MICROSTRUCTURE MODELLING OF CERAMIC TILE SYSTEMS AND FROST RESISTANCE CHARACTERISTICS

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ABSTRACT

Frost resistance of ceramic tiles is one of the most important characteristics of these products, which is directly connected with the microstructure features of the final product: pore size distribution and pore permeability. As the microstructure of the final product (biscuit) is closely connected with the raw material characteristics and processing parameters, the study is focused on the quantification of these parameters with the aim of revealing the behaviour of the ceramic matrix during freezing action. Two groups of tiles were the subject of the investigation: one which failed in strong climate conditions-real systems, and a second, which involved model systems based on kaolinite / illite-carbonate compositions. The model samples were shaped by dry pressing and fired at 960 °C and 1050 °C in laboratory conditions. A promising tool in the procedure of modelling frost resistant ceramic tiles has been established, based on the correlation of pore size distribution of the fired tiles and model systems, freezing dilatation values and DSC results (-40 up to +40 °C).

***Key words**: frost resistance, ceramic floor tiles, model systems, DSC method, low temperature dilatation.*

1. INTRODUCTION

Regarding the frost resistance of ceramic tiles, two main factors influence this characteristic: the climatic conditions to which the ceramic material is exposed and its reactions to the frost action. There is no generally accepted theory which could describe how frost damage occurs in the case of materials such as ceramic tiles for outdoor areas, clay roofing tiles or facing bricks, but there is general agreement that the interactions between the material and the environmental characteristics (values of moisture content and temperature) play a dominant role [1] The properties of the raw material and the manufactory line also have a great influence on the frost resistance of the material. During the manufacturing process of ceramic tiles, the technological parameters of shaping, drying and firing play a crucial role in pore structure design and in the introduction of structure faults into the system. This fact affects the frost resistance characteristics of the ceramic systems.

The available testing methods for the frost resistance characterization could be classified as direct and indirect. Direct testing methods use the well-known repeated freezing/ thawing cycles in a climatic chamber, according to the different standard methods. Indirect testing methods are based on the fact that pore size distribution and pore structure play the main role regarding frost resistance characteristics[2]. Our investigations in the field of ceramic roofing tiles[3] have shown that the microstructure, particularly the glassy phase content plays a significant role in the ceramic response to the frost action. The presence of glass content was correlated with the sample freezing dilatation value at definite temperatures. The frost resistance prediction was confirmed in the standard procedure of 35 cycles of the freezing/ thawing procedure.

A number of ceramic tiles for the outdoor areas (water absorption less than 2 mass%), Panonia region, did not meet the quality demands in the particular kind of climatic conditions, i.e. temperature and moisture content fluctuations. The detected types of damage were chipping, with breaking-off of cone-shaped pieces of tile consisting not only of the glaze but also of the ceramic body. Our first investigation was dedicated to the density differences of the green tiles, correlated with the distortion phenomenon known as warpage of the ceramic biscuit. The idea was to keep the linear dimension in the standard limits[4] without significant changes in the raw material composition -tile producers' demands. The position of the press-die in the production line was taken into account; the end-die was marked as the critical parameter concerning the green tile density differences. As the frost resistant characteristics of the ceramic tiles, after a period of two years, dropped off - the problem of the prediction of the chipping phenomenon has been opened.

This paper proposes the product microstructure (biscuit) as the main object of the investigation in the experimental procedure of revealing the frost tile damage. Model systems were formed, based on the ceramic raw materials of the particular mineralogical composition (kaolinite or illite clay minerals) with the idea of explaining the clay material role in the ceramic biscuit microstructure formation, and consequently in the frost resistance characteristics of the ceramic tiles. The results obtained were correlated with the behaviour of the real systems (ceramic floor tiles).

2. EXPERIMENTAL WORK

2.1. MATERIALS

Real systems: The analyzed samples presented two opposite corner places of the A and B ceramic floor tile: a three-layer systems (biscuit /engobe/glaze - AEG and BEG samples); two-layer systems (biscuit /engobe- AE and BE samples); one layer-system biscuits A and B. The three-system pairs had the same raw material composition and processing parameters as the tile series which failed in the particular climate conditions showing damage known as the chipping phenomenon. The choice of sampling place (A and B) was made based on recent research work[4],[5]. The distortion phenomenon of the ceramic tiles was related with the position of the dies and ceramic powder agglomeration during the period of green tile preparation. Process parameters P = 25 MPa; Fast firing procedure - industrial roller kiln, $T_{máx}$ = 1180°C, ι = 44 min.

Model systems: Two types of raw materials formed the model systems: the ceramic clay material based on kaolinite, quartz and orthoclase (Al_2O_3/SiO_2 = 28,05/61,01; K_2O = 2.42%- system K) and the clay material based on illite, quartz and carbonates (Al_2O_3/SiO_2 = 9,88/47,83; CaO = 13.73 % - system IC). The values of the surface area of the two ceramic clay materials were different: K - 12.66 m^2/g; IC - 36.74 m^2/g. The two clay materials were the main components of the tile raw material composition used for the production of the ceramic floor tiles which failed in severe temperature fluctuation.

2.2. METHODS

Real systems: Pore Size Distribution-Hg Porosimetry 2000 WS; Frost resistance characteristics-Low Temperature Dilatation (-40 ÷ +40°C), Thermo Mechanical Analyzer 990, v = 10°C/min.

Model systems: Pore Size Distribution-Hg Porosimetry 2000 WS; Differential Scanning Calorimetry (DSC)- Du Pont 910 (-40 ÷ +40°C); Water absorption-EN 532/2 (1998); Frost resistance characteristics-Low Temperature Dilatation (-40 ÷ +40°C), Thermo Mechanical Analyzer 990. Sample dimension 5x5x2 mm.

3. RESULTS AND DISCUSSION

The aim of our investigation was to set up a method which could predict the chipping appearance in the case of ceramic floor tiles. The correlations of the real and the model ceramic systems behaviour in the laboratory conditions (Low temperature dilatation and Differential Scanning Calorimetry) presented the basis of the developed method.

3.1. REAL SYSTEMS

3.1.1. Pore size distribution

A difference of pore size distribution (interval 2.00 to 8.00 μm pores) based on Hg Porosimetry results and the total porosity values between both three layer systems AEG and BEG, was identified, Figure 1. The real model BEG possesses a higher total porosity (18.20%) than the AEG system (15.50%); even the values of the green densities were opposites: The A model has a penetration index value of 35, while the B model has an index value of 21.

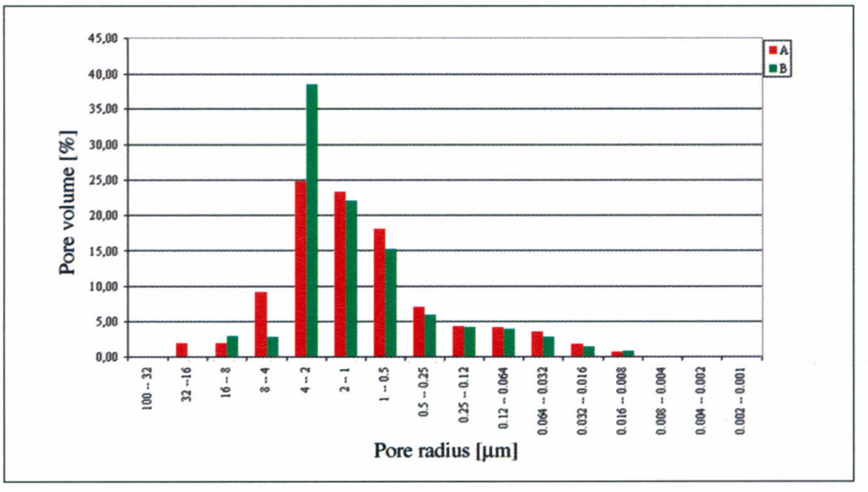

Figure 1. Pore size distributions of the biscuits A and B.

3.1.2. Frost resistance characteristics

Freezing procedure of the fired samples in dried conditions.

The glass and pore phase content in the tile structure is the dominant parameter which defines the dilatation values of the analyzed samples. The highest sample dilatation value means the most serious content of glass phase or the least pore phase content[6]. The two mono systems (A and B) have the same rate dilatation increase, but different total dilatation values, Figure 2. The presence of engobe (two-layer systems) and engobe + glaze (three-layer systems) dramatically changed the total dilatation value of the two biscuits. They namely influenced the decrease in the case of the B biscuit, but also the dilatation increase in the case of the A biscuit. Different dilatation results mean different step interactions among the three or two phases during the procedure of glass maturing and present the first significant value of the heterogeneity regarding the studied systems.

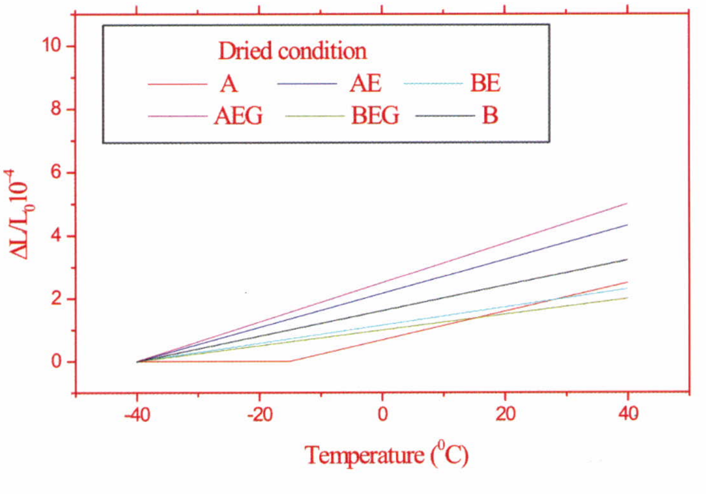

Figure 2. Low temperature dilatation values for the real systems A and B-dried conditions

Freezing procedure of water saturated samples

The behaviour of the water saturated samples, within the temperature interval -40 °C to +40°C. is shown in Figure 3. The first characteristic, which separates the biscuit samples, is the total dilatation value in the temperature interval -40°C up to the relaxing temperature $F_{temperature}$. The second characteristic is the period of latent dilatation, length E-F, Figure 3. The position of point E, determining the start of the melting process, signals the fact that biscuit B could be characterized as containing a smaller pore radius than biscuit A. Obviously biscuit A, due to the presence of larger diameter pores, starts its local strain release (ice melting process) later but in a stronger way than the B mono ceramic system. The attachment of engobe almost annuls these differences, but the glazes again open up the problem of sample heterogeneity. It is worth mentioning that the behaviour of the two systems is completely different from that of ceramic roofing tiles[3]. The absence of the brusque decrease of dilatation after point E is in good correlation with the water absorption values of the ceramic floor tiles (< 2 mass %) and the fact that pores with a diameter less than 100 nm could be the dominant parameter in frost behaviour[6].

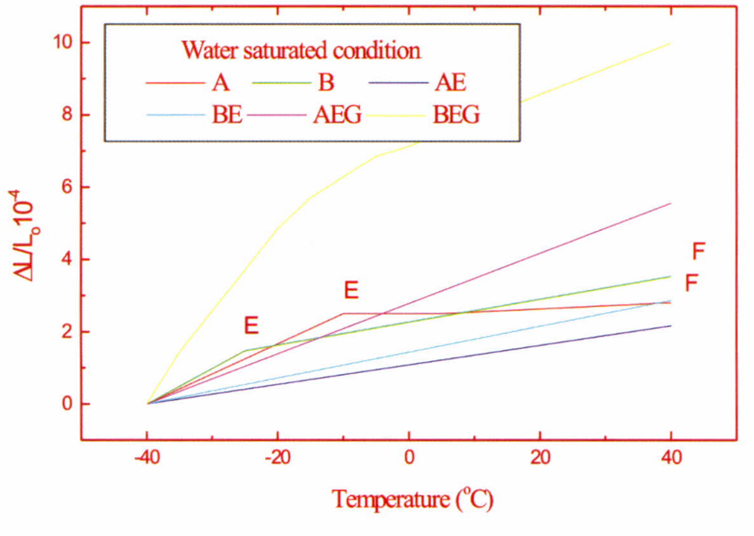

Figure 3. Low temperature dilatation values for the real systems A and B-water saturated conditions

3.2. MODEL SYSTEMS K AND IC

Process parameters: P = 25 MPa, sample dimension 25x5x5 mm; Thermal treatment-controlled process (T_{max} 960/1050°C), high temperature dilatometer, v = 10°C/min

3.2.1. Pores size distribution

The mineral composition of the ceramic raw materials and thermal treatment play the main role in the process of model pore structure formation. The illite-carbonate system IC could be characterized as the system with a dominant pore interval in the range 0.5 to 2.0 μm Figure 4, while the kaolinite system K could be characterized as the system with the dominant pore interval 0.5 to 0.064 μm, Figure 5. The temperature increase, 960°C to 1050°C, influenced pore enlargement, but diminished total porosity, Table 1.

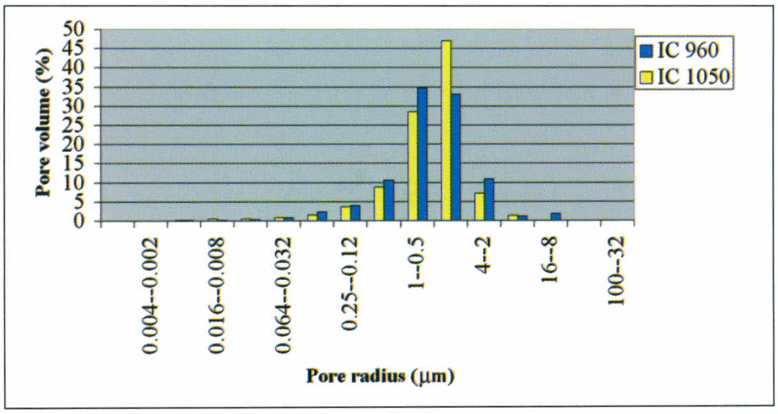

Figure 4. Pore size distribution of the model systems IC

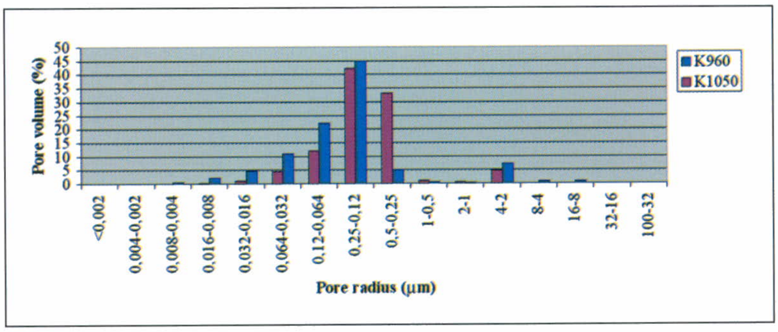

Figure 5. Pore size distribution of the model systems K

SYSTEM	IC 960	IC 1050	K 960	K 1050
Total porosity (%)	43.4	36.6	31.4	24.4

Table 1. Total porosity of model system IC and K

3.2.2. Phase composition of the ceramic systems IC and K

It is known that relatively slight forces keep the layers of the illite clay mineral together. The effort of CaO phase incorporation in the ex-clay system is the function of the degree of clay thermal disarrangement and the surface area of the obtained system [6]. The IC body presented a satisfying structure at 1050°C for a consistent silica-CaO system formation in the system K. The kaolinite system K possessed a stable structure up to 1050°C[7]. The thermal collapse of the plagioclase present, lowering the thermal decomposition of the entire body, partially supported the solid body reactions between CaO and SiO_2 components. Namely, the content of K_2O (2.42 mass%) brought about a glass phase with a high coefficient of viscosity, presenting a serious problem regarding the mixture of the tile raw mineral components.

3.2.3. Freezing procedure of the fired samples in dried conditions

Freezing dilatation examination for the model systems was performed in the same exploitation conditions as in the case of the real ones. The following increase of the total dilatation values could be noticed: illite carbonate system-IC /960°/ illite carbonate system /1050°/ kaolinite system /960°/kaolinite system /1050°/. The obtained results are in good correlation with the phase composition of the analyzed systems. Namely, the kaolinite system, due to the thermal collapse of the plagioclase components, possesses a noticeable quantity of K, Na glass phase which increased its total dilatation value in freezing dilatation condition (-40°C to +40°C) [3]. The illite glass phase of the IC ceramic system, on being saturated with Ca and Mg components, shows an insignificant increase in the total freezing dilatation value with the temperature firing changes of this system (960 to 1050°C), Figure 6.

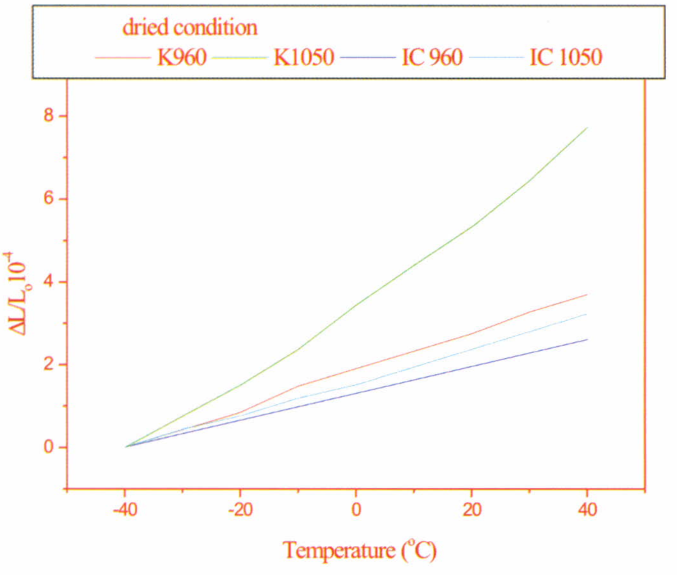

Figure 6. Low temperature dilatation values for the model systems K and IC- dried conditions

3.2.4. Freezing procedure of water saturated samples

Regarding the obtained results, Figure 7, it is obvious that the most unstable system is the illite carbonate IC system. It shows a brusque dilatation changes at -12°C, whose temperature is pushed almost to zero in the case of the system IC 1050. The kaolinite system, which was less sensitive to the temperature changes, could form a more stable system than the IC system.

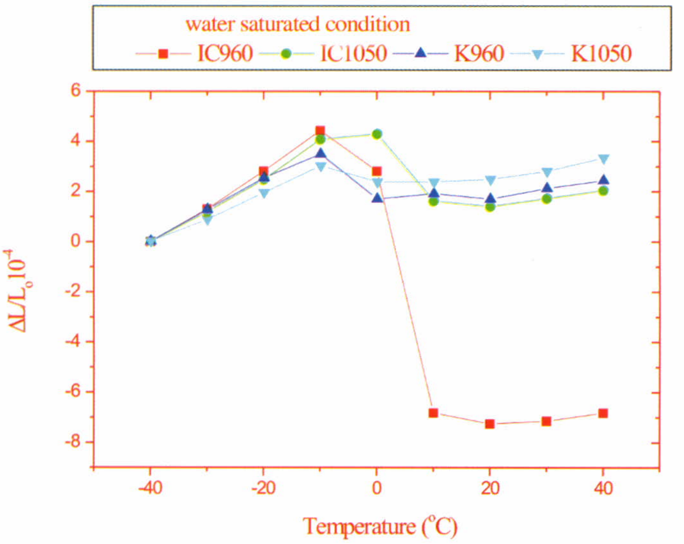

Figure 7. Low temperature dilatation values for the model systems K and IC -water saturated conditions

3.2.5. *Differential Scanning Calorimetry (DSC).*

The exothermic maximum of the DSC analysis, Figures 8-11 was used to determine the pore size diameter values[2] which played the main role in the water freezing process in the specific ceramic system. The formation of ice in the case of K systems is noticed in smaller pore diameters than in the case of the IC systems. This fact is in good correlation with the values of the dominant pore interval determined by Hg porosimetry, Figures 4 and 5.

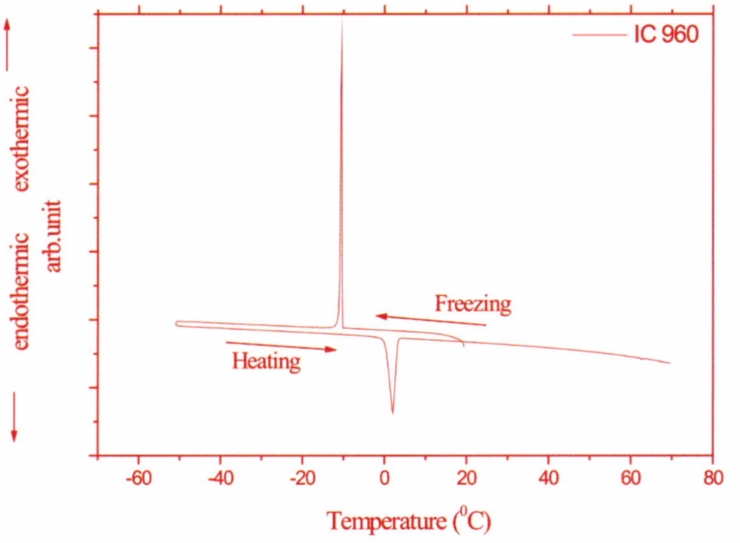

Figure 8. DSC results-IC 960 system

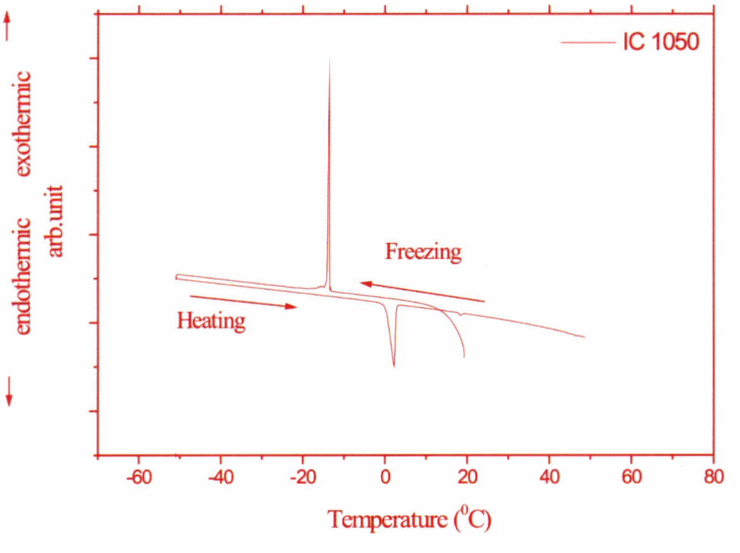

Figure 9. DSC results-IC 1050 system

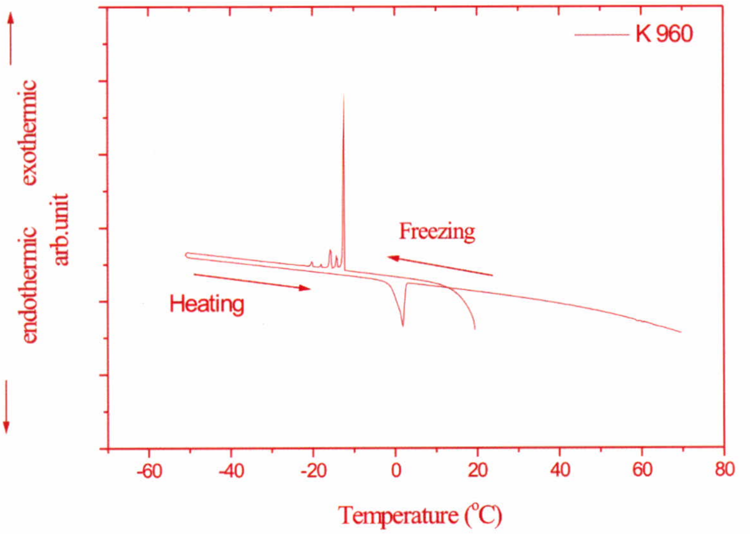

Figure 10. DSC results-K 960 system

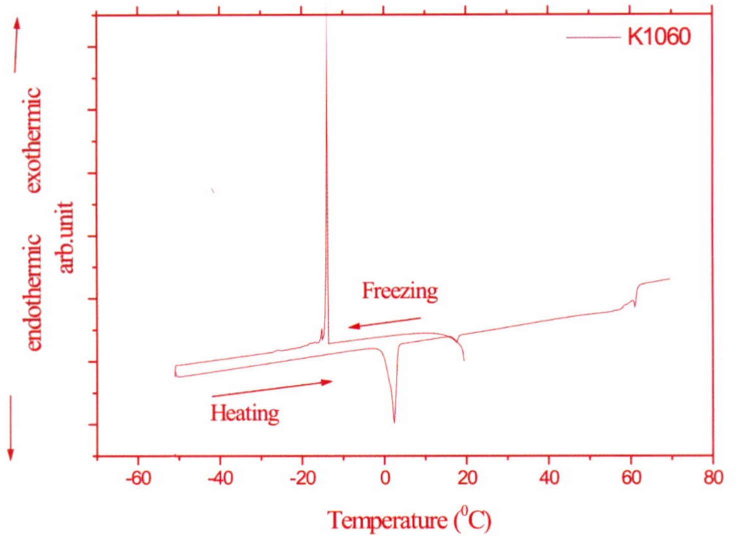

Figure 11. DSC results-K 1050 system

The existence of a difference between the amount of ice formed during the freezing/thawing processes enables calculating the amount of ice that formed during the heating procedure of the analyzed systems. Its origin could be the result of pore wall morphology and/or the presence of active centres which evidently are functions of the mineralogical characteristics of the defined raw material and the thermal treatment. A larger quantity of pore walls active centres means a stronger adhesion of the ice to the ceramic matrix [1]. This phenomenon is more developed in the case of the K than the IC systems. Note that the difference in ice amount between the freezing/thawing procedure also exists inside the system groups K and IC, but this fact is less pronounced in comparison with the difference between the K and IC systems, Table 2. The conclusion could be that the mineralogical composition of the model influences the characteristics of the ceramic matrix more seriously than the temperature of the thermal treatment (960/1050°C).

System	IC 960	IC 1050	K 960	K 1050
Freezing temperatures, T°C	-10	-13.5 -14.5	-12.3; -13.0; -13.5 -14.2; -21	-13.8 -15.2 -16.9
Pore diameters[2], μm	0.5	0.15-0.2	0.05-0.25	0.15-0.1
Amount of water transformed in ice (%)	75.6	53.9	54	45.7
Ice amount obtained during freezing process (%)	81	84	72	66
Ice amount obtained during heating (%)	19	16	28	34

Table 2. Results of the DSC analysis

Comparing the low temperature dilatation results of the real and model systems, Figures 2,3 and Figures 6,7 there are obviously interior mass strains in the K model due to unfinished thermal reactions. The respective behaviour of the biscuit systems A and B, Figures 2,3, is influenced by the kaolinite clay mineral (K model) presence which plays a decisive role in the appearance of the frost damages due to the unfinished reactions at the analyzed temperatures (960/1050°C- model K; 1180°C - B). This influence is stronger in the case of the B biscuit. Obviously, in the green state it contains a significant quantity of kaolinite clay mineral which fails to approach the crucial microstructure. The presence of engobe kept the strains in a defined range, Figures 2 and 3, while the glaze again opened up the problem of tile microstructure heterogeneity and the frost resistance characteristics failure (freezing linear dilatation).

4. CONCLUSION

The current research of the relationship between the mineralogical compositions of the model systems (kaolinite/illite-carbonate) and their behaviour in the specified temperature range (- 40°C up to + 40°C) implies the significance of tile phase composition for obtaining a frost stable system. The highest frost resistant ceramic floor tile is obtained when the thermal reactions in the ceramic tile are almost finishing (A real system, IC model system). The relationship established could be a promising method for revealing the degree of phase formation and the microstructure which could be stable under the frost attacks.

REFERENCES

[1] LINDMARK S.: Mechanism of salt frost scaling of portland cement-bound materials; studies and hypothesis, Licentiate Thesis, Lund Institut of Technology, Division of Building Materials, (1998).

[2] RAVAGLIOLI, A.: Evaluation of the frost resistance of pressed ceramic products based on the dimensional distribution of pores, Trans I Brit. Ceram. Soc 75, (1976).

[3] RANOGAJEC J., A. MESAROS, P. KERMECI, M. RADEKA , S. VOJNIC: Microstructural approach to frost resistance of ceramic roofing tiles, Istanbul, 8 ECERS, (2003).

[4] HIP, B.B., DOMONKOS, K.A., KILIBARDA-SABOTIC, R., AROKSALASI, L., RANOGAJEC, J., KANAZIR, J., MARINKOVIC-NEDUCIN, R.: Design of Green and Fired Microstructure of Ceramic Wall Tiles, 7 ECERS, Proceedings-Part 3, pp.1783-1786, (2002).

[5] HIP, B.B., DOMONKOS, K.A., KILIBARDA-SABOTIC, R., RANOGAJEC, J.,MARINKOVIC-NEDUCIN, R.: Un nuevo diseño de la microestructura en crudo y cocido en la producción de revestimientos cerámicos, VI Congreso Mundial de la Calidad del Azulejo y del Pavimento Cerámico, Qualicer 2000, Castellón, España, 103.

[6] RANOGAJEC, J., RADEKA, M., KASAS, K., MESAROS-BORBELJ, A.: Mineralogical composition of ceramic raw material and frost resistance characteristic of the final product. In press.

[7] BELNOU, F., GOEURIOT, D., GOEURIOT, P., VALDIVIESO, F.: Nano and Micrometric Particles Dispersion in Traditional Ceramics, 7 ECERS, Proceedings-Part 3, pp. 1735-1738, (2002).