

CHARACTERIZATION OF GLASS-CERAMICS CONTAINING INDUSTRIAL WASTE**RŪPNIECISKOS ATKRITUMUS SATUROŠAS STIKLKERAMIKAS RAKSTUROJUMS****I.Rozenstrauha**

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Keywords: glass-ceramic, industrial waste, composite materials, recycling, thermal treatment, sintering

Introduction

The main aim of this study was to synthesise new composite materials that contain industrial waste, which can find applications in the field of building construction. In this way the amount of industrial by-products is reduced. A second target was the neutralisation of ecologically harmful waste, converting them to natural minerals, in order to deposit them into geological formations without potential ecological hazards.

There are already in the literature several suggestions on how industrial waste could be utilized, e.g. as a filler or as additives in concrete, incorporated in ceramic materials or roads and pavements [1-2]. One possibility to recycle industrial waste though, is the production of glass-ceramic materials by thermal treatment [3]. Glass-ceramics are fine-grained polycrystalline materials formed when glasses of suitable composition are heat treated, thus undergoing controlled crystallisation to the lower energy, crystalline state. However, only specific glass compositions are suitable precursors for glass-ceramics. Some glasses are too stable and difficult to crystallise, such as ordinary window glass, whereas others crystallise too readily in an uncontrollable manner resulting in undesirable microstructures. Secondly, heat treatment is a critical factor in attaining acceptable and reproducible products [4].

In this work, for the production of glass-ceramic we investigate a method which is based on powder technology. This is a well known methodology, which is also energetically favourable in comparison to other methods, and can be applied in Latvia.

Experimental

1. Raw materials

The possibilities to apply peat ash, fly ash, metallurgical slag and other Latvian raw mineral materials in order to acquire dense, frost resistant, chemically durable building materials, has been studied in the past [5-7].

The production of glass-ceramic materials from Latvian industrial waste has been already investigated: steel cooling refuse, aluminium scrap metal processing waste, etching refuse, waste glass and lime-free clay. Steel cooling refuse is a by-product generated during the cooling of carbon steel slabs in water, after the hot rolling mill process, and it contains >90 % Fe oxides and some trace elements, such as Cr, Mn, As and Ni [8].

According to semi-quantitative x-ray fluorescence (XRF) analysis the aluminium scrap metal processing waste contains alumina (24%), metallic aluminium (7%), potassium and sodium chlorides (in total 4.8%), aluminium chloride (2.9%), aluminium nitride (4.8%), quartz (5.6%), iron oxide (3.4%), small amounts of sulphates and several non-soluble oxides.

Data obtained by XRD mineralogical analyses indicated that this waste contains corundum (Al_2O_3), metallic aluminium (Al), aluminium iron oxide (FeAl_2O_3), quartz (SiO_2), iron sulphite (FeSO_3), aluminium chloride (AlCl_3), gibbsite ($\text{Al}(\text{OH})_3$), aluminium nitride (AlN), while steel cooling refuse contains hematite (Fe_2O_3), magnetite (Fe_3O_4), FeO and oxide of iron chromite ($(\text{Fe}_{0.6}\text{Cr}_{0.4})_2\text{O}_3$) [7,9]. The chemical and mineralogical composition of waste glass and clay has been previously discussed. The composition of waste glass is the following: SiO_2 , Al_2O_3 , CaO, Na_2O , MgO, K_2O , TiO_2 , whereas

lime-free clay from the Latvian deposit Liepa contains SiO₂, CaO, MgO, SO₃, Na₂O, K₂O and some trace elements [9,10].

2. Experimental procedures

In order to produce dense glass-ceramics, it is necessary to reach the suitable ratio of glass and crystalline phases during the sintering process. Taking into account the chemical and mineralogical composition of the selected waste materials, various mixtures were prepared. According to their sintering behaviour, two more suitable compositions, labelled “E1” and “E2” were selected, as shown in Table 1. Both compositions contain the same raw materials in similar quantities, only the glass and clay content differs.

Table 1

Waste containing mixtures used for the fabrication of glass-ceramics

Composition, wt %	E1	E2
Steel cooling refuse	30	30
Aluminium scrap metal processing waste	30	30
Waste glass	20	10
Clay	20	30

The mixtures were milled in a ball mill for 24h in water (60 wt% solid) in order to homogenise the powders, and subsequently dried to about 12 to 14% humidity.

The humid powders were sieved (aperture 0.5 mm) and cylindrical samples (20 mm diameter) were pressed uniaxially at room temperature at a pressure of 50 MPa. The powder compacts were sintered in a commercial electrical furnace (make of NABERTHERM) in air using the following sintering conditions: heating and cooling rates of 3 K/min and a sintering time of 120 min. The sintering temperature was varied between 980 and 1110°C. The bulk density and water uptake of the sintered samples were determined according to standard procedures [11,12]. X-ray diffraction (XRD) analysis (Philips PW 1710) of the waste mixtures and sintered samples was conducted. The microstructure of selected samples was also studied using stereo light microscopy (Leica M420). The mechanical properties of the glass-ceramic composite materials were determined by compression. The specimens were shaped to a parallelepiped 15.0±0.1 mm long, 6.0±0.03 mm wide, and 6.0±0.03 mm thick. The compression tests were carried out on an Instron-4301 testing machine (Great Britain). The deformation rate (the rate of traverse motion of the testing machine) was 0.5 mm/min. The tests were continued up to failure of the specimens. At least eight parallel samples were tested for each composition.

Results and discussion

The results of both bulk density and water uptake of the produced glass-ceramics are depicted in Figure 1 in the temperature range of 1100 to 1240°C. These data were used further to estimate the functional properties of glass-ceramics.

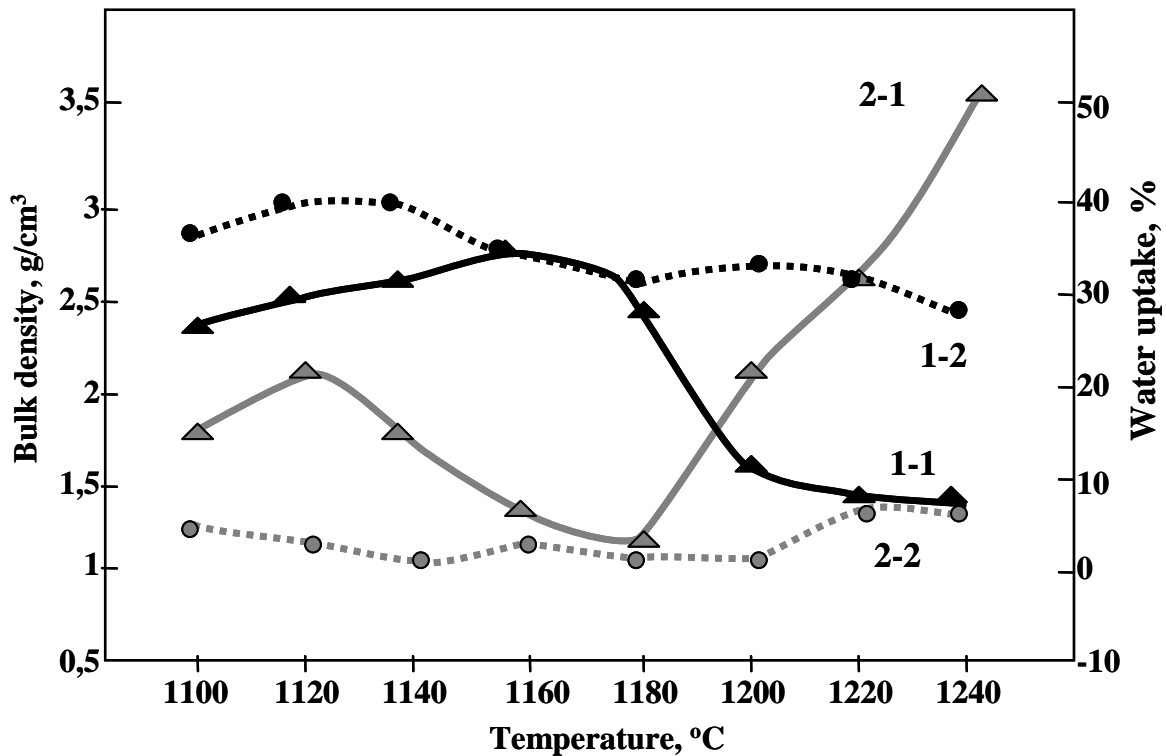


Fig. 1. Bulk density and water uptake of the waste containing mixtures (E1 and E2) versus sintering temperature. Abbreviations: 1-1 – bulk density of composition E1 and 1-2 – bulk density for composition E2; 2-1 – water uptake for composition E1, 2-2 – water uptake for composition E2.

In temperatures lower than 1140°C the water uptake of both compositions is 5-18 %, whereas bulk density slightly increases. In these temperatures the sintering of both mixtures is not observed. It can be thus assumed, that the two mixtures have pores large enough to attract large volumes of water (Figure 1). However, in the temperature range from 1140°C to 1180°C sintering was initiated, resulting to the decrease of porosity. This is suggested by the lowest water uptake of both materials (0.9 and 5.5%, respectively) as well as from the highest bulk density (2.52 g/cm³ for composition E2 and 3.24 g/cm³ for composition E1). In temperatures higher than 1180°C the water uptake increases rapidly for the sample with composition E1, due to its high content of waste glass (20%), compared to the sample with composition E2 (waste glass content of 10%; Table 1, Figure 1). During the thermal treatment of the above mentioned temperatures, waste glass with high alkaline content releases its volatile component promoting a porous structure with a decreased bulk density - up to 1.4 g/cm³ for the sample with composition E1 (Figure 1). Values for the properties of the synthesised materials are given in Table 2.

Table 2

Properties of sintered glass-ceramic materials from mixtures E1 and E2

Properties	E1	E2
Sintering temperature, °C	1160	1160
Thermal shrinkage, %	30	25
Water uptake, %	0.93	5.53
Bulk density, g/cm ³	2.52	3.24
Colour of the glass-ceramics	brown	dark grey
Chemical durability	Durable in acidic, alkaline and neutral medias	

These values are comparable to those obtained by other authors on sintered glass-ceramics produced from silicate wastes [4,7]. The results of mechanical tests of these materials are given in Table 3.

Table 3

Mechanical characteristics of glass-ceramic composite materials

Material	Compression	
	σ^* , MPa	E, MPa
E1	50.64±17.71	1148.0±179.3
E2	89.92±17.46	1303.0±231.0

A comparison between the glass-ceramic composites shows that a change in the matrix-filler ratio influences the mechanical characteristics of this material. A higher content of clay in composition E2 increases the elastic modulus (E) and the breaking strength (σ^*). Also a higher density of the glass-ceramics material increases the E and σ^* (Tables 1, 2, and 3).

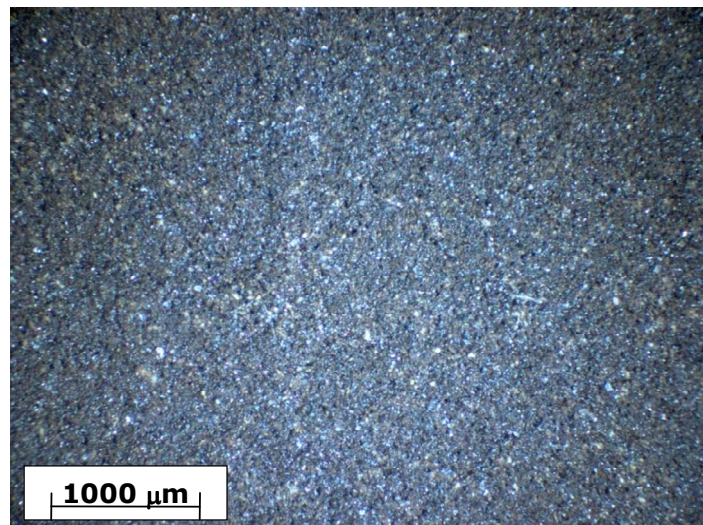


Fig. 2. Microstructure of glass-ceramic material E1

According to data obtained by XRD analysis the sintered glass-ceramic, which contains steel cooling refuses and waste of aluminium scrap metal processing, has the following crystalline phases: hematite (Fe_2O_3), spinel (FeAl_2O_4), quartz (SiO_2) and christobalite (SiO_2) [8]. These crystalline phases are thought to be responsible for the reasonably good mechanical strength of the materials [4,7].

The microstructure of sintered materials obtained by light microscopy analyses reveals a regular distribution of crystalline, glassy and pore phases without incorporation of big crystals (Figure 2). Thus it could be assumed, that the general crystalline phase is composed of small-sized spinel crystals, which can generally give an optimum strength of the obtained materials [5].

Considering the low water uptake and mechanical properties, the produced composite materials could be regarded as corresponding to the group BI of the standard LVS EN 176:1991 „Pressed ceramic tiles

with the low water uptake" ($E < 3\%$) and to the criteria for building ceramics according to LVS 163-3:1999. Potential applications are in the production of "unglazed ceramic tiles for road pavement and exterior walls from stone ceramics" (code – 690790910) [14-16].

Conclusions

We produced a new composite material, a glass-ceramic made from Latvian industrial waste, such as steel cooling refuse, waste glass, aluminium scrap metal processing waste and lime-free clay (bulk density 2.52 – 3.24 g/cm³; water uptake 0.95 - 5.5 %). According to water uptake these new materials meet the BI group requirements stated in the LVS EN 176 standard „Pressed ceramic tiles with the low water uptake" ($E < 3\%$).

The mechanical strength of the produced materials shows comparable results to other waste glass-ceramics and meets the requirements of Latvian standards for building ceramics LVS 163-3:1999 "Ceramic materials – ceramic tiles. Criteria of safety".

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Rozenštrauha I., Lodiņš E., Krāģe L., Fiļipenkov V., Chatzitheodoridis E. Rūpnieciskos atkritumus saturošas stiklkeramikas raksturojums.

Darbā pētītas stiklkeramikas kompozītmateriālu iegūšanas iespējas no mazkarbonātu māliem un rūpnieciskajiem atkritumiem: metalurģiskās rūpniecības tēraudliešanas nobīrām, atgāju stikla no stiklašķiedras rūpnīcas un alumīnija pārstrādes ražotnes atkritumiem. Pamatojoties uz izejmateriālu termisko īpašību un ķīmiskā sastāva pētījumiem, veidotas dažādas atkritumu kompozīcijas, kā iegūšanas metodi izmantojot pulvertehnoloģiju. Saķepšanas temperatūru intervālā 1140 – 1180 °C sintezēti blīvi stiklkeramikas kompozītmateriāli ar tilpummasu 2.52 – 3.24 g/cm³ un ūdens uzsūci 0.95 - 5.5 %. Ņemot vērā materiālu zemo ūdens uzsūci un noteiktās mehāniskās īpašības (elastības moduli $E = (1150 - 1300) \pm 200$ MPa un lieces izturību $\sigma^ = (50,6 - 89,9) \pm 15,0$ MPa), iegūtie kompozītmateriāli atbilst LVS EN standartā 176:1991 “Presētas keramikas flīzes ar zemu ūdens uzsūci” ($E < 3\%$) noteiktajai grupai BI un keramisko būvmateriālu standartā LVS 163-3:1999 noteiktajiem kritērijiem. Potenciālās materiālu izmantošanas iespējas ir, izgatavojot “neglazētas keramikas flīzes ielu segumiem un ārējai sienu apdarei no akmensmateriāliem” (kods - 690790910).*

Rozenstrauha I. , Lodins E. , Drille M. , Krage L. , Filipenkov V., Chatzitheodoridis E. Characterization of glass-ceramics containing industrial waste.

In the present study the preparation of glass-ceramic composite materials containing lime-free clay and industrial waste: steel cooling refuse from metallurgical plant, waste glass from waste fibre production, aluminium scrap metal processing waste were investigated. Taking into account the thermal properties and chemical composition of raw materials, various waste containing glass-ceramics composites were prepared by powder technology. Dense glass-ceramic composite materials (bulk density 2.52 – 3.24 g/cm³; water uptake 0.95 - 5.5 %) were produced in sintering temperature range from 1140°C to 1180°C. Considering the low water uptake and values of mechanical properties determined (the modulus of elasticity $E = (1150 - 1300) \pm 200$ MPa and the compressive strength $\sigma^ = (50,6 - 89,9) \pm 15,0$ MPa), the produced composite materials could be regarded as corresponding to the group BI of the standard LVS EN 176:1991 „Pressed ceramic tiles with the low water uptake” ($E < 3\%$) and to the criteria for building ceramics according to LVS 163-3:1999. Potential application is the production of “unglazed ceramic tiles for road pavement and exterior walls from stone ceramics” (code – 690790910).*

Розенштрауха И., Лодиньш Э., Дрилле М., Краге Л., Филипенков В., Чатзитхеодоридис Э. Характеристика стеклокерамики, содержащей промышленные отходы.

В данной работе исследованы возможности получения стекло-композитных материалов, используя малокарбонатные глины и промышленные отходы: отходы в металлургическом производстве стального литья, отходы стекла в производстве стекловолокна и алюминиевые отходы при переплавке алюминиевого лома. Подобраны различные композитные смеси из промышленных отходов. Подбор смесей основан на зависимости их термических свойств от химического состава. В работе использована порошковая технология. В температурном интервале 1140 – 1180 °C получены плотные стеклокерамические материалы с плотностью 2,52 – 3,24 г/см³ и водопоглощением 0,95 – 5,50 %. По низкому водопоглощению полученных материалов, а также их механической прочности (модуль эластичности $E = (1150 - 1300) \pm 200$ МПа и прочность на изгиб $\sigma^ = (50,6 - 89,9) \pm 15,0$ МПа) композитные материалы соответствуют группе BI ($E < 3\%$) стандарта LVS EN 176:1991 «Прессованные керамические плитки с низким водопоглощением» и отвечают критериям стандарта строительных материалов LVS 163:1999. Потенциальная сфера применения – «неглазированные керамические плитки для покрытия дорог и внешней отделки стен из каменных материалов» (код – 690790910).*