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Research Article

Comparative Study of the Thermal Shock Resistance of an Industrial Tableware Porcelain

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The effect of the glazed layer and firing conditions (temperature and duration) on the thermal shocks behavior of tableware porcelains has been studied. Two types of glazed layers and three firing conditions, used industrially in the commercial porcelains manufacture, are used in this investigation. Repeated thermal shock tests showed that the glazed layer with higher alumina/silica ratio is more resistant to thermal shocks and that the slow firing cycle, even at a relatively low temperature, is very beneficial for the thermal shock resistance of the porcelain matrix. Three-point bending tests showed that the crazing phenomenon, which affects the glazed layers as well as the porcelain matrix, does not affect significantly the mechanical resistance of these materials.

1. Introduction

The fine and translucent porcelains are used generally to produce tableware, household kitchen utensils, sanitary ware, laboratory materials, electric insulators, sparkplugs for combustion engines, and biomedical organs (such as teeth, disc, or body). Tableware porcelains are often coated with a silica-glazed layer to increase their water resistance, whitening, smoothing, and shining properties. However, repeated thermal shocks lead to the formation of randomly distributed surface cracks and crazes which are attributed principally to the relaxation of compressive stresses and to the difference between the thermal expansion coefficients of the glazed layer and the porcelain matrix [1–3]. The nucleation and the evolution of these cracks depend also on the chemical composition of the glazed layer and the firing process [1, 4–16].

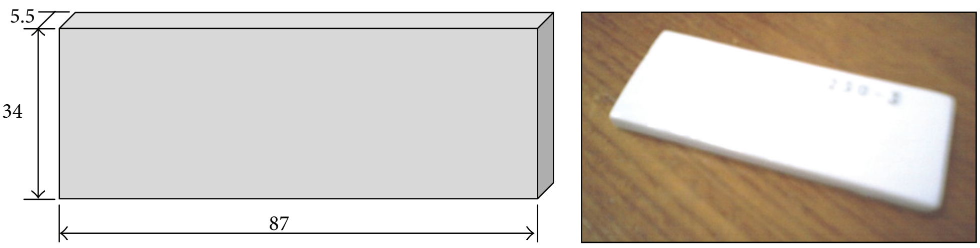
During the last few decades, many works have been devoted to the study of thermal shock resistance of metallic-coated or -glazed porcelains used in dental biomaterials. In particular, the phenomenon of crazing has been extensively investigated due to its detrimental consequences when these crazes become a nesting site for bacteria [17, 18]. However, studies devoted to the tableware porcelains are very limited and do not reflect the commercial importance and the general use of these materials in our daily life. The few performed studies are aimed at determining the effect of parameters such as microstructure, firing conditions, and quartz content on the mechanical and physical properties of porcelains. These results which are sometimes contradictory have been based on three main hypotheses such as the presence of fine mullite needles [5, 6, 8], the dispersion strengthening of the vitreous porcelain structure [9], and the reinforcement of the matrix by the development of compressive residual stresses [1, 7, 10, 11].

The thermal shock resistance of porcelain, as one of a ceramic family, is usually evaluated by the water-quenching method in which specimens are heated to a particular temperature and then quenched in water bath. This test method for the determination of thermal shock resistance by water quenching is commonly used and has been standardized in the ASTM C1525. Thermal shock resistance is graded by the critical temperature difference (ΔT_{Max}) which describes the maximum change in instantaneous temperature that can occur without the initiation of cracks.

The main objective of this work is to present a comparative study in order to determine the effects of glazed layers and firing conditions on the thermal shock resistance of an industrial tableware porcelain. Repeated thermal shock tests are performed on six porcelain grades to reproduce

Table 1: Chemical composition (wt.%) of the glazed layers.

Family	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O
230	72,29	12,48	0,90	0,54	2,51	6,45	0,56	4,27
302	66,90	17,20	0,90	0,54	2,22	7,70	0,45	4,09



(a) Sample geometry (size in mm)

(b) Sample photography

Figure 1: Sample geometry.

the thermal crazing similar to the one that appeared in service on the same materials. The crack nucleation and propagation have been studied in terms of number and length. The results are analyzed as a function of the number of thermal shocks applied to the material. The evolution of the mechanical properties of the studied materials as a function of the number of thermal shock cycles has been studied using three-point bending tests.

2. Experimental Procedure

2.1. Materials and Sample Preparation. The samples used in this investigation, provided by the Tunisia porcelain company, are prepared from porcelain of 50% kaolin, 25% quartz, and 25% feldspar. The samples are classified in two glazed layer families: 230 and 302. The chemical compositions of the two glazed layers are indicated in Table 1. Three grades (1, 2, and 3) have been prepared from each family using different firing conditions (temperatures and duration) as follows:

(1) firing at 1340°C during 25 hours using a tunnel furnace;

(2) firing at 1360°C during 7.5 hours using a fast-firing furnace (length 36 m);

(3) firing at 1370°C during 7.5 hours using a fast-firing furnace (length 60 m).

For example, grade 230-2 designates the porcelain sample from the family 230 subjected to firing at 1360°C during 7.5 hours using a fast-firing furnace (length 36 m).

Test samples (Figure 1) of prismatic shape ($87 \times 34 \times 5.5$) are obtained with the same manufacturing processes. These samples present a *glazed face* and a *normal face* that represent the original structure of the porcelain material. Designations which are *glazed face* and *normal face* will be preserved carefully in this study in order to determine their thermal shock behavior.

2.2. Bending Tests. The mechanical properties of the six porcelain grades used in this investigation have been determined using a 3-point bending tests with a span (l) of 50 mm and a crosshead speed of 1 mm/min on a MTS system. Young's modulus and the maximum stress have been determined by expressions (1) and (2), respectively:

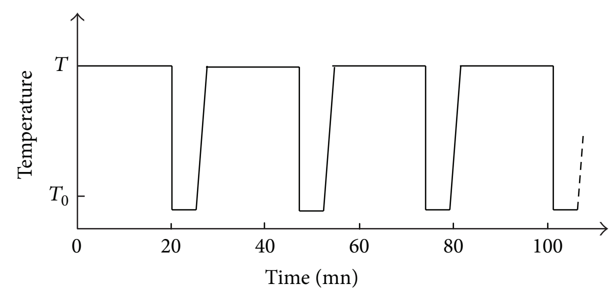


Figure 2: Thermal shock cycle applied to samples.

$$E = \frac{Cl^3}{48 I_{Gz}}, \tag{1}$$

$$\sigma_{\max} = \frac{3}{2}\,\frac{F_{\text{Max}} l}{bh^2}. \tag{2}$$

In these equations, $C = F_{\text{Max}}/y_{\text{Max}}$ is the slope of the force-deflection curve, $I_{Gz} = bh^3/12$ is the quadratic moment, F_{Max} and y_{Max} are force and deflection at fracture, respectively, l is the span, and b and h are the width and the thickness of the sample, respectively.

2.3. Thermal Shock Tests. To reduce the error margin, thermal shock tests have been applied simultaneously to sets of three different samples. The thermal cycle applied to each set is illustrated in Figure 2. It consists of a heating phase to T for 20 minutes followed by water quenching to ambient temperature $T_0 = 20^{\pm 2}$ °C. The intermediate transfer phase of the samples between the furnace and the water bath has been neglected since it is done very quickly (few seconds). The thermal shock resistance ($\Delta T_{\max}$) is estimated [19] using the following relationship:

$$\Delta T_{\max} = \frac{(1-\nu)\,\sigma_{\max}}{E\alpha}, \tag{3}$$

Table 2: Maximum force and deflection for the studied porcelain grades.

Grade	230-1	230-2	230-3	302-1	302-2	302-3
Average maximum force F_{Max} (N)	750	1025	700	850	950	800
Average maximum deflection y_{Max} (mm)	0.11	0.12	0.11	0.12	0.13	0.11

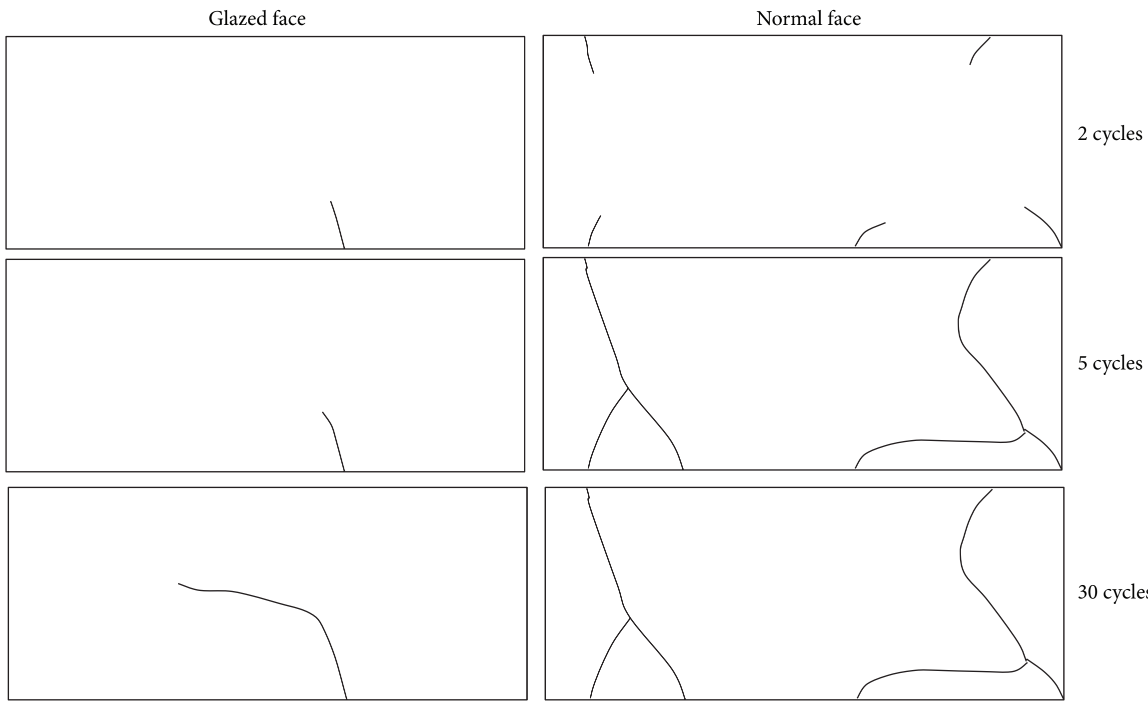


Figure 3: Surface cracks evolution by thermal shocks of the grade 302-3 at $\Delta T = 230\,^{\circ}$C.

where σ_{max} is the maximum fracture stress, E is Young's modulus, ν is Poisson's ratio, and α is the thermal expansion coefficient of glazed layers.

2.4. Cracks Characterization. The samples used in the thermal shock tests have been initially examined by macrographic observations in order to verify the absence of surface defects (scratches, scraping, bubbles, etc.). After every thermal shock cycle, both *glazed face* and *normal face* of the sample are macrographically examined, and the generated cracks due to the thermal shocks are scanned for qualitative and quantitative analyses.

3. Results

3.1. Mechanical Resistance of the Initial State Material. Three-point bending test results obtained on the studied material in the initial state for different grades are summarized in Table 2. The evaluated properties are the mechanical stress, Young's modulus, and the thermal shock resistance. All these properties are determined using (1), (2), and (3), respectively, with a Poisson's ratio $\nu = 0{,}25$, thermal expansion coefficient $\alpha = 44 \times 10^{-7}(^{\circ}\text{C})^{-1}$ for 230 family, and $\alpha = 43 \times 10^{-7}(^{\circ}\text{C})^{-1}$ for 302 family. The results are shown in Table 3.

3.2. Thermal Shock Resistance. We assume that the nucleation stage is achieved, after a number of thermal shock cycles,

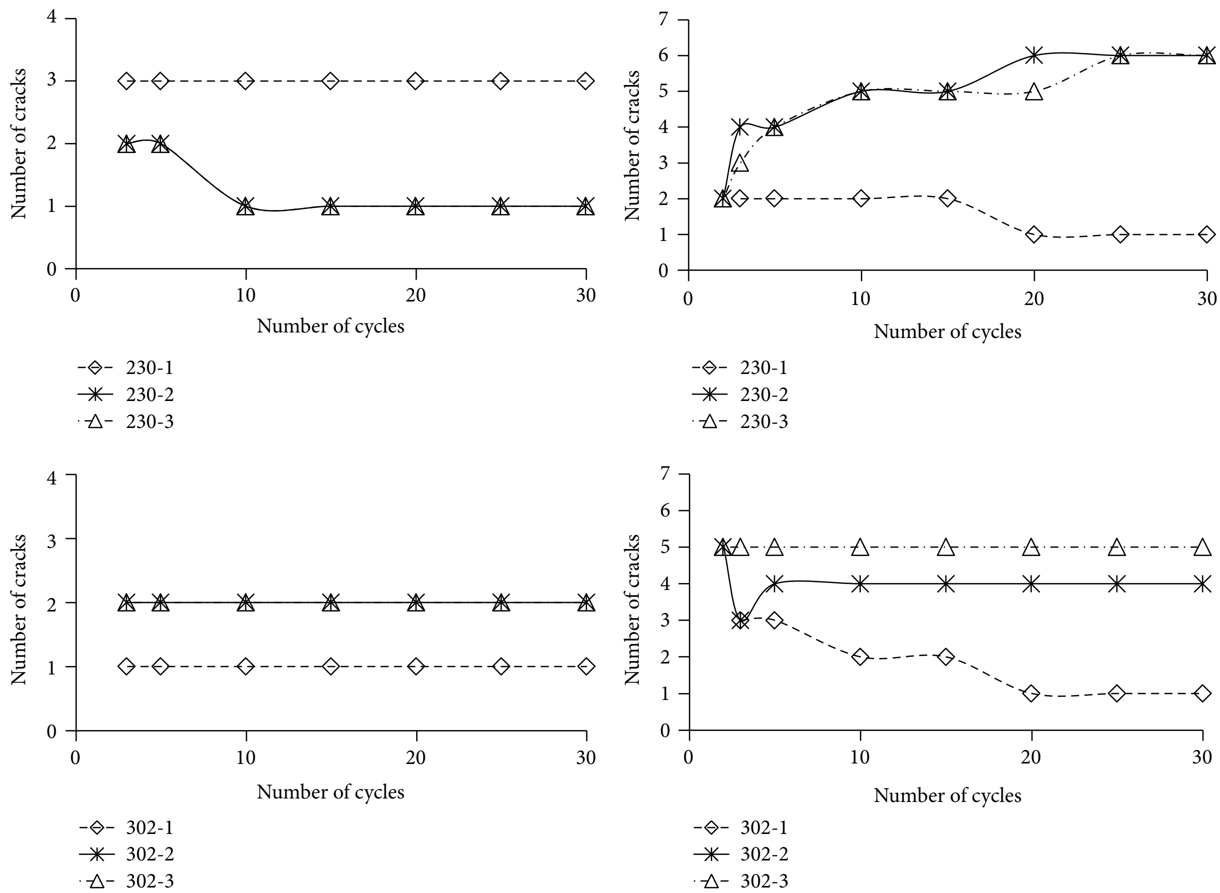
Table 3: Estimated mechanical and thermal properties of the studied porcelain grades.

Grade	230-1	230-2	230-3	302-1	302-2	302-3
Mechanical stress σ_{max} (MPa)	55	75	51	62	69	58
Young's modulus E (GPa)	38	47	35	39	40	40
Thermal shock resistance ΔT_{Max} (°C)	236	258	236	258	279	236

when the surface of the sample presents one or several detectable cracks that could be observed by macrographic examination [2]. For example, Figure 3 shows the cracks' cartography of the *glazed face* and *normal face* of the grade 302-3 produced by cyclic thermal shocks at $\Delta T = 230^{\circ}$C.

3.2.1. Number of Cracks. The number of cracks is defined by the number of all observed cracks, by macrographic examination, on the sample surface. For example, Figure 4 illustrates the number of cracks as a function of thermal shock cycles at $\Delta T = 230^{\circ}$C for the studied grades.

3.2.2. Length of Cracks. The total length of cracks is defined as the sum of lengths of all existing cracks. Figure 5 illustrates



(a) *Glazed face* (b) *Normal face*

Figure 4: Number of cracks as a function of the number of thermal shock cycles at $\Delta T = 230^{\circ}$C.

the evolution of the crack length as a function of the number of thermal shock cycles generated at $\Delta T = 230^{\circ}$C for the studied grades.

Results of thermal shock tests showed that the number and the total length of the formed cracks stabilize in both faces at a maximum of 20 cycles for $\Delta T = 230^{\circ}$C and after the first 2 cycles for $\Delta T = 280^{\circ}$C. For $\Delta T = 180^{\circ}$C, no cracks have been detected after 30 thermal shock cycles.

For $\Delta T = 230^{\circ}$C ($T = 250^{\circ}$C) the following can be shown.

(i) The number of cracks on the *normal face* for grades 2 and 3 is higher than that on the *glazed face*, whereas it is comparable on both faces for grade 1. This number decreases in some cases where certain cracks undergo junction by coalescence that often occurs by the creation of triple points or by the interconnection of two cracks.

(ii) No new cracks appeared after the first five cycles on both faces for all the studied grades.

(iii) The total length of cracks is higher on the *normal faces* than on the *glazed faces* for all the grades.

(iv) For the porcelain matrix, the slow-firing process applied to grade 1, although is performed at a relatively low temperature, seems to have a beneficial influence on the thermal shock resistance (Figure 6);

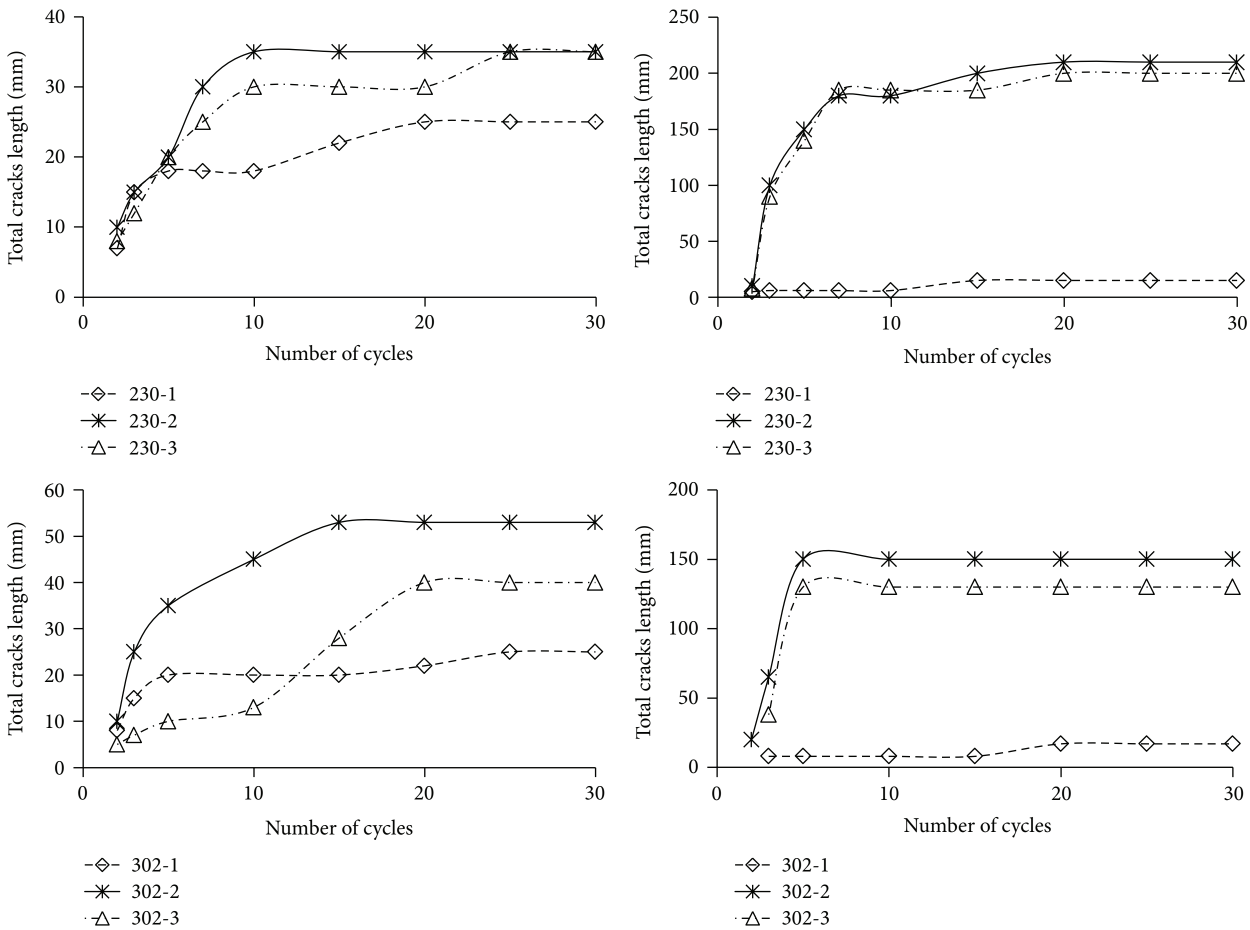
(v) The crack propagation is very brutal on the *normal face*, whereas these cracks grow much slower and often stopped on the *glazed face* (Figure 3).

3.3. Mechanical Resistance Evolution. The mechanical resistance degradation of the porcelain grades used in this study by thermal shock has been studied in terms of the isotropic damage (D) given by the following expression:

$$D = \frac{\left|\sigma - \sigma_0\right|}{\sigma_0}, \tag{4}$$

where σ_0 and σ are the mechanical resistance of the material in the initial state and after the thermal shocks, respectively.

Table 4 gives the damage by thermal shocks after 30 cycles at $\Delta T = 230^{\circ}$C for the different grades. It is clear that the damage by thermal shocks at $\Delta T = 230^{\circ}$C is lower for grade 1, whereas it is comparable for other grades. This result is in good agreement with the rate of cracking (Figure 4). However, a damage of 2.4% has been produced for grade 1



(a) *Glazed face*

(b) *Normal face*

Figure 5: Total length (mm) of cracks as a function of the number of thermal cycles $\Delta T = 230^{\circ}$C.

Table 4: Damage of the studied grades by thermal shocks at $\Delta T = 230^{\circ}$C.

Grade	230-1	230-2	230-3	302-1	302-2	302-3
Damage D (%)	6	12	11,5	6,5	11	10

after 30 thermal shock cycles at $\Delta T = 180^{\circ}$C for which no crack has been macrographically observed. Grades subjected to thermal shocks at $\Delta T = 280^{\circ}$C lost 50% of their mechanical resistance after the first applied cycle.

4. Discussion

At $\Delta T = 180^{\circ}$C ($T = 200^{\circ}$C), the studied industrial porcelain grades did show good resistance to the thermal shocks and no cracks have been detected until 30 cycles, whereas, for $\Delta T = 230^{\circ}$C ($T = 250^{\circ}$C), a network of cracks had been developed on both *glazed* and *normal faces* of the six studied grades. These results are in good agreement with the theoretical evaluations of the thermal resistance provided in Table 3.

The phenomenon of crack arrest, which is very remarkable on the *glazed face*, can be attributed to the presence of precipitates in the glazed layer which serve as obstacles to brutal propagation of these cracks. In particular, it has been confirmed [20–22] that the presence of TiO_2 in the chemical composition of a vitreous structure facilitates the nucleation and the growth of these precipitates. Furthermore, this precipitation is strongly favorable by the relatively high firing temperature.

The glazed layer of 302 family showed a more attractive behavior than that of 230 family. This result consolidates the assumption that the high alumina/silica ratio improves the mechanical resistance of the glazed layer.

The brutal propagation of cracks in the *normal face*, occurred usually by coalescence, is confirmed for this type of materials and reflects the amorphous structure of the porcelain matrix. The slow firing process, although performed at a relatively low temperature (grade 1), is very beneficial for the thermal shock resistance of the porcelain matrix. However, this process did not show a considerable effect on the thermal shock behavior of glazed layers. For identical firing durations (grades 2 and 3), the relatively low difference of the firing temperature did not show a significant effect on thermal shock resistance.

The evolution of developed cracks by thermal shocks at $\Delta T = 230^{\circ}$C stops after the first 20 cycles for the six grades. This result can be attributed, as confirmed in the literature

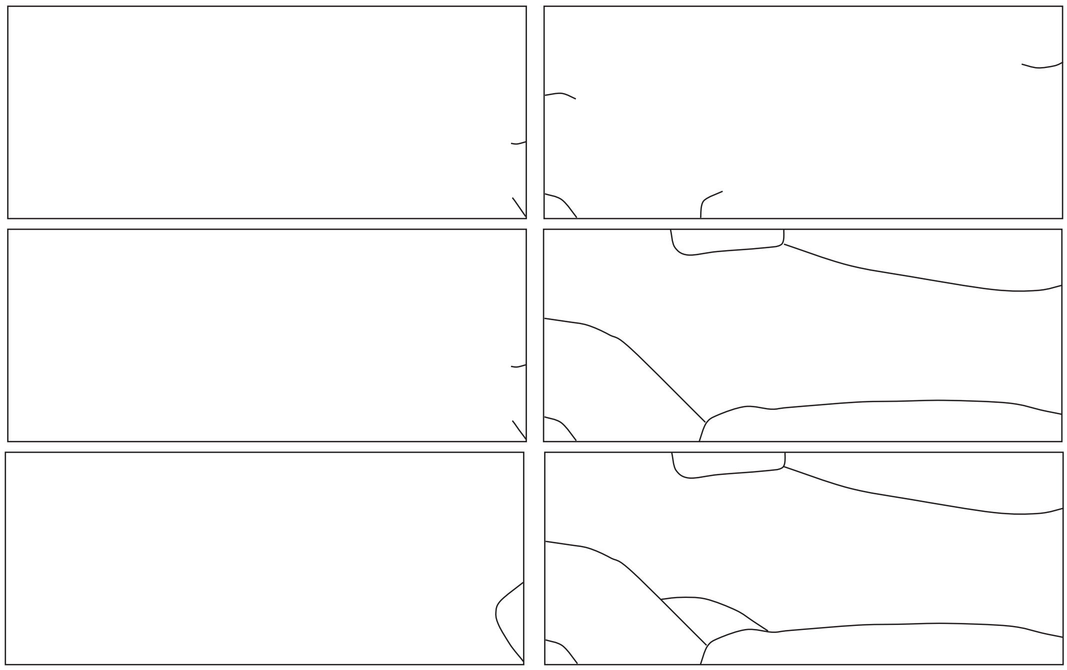


Figure 6: Cracks cartography on the *normal face* of grades 230-1 and 230-2 after cyclic thermal shocks at $\Delta T = 230^{\circ}$C.

[2, 3, 17, 18], to the relaxation of compressive stresses. These last ones are related to the evolution of the porcelain matrix microstructure during firing process, and they are more important when the firing duration is shorter [7, 9–11]. The few crazes observed on the *glazed face* can be related to the delamination phenomenon [3, 23] occurred at the glazed layer-porcelain matrix interface due to their different thermal expansion rate.

The damage, after 30 cycles of thermal shock at $\Delta T = 230^{\circ}$C is relatively low (the maximum value is 12%). In addition, a damage of 2.4% after 30 cycles thermal shocks at $\Delta T = 180^{\circ}$C has been obtained even though no cracks have been detected by macrographic observation. This puts in question the method usually used to detect and to follow the evolution of generated thermal shock cracks. In addition, these results led to classify the observed cracks into the crazing phenomenon that consists of the generation of randomly oriented superficial cracks which do not affect considerably the mechanical behavior. However, crazed tableware porcelain should be generally avoided for food contact as the cracks can harbor bacteria.

5. Conclusions

Thermal shock tests have been performed on six grades of an industrial porcelain in order to compare their behavior to thermal shocks. The studied grades differ by the glazed layers 230 and 302 and by the firing conditions (1, 2, or 3). Test samples have glazed and normal faces.

At a difference of temperature of $\Delta T = 180^{\circ}$C, the studied industrial porcelain showed a good resistance to thermal shocks. However, for $\Delta T = 230^{\circ}$C, a network of cracks has been developed on the glazed and the normal faces.

The thermal shock resistance of glazed layer is more important than of porcelain matrix. However, the two glazed layers show a similar behavior to thermal shocks in terms of crack initiation and propagation with a minor advantage for the 302 family.

The slow firing, even performed at relatively low temperature (grade 1), has a very beneficial effect on the thermal shock resistance of the porcelain matrix. For the same firing duration (grades 2 and 3), a small difference in firing temperature does not have a considerable effect on the thermal shock resistance.

The crazing produced by thermal shocks does not have considerable effect on the structural damage that varies between 6 and 12% at $\Delta T = 230^{\circ}$C. This damage is attributed to the compression stress relaxations in the porcelain matrix and to the delamination at the interface between the porcelain matrix and the glazed layer.

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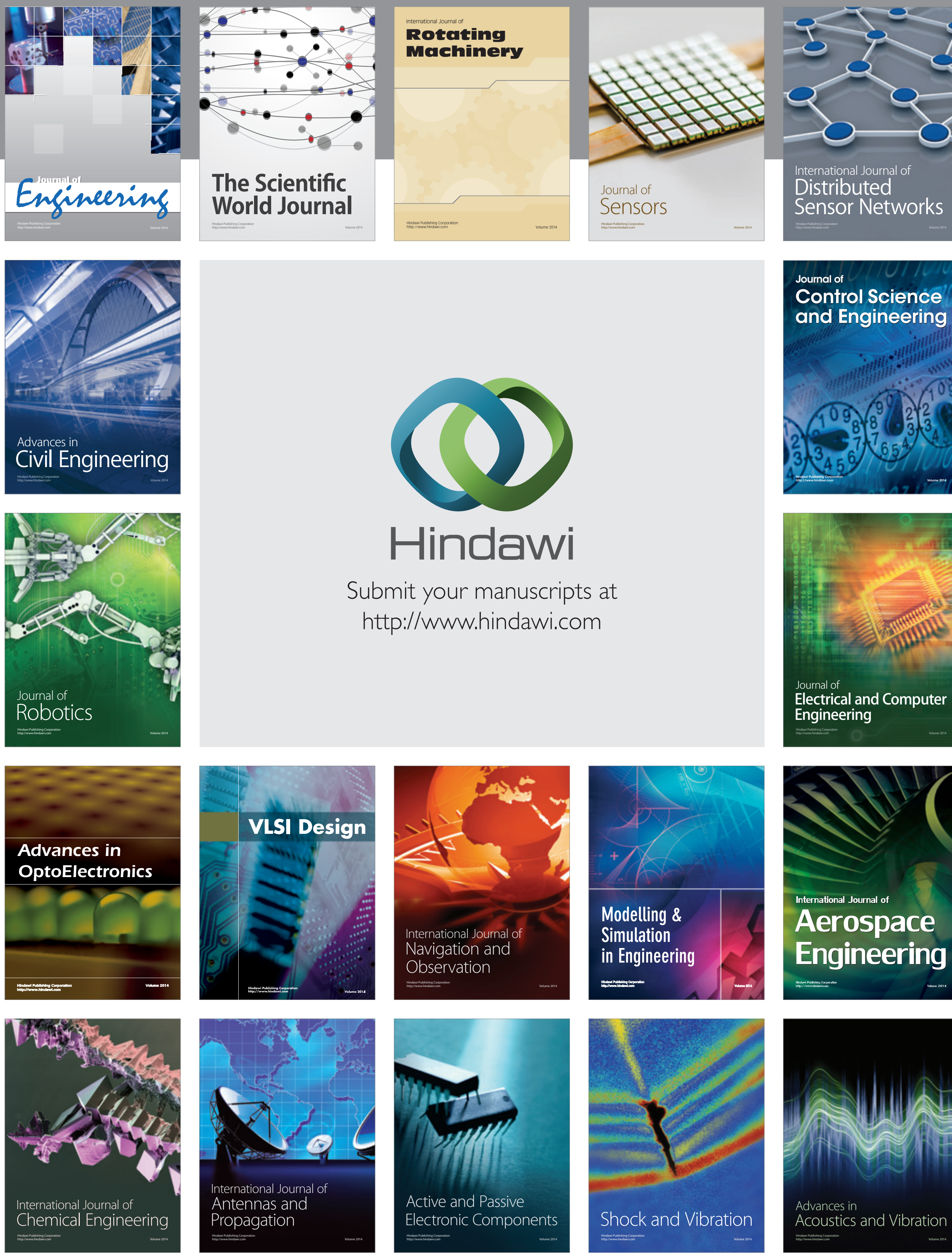
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