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Microstructure and Scratch Resistance of Ceramic Surfaces

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Introduction

In order to gain a fundamental understanding of material removal mechanisms and damage morphology in brittle materials, such as ceramics, several studies using both static indentation and scratch test have been conducted. Since the 1980's, it is known as the results of a scratch test provides information concerning the cracking of brittle materials, close to those induced by the indentation test, [1]. As regards, while hardness determination represents the result of a static indentation test, involving only a normal load applied to an indenter having different tip geometry (spherical, conical or pyramidal) and coming into contact with the surface of the material to be analysed, in the scratch test the normal load, L_N, is applied to an indenter with the same geometry, but into contact with the surface of a moving sample. The effects induced on the surface of the sample by the combination of the normal and tangential loads, (L_N and L_T) overcoming, under definite conditions, the strength of the material, lead to an elastic-plastic deformation the effect of which is the formation of a scar.

The scratch test technique is commonly adopted to evaluate the adhesion of hard ceramic coatings [2], but it can be used also to characterise bulk ceramics. The interest is due to the fact that, several cracking mechanisms likewise to what happens under a sharp indenter. In this context elastic/plastic deformation, median, radial and lateral cracks and material removal can contribute to clarify the mechanisms involved in wear phenomena as abrasion and machining of brittle materials [3-5]. Since the sliding wear can be considered as result of multiple scratches, this experimental technique provides also further information on the abrasion resistance of ceramic surfaces [6,7].

The materials used in several building applications, such as ceramic tiles or glass mosaic tesserae, need to have working surfaces characterised by very high scratch resistance. It is well known as chipping and cracks are able to strongly decrease both the mechanical performances, in particular hardness and wear resistance and the aesthetic, loss of brightness, discolouration effects, material removal. Besides, the presence of cracks and areas from which the material was removed, increasing the surface roughness, favours storage of powders and other dirty agents, preventing an efficient cleaning action.

Referring to ceramic tiles, the EN 101 Standard [8], was removed due to the poor meaningfulness and operator influence in other words, because of unreliable results. In spite of the always stronger quality requirements, no alternative standard method till now has been suggested.

The aim of the present study is to assess the possibility to apply the scratch test method to silicate based ceramics, to correlate the results with the working surface characteristics and to understand which are the parameters more affecting the results. To reach this target, the test method and parameters reported in the ISO 20502 Standard [9] were adopted.

Experimental

For the present work different commercial ceramic products were chosen: *i)* unglazed tiles, two porcelain stoneware products presenting different working surface conditions, as fired and polished; *ii)* glazed tiles, three single-fired glazed products characterised by different glaze microstructure and *iii)* two vitreous mosaic tesserae with different composition and colour.

The average and maximum surface roughness, R_a and R_M, of the working surface of all the samples, were measured by using a roughnessmeter (Hommel Tester, T2000, D), according to the test method recommended in the EN 623-4 Standard. Vickers hardness measurements were performed by using a semiautomatic hardness tester (Zwick 3212, D), applying an indentation load of 9.81N, for porcelain stoneware samples, and of 1.0N for the glazed tile.

The mineralogical phase composition of the glaze layers was assessed by X-ray diffraction analysis (PW3830, Philips, NL), carried out directly on the glaze surfaces. Since all the tested specimens had the same geometry and were analysed in the same conditions, even if it was not possible to obtain a quantitative analysis of the phase composition, the qualitative comparison of the relative intensity of the peaks in the XRD spectra, make it possible to evaluate the level of crystallinity in the different glazes.

The scratch test was performed on the surfaces of suitable specimens (~10x20mm) by using a specific instrument (Revetest Scratch Tester, CSM Instruments SA, CH), equipped with a stylus indenter Rockwell C diamond, cone angle 120° and tip radius 200µm, which was drawn at a constant speed across the surface to be tested, under progressive loading at a fixed rate.

Figure 1 reports the sketch of the instrument: the system is equipped with a tangential force L_T, sensor, a penetration depth P_D sensor, and an acoustic emission sensor. During the test, the applied load, L_N, the penetration depth, P_D, the tangential load, L_T, and the acoustic emission result of the fracture of the material, are continuously measured and recorded. So, it is possible to evaluate the friction coefficient at the contact between indenter and material, $\mu=L_T/L_N$, the penetration depth, P_D, and the residual depth, P_R as difference (P_D-P_E), where P_E represents the elastic recovery of the deformation. Obviously, to calculate these test parameters is necessary to perform firstly a pre scan to provide the profile of the surface and a post scan to evaluate the elastic recovery. P_D can be obtained by the difference between the penetration depth during the test and the profile measured in the pre-scan phase, while the residual depth is the difference between the depth measured during the post scan and the pre scan.

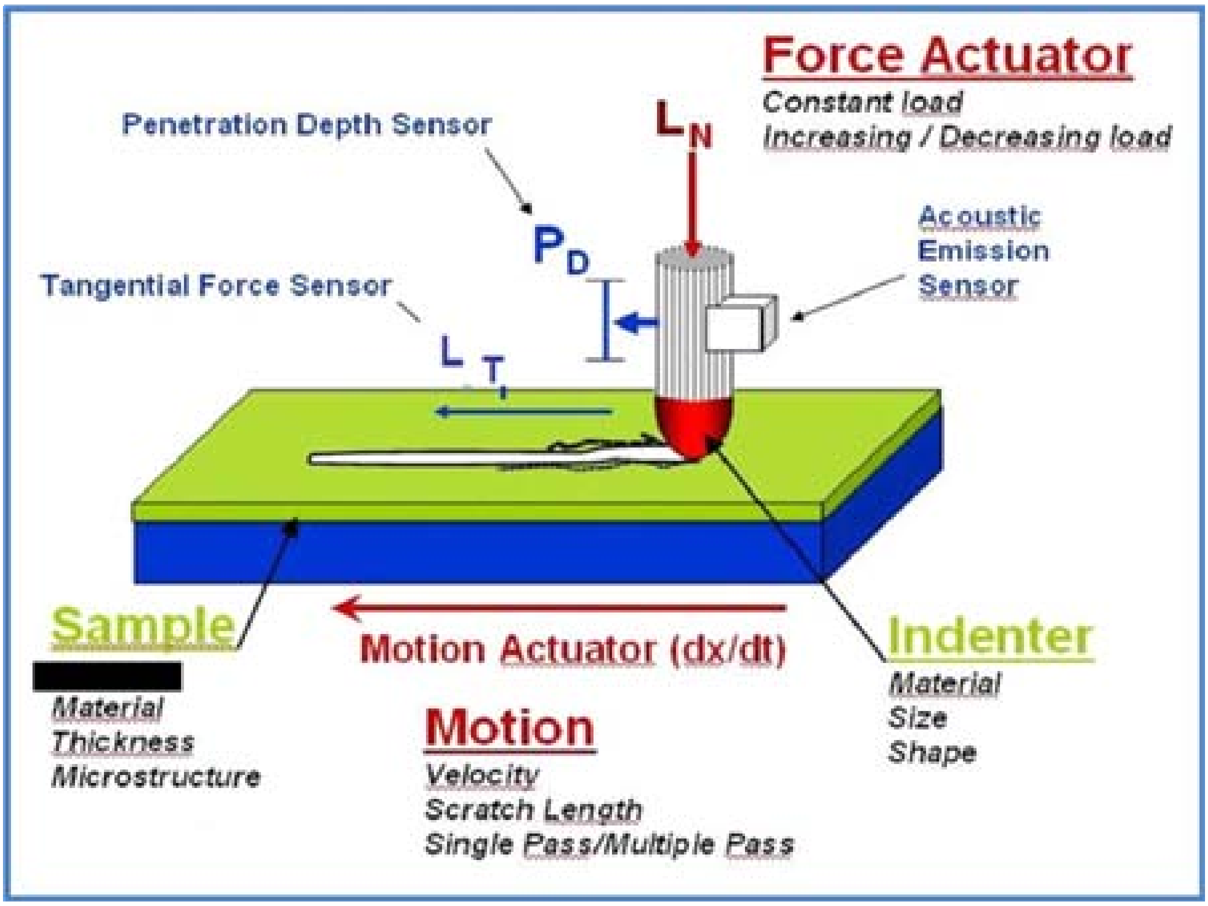


Figure 1 – Sketch of the instrument

The failure events at the surface materials can be detected both by direct microscopic observation, the most reliable method to detect and differentiate the kind of damages, and by elastic waves, generated as a result of the formation and propagation of micro cracks. This last one can be also influenced by micro cracks generated by the surface roughness of the sample.

As output of the scratch test, two values of critical normal load L_C, defined as the smallest load at which a recognisable failure occurs, are normally considered. In particular, in the lower applied load regime, the generated stresses result in conformal or tensile cracking of the surface, which still remains fully compact. The onset of these phenomena defines a first critical load. In the higher load regime, one defines another critical load which corresponds to the onset of material detachment by spalling and chipping. So, it is possible to recognise two values of critical normal loads, characterising the materials: L_{C1}, the value of the normal load at which the first hertzian ring crack is visible; L_{C2}, the value of the normal load for which a catastrophic fracture with detachment of material is observed.

In the present investigation, the scratch tests were performed by adopting an increasing load of 10.0N/mm in the range 0.9÷80.0N, with a sliding speed of 10.0mm/min on a sliding distance of 5.0mm.The scratch tracks were observed by an optical microscope and scanning electron microscope (SEM, Zeiss EVO 40, D) to identify the critical loads L_{C1} and L_{C2}, and the fracture mechanisms involved.

Results and Discussion

The roughness parameters, R_a and R_M, measured for the porcelain stoneware surface in the as fired, labelled AF, and polished, labelled P, condition are reported in Table I. The polishing operation drastically decreases the surface roughness for all the samples, even if for some of them a decrease in the hardness values, Table I, is also observed. It is well known as the industrial polishing procedure of such kind of product is able to strongly increase the aesthetic and the brightness [5,10], but induces several kinds of surface flaws (uncovered pores, scratches,…) not completely removed by the final polishing steps [6].

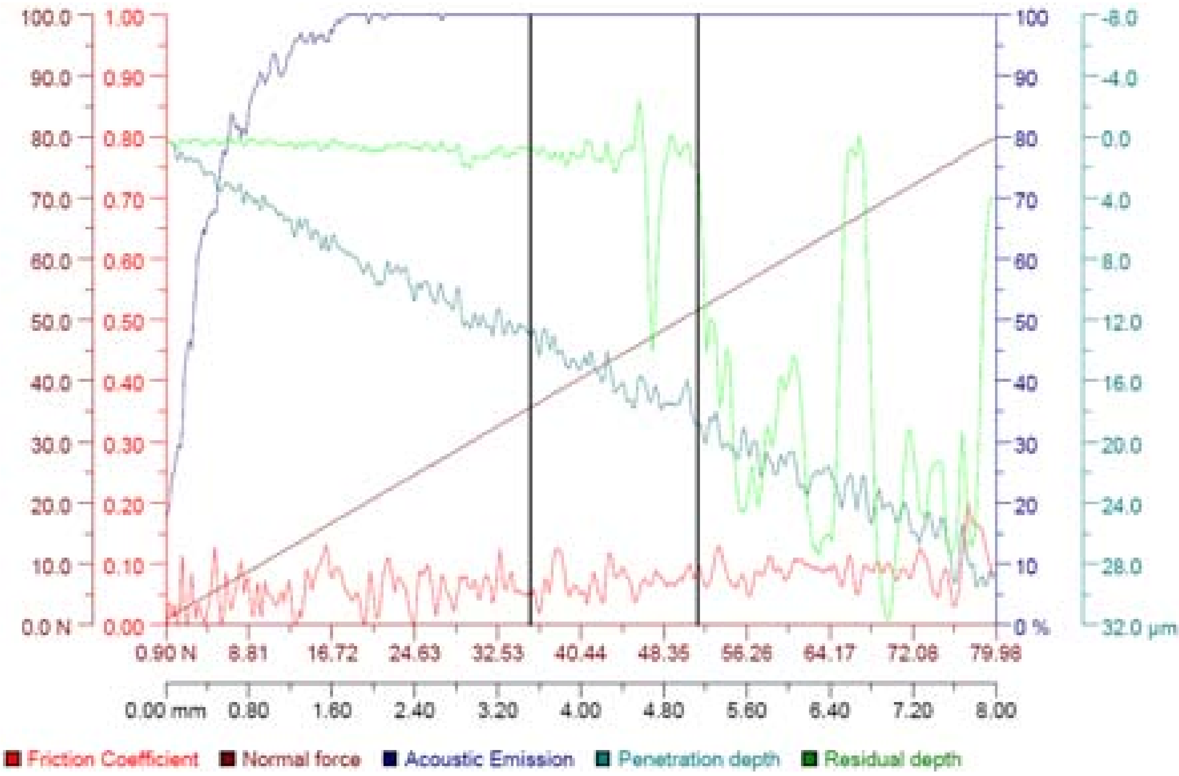
Table I – Roughness parameters, R_a e R_M, and Vickers hardness values

Campione	AF-1	P-1	AF-2	P-2	T-1	T-2	T-3
R_a, □m	2,4	0,26	2.9	0.19	0.94	0.59	0.70
R_M, □m	17,2	7,05	25.6	7.03	7.18	4.33	4.96
HV, GPa	7.5	6.0	7.1	6.2	7.7	7.4	6.9

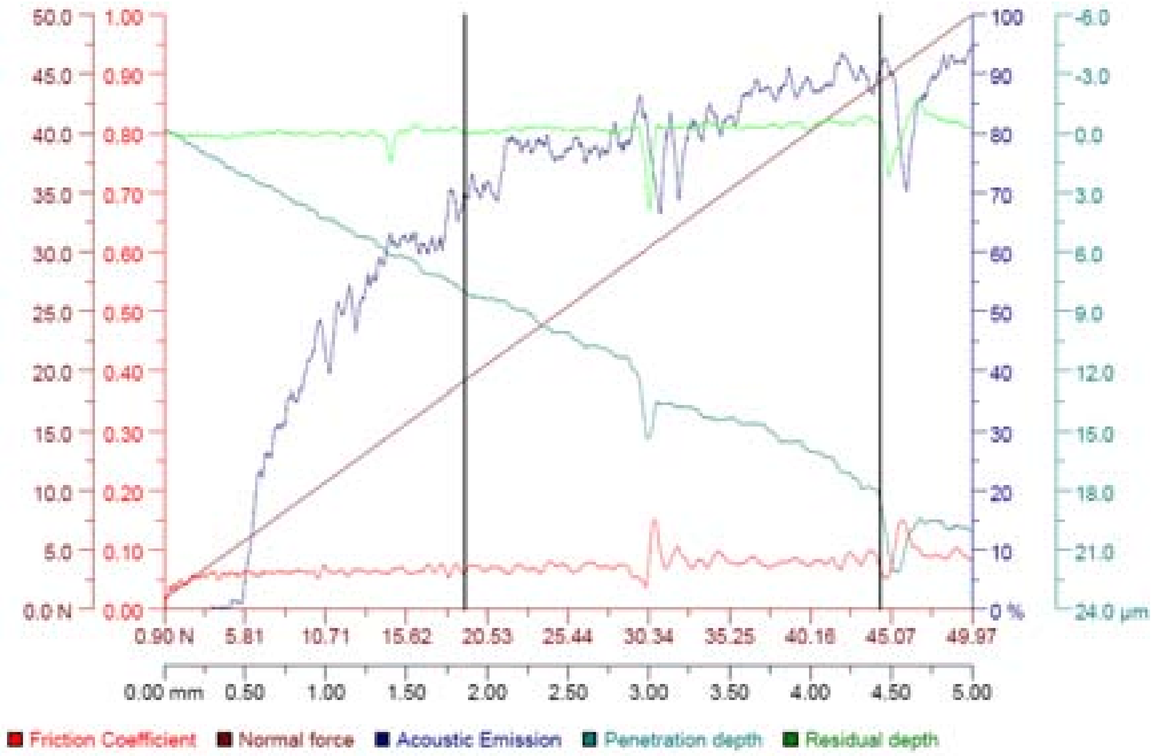
Table II - Critical load values for the porcelain stoneware tile samples

Sample	AF-1	P-1	AF-2	P-2
L_{C1} (N)	32.5	19.2	17.9	12.65
L_{C2} (N)	50.9	44.0	53.6	49.3

In Table II, the results of the scratches tests in terms of L_{C1} e L_{C2} are reported, for the porcelain stoneware products. It is rather clear as the polishing operation causes a general decrease of the critical loads, more evident for the L_{C2} values. This behaviour can be explained taking into account the changes of surface morphology and flaws caused by the polishing operation [9]. Even if the higher values, in particular of the L_{C1} for the as fired products, could be partially related to the difficulty with which the hertzian cracks can be recognised on this rougher surface.
The analysis of the report curves for this kind of the samples does not allow to identify the critical load points. In Fig. 2, the scratch reports for the samples AF-1 and P-1 are shown, similar behaviour is observed by sample 2.



a)



b)

Figure 2 - Scratch report a) of sample AF-1, b) of sample P-1.

For the as fired samples, it is evident as the acoustic emission curve is very irregular with no connection with the critical load, the values of which were detected only with the aid of the optical microscope, by observing the scratch morphology. Acoustic emission values are strongly influenced by the surface morphology of the sample to be tested, and for the rather rough surface of the as fired sample, small cracks immediately form at the first contact between the surface asperities and the indenter tip. As a consequence, drastic variations are recorded by the acoustic emission detector [7]. Such small cracks, in any case, don't cause the formation of a continuous scratch fracture or the formation of hertzian cracks. A similar irregular trend is reported also for the friction coefficient curve.

For the polished surface, characterised by reduced roughness and hardness, both the acoustic emission and friction coefficient curves show a more regular behaviour, compared to the corresponding as fired, even if the formation of the first hertzian cracks, and then the critical loads value, can be detected only by microscopic observations.

Of the three glazed tile samples tested, only the glaze of T-3 is completely amorphous, while T-1 and T-2 samples have glazes layers with different kinds and amounts of crystals phases embedded in a glassy matrix. In particular, T-1 presents a rather low amount of glassy phase, zircon is the main crystalline phase with a small amount of plagioclase and quartz, while for T-2 the degree of crystallization is low, with the presence of a calcium-zinc silicate (petedunnite), celsian, magnetite, plagioclase, zircon and quart. The results of the scratch test for the glazed tiles, Table III, underline as the amorphous glaze of T-3 is characterised by the lowest value of L_{C1} and L_{C2}. For T-1 and T-2, while no very large differences exist for L_{C1}, whose values are all in the same range, more evident differences are found for the L_{C2} values.

Table III - Critical load values for the glazed tile samples

Sample	T-1	T-2	T-3
***L_{C1}* (N)**	15.8	14.4	9.1
***L_{C2}* (N)**	49.4	33.4	27.8

In particular it is possible to correlate them with the different levels and kinds of crystalline phases, present in the samples. In fact, T-1, characterised by a large amount of newly formed crystals, with elongated habitus, presents higher resistance to the advancing and branching of cracks, that means also higher L_{C1} and L_{C2}. Due to the rather high surface roughness (caused by the protruding crystals) in T-1 and T-2, both the curves of the friction coefficient and acoustic emission result to be irregular from the very beginning of the test, as observed for the porcelain stoneware tile products, so the critical load values have been identified by the optical microscope. From the analysis of the scratch report of these glazed products (Fig. 3), it is evident as the destruction of the surface, at the load value of L_{C2}, is so severe, that a sudden fall of the penetration depth can be recorded starting from this point, as revealed by the observation by the optical microscope (Fig. 4).

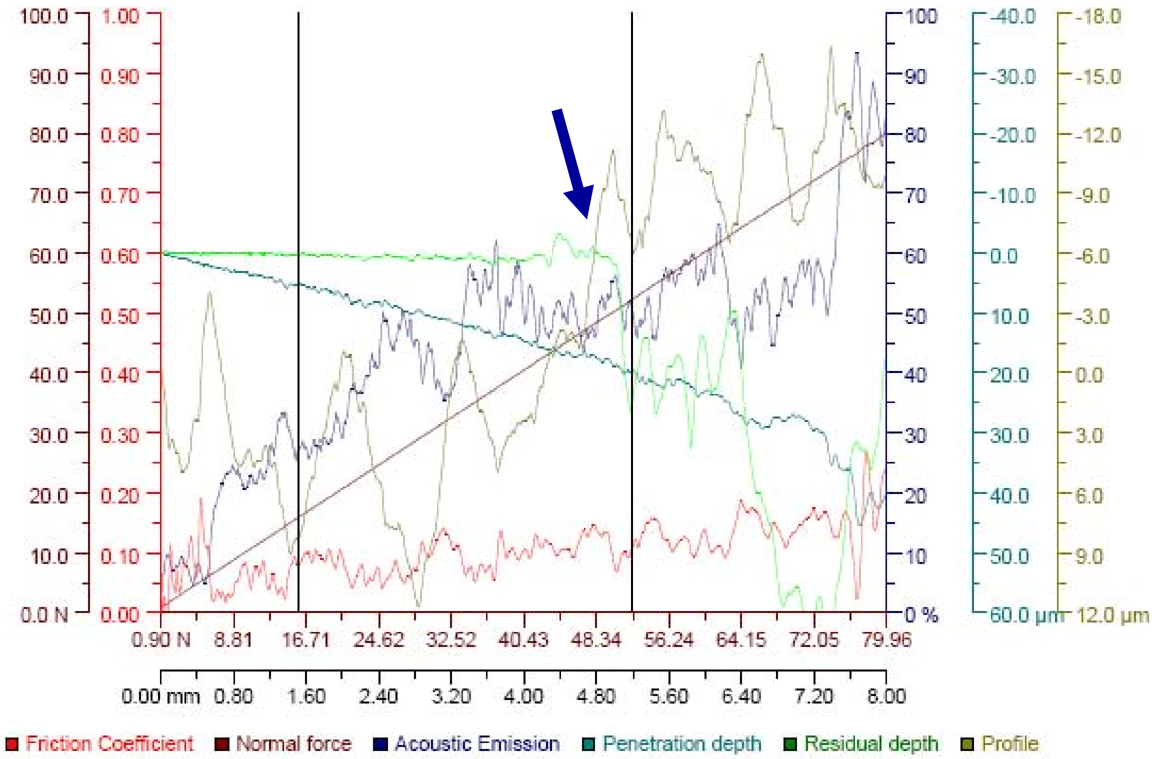


Figure 3 - Scratch report of sample T-1. The arrow identify, in the penetration depth curve, the L_{C2} position.

In Table IV, the results of the scratch test for the vitreous mosaic tesserae are reported. These materials are coloured glasses, in rather thick specimens, with a similar surface microsturcture and present rather similar L_{C1} and L_{C2} values. The test report, for G3, but similar trend are presented by the other samples, is shwon in Fig. 5. For this class of material, due to their surface morphology, it is possible to directly recognise the critical applied loads from the analysis of the acoustic emission and the penetration depth curves. In fact, for very smooth surfaces, as these mosaics glassy products are, the acoustic emission is very low at the beginning of the scratch test; then it suddenly increases when the first ring cracks form (Fig. 6). We can observe also the drop in the penetration depth curve when L_{C2} is reached, as revealed by the morphological observation (Fig. 7).

Table IV - Critical load values for vitreous mosaic tesserae samples

Sample	G-1	G-2	G-3
L_{C1} (N)	15.5	17.8	11.1
L_{C2} (N)	36.3	35.5	39.0

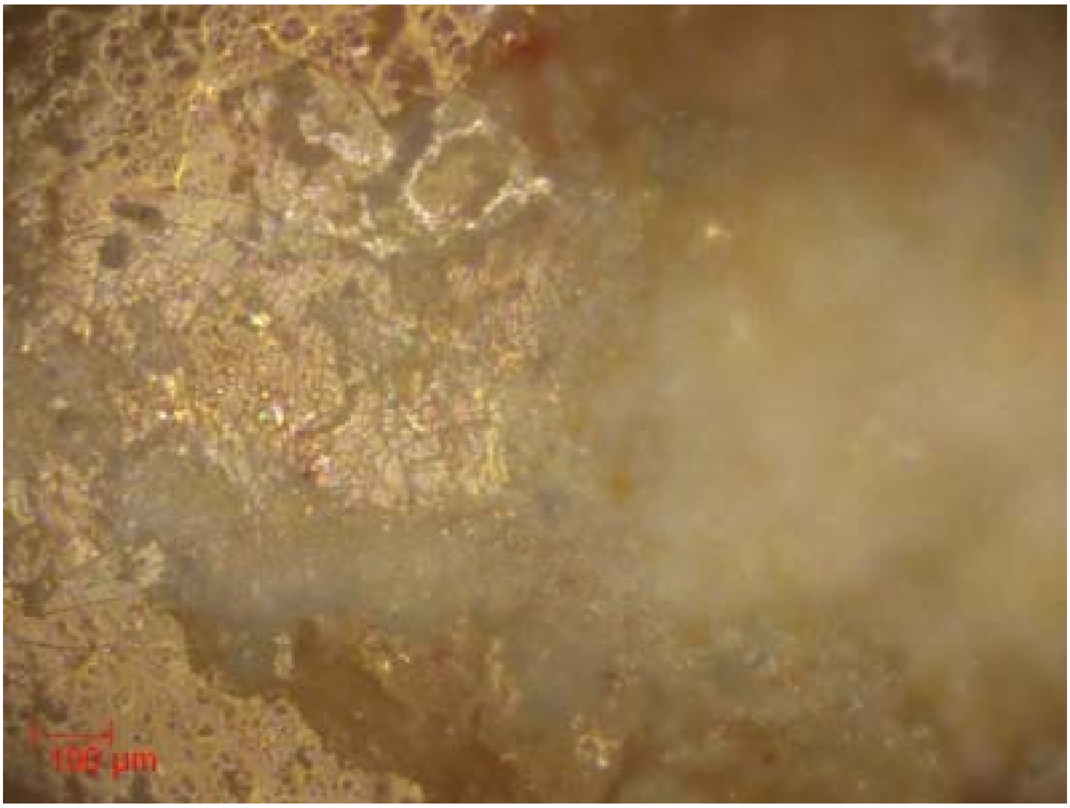


Figure 4 - Optical micrograph of part of the scratch of sample T-1, at the L_{C2} position.

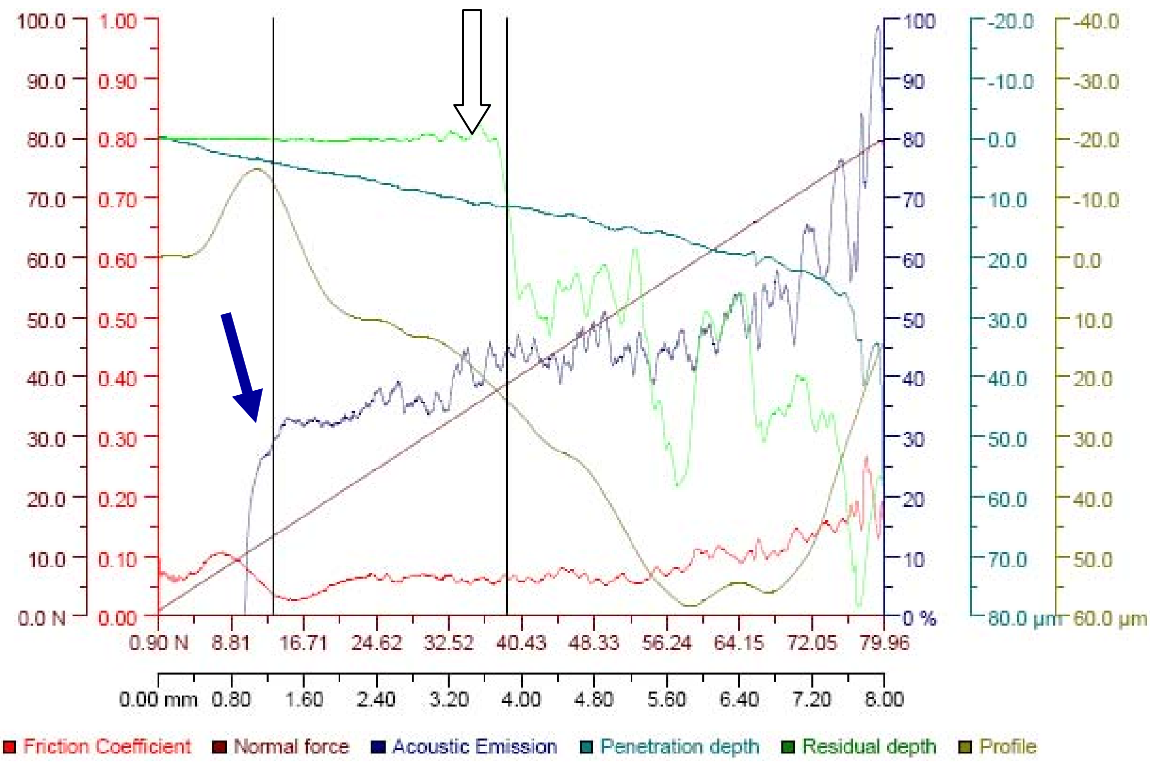


Figure 5 - Scratch report of sample G-3. The arrow identifies, in the acoustic emission curve, the L_{C1} position. The blank arrow identifies, in the penetration depth curve, the L_{C2} position

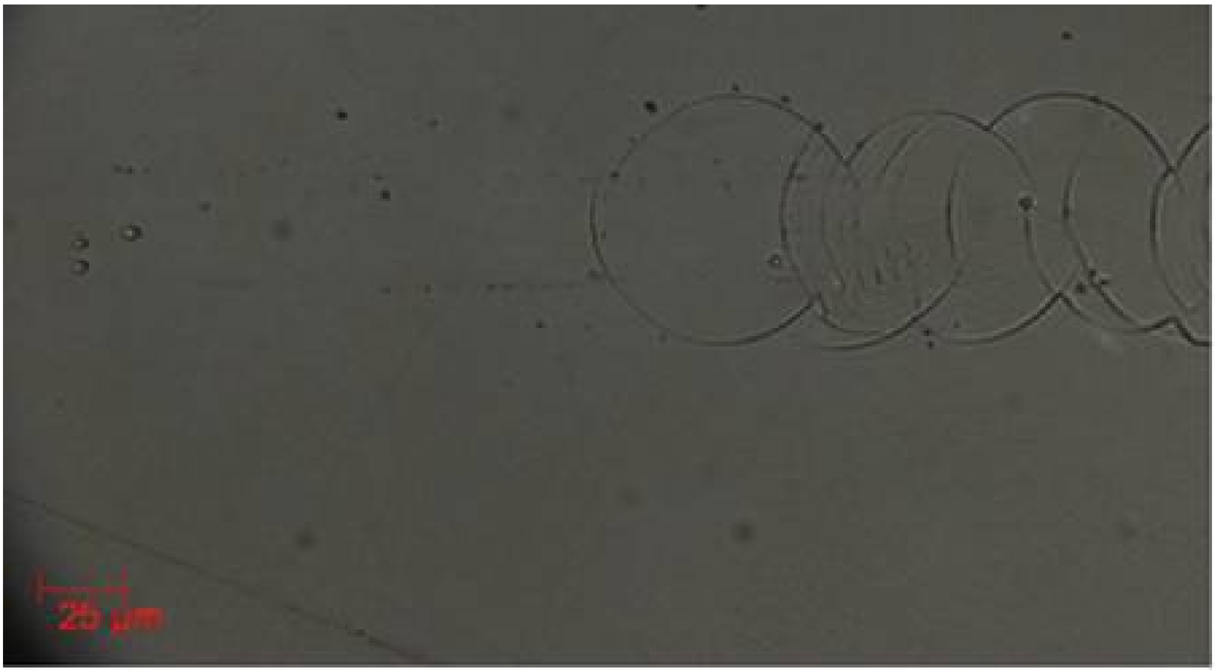


Figure 6 - Optical micrograph of part of the scratch of sample G-3, at the L_{C1} position. Hertzian cracks are visible.

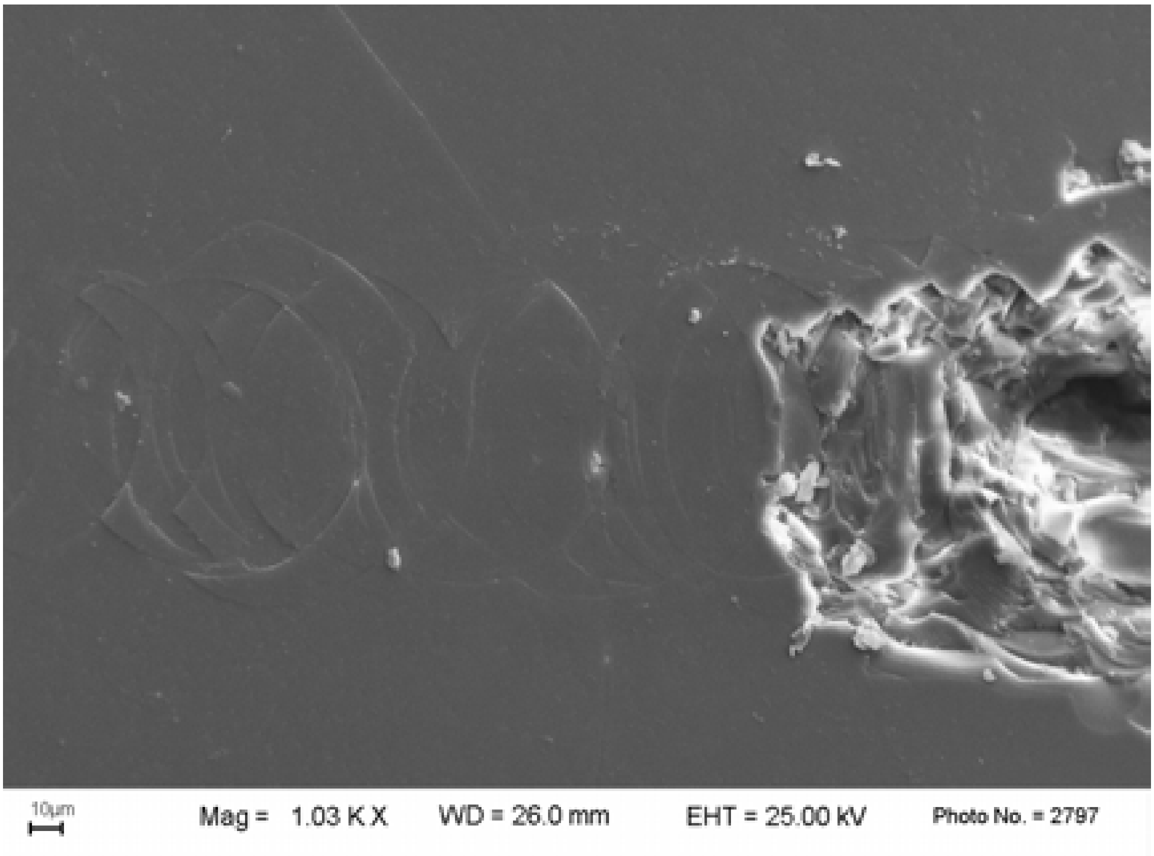


Figure 7 – SEM micrograph of part of the scratch of sample G-3, at the L_{C2} position. Severe fracture of the surface is visible.

Conclusion

Scratch tests have been performed on the surface of ceramic elements, such as ceramic tiles (unglazed and glazed) and vitreous mosaic tesserae, to be used in building application, characterised by different composition and microstructure.

The analysis of the test results, obtained by using an automatic scratch tester (Revetest Scratch Tester CSM Instruments SA, CH), allows to conclude:

- - in the frame of the performed tests, a satisfactory reproducibility of the measurements has been found;
- - the technique allowed to discriminate products, characterized by different surface microstructures, and among the same class of product, the more resistant one;
- - further works is foresee to assess the possibility to standardize this test methodology.

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