CRACK PATHS AND TOUGHENING MECHANISMS IN STEEL-PORCELAIN STONEWARE CERAMIC MATRIX COMPOSITES

G. Pellicelli[(1)], L. Esposito[(2)], E. Rambaldi[(2)], A. Tucci[(2)]

[(1)]Granitifiandre S.p.A., Castellarano (RE), I.
[(2)]Centro Ceramico Bologna, Bologna, I.

ABSTRACT

The introduction of the Double Charge Technology (DCT) can be considered one of the most important technological contributions to the aesthetics of the working surface of porcelain stoneware tiles. The shaping process allows, without involving the ceramic body below, to realize surface layers with diversified aesthetic content, saving a consistent amount of more expensive raw materials. Porcelain stoneware tiles with a layer containing a 2.4wt% of stainless-steel powder were recently produced by DCT, conferring to the working surface a peculiar aesthetic effect.

The work reports the results of an extensive microstructural SEM observation aimed to analyse the interface stainless-steel particles-ceramic matrix and clarify the role of the metal in the material behaviour and the reinforcing mechanisms. In this framework, particular attention was put both on the deflection and trapping of the cracks and the yielding of the metal particles. The results represented the input to explain the data of mechanical characterisation, i.e. fracture toughness, flexural strength and Young's modulus. Besides, to foresee the prospects of development of these innovative tiles, the investigation was extended to the preparation and characterisation of other materials manufactured with the same silicate-based ceramic matrix, but containing increasing weight percentages of the same stainless-steel powder.

1. INTRODUCTION

The requirement of reliable structural components encouraged the development of innovative materials. In this regard, advanced ceramic materials, which are particularly attractive for their intrinsic properties, found serious restrictions to intensive use in structural applications due to their low fracture resistance. The efforts produced to overcome the problem was partly crowned with success, preparing zirconia based ceramics and composite materials, reinforced with a second phase as whiskers, fibres and particles. Exploiting different and concurrent toughening mechanisms[1], significant improvements of fracture toughness were achieved. Many aspects and mechanisms were clarified, defining also some intrinsic limits to the attainable reinforcement of ceramic matrix. Recently, other developments related to the micro and nanocomposites have been pointed out[2].

Until now, in the field of ceramic tiles, few attempts were pursued to reinforce the matrix [3-5] and the research and the development of innovative materials exhibiting toughening mechanisms, are almost completely lacking. In this framework, the results obtained using as reinforcement phase short fibres were not satisfactory, due to the difficulties encountered in the preparation of the slurry and in the achievement of a good interface fibres-ceramic matrix[5]. In contrast, encouraging results for the desired increase in fracture toughness were obtained by adding second phases in form of advanced ceramic powders[6] and wollastonite fibres[7]. This solution allowed a better homogenization, consequently ensuring a good interface between second phase and ceramic matrix.

Recently, with the aim to confer to the working surface a new aesthetic effect, porcelain stoneware tiles with a surface layer containing a 2.4wt% of stainless-steel powder were produced by using the DCT. The study, dealing with the material of the surface layer as a metal-ceramic matrix composite, was addressed to investigate the dependence of the behaviour of the material on the stainless-steel particles. In order to go further into some aspects and foresee the expectations of development of these innovative tiles, the investigation was extended to the preparation and characterisation of other samples manufactured with the same silicate-based ceramic matrix and increased the weight percentages of stainless-steel powder.

Referring to the advanced materials, the metal-ceramic matrix composites on one hand exhibit higher hardness, wear resistance and stiffness than the metal introduced and on the other, higher fracture toughness, thermal and electrical properties than the monolithic ceramic matrix. This behaviour is related to the plastic deformation, i.e. the yield strength of the metal, and it was found that the toughening mechanism is governed by the percentage and dimension of the particles and the nature of the interface metal-ceramic matrix[8,9]. The toughening mechanisms depend on a good adhesion at the interface metal particles-ceramic matrix and on the characteristics of the constituent phases, in particular the linear thermal expansion and the Young's modulus. To induce a compressive stress field in the matrix the necessary condition is $\alpha_p > \alpha_m$. On the basis of these remarks, a characterisation to clarify the changes and the effects due to the introduction of the stainless-steel particles in a silicate-based ceramic matrix was undertaken. An analysis addressing the deflection of the cracks was performed, relating the results to the data obtained from the characterisation of the samples.

2. EXPERIMENTAL

The main characteristics of the powder of stainless-steel AISI 316L introduced in the products are reported in Table 1 and Table 2. In Figure 1, a micrograph of the stainless-steel powder is reported, the average particle size lies in the range 250÷600µm.

C	Si	Cr	Ni	Mo	Mn
<0.03	0.5	17	12	2.5	1.5

Table 1. Average chemical composition of the stainless-steel AISI 316L.

r (g/cm^3)	E (GPa)	R (GPa)	R_p (GPa)	* ax10^{-6}°C^{-1}
8.1	193.0	0.6	0.2	18
				*(20÷500°C)

Table 2. Physical-mechanical characteristics of stainless steel AISI 316L.

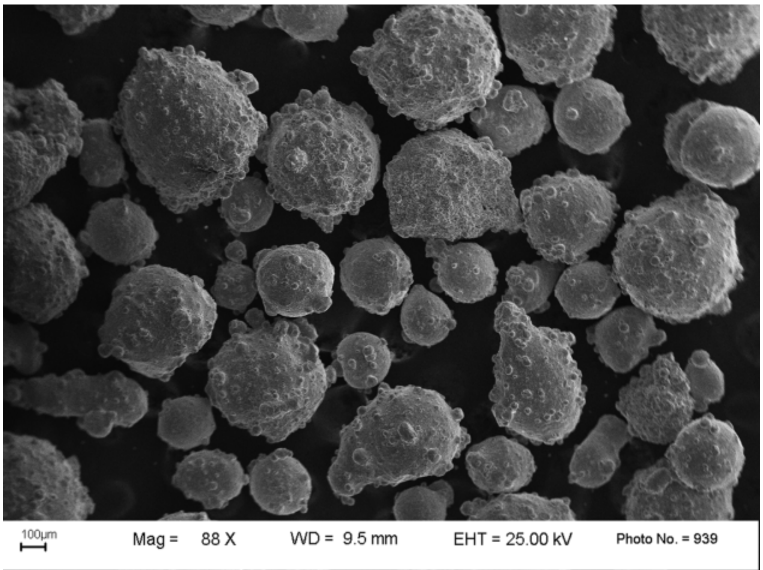


Figure 1. SEM micrograph of the stainless-steel particles.

Stoneware tiles 60x60cm, denoted DMD-BLUE, produced by DCT, with a surface layer containing a 2.4wt% of stainless-steel 316L powder were considered. Considering that the mix used for the surface layer and for the body mix were labelled BLP-94 and AZ-29, respectively, to clarify the dependence of the behaviour on the metallic powder, tiles having the same nominal size with a surface layer not containing stainless-steel powder, denoted BLP-94/AZ-29, were produced by DCT. Other tiles were manufactured using both the mix of the surface layer (the matrix material) and the mix of the ceramic body alone, called BLP-94 and AZ-29, respectively. This allowed investigation separately of the properties of the two materials and their mutual influence, when coupled. The influence related to the presence of the stainless-steel powder in the tiles was investigated, by introducing in the mix of the surface layer, increasing weight percentages of stainless-steel powder, 2.4, 4.8, 7.2 and 32.0 denoted in the following Mix 1, Mix 2, Mix 3 and Mix 4, respectively. With these mixes, tiles of the same nominal size and thickness were produced and characterised. It has to be noted that the working surface of all the tiles expressly produced for the present investigation was subjected to polishing, by an industrial machining line.

Flexural strength, σ, and elastic modulus, E, were measured by subjecting to 3-point, specimens cut from the tiles, in form of rectangular bars 80.0x16.0x8.5mm, using an universal machine (10/M, MTS, USA), equipped with a bending fixture 60mm rollers span L, adopting a crosshead speed of 5.0mmmin^{-1}. The load P monitored as a function of the deflection f of the specimen, measured by an extensometer into contact with the surface subjected to tensile stress, allowed calculation of the elastic modulus, E. All the tests were performed subjecting to tensile stress the polished working surface. Vickers hardness was evaluated only on the polished samples cut from the tiles produced with the mix of the surface layer, BLP-94, while the determination of fracture toughness, involved the matrix material (the mix of the surface layer) and the two materials containing 7.2 and 32.0wt% of stainless steel powder, Mix 3 and Mix 4 respectively. Fracture toughness was evaluated by SENB technique, subjecting to 4-point bending test at a crosshead speed of 0.10mmmin^{-1} bars 45x4x7mm in which a notch of 1.75mm depth was introduced to have a ratio a/h = 0.25, where a is the depth of the notch and h is the thickness of the specimen.

The properties of the constituent phases and the results of an extensive microstructural investigation and fracture surface analysis represented the input data to investigate the behaviour of the materials. The reinforcement mechanisms were accurately investigated analysing, with the aid of a scanning electron microscope, SEM, (Zeiss EVO 40, D), equipped with an energy dispersion X-ray attachment, EDS, (Inca, Oxford Instruments, UK), the fracture surface, the yielding of the metallic particles and the path deflection of the cracks arisen from the corners of impressions left on the surface by Vickers indentation technique.

3. RESULTS AND DISCUSSION

In Table 3 and Table 4 are presented the results of the mechanical characterisation. The characteristics of the matrix material. BLP-94, are the highest. When the matrix material is coupled by DCT with the ceramic body, the characteristics strongly decrease, approaching the values exhibited by the AZ-29 material alone. This behaviour was attributed to the lower properties of the ceramic body; the contribution to the resistance of the surface layer can be considered negligible, if compared with that of the ceramic body.

SAMPLE	σ (MPa)	E (GPa)
AZ-29	69.1±3.0	57.4±2.9
BLP-94	82.3±3.0	68.7±6.7
BLP-94/AZ-29	71.7±3.0	55.9±4.1
DMD-BLUE	67.3±4.5	58.7±2.1
Mix 1	70.2±5.0	66.8±3.1
Mix 2	67.0±4.8	64.0±3.1
Mix 3	63.8±3.7	61.6±2.0
Mix 4	44.6±7.0	49.0±2.9

Table 3. Flexural strength, σ, and elastic modulus, E.

SAMPLE	HV (GPa)	K_{IC} (MPa√m)
BLP-94	6.01±0.53	1.40
Mix 3	---	2.32
Mix 4	---	1.24

Table 4. Vickers hardness, HV, and fracture toughness, K_{IC}.

The same conclusions can be drawn by analysing the results obtained for the DMD-BLUE, the commercial product, containing in the surface layer a 2.4wt% of stainless-steel powder. The results confirm that the percentage of metallic powder, rather low, is not able to introduce significant variation in the mechanical behaviour of the material.

The results of the samples obtained with the single mixes underline how, up to an amount of 7.2wt% of metal addition, not very meaningful changes connected with the bulk mechanical characteristics are evident. While the presence of 32.0wt% of stainless steel, sample Mix 4, determines a drastic drop of the elastic properties.

In Table 4, Vickers hardness and fracture toughness values are reported. The ceramic matrix, BLP-94 sample, presents a value of K_{IC} of 1.40MPa√m, a usual value for porcelain stoneware products[5,10]. The value determined for Mix 3, 2.32MPa√m, shows a strong increase of toughness, but the value found for Mix 4, 1.24MPa√m, results to be lower than that of the ceramic matrix. The toughening effect depends both on the properties of the second phase and on its percentage in the matrix.

The SEM analysis of the tested samples, both of the surface and of the fractured body, allowed clarification of the results obtained. For Mix 1, Mix 2 and Mix 3, rather good adhesion at the interface metal particle-ceramic matrix was observed. In Figure 2, the fracture surface of a specimen of Mix 2 is reported, where a round metal particle appears to be well wetted by the ceramic matrix. In this way, the metallic inclusions are firmly bonded to the ceramic matrix, contributing to favour the ductile deformation of the metal, when stressed.

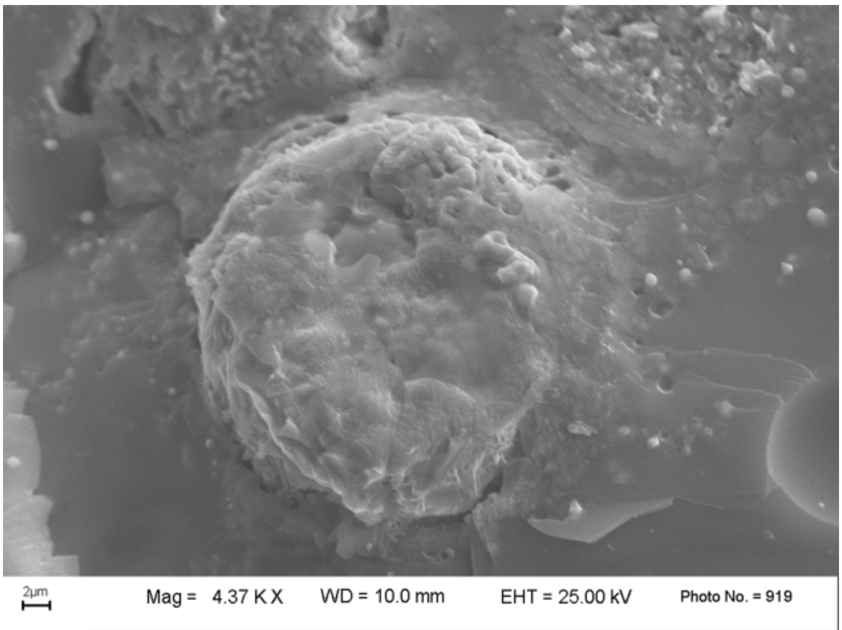


Figure 2. SEM micrograph of Mix 2, a round metal particle adhering well to the ceramic matrix.

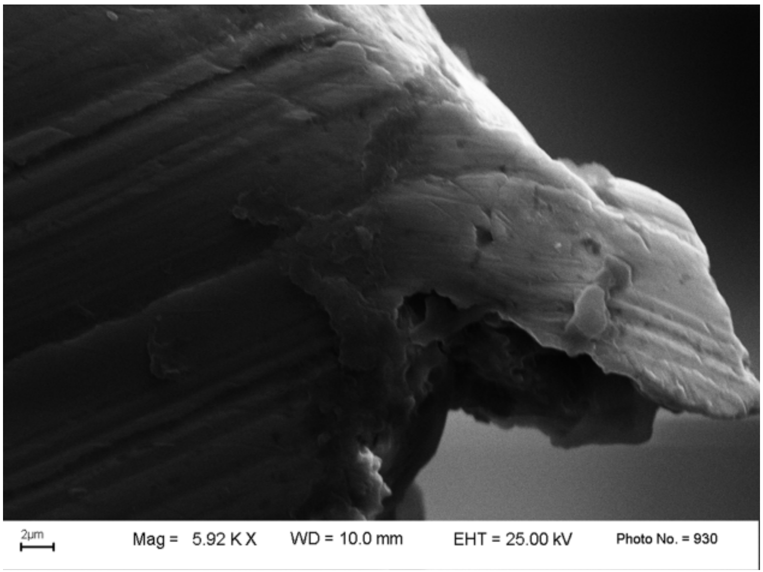


Figure 3. SEM micrograph of Mix 3, showing the elongated deformed area of the metal particle.

The analysis of their fractured surfaces evidenced considerable plastic deformation, contributing to create a bridge bonding between the surfaces of the growing crack. In Figure 3, for Mix 3, the ductile fracture of a metal particle at the surface of a fractured bar is shown. Some Lüders bands are also evident[11].

The analysis of Vickers impressions, left on the polished surfaces, was addressed to observe the deflection of the median-radial cracks. The large metal spheres blunted the crack paths, as observed in Figure 4 and Figure 5;

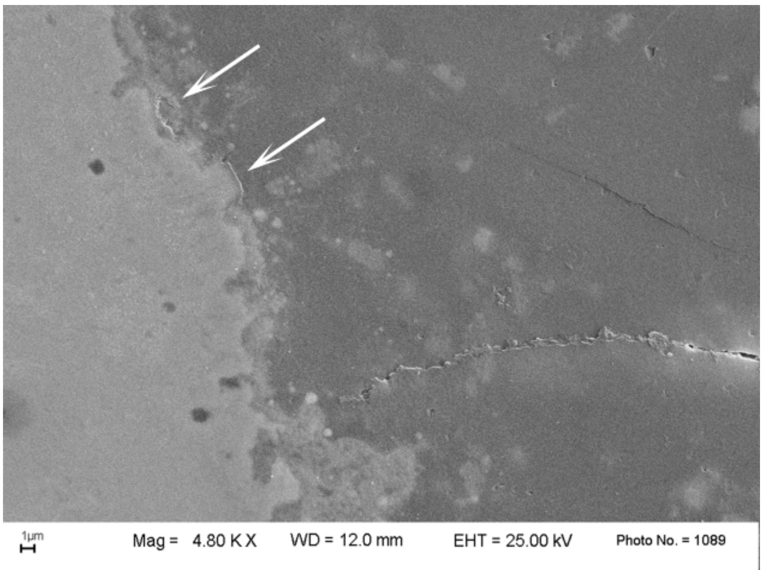


Figure 4. SEM micrographs of the polished surface of Mix 2, crack path blunted by a metal particle. The arrows underline the metal detachments.

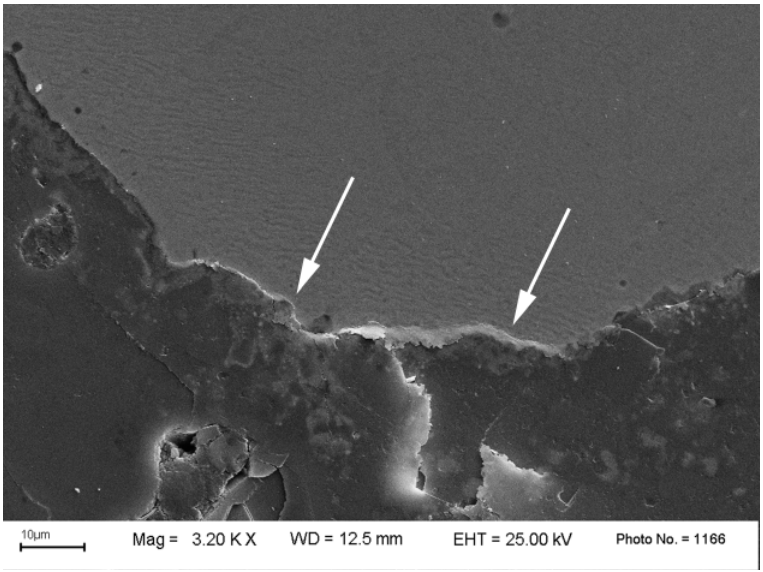


Figure 5. SEM micrographs of the polished surface of Mix 3, crack path blunted by a metal particle. The arrows underline the metal detachments.

at the same time partial detachments of the particle, pointed by the arrows, contribute to the loss of the fracture energy. If the fracture energy is rather high, the crack grows around the metal particle, Figure 6. Both the mechanisms led to significant toughening of the composite material.

Taking into account that the linear thermal coefficient of porcelain stoneware lies in the range $7\div8x10^{-6}{}^{\circ}C^{-1}$, lower in comparison with that of the metal added (Table 2), during the cooling phase, in the matrix around the metal particles, a compressive hoop stress field and a radial tensile stress field develop. This latter tensile stress

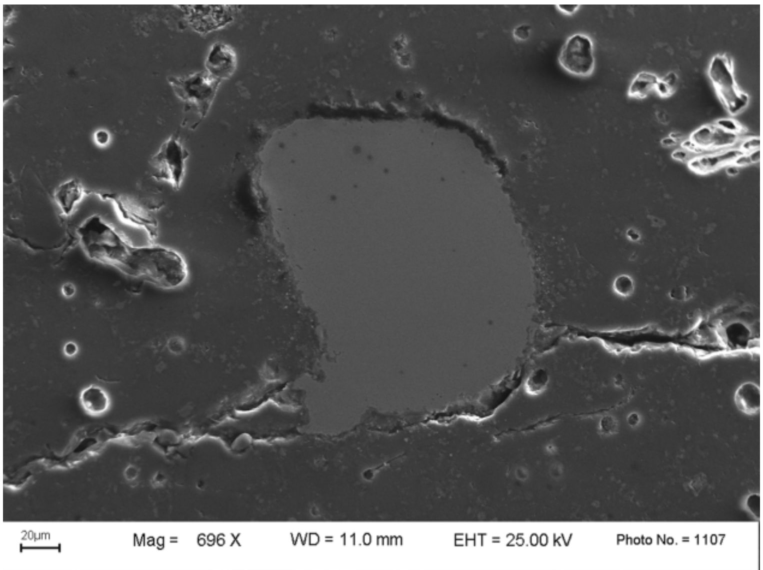


Figure 6. SEM micrographs of the polished surface of Mix 3, showing a crack deflected around metal particles.

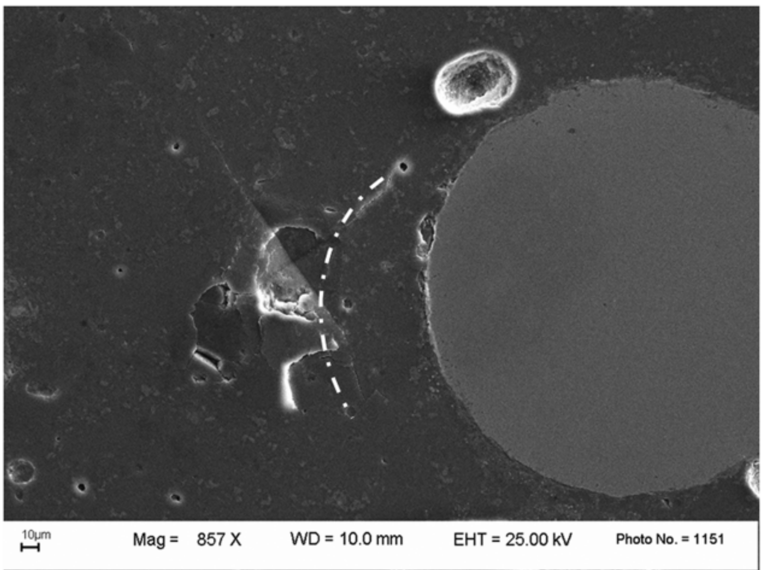
at the metal ceramic interface could cause, in case of a poor adhesion, a debonding of the metal particles. Altogether, this residual stress field produces a closure effect of the advancing cracks along the radial direction and a deflection of the cracks growing along a circumferential trajectory as on the other hand, shown in Figure 7 a) and b), where it is possible to verify these effects involving the median-radial cracks emerging from the corners of a Vickers impression. These phenomena have to be considered toughening mechanisms.

SEM observations of the polished surfaces, Figure 8, showed at the interface metal-ceramic matrix, the presence of a light grey layer, in which the EDS analysis revealed the presence of large amount of chromium. Moreover, the same analyses performed in the area of the metal particles contiguous to ceramic material pointed out a depletion of chromium in comparison with the content found in their inner area. It is known that, when thermal treated, the stainless steel, used in this study, presents at temperatures >600°C a segregation of carbides that go in solution at temperatures >800°C.

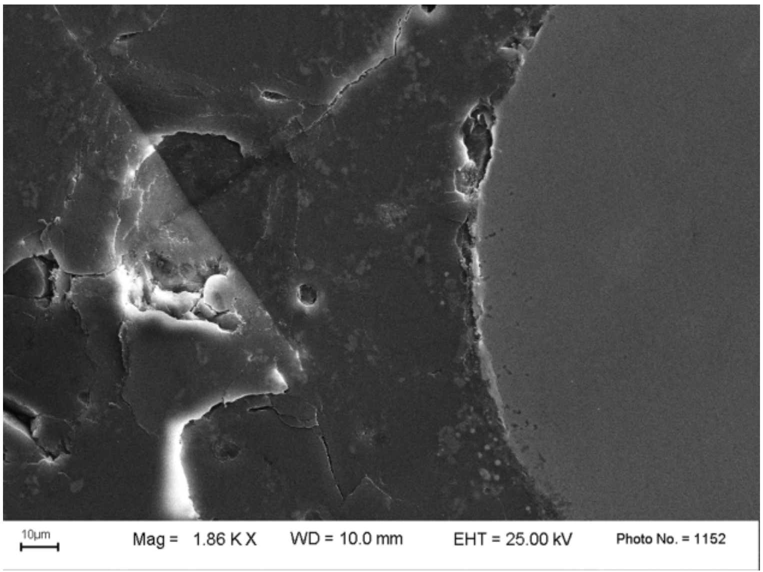
If in the range of temperature 850-450°C the cooling phase is not fast, the precipitation and coalescence of chromium carbides at the grain boundary takes place. Since, the cooling phase of porcelain stoneware tile process does not foresee a quenching treatment, it is clear that the outer chromium layer was built during the processing of the ceramic tile. This chromium rich layer appears to be rather compact and seems to improve the adhesion to the ceramic matrix.

All the mechanisms, till now described, are present in all the tested samples, but in the Mix 4 the very high percentage of metallic particles, causes a degradation of the material. The specimens subjected to flexural test, showed in the ceramic matrix around the metal particles the presence of a wide diffusion of chromium, with evident deterioration of the interface metal-ceramic matrix. These observations suggested that in this case, the metal particles operated as inclusions rather than as reinforcing elements. The results were strengthened by the decrease of elastic modulus and fracture toughness data.

The behaviour of the Mix 4 material was attributed to the excessive percentage of metallic particles embedded in the matrix. The probable non homogeneous distribution of the metal particles in the powder, due to their high percentage and the presence of agglomerates, caused, during the firing step, their joining, giving rise to a non-homogeneous microstructure. This determined a degradation of the properties of the material. Furthermore, a wider diffusion of chromium from the metal particles to the ceramic matrix could have favoured oxidation phenomena at their surface, compromising the nature of the interface metal-ceramic matrix. Consequently, in this material, the metal particles acted as inclusions rather than as reinforcing elements. The decrease of the mechanical characteristics confirms these observations.



a)



b)

Figure 7. SEM micrographs of the polished surface of Mix 3: a) crack deflection, b) magnification.

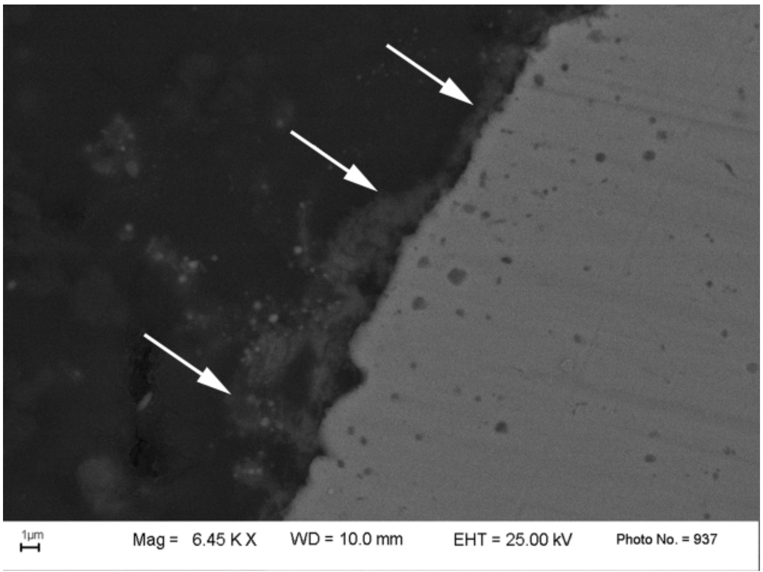


Figure 8. SEM micrographs of the polished surface of Mix 2, the chromium rich layer is arrowed.

4. CONCLUSIONS

In the present work the results of an extensive characterisation of innovative porcelain stoneware tiles produced by the DCT is presented. Since the surface layer, a silicate-based ceramic, contains a dispersion of stainless-steel particles, the material was considered and treated as a metal-ceramic matrix composite.

The results obtained, analysing the nature of the interface metal particles-ceramic matrix, the fracture surfaces and the experimental data of mechanical characterisation showed different reinforcing mechanisms, acting at the interface metal-ceramic matrix.

The precipitation and coalescence of carbides, during the cooling step of the industrial process, favoured a good adhesion, even if the change in composition at the surface of the metallic particles is able to alter the characteristics of the alloy. The mechanical degradation found in Mix 4 material, containing the highest percentage of metal particles, can be also looked on from this point of view.

REFERENCES

[1] A.G. Evans. Perspective of the development of high-toughness ceramics. J. Am. Ceram. Soc., 73 [2] (1990), 187-206.

[2] J.S. Moya, S.L. Esteban, C. Pecharromàn. The challenge of ceramic/metal microcomposites and nanocomposites. Prog. Mater. Sci., 52 (2007), 1017-1090.

[3] C. Leonelli, F. Bondioli, P. Veronesi, M. Romagnoli, T. Manfredini, G.C. Pellacani, V. Cannillo. Enhancing the mechanical properties of porcelain stoneware tiles: a microstructural approach. J. Europ. Cer. Soc., 21, 785-793, (2001).

[4] M. Dondi, G. Ercolani, C. Melandri, C. Mingazzini, M. Marsigli. The chemical composition of porcelain stoneware tiles and its influence on microstructural and mechanical properties. Interceram, Vol. 48 No. 2 (1999) 75-83.

[5] C. Palmonari, L. Esposito, A. Tucci, G. Timellini. Short fibre reinforced ceramic tiles: microstructural aspects and implications. Silic. Ind., 3-4 (1996) 91-96.

[6] A. Tucci, L. Esposito, L. Malmusi, E. Rambaldi. New body mixes for porcelain stoneware tiles with improved mechanical characteristics. J. Europ. Cer. Soc., 27, 1875-1881, (2007).

[7] W.H. Tuan, S.C. Chen. Fiber-reiforced ceramic tile. Am. Ceram. Soc. Bull., 83 [6] (2004), www.ceramicbulletin.org.

[8] H. Prielipp, M. Knechtel, N. Claussen, S.K. Streiffer, H. Müllejans, M. Rühle, J. Rödel. Strength and fracture toughness of aluminum/alumina composites with interpenetrating networks. Mat. Sci. and Eng. A197 (1995) 19-30.

[9] P. Agrawal, C.T. Sun. Fracture in metal-ceramic composites. Compos. Sci. Technol., 644 (2004), 1067-1178.

[10] P.M. Tenorio Cavalcante, M. Dondi, G. Ercolani, G. Guarini, C. Melandri, M. Raimondo, E. Rocha e Almendra. The influence of microstructure on the performance of white stoneware. Ceramics International 30 (2004), 953-963.

[11] R.C. Juvinal. Engineering considerations of stress, strain and strength. McGraw-Hill, (1967), 66.