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Silica Crown Refractory Corrosion in Glass Melting Furnaces

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Abstract:

The critical parameters of silica refractories, such as compressive strength, bulk, density, quantity of silica, microstructure and porosity were evaluated of unused and used bricks to line the crowns of glass furnaces, when the rate of corrosion of crowns were about 2 times greater. The change of these parameters, the chemical composition and formation of the microcracks in the used silica refractories material were studied.

It was established that the short time at service of container glass furnace crown can be related to low quality of silica brick: high quantity of CaO and impurities, low quantity of silica, low quantity of silica, transferred to tridymite and cristobalite and formation of 5 -10 μm and more than 100 μm cracks in the crown material. The main reason of corrosion high quality silica bricks used to line the crown of electrovacuum glass furnace is the multiple cyclic change of crown temperature at 1405 – 1430 ^{o}C range in the initial zone of crown and at 1575 – 1605 ^{o}C range in the zone of highest temperatures.

Keywords: *Crown refractories, α-quartz, Tridymite, Cristobalite, Corrosion.*

1. Introduction

Silica is preferred material for crown construction of glass melting furnaces, in terms of cost, strength and of defect potential. Corrosion of refractory silica brick of glass melting furnaces is a serious problem, because the degradation of dinas can exactly be assessed only after a campaign when the furnace is partially or totally disassembled [1, 2].

Long service duration at glass melting furnaces is the main reason of small number of these studies [1-10]. Corrosion tests to predict degradation of refractories usually employ small specimens, exposed to accelerated working conditions, that might not be simulative of actual industrial conditions [3].

R.H. Nilson, S.K. Griffiths, N.Yang et al. [5] report equilibrium calculations for the Na_2O - SiO_2 system, which predict the formation of a variable-composition liquid-solution phase as a function of key furnace variables. The calculations indicate that gas-phase NaOH concentrations less than approximately 15 ppm will not react with the silica refractory under either air-fired or oxy-fired conditions, since this is the smallest equilibrium NaOH partial pressure in a system, containing crystalline SiO_2 (either cristobalite or tridymite) in equilibrium with a variable composition sodium-silicate liquid phase at refractory temperatures in the range 1400 – 1700 ^{o}C. The results of calculations are used to define a critical temperature, above which corrosion is not expected to occur for a given NaOH (g) partial pressure. Thermodynamic calculations indicate a higher driving force for NaOH (g) to react with silica refractories under oxy-fuel firing conditions [5, 6].

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A study of the thermal shock resistance of coke-over dinas under laboratory conditions was carried out by E.K. Akselrod and I. Portnova [7]. The effect of the porosity of dinas on its thermal shock resistance was determined by the conditions of thermal loading of the specimens. The moderate test regimes (small number of thermal cycles, air cooling of specimens) lead to a parabolic dependence of thermal shock resistance on the porosity. In this case, the minimum thermal shock resistance is shown by the specimens, having 17-19 % porosity. Increasing the severity of the test conditions (increasing the number of thermal cycles, water-spray cooling of the specimens) alters the nature of the relationship between thermal shock resistance and porosity: the parabolic relationship changes into a linear relationship. The low porosity (15-16 %) specimens show a decreased thermal shock resistance, the highest thermal shock resistance is exhibited by the dinas specimens having 19-21 % porosity.

Critical parameters of refractories such as microstructure, porosity and mechanical properties have been evaluated in corrosion studies [8, 9]. E.Z. Korol, V.M. Panferov et al. [9] studied the deformation and strength characteristics of the dinas specimens (drawn from the industrial walling and checker-work products before and after service) under uniaxial tension and compression at the temperature up to 1600 ^{o}C. It was established that ultimate strength of dinas decreases with increasing test temperature and that the load-bearing capacity is insignificant at 1570-1600 ^{o}C. When dinas specimens were subjected to cyclic heating (1250↔1450 ^{o}C) in the laboratory tests as well as during service in a hotblast stove operating under alternating oxidizing and reducing environmental conditions, dinas bricks exhibit embrittlement and softening (their tensile and compressive strength characteristics differ by almost 10 times).

The obtained data showed that the limiting temperature at which the strength characteristics of dinas abruptly decrease under a constant stress and multiple cyclic actions of alternating atmospheres amounts to 1600 ^{o}C.

Current research includes the study of influence of quality, microstructure and alternating changes of temperature to the duration of service of silica crown of glass melting container and electrovacuum furnaces.

The objective of this research was to analyze and to determine the sources of the corrosion of silica crown refractory in glass melting furnaces.

1. Experimental procedure

The phase composition was analyzed by X-ray diffractometer DRON-6 with Bragg-Bretano geometry using Ni-filtered CuK_{α} radiation and graphite monochromator, operating with 30 kV voltage and emission current of 20 mA. The step-scan covered the angular range 5-70^{o} (2Θ) in steps of 2Θ = 0.02^{o}. Diffraction curves were additionally recorded in step times 1.0 s and step size of 0.01^{o} (2Θ) from 19 to 25^{o}. For diffraction profile refinement under the pseudo Void function and for description of the diffractional background under the 3rd degree Tschebyshev polynomial, we used a computer program X-fit. The reliability of method is 98 %.

The structure and texture of the dinas samples were investigation using an OLYMPUS CX31LBSF optical microscope. Photos were made with an attachment to an OLYMPUS C-50502 camera with total magnification x 40.

Microstructures of the samples were studied by scanning electron microscopy (SEM) (model Oxford ISIS Leo 440i, UK), using an accelerating voltage of 20 kV and a working distance of 10 mm.

The chemical composition of samples was determined by classic chemical methods of analysis of insoluble silicate materials.

The percentage of Na^{+} and K^{+} was determined by flame photometer FPLI.

The compressive strength of silica brick specimens was determined by hydraulic press CU – 2, the rate of load augmentation was 6 - 8 kN/s.

2. Results and discussion

The aim of this study was to examine the examples of dinas bricks used in electrovacuum glass melting furnace, as their corrosion was accelerated twice. The qualitative data of three inner dinas bricks used in electrovacuum furnace were compared. The photos of the maintained dinas bricks are presented in Fig. 1.

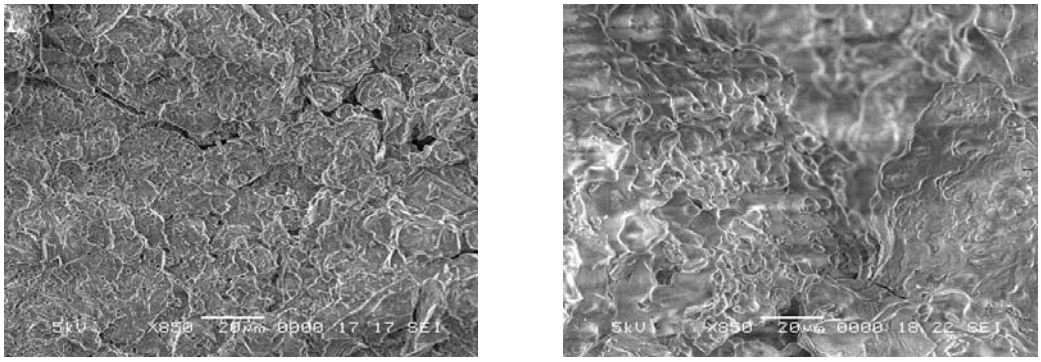
a b

Fig.1. The photos of used dinas bricks: a) from the crown of container glass furnace; b) from the crown of electrovacuum glass furnace.

After the comparison, the structure, texture, colour and quality of the dinas bricks used in different furnaces occurred to be different. The quality of dinas bricks used in container glass furnace (Fig.1a) was not enough good as the low temperature α-quartz formed tridymite and crystobalite of the average quality (contained 15-20 % α-quartz in the brown coloured layer) only or even of unsatisfactory (the quantity of α-quartz was larger than 20 % in the greenish-white coloured layer). The insufficient grade of α-quartz modification into tridymite and crystobalite, and too large amount of CaO could have become the main reason for accelerated corrosion of dinas crown because of transformation of the modifications of α-quartz into tridymite and crystobalite in the crown of the glass tank furnace, also because of big inner strains had formed during the process of these modifications [11].

Meanwhile the dinas bricks used in electrovacuum furnace (Fig. 1b) were of good quality. The equal light brown colour of the whole brick proved that the grade of α-quartz modification into tridymite and crystobalite was high (α-quartz less than 6 %). Thus the insufficient grade of α-quartz high temperature modifications could not had been the reason for the accelerated corrosion of furnace crown.

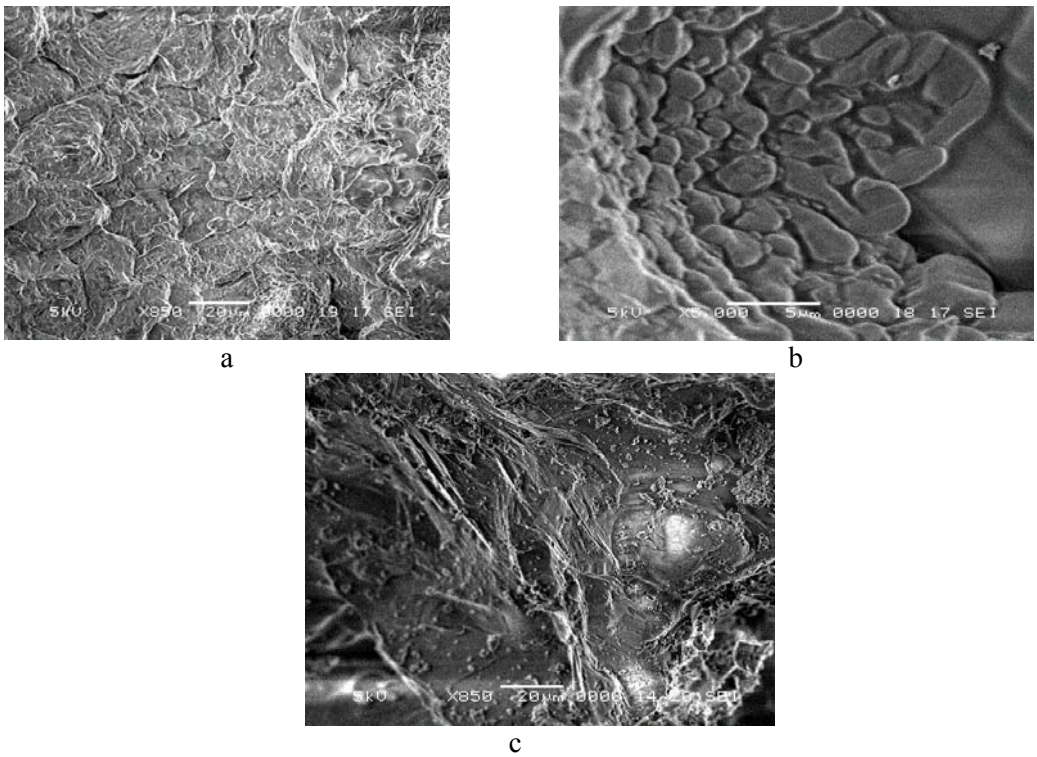
In order to find the reasons of the accelerated corrosion of dinas bricks used in glass tank furnaces, the following data of original and used dinas bricks as the porosity, the proportion of the quantity of tridymite and crystobalite, chemical composition, the possibilities of the formation of other minerals from the reactions of glass melt's vapours with dinas bricks used in glass furnace crowns, also the microstructure changes formed in dinas bricks during the exploitation process were examined.



a b

Fig.2. Microstructure of used material in electrovacuum glass furnaces crown: a) dark-coloured layer, b) white-coloured layer

After the SEM analysis of the microstructure of the maintained dinas bricks was performed, it was established that not only the coalescence of micropores of 3-5 μm in length in the brown-coloured layer occurred and micro cracks of 5-10 μm in length during the process had formed, but much larger (> 100 μm) cracks were formed which could have accelerated the corrosion of the crown (Fig. 2a) [12, 13, 14]. The microcracks (of 10-15 μm in length) were found in the white-coloured layer of the dinas (Fig. 2b).



a b

c

Fig. 3. Microstructure of used material in electrovacuum glass furnaces crown: a) yellow-coloured material with microcracks, b) partially melted and thickened quartz grains, c) microstructure of glassy mass.

The cracks of the larger length were not found in the yellow-coloured layer of the dinas used in the electrovacuum furnace, although the microcracks of 15-20 μm in length were seen clearly (Fig. 3a). The main mass of this kind of dinas was formed by partially

melted and thickened quartz grains (Fig. 3b), and the microstructure changed distinctly towards the half-melted outer white-coloured layer of the brick: a large amount of insertions of melted phase and of small plate form phase appeared (Fig. 3c). The outer half-melted white – coloured layer of the dinas bricks consisted mainly from amorphous phase with very tiny round crystals (0,5-1 μm) and comparatively large dendrite crystals.

X-ray diffraction, chemical analysis and flame photometry were used to analyse the chemical and mineralogical composition of dinas.

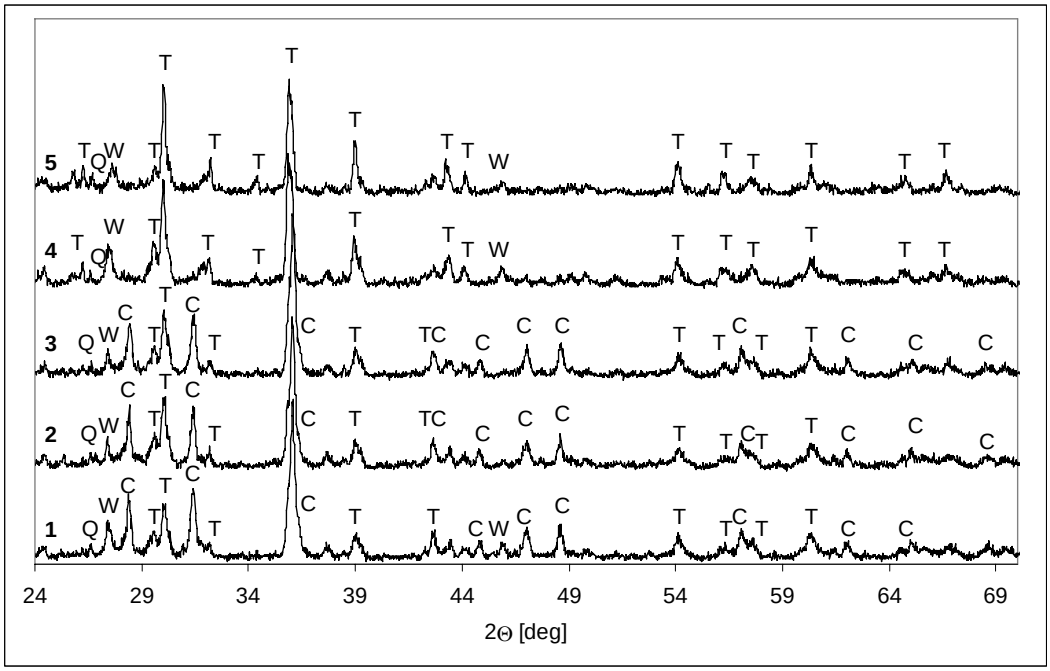


Fig. 4. X-ray curves of used material in electrovacuum glass furnace crown: 1, 2, 3 different compounds of unused dinas bricks (1 – yellow-coloured mass, 2 – brown-coloured domains, 3 – white inclusions); 4 – used dinas brick's material; 5 – glassy mass of used dinas brink. Indexes: T – tridymite, C – cristobalite, Q – quartz, W – pseudo-wollastonite.

Using X-ray diffraction analysis (Fig. 4) it has been established that dinas material, which was used in electrovacuum glass furnace roof, consisted of tridymite, crystobalite, α-quartz, also it contained pseudo-wollastonite mineral, which had formed due to reaction of the vapours over melts with SiO_2 of dinas in high temperature.

According to the X-ray diffraction analysis, during the process of dinas exploitation in the furnace crown, crystobalite changed into tridymite. As one can see in the Fig.4, the curves number 4 and 5 demonstrate that the peaks of 0,31365; 0,28440; 0,24881; 0,20194 and 0,19301 nm height common to crystobalite disappears, while the intensity of peaks of 0,29755; 0,27812; 0,24974; 0,23110; 0,20839; 0,16951; 0,16373 0,15332 and 0,14145 nm, common to tridymite, rises sharply.

It is well known that the volume of crystal lattice changes during the modifications of SiO_2, and this is a reason of formation of big internal strains in the material.

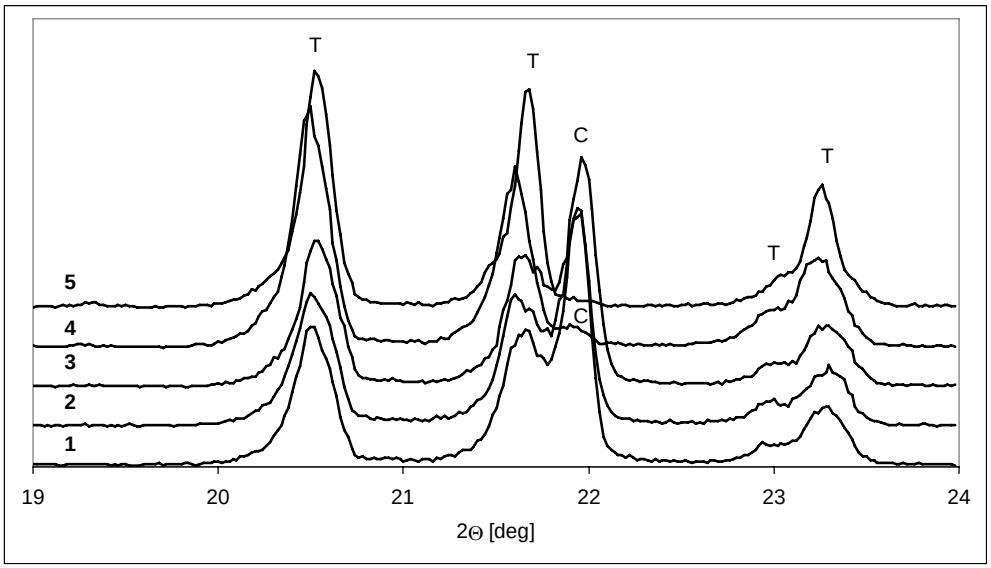


Fig. 5. X-ray curves of cristobalite transformation to tridymite in glass furnaces crown's material: 1, 2, 3 different compounds of unused dinas bricks (1 – yellow-coloured mass, 2 – brown-coloured domains, 3 – white inclusions); 4 – used dinas brick's material; 5 – glassy mass of used dinas brink.
Indexes: T – tridymite, C – cristobalite.

The process of transformation of crystobalite into tridymite can be best seen (Fig. 5) in the area of the largest intensity peaks ($2\Theta=20 - 24^{o}$) of the diffractive reflection: in the 4 and 5 curves the 0.40429 nm peak of crystobalites disappears and the intensity of 0.43283 nm peak common to tridymite increases almost twice.

The cristobalite- tridymite transformation was studied by H. Lemmens et al. [15] who, using high-resolution electron microscopy on the cristobalite phase of $(Si_{0,9}, Ge_{0,11})O_2$, observed atomic-scale twins and tridymite-like stacking faults on $(111)_{\beta}$ planes, some producing polytypic structures, particulary a four-layer polytype. These led to the suggestion that the cristobalite- tridymite transformation involves a shear along (111) coupled with tunnelling of Si(Ge) trough a triangle of oxygens.

P.I. Heany [16] and other authors [17, 18] have been established that the tridymite-cristabolite transformation is also reconstructive, like another quartz modifications, but since both have similar layer units (parallel to 0001 in tridymite and (111) in cristobalite) it may proceed with more limited atomic movements.

The reconstructive transformation tridymite-cristobalite was studied also by X-ray diffraction single-crystal pression methods by H. Schneider and O. W. Florke [19] who used untwined tridymite (pseudo-ortorombic) from a refractory block heated to 1500-1620 ^{o}C the cristobalite produced is strongly oriented with respect to the tridymite.

The dominating crystal phases of the examined dinas material used in the glass melting tank furnace are α-quartz, tridymite and crystobalite, also sodium aliumosilicate which forms from the vapour and SiO_2 of dinas.

The data of the chemical analysis of the initial and exploited dinas bricks are given in the Tab. I.

Tab. I. Chemical composition of dinas bricks

Materials	Chemical composition, weight %				
	SiO_2	Fe_2O_3	CaO	K_2O	Na_2O
Container-glass melting furnace greenish-coloured dinas	87.73	0.72	3.79	-	-
Container-glass melting furnace-white coloured dinas	81.44	0.734	2.16	-	-
The partially melted 2 – 2.5 mm thickness layer of the surface of container-glass melting furnace	74.00	1.51	3.76	1.87	1.09
Melted 4 – 6 mm thickness deeper darker-coloured layer of container-glass melting furnace	79.00	1.66	3.64	1.94	1.10
The light brown coloured bulk of exploited dinas in electrovacuum glass melting furnace	96.68	0.29	3.30	-	-
The primary dinas bulk of electrovacuum glass melting furnace: yellow-coloured brown-red coloured white coloured	95.73 95.65 97.19	0.41 0.37 0.38	3.40 2.80 2.80	- - -	- - -
The white-coloured partially melted surface layer up to 3 mm thickness of electrovacuum glass melting furnace Glassy mass	90.00 92.14	0.46 0.17	2.95 2.40	0.57 -	1.23 -

The data of chemical analyses proved the low quality of dinas exploited in container-glass melting furnace: it had small amounts of SiO_2 (about 80 %) in its different layers, and large amounts of CaO and alkali oxides if compared to the requirements. The material of electrovacuum furnace dinas had large (about 97 %) quantities of SiO_2, and it lessened up to 90 % only in the surface partially melted layer as result of the chemical reaction with base oxide emissions that vapour from the glass melt.

The characteristics of dinas bricks used in electrovacuum furnace indicated the highest quality that is required for the high quality refractory dinas: its density was 2330 kg/m^3, its strength was of 37.7 MPa, 8.87 % of open porosity, the quantity of SiO_2 was 96.43 %. But the X-ray diffraction revealed that the crystobalite phase dominated in this dinas. The highest quality dinas must contain 50 -70 % of tridymite and 30 -20 % crystobalite. The strength of used dinas lessened up to 33.8 MPa, but it remained enough strong.

The quality of the dinas used in electrovacuum glass melting furnace matched the qualitative requirements for the highest quality refractory materials thus the formation of microcracks and the process of accelerated corrosion was influenced only by periodic temperature fluctuations of the flame torch and the cyclical fluctuation of the glow temperature of the furnace crown: at the supply boot the temperature periodically fluctuated from 1405 to 1430 ^{o}C, in the crown of the highest temperature zone it fluctuated from 1527 to 1550 ^{o}C and when the coefficient of the light transmission of the glass periodically was changed from τ = 48.5 to τ = 56.5 %, the temperature of this zone fluctuated from 1575 to 1605 ^{o}C.

3. Conclusions

The reasons for the accelerated corrosion of the crown could be the insufficient grade of the modification of α- quartz into tridymites and crystobalites, large amount of admixtures and the large amount of CaO in the initial bricks, also the cyclic fluctuation of temperatures in the range of 1570 – 1550 ^{o}C in the vault.

Even using the initial dinas bricks of high quality, the cyclic change of crown's temperature (when the temperature changes in the 25-30 ^{o}C interval), becomes the important reason of significant acceleration of crown's material corrosion rate.

References

1. M. Velez, J. Smith, R. E. Moore, Ceram. (Brazil), 43, (1997), 180.
2. M. Karakus, R. E Moore, In Corrosion of Materials by Molten Glass, (1996), 179.
3. M. Velez, M. Karakus, M. R. Reidmeyer, W. D. Headrick, R. E. Moore, Ceram. (Brazil), 47, (2001), 113.
4. M. D. Allendorf, K. E Spear, J. Electrochem. Soc., 148, (2001), 59.
5. R. H. Nilson, S. K. Griffiths, N. Yang, P. M. Walsch, M. D. Allendorf, B. Bugeat, O. Marin, K. E. Spear, G. Pecoraro, Glass Sci. and Technol., 76, (2003), 136.
6. A. V. Faber, O. S. Verheijen, Ceram. Eng. Sci. Proc. 18, (1977), 109.
7. E. K. Akselrod, A. I. Portnova, Refract. Industr. Ceram., 26, (1985), 587.
8. C. A. Paskocimas, E. R. Leite, E. Longo, W. Kobayashi, M. Zorrozua, J. A. Varela, in: Proc. 58th Conference on Glass Problems, The American Ceramics Society, 19, 2008, p. 89-98.
9. E. Z. Korol, V. M. Panferov, V. L. Bulakh, N. V. Pitak, Refract. Industr. Ceram., 27, (1986), 323.
10. Ch. A. Schacht, Refractories Handbook, CRS Press, New York, (2004).
11. Ch. Bray, Dictionary of glass. Appendix of tables. A. Black, London, 1995.
12. E. le Bourhis, Glass. Mechanics and Technology, Weinheim, 2008.
13. J. Vernon, Introduction to Engineering Materials, 4 th ed., Palgrave Macmillan, New York, 2003.
14. J. E. Shelby, Introduction to Glass Science and Technology, 2 nd ed., Cambridge: Royal Society of Chemistry, 2005.
15. H. Lemmens, M. Czank, G. Van Tendeloo, S. Amelinkx, Phis. Chem. Min. 27, (2000), 97.
16. P. J. Heaney, Rev. Min. Geochem., 29, (1994), 1.
17. A. B. Thompson, M. Wennemer, Amer. Min., 64, (1979), 1010.
18. M. Wennemer, A.B. Thompson, Schweiz. Min. Petr. Mitt., 64, (1984), 53.
19. H. Schneider, O. W. Flocke, Z. Krist., 175, (1986), 165.

***Садржај**: Критични параметри ватросталног силицијума, као што су тврдоћа на притисак, величина, густина, микроструктура и порозност, рачунати су за некоришћене и коришћене цигле које се користе као кров за стаклене пећи, када је брзина корозије 2 пута већа. Проучавани су промена ових параметара, хемијски састав и микропукотине у коришћеном ватросталном материјалу.*

Утврђено је да је кратко време издржљивости цигли на крову пећи повезано са лошим квалитетом цигли од силицијума: висок садржај CaO и нечистоће, мала

количина силицијума, прелазак у тридимит и кристобалит и формирање 5 -10 μm и већих од 100 μm пукотина у кровном материјалу. Главни разлог корозије високо-квалитетних силицијумских цигли употребљених за кров електровакуумске стаклене пећи је у цикличним променама температуре крова у опсегу 1405 – 1430 ^{o}C у иницијалној зони крова и у опсегу 1575 – 1605 ^{o}C у високо-температурској зони.

Кључне речи: *ватростални кров, α-кварц, тримидит, кристобалит, корозија.*