New glass-ceramic by Fe-Ni wastes with improved structure and properties

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Introduction

Iron-rich natural and artificial silicate products are widely used as tilling and paving materials. It is interesting to remember that (as it is shown in Fig. 1-a) natural basaltic slabs were used as pavements in the Roman Empire two millennia ago. Iron-rich silicate melts are also widely used in the petrurgy, which is based on re-melting and crystallization of basalt rocks to produce tiles, tubes, bends and basalt fibre. The perurgy started its development in the first decades of the twenties century and practically can be considered as predecessor of the glass-ceramics industry. As an example, in Fig. 1-b is shown a typical modern application of petrurgical paving tiles.

A part of the most interesting studies with glass-ceramics by industrial wastes also are related to iron-rich compositions. Typical for this kind of materials are the low melting temperatures and the short crystallization cycles, coupled with the excellent mechanical characteristics and good chemical durability.

In the present work are summarises results of complex research on a glass-ceramic, obtained after vitrification of a mix of hazardous residues from ferronickel smelting plant. The used metallurgical wastes originate from the ferronickel smelting plant FENI INDUSTRY – Kavadarci, Republic of North Macedonia, which amounts of such residues surpass 1 million tons per year.


a

b

Fig. 1 Ancient Roman road (*a*) and modern petrurgical basalt tiles (*b*)

Experimental

A mix of hazardous residues from a ferronickel smelting plant (70 wt %) are blended with glass cullet (30 wt %) and vitrified at moderate temperature of 1400 ºC. The optimal heat-treatment regime for transformation of the obtained glass into glass-ceramic is evaluated by fast non-traditional methods: the nucleation step is estimated by DTA analysis, while the crystallization step – by pycnometric measurements.

The evolution of crystallization process and the development of glass-ceramic structure are studied in detail by XRD, SEM, EDS and TEM. Additional information for the morphology of final glass-ceramics is obtained by FE-SEM.

The mechanical properties of the final glass-ceramic, such as compressive and bending strength, as well as Vickers micro-hardness and fracture toughness are evaluated.

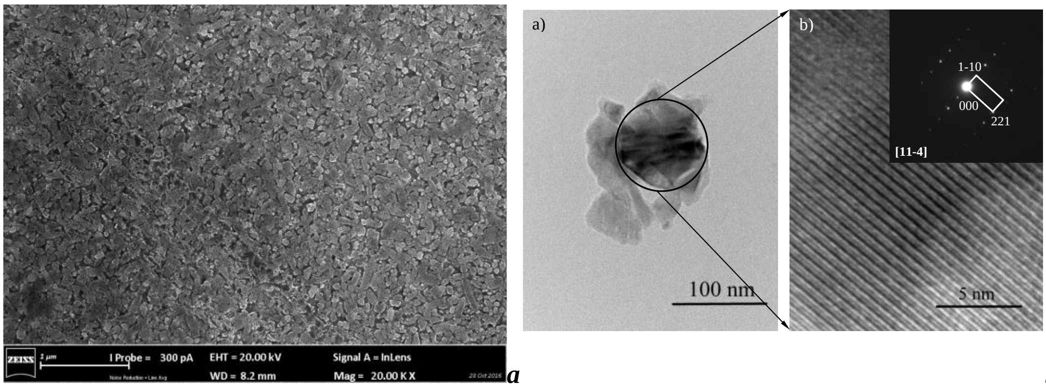
Finally, the chemical durability of the initial industrial wastes and obtained glass and glass-ceramic are estimated by Toxic Characterization Leaching Procedure (TCLP).

Results and Discussion

The DTA and pycnometric results elucidate that the optimal heat–treatment for the crystallization can be two- step: 45-60 min at 650 ºC for nucleation and 45-60 min at 730-740 ºC for crystal growth. These temperatures and times are lower and shorter, respectively, than ones used for the productions of the traditional glass-ceramics by industrial wastes. It is highlighted that, due to the presence of 1.5 wt.% chromium oxides and high amounts of iron and magnesium oxides in the parent glass, the studied crystallization process is peculiar. It starts during the melt cooling with the precipitation of preliminary Fe-Mg-Cr spinel crystals, which then act as centres for epitaxial growth of pyroxene phase. At the same time, due to liquid-liquid immiscibility, the main amorphous phase is characterized by a nonhomogeneous binodal structure, which becomes finer after the nucleation treatment. As a result, pyroxenes with sizes below 200 nm are formed as main crystal phase during the crystallization step. The total crystallinity of this complex arrangement is estimated at about 55-60 wt. %. The main structure of the glass-ceramic is shown in the Fig. 2-a, while in Fig. 2-b is demonstrated an individual pyroxene nano-crystal.

Due to attained nano-crystalline structure the final glass-ceramics is characterised by excellent mechanical characteristics: bending strength - 120 MPa, Vickers hardness - 9 GPa and fracture toughness - 1.6 MPa $m^{1/2}$.

The results of the TCLP test after the vitrification demonstrate that the concentration of the measured heavy metals decreases by two to four orders of magnitude in comparison with the values for the initial harmful wastes, so that the glass can be characterised as entirely inert material. After the controlled crystallization the chemical durability of the glass-ceramic increases additionally.



a **b**

Fig. 2 FE-SEM image of the main glass-ceramic structure (*a*) and TEM photos of single pyroxene mono-crystal (*b*)

Conclusions

The investigated glass is obtained using a mix of industrial wastes from ferronickel production and glass rejects. It is easy melted and is characterized by a spontaneous trend for bulk crystallization due to fast precipitation of Cr-rich preliminary spinel phase. In addition, due to tendency for liquid-liquid immiscibility, the final glass-ceramic is obtained after a very short and low-cost thermal cycle. This crystallization process, which is untypical for the traditional glass-ceramics by industrial wastes, leads to a complex and intriguing structure of the final material. The main arrangement (at about 80-85 vol %) is formed after crystallization of pyroxene phase composed by mono crystals with size of 150-200 nm. As a result, the glass-ceramic is characterized by very high mechanical characteristics. Notwithstanding of the huge amount of harmful wastes in the glass batch the TCLP test confirm that the vitrification of used industrial residues is extremely effective way to capture the heavy metals into the glass-ceramics structure.

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