Influence of glass compositions, sintering rate and holding temperature on the sinter-crystallization of vitrified industrial wastes

A. Karamanov[1], N.B. Jordanov[1], V. Savic[2]

[1]Institute of Physical Chemistry, Bulgarian Academy of Sciences, Bl. 11, Acad. G. Bonchev Str., 1113, Sofia, Bulgaria
[2]Institute for Technology of Nuclear and Other Mineral Raw Materials, Bulevar Franš d'Eperea 86, 11000, Belgrade, Serbia
Keywords: virification, glass-ceramics, sintering
Presenting author e-mail: karama@ipc.bas.bg

Introduction

The technique of sinter-crystallization, which permits the manufacture of specimens with complex shapes or composite materials, has been proposed by many colleagues as an alternative for the synthesis of various glass-ceramics by inorganic technogenic industrial wastes. It is a promising approach because gives a possibility to use glasses with lower degree of homogenization and refining, which significantly reduces the melting price. In addition, contrary to the traditional bulk glass-ceramics, which are produced by two step long thermal cycle (for bulk nucleation and subsequent crystal growth, respectively), the sintered glass-ceramics are usually obtained by short one step heat-treatment. However, in many cases the relationship between the sintering and the crystallization of used glass powders or frits, which carries out during the thermal treatment, is not well elucidated and thus several of the synthesis made are not well optimized.

In the present work attempt to show the impact of parent glass composition, heating rate and holding temperature on the final structure of sintered glass-ceramics is made. As examples four different glasses obtained by vitrification of diverse industrial wastes are used.

Experimental

The industrial wastes used were fly ash from a thermal power plant, FA, sugar beet factory lime, CS, municipal solid waste incinerator bottom ash (fraction > 2 mm), MSWA, and iron furnace slag, IS. The batches were obtained by mixing: 75 % FA with 25 % CS (composition CS); 37.5 % FA with 25 % CS and 37.5 % cullet from container glass (composition LCS), 100 % MSWA (composition MA); 70 % IS with 30% industrial sand (composition ISS). The glasses were melted for 1 at 1500ºC (composition CS and LCS) and 1400ºC (compositions MA and ISS) and then were milled below 63 microns. "Green" samples with 50×5×4 mm size have been prepared by wetting with 8 % wt. PVA solution, followed by uniaxial pressing of 100 MPa.

The sintering was carried out using contactless optical dilatometer or hot stage microscopy at different heating rates and holding temperatures, appropriated for each of the composition. The structures of samples were studied by SEM, the phase composition – by XRD and the porosity - by gas pycnometry.

Results and discussions

Table 1. Chemical compositions

	CS	LCS	MA	ISS
SiO_2	51.8	50.3	42.7	49.2
TiO_2	0.7	0.5	1.3	0.7
Al_2O_3	14.8	10.4	11.2	5.1
Fe_2O_3	3.0	3.7	4.5	5.5
MgO	2.7	1.4	4.0	1.1
CaO	26.1	30.8	19.5	18.6
BaO	-	-	-	10.9
MnO	-	-	-	5.8
K_2O	0.7	0.7	1.8	0.7
Na_2O	0.2	2.3	10.3	0.1
other	-	-	4.1	1.2

The results for the chemical compositions of parent glasses are summarised in Table 1. They are typical for the vitrified industrial wastes and show mainly SiO_2, Al_2O_3 and CaO, together with some iron oxide; MA also contain elevate amount of Na_2O, while ISS - BaO and MnO.

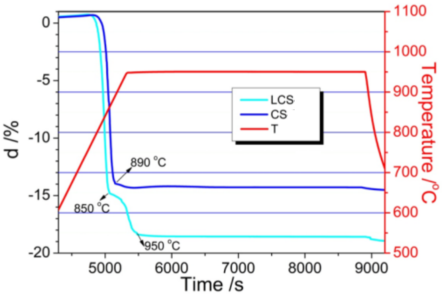

Fig. 1

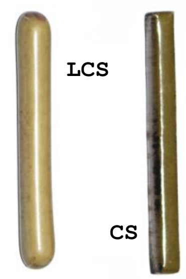

Fig. 2

Fig. 1 show the densification of CS and LCS by optical dilatometer at 20ºC/min and 1 h crystallization at 950ºC; thus obtained samples are presented in Fig. 2. Both glass-ceramics are perfectly sintered, but in CS a certain smoothing the edges is observed, while in LCS definite softening and deformation are evident. The sintering is taking place rapidly during the heating step and completes at 850 and 890ºC, respectively. During the crystallization step additional shrinkage is not observed in CS, while in LCS deformation shrinkage down to 19 % carries out; after ~ 20 min., due to the slow crystallization, this deformation process terminates. XRD results, after

1 h at 880ºC, explain this different behaviour: the crystallization in LCS yet is in initial phase, while is CS it is nearly complete with the formation of -30 % crystal phases (mainly anorthite). If lower heating rate of 5ºC/min is applied, the sintering remains completed in both glass-ceramics but the deformation trend decreases.

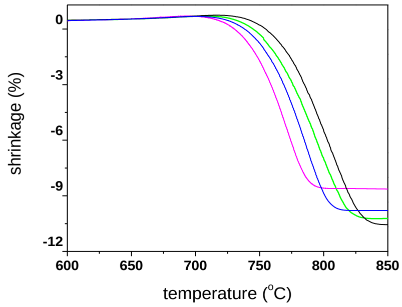

Fig. 3

Fig. 4

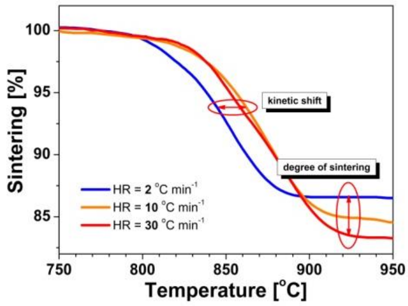

Fig.5

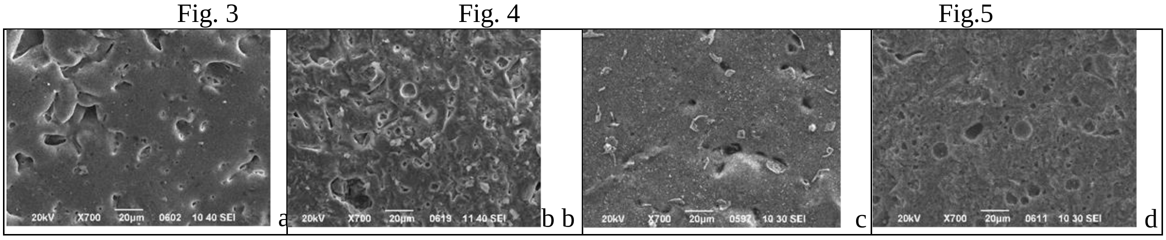

Fig. 6 SEM images of MA after 1 h at 950ºC: surface (*a* and *c*) and fracture (*b* sand *d*) at 5 and 20ºC/min.

Fig. 3 shows the non-isothermal sintering of MA at 2, 5, 10 and 20°C/min. Due to lower viscosity the sintering in this composition completes yet at 820-830°C and the crystallization step is at about 900ºC. It is evident that at lower heating rates the densification is partially inhibited, which can be explained by some slow phase formation during the heating. The porosity of final samples decreases with the rise of heating rate. At 2ºC/min the porosity is ~18% and mainly is open, at 5ºC/min it decreases to ~13% and starts the transformation of open into closed porosity. At higher heating rate the open porosity is eliminated and the closed porosity decreases to 8-9%. This is confirmed by Fig. 6, where SEM images of the surfaces and the fractures of samples, obtained at 5 and 20°C/min, are shown. The presence of some open porosity at low heating rate, as well as the decreasing of closed porosity at high heating rate are evident. In Fig. 4 are presented photos of an initial green sample and the glass-ceramics, obtained at 5 and 30°C/min, which confirms the improvement of the sintering at higher heating rate and the absence of additional shrinkage or deformation during the crystallization. The variation of heating rate also leads to different colours of the samples. Probably, the more intensive brown colour at higher heating rate is as a result of an uncompleted oxidation of the iron oxides. In fact, Fe^{2+} oxidation into Fe^{3+} in similar glass powders is a time depending process, which carries out near to the glass transition range. The crystallinity of MA is a little higher than in CS and the main crystal phases are gehlenite and pyroxene.

Fig. 5 shows isothermal hot-stage microscopy plots of ISS at different heating rates. The results are somewhat similar to ones of MA (i.e. the sintering improves at higher heating rate), but an interesting overlapping of the curves at 10 and 30°C/min is observed. This is another consequence of the presence of higher amounts of iron oxide (combined in this composition with certain MnO). It can be supposed that at lower heating rates the oxidation of the Fe^{2+} and Mn^{2+} practically completes, while at 30°C/min some no oxidized Fe^{2+} remains during the sintering. Since Fe^{3+} plays the role of intermedia oxide, which partially increases the viscosity, while Fe^{2+} and Mn^{2+} are typical modifiers, which contrary decrease the viscosity, the sintering is additionally "accelerated" at higher heating rates. The crystallinity of ISS glass-ceramics, obtained after 30 min step at 950°C is similar to one of MA, but, due to the lower amount of Al_2O_3 and higher % of iron and manganese oxides, the main crystal phase are pyroxene solid solutions.

Conclusions

In the studied glass-ceramics the sintering takes place mainly during the heating and the reached degree of densification depends on the crystallization trends of parent glasses. At lower crystallization ability (LCS and partially CS) deformation might carry out and lower heating rates and prolonged crystallization at inferior temperatures are required. Contrary, when the crystallization trend is higher (MA and ISS) the sintering improves at higher heating rates and shorter crystallization step at higher temperature is possible. When the composition contains bigger percentages of iron and manganese oxides, the sintering might be additionally accelerated at higher heating rates due to uncompleted low temperature oxidation of these oxides.

Acknowledgements: This research was financially supported by the projects KP-06-N67/13 (Bulgaria) and 451-03-66/2024-03/200023 (Serbia).