

Iron-Rich Sintered Glass-Ceramics from Industrial Wastes

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In this study, sintered glass-ceramics made up of jarosite (a hazardous industrial waste) have been obtained by sintering high-iron-content glasses. Thermal gravimetry and differential thermal analysis, carried out in different atmospheres, have been utilized to explain the phase formations in the volume and iron oxidation on the surface of the glass particles. Low-angle XRD technique has been used to investigate the distribution of the phases formed on the surface of the glass during heating. The variation of density of the powder and bulk samples has been used to investigate the kinetics of phase transformation. The value of the Avrami constant, n , has been obtained as 1.33, which corresponds to the three-dimensional diffusion growth on a fixed number of nuclei. The sinter-crystallization process has been defined to yield a 40 wt% crystal phase. The results of this study have opened the possibility of preparing glass-ceramics with an original appearance, somewhat similar to that of granite, by reevaluating industrial wastes.

I. Introduction

GLASSES and glass-ceramics are suitable media to immobilize regulated heavy metals and recycle inorganic hazardous wastes. This methodology was proposed by Kitaigorodski in 1959, and "Slagsitalls"—glass-ceramics for building applications made out of furnace slags—are still marketed in the former Soviet Union.^{1,2} Similar products were developed in England^{2,3} and other countries.^{4,5} All of these materials are characterized by excellent properties but the appearance is inferior to that of natural stones or traditional ceramics.

One way to improve the appearance of this class of glass-ceramics is to use the technology of sinter-crystallization of glass frits, used for the first time in the production of marble-like "Neoparies" material,^{2,6} the production of which started in 1974 in Japan. This building material is made up of 30–35 wt% wollastonite ($\text{CaO}\cdot\text{SiO}_2$) crystal phase which gives, after heat treatment, an appearance similar to marble coupled with outstanding mechanical and chemical properties.

More recently, glass-ceramics based on other raw materials⁷ and industrial wastes^{8,9} were developed using the technique of sinter-crystallization of frits. The main crystal phases formed after crystallization are pyroxenes or plagioclases.

In principle, these sintered glass-ceramics are characterized by an appearance similar to that of natural stones, because during the heat treatment the crystallization starts from the surface to the inside of each grain. The crystal size is on the order of millimeters and the different particles can be easily distinguished in the structure of the materials; as a result, the appearance imitates the grained structure of marble and granite.

In the present work, the results obtained in the synthesis of sintered glass-ceramics based on Jarosite,^{10–12} hazardous waste arising from the hydrometallurgical process for producing zinc metal,¹³ are summarized. In comparison with the other previously investigated sinter-crystallization glass-ceramics, in this study some differences are observed:

- In iron-rich glass compositions, the sinter-crystallization process is more complicated because pyroxene is formed preferentially in the bulk while hematite (Fe_2O_3) is formed on the surface as a result of the oxidation of FeO .

- Magnetite (Fe_3O_4) also crystallizes in the bulk of the glass but its formation is influenced by the initial ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$, by the particle size distribution, and by the sintering conditions.

In this study, the phase formation in the volume and on the surface of the glass particles is explained by differential thermal analysis (DTA) and thermal gravimetry (TG) carried out in different atmospheres and by X-ray diffraction (XRD). The crystallization kinetics are investigated by measuring the variation of density of the glass during the crystallization process.

II. Experimental Procedure

Different glass compositions were prepared by mixing jarosite, granite waste, quartz sand, limestone, and Na_2CO_3 . The melting was carried out in a super-kanthal furnace at 1450°C utilizing alumina crucibles and by keeping this temperature constant for 2 h. The main part of the melt was quenched in water and the frit obtained was broken and sieved. Two fractions were obtained: from 2 to 5 mm and less than 0.5 mm, respectively. The remaining part was poured into a stainless steel mold and cut into small specimens for subsequent thermal treatment.

Table I reports the chemical analysis of jarosite waste (JW), wastes from the granite sawing (GW), and one of the glass compositions investigated during the experimental activity (S3). The S3 batch had the following composition: JW, 42.5 g; GW, 30 g; SiO_2 , 31 g; CaCO_3 , 12.5 g; Na_2CO_3 , 10.3 g.

The crystallization process was investigated by DTA techniques (Netzsch STA 409 apparatus), at a heating rate of 10°C/min. About 120 mg of glass powder (200–300 μm size) was thermal treated in air and in nitrogen atmospheres. Bulk glass, with approximately the same weight, was investigated in air only.

Isothermal and nonisothermal treatments were made using powder and bulk glass fractions. The crystalline phases formed were determined by XRD (Philips PW 1830 apparatus and $\text{CuK}\alpha$ radiation). The crystalline fraction, developed during the thermal treatment, was estimated by comparing the areas of amorphous halo in the parent glass and in the crystalline samples. The ratio between different phases was obtained by comparing the intensities of the mean peaks of each one.^{2,14} Low-angle XRD analysis was employed to highlight the phases formed on the surface of the glass.

The crystalline fraction developed in isothermal conditions was also evaluated by measuring the change of the density between the parent glass and the heat-treated sample. For this series of tests, a He displacement pycnometer (AccyPyc 1330) was utilized. The experimental error associated with our mea-

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Table I. Chemical Compositions of Jarosite Waste (JW), Granite Scraps (GW), and Parent Glass (S3)

	Composition (wt%)		
	JW	GW	S3
SiO ₂	3.7	70.2	53.8
Al ₂ O ₃	0.3	12.1	3.7
Fe ₂ O ₃	49.3	1.6	21.7
CaO	0.1	5.2	8.7
MgO	0.2	0.6	0.2
ZnO	5.6		2.4
PbO	3.6		1.5
Na ₂ O		2.9	6.9
K ₂ O		3.3	1.0
LOI	37.2	4.1	

surements, employing a 3–4 glass sample, was evaluated as $\pm 0.001 \text{ g/cm}^3$. A detailed description of the methodological approach and experimental procedure is reported elsewhere.¹⁵

The oxidation process of Fe²⁺ to yield Fe³⁺ was investigated at 620° and 680°C by thermal gravimetry (Cahn 1000 apparatus). In this series of experiments about 4 g of powder sample was suspended in the microbalance and heated in air for up to 6 h. The weight gain was recorded as a function of time.

The sintering ability of the glass was investigated by placing different fractions in alumina forms and heat-treating at different temperatures. After grinding and polishing, the surface of the samples was observed by optical microscopy.

III. Results and Discussion

(1) Surface and Bulk Crystallization

With the aim of investigating the influence of the particles size on the crystallization behavior of the parent glass, when heat-treated in different atmospheres (air and nitrogen), simultaneous thermal analyses, TG and DTA, were carried out in the 20–1200°C temperature range.

In Fig. 1, the DTA plots (solid line) and the TG (dashed line) are reported for the powder samples (200–300 μm), heat-

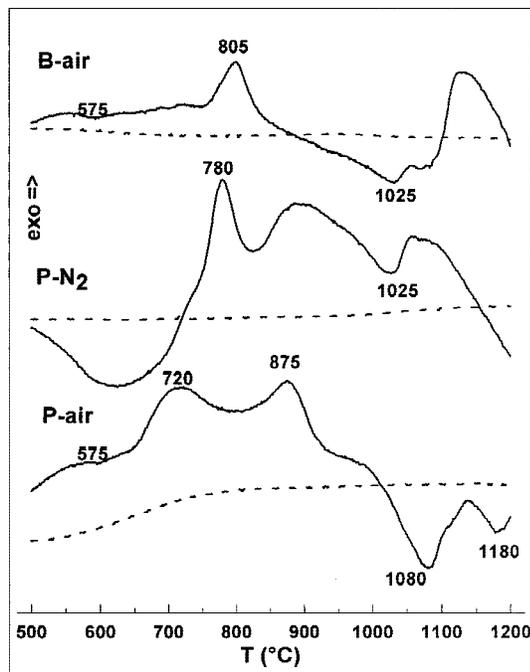


Fig. 1. DTA plots (solid lines) and the TG (dashed lines) of the powder samples, heat-treated in air (**P-air**) and nitrogen atmospheres (**P-N₂**), and for the bulk sample, treated in air (**B-air**).

treated in air and nitrogen atmospheres (labeled **P-air** and **P-N₂**) and for the bulk sample, treated in air (labeled **B-air**). The TG trace of **P-air** sample shows a detectable increase in weight, about 1%, taking place after 620°C. This weight change is connected with an exothermal effect having its maximum at 720°C. The crystallization peak occurs, in the same graph, at 875°C while two melting points are noticeable at 1080° and 1180°C, respectively. When the powder sample is heat-treated in N₂ atmosphere (**P-N₂**), with the same thermal schedule, no TG variation is detected and the only exothermal peak is the one relative to the crystallization. Only one melting point is evident and, in this case, it occurs at a lower temperature (1025°C). Finally, when a bulk sample is heat-treated in air (**B-air**) no TG variation appears in the trace; the crystallization exo-peak occurs at 805°C and the melting endo-peak at 1025°C, respectively.

Aiming at ascertaining the differences in the evolution of phase formation and melting, related to the sample sizes, powder (**P**) and bulk (**B**) samples were heat-treated in air with the same heating regime and immediately analyzed by XRD. The spectra are presented in Figs. 2 and 3 for the **P** and **B** samples, respectively. After the **P** sample was treated for 2 h at 950°C (Fig. 2(a)), the crystal phases formed were identified as pyroxene solid solution and hematite with a ratio pyroxene/hematite of about 2 and a percentage of crystal phases estimated at about 30–35% wt%. In Figs. 2(b) and (c) the spectra of the same **P** sample after heating at 1050° and 1150°C, respectively, are shown in Fig. 2(b), pyroxene and hematite peaks are still present in the spectrum while in Fig. 2(c) only hematite remains because the pyroxene is melted. The sample **B**, treated for 2 h at 950°C (Fig. 3(a)) shows pyroxene and magnetite peaks with

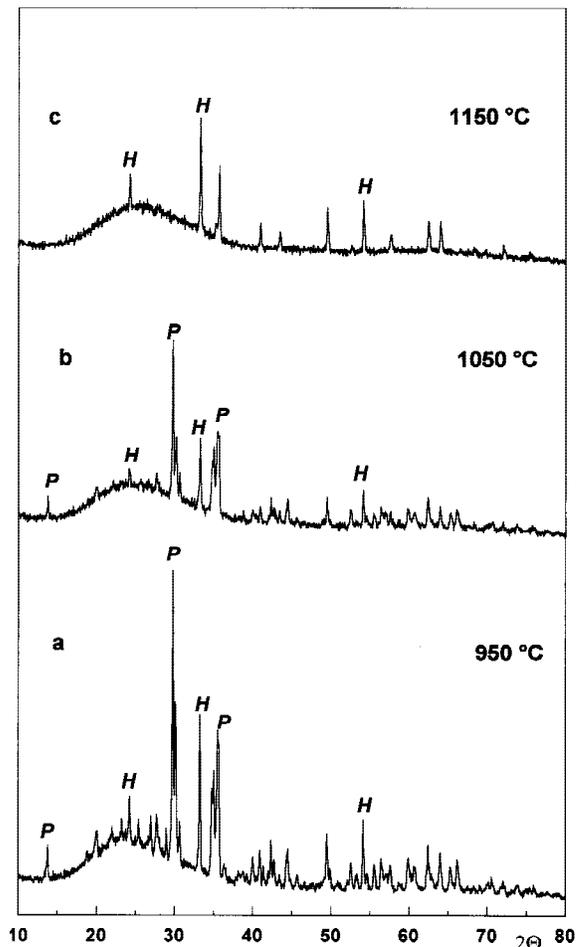


Fig. 2. XRD spectra of the powder (**P**) samples, treated at different temperatures: (**P**) pyroxene, (**H**) hematite.

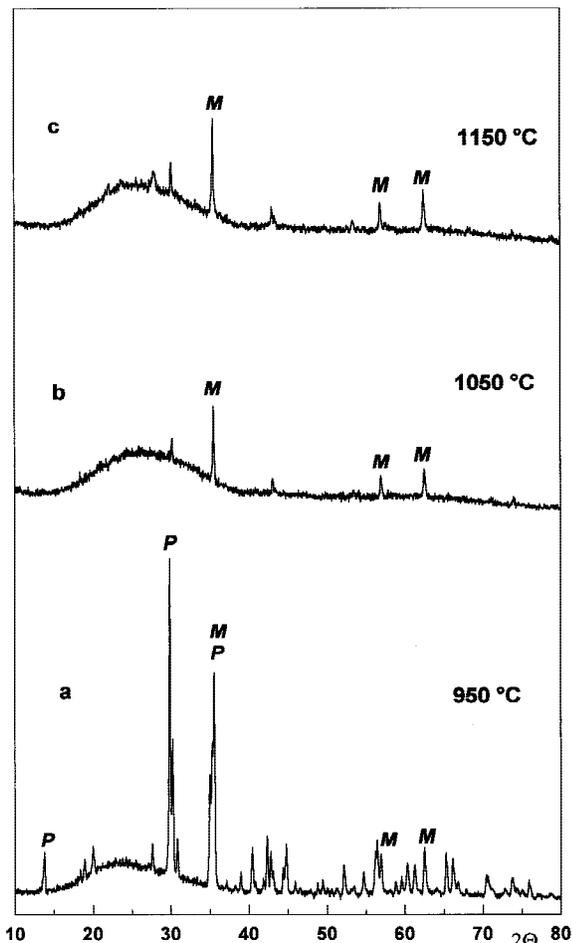


Fig. 3. XRD spectra for the bulk (B) samples, treated at different temperatures: (P) pyroxene, (M) magnetite.

a pyroxene/magnetite ratio of about 4 and a degree of crystallization of about 40–45 wt%. Heating the B sample up to 1050°C (Fig. 3(b)) results in the melting of pyroxene with only magnetite remaining in the spectrum. At 1150°C (Fig. 3(c)) the spectrum does not appreciably change.

Low-angle XRD was used to investigate the distribution of the phases formed on the surface of the glass during heating. Figure 4(a) shows the spectrum of the surface of the glass heat-treated for 2 h at 950°C. After the surface was polished for some fraction of a millimeter, the analysis was repeated and the spectrum is shown in Fig. 4(b).

The comparison highlights that in air conditions, hematite is prevalent on the surface of the glass due to the oxidation of Fe^{2+} , while in the bulk of the glass, pyroxene is the main crystal phase. Optical microscopy and visual inspection confirmed the presence of about 0.1 mm thick red-brown hematite phase on the surface of the glasses. Similar results on hematite formation were obtained in another study using SEM observation on the surface of jarosite glasses.¹²

The DTA and XRD results can be explained by considering that oxidation in the P sample takes place at a low temperature, 720°C, as highlighted by the DTA peak and the TG weight gain. Oxidation leads to a decrease of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, which increases the viscosity, making the crystallization process more difficult to achieve. The pyroxene melting temperature in the P-air sample is higher than in the B-air and P-N₂ samples (1080°C instead of 1025°C) probably because the composition of the parent glass is changed, due to the surface oxidation phenomenon.

Isothermal treatments were carried out at 620° and 680°C on the P sample as a function of time. By increasing the tempera-

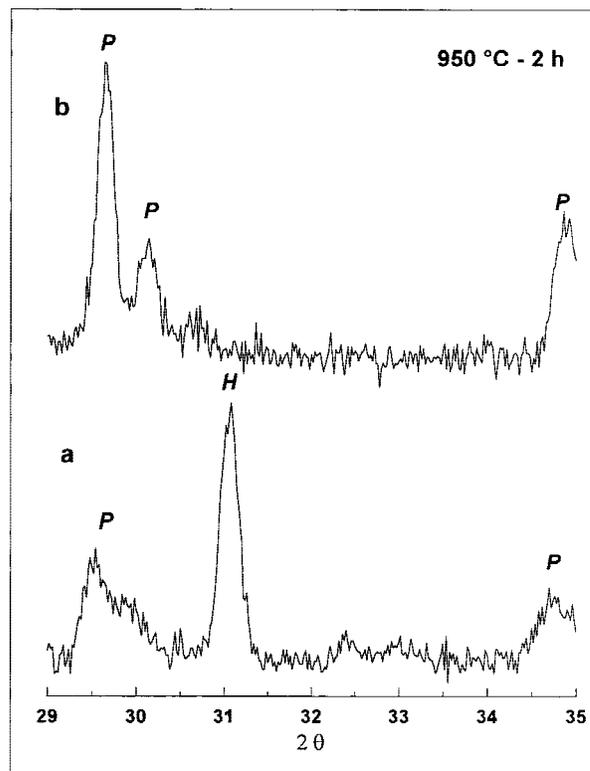


Fig. 4. Low-angle XRD: (a) surface of the glass heat-treated for 2 h at 950°C; (b) after polishing the surface.

ture, the weight gain increases rapidly for the first 60 min and then asymptotically. No appreciable weight gain was detected by heat treatments at temperatures below T_g (24 h at 550°C) where the diffusion process and structural changes are practically inhibited. By plotting the weight gain ($\Delta(\text{wt})$) as a function of the square root of time ($\tau^{0.5}$), two straight lines are obtained whose slope can be related to the diffusion of Fe^{2+} , from the bulk to the glass surface. The results are shown in Fig. 5.

In a different series of experiments, the kinetics of phase transformation, i.e., the degree of phase transformation (α), was investigated by measuring the variation of density of the P and B samples in isothermal conditions, at 680°C. The following relation was utilized:¹⁵

$$\alpha(\tau) = [(\rho - \rho_0)/(\rho_m - \rho_0)]\rho_m/\rho \quad (1)$$

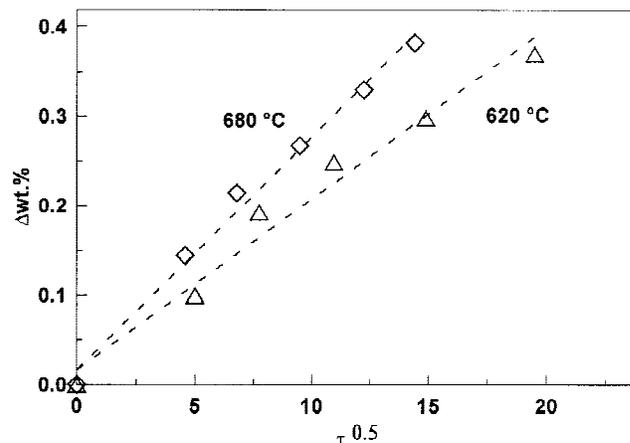


Fig. 5. Differential weight gain as a function of the square root of time of P samples.

where ρ_0 is the initial density of the glass, ρ_m is the maximum density obtained for this composition, and ρ is the density measured at time τ .

As highlighted by Fig. 6, for the **B** sample, the evolution of the crystalline phases sensibly influenced the variation of density, since the initial glass density was measured as 2.79 g/cm³ and increased up to 2.96 g/cm³ after 300 min heat treatment. Regarding the **P** samples, the density change was negligible, since the crystallization process in the powder samples was inhibited due to the chemical composition change, as a result of the surface oxidation.

The bulk crystallization kinetics were then investigated by using the Avrami equation in the form

$$\alpha(\tau) = 1 - \exp(-a\tau^n) \quad (2)$$

where α is the degree of phase transformation, a is a constant, and n is an integer which depends on the growth direction and the mechanisms of nucleation and crystal growth.

By taking the logarithm of Eq. (2) twice, the value of the Avrami constant, n , may be calculated by the slope of the experimental line. In our case, the value obtained is $n = 1.33$, which is close to the value of 1.5, corresponding to the three-dimensional diffusion growth on a fixed number of nuclei.² Similar results were previously obtained for other iron-rich compositions.^{16–18}

(2) Sintering Thermal Schedule

Using the **P** fraction, complete sintered samples were obtained at about 1000°C after 20–30 min, while using the large particles (**B**), the sintering process at the same temperature was not completed even after 5 h. However, in this latter case, by increasing the temperature by about 20°C, a complete sintering could be obtained after 20–30 min. This difference in the sintering ability of **P** and **B** fraction can be explained by considering the following:

(1) According to the Frenkel model, particles with a small size have a higher tendency toward sintering due to the high specific surface. Moreover, during the thermal treatment, a low percentage of crystal phase is formed in the **P** fraction thereby favoring the sintering.^{19,20}

(2) On the other hand, a higher degree of crystallization is formed in the **B** fraction, which leads to sintering times of hours at 1000°C. By raising the temperature a few degrees above the liquidus point of pyroxene, 1020°C in our composition, sintering is achieved in a few minutes.

After grinding and polishing, the sintered samples obtained from fraction **P** are red-brown while the ones obtained from the large **B** fraction show a dark green-black color. By mixing these two fractions, with different grain size distribution in different percentages, an agreeable chromatic granite like ef-

fect is obtained by adjusting the combination of red-brown hematite and green-black pyroxene.²¹ Figure 7(a) shows an optical-microscope picture of the boundary between large black particles and small grains with surface hematite formations (light spots in the picture). Figure 7(b) is an enlargement of small particles after prolonged polishing in which the surface hematite layer is evident.

By taking the experimental results into account, the heat-treatment regime was defined as follows:

(1) The first step, 45–60 min at 700°C, corresponds to the surface oxidation process, which yields the hematite formation on the surface of the **P** fraction.

(2) The second step, 20–30 min at 1029°C, is for the sintering of the grains. The temperature corresponds to the melting of the pyroxene formed in the volume of the **B** fraction.

(3) The third step, 40–60 min at 750–800°C, corresponds to the recrystallization of pyroxene in the bulk of the material, yielding to about 40 wt% crystal phase. The pyroxene recrystallization can also be obtained by slow continuous cooling.

IV. Conclusions

In the thermal treatment of glasses the surface crystallization is more frequent than internal crystallization but, as noted by Zanotto,²² the mechanism of surface crystallization is still a matter of controversy.

The present work is an attempt to highlight some typical features of surface and bulk crystallization in high-iron-content compositions. In this case, the process seems to be more complex than in other systems due to the formation of different crystalline phases: hematite on the surface and pyroxene solid solution and magnetite in the bulk. The ratios between these phases is regulated by the initial glass composition and Fe²⁺/Fe³⁺ ratio, by the particle size distribution, and sintering conditions.

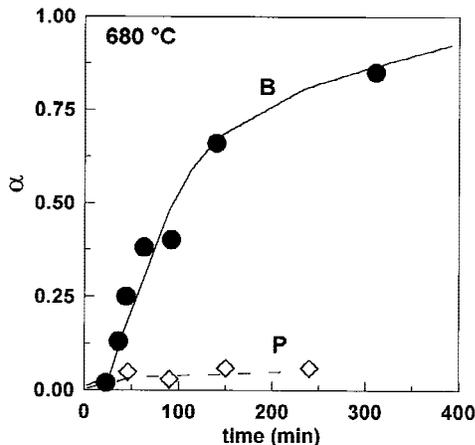


Fig. 6. Degree of transformation, α , as a function of the time of **B** and **P** samples at 680°C.

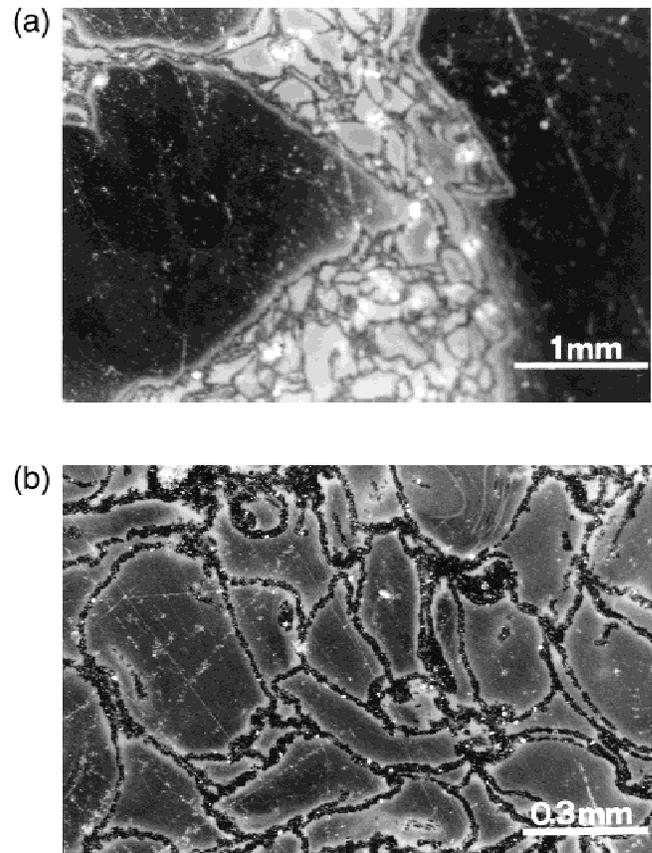


Fig. 7. Optical-microscope pictures of sintered glass-ceramic samples.

Taking advantage of the surface crystallization phenomena, the results of this study open the possibility of preparing sintered glass-ceramics with an original appearance, somewhat similar to that of igneous natural stones, by reevaluating jarosite and granite industrial wastes.

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