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Thermal Shock Properties of Glass-ceramics Synthesized From a Glass Frit

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Abstract:

In this study, the behavior of glass-ceramics synthesized from a glass frit of FFW (Final Flotation Waste) originated from the RTB Bor Company was investigated. Thermal shock resistance was monitored in order to assess the possibility of application of such waste material. Thermal shock of the samples was conducted using water quench test. Image analysis and ultrasonic measurements were used as nondestructive methods for quantification of thermal shock damage at the surface and in the bulk of the specimens. Phase composition of samples was determined by X-ray powder diffraction (XRPD). The degradation level of samples was about 43 % after 20 cycles of water quench tests. The results pointed out that glass-ceramic material exhibited good thermal shock resistance.

Keywords: *Final Flotation Waste (FFW); Glass-ceramic; Thermal shock; Image analysis; Ultrasonic velocity.*

1. Introduction

Extraction of copper, particularly flotation enrichment and pyro-metallurgical processing, results in the formation of waste materials which produce major environmental pollution problems. Flotation waste dumps and slag from smelters degraded large areas of land and cause permanent pollution of soil, water, and air. Utilization of waste that predominantly consists of silicate (consisting of fayalite, magnetite, and glass) [1,2] is extremely significant, not only because of reduction of the amount of industrial waste, but also as a potential raw material for the launch of new technology initiatives. Recycling of industrial waste material is a very frequent subject of numerous works [2-8], in which a glass-ceramics is being obtained by the process of vitrification.

For the most of ceramic or refractory materials, thermal shock resistance is one of the main properties to be investigated. Most of the tests for the determination of thermal shock resistance are based on heating and quenching sample into a different medium (water or air). The number of cycles that samples withstand represents the measure of their thermal stability

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[9-16]. It is well known that rapid temperature changes result in loss of strength and material degradation at the surface and in the bulk. The velocity of ultrasonic waves through the sample depends on the density and elastic properties of the material. The development of the samples damage was monitored by measuring the velocity of ultrasonic waves during the thermal shock.

The goal of this paper was to examine thermal shock characteristics of glass-ceramics synthesized from a glass frit of FFW in order to determine possibilities of its novel applications.

2. Experimental

2.1 Materials

FFW was sampled at the end of flotation process [2] just before transport to the landfill. Tab. I show chemical composition of FFW that was determined by using the X-ray fluorescent analysis (PANalytical AXIOS XRF Spectrometer).

Tab. I Chemical composition of FFW.

Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	K_2O (%)	MgO (%)	ZnO (%)	SO_2 (%)	CuO (%)	TiO_2 (%)	Na_2O (%)	Mn_3O_4 (%)	P_2O_5 (%)
52.10	34.27	4.89	4.58	1.22	0.79	0.79	0.50	0.49	0.36	0.31	0.07	0.07

The phases ratio of FFW was determined by the Powder Cell (PCW) program using the structural models of fayalite [17], magnetite [18], and hematite [19]. The results of XRPD analysis showed that FFW is composed of fayalite (75.0 %) and magnetite (25.0 %) as presented in Fig. 1.

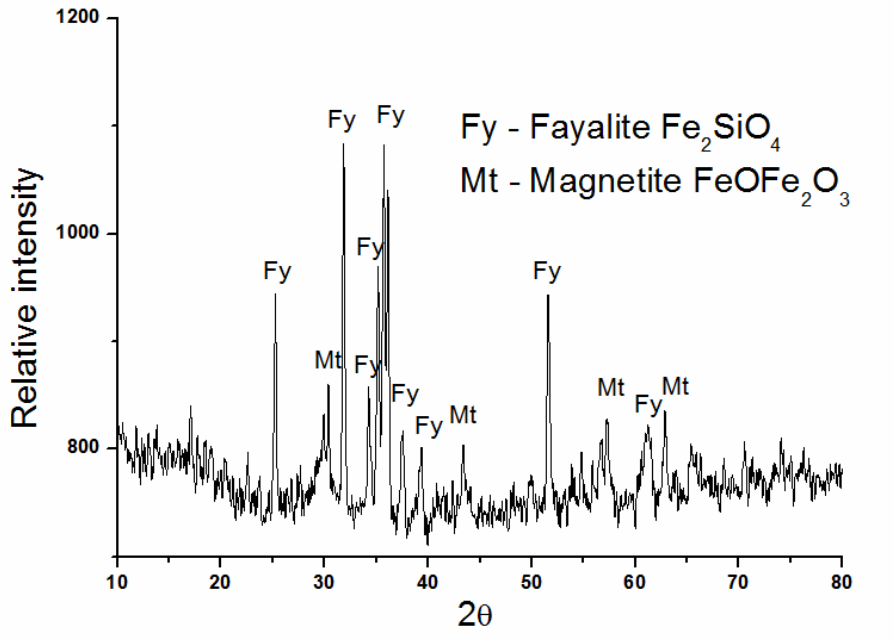

Fig. 1. X-ray powder diffraction diagram of FFW.

2.1.1 Samples preparation and characterization

In order to obtain a frit, the samples of FFW were thermally treated at 1300 °C, for 2 - 4h, then rapidly cooled in water and pulverized in the vibrating mill. Thereafter samples were sintered at a temperature of 1100 °C, for 4h. The XRPD pattern of the glass-ceramic sample is shown in Fig. 2. The magnetite from FFW is transformed by strong oxidation into the hematite, and fayalite is transformed into the hematite and amorphous glass [2,3,20,21].

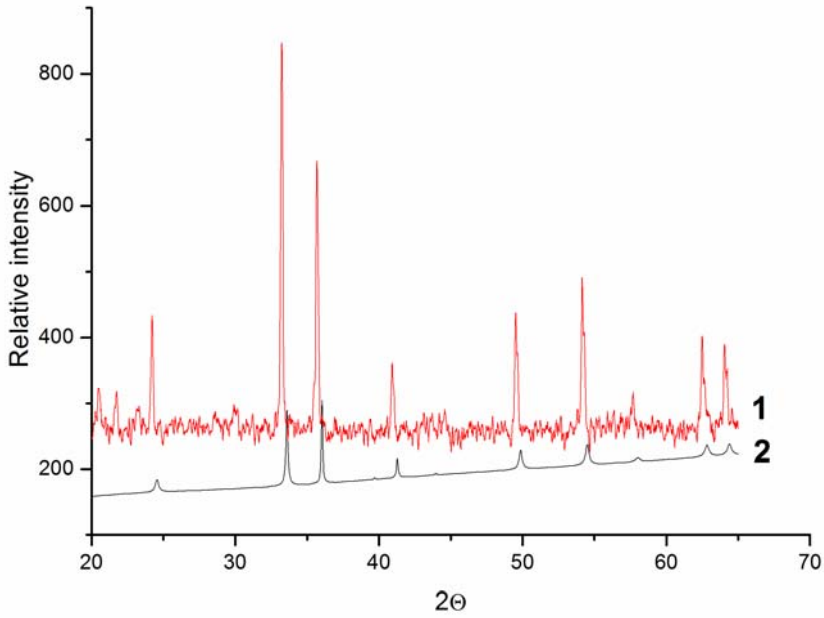

Fig. 2. X-ray powder diffraction diagram: 1) glass-ceramic, and 2) theoretical diagram of hematite [19].

Fig. 3 presents resulting glass-ceramics with bubble structure (the diameter of caverns varies from 0.02 to 0.03 mm, rarely above 1 mm) (Fig. 3a). Such structure is a consequence of the emanation of gasses due to heat treatment. The microstructure of synthesized samples consists of the glass and crystals of hematite (Fig. 3b). That is a solid solution with two phases: hematite and magnetite. The crystals are anhedral, rarely subhedral, with a diameter mainly below 10 μm.

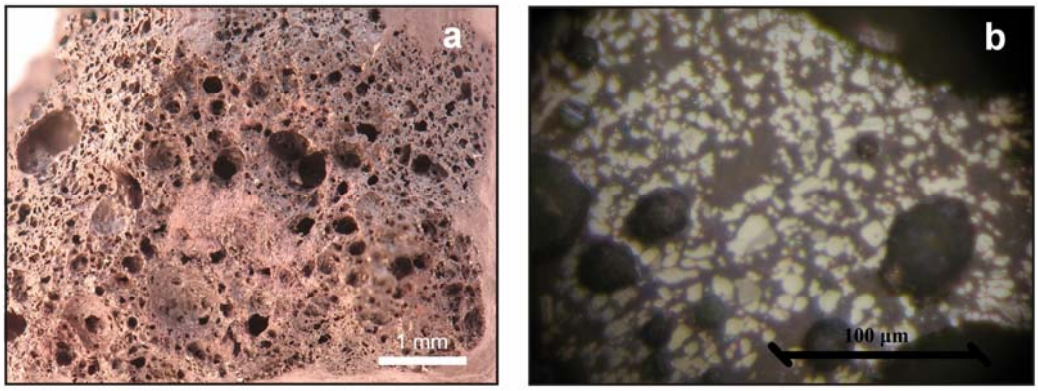

Fig. 3. Glass-ceramic samples: a) Macro photograph, and b) SEM microphotograph.

2.2. Methods

2.2.1 Water Quench Test

Thermal shock behavior of the samples was investigated using water quench test experimental method (ICS 81.080 SRPS B.D8.308). Samples were cylindrically shaped with the same length and diameter (1 cm). Each thermal shock cycle consisted of several consequent steps of rapid cooling into the water [16,22-26]. At first, the samples were dried at 110 °C for 24 h; then heated in an electrical furnace at 950 °C for 15 minutes. After that, the samples were cooled in the water for 3 minutes and dried. This procedure was repeated until the appearance of the first cracks (fracture). The number of such cycles before the appearance of cracks is taken as a measure of material thermal resistance. The standard fracture is defined as complete degradation of a sample, or 50 % or more of sample surface degradation that was coherent prior to this test.

2.2.2 Image analysis

For the determination of the degradation level of samples, image analysis was applied using Image Pro Plus Program. Samples were photographed before and during the test, in order to measure the degradation level.

2.2.3 Ultrasonic Pulse Velocity Testing

Various publications have dealt with the practical application of Ultrasonic Pulse Velocity Testing (UPVT) to non-destructively characterize and monitor the properties of industrial refractory materials. The UPVT method has been considered in detail in the literature [16,27-29]. Briefly, pulses of longitudinal elastic stress waves are generated by an electro-acoustical transducer that is held in direct contact with the surface of the refractory under test. After traveling through the material, the pulses are received and converted into electrical energy by a second transducer.

The ultrasonic pulse velocity (V) and dynamic modulus of elasticity (E_{dyn}) are calculated based on the equations (1) and (2) well documented in the literature [16,27-29].

$$V = \frac{L}{T} \text{ (m/s)} \tag{1}$$

where L is the path length (m) and T is the transit time (s).

$$E_{dyn} = V^2 \cdot \rho \cdot \left(\frac{\left(1 + \mu_{dyn}\right) \cdot \left(1 - 2\mu_{dyn}\right)}{1 - \mu_{dyn}} \right) \tag{2}$$

where ρ is the bulk density (kg/m^3) and μ_{dyn} is the dynamic Poisson ratio.

The measurement of ultrasonic velocity was performed using the OYO equipment, model 5210, according to the standard testing procedure (SRPS D. B8. 121.). Young's modulus of the samples was calculated using ultrasonic velocities obtained by UVPT [27-30].

3. Results and Discussion

The samples were experimentally investigated until 20 cycles of thermal shock. An example of the sample surface visage after the certain number of test cycles is shown in Fig.

4.

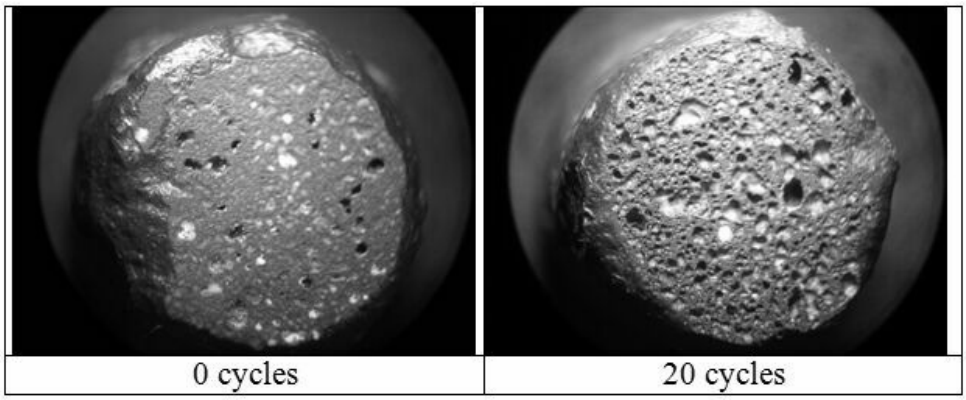

Fig. 4. An example of the sample surface visage before and after the water quench test.

The dependence between the level of degradation and a number of water quench test cycles (N) is presented in Fig. 5. The level of degradation is defined as P/Po (where P is damaged surface area and Po is undamaged surface area). It is important to note that the certain level of degradation was observed in the samples even before the quenching (22 %). This level of degradation will affect thermal shock behavior of the samples, thus, a higher level of degradation will lead to a lower thermal stability. The obtained level of degradation after 20 cycles of thermal shock test was 43 %. Such degradation level pointed out the good thermal stability of the samples. A very strong linear correlation was observed (R^2=0.957) between the level of degradation and the number of water quench test cycles.

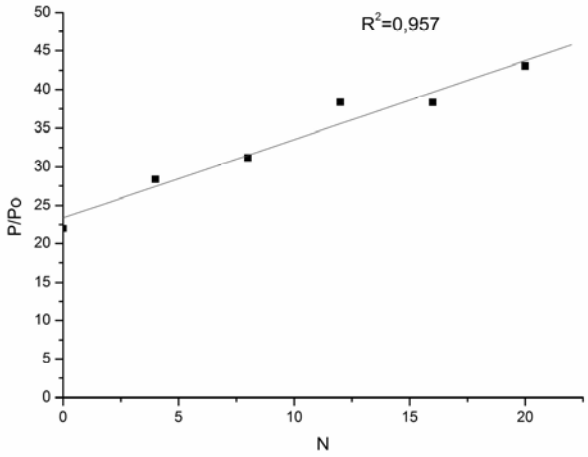

Fig. 5. Level of degradation of the samples (P/Po) versus number of quench cycles (N).

UPVT measurements pointed out that significant changes in ultrasonic velocities, both longitudinal and transversal, (Fig. 6a), as well in Young modulus of elasticity (Fig. 7a) were observed after only 4 cycles of quenching: decrease of ultrasonic velocities was about 40 % and Young modulus of elasticity decreased about 57 %. When the test was continued, the changes were not such rapid, and at the end of the experiment, ultrasonic velocities were less than one-half of the velocities measured before the quenching. After 20 cycles of quenching, Young modulus of elasticity decreased for about 76 %.

Accordingly, similar changes of ultrasonic velocities and Young modulus of elasticity as a function of degradation level can be noticed (Fig. 6b and Fig. 7b).

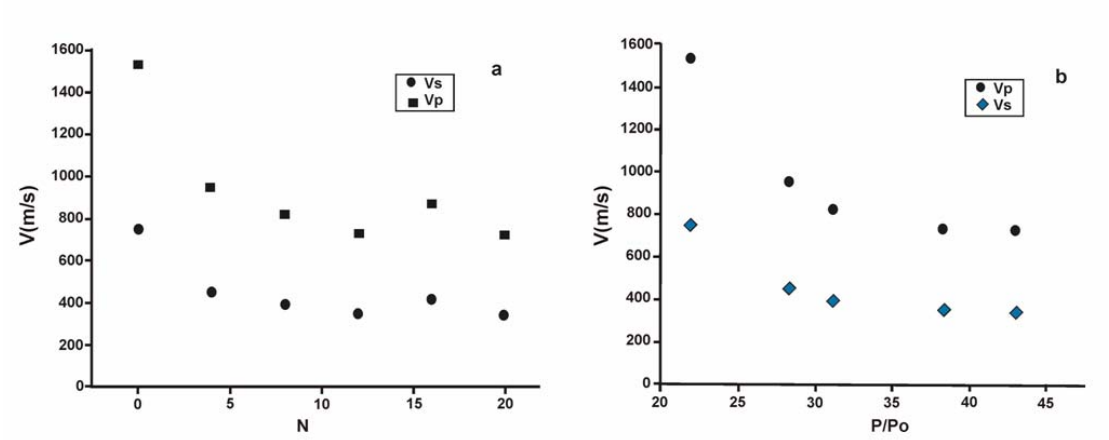

Fig. 6. Changes of ultrasonic velocity versus: a) number of quench cycles (N), and b) level of degradation.

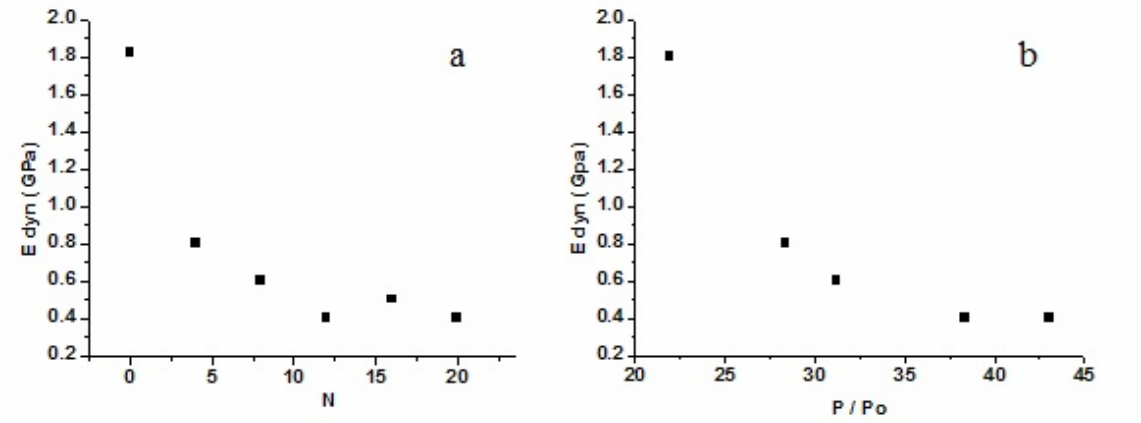

Fig. 7. Changes of Young modulus of elasticity versus: a) number of quench cycles (N), and b) level of degradation.

Results of UPVT measurements suggest that sampled material was very stable. These results indicate that the number of nucleated cracks did not resolute in the rapid degradation of strength and Young modulus of elasticity, thus, samples showed an excellent thermal shock behavior.

Knowing the compressive strength of the material before the exposure to the thermal shock testing, and ultrasonic velocity before and after testing, the compressive strength values were calculated from the equation (3) [16,22-24,30]:

$$\sigma = \sigma_0 \cdot \left(\frac{V_{P,S}}{V_{P0,S0}} \right)^n \tag{3}$$

where σo is a compressive strength of the material before the exposure to the thermal shock testing (σo was determined experimentally), $V_{P,S}$ is the velocity of ultrasonic waves (longitudinal and transversal) after testing, $V_{P0,S0}$ is the velocity of ultrasonic waves

(longitudinal and transversal) before testing, and n is material constant (n = 0.488). Calculated compressive strength values in relation to the initial strength value as a function of number of quenching cycles are presented in Fig. 8a. As can be seen, compressive strength was 80 % of the initial strength (σo) after 4 cycles and it remained almost constant (approximately 70 % of the initial strength) until the end of the experiment (Fig. 8a). Similar dependence of calculated compressive strength values in relation to the initial strength value as a function of degradation level can be observed in Fig. 8b.

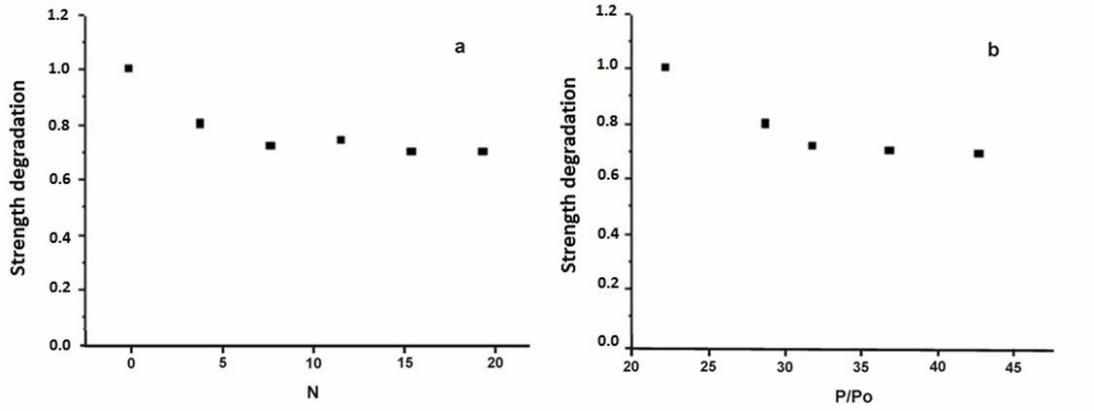

Fig. 8. Strength degradation versus: a) number of quench cycles (N), b) level of degradation.

4. Conclusion

Glass ceramic samples were synthesized using glass frit of FFW (final flotation waste) as basic material. The thermal shock resistance was investigated using the water quench test accompanied with the image analysis and UVPT.
Obtained results pointed out that:

- FFW could be successfully used for the synthesis of the glass-ceramic materials.
- Obtained glass-ceramic material showed good thermal shock resistance. After 20 cycles of water quench tests, the level of degradation was about 43 %.
- Results of the thermal shock stability testing suggested that glass-ceramic samples could be used in the applications with the rapid temperature changes.

Acknowledgements

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Садржај: *У раду је испитана, синтетисана стакло-керамика добијена из стакленог фрита дефинитивне флотацијске јаловине пореклом из РТБ-а Бор. Термо стабилност је праћена у циљу испитивања могућности примене отпадног материјала. Термостабилност синтетисане стаклокерамике (добијене синтеровањем фрита на 1100 °C / 4h) испитана је праћењем степена оштећења на основу промене брзине простирања ултразвучног таласа и Јунговог модула еластичности, сукцесивним подвргавањем термошоку. Коришћењем стандардне методе наглог хлађења у води*

праћен је термо шок узорака. Анализа слика и ултразвучна мерења су коришћени као недеструктивне методе за одређивање степена разарања узорка. Фазни састав узорака је одређен рендгенско дифракционом анализом праха (XRRPD). Ниво оштећења узорака је око 43 % после 20 циклуса, што указује да добијени стаклокерамички материјал има висок ниво отпорности на термошок.
Кључне речи: *Дефинитивна флотацијска јаловина; Стакло-керамика; Термо шок; Анализа слике; Ултразвучна брзина.*