THE COMPOSITE APPROACH FOR THE REINFORCEMENT OF CERAMIC FLOOR TILES

P. Descamps, J. Tirlocq, M. Deletter, F. Cambier

Belgian Ceramic Research Centre - BCRC - Mons - Belgium

1. ABSTRACT

In this work, the wear resistance of unglazed floor tiles has been significantly improved by the presence of non-conventional mineral phases either added (like, for instance, alumina, zircon or spinel) or crystallized during the firing stage (especially β-spodumene).

In the former case, the mechanical characteristics slightly decrease because the additional phase reduces the compaction ability and introduces agglomerates, therefore increasing the critical flaw size. In contrast, in situ crystallization of β-spodumene allows enhancing both strength and toughness values, indicating that the well dispersed alumino-silicate phase favours reinforcement mechanisms. In addition, as β-spodumene formation, which takes place at a lower temperature than the vitrification process, consumes large quartz amounts, uncracked samples can be obtained using fast firing conditions.

2. INTRODUCTION

In unglazed floor tiles, the major crystallized phase is usually mullite (3 Al_2O_3. $2SiO_2$) even if the precipitation of secondary phases can also take place (anorthite, sapphirine, ...) as a result of the presence of various oxides (CaO, MgO,...) in the global composition. Such crystalline phases are characterized by higher Young's modulus (E) and hardness (Hv) compared to those of the surrounding glassy phase.

In addition, the dispersed crystalline population gives rise to an increase of the crack growth resistance of the tiles with, as a consequence, an improvement of their wear resistance. According to this principle, several authors [1, 2] have focussed their attention on the kinetic of mullite crystallization as a function of the Al_2O_3/SiO_2 ratio and the firing conditions. However, up to now very few works refer to the study of wear reinforcement phases selected according to specific criteria such as, for instance, those outlined below :

- high hardness
- specific grain morphology allowing direct crack interaction reinforcement mechanisms
- thermal mismatch with the surrounding phases able to put the surface of the tile under compressive stresses, etc.

In this work it is proposed to enhance the wear improvement and in some cases, the mechanical properties of floor tiles either by inducing in situ-crystallization of non-conventional phases or by adding hard mineral particles into the raw mixture. Concerning the in-situ crystallization route, compositions have been adapted in order to favour the occurrence of lithium and barium compounds like for instance β-spodumene or celsian

For the former one, a previous work performed in BCRC [3] already proved that presence of spodumene in the sintered bodies leads to some improvement of both the wear resistance and the mechanical characteristics. However, due to the especially high rate of crystallization of lithium alumino silicate which in addition occur at relatively low temperature (T_c = 950 °C for the β-eucryptite which transforms into β-spodumene when increasing temperature to 1000-1050 °C), full densified materials can only be obtained after a long firing time.

In the present work, compositions were slightly modified by addition of various amounts of baddeleyite (ZrO_2) which acts as crystallization inhibitor for lithium alumino-silicate phases [4] in order to delay the spodumene formation, and therefore allow to overcome this problem of densification.

---

[1] M. Dondi, B. Fabbri, T. Manfredi and G.C. Pellacani, *Microstructure and Mechanical Properties of Porcelainized Stoneware Tiles,* Fourth Euro-Ceramics - Vol. 11, pp 319-26, Ed. C. Palmonari, Pub. Gruppo Editioriale Faenza Editrice S.p.A. - Italy (1995)

[2] L. Barbieri, L. Bonfatti, AM. Ferrari, C. Leonelli, T. Manfredi and D. Settembre, *Relationship Between Microstructure and Mechanical Properties in Fully Vitrified Stoneware,* Proc. 8th Cimtec, World Ceramic Congress, Firenze - Italy, 28 june-4 july 1994.

[3] J. Tirlocq, P. Descamps, M. Deletter and F. Cambier, *Wear Resistant Floor Tiles Composition obtained by the Crystallization of Lithium Compounds,* Proc. of the 6th Conf. of the EcerS, Extended Abstracts - Vol. 2, pp 317-318, Pub. University Press - Cambridge - UK (1999)

[4] J.Y. Hsu and R.F. Speyer, *Influences of Zirconia and Silicon Nucleating Agents on the Devitrification of* Li_2O-Al_2O_3-6.SiO_2 *Glasses,* J. Am. Ceram. Soc., 73 (12), pp 3585-3593 (1990)

For the mineral route (the 2nd one), the research work started with corundum addition, this phase being introduced into the bulk composition in various amounts and grain size ranges. In a second stage, other mineral phases, especially selected for their hardness (mullite, zircon, spodumene, andalusite, spinel, olivine) were incorporated into the raw mixture.

In all the cases, the experimental study was focussed on the thermal compatibility, the cohesive strength at the boundary and the chemical inertness of the reinforcement phase with respect to the matrix. With the purpose of reducing production costs, two-layer floor tiles were fabricated in plant. These tiles, whose reinforcement phase addition was limited to the top layer, were carefully analyzed in order to detect if any kind of damage such as excessive strain mismatch, spalling or interface delamination occurred during the sintering process.

3. RESULTS AND DISCUSSION

3.1. 1ST ROUTE : IN SITU CRYSTALLIZATION

3.1.1. β-spodumene formation

3.1.1.1. Composition optimization

In a previous work [3], it has been demonstrated that even without nucleating agents (ZnO, TiO_2,...), the crystallization rate of β-spodumene remains very fast, therefore increasing the matrix viscosity. In addition, β-spodumene grains, due to their particular shape [5, 6] tends to favour at relatively low temperature the formation of a stiff network counteracting any further shrinkage. As a consequence, densified materials can only be achieved after very long soaking time (10 hours), even when fluxing agent content is increased. In order to overcome this problem, various amounts of baddeleyite were added (1, 2 and 3 wt/%) to the raw mixture (table 1), taking into account that this mineral lowers the rate of formation of the lithium alumino-silicate compounds.

Components	SiO_2	Al_2O_3	Li_2O	MgO	K_2O	Na_2O	CaO	Others	SiO_2/Al_2O_3 ratio
Content %	71.9	18.6	2.8	2.7	2.4			1.6	≈ 3.9

Table 1. *Composition of the raw mixture favourable the β-spodumene crystallization*

The green compacts, obtained by uniaxial pressing (400 kg/cm^2) were sintered in the 1000-1150 °C temperature range, keeping the same temperature increase rate as previously : 1.4 °C/min but, selecting a shorter soaking time, i.e. 1 or 2 hours. As illustrated by figure 1, which refers to a soaking time of 1 hour, the increase in ZrO_2 content leads, above 1100 °C, to density values which are at least equal to those

---

[3] J. TIRLOCQ, P. DESCAMPS, M. DELETTER AND F. CAMBIER, *Wear Resistant Floor Tiles Composition obtained by the Crystallization of Lithium Compounds,* Proc. of the 6th Conf. of the EcerS, Extended Abstracts - Vol. 2, pp 317-318, Pub. University Press - Cambridge - UK (1999)

[5] P. VOMACKA, O. BABUSHKIN AND R. WARREN, *Zirconia as Nucleating Agent in a Yttria-Alumina-Silica Glass,* J. Eur. Ceram. Soc., 15, pp 1111-1117 (1995)

[6] R. RAJ AND C.K. CHYUNG, *Solution-Precipitation Creep in Glass Ceramics,* Acta Metall., 29, pp 159-166 (1981)

corresponding to the previous long firing conditions. As expected, this improvement of the sintering process complies with the fact that lithium alumino-silicate phase formation is actually delayed (figure 2a).

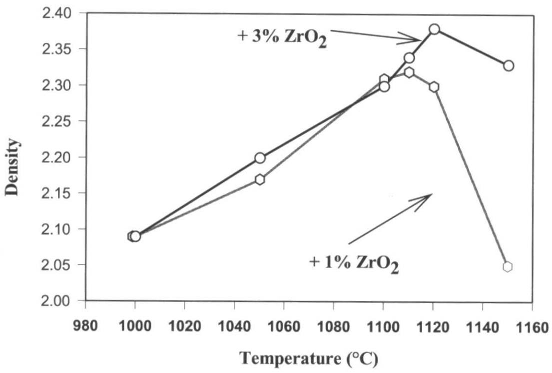


Figure 1. *Effect of ZrO_2 content on densification ability of the Li_2O containing composition reported in table 1*

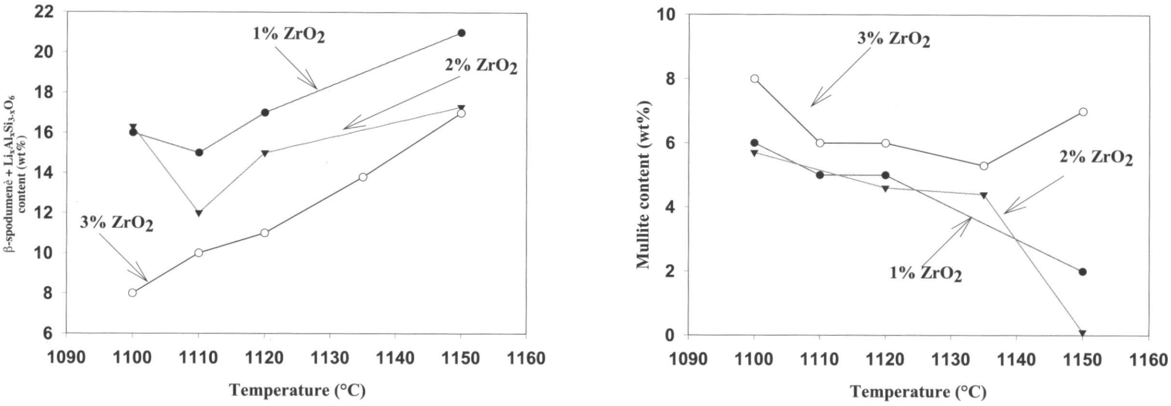


Figure 2. *Effect of ZrO_2 addition on crystallization of (a) Li alumino-silicate phases - (b) mullite (composition reported in table 1)*

As the formation of those phases consumes both Al_2O_3 and especially SiO_2, their crystallization necessary occurs at the expense of the mullite formation.

Thanks to baddeleyite addition, it is therefore possible to enhance the final mullite content (figure 2b) which also acts as reinforcement phase for ceramic tiles and can obviously takes place in the improvement of the wear behaviour.

3.1.1.2. Mechanical properties and wear measurement

Mechanical characterization and wear measurement were restricted to fired bodies containing 2 and 3 wt% in ZrO_2* and with the highest density values. The Young's modulus (E), the flexural strength (σ_F) and the toughness (K_{IC}) as well as the deep abrasion resistance (measured according to EN 102 standard) of the selected materials are included in table 2.

For all the improved compositions, the σ_F and K_{IC} values are higher than those corresponding to a commercial material (taken as reference). The E values also appear especially high, that can be considered as a consequence of both the higher density and cristallinity levels.

ZrO_2 content M	Firing conditions	Bulk density	E (GPa)	σ_F (MPa)	K_{IC} (MPa$\sqrt{m}$)	Wear volume (mm^3)
2 wt %	T = 1120 °C – 1h	2.36	64	66	1.32	111.4
	T = 1120 °C – 2 h	2.33	64	67	1.36	118.6
	T = 1135°C – 1 h	2.32	64	72	1.43	111.4
3 wt %	T = 1100 °C – 2 h	2.34	61	63	1.09	147.2
	T = 1110 °C – 1 h	2.34	62	58	1.17	129.3
	T = 1110 °C – 2 h	2.35	63	58	1.23	126.9
	T = 1120 °C – 1 h	2.38	65	58	1.27	112.8
	T = 1120 °C – 2 h	2.37	65	66	1.19	111.4
	T = 1135°C – 1 h	2.36	67	78	1.46	115.7
	T = 1135 °C – 2 h	2.28	64	72	1.35	127.7
	T = 1150 °C – 1 h	2.31	67	74	1.37	110.0
Reference	T = 1200 °C – 1 h	2.40	62	57	1.18	123

Table 2. *Bulk density, mechanical properties and abrasive wear measured on β-spodumene reinforced materials containing 2 and 3 wt % in* ZrO_2

In spite of very similar density values, it must be pointed out that toughness and, to a lesser extent, Young's modulus and strength tend to slightly increase when the sintering temperature is increased. This is very likely due to the fact, that, once the densification process is complete, crystallization and growth of β-spodumene grains can still proceed, increasing the total amount in reinforcement phases. In addition to their high mechanical properties, the samples obtained from the new compositions mostly present a reduced wear volume compared with this of the reference material (up to 10 % reduction in the most favourable case).

3.1.1.3. Attempts towards fast firing conditions

Taking into account the larger quartz consumption as a result of lithium aluminosilicate phase formation, it can reasonably be assumed that the deleterious α-β phase transformation [7], which occurs during cooling down can be minimized.

Therefore, the following faster sintering conditions have been adopted.

Temperature increase rate : 10 °C/min
Sintering temperature : 1150 °C
Soaking time : 30 min
Cooling down rate : 10 °C/min

The following table summarizes the density and porosity values as well as the mineralogical analysis of samples containing various amounts of ZrO_2 and fired according to the above accelerated conditions.

Additional ZrO_2 content (wt%)	Bulk density	Porosity (%)	Amount of reinforcement phase (wt%)	
			Mullite	β-spodumène+$Li_xAl_xSi_{3-x}O_6$
1	1.92	19.2	-	33
2	2.35	0.13	5	12
3	2.38	0.08	6	14

Table 3. *Physical and mineralogical analysis of samples obtained using faster sintering conditions (composition reported in table 1).*

---

[7] C.A. JOUENNE, *Traité de Céramiques et Matériaux Minéraux,* Pub. Editions Septima-France (1979).

Additional ZrO_2 content	E (GPa)	σ_F (MPa)	Wear volume (mm^3)
2	68 ± 1	79 ± 4	139-147
3	69 ± 1	86 ± 7	123-131

***Table 4.** Mechanical characteristics and abrasive wear measured on the densest samples obtained using faster sintering conditions (composition reported in table 1)*

From examination of table 3, it is clear that there is a threshold ZrO_2 content to get a hindering effect on lithium alumino-silicate phases formation since only the 1 wt % ZrO_2 material is far from being completely densified.

The mechanical properties as well as the wear volumes of the densest bodies, reported in table 4, clearly emphasize that the E and σ_F values are even higher than those measured on samples sintered using a longer firing cycle (see table 2). However, as a consequence of their lower content in crystalline phases (i.e. mullite and spodumene), their wear behaviour is not improved compared with the reference material. Nevertheless, it must be pointed out that those values remain quite acceptable especially in comparison with those of most fast fired products commercially available.

3.1.2. Celsian formation

Taking into account the phase diagram $BaO-SiO_2-Al_2O_3$ [8], celsian as well as mullite formations require a high Al_2O_3/SiO_2 ratio compared with the composition intended for β-spodumene crystallization. Such high ratio could give rise to an increase of the sample refractoriness unsuitable for obtaining high density levels. However, the dilatometric curve shown at figure 3 proves that densification starts at relatively low temperature (T < 900 °C) very likely due to the presence of BaO acting as additional fluxing agent before celsian crystallization occurs.

After the densification onset, the dilatometric curve does not display any particular feature indicating that the shrinkage process is slowed down by the reinforcement phase formation or by progressive depletion in Al_2O_3 and SiO_2 .

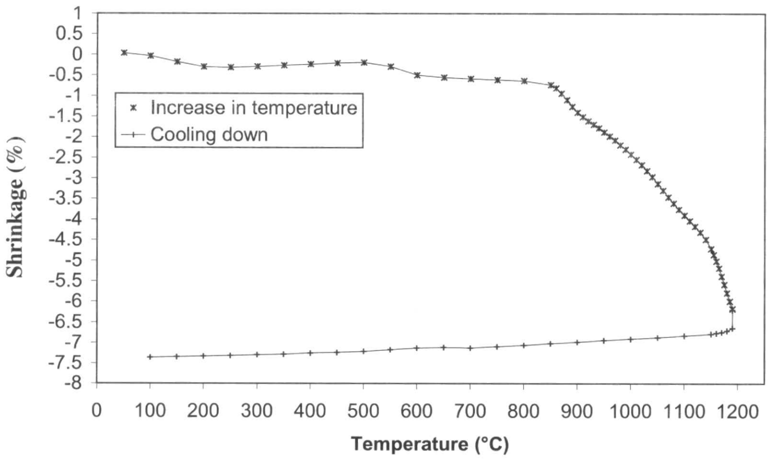


***Figure 3.** Dilatometric curve of an Al_2O_3 rich composition (ratio $Al_2O_3/SiO_2 \cong 0.41$) favourable to celsian crystallization.*

---

[8] E. LEVIN, C.R. ROBBINS AND H.F. MURDIE, *Phase Diagrams for Ceramics*, Pub. The Am. Ceram. Soc. - USA, fig. 556, p 195 (1964)

On the basis of these promising results, samples have been prepared from a high Al_2O_3 content composition (table 5), with the aim to crystallize celsian as main reinforcement phase. According to literature, in addition to BaO, small amount of calcium fluoride has been incorporated into the raw mixture in order to favour celsian formation at the expense of β-hexacelsian [9, 10]. Precisely, this last phase must be avoided as it undergoes around 300 °C a reversible phase transformation (with a volume expansion of about 4 %) which is necessary deleterious [11, 12]. On the basis of dilatometric curve, the green bodies were sintered at 1175 and 1200 °C, respectively while keeping the 1 or 2 hours soaking time.

Component	Content (wt%)
SiO_2	60.8
Al_2O_3	27.8
MgO	0.7
TiO_2	1.2
K_2O	1.5
Na_2O	0.7
CaO	1.0
BaO	4.1
CaF_2	0.5
Others	1.7
SiO_2 / Al_2O_3 ratio	2.19

Table 5. *Raw mixture intended to favour celsian formation.*

Firing conditions	Bulk density	% of theoretical density	Porosity (%)	Mineral phase content (wt%)				
				α-Quartz	Mullite	Celsian	Cristobalite	Al_2O_3
1175 °C 1h	2.45	91	0.29	9	20	7	< 1	-
1175 °C–2h	2.46	91	0.12	8	18	5	-	2
1200 °C–1h	2.48	92	0.05	6	19	5	-	-
1200 °C–2h	2.47	92	0.03	5	17	3	-	2
1175 °C–1h	2.44	92	0.82	10	14	Traces	-	-
1175 °C–2h	2.49	93	0.12	12	20	4	-	2
1200 °C–1h	2.51	94	0.04	11	15	traces	-	2
1200 °C–2h	2.50	94	0.04	9	15	traces	-	2

Table 6. *Physical and mineralogical characteristics of celsian reinforced samples (composition reported in table 5)*

As shown by the values reported in table 6, the measured bulk densities are high and the open porosity values appear very low (< 0.3 %).

In addition, RX diffraction data confirm that the fired samples effectively contain celsian even if :

- first, the measured content is lower than the expected one (theoretical value = 10 %)
- secondly, the amount of barium alumino-silicate phase decreases when increasing either the soaking time or the firing temperature.

---

[9] M.C.G. VILLAR, C.G MONZONIS AND J.A. NAVARRO, *Reactions Between Kaolin and Barium Carbonate : Influence of Mineralizers-1. Quantitative Study,* Trans. J. Br. Ceram. Soc., 82, pp 69-72 (1983)

[10] C.H. DRUMMOND, W.E. LEE, N.P. BANSAL AND M.J. HYATT, *Crystallization of a Barium-Aluminosilicate Glass,* Ceram. Eng. Sci. Proc., 10 (9, 10), pp 1485-1502 (1989).

[11] H.C. LIN AND W.R. FOSTER, *Studies in the System BaO-Al_2O_3-SiO_2 - I. The Polymorphism of Celsian",* The Am. Miner., 53, pp 134-144 (1968)

[12] W.E. LEE, M. CHEN AND P.F. JAMES, *Crystallization of Celsian ($BaAl_2SiO_8$) Glass,* J. Am. Ceram. Soc., 78 (8), pp 2180-86 (1995)

Afterwards, the mechanical properties and the wear resistance have been determined (table 7). But, at the opposite to β-spodumene reinforced materials, even if the strength and the Young's modulus reach quite high values, the wear volume appears in all the cases larger than that of the reference material. Such a decrease of the wear resistance could be associated with the lower hardness of celsian ($H_{mohs} \approx 6$) compared with that of mullite ($H_{mohs} \approx 7$), whose content is lower than for the reference material (≈ 30 %) and/or to a lack of cohesion at the interface celsian grain/matrix, which favours grain pull out phenomenon during the abrasive test.

Firing conditions	σ_F (MPa)	E (GPa)	Wear volume (mm^3)
1175 °C – 1 h	80	-	151
1175 ° C – 2 h	80	-	159
1200 °C – 1 h	73	67	158
1200 °C – 2 h	81	-	159
Reference material 1200 °C – 1 h	57	62	123

Table 7. *Mechanical properties and abrasive wear measured on celsian reinforced bodies (composition reported in table 5)*

3.2. 2ND ROUTE : HARD MINERAL PARTICLE ADDITION

As already mentioned, the work is dealing with α-Al_2O_3 (corundum) addition into an industrial clay/feldspar raw mixture which is usually used to prepare the reference material. In a second stage, the study was extended to the following alternative phases : mullite, zircon, olivine, spinel, andalusite, spodumene, while keeping the same grain size range as this allowing to obtain the best results for corundum reinforced materials.

3.2.1. α-Al_2O_3 additives

Various amounts (5, 10, 15 wt %) of sieved α-Al_2O_3 powders, with different grain size ranges (40-106, 140-200, 200-250 μm) were incorporated into the raw mixture and the so obtained green bodies sintered in the same conditions as those used in plant for the reference material (increase in temperature and cooling down: 1.4 °C/minute, sintering temperature: 1200 °C, soaking time 1 hour). Additional firing tests with a longer soaking time (2 hours) were also carried out in order to counteract the possible hindering effect of the mineral on the densification process. After firing, most samples appear well densified for both soaking times, even if the measured densities deviate from the theoretical values when the corundum content increases.

Conversely to what was expected, the densification process is not completed for the finest α-Al_2O_3 grain range (40-106 μm) only (figure 4). This effect must be imputed to the higher number of grains for a same amount of reinforcement phase which lowers the distance from particles to particles. As a consequence, particles interaction reduces mixture compaction ability and, possibly, the vitrification process itself.

Otherwise, as proved by XRD measurements (table 8), corundum neither solves into the glassy phase nor affects mullite crystallization, whatever the grain size used.

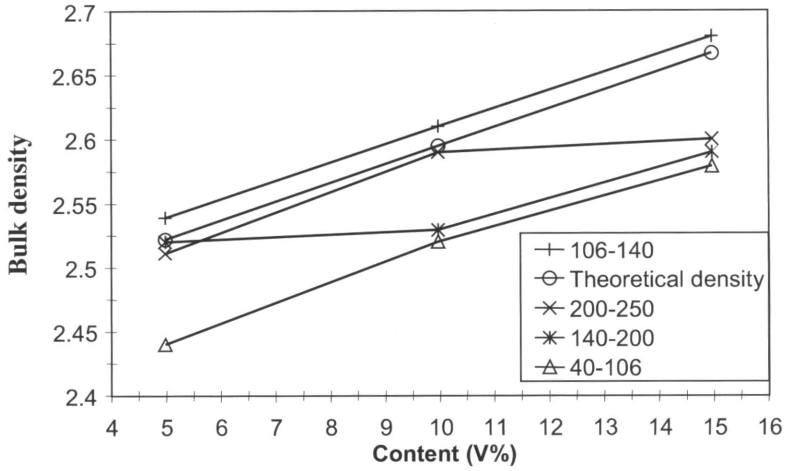


Figure 4. *Bulk density as a function of the* α-Al_2O_3 *content for various grain size ranges*

Granulometric range	Amount in α-Al_2O_3 phase added (wt%)	Mineral phase analysis (wt%)				Linear shrinkage (%) *
		Al_2O_3	α-quartz	Mullite	Cristobalite	
40-106 μm	5	4	15	18	2	7.3
	10	9	16	19	2	7.3
	15	13	13	16	1	6.8
106-140 μm	5	5	15	19	1	7.4
	10	8	14	20	3	7.6
	15	15	14	15	1	6.4
140-200 μm	5	5	16	20	1	7.3
	10	9	16	19	2	7.7
	15	13	13	17	1	6.8
200-250 μm	5	4	16	20	1	7.4
	10	8	15	18	1	6.6
	15	17	13	15	1	6.4

* value of a reference material (sample without additional phase) : 7.6 %

Table 8. *XRD analysis and shrinkage during sintering of* α-Al_2O_3 *containing samples (T = 1200 °C, t = 2 h).*

Especially for the smallest grain size range, the shrinkage resulting from the sintering stage is very similar to that of the reference material, independently of the alumina content. It is the same for larger grain sizes (106-140 and 140-200 μm) provided that the Al_2O_3 amount does not exceed 10 wt %. A very similar shrinkage level for materials containing mineral loads to the reference one is particularly interesting with regard to the manufacture of floor tiles, whose reinforcement phase is limited to the top layer. In such conditions, indeed delamination effect could be avoided. Moreover, even if in some cases, some surface stresses could be induced as a consequence of the slightly lower shrinkage of the α-Al_2O_3 containing surface layer, they are compressive in nature and could therefore even give rise to some strength improvement. The wear behaviour has been determined on fired bodies issued from all the tested compositions (always according with the EN 102 standard) whereas the mechanical properties have been measured on those whose mineral grain size corresponds to the following range : 106-140 μm.

The results obtained are reported in tables 9 and 10. Except for the samples containing the finest α-Al_2O_3 powder (40-106 μm), i.e. those having the lowest relative bulk density values, a significant reduction of the wear volumes can be observed compared with that of the reference material.

Granulometric range	α-Al_2O_3 content (wt %)	Wear volume (mm^3)	Wear reduction (%)	Wear volume (mm^3)	Wear reduction (%)
		T=1200°C - t=1h		T=1200°C - t=2h	
Reference	0	117	-	117	-
40-160 µm	5	136	-	109	7
	10	127	-	114	3
	15	114	≈ 3	107	9
106-140 µm	5	116	≈ 1	106	9
	10	99	≈ 15	101	14
	15	121	-	110	6
140-200 µm	5	101	≈ 14	104	11
	10	105	≈ 10	102	13
	15	109	≈ 7	109	7
200-250 µm	5	104	≈ 11	101	14
	10	116	≈ 1	102	13
	15	123	-	114	3

Table 9. *Abrasive wear volumes measured on fired bodies whose the α-phase was incorporated in various amounts and grain size ranges*

α-Al_2O_3 (wt %)	Soaking time (h)	E (GPa)	σ_F (MPa)
5	1	76	88
10	1	75	74
15	1	75	62
5	2	75	83
10	2	78	85
15	2	75	65

Table 10. *Mechanical characteristics of fired bodies whose α-Al_2O_3 grain size ranged between 106 and 140 µm*

It must be pointed out that for coarser corundum grains, an increase of the soaking time (from 1 to 2 hour) allows to improve the wear behaviour especially for phase contents equal or upper than 5 wt %. Concerning the mechanical characteristics, the Young's modulus is relatively unaffected by α-Al_2O_3 addition as a consequence of the high degree of densification obtained whereas the modulus of rupture values only drop for the largest phase content (15 wt %). Nevertheless, σ_F values are in all cases very high as a consequence of a careful control of the process, at the laboratory scale.

Microstructural observations (by SEM) have been performed on samples having the largest alumina amount in order to highlight possible cracks formation, especially around neighbouring grains. These observations confirm that the cohesive strength at the grain/matrix interface is very likely strong as no particle pull out resulting from samples polishing occurred and the α-Al_2O_3 phase can not be distinguished from the matrix on secondary electron image (SEI).

Back scattered electron micrographs (Compo mode) on which corundum grains are revealed do not present an especailly higher level of cavitation near the grain/matrix boundaries (figure 5) and furthermore, no crack formation or density gradient can be observed around contiguous grains (figure 6).

Those microstructural features are in agreement with the better wear resistance resulting from corundum addition as well as with the low grain pull out in the wear tracks.

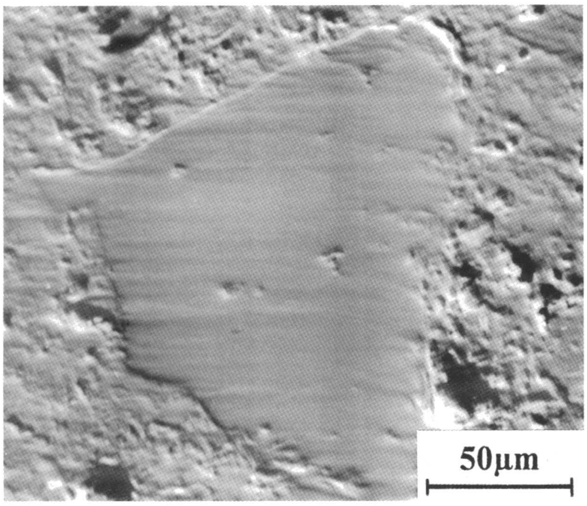


Figure 5. *BSE micrograph of a single α-Al_2O_3 grain.*

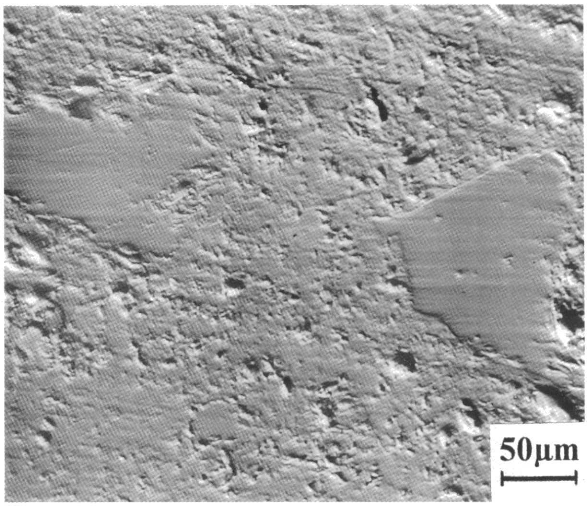


Figure 6. *BSE micrograph showing no microcrack or density gradient around continuous α-Al_2O_3 grains*

3.2.2. Alternative phases addition

The other possible reinforcement phases previously mentioned have been introduced into the same commercial raw mixture as for α-Al_2O_3 addition. According to the results obtained for this latter mineral, the 106-140 µm grain size range was selected. In order to easily compare the reinforcement ability of phases varying in density, their content has been expressed in volume % (in place of wt %) and corresponds to 3.36, 6.83 and 10.43 vol%, respectively.

Once sintered in the same conditions as for α-Al_2O_3 reinforced materials, the samples were fully characterized. Whereas for zircon addition (figure 7), the densities are close to the theoretical values, additions of sintered mullite, andalusite and α-spodumene (natural phase) rather tends to hinder densification; the effect being still enhanced when the amount in such minerals becomes higher (figure 8). For other phases (spinel and olivine), even if deviation from theoretical densities is extended compared with zircon addition, the values reached remain nevertheless reasonably good.

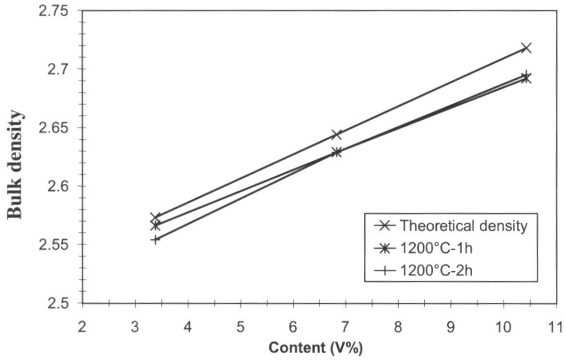


Figure 7. *Bulk density as a function of the zircon content for the 106-140 µm grain size range*

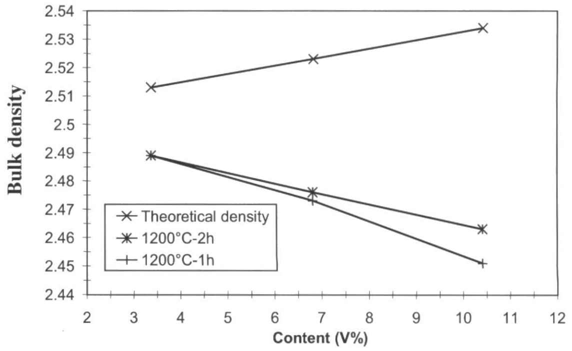


Figure 8. *Bulk density as a function of the sintered mullite content for the 106-110 µm grain size range (a same variation was observed for andalusite and (β–spodumene)*

According with SEM observation, the lack of densification for both mullite and andalusite can be attributed to the grain shape (sharp edges) which reduces compaction ability with as consequence lower green densities. Indeed, as shown on SEM micrographs, porosity is preferentially located in the neighbour of grains of the reinforcement phase (indicated by arrows in figure 9) and still increases in areas where phase dispersion is less homogeneous (figure 10).

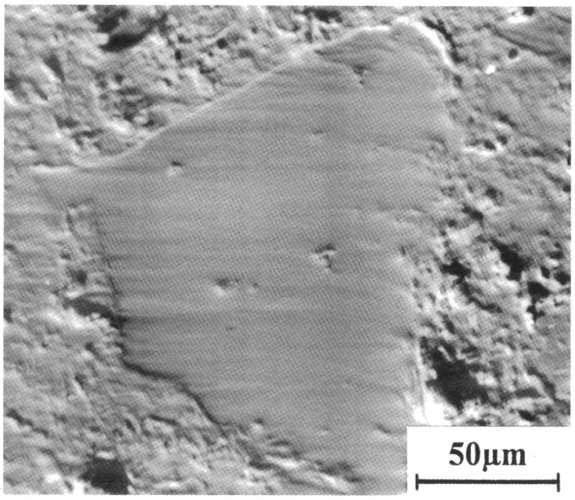
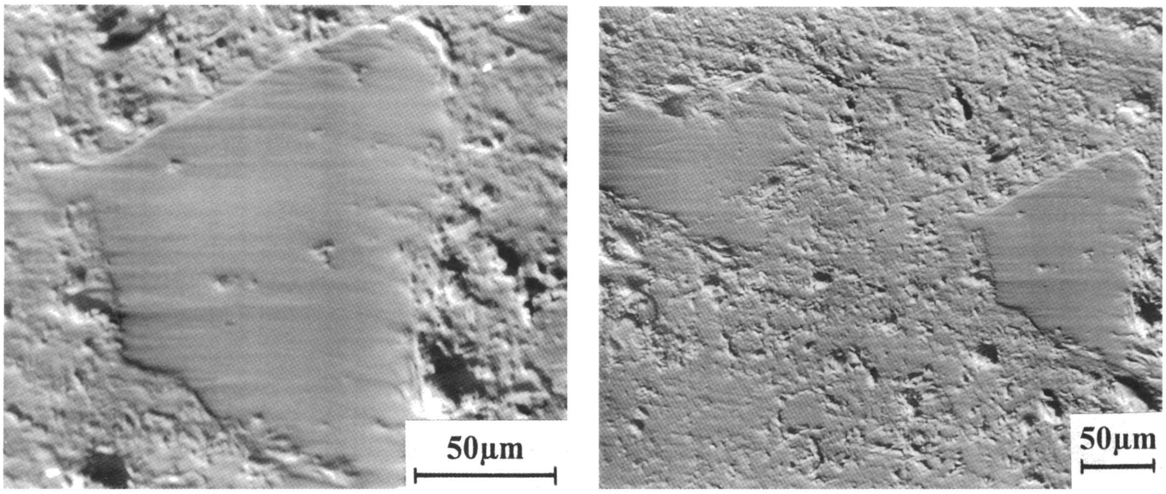


Figure 9. *BSE micrograph of the microstructure of a sample containing andalusite as additional phase.*



(a) (b)

Figure 10. *Agglomerate inside a sample containing andalusite : (a) BES micrograph - (b) corresponding EDX image (Al)*

At the opposite, for α-spodumene containing samples, the low bulk densities are mainly due to the α-β phase transformation which occurs during firing as its associated volume expansion induces microcracking, of the transformed grains mainly.

For mullite containing samples, the problem has been overcome by using a fused powder in place of a sintered one. In addition to the improvement of the densification process mullite content of the fired bodies appears larger due to the lower reactivity of the fused grade, therefore reducing its solubility into the glassy phase. Concerning spodumene, by applying a preliminary annealing treatment, powder has been introduced under its β form in the raw mixture which allows to avoid the deleterious effect of the phase transformation.

The mechanical characteristics of the various sintered samples are summarized in table 11. In this table, are also reported the wear resistance of those having the highest densities and strength values.

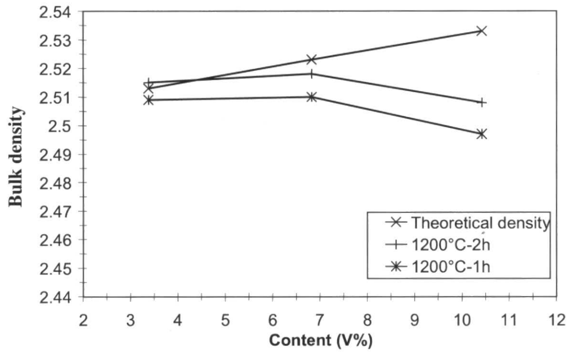


Figure 11. *Bulk density as a function of the fused mullite content for the 106-110 µm grain size range.*

In this table, the wear has only been expressed in term of reduction, compared with the reference material,. because its wear volume, checked for each composition, is not completely stable.

Reinforcement phase	Soaking time (h)	Phase content (vol %)	Linear Shrinkage (%)	E (GPa)	σ_F (MPa)	Wear reduction (%)
Zircon	1	3.36	7.2	73	74	3
Zircon	1	6.83	6.8	73	68	not improved
Zircon	1	10.43	6.2	72	55	-
Zircon	2	3.36	7.2	74	77	not improved
Zircon	2	6.83	7.0	74	65	not improved
Zircon	2	10.43	6.4	73	54	-
β-Spodumene	1	3.36	6.7	71	82	not improved
β-Spodumene	1	6.83	6.0	69	83	not
β-Spodumene	1	10.43	5.2	69	78	–
β-Spodumene	2	3.36	6.8	72	79	5
β-Spodumene	2	6.83	6.1	69	78	not improved
β-Spodumene	2	10.43	5.2	67	71	-
Spinel	1	3.36	7.1	72	71	not improved
Spinel	1	6.83	7.0	73	66	not improved
Spinel	1	10.43	6.2	74	63	-
Spinel	2	3.36	7.2	74	76	5
Spinel	2	6.83	6.8	73	68	4
Spinel	2	10.43	6.3	75	68	-
Fused Mullite	1	3.36	7.2	74	83	not improved
Fused Mullite	1	6.83	6.7	70	77	not improved
Fused Mullite	1	10.43	6.2	67	63	-
Fused Mullite	2	3.36	7.1	76	84	6
Fused Mullite	2	6.83	6.7	75	77	2
Fused Mullite	2	10.43	6.3	71	69	-
Andalusite	1	3.36	7.3	76	88	5
Andalusite	1	6.83	6.7	68	61	-
Andalusite	1	10.43	6.2	65	57	-
Andalusite	2	3.36	7.2	73	85	9
Andalusite	2	6.83	6.8	68	64	-
Andalusite	2	10.43	6.2	64	57	-
Olivine	1	3.36	7.2	72	82	-
Olivine	1	6.83	6.7	66	60	-
Olivine	1	10.43	6.4	63	54	–
Olivine	2	3.36	7.2	71	71	–
Olivine	2	6.83	6.7	66	64	–
Olivine	2	10.43	6.5	60	44	–

Table 11. *Shrinkage during densification, mechanical, properties and wear resistance of samples containing various amounts of alternative phase (sintering T° : 1200°C).*

In most cases (spinel, zircon, mullite, annealed spodumene), E values do not significantly change in spite of the increase in additional phase content. At the opposite, the strength slightly decreases, proving that large grains or agglomerates of the reinforcement phase enhance the critical flaw size.

Especially for andalusite and olivine, a decrease of both the E and σ_F values as a function of the phase content can be emphasized. For the former one, the drop of the mechanical properties can be explained by the lower compaction ability of the powder mixture, whereas for olivine it is rather due to a phase decomposition at elevated temperature. Indeed, according with literature [13], at high temperature olivine transforms into smaller forsterite grains linked between them by a partly microcracked low strength glassy phase (figure 11).

Taking into account the mechanical properties values, deep abrasion tests have been carried out on the best materials, i.e. those containing 3.36 and 6.83 vol% of minerals. Even if in some cases, an improvement can be obtained compared with the reference material, it is nevertheless obvious that its extent remains lower than for alumina-reinforced bodies (see table 9).

3.2.3. Fabrication of two layer floor tiles in plant

Two layer floor tiles (30 x 30 cm), whose reinforcement phase (α-Al_2O_3) was only introduced into the top layer, were fabricated in plant (figure 12a).

Based on the recorded mechanical characteristics and levels of wear reinforcement, the following compositions have been selected (table 12).

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Content in raw feldspar/clay mixture	100	95	90	90	95	90
Content in unsieved α-Al_2O_3 powder (<200μm)	0	5	10	0	0	0
Content in α-Al_2O_3 : size range : 106-140 μm	0	0	0	10	0	0
Content in α-Al_2O_3 : size range : 140-200 μm	0	0	0	0	5	10

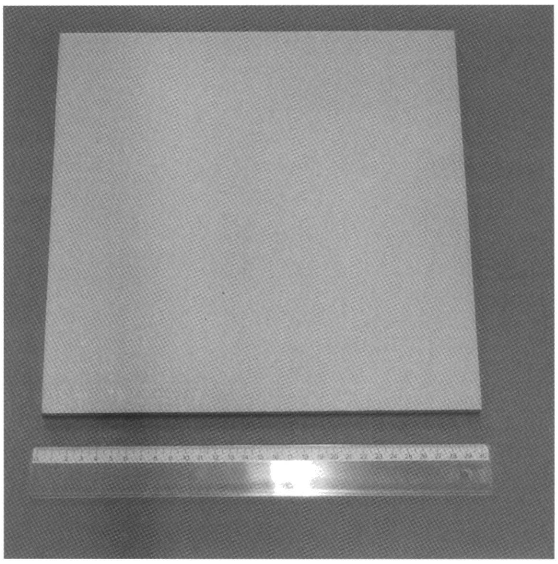
Table 12. *Compositions of the two-layer floor tiles fabricated in plant (thickness of the top layer ≅ 4 mm)*

Tiles containing the as-received industrial powder have also been prepared taking into account that this powder exhibits a relatively large mean grain size (≈ 70 μm) and only 10 vol% of grains smaller than 30 μm. Indeed, even if in this case, the reinforcement can be presumed to be lower, the fabrication costs can be reduced by suppressing the sieving or the elutriation stage.

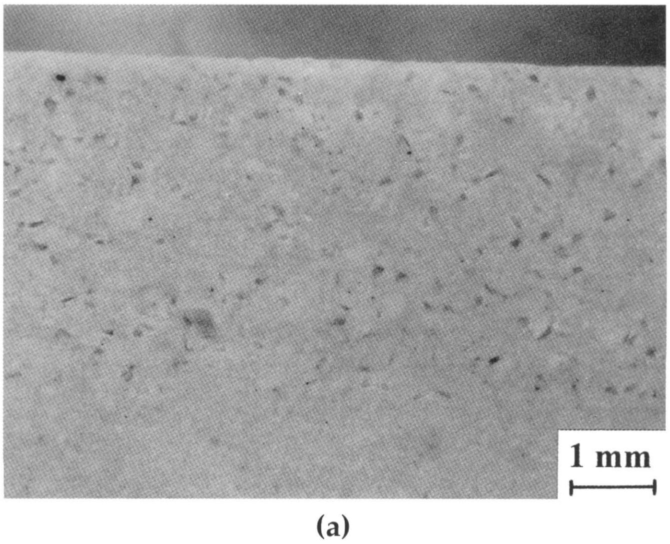
---

[13] J. Tirlocq, W. Pasek and M. Colson, *Etude Comparative de deux Silicates de magnésium, la Dunite et l'Olivine, en tant qu'Agents d'Eliminations du Potassium en Haut Fourneau,* Silicates Industriels, 1-2, pp 15-24 (1992)

For all the fired tiles, no particular strain or microcracking at the interface between the two layers (top and main) can be observed in spite of the large size of the tiles and of a little thermal expansion discrepancy between the layers (figure 12b).



(a)



(a)

Figure 12. *Two layer floor tiles fabricated in plant : (a) large size floor tile containing 10 wt% of* α-Al_2O_3 *(range 140-200 µm) in its top layer - (b) cross section of the same tile showing no delamination effect.*

However, at the opposite to the laboratory samples, no significant wear improvement can be obtained. This difference can very likely be imputed to both the lower pressing load (350 in place of 400 kg/cm^3) and to the lower sintering temperature (1180 in place of 1200 °C) adopted in plant. At present time, complementary tests using more suitable processing conditions are performed in collaboration with our industrial partner.

It must be noted that for the others minerals additions, the shrinkage of samples containing low and intermediary phase contents is closer to this of the reference material, that also allows to foresee the industrial fabrication of free of defect two layer tiles.

4. CONCLUSION

The purpose of the present work was to improve both the wear resistance and the mechanical characteristics of floor tiles, either by inducing in-situ crystallization of lithium and barium alumino-silicates or by adding hard mineral particles (corundum, spinel, mullite, andalusite, spodumene, zircon, olivine) into the raw mixture.

Concerning the former route, best results were obtained for β-spodumene reinforced materials prepared starting from compositions containing larger amounts in baddeleyite (2 and 3 wt%). Indeed, for such compositions, lithium alumino-silicates phases formation is found to be delayed, therefore allowing to reach high densification levels. Due to the joint formation of mullite and β-spodumene, the fired samples exhibit higher mechanical properties (σ_F, K_{IC}, E) as well as an improved wear resistance compared with a reference material.

In addition, when β-spodumene formation takes place, most of the quartz initially present in the raw mixture is consumed, therefore allowing to fasten firing conditions without inducing cracking or excessive strain.

In spite of the high Al_2O_3/SiO_2 ratio required to ensure celsian crystallization, dense bodies were nevertheless obtained. However, even if this mineral acts as reinforcement phase giving rise to high strength values, the wear resistance appears rather low. This is presumably due to the relatively low hardness value of this barium-alumino-silicate, whose formation occurs at the expense of mullite.

The other route, based on mineral particles addition, also leads to some improvement of the wear resistance, especially when corundum is selected as reinforcement phase.

However, following this alternative route, the σ_F values are systematically lower than for a reference material (without additional phase) because large mineral grains or agglomerates necessarily increase the critical flaw size.

Always compared with the reference material, the shrinkage does not seem markly hindered by mineral addition therefore, allowing to foresee two layers tiles fabrication whose mineral phase addition is restricted to the top layer.

Indeed, free of defect tiles (like for instance spalling, large strain or delamination at the presumed weakly stressed interface between the main and the top layer), have been successfully processed and sintered in plant.

ACKNOWLEDGEMENT

The authors thank the Ministry of Economic Affairs, the Brussels, Walloon and Flemish Regions for funding this work.