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FROST RESISTANCE CHARACTERISTICS AND PORES STRUCTURE OF CERAMIC TILES

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SUMMARY

One of the criteria of ceramic tiles quality is their stability in the range of low temperatures. Texture and structure characteristics (content of glass and crystal phase) of ceramic tiles play the dominant role in this field. The aim of our investigation was the frost resistance prediction of the fired ceramic samples made from two types of clay materials (kaolinite/illite system and illite/carbonate system). The clay powders of define characteristics were shaped by dry pressing, 25 MPa, and fired in laboratory conditions at the temperature of 960 and 1050°C (soaking time 90 min). Mechanical values of the fired samples (bending strength and values of Vickers hardness) were correlated with the pore structure values (total pore volume) as well as with the microstructure characteristics. The frost resistance of the ceramic systems was examined by the standard procedure of freezing/thawing (35 cycles, EN 539-2) and with a low temperature dilatometer (water saturated samples-24h). The system (final temperature - 1050°C) containing glass phase, formed after the thermal collapse of illite clay minerals, showed better frost resistance characteristics in comparison with the kaolinite system. The state of unfinished reactions in the case of kaolinite system could be the reason of the inappropriate characteristics. Both ceramic systems (K and IC) fired at 960°C did not show any differences in the investigated area - frost resistance properties.

KEY WORDS:

frost resistance, ceramic tiles, pore structure, mechanical properties

1. INTRODUCTION

The life cycle of the ceramic tiles is determined by their frost resistance. Several mechanisms of frost action could be present [1]:

- Volumetric expansion mechanism; the destruction of ceramics occurs if the pore structure is water filled over 91% due to the fact that water conversation into ice involves a 9% increase in total volume;

- Micro ice lenses mechanism; during freezing the ice is first formed in coarser pores while the unfrozen water is present in finer neighboring pores. Water moves into coarse pores and the micro ice lenses mechanism is formed;
- Hydraulic pressure mechanism; due to lower energy level of the ice than of the unfrozen water, in largest pores water freezes first and the ability of the ice to expand in smaller pores, saturated with unfrozen water, is limited. This causes large hydraulic pressures in the entire ceramic system and subsequently its deterioration.

The specified mechanisms would be developed only if the interactions between the material and environmental characteristics (values of moisture content and temperature) exist.

Frost resistance is directly connected with microstructure, texture and mechanical properties of the final product: content of glassy/amorphous and crystal phase, total pore volume, bending strength and hardness. Properties of raw materials and manufactory lines (shaping, drying and firing process) have a great influence on these characteristics. This work gives a correlation among those properties with the aim to predict the stability of the final product in the range of low temperatures. Furthermore, the investigation [2] has shown that the amount of glassy phase plays a significant role in the ceramic response to the frost action. Finally, prediction of the frost resistance was confirmed by the standard procedure of 35 cycles of freezing/thawing.

2. EXPERIMENTAL PROCEDURE

Materials

Model systems: two types of clay materials were used, system K - ceramic clay material based on kaolinite, quartz and orthoclase (Al_2O_3/SiO2=28.05/61.01; K_2O=2.42 mass%) and system IC - clay material based on illite, quartz and carbonates (Al_2O_3/SiO2=9.88/47.83; CaO=13.73 mass%).

Procedures and Methods

Procedures: shaping pressure (25Mpa), dimensions of green products 5x5x25mm; material moisture content K system - 1.17 mass%, IC system - mass 2.12%; thermal treatment-controlled firing process Tmax=960/1050°C, soaking time 90 min; low temperature dilatation measurements (freezing dilatation) - "water dried" samples, "water saturated" samples (24h water pretreated samples; Twater=21°C), thawing rate 10 °C/min; bending strength, crosshead speed 0.2mm/min; Vickers hardness, load 5kg.

Methods: Pore Size Distribution - Hg Porozimetry 2000WS; Differential Scanning Calorimetry (DSC) - Du Pont 910 (-40 H-+40°C); Water absorption after 24h- EN 532/2 (1998); Water absorption after 4h in boiling water - ASTM C-373/88; Bending strength - JUS B.D8.066 (Laboratory press Instron 1122); Vickers hardness - JUS C.A4.030; Frost resistance characteristics - Low Temperature Dilatation (-40 up to +40°C), Thermo Mechanical Analyzer 990; Frost resistance characterization - EN 539/2; Scanning Electron Microscopy (SEM) - JEOL, ISM-35.

RESULTS AND DISCUSSION

Pore size distribution

The increase of firing temperature, from 960 to 1050°C, leads to the pores enlargement and diminishes the total porosity of the final system, Table 1 and Figure 1.

As far as the pore size distribution is concerned, system K could be characterized as the one with the dominant pore interval in the range 0.064 to 0.5 um, while the IC system could be characterized as the system with the dominant pore interval 0.5 to 2.0 um.

Table 1. Total porosity of the fired model systems **K** and **IC**

System	**IC960**	**IC1050**	**K960**	**K1050**
Total porosity [%]	43.4	36.6	31.4	24.4

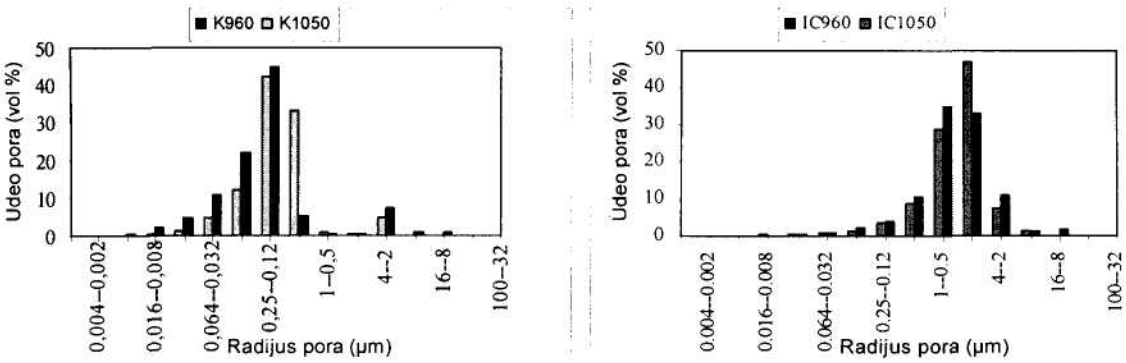

Figure 1. Pore size distribution of the model systems K (left) and IC (right)

MICROSTRUCTURE OF THE MODEL SYSTEMS K AND IC

It is known that relatively slight forces keep the layers of illit clay mineral together and that during firing process carbonate dissociate to CaO and CO2 (case of the IC systems). The presence of free CaO makes this system less meltable and the CO2 release increases its porosity, Table 1 and Figure 2.

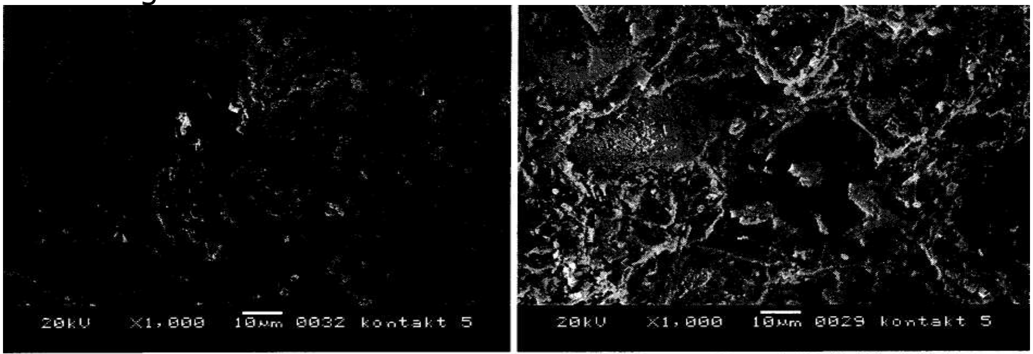

Figure 2. SEM pictures of the fired model system **IC** at 960 (left) and 1050°C (right),x1000

Contrary to the IC, the K systems posses a low carbonate content, but due to the thermal transformations within Al_2O_3-SiO_2 composition a considerable amount of amorphous/glassy phase and a sealed porosity is formed, Figure 3.

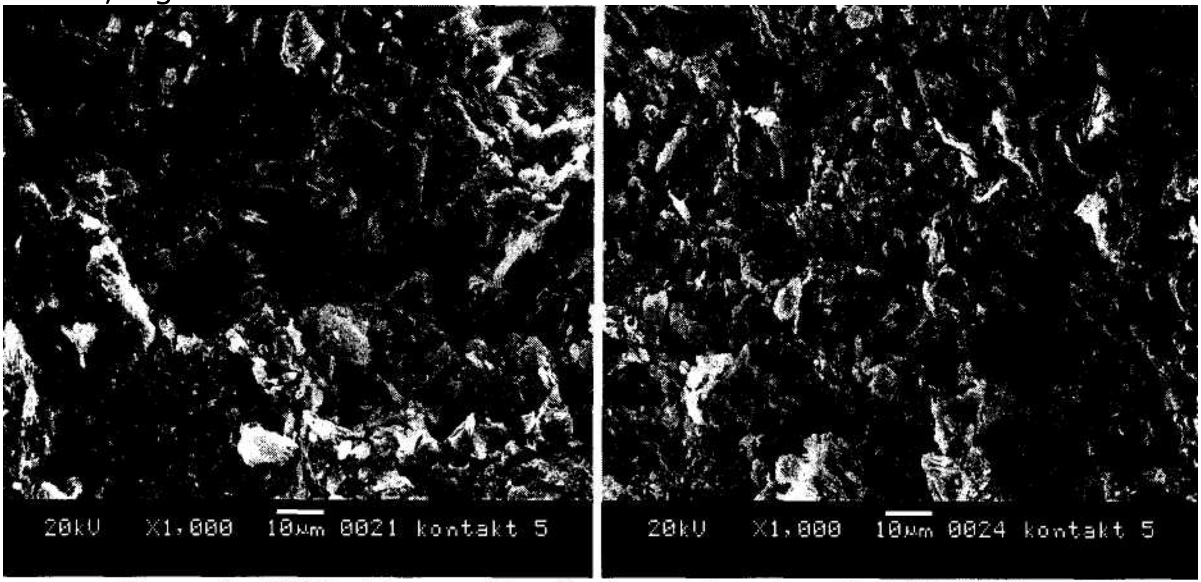

Figure 3. SEM pictures of the fired model system **K** at 960 (left) and 1050°C (right),x1000

Freezing procedure of the fired samples in water dried conditions

The total porosity and content of glassy phase define the dilatation values of the analyzed samples [3]. Regarding the obtained results the following increase of the total dilatation values could be noticed: IC system/9607-> IC system/10507-> K system/9607-» K system/10507, Figure 4. These results are consistent with the microstructure and pores structure of the analyzed systems, Figures 2 and 3, Table 1. Namely, the highest sample dilatation value, the case of the system K/10507, is the result of the glassy/amorphous phase domination, Figure 4, and the smallest amount of pore phase, Table 2, [3].

Freezing procedure of the fired water saturated samples

In the view of the obtained results, Figure 4, the K system/1050/ shows the lowest fluctuations of the total dilatation values with the temperature changes, predicting the fact of being the most stable system in temperature range -40 -r +40°C.

Table 3. Saturation coefficient of the fired model systems **K** and **IC**

System	**Water absorption after 24h [mass%] C**	**Water absorption after 4h in boiling water [mass%] B**	**Saturation coefficient [1] C/B**
IC960	18.99	19.43	0.98
IC1050	19.02	19.61	0.97

K960	14.09	14.37	0.98
K1050	11.45	11.46	0.999

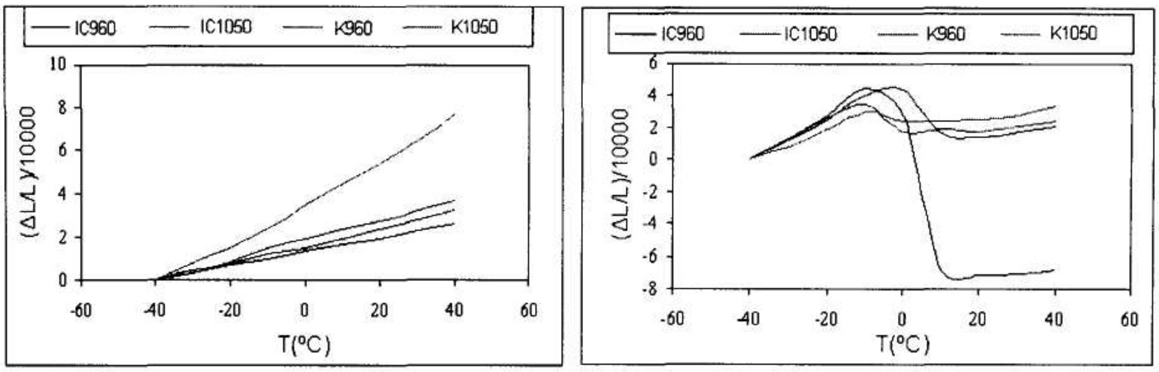

Figure 4. Dilatation values for model systems **K** and **IC** in "water dried" (left) and "water saturated" condition (right)

Differential Scanning Calorimetry (DSC)

The exothermic maximum of the DSC analysis, Figure 5, were used for pore size diameters determination [4]. According to the obtained results, Figure 5 - point A, in K systems is noticed the formation of stable size nucleus of ice crystals in smaller pores than in the IC systems. This result is in good correlation with the dominant pores interval of the analyzed systems. Due to the existence of the difference between the total amount of ice formed during freezing and heating it is possible to calculate the ice amount formed in analyzed samples during the heating procedure, Table 2. The possible reason for the existing difference in the ice amount, considering the two systems, could be the pore wall morphology and/or the presence of active centers, which are related to the mineralogy of the raw material and the firing process.

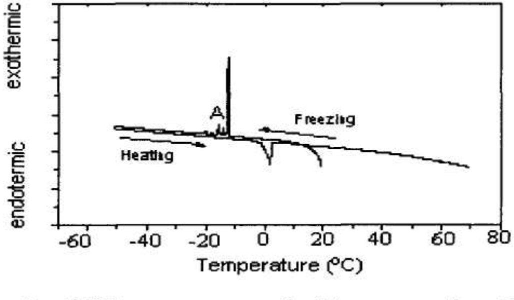

Figure 5. DSC measurements (the example of **K**960)

Table 2. Results of DSC analysis of the model systems **K** and **IC**

System	**IC960**	**IC1050**	**K960**	**K1050**
Amount of water transformed into ice [%]	75.6	53.9	54	45.7
Ice amount obtained during freezing process [%]	81	84	72	66
Ice amount obtained during heating process [%]	19	16	28	34

Relating freezing dilatation values to the total amount of ice, the following mechanisms of frost deterioration could be present: volumetric expansion, as the degree of sample water saturation is between 0.97-1, Table 3, and hydraulic pressure mechanism, the inevitable mechanism due to the presence of unfrozen water (specifically the case of K systems present. Moreover, according to the DSC measurements, Figure 5, the ice interactions with pore walls is also present. We assumed that the mechanism of micro ice lenses formation is negligible due to the obtained saturation values.

MECHANICAL PROPERTIES

With the increase of the firing temperature the values of bending strength and hardness increase, Table 3. The achieved results are in good correlation with the texture and microstructure characteristics of the systems. Namely, the K systems have higher values of mechanical properties due to the lower values of the total porosity and considerable amount of amorphous phase in contrary to the IC systems. Moreover, the observed lower values of mechanical properties after cycling compared to the earlier ones, for the same firing temperature, could be the result of the micro cracks occurrence, influenced by the freezing

CONCLUSION

The obtained results of this work indicate that the microstructure (especially the content of glassy phase) as well as the interaction between the material and environmental characteristics (values of moisture content and temperature) plays the main role in frost resistance of ceramic tiles. Moreover, the significance of mineralogical properties of raw material and the degree of unfinished reactions on the frost resistance properties were revealed. The highest frost resistant ceramic system is reached when the thermal reactions in the ceramic tile are almost finishing; as in the case of the IC1050 model system. The K model systems due to the unfinished reactions possess inappropriate frost resistance characteristics, but on the other hand, his mechanical properties were crucial in appearance of the first micro crack during freezing thawing procedure.

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