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Synthesis of wall-covering glass-ceramics from waste raw materials

Alexander Karamanov and Ivan Gutzow
Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia (Bulgaria)

Ivan Chomakov and Jancho Christov
Higher School of Chemical Technology, Burgas (Bulgaria)

Lyubomir Kostov
Staklomat Company, Sofia (Bulgaria)

The possibility of producing glass-ceramic wall-covering materials from waste raw materials by sintering and crystallization of the frit is demonstrated. The compositions used are given and suggestions concerning the synthesis are made depending on the type of the initial waste materials.

Herstellung von Glaskeramik als Wandverkleidung aus Abfallprodukten

Es wird die Möglichkeit untersucht, aus industriellen Abfallprodukten durch ein Sinterkristallisationsverfahren Glaskeramiken für architektonische Zwecke herzustellen. Es werden die Zusammensetzungen der verwendeten Materialien angegeben und Vorschläge gemacht, wie die Synthese der verschiedenen Abfallstoffe durchzuführen ist.

1. Introduction

The utilization of waste products from industry belongs to the ecological challenges in developed countries. Of particular interest is the production of new materials substituting natural products whose processing disturbs the environment.

In this connection, the present paper describes an attempt to show the possibility of using waste products from metallurgical and ore-dressing plants as well as ashes from electric power stations for the production of wall-covering glass-ceramic materials which, in addition to their attractive appearance similar to that of granite, possess physico-mechanical properties exceeding those of natural wall-covering materials.

Some of the waste raw materials mentioned have chemical compositions allowing their application in the glass industry. In some cases a small amount of the waste product is added to the batch, which contributes to reducing the duration of fining and homogenization of the melt as well as to a lowering of the glass melting temperature. However, the main application of waste products in the glass industry is associated with the production of wall-covering glass-ceramics. The most usual materials of that kind are the slagsitalls [1 and 2]. They are obtained mainly by a rolling process followed by crystallization of a melt containing about and above 50 % waste materials. The products obtained have very good physico-mechanical and thermal properties as a result of the relatively high percentage of crystalline phases distributed uniformly in the whole volume and consisting of crystals with sizes ranging from 0.1 to 1 µm. However, slagsitalls and other similar materials have an appearance that cannot compete with natural covering materials. In addition, the relatively great aggressiveness of the melt requires the use of special refractory materials.

Another type of tiling glass-ceramics from waste materials is obtained by sintering a mixture of an inert material (containing waste) and the frit of a suitable partially crystallizing glass. A material of that kind is, for instance, steklokremnesit [3]. It has a more attractive appearance in comparison with slagsitalls but is inferior to them in its physico-mechanical properties and, above all, because of its inhomogeneity.

There are also other kinds of glass-ceramic wall-covering materials that are produced by sintering and crystallization of the frit. These are the Japanese "Neoparies" [2 and 4] with β-wollastonite ($CaO \cdot SiO_2$) as the main phase and a similar material developed by a Bulgarian team [5], the major crystalline phase in this case being diopside ($CaO \cdot MgO \cdot 2SiO_2$). These two kinds of materials have an appearance similar to that of natural marble and physico-mechanical and thermal properties that considerably surpass the properties of natural wall-covering materials and are close to those of slagsitalls. The size of the needle-like crystals formed in

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these cases is in the order of millimetres. This and the circumstance that surface crystallization of the separate grains takes place determine the excellent appearance of these products.

The purpose of the present paper is to demonstrate the possibility of obtaining wall-covering glass-ceramics by sinter-crystallization of frits, a high percentage of industrial waste material being used.

2. Experimental

The initial waste raw materials used were granulated blast furnace slag (A) from metallurgical processes, a waste product (B) from the copper-producing industry and ash (C) from a coal-fired electric power station. These waste materials are common in all industrial countries. The chemical compositions (in wt%) of the materials used are presented in table 1. They are typical of the respective industrial waste raw materials.

Table 1. Chemical compositions (in wt%) of the waste materials used

	A	B	C
SiO_2	38.7	52.4	49.1
TiO_2	–	–	0.9
Al_2O_3	6.6	13.2	23.8
Fe_2O_3	0.6	10.1	9.7
CaO	41.8	7.2	6.7
MgO	2.3	7.1	1.8
BaO	3.4	–	–
MnO	2.5	–	0.1
CuO	–	0.8	–
Na_2O	0.5	1.2	0.7
K_2O	0.7	3.0	2.2
S^{2-}	1.6	0.6	0.4
weight loss on ignition	1.3	4.4	4.6

The comparison of the compositions with a view to their use for the preparation of glass-ceramics reveals significant differences. Composition A displays a very high percentage of CaO, whereas the simultaneous presence of large amounts of Fe_2O_3, CaO and MgO is characteristic of composition B, and high Al_2O_3 content is typical of composition C.

Using the described waste products, a series of glasses was melted at 1450 to 1500 °C in a furnace with super-kanthal heating elements utilizing corundum crucibles. The temperature was kept constant for 2 to 3 h. The compositions of some of the glasses are included in table 2. The last line of table 2 gives the percentage of the waste material participating in the corresponding batch composition. The kind of waste material is indicated by the corresponding letter as given before. The other raw materials employed were quartz sand, borax, limestone, dolomite and technical Al_2O_3, $BaCO_3$, ZnO, NiO, MnO and Na_2CO_3. For comparison, table 2 also shows the compositions of "Neoparies" (N), of the marble-like Bulgarian material (BM) and of slagsitalls (S).

The melts were fritted and the frits obtained were broken and sieved. Fractions with grain sizes of 1 to 10 mm were placed in refractory forms (having the dimensions $(12\times12\times3)\,cm^3$) with dismountable boards. After that the forms containing the frits were heated in a resistance furnace with a heating rate of 5 to 7 K/min up to a definite temperature for each composition. After keeping the temperature constant for 1 h, the samples were cooled to room temperature with a rate of 3 to 5 K/min and then taken out of the forms. The constant temperature to be maintained for each composition was determined by the requirement to achieve complete sintering and a relatively smooth surface of the samples.

The compositions of the samples can be divided into groups not only on the basis of the waste raw materials used but also according to their oxide contents. Compositions A1, B1 and C1 with a total $CaO+MgO+Fe_2O_3$ content of less than 20 % are closer to the marble-like glass-ceramics obtained in this way. The other group of compositions comprises A2, B2 and C2, in which the $CaO+MgO+Fe_2O_3$ content exceeds 20 %. These compositions are closer to that of slagsitalls. It should be noted that compositions A1, B1 and C1 exhibit mainly surface crystallization of the separate grains, while in the case of A2, B2 and C2 there is also bulk crystallization irrespective of the fact that no additional nucleating agents have been participating.

The samples obtained have a smooth surface, their colour ranges from light to dark brown and they are very appropriate for use as covering materials. After cutting and polishing, the appearance is considerably improved especially with samples obtained from compositions A1, B1 and C1, which are similar to high-quality granites.

Figure 1 shows the results from X-ray phase analysis of the samples obtained. The crystalline phases are: β-wollastonite, diopside and anorthite ($CaO\cdot Al_2O_3\cdot 2SiO_2$). It is worth noting that according to the X-ray analysis these are cases of solid solutions rather than of pure phases. It is well-known that diopside is a typical representative of pyroxenes and allows incorporation of FeO, MnO, Fe_2O_3, Al_2O_3 and Na_2O. Solid solutions are also formed by β-wollastonite, and substitution of Fe^{2-}, Mn^{2-} and Mg^{2-} for Ca^{2-} ions is possible. Anorthite belongs to the large group of plagioclases. Table 3 shows the crystalline phases formed in each composition. They are denoted by the corresponding letter.

Some physico-mechanical and thermal properties of the synthesized samples have been investigated and the corresponding results are given in table 3. Tests on the bending strength have shown that in none of the samples it is below 30 MPa. This value is twice as high as that of natural marbles and granites.

Table 2. Compositions (in wt%) of the initial glasses

	A1	A2	B1	B2	C1	C2	N	BM	S
SiO_2	59.3	58.9	58.1	57.0	57.5	57.3	59.3	58.7	54.0 to 62.0
TiO_2	–	–	–	–	0.3	0.4	–	–	–
Al_2O_3	7.0	7-2	6.7	7.1	7.0	10.5	7.1	6.6	5.0 to 15.0
B_2O_3	1.0	–	2.0	–	–	–	1.0	2.2	–
Fe_2O_3	0.3	0.4	5.3	5.6	2.8	4.3	–	–	0.2 to 1.5
CaO	16.7	20.1	7.0	19.9	16.5	19.0	17.1	10.7	21.0 to 31.0
MgO	0.9	1.1	5.0	3.8	0.5	1.6	–	7.7	1.0 to 7.0
BaO	3.1	1.6	4.5	–	3.9	–	4.0	3.7	–
ZnO	5.0	3.5	5.5	–	6.3	–	6.5	5.3	0.5 to 5.0
NiO	0.7	–	–	–	–	–	–	–	–
CuO	–	–	0.4	0.4	–	–	–	–	–
MnO	1.0	1.2	–	–	–	1.4	–	–	0.5 to 2.5
Na_2O	4.7	5.7	4.0	4.7	4.6	4.5	3.0	5.1	1.0 to 8.0
K_2O	0.3	0.3	1.5	1.5	0.6	1.0	2.0	–	1.0 to 4.0
share of waste material in wt%	37.8	45.6	45.9	45.7	24.8	37.1	–	–	–

In table 3 are also given the results of the chemical resistance of the materials. Grained glass-ceramic samples (with sizes from 0.4 to 0.5 mm) were used according to a standard procedure in which about 2 g samples were treated at 95 °C for 1 h in 65 to 70 cm^3 solution (0.01 mol/l HCl and 0.01 mol/l NaOH, respectively). Table 3 gives percentage of weight loss of the samples under the described conditions of experimentation. Additional determinations were made of the hydrolytic class (DIN ISO 719 [6]) of the initial C1 glass and the corresponding glass-ceramics. It turned out that the durability of the glass corresponds to the second hydrolytic class and after its crystallization to the first hydrolytic class.

The densities obtained are of the order of those for natural wall-covering materials. The thermal expansion coefficients are commensurable with or lower than those for marbles and granites. The microhardness values are in most cases higher than those for granites, which leads to a higher wear resistance. It should be noted that the increasing microhardness is a result rather of the total amount of the crystal phases formed than of the nature of the phases separated in the materials. The chemical durability of materials corresponds to that of glasses and glass-ceramics of high chemical resistance.

3. Discussion

On the basis of the present investigation and the appearance of the samples obtained it may be concluded that the production of sintered wall-covering glass-ceramics from waste raw materials is possible. In physico-mechanical properties the samples obtained by sintering and crystallization of the frit surpass natural building materials, while in appearance they are much better than slag-sitalls.

The percentage of the waste raw materials that may be used depends mainly on its chemical composition and on the major crystalline phase formed. In the case of a waste raw material with a high CaO concentration (composition A) it is advisable to synthesize material forming mainly $CaO \cdot SiO_2$ or solid solutions on its basis. In the presence of large amounts of MgO and FeO (or Fe_2O_3) (composition B) it is better to look for products in which the pyroxene solid solutions are prevailing. The high

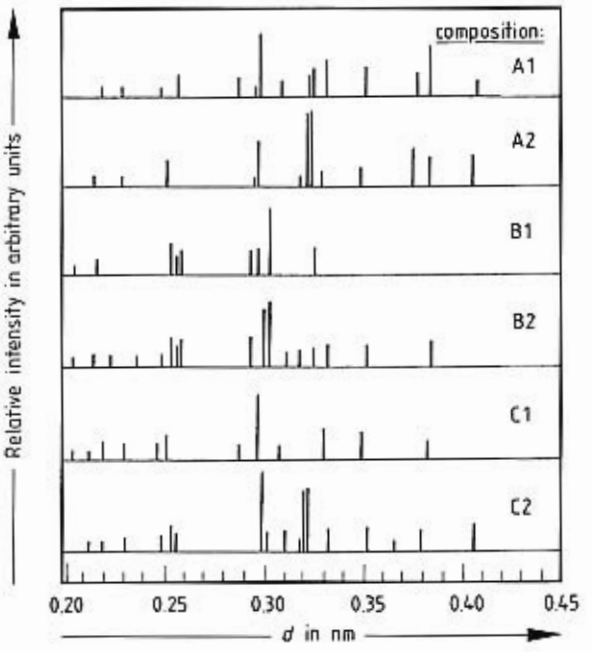

Figure 1. Schematic presentation of X-ray patterns of the samples obtained. The phases crystallized are (the d values (in nm) are given in the respective brackets): β-wollastonite (0.297, 0.383, 0.352, 0.331, 0.247), diopside (0.299, 0.253, 0.289, 0.252, 0.323), and anorthite (0.320, 0.318, 0.404, 0.326, 0.312).

Table 3. Properties of the synthesized samples

	A1	A2	B1	B2	C1	C2
density in kg/m³	$2.8 \cdot 10^3$	$2.9 \cdot 10^3$	$3.0 \cdot 10^3$	$2.8 \cdot 10^3$	$2.7 \cdot 10^3$	$2.7 \cdot 10^3$
hardness in MPa	582	623	586	745	493	579
coefficient of thermal expansion at 20 to 400 °C in $10^{-6}K^{-1}$	6.04	6.58	6.84	5.55	5.72	7.61
chemical resistance given as loss in wt%						
in solutions 0.01 mol/l HCl	1.0	0.7	0.3	–	1.4	1.2
in solutions 0.01 mol/l NaOH	0.8	0.5	0.5	–	1.0	0.6
ϑ_{max} in °C	1100	1150	1050	1150	1000	1100
crystalline phases	W,A	A,W	D	D,W	W	W,A

Al_2O_3 percentage in composition C does not allow the use of a large amount of this waste product if the mentioned main phases are to be expected. Of course, a composition forming $CaO \cdot Al_2O_3 \cdot 2SiO_2$ or another aluminosilicate as a major phase may be synthesized. But in this case the melting temperature of the initial melt would rise, which is not very favourable from a technological point of view.

On the other hand, the significant increase in the amount of the crystalline phase formed (which is mostly accompanied by a larger amount of the waste product used) in the order of the percentage of crystalline phase appearing during the production of the slagsitalls leads also to bulk crystallization. This results in an increasing sintering temperature. In this case the crystallization proceeds before the sintering and inhibits it. In addition, the amount of the residual glass phase is in this case lower. The most important thing is that, due to bulk crystallization, the appearance of the products is unsatisfactory. After polishing the separate grains are not discernible and the appearance is too homogeneous. In contrast to the samples obtained from compositions A2, B2 and C2, in the cases of samples of compositions A1, B1 and C1 the percentage of crystal phase formed is even lower than 30 to 40 %. As a result of the predominating surface crystallization, separate grains are visible and the appearance of the samples is similar to that of some high-quality granites.

4. References

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