

Surfaces of refractory products modified by low-temperature plasma in glass manufacturing

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Abstract. The paper describes the production of strong and thermally resistant refractory materials modified by low-temperature plasma. Mechanical and physical tests are presented in this paper for determination of thermal resistance, density, and ultimate compressive strength. X-ray phase analysis and scanning electron microscopy are conducted to determine a phase composition of specimens before and after bake-out. It is shown that plasma treatment results in a formation of a non-porous vitreous layer which is X-ray amorphous and saturated with silicon dioxide and alumina oxide. Moreover, refractory materials exhibit 4-9% strengthening.

1. Introduction

Refractory materials and the equipment used for glass manufacturing allow considerably to increase service life of basic production facilities and reduce both energy and manufacturing costs. At the same time, the improved quality of refractories meets the world standards making them more available and attractive to customers. Applications of the advanced nanodispersed materials of high quality and innovative technologies provide the unique superior performance characteristics of manufactured products [1].

The requirements for glass manufacturing are being constantly improved including cost reduction, environmental standards (energy saving, NO_x emission, etc.), the quality of glass containers and flat glass. Along with the use of contemporary glass manufacturing technologies, a choice of refractories intended for the construction of glass tank furnaces is another possibility of their well positioning because they considerably define the quality of products and extend the life of a furnace.

In glass tank furnaces, electrocast refractory materials are mainly used within zones contacting with glass mass. Zirconia-containing materials such as alumina/zirconia/silica (AZS) are usually suitable for electric furnaces because corrosion resistance of these refractories increases with the increase of zirconium oxide (ZrO₂). Therefore, in contact zones, for example, furnace throats, it is reasonable to use such materials as Refel 1240 or Monofrax CS-5 with the highest ZrO₂ content (41% and 39.5% respectively). The intensive forced convection within this zone is caused by a severe erosion of refractory. This fact should be thoroughly studied because the change of the furnace throat area disturbs the smooth operation of the furnace process resulting in glass defect formation. Areas adjacent to the furnace throat are also considered to be contact zones because the refractory components while entering the glass mass, say in a refining zone, do not melt and generate glass defects too. In not numerous contact zones, the use of such refractories as Refel 1532 or Monofrax CS-3 with ZrO₂ content of 32-34% seems to be sufficient. A well-chosen bake-out schedule for production of electrocast refractory materials is also a crucial aspect for contact zones in which they



must exhibit superior corrosion resistance to glass melting. Baking parameters have a significant effect on the structure of material, and in particular on a crystalline bond between ZrO_2 and Al_2O_3 and phase distribution in the structure of refractories. A solid crystalline bond is a prerequisite for superior corrosion resistance of refractories.

Besides AZS 41, such products as Refel 1240 FVMo and Monofrax have shown good results in protecting refractory linings against chemical attack. Refel 1240 FVMo is a product, composed of fused cast 41% ZrO_2 material reinforced with a molybdenum insert. It has performed extremely well in refractory masonry of more than 20 glass tank furnaces. The similar behavior has been demonstrated by the refractory based on Cr_2O_3 obtained by isostatic molding technique [2].

Metpump AZS and Met-Silcast refractories find use, for example, as refractory blocks for those parts of furnaces which are subjected to severe high temperature operational conditions. However, exudation of the glassy phase from the surface of the refractory can occur in using these products.

This paper mainly focuses on the production of hot-strength, thermal shock and creep resistant refractory materials similar to Metpump AZS and Met-Silcast products designed by Magneco/Metrel, Inc., USA, with the formation of a fused layer on the material's surface using the low-temperature plasma (LTP).

2. Experimental procedure and results

The process of preparation of test specimens includes the following major stages: preparation of a raw mixture, molding, drying, and baking.

To obtain refractories of the types Met-Silcast and Metpump AZS 20, 14 wt.% and 10 wt.% mass ratios are respectively selected for these types of specimens. A binder is then added to the refractory powder in desired proportions and mixed until a uniform mixture is obtained. Compositions of the raw mixtures are given in the Table 1.

Table 1. Raw mixture compositions.

Composition	Refractory type	Binder (wt.%)
1	Met-Silcast	14
2	Metpump AZS 20	10

At the next stage, test specimens having 50x50x30 mm size are prepared using the vibratory compaction molding technique and vibratory compaction. Specimens are then dried and fused at temperature not higher than 950 °C.

Mechanical and physical properties of specimens such as thermal shock resistance, density, and ultimate compressive strength obtained are then tested.

For the thermal shock test, the surface of specimens is treated with LTP jet generated by a plasmatron at the following operating parameters: $T \sim 3000\text{--}5000^\circ\text{C}$, $V = 190\text{ V}$, $I = 340\text{ A}$, plasma propagation velocity $v = 0,07\text{ m/s}$ [3-6]. The quality of plasma-treated surfaces was detected by the scanning electron microscope (SEM) with 800x magnification. SEM images of the surfaces before and after LTP treatment are presented in Figures 1 and 2.

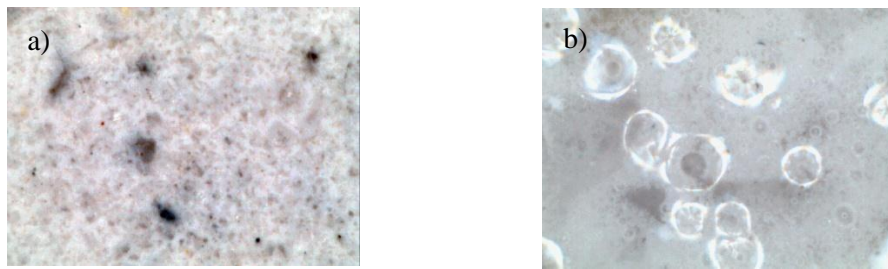


Figure 1. SEM of the type Met-Silcast specimen: before (a) and after (b) plasma-treatment.

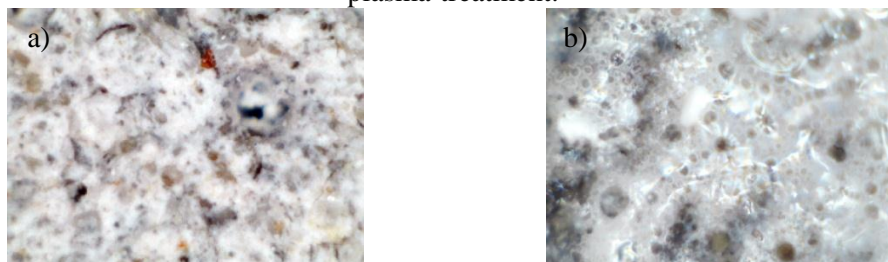


Figure 2. SEM of the type Metpump AZS 20 specimen: before (a) and after (b) plasma-treatment.

SEM analysis shows no crack formation after the plasma treatment. As illustrated in Figures 1 and 2, the porosity of the surface in both types of specimens decreases up to a complete pore elimination, and some of them are closed by fusion. The both types of specimens exhibit thermal shock resistance, however, the surface of the type Met-Silcast specimen is smoother and more uniform. As for the type Metpump AZS 20 specimens, their surface is uneven. This unevenness is the glassy phase, and it is possible to gain more even fusion choosing the appropriate mode of plasma treatment either by increasing its velocity or moving the specimen away from the plasma jet.

The density of refractory specimens is detected by the mass-volume ratio, and equals to 1770 kg/m^3 and 2960 kg/m^3 for the types Met-Silcast and Metpump AZS 20 specimens, respectively.

The test machine INSTRON-3382 equipped with the load transducer was used in this experiment to measure the ultimate compressive strength and the load applied. Measurements were conducted at 24°C at 2 mm/min . The stress-strain curves of compression states are presented in Figures 3 and 4 for both types of specimens.

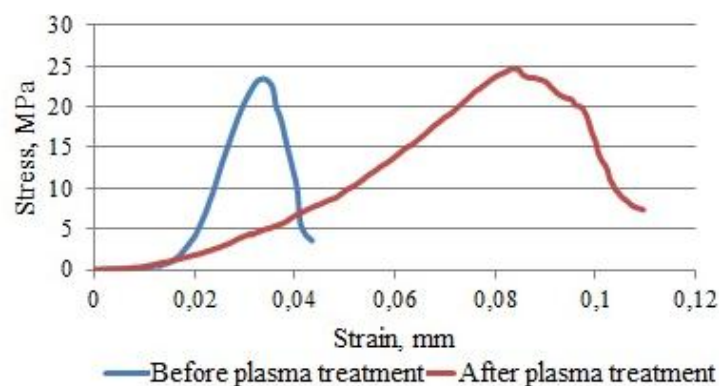


Figure 3. Stress-strain curves of compression for the type Met-Silcast specimen.

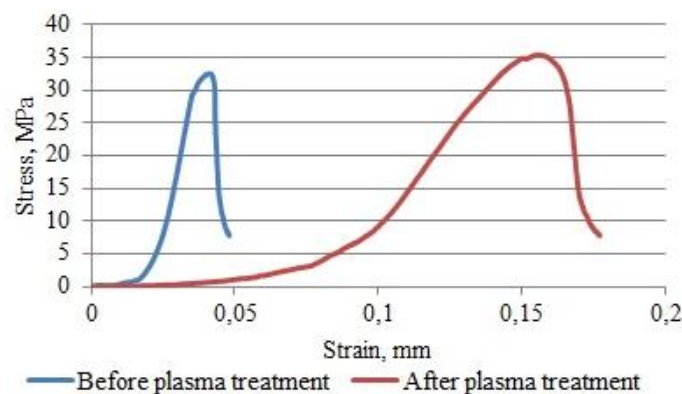


Figure 4. Stress-strain curves of compression for the type Metpump AZS 20 specimen.

The ultimate compressive strength for the type Met-Silcast specimen is 23,4 MPa. After the LTP it reaches 24,5 MPa, i.e. increases by 4%. The ultimate compressive strength for the type Metpump AZS 20 specimen is 32,5 MPa. After the LTP it reaches 35,4 MPa, i.e. increases by 9%.

Phase composition before and after the bake-out process was determined by the X-ray diffraction method. The resulting microstructure in the modified specimen surfaces was examined using scanning electron microscope Quanta 200 3D.

Figure 5 shows the X-ray diffraction diagram of the type Met-Silcast specimen before and after surface modification.

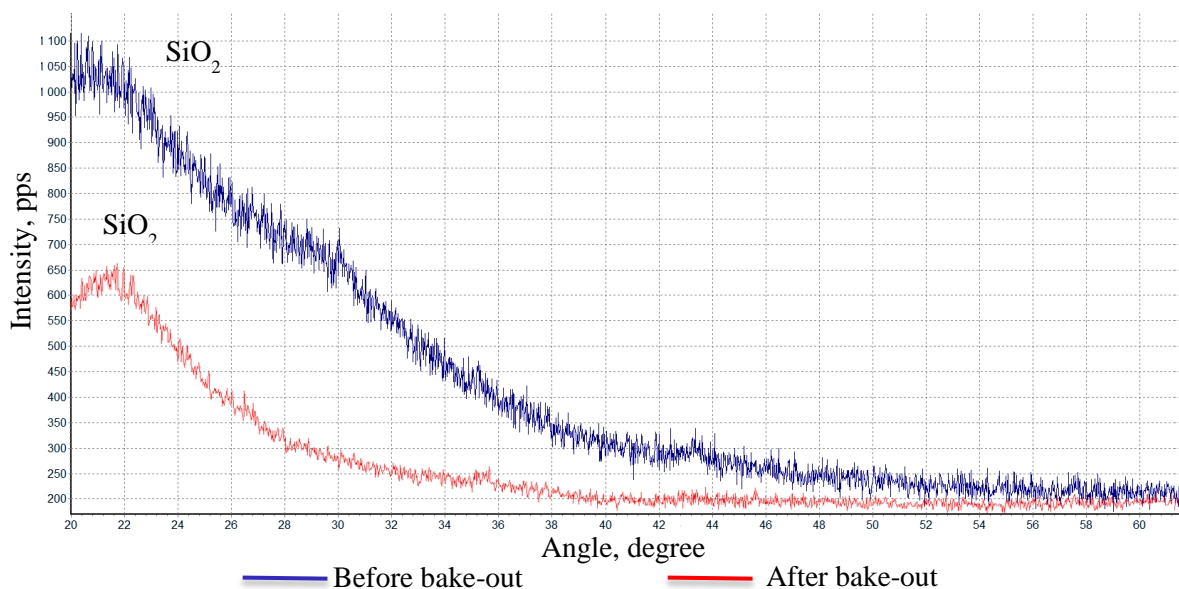


Figure 5. XRD patterns for the type Met-Silcast specimens.

XRD patterns presented in Figure 5, show that the amorphous behavior of the type Met-Silcast specimen microstructure is not changed before and after bake-out. These specimens are mainly characterized by a glassy phase saturated with silicon oxide.

Results of the qualitative X-ray diffraction analysis of the type Metpump AZS 20 investigated specimens are presented in Figure 6.

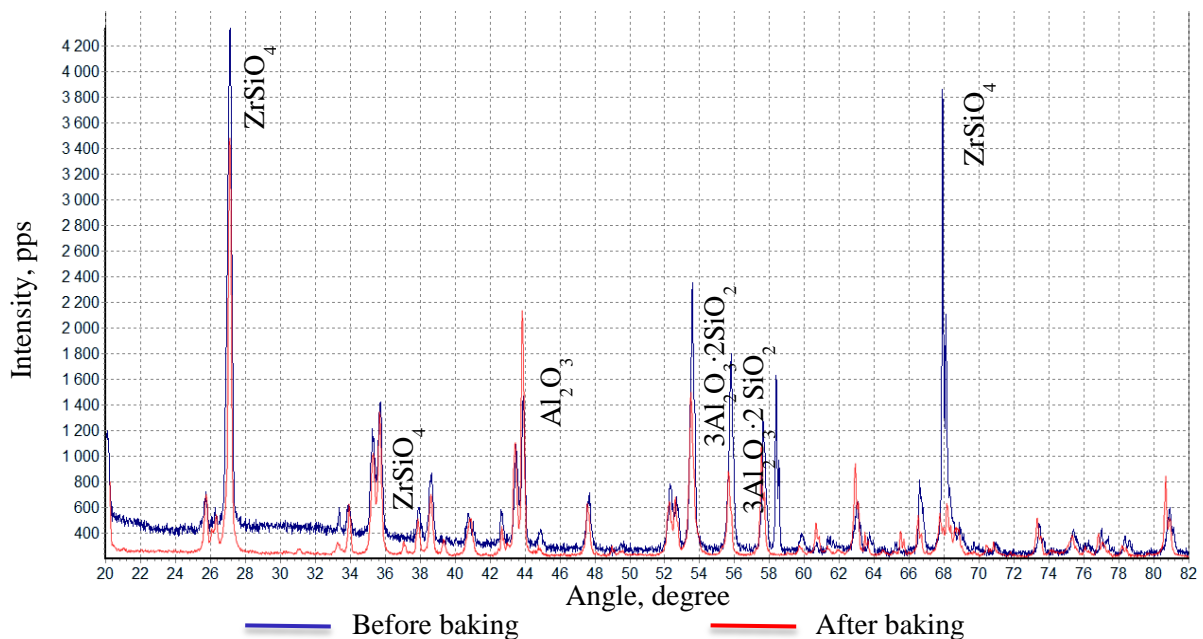


Figure 6. XRD patterns for the type Metpump AZS 20 specimens.

The original specimen of the type Metpump AZS 20 is represented by phases: zircon (ZrSiO_4 , $d = 0,328; 0,251; 0,138$ nm), alumina (Al_2O_3 , $d = 0,208$ nm), and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, $d = 0,171; 0,164$ nm). The XRD analysis showed that after bake-out some of crystalline phases in this type of specimens were partially changed. This is because the recrystallization of zirconia-containing compounds and formation of mullite-like phases.

Figure 7 shows scanning electron micrograph surfaces of specimens modified by bake-out carried out at Tomsk Core Facility Centre for Materials Science.

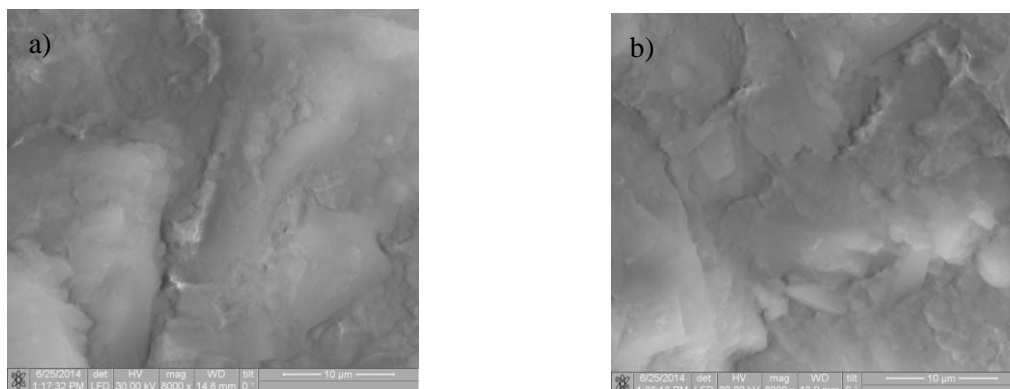


Figure 7. SEM of the types Met-Silcast (a) and Metpump AZS 20 (b) specimens: before (a) after bake-out.

SEM analysis proves results of X-ray investigations, i.e. the type Met-Silcast specimens comprise mainly a uniform homogeneous microstructure having small cracks in some places. As for the type Metpump AZS 20 specimens, they have a grain microstructure.

3. Conclusion

The plasma treatment of specimens of the type Met-Silcast resulted in the formation of a smooth non-porous vitreous layer. Strength properties of this specimen type are increased by 4%. Modification of the type Metpump AZS 20 specimens with plasma treatment resulted in a non-porous uneven vitreous layer. Its ultimate compressive strength increased up to 9%. The non-porous vitreous layer was X-ray amorphous and saturated with silicon dioxide (the type Met-Silcast specimens) and alumina oxide (the type Metpump AZS 20 specimens).

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