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Preparation of basalt-based glass ceramics

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Abstract: Local and conventional raw materials–massive basalt from the Vrelo locality on Kopaonik mountain–have been used as starting materials to test their suitability for the production of glass-ceramics. Crystallization phenomena of glasses of the fused basalt rocks were studied by X-ray phase analysis, optical microscopy and other techniques. Various heat treatments were used, and their influences, on controlling the microstructures and properties of the products were studied with the aim of developing high strength glass-ceramic materials. Diopside $CaMg(SiO_3)_2$ and hypersthene ($(Mg,Fe)SiO_3$) were identifies as the crystalline phases. The final products contained considerable amounts of a glassy phase. The crystalline size was in range of 8–480 μm with plate or needle shape. Microhardness, crashing strength and wears resistence of the glass-ceramics ranged from 6.5–7.5, from 2000–6300 kg/cm^2 and from 0.1–0.2 g/cm, respectively.

Keywords: glass-ceramics, microstructure, mechanical properties.

INTRODUCTION

A glass-ceramics is a multi-phase material obtained by directed crystallization of glass, which show special characteristics. Namely, due to changing the thermal treatment conditions, material can be produced with predetermined properties.[1]

The development of glass-ceramics from industrial grade raw materials containing diopside or pyroxene type phases has been accomplished in the last 20 years.[2,3] Basalt is a cheap and abundant raw material which can be exploited for the development of glass-ceramics.[4,5] Starting from basalt with identical chemical and mineralogical composition, after its melting, adequate selection of nucleation temperature and crystal growth, the type and amount of crystalline phase can be changed in relation to the amorphous phase.[6]

The aim of this work was to define the conditions of thermal treatment of a natural, basalt-based raw material to obtain a glass-ceramics having good mechanical abrasion resistance.

EXPERIMENTAL

Basalt rock, taken from the Vrelo locality on Kopaonik mountain, was used as the starting material. The basalt was crushed and ground and a fraction 0.1 < to < 0.4 mm was prepared in order to comply with the requirements of traditional glass production technology for obtaining glassy melts. The material was melted with no additives, in a 5 liter chammote ladle, in a gas furnace, within the temperature range of 1250 ºC – 1300 ºC.

The obtained melt was crystallized in an electric furnace at 950, 1000 and 1050 ºC during 3–8 h intervals. The microstructure, number and size of the crystal were determined using an optical microscope.

The mechanical characteristics of the obtained glass ceramic material were tested with ultrasound. The crushing strength, hardness and wear resistance were also determined.

RESULTS AND DISCUSSION

The tested basalt sample was an opulent and compact black rock with a clearly visible porphyry structure 1–3 mm in diameter. The sample was rather fine grained and cryptocrystalline. The results of chemical analyses (Table I) show the presence of the following oxides:

TABLE I. Chemical analysis of basalt (wt%)

SiO_2	Al_2O_3	TiO_2	Fe_2O_2	FeO	MgO	CaO	MnO	Na_2O	K_2O	H_2O	Σ
49.33	16.13	1.94	3.81	2.68	6.48	8.87	0.14	3.30	2.70	1.57	100.4

The content of SiO_2 is below 50 % which is of special importance for the melting and casting procedures because of the lower melt viscosity. The viscosity reduction is caused by high Fe_2O_3, MgO and CaO contents. The content of alkalies (6 %) significantly reduces the melting temperature. Althought the TiO_2 content is negligible, its presence is important because of mineralizing properties.

The mineralogical composition was determined by XRD. The following phases were found: plagioclase, pyroxene, amphibole and glassy phase. The present amounts of plagioclase and pyroxene were nearly identical, while the content of amphibole and glassy phase was rather small. Two phases of pyroxene were found : deopsidal and hypersthenic, the reflections of diopside being stronger.

The chemical and mineralogical composition of the basalt enabled its melting at comparatively low temperature (1140 – 1160 ºC), where a homogenous melt was obtained which quickly lost its gaseous phase.

Thermal treatment of basalt melt

By crystallization of the basalt melt at various temperatures for different times, glass-ceramic products are created that differ in their microstructural and physical characteristics. The microstructures of the glass ceramic obtained at 1050 º, 1000 º and 950 ºC for 3 and 8 h are shown in Figures 1, 2, 3, 4, 5 and 6.

The microstructural investigations show that all the glass ceramic products have an incertal structure. In the basic glassy mixture the development of staky pyroxene around regularly arranged crystallization centers is obvious. The stakes cross-over one another, forming an intertangled dense network. In the glass ceramic formed by crystallization at 1050 ºC (Fig. 1 (a, b)), the pyroxene stakes are rather large because there was enough space for their development. In the glass ceramic formed at 1000 ºC(Fig. 1 (c, d)), the pyroxene crystals show radial ray shape development and their dimensions are smaller compared to the crystals formed by heat treatment at 1050 ºC. The glass ceramic formed by crystallization at 950 ºC have even smaller grain size then the glass ceramics formed at 1000 ºC (Fig. 1 (e, f)).

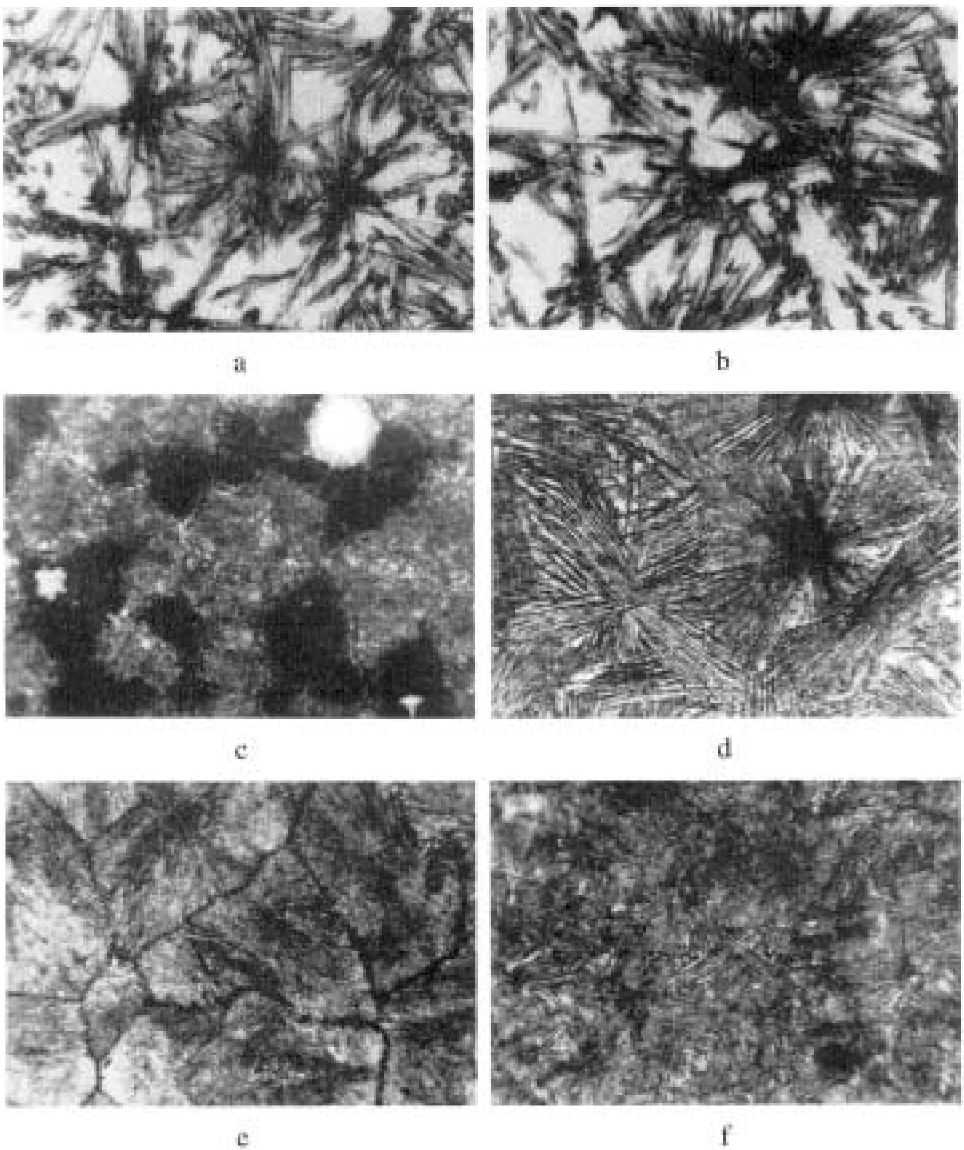

Fig. 1. Microstructures of glass ceramic obtained at 1050 ºC (a – 3 h), (b – 8 h); 1000 ºC (c – 3 h), (d – 8 h) and 950 ºC (e – 3 h), (f – 8 h). Magnification 50X.

With decreasing crystallization temperature, the number of directly formed glass ceramics nuclei increases, thus influencing the structure. A more dense distribution of crystallization centers suppresses crystal growth, resulting in a comb-shaped structure at 950 ºC. The influence of crystallization temperature and time on the number and dimension of the crystals is given in Table II.

TABLE II. Number and dimensions of the crystals as a function of crystallization temperature and time

Temperature/ºC	Time/h	No. of crystal/mm^2	Length/μm	Width/μm
1050	8	288	320–480	16–32
	3	264	320	16–32
1000	8	1920	200	8
	3	2100	170	8
950	8	870	16–32	4
	3	9400	8–16	3

The highest crystallization temperature (1050 ºC) enables glass ceramics with the greatest portion of glassy matter and relatively small number of crystals to be obtained. If the crystallization temperature is decreased by 50 ºC (1000 ºC), glass ceramics with less glassy matter are obtained, but with a rather large number of crystals of smaller dimensions. If the crystallization time is increased, the number of crystals decreases, but their dimensions increase. The higher degree of crystallization of the glass ceramics obtained at the longer crystallization time was confirmed by XRD method.

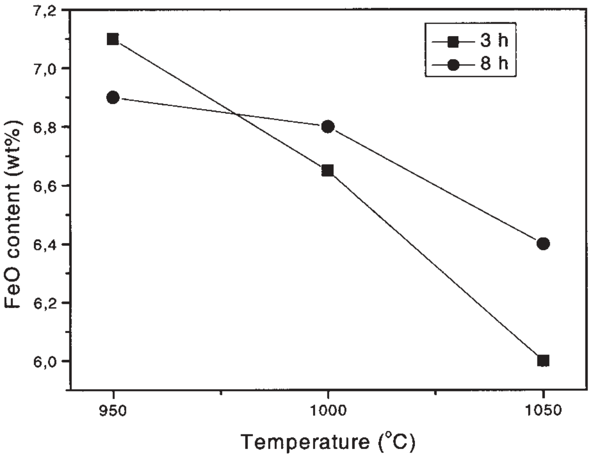

Fig. 2. Effect of temperature on the oxidation state of the sintered bodies.

The results of X-ray examination showed diopside (di) and hypersthene (xi) phases, the intensity of which changes depending on the temperature and time of crystallization. Diopside phase growth is favored by decreasing crystallization temperature, as well as by prolonged annealing time. However, the amount of the hypersthene phase decreases with both increasing temperature and crystallization time (Table III). The reason is the oxidation of FeO into Fe_2O_3 which cannot enter the hypersthene structure.[7] The effect of temperature on the oxidation state of liquid basalt in air shows that higher temperatures produce a

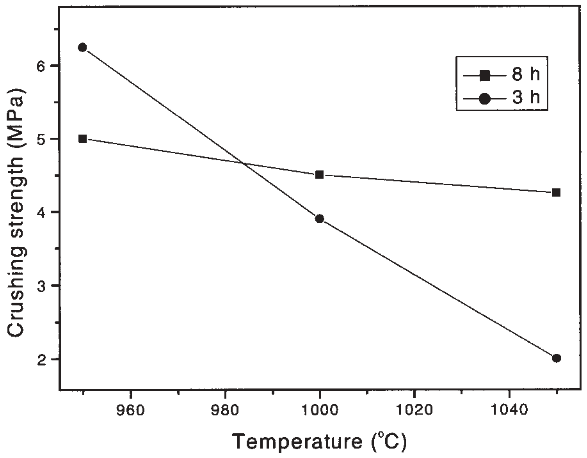

Fig. 3. Crushing strength as a function of temperature and annealing.

significant amount of iron in the ferric (Fe^{3+}) state.[8] FeO oxidation increases with temperature and extension of crystallization time (Fig. 2).

TABLE III. Evolution of the crystalline phases (di – diopside, xi – hydpersthene) as a function of the sintering time and temperature

Temperature/ºC	Ratio di/(xi+di)	
	3 h	8 h
1050	0.52	0.59
1000	0.64	0.73
950	0.82	0.90

TABLE IV. Hardness and wear resistance of glass ceramic products obtained by crystallization at different temperatures

Temperature/ºC	Time/h	Hardness/moss	Wearing resistance/(g/cm)
1050	3	6.5	0.20
	8	6.0	0.23
1000	3	6.9	0.16
	8	7.0	0.14
950	3	7.2	0.11
	8	7.5	0.10

A study of the crushing strength showed that glass ceramics of denser structure and finer crystals exibit higher fracture strength (Fig. 3). A study of the mechanical properties using the ultrasonic method confirmed that the values of the modulus of elasticity are the lowest for the glass ceramic sample crystallized at 1050 ºC as a result of the increased amount of glassy phase.

Hardness and wear resistance testing (Table IV) showed that the highest values were found in the glass ceramic obtained by crystallization at 950 ºC. Its hardness increases with prolonged soaking time.

CONCLUSION

The chemical and mineral compositon of basalt from the Lokva area (Kopaonik mountain) enables melting at relatively low temperatures (1040 – 1060 ºC). Its melt has the ability to crystallize, and glass ceramics of pyroxene phase composition with small portions of glassy phase are obtained. Crystallization at 950 ºC produces a more homogeneous structure compared to glass ceramics obtained at 1000 ºC and 1050 ºC. Crystallization at 950 ºC gives a spherulitic structure resulting in the most favorable mechanical properties.

Glass ceramics based on basalt are suitable for the formation of material which could be used in areas where high hardness and high wear resistance are required.

ИЗВОД

ДОБИЈАЊЕ СТАКЛО-КЕРАМИКЕ НА БАЗИ БАЗАЛТА

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Домаћа индустријски доступна сировина базалт из Врела са Копаоника је испитивана са циљем да се утврди њена подесност за производњу стакло–керамике. Кристализација базалтног растопа је проучавана рендгенском структурном анализом, оптичком микроскопијом и другим техникама. Различитим топлотним третманима је контролисана микроструктура и особине производа. Главне кристалне фазе су диопсид ($CaMg(SiO_3)_2$) и хиперстен ($(Mg,Fe)SiO_3$), мада је уочена и значајна количина стакласте фазе. Кристали су се развили у облику пљоски и иглица са дужином од 8–480 μm. Микротврдоћа (по Mossu) се креће од 6,5 до 7,5, док је притисна чврстоћа од 2000 до 6500 kg/cm^2 и отпорност на хабање од 0,1 до 0,2 g/cm.

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