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NEUTRALIZATION OF HAZARDOUS WASTE IN VITREOUS MASS OF GLASS

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ABSTRACT

The paper presents studies concerning the neutralization of hazardous waste containing metal ions by embedding them in vitreous matrix which are chemically stable materials. The main analysed factors are: chemical composition of the charge based on packaging glass waste, amount influence of waste added in the charge on the physical-mechanical properties of analysed materials, the structure and the capacity for inclusion of metallic oxides from hazardous waste, the thermal treatment of vitreous or vitreous-ceramic materials.

KEYWORDS: glass, oxides, hazardous waste, structure

1. Introduction

Through the neutralization of dangerous waste in the matrix of oxidic glasses which are stable from the chemical point of view, the polluting potential of the waste decreases substantially [1].

The recovery of glass waste in view of elaborating the vitreous matrix for the inertisation of dangerous waste was studied in the present paper due to the fact that it represents a research field which may reveal very important technical and economic advantages.

Through incorporating various composites (some metal oxides, salts, heavy metal hydroxides) into the vitreous matrix, decorative glasses may be obtained, whose colour varies in keeping with the nature of the metallic ion, the quantity added and the work temperature [2].

Vitroceramic materials may combine specific properties to ceramic and specific properties to glass. To obtain the designed properties, the stabilisation of the appropriate chemical composition and the achievement of an adequate thermal treatment must be taken into account.

The concept of controlled crystallisation involves the separation from the vitreous phase of a crystalline phase under the form of fine crystals, whose number, growth speed and final size are controlled through an appropriate thermal treatment [3]. The inertisation of wastes in the vitreous matrix mainly consists in their incorporation through melting in a glass with a particular composition, which allows the incorporation of certain chemical elements present in the waste [4, 5].

The complexity of the correlation between the chemical composition and the properties of the base glass functioning as a vitreous matrix which incorporates the waste makes the choice of composition be of a a great importance.

The production of vitroceramics with improved properties is highly dependent on the phases of the crystalline microstructure developed during the heat treatments of the base glass.

Some glass compositions have their own crystallisation centres, but others need specific components to be added so as to ensure the internal formation of crystallisation centres. In glass factories, glass chips are used to a high extent (almost up to 100%) in the fabrication process as raw material, also known as adding material.

2. Experimental results

In present are known three broad categories of vitro-ceramic materials used for their special properties. The first is based on a base glass with a composition close to eutectic Al_2O_3-SiO_2-MgO system (MAS), the second system becomes very important is ternary system Li_2O-Al_2O_3-SiO_2 (LAS), the third class of vitro-ceramic materials refers to those which contain the main crystalline phase keatitul (polymorphic form of SiO_2) from the system

Al_2O_3-SiO_2 (AS), with outstanding thermal properties.

Results for stoichiometric compositions 2CaO Na_2O 3SiO_2 (NC_2S_3) and 2Na_2O CaO 3SiO_2 (N_2CS_3) which are based on the ternary system SiO_2-CaO-Na_2O, Figure 1, were discussed by Gonzales - Olivier and James [4] which studied nucleation speeds, viscosity and thermodynamic data in stationary regime.

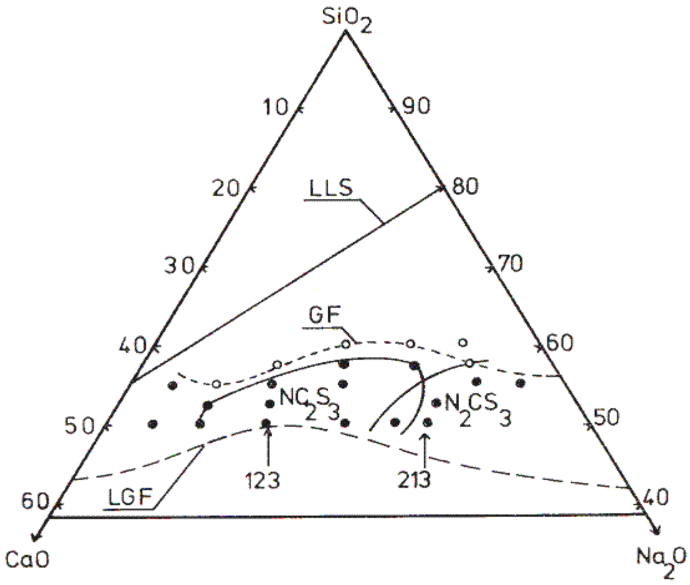

Fig. 1. *Section of Na_2O-CaO-SiO_2 system with compositional fields vitrogene (GF, LGF) with imiscibilitaty (LLS) and crystallization in volume of the N_2CS_3 NC_2S_3 compounds [3]*

Table 1. *The main stages in the elaboration of glass*

No	Name of stage	Temperature range
1	Formation of silicates in the solid phase and of the first melt volumes	It begins at 300 ° C and ends at 800 - 1000^{o}C
2	Glass formation	It begins at 800 – 1000^{o}C and ends at 1300 – 1500^{o}C
3	Refining of the glass melting	1350 – 1550^{o}C
4	Homogenization of the glass mass	It begins at the upper limit of the melting interval and ends at temperatures corresponding to the glass clarification
5	Cooling of the glass mass	At temperatures 200-600^{o}C lower than those of the melting interval

More types of glasses go into the recycling flux, each having different chemical compositions and physical properties. The most frequently used vitreous material is the glass based on silicon dioxide (SiO_2), sodium carbonate (Na_2CO_3), calcium carbonate ($CaCO_3$) or limestone and other minor additives.

Most of the recycled glass is made up of packaging and plane surface glass. The main stages in the treatment and elaboration of glass are shown in table 1.

The samples were made of chipped packaging glass, aluminium oxide, zinc oxide, arsenic trioxide, metal oxide wastes with a granulation of under 300µm. The casting form were filled with these chipped materials which were heated in an oven with silit bars, at a temperature of up to 1450^{o}C.

The quantity and the dimensions of the pieces of glass, as well as the metallic oxide resulting from industrial waste are of a great importance for the melting time, and also for the end product. The granulation of the transparent glass chips which change colour following melting and in the presence of oxides plays an important role in the colour homogeneity and uniformity. The smaller the granule size, the better the colour uniformity. The homogenisation of the glass melt consists in the levelling of the physical and chemical characteristics of the whole mass of glass, a phenomenon which is usually based on reciprocal solubility.

The non-uniformity of colour may appear as a result of an insufficient mixing of the chips with the waste which contains a certain metallic oxide that influences the structure of the glass.

The intensity of the colour and its nuance depend on the concentration of oxide, the valence of the colouring ion, the latter's modification due to the atmosphere of the oven and the chemical composition of the glass. An extremely important role in finalising the homogenisation of the glass is played by high temperature diffusion, at the atom-molecular level. In glass melts, diffusion is the slowest stage and it depends especially on raising the temperature, which also leads to a reduction in viscosity.

Glass without gas bubbles is obtained through refining the glass melt during its elaboration.

Figure 2 presents a sample of dark green glass obtained with the aid of iron oxide resulting from the scale, which is a waste from the metallurgical industry, grinded at sizes of under 200 µm, in a reducing medium.

The used materials for obtaining vitreous materials when added waste with nickel ions are presented in charge, are presented in table 2.

Fig 2*. Green glass obtained by adding in charge of iron oxide*

Table 2*. Raw materials for glasses which neutralisation wastes containing nickel oxide*

Materials charge	wt (%)
Waste glass	63.37
Aluminium oxide	12.25
Zinc oxide	17.42
Arsenic trioxide	0.47
Waste with nickel oxide content	6.48

The melting temperature has increased to over 1450^{o}C through adding the concentration of nickel oxide. After the temperature of 1450^{o}C was reached, it was maintained at this temperature for 150 minutes in view of homogenisation and degasification.

Fig. 3*. Glass with nickel oxide after thermal treatment*

The melt from the refractory crucible was poured into the preheated refractory metal form. The samples obtained through casting were subjected to a thermal treatment of afterglow at a temperature of 600ºC. NiO can be introduced as $Ni(OH)_2$ which decomposes during melting.

Depending on glass composition and melting temperature, glass shades range from yellow to brown, violet or gray. After maintaining the temperature at 600ºC for 2 hours, the oven was stopped and the samples were left inside until completely cooled. Following the afterglow thermal treatment, the sample is gray-green in colour, Figure 3.

The obtained samples were analysed at the SEM in view of emphasising their structure and the inclusions present in their mass. Figure 4 presents the structure of the glass sample, for their obtaining were used green glass waste, other oxide additions and waste containing iron oxide.

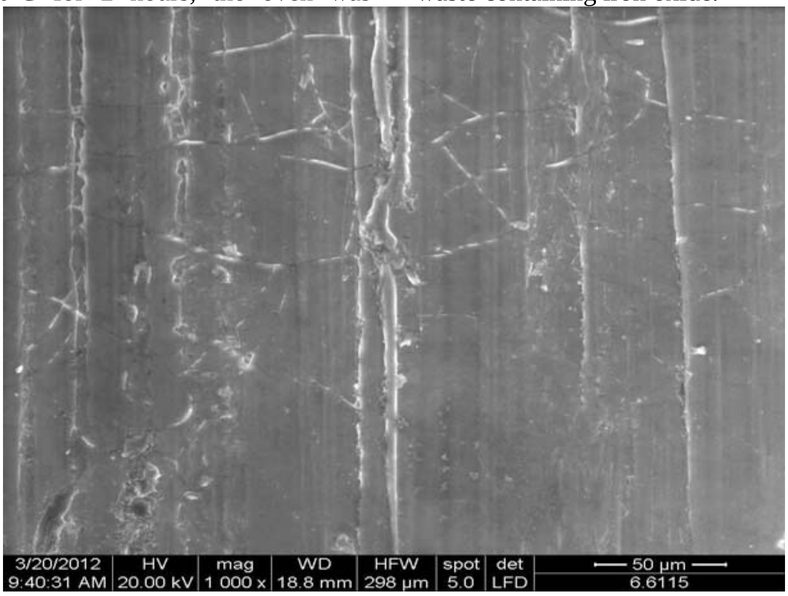

Fig. 4. *Microstructure of a green glass plate with iron oxide*

For casted glass, the base structure is amorphous, which is specific to a vitreous mass. Figures 5 and 6 present the microstructures of the studed glasses which were achieved through the re-melting of glass wastes mixed with othercomponent such us dried mud which contains nickel ions, following then the casting and the afterglow thermal treatment.

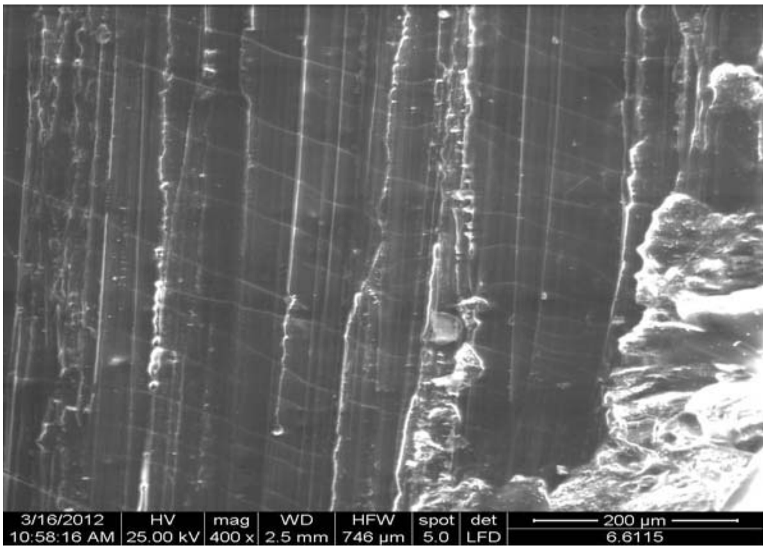

Fig. 5. *Microstructure of glass with nickel oxide, thermally untreated*

In the microstructures of glasses obtained by re-melting of glass waste in the presence of iron oxides or nichel and other components, has revealed the presence of crystals in the vitreous matrix which is specific to oxide glasses.

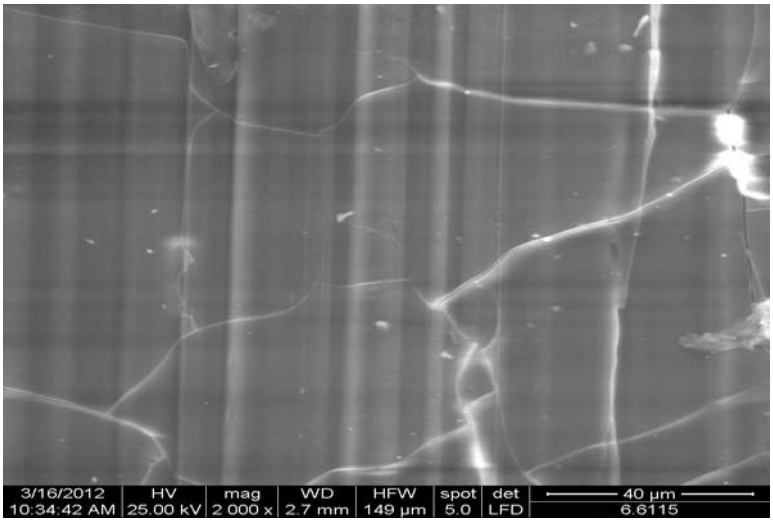

Fig. 6. *Microstructure of glass with nickel oxide, after thermal treatment*

The crystals formed thanks to the thermal of the vitreous phase have determined at the same time a gradual change in the composition and structure of the base glass.

4. Conclusions

The main conclusions of these experimental researches are:

1. Incorporating metallic oxides (contained by industrial waste) into the vitreous matrix determines the decrease of their polluting effect, favourably influences on the temperature of elaborating or thermally treating of the vitreous or vitroceramic materials, and sometimes improves their physico-mechanical properties.

2. Crystals formed as a result of neutralization of waste with metal oxide content in the vitreuos matrix and of the thermal treatment determining at the same time a gradual change in the composition and structure of the base glass.

3. To ensure the designed properties of the glasses, the establishing of the appropriate chemical composition and achieving an adequate thermal treatment are very important.

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