Glassceramics from Industrial Waste Prepared in a Microwave Furnace

Milota Kováčová*[1], *Michal Lovás* and *Štefan Jakabský

This work presents the study of glassceramics from nickel leaching residue used as a heavy metal carrier (Cd, Pb) prepared by microwave vitrification. The Vicker`s microhardness, chemical durability and magnetic susceptibility of vitrified waste was tested. The glassceramics containing 40-50 % of nickel leaching residue with a high microhardness and very good chemical durability was obtained in a short time of heating (45 minutes).

Keywords: *waste, nickel leaching residue, microwave vitrification, leaching, microhardness*

Introduction

Vitrification is a well-established technology that involves the conversion of waste into a stable and homogeneous glass through thermal treatment of fusion with the possible additional modification of the starting composition with glass-forming additives (Colombo et al., 2003). Vitrification was applied for the first time at the end of the 1970s to the immobilization of liquid high-level radioactive waste (Ojovan et al., 2005).

Glassceramics were developed in the 1950s and today find a wide variety of applications in different technological fields (Strnad, 1983).

Glassceramic method, based on nucleation and crystallization, has been used for the disposal of a wide variety of non-nuclear inorganic waste originating in both industrial and mineral processes (Rawlings et al., 2006). In this case, waste is transformed into valuable products for following use such as ceramic floor tiles, abrasives and concrete additives. Among industrial waste, special attention is paid to those with high iron oxide content, which leads to glassceramic materials characterized by high mechanical strength and good chemical stability. In the last few years, iron-rich glass-ceramics have been obtained from zinc hydrometallurgy waste (Romero et al., 1998), electric arc furnace dusts (EAFD) from steel production (Kavouras et al., 2007; Pelino et al., 2002), copper flotation wastes (Karamanov et al., 2007) and coal ashes (Francis et al., 2002).

Microwave energy has a wide use in waste technology (Appleton et al., 2005) and was also recently used for vitrification of radioactive waste (Komarov et al., 2005) and MSWI fly ash (Chou et al., 2009).

Microwave heating has several characteristics that are not typical in conventional heating, including volumetric heating, rapid heating and selective heating of materials depending on their dielectric properties (Bykov et al., 2001). It has been generally observed that microwave sintered products possess finer microstructures and other unique features leading to considerable improvement in the mechanical properties (Agrawal, 2006).

The paper deals with the microwave vitrification of nickel leaching residue (NLR) from the former nickel hydrometallurgy plant in Sereď (Slovakia) used as a model carrier of heavy metals (Cd, Pb). The microhardness, chemical durability and magnetic susceptibility of glassceramics were studied.

Material and Methods

The chemical composition of NLR and raw materials is shown in Table 1. The heavy metal ions Cd^{2+} and Pb^{2+} were precipitated from $CdCl_2.2.5H_2O$ and $Pb(NO_3)_2$ in a concentration 10 mg of ions per 1 g of NLR. 9 mixtures described in Table 2, with NLR in 40-50 % weight range, have been prepared. Their theoretical chemical composition is shown in Table 3.

Microwave vitrification was carried out in a microwave furnace Panasonic NN-Q453 with frequency 2.45 GHz and output 1000 W. The mixtures were placed in an upper thermal isolated crucibles were heated for 45 minutes. When the samples achieved the melting temperature, the sample flowed down through the hole from the upper crucible into the bottom crucible where slowly cooled down in the microwave furnace.

The microstructure of glassceramics was studied by light microscopy (metallographic microscope Olympus GX71) of polished samples.

[1] *Ing. Milota Kováčová, PhD., RNDr. Michal Lovás, PhD., Ing. Štefan Jakabský, PhD.*, Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, Košice, 043 53, Slovakia, kovacova@saske.sk

Indentations for Vicker`s microhardness testing (model Leco) were made with a constant load 50 g and dwell time of 10 s on the polished samples.

The chemical durability of nickel leaching residue with precipitated heavy metals before vitrification and vitrified samples were evaluated by the toxicity characteristic leaching procedure (TCLP, US Environmental Protection Agency). The dried waste and vitrified sample (with size under 1 cm) were placed in extraction fluid and stirred for 18 hours. The extraction fluid with pH 2.88 ± 0.05 was used for nickel leaching residue and with pH 4.93 ± 0.05 for vitrified samples. The concentrations of heavy metals in the TCLP extracts were analysed by ASS method (Varian Specter AA-30).

Magnetic susceptibility was measured by a Kappabridge KLY-2, Geofyzika Brno in a magnetic field intensity of 300 Am^{-1} with homogeneity of 0.2 % at frequency 920 Hz.

Tab. 1. Chemical composition of the raw materials used in mixtures (wt%).

	NLR	glass	andesite	dolomite	glass sand	soda
SiO_2	15.21	72.4	56.38	0.59	99	-
Al_2O_3	4.72	1.7	18.86	0.34	-	-
Fe_2O_3	44.85	0.05	6.8	0.29	-	-
FeO	23.13	-	4.92	-	-	-
CaO	3.55	9.6	8.69	29.61	-	-
MgO	2.67	1.7	2.52	22.47	-	-
TiO_2	0.13	-	0.85	-	-	-
MnO	0.42	-	0.13	-	-	-
K_2O	0.19	0.6	1.13	0.11	-	-
Na_2O	0.16	13.8	2.89	0.04	-	57
P_2O_5	0.06	-	0.12	-	-	-
SO_3	0.12	0.18	-	-	-	-
CuO	0.005	-	-	-	-	-
Cr_2O_3	3.34	-	-	-	-	-
NiO	0.38	-	-	-	-	-
BaO	-	0.2	-	-	-	-
LOI	-	-	1.27	46.35	-	-

LOI – loss on ignition

Tab. 2. Chemical composition of NLR and additives.

sample	NLR	glass	andesite	dolomite	sand	soda
1A	50	-	40		10	
2A	50	-	20	10	20	
3A	50	-	20		20	10
4A	50	-	30	10	10	
5A	50	-	30		10	10
6G	50	40	-		10	
7G	40	50	-	10		
8G	40	25	-	10	25	
9G	40	10	-	5	30	15

Tab. 3. Theoretical chemical composition of glassceramics.

sample	SiO_2	Fe_2O_3	FeO	Al_2O_3	CaO	MgO	Na_2O	K_2O
1A	39.97	20.04	13.29	9.94	5.25	2.11	1.16	0.45
2A	38.65	19.69	12.30	6.21	6.47	3.86	0.58	0.24
3A	38.59	19.66	13.78	6.17	3.51	1.61	6.41	0.23
4A	34.39	19.88	12.80	8.09	7.34	4.11	0.87	0.35
5A	34.32	19.85	12.80	8.06	4.38	1.86	6.70	0.34
6G	46.38	19.31	11.32	3.08	5.61	1.79	5.52	0.24
7G	42.27	15.48	9.06	2.80	9.18	3.98	6.90	0.31
8G	48.92	15.47	9.06	2.38	6.78	3.56	3.45	0.16
9G	53.87	15.46	9.06	2.11	3.86	2.18	10.14	0.07

Results and discussion

Microwave heating is characterized by selective heating where the high-loss NLR is heated firstly and then the other components of the mixture are heated by thermal conductivity from it. The glassceramics was prepared by petrurgic method which is based on nucleation and crystallization during slow cooling. This method is used for the product from fused rocks (peturgy). In these materials, an uncontrolled crystallization takes place during cooling and as a result a course-grained structure is obtained (Karamanov et al., 2001). The homogeneity of glassceramics in the experiments improves the system of overflowing in crucibles, which is connected with the glassceramics composition and their viscosity. The samples 5A, 6G, 8G and 9G that flowed to the bottom crucible were without big pores in the structure. These samples were polished and light microscopy and Vicker`s microhardness were studied on them. For the glasseceramics with high iron content is typical dendritic structure (Huang et al., 2004; Romero et al., 1998) as is shown in Fig. 1 (sample 6G).

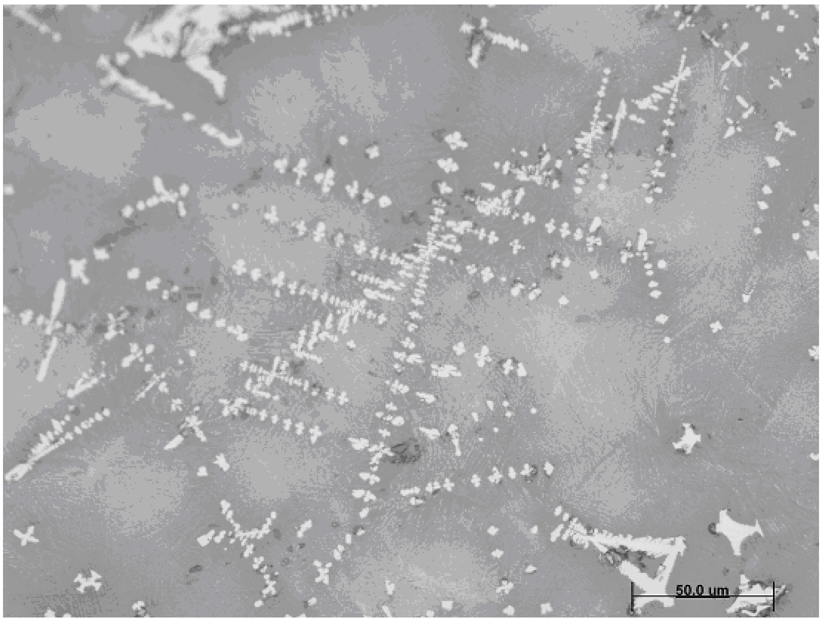

Fig. 1. Dendritic structure - sample 6G.

The Vicker`s microhardness was measured in the matrix and white zones identified in the pictures from the light microscopy (Fig. 2). The measured values with standard deviations are described in Tab. 4. The microhardness reached higher values in the white zones.

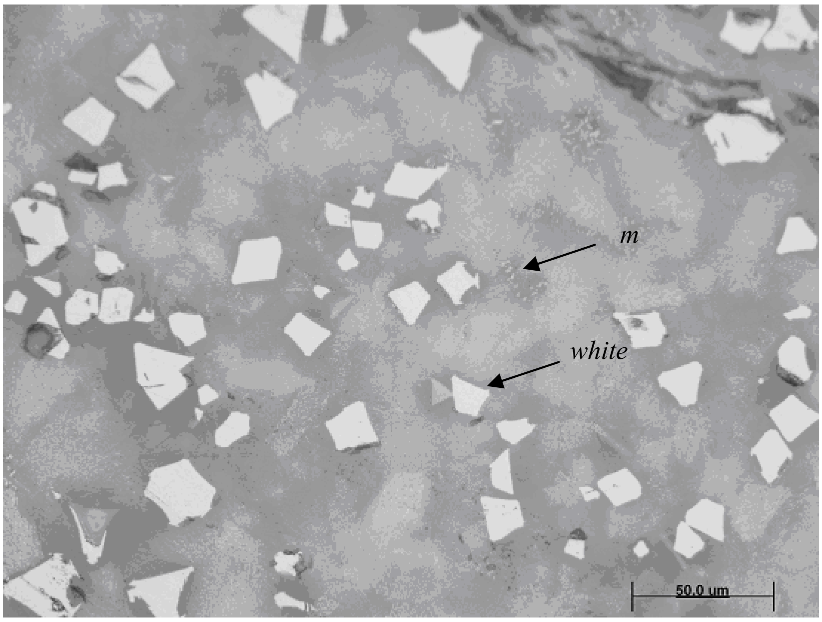

Fig. 2. Matrix and white zones – sample 5A.

Tab. 4. Vicker`s microhardness (GPa).

sample	matrix	white zone
5A	7.07 ± 0.36	12.37 ± 1.74
6G	7.79 ± 0.68	11.99 ± 1.09
8G	7.58 ± 0.77	12 ± 1.36
9G	6.24 ± 0.65	12.41 ± 1.5

In Table 5, the results of TCLP test of nickel leaching residue with precipitated heavy metals before and after vitrification and limit values are shown. The concentrations of cobalt and lead in glassceramics were compared with concentrations before vitrification. Microwave vitrification significantly reduces the leachability of heavy metals. The measured values are under limit of Cd and Pb.

Tab. 5. TCLP test results (mg.l^{-1}.)

	Cd	Pb
before vitrification	501.9	102
after vitrification		
1A	0.10	0.21
2A	0.06	0.17
3A	0.35	0.33
4A	0.13	0.25
5A	0.13	0.47
6G	0.06	0.15
7G	0.76	0.50
8G	0.06	0.17
9G	0.31	0.20
TCLP limit	1	5

The magnetic susceptibility of raw materials and vitrified samples are shown in Table 6 and 7. The magnetic susceptibility of glassceramics does not exactly correlate with the iron content. According to the previous study (Kováčová et al., 2008), it depends on the magnetic state that is influenced by grain size.

Tab. 6. Magnetic susceptibility of raw materials.

Sample	Magnetic susceptibility x10^{-6} jSI
NLR	135 222
glass cullet	247
andesite	2 682
dolomite	36
glass sand	34

Tab. 7. Magnetic susceptibility of vitrified samples.

Sample	Magnetic susceptibility x10^{-6} jSI
1A	208 886
2A	192 478
3A	214 994
4A	170 001
5A	240 348
6G	169 627
7G	81 011
8G	130 588
9G	115 311

Conclusion

Microwave vitrification was applied as a suitable method for the stabilization of heavy metal carriers. The mixtures used in the experiments were able to inertize 40-50 % of nickel leaching residue. The glassceramics with a high microhardness and very good chemical durability was obtained in a short time of heating.

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