Journal of the University of Chemical Technology and Metallurgy, 41, 2, 2006, 187-192

THE VITREOUS MATRIX PROCESSING OF A WASTE RESULTING FROM ELECTROCHEMICAL DEPOSITION PROCESSES

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Received 07 December 2005
Accepted 15 February 2006

ABSTRACT

The vitreous or vitro-ceramic matrix processing is a promising modality of immobilizing and recycling industrial inorganic wastes (sludges, slag and ashes). The paper studies the immobilizing of wastes resulting from an electrochemical deposition process of Urbis type in a chemically stable vitreous matrix. As a raw material, which by melting may become a stable vitreous matrix with high capacity of Urbis wastes incorporation, basalt may be taken into consideration.

Four compositions were prepared for experiments. The meltings were realized in alumina crucibles in an electric oven heated with silica carbide bars at 1400-1450° C, with a limit to 1450° C, for 2-3 hrs and annealing treatment, at temperatures in the range of 600-650° C, for 30 minutes. The obtained glasses were characterized in order to obtain useful products, as compared to domestic glasses used in the domestic glass factory STAR GLASS Targu-Jiu.

The obtained results showed that the glasses with variable contents of Urbis wastes may be utilized by the industry for the production of domestic products.

Keywords: urbis wastes, vitreous matrix, melting, basalt.

INTRODUCTION

The vitreous or vitro-ceramic matrix processing is a promising modality of immobilizing and recycling industrial inorganic wastes (sludges, slag and ashes).

The immobilizing of dangerous wastes in a vitreous matrix has the following main advantages [1,2]:

- allows for reducing of wastes volume;
- the matrix is chemically stable;
- means of recovery can be found;
- another utilization alternative is offered, certainly contributing to the durable development of society.

According to norms and regulations in this domain, it is considered that there may be inert liquid, paste or solid industrial wastes, of a mineral nature, with a predominant content of little soluble compounds of toxic metals such as:

- wastes in the form of aqueous suspensions: slimes containing hydroxides of toxic metals, resulting from electro-deposition processes;
- solid wastes: ashes and slags resulting from combustion processes.

To each waste category correspond certain treatment technologies for turning them into an inert material.

Immobilizing procedures of toxic compounds (heavy metals, inorganic compounds, etc.) by immobilizing in solid matters

The stabilization technologies refer to:

- cold processing, by stabilization in inorganic (cement) or organic matrices,
- heat processing, by immobilizing of wastes in a vitreous matrix.

By incorporating wastes in complex matrices, in an appropriate ratio, the polluting potential decreases, so that the wastes may be either stored safely, or reused in different ways.

The good chemical stability of glasses led to their utilization for the incorporation of toxic substances for their storage with minimum risks of spreading into nature of dangerous compounds.

The complexity of the correlation between the chemical composition and the properties of the basic glass assigned as the vitreous matrix incorporating the waste makes the choice of the composition a huge responsibility.

This paper studies the immobilizing of Urbis type wastes resulting from electrochemical deposition processes in a chemically stable vitreous matrix, as well as the possibility of obtaining useful products by recovery.

EXPERIMENTAL

Raw materials overview

Urbis wastes – characteristics. In the electrochemical deposition process at the URBIS Factory in Bucharest a residue with an average oxide composition presented in Table 1 is produced.

From the Table 1 the higher quantity of Al_2O_3, Fe_2O_3, CuO, MgO and Cr_2O_3 is evident but the high content of PbO, considered a compound with polluting potential, can not be neglected.

Table 1. The oxide composition of Urbis residue.

Oxide	Al_2O_3	Cr_2O_3	CuO	Fe_2O_3	MgO	PbO	P_2O_3	SiO_2	SnO	ZnO	NiO
%	22,89	7,41	10,81	14,74	8,59	6,34	0,19	5,44	0,58	12,64	10,37

Table 2. The oxide composition of basalt.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	pB(%)
%	47,93	15,43	8,45	10,49	10,67	3,24	1,32	2,47	59,55

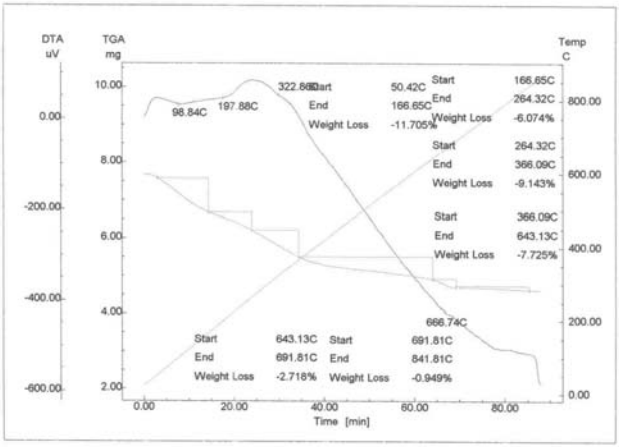

Fig. 1. Differential thermal analysis of the Urbis waste.

The differential thermal analysis executed on the waste sample evidences the loss during total calcination of 38,28 %, representing mostly water in various forms: free, hygroscopic or chemically bound. These data are relevant for a mainly gel-like structure of the waste, the composition of which seems to be made up of hydroxides.

Basalt. As a raw material, which by melting may becomes a stable vitreous matrix with high capacity of Urbis wastes incorporation, basalt may be taken into consideration.

From the point of view of the chemical composition, basalt meltings are silicate meltings whose oxide composition is presented in Table 2.

Glasses synthesis

• Mixtures preparation

The composition of the basic glass and the capacity of incorporation into the melting of the waste are determining factors that must be taken into consideration.

This is why most of the vitreous matrices have different compositions, "adjustable" to the waste type.

For experiments four compositions were chosen. Table 3 shows the dosage of the components assuring the oxide composition of the synthesized glasses, presented in Table 3.

The residue was dried, grinded and passed through a 0.22 mm sieve. The basalt was grained and grinded just as the residue. Grinding to particles smaller than 0.22 mm was used for both components for a better homogeneity and for increasing the melting speed of the mixture. The homogenization of the components weighted according to Table 3 was effected by grinding for 15-20 minutes.

Table 3. The dosage of the components.

Components	Sample 1	Sample 2	Sample 3	Sample 4
Basalt, g	65	85	75	63
Urbis waste, g	35	10	20	30
Na_2CO_3, g	-	5	5	7

• **The elaboration of meltings**

The meltings were made in alumina crucibles, in an electric oven heated with silica carbide bars, the raw materials mixture being gradually added, after the temperature reached 1400 – 1500°C. After the mixture was poured into the crucible, the melting was maintained at 1450°C for 2-3 hrs.

The meltings were poured into special metal shapes; in order to determine the dilatation curves, they were annealed at temperatures in the range of 600 – 650°C for 30 minutes and then left in the oven to cool.

During the pouring of sample 1 it was noticed that the melting was very viscous and, although it seemed homogeneous, it did not flow from the crucible to obtain the necessary shape for the determination of the dilatation curve. That is why it was decided to continue the preparation of this sample by adding of 3 g and 6 g respectively of Na_2CO_3.

During the pouring of samples 2, 3, 4 it was noticed that the melting is well done, is homogeneous and can be poured into a special metallic shape. It was noticed, however, that it did not have the viscosity required for making fibers.

Since sample 1 did not flow from the crucible, it was not characterized. For the rest of the samples, the following determinations were made:

1. Density determination by the hydrostatic weighting method [8];

2. Determination of linear thermal dilatation curves, with a Weiss type differential dilatometer [8];

3. Hydrolitic stability determination, by the conductometric method [8].

RESULTS AND DISCUSSION

Basalt is the most widely spread volcanic rock to be found in the earth surface, having the following mineral composition [3]:

• vitreous mass of approx. 45 %;

• pyroxenes of approx. 30 %;

• plagioclase feldspar (potassium aluminosilicates, sodium, calcium) of approx. 5 %;

• hematite, limonite (oxides, iron hydroxides) of approx. 17 %;

• other minerals 3 %.

Basalt is well-known as a natural polyphase chemically resistant complex.

The good long-term chemical stability, the possibility of being melted at relatively low temperatures (approx. 1400°C) and of being obtained in the vitreous state without difficulties, as well as the fact that it represents an abundant cheap raw material are the main arguments in favor of using basalt (along with other additions) as a vitreous matrix for the incorporation of wastes with polluting potential.

It must be added that, due to the remarkable capacity of basalt meltings of fibrillating, it is expected that, from certain glass compositions with different quantities of Urbis residues, fibers that can be used in different fields, within further research can be obtained.

The preparation of the glasses compositions was made on the basis of the basicity weight factor concept (pB).

Baltγ and coworkers [4-7] used as a measure of basicity the weight of the ionic character of the binding, based on the ionizing potential. Since basicity is a property of atoms and compounds, not of the binding, there was introduced the notion of a basicity weight factor, pB, equal numerically to the influence of the ionic character of the binding of an element with oxygen.

It reflects the way of reaching equilibrium, within the established binding, between the electrons acceptor force of the respective element and the electrons donor force of oxygen, the latter being determined by the electrons acceptor capacity of the partner atom which depends on the ionizing potential, P_i, and on the coordination number, NC, according to the relation determined by P. Baltγ and D. Radu [3,6,7].

$$\lg pB = 1{,}9\ (NC)^{0{,}02} - 0{,}023\frac{P_i}{NC} \qquad (1)$$

resulting in pB in % as compared to pBO_2 = 100%.

For oxidic compounds such as silica glasses, pB is calculated by summing up the products of pB_i and the mass fractions of component oxides.

For an oxidic compound, the basicity weight factor results from the relation [3,6,7]:

$$pB = \text{“}pB_i\text{”}c_i \qquad (2)$$

where: pB_i is the basicity weight factor of the i oxide;

Table 4. Oxidic compositions of synthesized glasses.

Oxide	Sample 1	Sample 2	Sample 3	Sample 4
SiO_2	43,5	42,7	37,52	33,15
Al_2O_3	15,97	16	16,01	16,61
Fe_2O_3	9,29	8,94	9,45	10,09
CaO	9,41	9,17	7,93	6,86
MgO	10,57	10,32	10,07	9,96
Na_2O	2,93	4,61	6,06	5,73
K_2O	1,19	1,14	1,01	0,87
TiO_2	2,23	2,18	1,89	1,63
Cr_2O_3	0,84	0,87	1,73	2,57
CuO	0,98	0,99	2	3,04
NiO	1,04	1,05	2,13	3,19
PbO	0,08	0,08	1,30	1,95
P_2O_5	0,63	0,64	0,2	0,3
SnO	0,07	0,06	2,6	3,89
ZnO	1,27	1,25	0,12	0,16
TOTAL:	100	100	100	100
pB (%)	**64,11**	**64,57**	**65,98**	**66,82**

The basicity weight factor, pB, of basalt is 59,55 %.

c_i – the concentration in mass fractions.

As previously shown, four basic compositions were prepared. Their oxidic compositions are presented in Table 4.

The basic idea was the immobilizing in the basalt matrix of a residue content as large as possible, in the conditions of maintaining the meltings workability for the preparation of useful products.

The results presented in Table 4 show that the influences of basicities of the synthesized glasses have an increasing tendency, this being justified by the Na_2CO_3 but also by the basic compounds contribution brought in by the residue (glass 3 as compared to glass 4). The increase of the glasses influence basicity lead to the increase in the crystallization tendency, a phenomenon that was observed during the whole annealing treatment.

In Table 5 the compositions of domestic glasses currently used in the manufacturing of domestic glass STAR GLASS Tg – Jiu are presented.

Table 6 presents the characteristics of the synthesized glasses (of the three samples whose melting could be processed: samples 2, 3, 4).

In Table 7 characteristics of domestic glasses from the glass factory STAR GLASS Tg-Jiu, experimentally determined in the laboratory, are presented.

Table 5. The oxidic composition of domestic glasses and pB values.

Oxide	White domestic glass, %	Blue domestic glass, %
SiO_2	73,37	60,96
B_2O_3	0,26	2,83
Al_2O_3	0,29	0,23
Na_2O	13,95	13,20
K_2O	3,04	4,41
CaO	8,36	3,84
MgO	0,7	0,1
PbO	-	14,41
Fe_2O_3	0,03	0,02
Cu	-	-
Sn	-	-
pB (%)	59,3	61,3

The characteristics of the synthesized glasses were compared to those of some domestic glasses from the STAR GLASS Tg-Jiu factory.

The main properties of the synthesized glasses with a variable content of Urbis waste are comparable and compatible with the ones of the industrial glasses currently used for domestic products.

For a more suggestive interpretation of the influence of the waste addition on some of the glasses properties, Figures 1 and 2 present the density variation and the dilatation coefficient with the waste content added in the basalt matrix.

Table 6. Synthesized glasses characteristics.

Characteristics	Measurement unit	Basalt sample	Sample 2 (10%)	Sample 3 (20%)	Sample 4 (30%)
Preparation temperature	^0C	1400	1450	1450	1450
Vitreous tranzition temperature, T_g	^0C	690	625	657	615
Annealing temperature	^0C	-	600	650	600
Density, d	g cm^{-3}	2,8900	2,8005	2,8792	2,8974
Thermal dilatation coefficient, α	K^{-1}	$47 \cdot 10^{-7}$	$98,95 \cdot 10^{-7}$	$96,54 \cdot 10^{-7}$	$105,42 \cdot 10^{-7}$

Table 7. Characteristics of domestic glasses.

Characteristics	Measurement Unit	White domestic glass	Blue domestic glass
Preparation temperature	^0C	1450	1450
Vitreous transition temperature, Tg	^0C	619	620
Annealing temperature	^0C	600	610
Density, d	g cm^{-3}	2,8076	2,8441
Thermal dilatation coefficient, α	K^{-1}	$101 \cdot 10^{-7}$	99,41

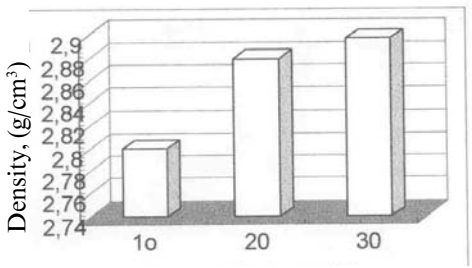

Fig. 2. The density variation with the waste content.

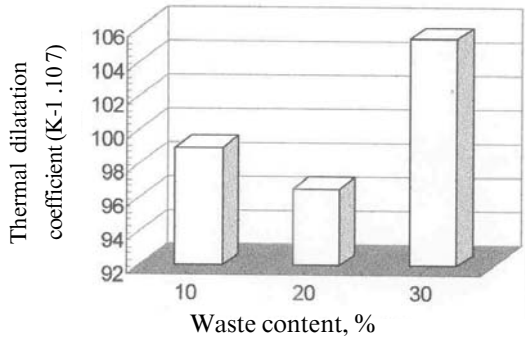

Fig. 3. The dilatation coefficient variation with the waste content.

The sample density with the highest waste content has, as expected, the highest value, because it correspondingly increases the heavy metals oxides content, whose specific heavy weights contribute to the density increase.

The thermal dilatation coefficient of the sample with the highest waste content (sample 4) has the highest value, because it increases correspondingly the modifying oxides content which depolymerizes the structure, creates asymmetry centers and determines the anharmonizing of thermal oscillations and, subsequently, the increase of the thermal dilatation coefficient.

The graphic representation of the conductance variation with time is evidenced for each of the studied glasses in Fig. 4.

The graphic representation of the conductance variation with time is even more suggestive for each of the studied glasses.

From the analysis of the presented results, it is concluded that for all three glasses, the conductance of the suspension increases in the first 10-20 minutes, after which it does not vary significantly, which means that it is possible that the interdiffusion and reaction processes take place at very low speeds. From Fig. 4 it

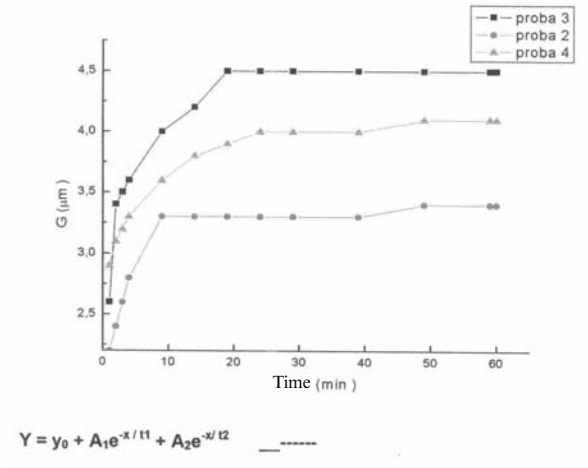

Fig. 4. The conductance variation with time.

results that the sample with the highest hydrolytical stability is sample 2, with a waste content of 20 % and pB = 65,98 %.

CONCLUSIONS

The composition of the basic glass and the capacity of waste incorporation in the melting are the determining factors that must be considered.

The immobilizing of the Urbis waste in a basalt matrix was possible in lab conditions only by adding a fluidizing compound, in order to obtain a melting with processing properties.

The syntesized glasses with a variable Urbis waste content may be used for the production of domestic products.

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