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THERMAL AND ENVIRONMENTAL CHARACTERISTICS OF GLASS PRODUCED FROM METALURGICAL WASTES

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Abstract

The subject of this study is glass produced by mixed metallurgical waste from ferronickel production, aimed for further production of glass-ceramic. Characterization of waste materials includes determination of chemical and mineralogical composition and standard leaching test. The waste materials contain several heavy metals (Fe, Ni, Mn, Zn, Cr) which exceed the applied limits and can be potential hazard to the soils. On the other hand, the waste mixture contains sufficient amount of glass-forming component - SiO_2. The components in the waste mixture aimed for glass production were in the ratio as they are produced in the Fe-Ni smelter (flay ash:electro-furnace slag:converter slag = 1:10:1). Thermal characterization of the glass was performed by means of hot stage microscopy (HSM) and DTA analysis, where the temperatures of sintering, softening, smelting and crystallization were determined. The results highlight that fine-crystalline glass-ceramic with high crystallinity can be obtained. Standard leaching test has shown that the concentration of all heavy metals is bellow applied limits for 5 to 400 times. Thus, the produced glass is environmental safety product.

Keywords**:** fly ash, electric furnace slag, converter slag, glass, glass-ceramic

1. Introduction

Disposal or stabilization of waste materials from metallurgical industry such as slags, dust, hydrometallurgical by-products etc., is not an easy task because of the complex composition and high content of regulated heavy metals as well as different local circumstances. Often, recovery of some metal can not be economic efficient or the recovery procedure produce new waste. Disposal of waste containing heavy metals can be hazardous to environment. Vitrification of hazardous wastes, i.e. transformation of waste materials to glass can be considered as an environmentally compatible stabilization process. It is considered as an ultimate method for immobilization hazardous wastes, because during glass melting, the harmful elements are chemically bonded in a durable amorphous network [1-3]. This significantly reduces their solubility and, in addition, drastically decreases waste in volume. On the other hand, depending on the composition, with or without any additives, the waste-based glass can be transformed to glass-ceramic with properties comparable or better than commercial ones. This is illustrated by numerous researches focused on using slags originated from iron and steel production for production of glass or glass-ceramic [4-10]. The research of Karamanov and co-workers was directed on production of glass and glass ceramic from by-products originated from zinc and copper hydrometallurgical production [11-15]. All these studies highlight good chemical, physical and mechanical properties of the produced glass or glass-ceramic, close or even better than those produced from virgin raw materials. Besides technical and economic effects, this route of processing metallurgical waste materials was shown as environmental efficient. According to various standard leaching tests [16], the glass and glass-ceramic products based on metallurgical waste, are environmental friendly materials.

The aim of this study is vitrification of solid waste from ferronickel smelting plant, such as dust, slag from electro-furnace and converter slag. Characterization of waste materials and produced glass is directed to estimate their possibility for further production of glass-ceramic as well as to determine their environmental impact.

2. Experimental

Dust (D), electro-furnace slag (EFS) and converter slag (CS) from ferronickel smelting plant in R. Macedonia, were used as a raw material for glass production. Their annual production is in ratio D:EFS:CS = 1:10:1. The content of different type of waste was in this ratio within the waste mixture aimed for vitrification.

Chemical composition of the waste materials was determined by X-ray fluorescence (XRF) spectrometer (Model XRF ARL 9900). Mineralogical analysis was carried out by X-ray diffraction method using Philips APD 15 diffractometer, operating at CuKα-radiation. Diffraction data were collected at a constant rate of $0.02^{o}\cdot s^{-1}$ over an angle range of $2\theta = 5–90^{o}$.

To determine environmental impact of the waste materials, standard leaching test – TCLP (Toxicity Characteristic Leaching Procedure) was performed. Shown in Table 1 are the leaching test conditions. Concentrations of heavy metals after testing were measured by atomic absorption spectroscopy (AAS) using the instrumentation Perkin Elmer AA400.

Table 1. Leaching conditions according to TCLP test

Solvent	CH_3COOH
pH	5
Volume of the solution	2 L
Weight of solid phase	100 g
s:*l* ratio	1: 20
Intensity	30 rpm
Duration	24 h

To correct the content of MgO and Cr_2O_3 in the waste mixture (WM), standard glass (SG) powder was added in ratio WM:SG = 7:3. Waste materials and the standard glass were homogenized and melted in chamber furnace at 1450°C for 1 h.

Thermal characteristics of the produced glass were studied by means of hot stage microscopy (HSM) and differential thermal analysis (DTA). A glass sample was observed in heating microscope MISURA HSML. The sample was heated from ambient to 1300°C with heating rate of $1^{o}C\cdot min^{-1}$.

During the heating reduction of dimensions and characteristic temperatures were recorded. DTA measurements were performed using a Perkin Elmer PYRIS

Diamond Thermogravimetric/Differential Thermal Analyzer. The studied material was heated in the temperature interval of 25ºC÷1100ºC by heating rate of 20ºC·min^{-1} air atmosphere.

The glass sample was undergoing on standard TCLP leaching test. The test conditions are the same as in previous case shown in Table 1.

3. Results and discussion

Chemical composition of the waste materials is shown in Table 2. All waste materials have high amount of Fe, especially converter slag (CS). So, these wastes could be used for Fe extraction, but, there is not smelter for iron production in R, Macedonia. Only in the dust Ni content is appropriate to be returned in the Fe-Ni production process. Annual production of these waste materials is 102.000 t dust, 1.135.000 t slag from electro-furnace and 109.000 t converter slag. The ratio of their production is approximately D:EFS:CS = 1:10:1. On the other hand, the dust and slag from electro-furnace contain high enough SiO_2 - glass forming component. Also, the waste mixture has appropriate content of SiO_2 (47.8%) for glass forming. But, MgO and Cr_2O_3 is high in the waste mixture (15.9 and 2.2 % respectively) and can cause spontaneous uncontrolled crystallization. Cr_2O_3 is not soluble in the glass, while in lower amount can improve the nucleation during transformation of glass to glass-ceramic. Thus, the composition of the waste mixture should be corrected in order to reduce the content of MgO and Cr_2O_3. For this purpose standard glass (SG) was added in the waste mixture in ratio WM:SG = 7:3.

Table 2. Composition (wt%) of dust (D), slag from electro-furnace (EFS), converter slag (CS), waste mixture (WM) in ratio D:EFS:CS = 1:10:1, standard glass and overall glass mixture in ratio WM:SG = 7:3

Item	D	EFS	CS	WM	SG	GM
SiO_2	37.5	53	1.9	47.8	71.4	55
MgO	14.5	16.9	6.2	15.9	3.3	12.1
CaO	2.3	2.4	15.9	3.5	9.8	5.4
Al_2O_3	1.8	2	0.3	1.9	0.6	1.5
Cr_2O_3	1	2.5	0.7	2.2		1.5
CoO	0.1	0.1	0.1	0.1		0.1
NiO	2.7	0.1	0.45	0.3		0.2
Fe_2O_3	30	14	60	19		13.3
FeO		9	19	9		6.5
Na_2O					13.3	4
K_2O					1.3	0.4

The waste mixture as well as the overall glass mixture is iron-rich. It is similar to a typical natural petrurgical raw material - basalt rock [17,18], containing typically Fe rich phases in glass-ceramic, also typical for waste-derived glasses, have been shown to impart functional properties to the final products [7]. As magnetic, electrical and thermal properties of glass–ceramics can be altered by controlling the crystalline phase concentrations, crystallisation kinetic studies of iron rich silicate waste derived glass-ceramic are important for optimising functional properties [7, 12].

According to XRD analysis (Fig. 1), iron is present as hematite (Fe_2O_3, i.e. Fe^{3+} form) and as non-stoichiometric mixed oxide with Cu, Zn and Cr ($Cu_{0.5}Zn_{0.5}Cr_{1.1}Fe_{0.9}O_4$) in the dust. The similar appearance of iron is in slag of electro-furnace – non-stoichiometric mixed silicate (forsterite) and non-stoichiometric Fe^{3+} oxide – maghemite. Converter slag contains Fe^{3+} as hematite and calcium iron oxide ($CaFe_2O_4$), Fe^{2+} as wuestite and mixed Fe^{3+} and Fe^{2+} oxide – hagnetite (Fe_3O_4). The glass forming component – SiO_2 is present as pure oxide quartz and silicates with other metals, mainly with Mg and Ca. According to the Fe content and appearance, it is 10–15 wt% iron oxides and it is characterized by high chemical durability and good resistance to abrasion and corrosion.

expected to produce glass similar to basalt based one [17].

The results of the TCLP test, carried out on the waste materials and produced glass are summarized in Table 3. There are several metals which exceed the applied limits and can be potential hazard to environment if the waste materials would be disposed at landfill. Ni, Mn, Zn, As and Cu are hazardous components in the dust, in the electric-furnace slag are Fe, Ni and Mn, while in converter slag are Fe, Ni and Cr. Concentration of Fe and Ni are to far from the applied limits.

One of possible and effective options to immobilize heavy metals is to capture them in glass matrix after vitrification of waste materials. So, next step in this research was vitrification of mixture of waste materials and standard glass. To ensure transformation of the mixture in liquid state, vitrification was performed at 1450°C for 1 hour. After cooling at ambient temperature, the produced glass was undergone to thermal investigations.

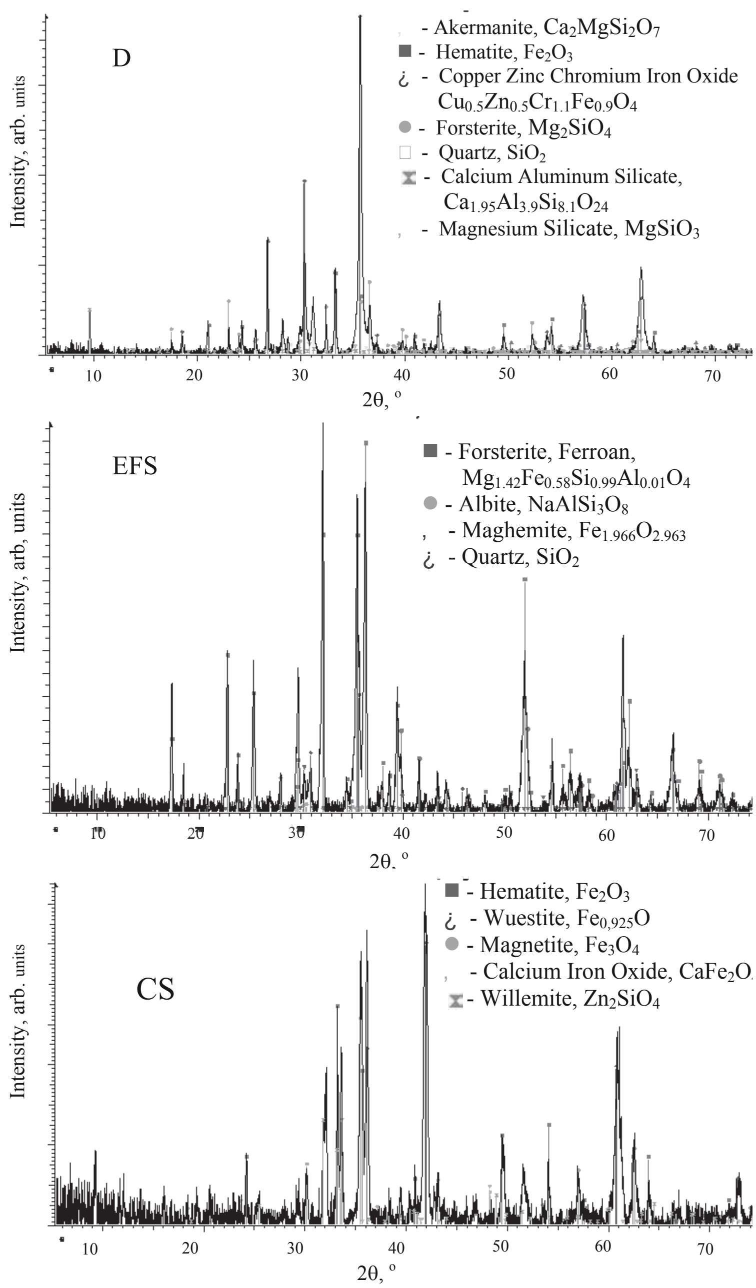

Figure 1. XRD spectra of the waste materials

Hot-stage microscopy is an analytical technique which combines the best properties of microscopy and thermal analysis to enable the characterization of the physical properties of materials as a function of temperature. During the measurements, video and pictures of the sample were recorded with registered reduction of dimensions. Also, a diagram temperature – change of dimensions (%) was constructed and determined temperatures of sintering, softening and melting were determined (Fig. 2). Produced glass shows high stability of dimensions and shape during the heating. The sintering occurs at high temperature (1167°C) at very short interval and practically this material does not sinter. At sintering temperature reduction of dimension is very low. Lowering of dimensions to 78.25% of starting ones reaches at softening temperature at 1222°C, but the shape is still stable. Forming of half-sphere occurs at 1245°C and melting point is 1251°C.

This is relatively low melting point, which contributes to more economically efficient process of vitrification of waste based glass. The HSM results, obtained by pressed glass powders, highlight that the sintering method is not appropriated for the investigated glass, because the traditional low-temperature densification is totally inhibited by intensive crystallization.

Table 3. Concentration of heavy metals in the solution after TCLP test

	D, $mg \cdot dm^{-3}$	EFS, $mg \cdot dm^{-3}$	CS, $mg \cdot dm^{-3}$	Glass, $mg \cdot dm^{-3}$	Applied limits, $mg \cdot dm^{-3}$
Fe	1	202	1155	0.416	2
Ni	6,1	2.7	19.2	0.311	2
Co	0.4	0.14	1.1	< 0.005	2
Cd	< 0.005	< 0.005	< 0.005	< 0.005	0.02
Cu	0.15	0.093	0.07	0.011	0.1
Mn	4.7	14.6	1.5	< 0.005	2
Pb	0.026	0.031	0.086	0.017	0.2
Zn	3.6	0.29	0.42	< 0.005	2
Cr	0.22	1.1	2.9	< 0.005	2
Sb	0.020	0.038	0.023	0.023	
As	1.2	0.011	0.18	0.009	5

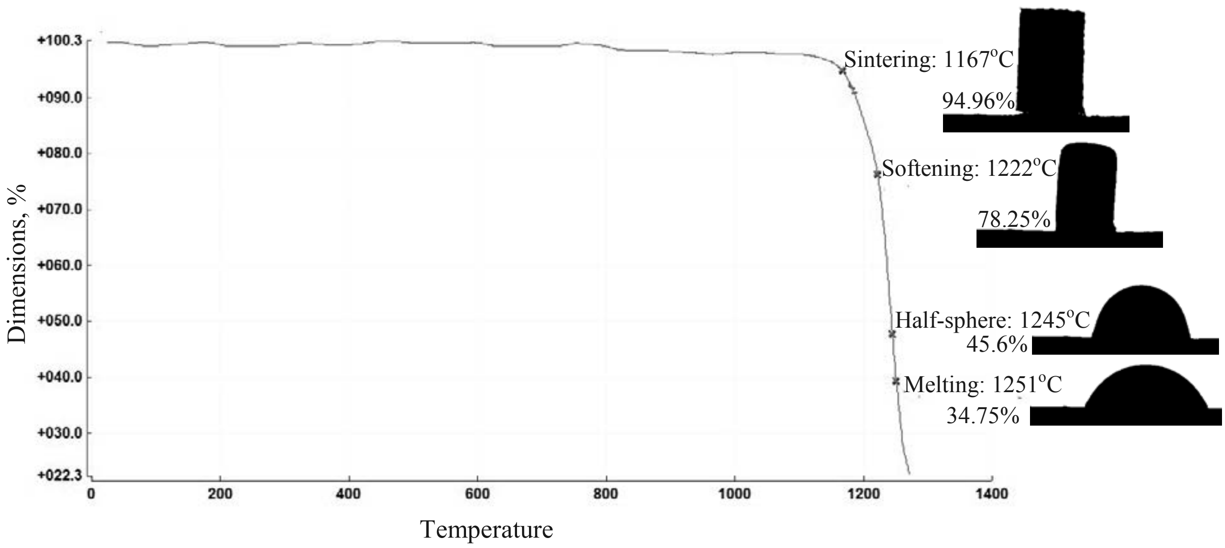

Figure 2. Change of dimensions as function of heating temperature registered by HSM

In order to determine how and at which temperature the studied glass crystallize, DTA analysis was performed at temperature region from ambient to 1100°C by heating rate of 20°C·min^{-1}. Crystallization of the waste based glass occurs at 800°C. The shape and the intensity of peak indicate intensive bulk crystallization. If we previously perform nucleation of glass with retention of heating at 650°C for 1 hour, the temperature of crystallization shifts to lower temperature of 785°C, while the intensity of the bulk crystallization increases. This points out that the waste based glass is appropriate for production of glass-ceramic and can be performed by two-stage process: firstly heating at 650°C to perform nucleation and crystal growth at 785°C.

At the same time, the preliminary DTA and density results demonstrate that this composition have good trend for bulk nucleation, giving possibility to obtain material with fine crystalline structure at low temperatures and short times.

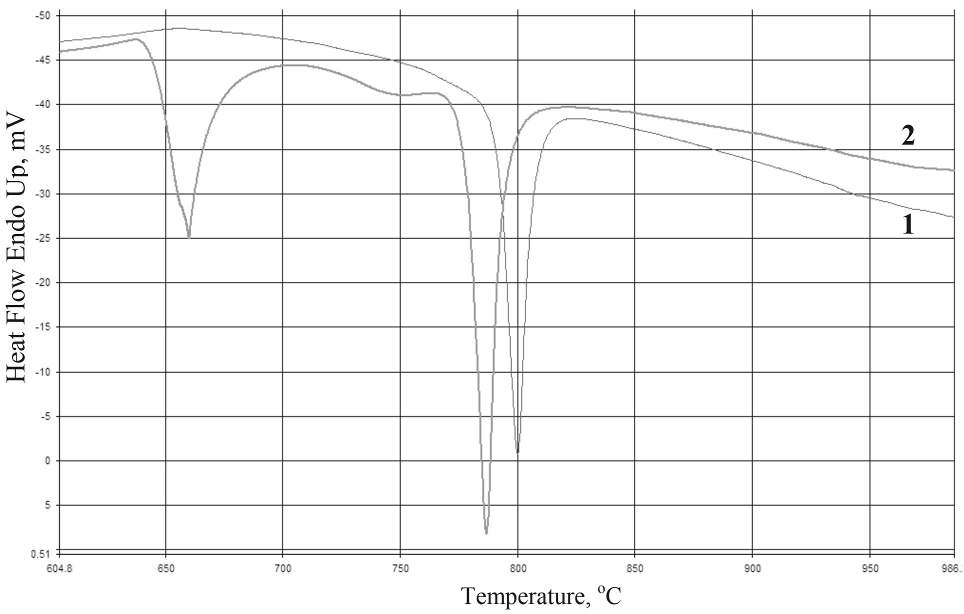

Figure 3. DTA curves of the studied waste based glass: non-nucleated (line 1) and nucleated at 650°C (line 2)

TCLP test of the produced glass was performed, in order to evaluate the environmental impact. The results of TCLP test are given in Table 3. The results show the vitrification procedure is successful and that the obtained glass demonstrates high chemical durability, corresponding to an inert material.

Conclusion

According to the obtained results from this study, we can draw several conclusions:
Waste materials from ferronickel production process contain components which are potential hazard to environment.
Waste materials contain glass-forming components enough, so they are appropriate for vitrification and further transformation of the produced glass to glass ceramic.
TCLP test of the produced waste based glass has shown that it is environmental friendly, i.e. the amount of all heavy metals in the leachate is far below the applied limits.
The produced waste based glass has shown very short interval of sintering at high temperature (1167°C) and low melting point, which point out on its economical efficient production at lower temperatures.
The produced glass showed intensive bulk crystallization at 800°C without previous nucleation. Nucleation at 650°C for 1 hour decreased the crystallization temperature to 785°C, as well as increased the intensity of the bulk crystallization. This offers possibility for efficient two-stage production of glass-ceramic from the studied glass: 1st stage of nucleation at 650°C and 2nd step crystallization at 785°C.

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References:

1. W. Vogel, “Glass Chemistry”, Springer-Verlag, Berlin, Heidelberg 1994
2. Festa D., Guadagnino E. Proprietà chimiche del vetro. Parte I: Generalità. Rivista della Stazione Sperimentale del Vetro, 5 (1995) 189-93.
3. P. Pisciella, S. Crisucci, A. Karamanov, M. Pelino, Chemical durability of glasses obtained by vitri®cation of industrial wastes, Waste Management 21 (2001) 1-9.
4. R. D. Rawlings, J. P. Wu, A. R. Boccaccini, Glass-ceramics: Their production from wastes - A Review, J. Mater. Sci., 41 (2006) 733-761.
5. H. Isa, A review of glass-ceramics production from silicate wastes, Int. J. Phys. Sci., 6 (2011) 6781-6790.
6. P. Colombo, G. Brusatin, E. Bernardo and G. Scarinci, Inertization and reuse of waste materials by vitrification and fabrication of glass-based products, Opinion in Solid State and Materials Science, 7 (2003) 225-239.
7. R. K. Chinman, A. A. Francis, J. Will, E. Bernardo, A.R. Boccaccini, Review. Functional glasses and glass-ceramics derived from iron rich waste and combination of industrial residues, J. Non-Cryst. Solid., 365 (2013) 63-74.
8. C. Fredericci, E. D. Zanotto and E. C. Ziemath, Crystallization mechanism and properties of a blast furnace slag glass, J. Non-Crystalline Solids, 273 (2000) 64-75.
9. N. A. El-Alaily, Study of some properties of lithium silicate glass and glass ceramics containing blast furnace slag, Glass Technology**,** 44 (2003) 30-35.
10. E. B. Ferreira, E. D. Zanotto and L. A. M. Scudeller, Glass and Glass-ceramic from basic oxygen furnace (BOF) slag, Glass Science and Technology, 75 (2002) 75-86.
11. A. Karamanov, M. Aloisi, M. Pelino, Vitrification of copper flotation waste, J. Hazar. Mater., 140 (2007) 333-339.
12. A. Karamanov, G. Taglieri and M. Pelino, Iron-Rich Sintered Glass-Ceramics from Industrial Wastes, J. Am. Ceram. Soc., 82 (1999) 3012-3016.
13. A. Karamanov, R. Di Gioacchino, P. Pisciella and M. Pelino, Viscosity of iron rich glasses obtained from industrial wastes, Glass Technol., 43 (2002) 34-38.
14. A. Karamanov, P. Pisciella and M. Pelino, The crystallisation kinetics of iron rich glass in di erent atmosphere, J. Europ. Ceram. Soc., 20 (2000) 2233-2237.
15. A. Karamanov and M. Pelino, Crystallization Phenomena in Iron Rich Glasses, J. Non-Cryst. Solids, 281 (2001) 139-151.
16. H. A. Van der Sloot, L. Heasman and Ph. Quevauviller, “Harmonization of leaching/extraction tests”, Elsevier, Amsterdam 1997
17. H. Beall and H.L. Rittler, Ceram. Bull. 55, 579, 1976
18. J. Hlavac, “The Technology of Glass and Ceramics: An Introduction”, Elsevier, Amsterdam, 1983.