Ponencia ref 34-HOT-PRESSED GRES PORCELLANATO BODY

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Abstract

Gres Porcellanato Tiles (unglazed and glazed) are the most popular covering materials used in the construction sector from several years and permanently develop by researcher and technologists but mainly by implementation new decorative technique. During last 15 years, the body composition and production methods becomes almost to perfection. Present, Gres Porcellanato material be characterized by high mechanical parameters, staying a very cheap material, in comparison to others use in engineering. In other hands, new production techniques, like Hot Pressing, becomes more and more chip and accessible. Comercial two gres porcellanato bodies have been sintered by Thermal Technology Hot-Press. The parameters of hot pressing process, sintering temperature: 1100, 1150 and 1200 Celsius degree and pressure 25 MPa. Comparing to commercial tiles parameters and to referee of standard requirements, the strong increasing of flexure strength and microhardness have been obtained. The differences in phase composition and microstructure have been discused. All results shows the possibility of develop technical parameters of the ceramic Gres Porcellanato bodies and perhaps find other application.

Introducton

Material used for production of „Gress Porcellanato" type ceramic tiles, has been implemented to industrial practice in the eighties of the last century. Since that time, its role in ceramic tile production is more and more important. This material characterizes with perfect technical parameters, such as: very low water absorbability, high mechanical bending strength, high abrasion resistance, high chemical resistance and high stain resistance. The parameters also comprise resistance to changeable climatic conditions, including freeze, water and sunlight resistance, and resistance to rapid temperature changes. Actually, potential of gres-type material is not fully adapted, what mainly results from technological and economical reasons. If manufacturing technology is concerned, we should not expect any essential turning point like change from tunnel kilns to roller kilns in second halt of the XX century. However, implementation of sintering under pressure/hot pressing (*synonim:* hot pressing) to standard production could introduce such turning point. From the point of view of technology development it is still „science fiction", but is hard to predict what is going to happen during the nearest decade. However, it is interesting, what properties will possess material obtained in conditions of sintering under pressure/hot pressing. The hot pressing technology was born in the forties of XX century, when pressing process was combined with contemporary action of high temperature. This problem is a subject of the present work.

Experimental procedure.

Two commercial bodies used for manufacturing of tiles of the type Gres Porcellanato taken from a company Ceramika Tubądzin were used in the examinations. Principal body parameters, marked with symbols MG-1 and MG-2, have been presented in Tables 1 and 2, and Figures 1 and 2. The only technological difference comprised drying granulates to moisture content equal to zero, what was necessary because of applied hot pressing technique. The

bodies were initially pressed under minor pressure in graphite mould and placed together in high-temperature press. Sintering process was conducted under uniform pressure P_{max} = 25 MPa, using three variable sintering temperatures (T_{max} = 1100; 1150 and 1200^{0}C). Three following stages were distinguished during process of sintering under pressure/hot pressing: application of initial pressure, heating accompanied with pressure growth, keeping in maximal temperature T_{max} and under maximal pressure P_{max} and cooling. Duration of the whole process amounted for about 120 minutes. Press *Thermal Technology Hot-Press* was used for sintering. After sintering, the samples were disc-shaped of the disc diameter of 90 mm and thickness of 8 mm. The discs were cut with diamond saw into suitable shapes: beams 60 x 9 x 8 mm, plates 60 x 60 x 8 mm and 8 x 8 x 8 mm. The following mechanical parameters were determined for the samples: mechanical bending strength, micro-hardness, resistance to brittle crushing K_{IC} and inward resistance to abrasion, (Table 3 and Fig. 3 - 4). Moreover, sintering degree was measured via calculation of water absorbability, apparent density and total porosity (Table 4). Examination of phase composition of sintered materials was also conducted (Figures 5 – 10), including microscope examination and phase microanalysis with use of scanning microscope method and X-ray micro-analyser (Figs 11 and 12).

Results and discussion.

The obtained results in broad range satisfied expectations of the authors, who planed their examinations only on the basis of data referring to oxides sintered under pressure. Contemporary action of temperature and pressure during sintering should facilitate mass transfer, densification rate and elimination of pores. However, behavior of liquid phase, which amount in such material in traditional sintering in roller kiln can range from 30 to over 60 %, is unknown. We were afraid that because of low alloy viscosity, that could cause plastic material flow during sintering and effect in mould and/or press damage. Influence of the atmosphere onto sintering process is also interesting, as the atmosphere because of graphite shape used and nitrogen presence, can be reductive, or at least neutral.

Obtained values of mechanical bending strength correspond to level of technical porcelain reinforced with addition of small amounts of Al_2O_3, or some chosen oxide materials. This maximum obtained value is twice higher than corresponding values obtained for the same materials sintered in commercial roller kiln. The same refers to values of inward abrasion. Obtained volumes of grinded material are from 30 to 60 % lower than corresponding volumes of materials traditionally fired. The same tendency is observed for measured values of micro-hardness and resistance to brittle crushing K_{IC}. Vickers micro-hardness and K_{IC} value was increase from 25 to over 40 %. Explanation of such great improvement of mechanical parameters is very difficult. Sintering degree of obtained materials is comparable with those obtained in traditional firing. Water absorbability, except single case, reaches values below 0,5 % by weight, what constitutes maximal permissible value for gres porcelanato material, and comparable with values obtained in ceramic tiles technology. Similar situation is observed for results obtained for bulk porosity and apparent density. Thus we can conclude that sintering degree is not responsible for growth of values of mechanical parameters. In general, phase composition of the materials is not different than composition of the materials traditionally fired. Crystals of α – quartz, crystalline phase of anorthoclase type and in some cases phase of sanidine type occur in all materials. However, both anorthoclase and sanidine structure is strongly disturbed and their composition is often non-stoichiometric. What interesting, phase analysis did not prove presence of mullite, which always occurs in materials traditionally fired. More data explaining changes of mechanical parameters were obtained in result of scanning microscope observations and point X-ray microanalysis. Comparison of microscope images of traditionally fired material (Fig. 13) with images of materials sintered under pressure allows drawing many conclusions. Materials sintered under prassure contain considerable smaller amount of the liquid phase. Size reduction/powdering of a sintered material sample and exposing them to action of hydrofluoric acid in temperature of 40^{0}C for a period of 24 hours, confirms this observation. Materials sintered under pressure contain 50 % less of the liquid phase. Quartz relicts, not melted during sintering process, are observed on all images. Their size is usually not coarser than 10 μm, although single coarser crystals can occur. Bigger crystals reaching size of 40 – 50 μm usually occur in traditionally fired materials. Other

crystalline grains similar in structure to sintered kaolinite aggregates are also interesting. X-ray microanalysis indicates that it is rather sanidine-type phase. Big agglomerates of fine bar and needle shaped crystals were also observed at large magnifications. They usually occur near quartz grains, what can suggest that presence of SiO_2 supports their crystallization. Shape of these crystals can indicate for mullite-type crystals. However, chemical microanalysis indicates also in this case for crystalline phases with admixture of other oxides. However, we should remember that it was not proved by X-ray phase analysis. In general, structure of materials sintered under pressure is fine crystalline, observed crystals have various shapes (from very fine needles to irregular sharp-edged big crystals). Shape, size and amount of the crystalline phase can be explained by improvement of mechanical parameters.

Conclusions.

1. The presented study describes potential of gres porcelanato-type materials/bodies. On the basis of such materials we can considerably improve mechanical parameters.
2. Examinations of sintering degree of materials/bodies sintered under pressure (hot pressed bodies), as compared with those fired traditionally in roller kiln, did not prove bigger differences.
3. Considering structure of tested materials/bodies, small amount of liquid phase and general knowledge on chemical corrosion of ceramic materials, we can expect high chemical resistance of gres porcelanato-type materials sintered under pressure (hot pressed bodies).
4. Actually, there are none technical possibilities of ceramic tiles manufacturing with use of sintering under pressure/hot pressing technique. However, these cheep materials can be used for other applications, where similar mechanical parameters, chemical resistance and accessibility of raw materials, are required.

Reference.

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Table 1. Chemical analysis of gres green bodies.

Tlenki	MG-1	MG-1
SiO_2	58,5	57,2
Al_2O_3	13,9	15,4
Fe_2O_3+ TiO_2	0,7	0,8
CaO + MgO	9,2	8,9
Na_2O + K_2O	5,3	4,8
strata prażenia	11,8	11,4

Table 2. Granulometric analysis of green bodies

Frakcje ziarnowe [μm]	MG-1	MG-1
	udział [%]	
> 600	2	1
400 – 600	13	9
300 – 400	13	10
250 – 300	44	40
180 – 250	14	19
125 – 180	7	14
<125	6	7
d_{50}	298	265

Table 3. Mechanical parameters of hot pressed materials.

Opis masy		Oznaczany parametr			
symbol	temperatura spiekania [^{0}C]	wytrzymałość mechaniczna na zginanie [MPa]	Mikrotwardość [GPa]	K_{IC} [Mpa $m^{1/2}$]	Odporność na ścieranie wgłębne [mm^3]
MG-1	1100	64,57 ± 2,65	74,56 ± 0,52	1,95 ± 0,06	87
	1150	122,13 ± 3,93	74,58 ± 0,48	2,00 ± 0,11	52
	1200	97,43 ± 2,97	74,58 ± 0,73	1,99 ± 0,16	55
MG-2	1100	84,35 ± 3,15	68,46 ± 0,88	1,91 ± 0,17	85
	1150	108,43 ± 3,51	68,38 ± 0,31	1,90 ± 0,11	59
	1200	114,72 ± 2,94	76,14 ± 0,54	2,10 ± 0,15	56
Klasyczne tworzywo gres	1200 (piec rolkowy)	52,7 ± 5, 32	54,54 ± 0,43	1,476 ± 0,09	115

Table 3. Porosity, density and water absorption of hot pressed materials.

Opis masy		Oznaczany parametr		
symbol	temperatura spiekania pod ciśnieniem [^{0}C]	Nasiąkliwość wodna [%]	Porowatość całkowita [%]	Gęstość pozorna [g/cm^3]
MG-1	1100	2,28 ± 0,04	5,55 ± 0,07	2,55 ± 0,06

	1150	0,05 ± 0,01	0,12 ± 0,03	2,57 ± 0,07
	1200	0,04 ± 0,02	0,09 ± 0,04	2,56 ± 0,04
MG-2	1100	0,22 ± 0,04	0,55 ± 0,11	2,52 ± 0,09
	1150	0,03 ± 0,01	0,07 ± 0,01	2,50 ± 0,02
	1200	0,08 ± 0,02	0,18 ± 0,04	2,42 ± 0,02
Klasyczne tworzyw gres	1200 (piec rolkowy)	0,05 ± 0,01	0,18 ± 0,06	2,38 ± 0,29

Fig. 1. MG-1 granulate

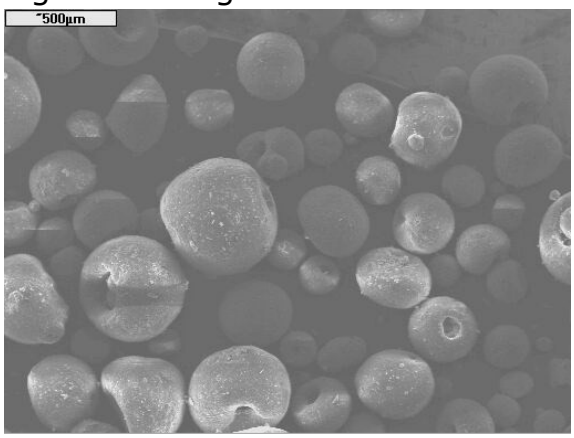

Fig. 2. MG-2 granulate

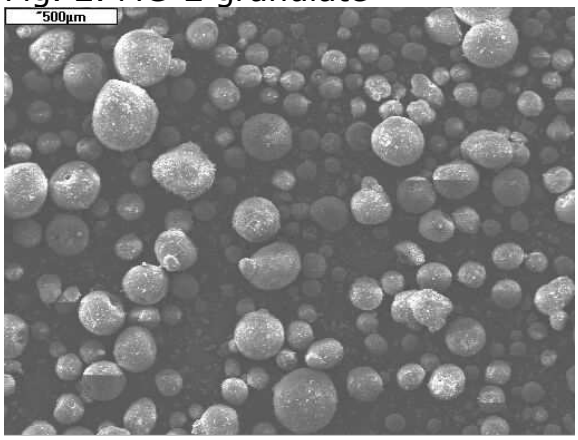

Fig. 3. Vickers microhardness identation of hot pressed MG-1 materials (3a- T_{max}=1100^{0}C; 3b - T_{max}=1150^{0}C; 3c - T_{max}=1200^{0}C).

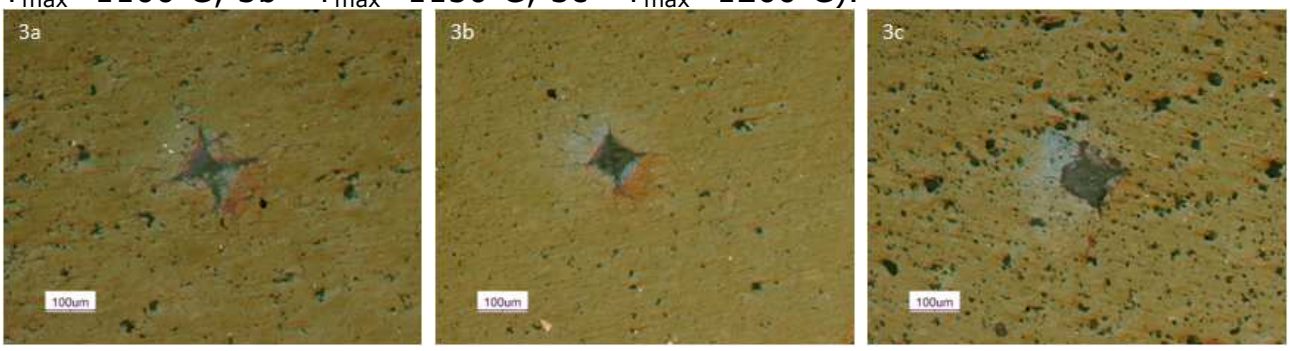

Fig. 4. Vickers microhardness identation of hot pressed MG-2 materials (4a - T_{max}=1100^{0}C; 4b - T_{max}=1150^{0}C; 4c - T_{max}=1200^{0}C).

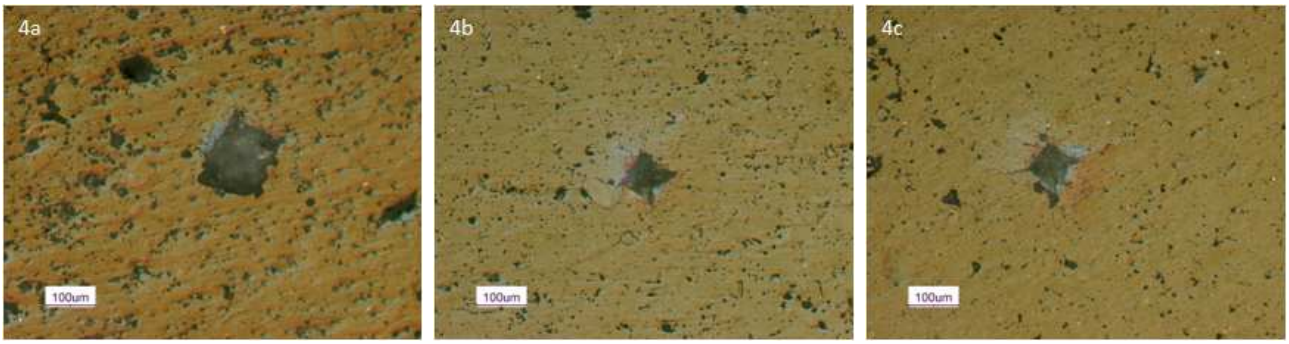

Fig. 5. X-ray analysis of of hot pressed MG-1 (1100^{0}C) materials.

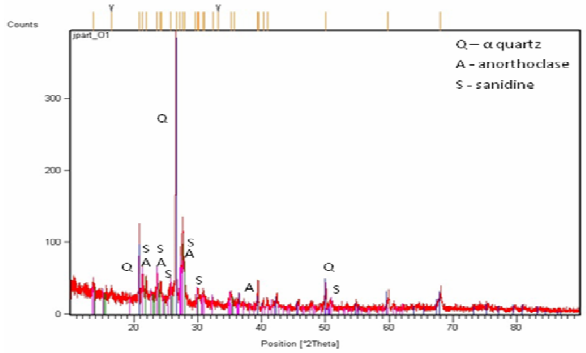

Fig. 6. X-ray analysis of of hot pressed MG-1 (1150^{0}C) materials.

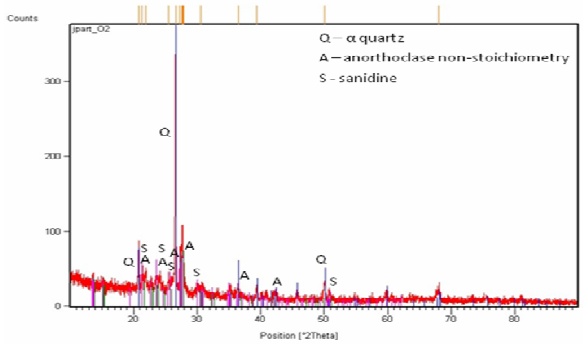

Fig. 7. X-ray analysis of of hot pressed MG-1 (1200^{0}C) materials.

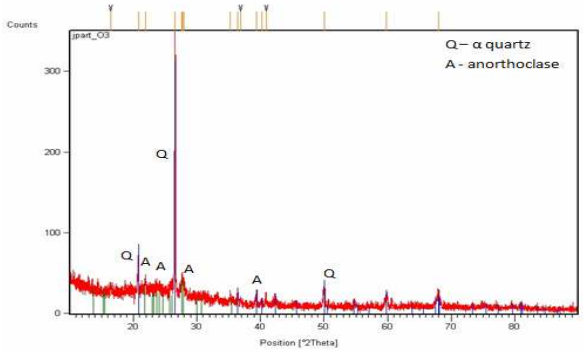

Fig. 8. X-ray analysis of of hot pressed MG-2 (1100^{0}C) materials.

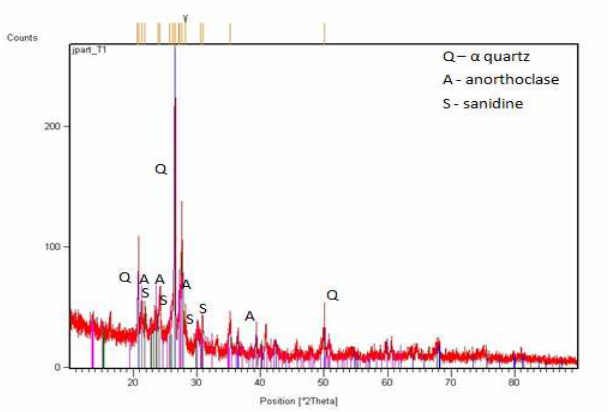

Fig. 9. X-ray analysis of of hot pressed MG-2 (1150^{0}C) materials.

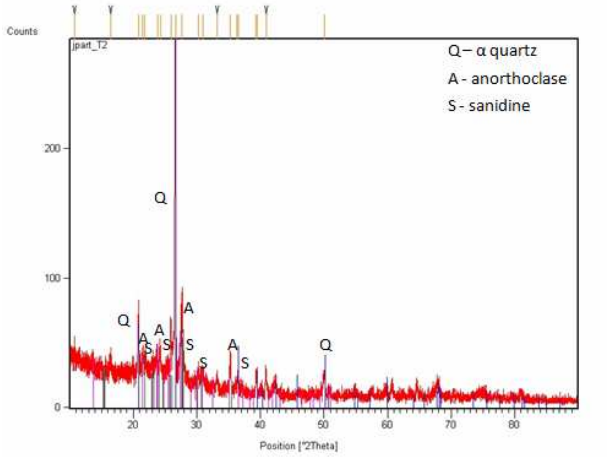

Fig. 10. X-ray analysis of of hot pressed MG-2 (1200^{0}C) materials.

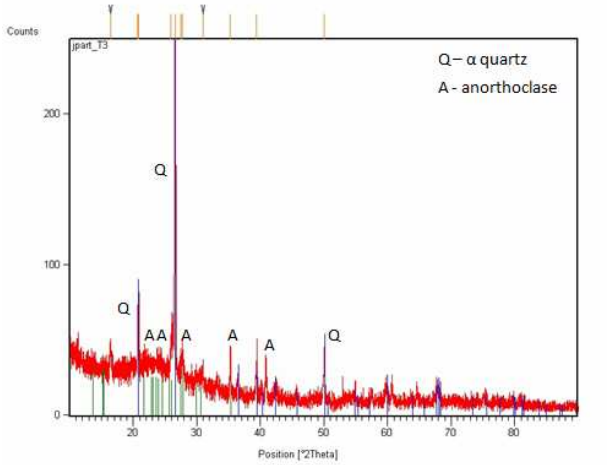

Fig. 11. SEM images of hot pressed MG-1 (11a- T_{max}=1100^{0}C; 11b - T_{max}=1150^{0}C; 11c - T_{max}=1200^{0}C).

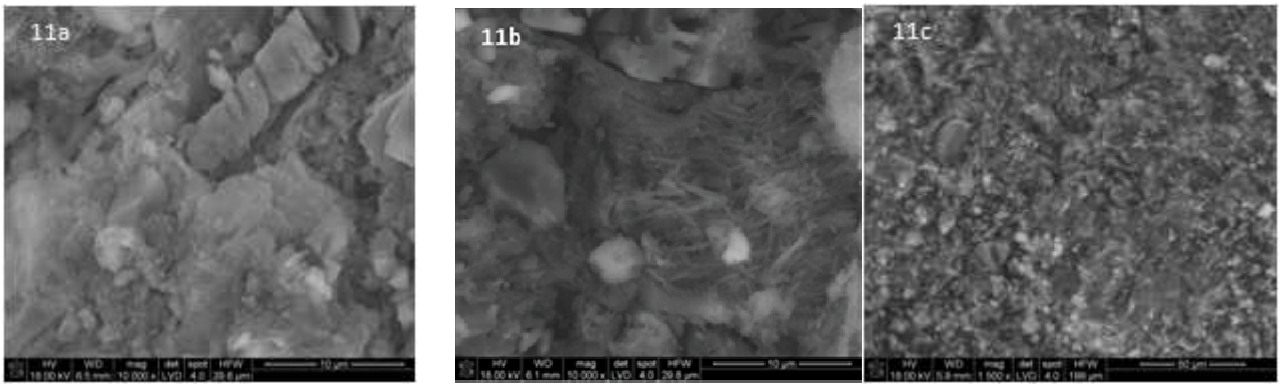

Fig. 12. SEM images of hot pressed MG-2 (12a- T_{max}=1100^{0}C; 12b - T_{max}=1150^{0}C; 12c - T_{max}=1200^{0}C).

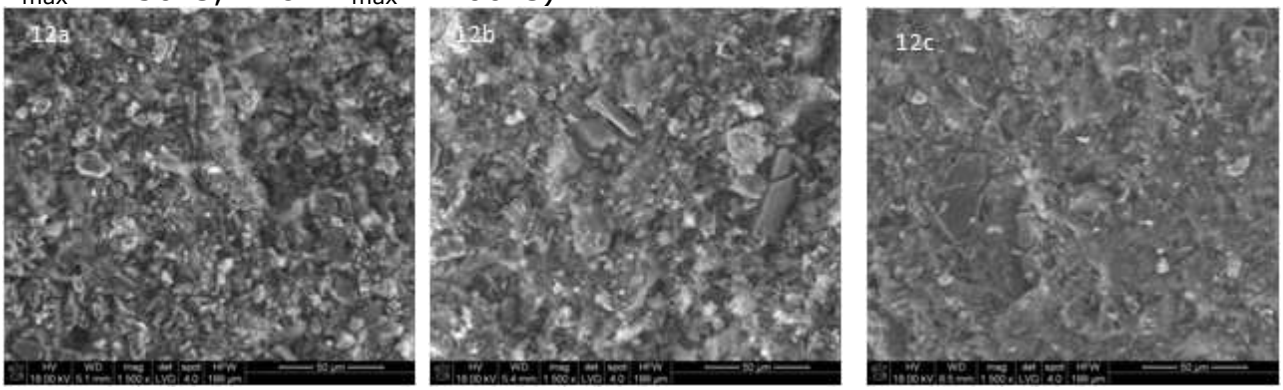

Fig.. 13. SEM images of MG-1 sintered in commercial roller kiln.