. This has an impact on the unit cell parameters of the formed melilite phases (Table 4). The unit cell parameters of the melilite phase are closer to those of gehlenite in compositions 3 and 4, i.e., closer to those in compositions with a high Al_2O_3 content. The unit cell pa-

rameters in compositions 1 and 6 that have a lower Al_2O_3 content deviate from those of gehlenite and tend to approximate the akermanite unit cell parameters. The unit cell parameters of the anorthite phase in compositions 1, 2 and 3, which have the highest anorthite content, correspond most closely to literature data [20]. Pyroxenes also tend to have isomorphic substitutions; however, the unit cell parameters of the formed pyroxene phases in the glass-ceramic samples did not differ significantly. It cannot be therefore expected that the phase compositions of pyroxene in the samples differ.

Common micro-structural features were observed in slag glass-ceramics № 1, 2, 3, 4, 5 and 6, which are represented in Fig. 5. A common structural feature of the samples was the presence of an

Table 4. Cell parameters of crystalline phases in glass-ceramics

Sample №	1	2	3	4	5	6	7
Cell parameters of melilite, Å							
a	7.748	7.759	7.696	7.702	7.728	7.752	7.701
c	5.042	5.046	5.065	5.047	5.038	5.037	5.074
Cell parameters of anorthite, Å							
a	8.182	8.178	8.185	8.212	8.109	8.128	8.199
b	12.885	12.895	12.879	12.956	12.953	12.959	12.911
c	14.147	14.155	14.165	14.238	14.236	14.211	14.188
α	93.315	93.527	93.328	94.300	93.601	93.434	93.215
β	115.577	115.606	115.586	115.641	115.545	115.649	115.710
γ	90.985	90.866	90.983	90.881	92.027	92.120	91.097
Cell parameters of pyroxene, Å							
a	9.676	9.709	9.709	9.709	9.509	–	9.709
b	8.752	8.752	8.752	8.752	8.752	–	8.752
c	5.368	5.350	5.335	5.335	5.354	–	5.351
β	105.060	106.517	106.299	106.299	105.060	–	106.263

amorphous phase densely enveloping the crystals. The obtained glass-ceramic materials had a finely dispersed crystalline structure showing microcrystals of ~3–4 μm. Idiomorphic crystals with a characteristic morphology that corresponds respectively to anorthite, melilite and pyroxene were identified in large rounded pores measuring up to 10–20 μm. The diversity in size and morphology of the crystalline phases illustrates the complex phase composition of the samples. The typical orientation of melilite and anorthite crystal slabs was perpendicular (transverse) to the boundary surface of pores. SEM observations confirmed the view that the inter-phase surface is a factor favorable for crystallization. The observed intensive crystallization in the above mentioned pores, where even amorphous mass linkage was missing, proves this. In addition to the larger, rounded pores, smaller pores of irregular shape were observed. There was a good sintering of the input powders. Different-sized pores were closed and did not lead to increase in the water absorption of samples, which was in the range 0.01–0.05%. Usually the dense microstructure without any pores is considered to be characteristic of glass-ceramics. On the other hand, the presence of pores is not without a precedent and has an explanation. For example, two types of closed porosity are well distinguished in diopside glass-ceramics [21, 22]: intergranular residual pores have an irregular shape and are characterized by a smooth surface, while intragranular induced crystallization pores have a semi-spherical shape and an indented polycrystalline surface. It is shown by Karamanov and Pelino [21, 22] that, due to the volume variation related to crystallization, spherical intragranular pores are formed in sintered glass-ceramics. The amount of the induced porosity is a function of the crystallization. In spite of the increase in porosity, the mechanical properties are improved with the rise in crystallinity. The pores observed in our study (Fig. 5) were typical intragranular induced crystallization pores.

Previous experiments have shown [14-16] that the thermal treatment of similar in composition monolithic slag glasses does not incur bulk crystallization. On the other hand, when thermally treated, pressed powders transform into strong and relatively dense materials with several crystalline phases. Therefore, in ceramic technology (sintering of glass powders) the process of crystallization proceeds much more intensively. The interphase surface stimulates the crystallization, which starts from the surface of the glass particles. Larger pores, in which the highest degree of crystallization was observed, also support the idea of the role of the surface. We consider that probably these pores were formed as a consequence of the glass crystallization The crystals formed in the amorphous matrix had a higher density than the density of the amorphous mass, which led to shrinking of the sample and the formation of induced porosity.

CONCLUSIONS

Glass-ceramics with good properties have been successfully synthesized from blast furnace slag (between 68 and 80%$_{mass}$), kaolin, Al_2O_3 and TiO_2 additives via sinter-crystallization technology. The
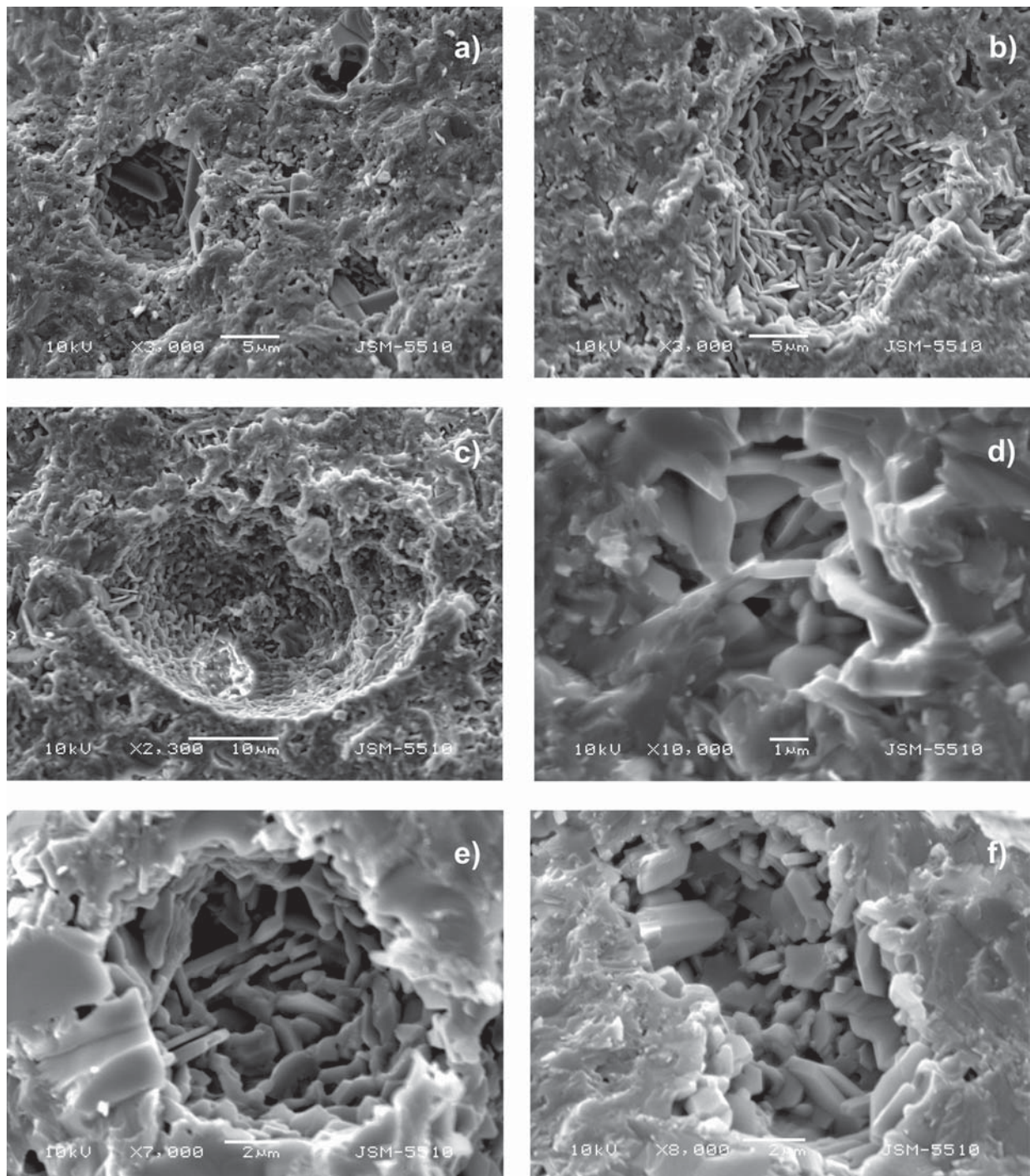
Fig. 5. SEM images of glass-ceramics samples: a) – 2; b) – 3; c) and d) – 4; e) – 5; f) – 6

final crystalline phases of glass-ceramics were melilite, anorthite and pyroxene. The batch compositions affected the phase composition of glass-ceramics. Glass-ceramic materials with a main phase in the form of melilite were obtained from the compositions with higher slag content (~ 80%).

Kaolin additive led to an increase of anorthite and the increase of Al_2O_3 content facilitated the crystallization of pyroxene. Therefore the use of additives could be applied to control phase composition. However, it is more important that glass-ceramic materials with a similar microstructure and promis-

ing properties were obtained within the scope delineated by the seven batches. Therefore, the unavoidable variations in the chemical composition of the used slag could change the phase composition of the obtained glass-ceramics, without having any significant impact on its structural characteristics and properties.

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ВЛИЯНИЕ НА СЪСТАВА ВЪРХУ КРИСТАЛИЗАЦИЯТА НА СИТАЛИ НА ОСНОВАТА НА ДОМЕННА ШЛАКА

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(Резюме)

Производството на ситали е считано като много ефективен метод за рециклиране и използване на различни типове промишлени отпадъци. Целта на настоящата работа е да изследва процеса на кристализация на ситали, получени по керамична технология чрез спичане на стъклени прахове. Първоначално са получени изходни стъкла от шихти, съставени от доменна шлака (68–80%$_{mass}$), каолин, Al_2O_3 и TiO_2. Ситалите са получени чрез едно-стъпална термообработка при 1000 °C на пресованите стъклени прахове. Кристализацията е изследвана с рентгено-фазов анализ и сканираща електронна микроскопия. Кристалните фази са определени като мелилит, пироксен и анортит. Съотношението между кристалните фази зависи от химичния състав на изходните стъкла. Установените различия в параметрите на елементарната клетка са във връзка с изоморфни замествания в кристалните фази и респективно променливия им състав. Микроструктурата на ситалите е в съгласие с повърхностен механизъм на зародишообразуване. Засилената склонност към зародишообразуване на фините стъклени прахове води до получаване на ситали с добри механични свойства.