POST-INDENTATION SLOW CRACK GROWTH IN VITREOUS MOSAIC TESSERAE

C. Alban[1], L. Esposito[2], E. Rambaldi[2], A. Tucci[2]

[1]TREND GROUP S.p.A., Piazzale Fraccon 8, 36100, Vicenza, I.
[2]Centro Ceramico Bologna, Via Martelli 26, 40138, Bologna, I.

ABSTRACT

Vickers indentation technique was used to investigate the slow crack growth (SCG) behaviour by stress-assisted reaction in vitreous mosaic tesserae, products widely used both in wall and floor covering. SCG was studied by exploiting the induced tensile stress field and the median-radial cracks emerging from the corners of Vickers impressions. On the working surface of four different samples of vitreous mosaic tesserae, a single impression was left, by adopting test parameters suitable to trigger well developed median-radial cracks.

Post-indentation slow crack growth was monitored, by measuring, after the removal of the indentation load under a light microscope, the increase of the median-radial cracks length considered as pre-existing cracks, at fixed intervals of time. To estimate the effects of the environmental conditions, the tests were conducted in air, having 40% of relative humidity, water and in alkaline solution, KOH 100g/l. The same tests were performed also on specimens of soda-lime glass (S-L G), considered as reference material. The different crack resistance behaviour of the materials was correlated to their chemical composition.

1. INTRODUCTION

In glasses and silica-based ceramics, pre-existing cracks can grow at an applied stress, below the threshold value. This behaviour, known as slow crack growth (SCG), is favoured by a stress-assisted reaction with humidity, through the dissociation of SiO2 and consequent forming of hydroxyl links. The class of the vitreous mosaics can also be included as silica-based ceramics. These products, widely used both in wall and floor covering, can be subjected to different stresses coming from the environment. The concomitant presence of cracks and residual tensile stress fields, due to impacts, static points force and falling objects, leads to damage of the working surface, causing a decrease of mechanical properties and, eventually, a loss of aesthetics and brightness. This condition represents the starting point for a stress-assisted reaction. Furthermore, during service, chemical and cleaning solutions and other different liquids and substances come into contact with the surface, the influence of which on crack propagation is, in these products, completely unknown.

The subcritical crack growth of soda-lime glass in contact with water is a function of the applied stress intensity factors and depends on the mobility and/or immobility of the alkali ions[1]. The behaviour of other glasses can be more complicated[2], depending on both the composition and the pH of the environment. The dependence of the safe-life and reliability of ceramics on the subcritical crack growth represents a critical design aspect and, because of its importance, this behaviour needs to be known in glasses and ceramics.

According to a general hypothesis, a crack does not grow if the applied tensile stress st does not reach the critical value. Nevertheless, in ceramic materials, cracks can grow at an intensity of the applied tensile stress below the threshold value. At room temperature, silica-based ceramics, in particular soda-lime-silica glass, fail by subcritical crack growth from pre-existing flaws, favoured by a stress-assisted reaction with water. In the case of the interaction between water and vitreous silica, a molecular mechanism for stress corrosion was also proposed, Figure 1[3,4].

This behaviour is present in other ceramics such as alumina, silicon nitride, porcelain and zirconia[5,6]. The interest concerns the crack behaviour in service conditions. If the applied stress triggers the slow growth of a crack, the applied stress intensity factor increases reaching the critical value and consequently the material fails.

Among the silica-based ceramics, a considerable part is represented by glazed ceramic tiles and vitreous mosaic tesserae. During service, the working surface of these products is subjected to concomitant loading conditions, thermal-mechanical and chemical, often causing complex and dangerous synergistic effects. Since these phenomena leave in the material, near the damage, a residual tensile stress field, in regard to silica-based ceramics, this condition may act as driving force for a stress-assisted reaction with the environment, also different from water.

Starting from these observations, the study of the evolutional behaviour of a crack, suitably introduced on the working surfaces of these products, the length of which can be easily measured, turns out to be rather interesting.

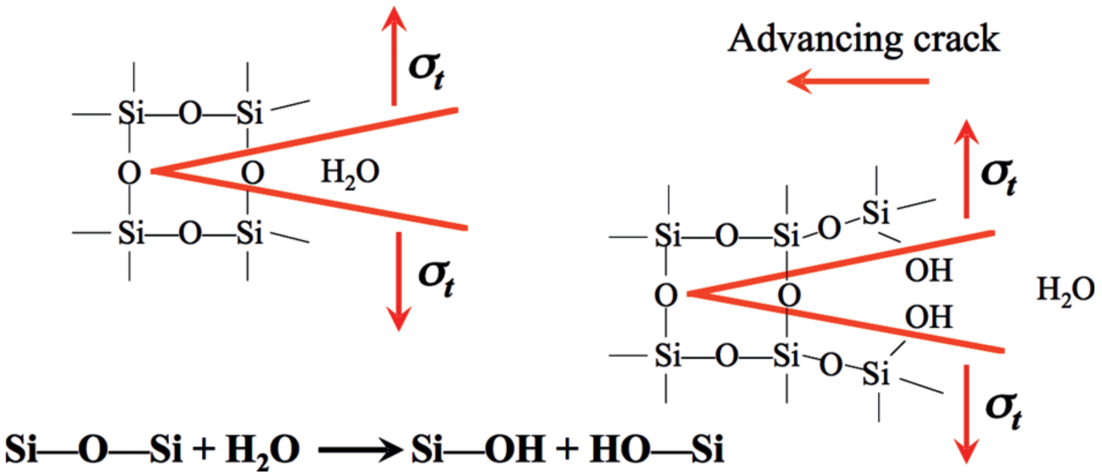


Figure 1. Qualitative molecular model of crack propagation in soda-lime glass.

The sensitivity to SCG of the working surface of glazed ceramic tiles was already presented[7]. With regard to soda-lime glass, it may be noted that, on the basis of its intrinsic characteristics, it results particularly sensitive to external loads. Usually, the surface of soda-lime glass products, as sheets, presents handling damages, such as scratches, grooves and, sometime, very large areas, from which the material has been removed. If this damage is linked to the presence of residual tensile stress field, induced by applied loads, the stress-assisted reaction with the environment can trigger, favouring the SCG phenomenon. That is also source of strength degradation of the material[8,9].

In the present investigation, starting from soda-lime glass, vitreous mosaic tesserae, having different chemical compositions, were considered. In a context of reliability and lifetime of these products, the advanced knowledge of their crack resistance behaviour turns out to be very important.

Considering Vickers indentation method as viable technique, to investigate the crack resistance behaviour, the SCG of four vitreous mosaic tesserae was evaluated in different environments: air having 40% of relative humidity, water and an alkaline solution of potassium hydroxide. The increasing of the median-radial cracks induced by Vickers indentation was evaluated by the difference among the median-radial cracks length, measured immediately after the test and after the leaching treatment, at fixed time intervals. The results were attributed to the different chemical composition and an attempt to correlate it with the crack resistance is presented.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

Four different samples of vitreous mosaic tesserae 50x50mm, denoted on the basis of their colour Transparent, Yellow, Blue and Red, were selected, Figure 2.

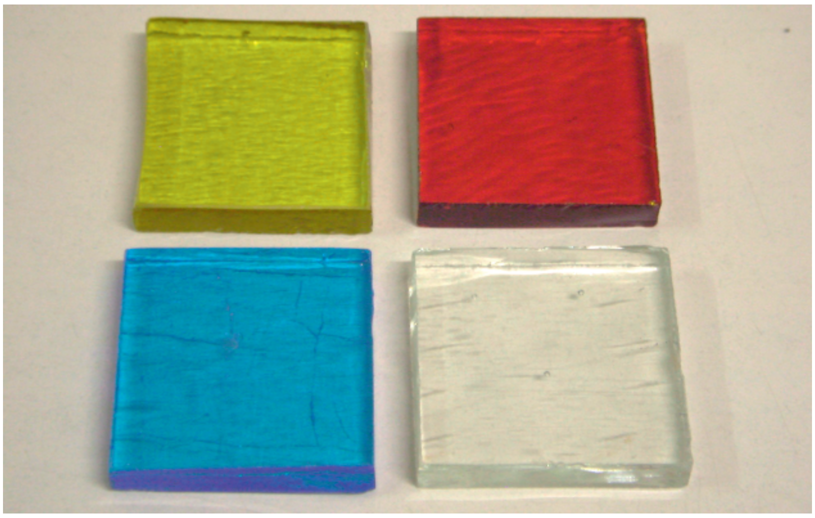


Figure 2. Vitreous tesserae on which the tests were performed.

The tesserae were cut directly from sheets 30x30cm obtained pouring the glass into a mould and subjecting to pressing. The sheets, successively annealed, followed a particular thermal cycle, able to remove the residual stresses induced by the previous process.

The chemical analysis of the vitreous tesserae and the soda-lime glass, denoted S-L G, determined by using an atomic emission spectroscopy (Perkin Elmer ICP - OES Optima 3200 XL, NL), are reported in Table 1 as percentages of moles. In Table 1, it is also shown the role of each oxide in the glass structure, such as glass former, F, intermediate, I, modifier, M, or a combination of roles, F/I, I/M, depending on the whole composition[11]. To rapidly decipher similarities or differences among the samples, the flux and the intermediate oxides were grouped as M + I/M and I + F/I, respectively, and assumed to act similarly, Table 2.

OXIDE	TRANSPARENT mol %	YELLOW mol %	BLUE mol %	RED mol %	S-L G mol %	ROLE
SiO_2	65.80	69.49	71.65	69.61	69.99	F
Al_2O_3	1.44	1.13	1.88	1.18	0.29	F/I
TiO_2	0.02	0.01	0.02	0.01	---	I
Fe_2O_3	0.02	0.04	0.04	0.05	---	I/M
CaO	5.66	4.89	8.13	0.89	12.19	M
MgO	0.11	0.11	0.08	0.27	3.60	M
K_2O	0.04	6.68	0.50	5.67	---	M
Na_2O	20.66	11.13	16.94	13.55	13.93	M
ZrO_2	0.05	---	---	---	---	F/I
CdO	---	0.11	---	0.13	---	I/M
CuO	---	---	0.31	0.22	---	I/M
ZnO	2.79	4.32	0.02	4.94	---	I/M
BaO	1.18	---	---	---	---	M
Sb_2O_5	0.17	---	---	---	---	F
SrO	0.02	---	---	---	---	M
SeO_2	0.13	---	---	0.18	---	F/I
B_2O_3	1.90	2.10	0.43	3.31	---	F

(F = glass former; I = intermediate; M = modifier).

Table 1. Chemical analysis of the vitreous mosaic tesserae and soda-lime glass, S-LG.

ROLE	TRANSPARENT	YELLOW	BLUE	RED	S-L G
F	67.87	71.59	72.09	72.92	69.99
F/I + I	1.64	1.14	1.90	1.36	0.29
M + I/M	30.49	27.27	26.01	25.72	29.72

Table 2. Synoptic table of the chemical analyses of the tested samples. (F = glass former; I = intermediate); M = modifier).

The fracture behaviour of the samples was investigated by Vickers indentation technique, exploiting the induced tensile stress field and the median-radial cracks emerging from the corners of the impression, Figure 3. In this context Vickers hardness was also evaluated adopting an indentation load P = 9.81N. The results are reported in Table 3.

Before each test, the surface of the specimens was cleaned with acetone and carefully inspected in order to find areas free from pre-existing cracks or other defects able to interact with the impression and the correlated phenomena. A single impression was left at the surface of the specimens, by adopting an indentation load P = 9.81N, to induce well developed median-radial cracks and a tensile stress field able to trigger the stress-assisted reaction with the environment. After the removal of the load, considering the median-radial cracks as pre-existing cracks, the post-indentation SCG was evaluated, measuring by light microscopy their length, at fixed intervals of time, every five minutes, for the first half hour, then, after half, one, two and tree hours, respectively. Each test lasted seven hours and involved eleven measurements.

For each sample, different specimens were tested. The crack propagation was evaluated, measuring the length of the median-radial cracks in different environments: air having 40% of relative humidity, water and alkaline solution, KOH 100g/l, as specified in the international standard EN ISO 10545-13 regarding the determination of the chemical resistance of ceramic tiles[12].

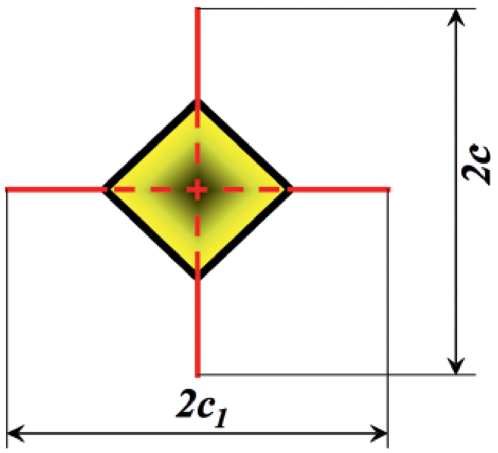


Figure 3. Vickers impression and median-radial cracks.

SAMPLE	$HV_{9.81}$ (GPA)
Transparent	5.1 ± 0.7
Yellow	5.1 ± 0.3
Blue	4.8 ± 0.1
Red	5.4 ± 0.5
S-L G	5.4 ± 0.8

Table 3. Vickers hardness of the tested samples.

The first measurement (the reference measurement at zero-time) was always performed in air, after the removal of the load. Immediately after, for the tests conducted in water and alkaline solution, the impression and the neighbouring surface area were covered with some drops of the specified liquids. Before each successive measurement, to avoid optical distortions, the area containing the impression was quickly dried and immediately covered with some drops of water and alkaline solution. To define the influence of the chemical composition of the glasses on the stress assisted corrosion, the tests were performed also on specimens of soda-lime glass, considered as reference material.

Referring to the symbols reported in Figure 3 and Figure 4, the crack resistance (SCG), in terms of average difference Δc_{im}, was calculated with the relation:

$$\ddot{A}c_{im} = c_{im} - c_{0m} \tag{1}$$

where c_{im} is the average length of the median-radial cracks measured at the i-observation and c_{om} is the average length of the median-radial cracks measured at zero-time, evaluated by the expression:

$$c_{im} = \frac{1}{4}\left(2c_{i1} - 2c_{i2}\right) \tag{2}$$

Adopting for the calculations the relation (2), the resulting crack length represents the average value of four median-radial cracks, taking thus into account a possible non homogeneous behaviour of the material. For each sample, the data calculated using the expression (1) were plotted together with the same of the soda-lime glass,

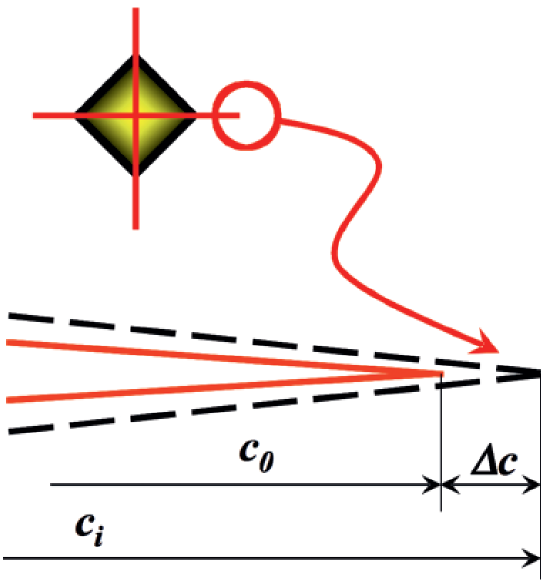


Figure 4. SCG in terms of $\Delta c_i = (c_i - c_0)$, referred to a single median-radial crack.

as a function of time. The curves $\Delta c_m = f(t)$ represent the average velocity of the propagation of the median-radial cracks and allowed comparison of the fracture behaviour and sensitivity to SCG of the different materials both towards the specified environments and in the light of their chemical composition.

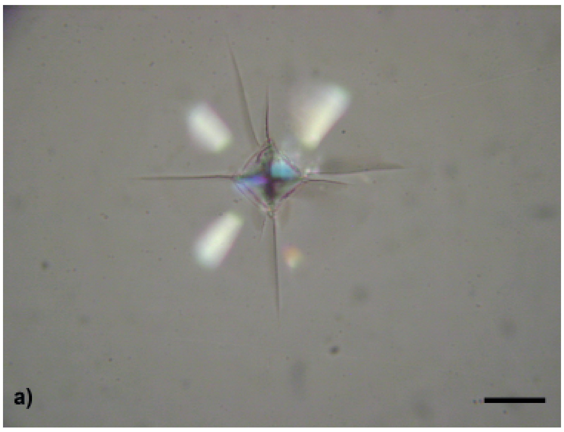
3. RESULTS AND DISCUSSION

The Vickers hardness results, Table 3, do not present significant differences, if compared with the data concerning the soda-lime glass, S-L G. The hardness behaviour does not seem to be influenced by the differences found in the chemical analysis, Tables 1 and 2.

The crack path was observed by the optical microscope. The amorphous nature of the glasses favours a good development of the median-radial cracks and its transparency allowed both the direct observation and analysis and the classification of the indentation cracking present also in ceramic materials[9,10], Figure 5. The fracture resistance of the selected products in terms of differences Δc_m as a function of time was analysed, comparing the effects due to the specified environmental conditions. The results are reported in three different diagrams respectively referred to air, having 40% of relative humidity, water and an alkaline solution, KOH 100g/l, Figure 6 a), b) and c). In the plots the results obtained of soda-lime glass are also reported. Since the behaviour of S-L G sample is in agreement with the results reported in literature[13-16], it can be considered a valid and reliable reference material.

Starting from the effects due to the air with 40% of relative humidity, Figure 6 a), it is interesting to note as, in the first half hour, the velocity of crack propagation is rather high for all the materials and decreases after 1h. The crack propagation stops, for the Yellow, Red and Blue samples, after 2h, while, for the S-L G and Transparent samples, after 4h. The similarities in the shape of the curves, corresponding to the S-L G and Transparent samples and, and the delay with which the cracks are stopped, compared to the behaviours of the other samples, can be correlated with their higher presence of M and I/M oxides, Table 2. It is well known that modifier oxides strongly destabilise the network structure of a glass, by making it more inclined to stress corrosion and, as a consequence, to lower their durability[11,17].

The differences in the SCG become more appreciable, when the tests are conducted in presence of water, Figure 6 b). The S-L G, Transparent and Yellow samples present values of Δc_m, higher in comparison with the same results, obtained in air environment. On the contrary, the Blue and Red samples show similar curves and not significantly different from those presented in air. All that can be justified again considering the relevant amounts of M and I/M oxides in the S-L G, Transparent and Yellow samples, higher than those present in the Blue and Red samples.



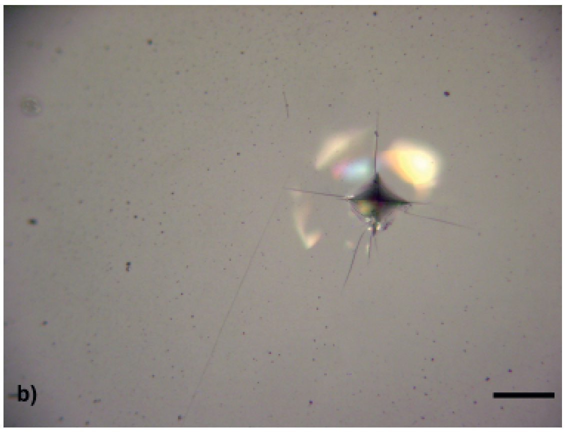
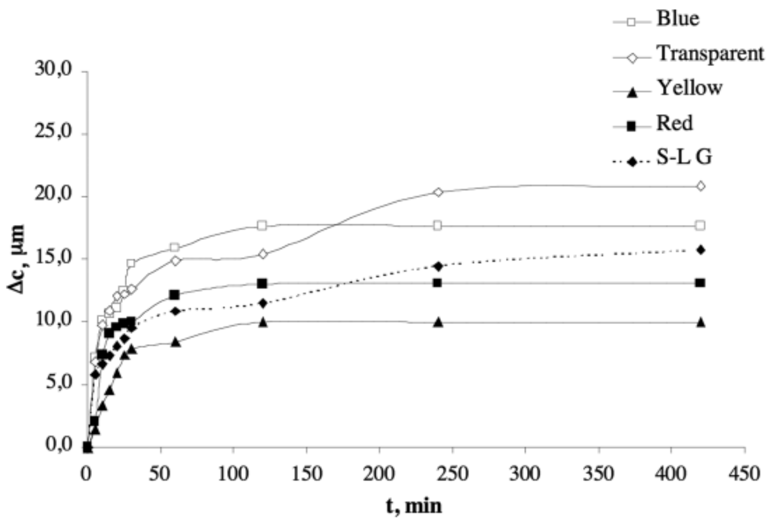


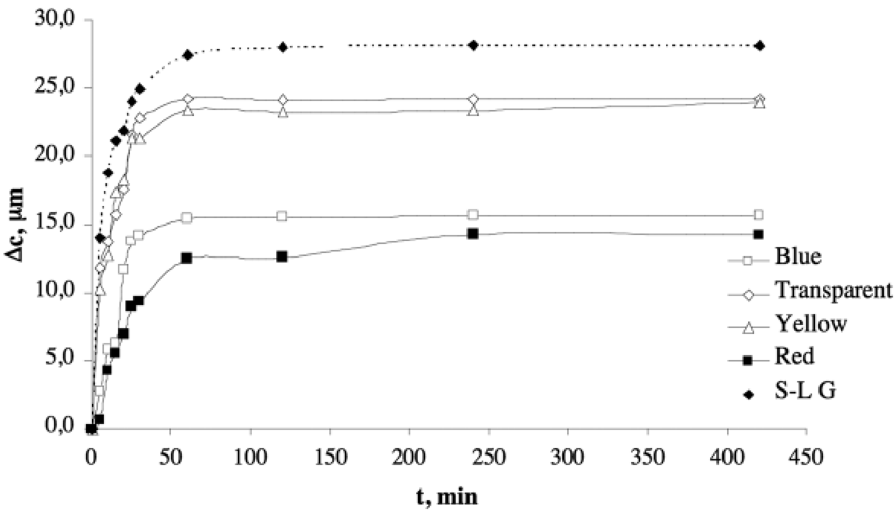
Figure 5. Light micrographs of Vickers indentations and the corresponding crack path of a) S-L G and, b) Red samples in air environment. The bar is 50 µm.

Due to its intermediate amount of M and I/M oxides, the Yellow sample shows a behaviour similar to the more stable glasses, the Blue and Red ones, in air environment, Figure 6 a), while, in the more aggressive water environment, Figure 6 b), it results similar to the S-L G and Transparent samples, for which the higher amount of M and I/M oxides cause a longer crack propagation[11,17].

The alkaline solution, Figure 6 c), affects the S-L G and Yellow samples in a rather similar way to the water environment. In the Blue and Red samples, the effect of the basic solution turns out to be stronger than the water, Figure 6 b), by increasing the crack propagation; the dissociation of SiO_2 and the formation of hydroxyl links is supported by the water present in the solution and KOH increases the effect of the stress-assisted reaction. The different behaviour of the Transparent sample, in which the effect of the KOH solution is less efficacious, compared to the other samples, may be due to the presence of zirconia and antimony oxide, Table 1. It is known that, in alkaline environment, zirconia, even if in low amount, plays a key role in the stabilizing of the glasses, by increasing their durability[17-19]. A not negligible effect may be due to the antimony oxide that, acting as strong former[20], is able to stabilize the network structure of the glass and thus to increase its chemical durability[21].



a)



b)

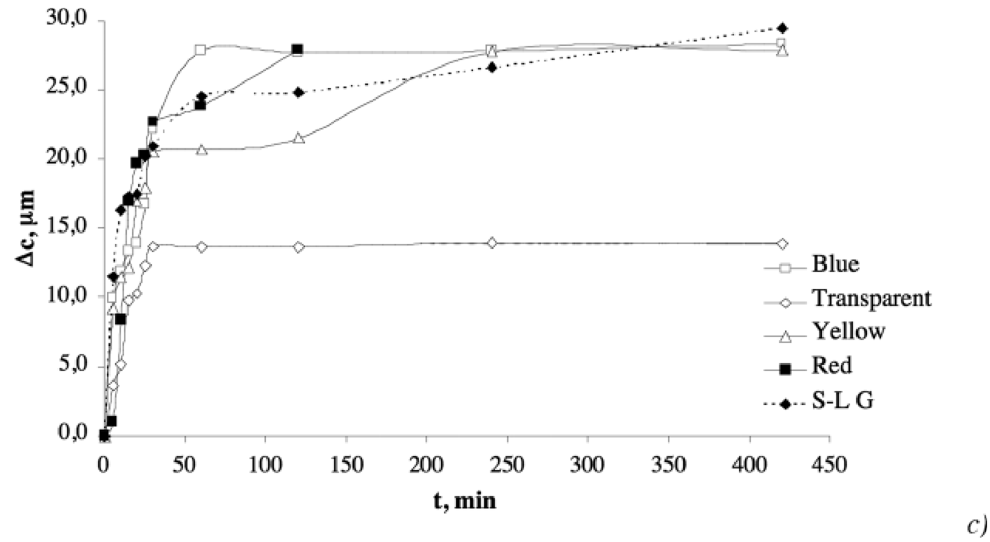


Figure 6. Δc_m as function of time, for the tested samples in a) air, b) water and, c) in alkaline solution, KOH 100g/l.

4. CONCLUSIONS

Four different samples of vitreous mosaic tesserae were selected to assess their crack resistance in terms of slow crack growth, SCG, from pre-existing flaws, by stress-assisted reaction in presence of different environments. For the investigation, Vickers indentation technique was considered, exploiting the induced tensile stress field and the median-radial cracks emerging from the corners of the impression.

On the basis of the results the following conclusions can be drawn:

- these products, rather widespread, are sensitive to the stresses coming from the environment;
- residual tensile stress fields and damage induced by impacts and points force favour the stress-assisted reaction, giving rise to a cracking evolution;
- air (humidity), water and alkaline solution, differently support as a function of time and glass composition, the stress assisted reaction and consequently the degradation of the material.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. A. Albertazzi and G. Bonvicini Ph.D., (Centro Ceramico Bologna) for the chemical analyses and the useful discussion.

REFERENCES

[1] S.M. Wierderhorn. Influence of water vapour on crack propagation in soda-lime glass. J. Am. Ceram. Soc., 50 (1967), 407-414.

[2] S.M. Wiederhorn. Subcritical crack growth in ceramics. In, Fracture Mechanics of Ceramics, Eds. Bradt, R. Hasselman, D.P.H. and Lange, F.F., Plenum Press N.Y. (1974), 613-646.

[3] T.A. Michalske and S.W. Freiman. A molecular mechanism for stress corrosion in vitreous silica. J. Am. Ceram. Soc., 66 (1983), 284-288.

[4] R.F. Cook. Crack propagation thresholds: A measure of surface energy. J. Mater. Res., 1 (1986), 852-860.

[5] S.W. Freiman, K.R. McKinney and H.L. Smith. Slow crack growth in polycrystalline ceramics. In, Fracture Mechanics of Ceramics, Eds. Bradt, R.C. Hasselman, D.P.H. and Lange, F.F., Plenum Press N.Y. (1974), 659-676.

[6] J.B. Wachtman. Subcritical crack propagation. In, Mechanical Properties of Ceramics, John Wiley & Sons, Inc. N.Y. (1996), 117-140.

[7] L. Esposito, D. Naldi, E. Rambaldi, A. Tucci. Slow crack growth (SCG) in glazed ceramic tiles. Oral presentation at the 10th European Ceramic Society Conference, Berlin, 17-21 June, 2007.

[8] D.C. Larsen, J.W. Adams, S.A. Bortz and R. Ruh, Evidence of strength degradation by subcritical crack growth in Si3N4 and SiC. In, Fracture Mechanics of Ceramics, Eds. Bradt, R.C. Evans A.G. Hasselman, D.P.H. and Lange, F.F., Plenum Press N.Y. (1983), 571-585.

[9] G.K. Bansal, W.H. Duckworth. Effects of moisture-assisted slow crack growth on ceramic strength. J. Mat. Sci., 13 (1978), 239-242.

[10] R.F. Cook and G.M. Pharr. Direct observation and analysis of indentation cracking in glasses and ceramics. J. Am. Cer. Soc., 73 (1990), 787-817.

[11] A. Varshneya. Fundamentals of inorganic glasses, Academic Press Inc., Harcourt Brace & Co. Publisher N.Y. State College of Ceramics, Alfred University, (1994).

[12] International Standard EN ISO 110545-13: Ceramic tiles - Determination of chemical resistance, (2000).

[13] P.J. Dwivedi, D.J. Green. Determination of subcritical crack growth parameters by in situ observation of indentation cracks. J. Am. Ceram. Soc., 78 (81) (1995), 2122-2128.

[14] V.M. Sglavo, D.J. Green. Influence of indentation crack configuration on strength and fatigue behaviour of soda-lime silicate glass. Acta Metal. Mater., 43 (3) (1995), 965-972.

[15] M. Yoda, Y. Yoshikava. Growth and Coalescence of Indentation Cracks in Glass. J. Am. Ceram. Soc., 70 (11) (1987), 301-302.

[16] M. Yoda. Subcritical crack growth in soda-lime glass under combined modes I and III loading. J. Am. Ceram. Soc., 73 (7) (1990), 2124-2127.

[17] G.W. Morey. The properties of glass. Reinhold Publishing Corporation N.Y. (1954).

[18] R.A. Eppler, D.R. Eppler. Glazes and glass coating. The American Ceramic Society, Westerville, Ohio, (2000).

[19] B. Karasu, M. Cable. The chemical durability of SrO-MgO-ZrO2-SiO2 glasses in strongly alkaline environments. J. Europ. Ceram. Soc., 20 (2000), 2499-2508.

[20] M. Nalin, M. Poulain, M. Poulain, S.J.L. Ribeiro, Y. Messaddeq. Antimony oxide based glasses. J. Non-Cryst. Sol., 284 (2001), 110-116.

[21] J.G. Wood, S. Prabakar, K.T. Mueller, C.G. Pantano. The effect of antimony oxide on the structure of alkaline earth alumino borosilicate glasses. J. Non-Cryst. Sol., 349 (2004), 276-284.