Ceramics International 42 (2016) 15199–15202

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Chemical tempering of porcelain tiles

Marcelo Dal Bó [a,*], Lucas Dominguini [a], André Zimmer [b], Sílvia R. Grando [b], Paloma Kaspari [b], Dachamir Hotza [c]

[a] Federal Institute of Education, Science and Technology of Santa Catarina (IFSC), Campus Criciúma, 88813-600 Criciúma, SC, Brazil
[b] Federal Institute of Education, Science and Technology of Rio Grande do Sul (IFRS), Campus Feliz, 95770-000 Feliz, RS, Brazil
[c] Graduate Program in Materials Science and Engineering (PGMAT), Department of Chemical Engineering (EQA), Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis, SC, Brazil

ARTICLE INFO

Article history:
Received 8 May 2016
Received in revised form
31 May 2016
Accepted 21 June 2016
Available online 22 June 2016

Keywords:
Mechanical properties
Diffusion
Strength
Chemical tempering

ABSTRACT

This work presents an innovative approach for strengthening porcelain tiles via chemical tempering, which consists in replacing cations with smaller ionic radius by similar cations with larger ionic radius. Na-containing porcelain tiles were immersed into molten KNO_3 bath. A concentration profile of Na and K in the cross section of porcelain tiles to a depth of 200 μm from the surface confirmed the ion exchange. Compressive stresses on the material surface were produced, leading to flexural strength of up to 54.5 MPa (~74% increase) after chemical tempering at 360 °C during 5.5 h.

1. Introduction

Porcelain stoneware is a ceramic tile with outstanding technical and esthetic properties. Porcelain tiles present specific characteristics as low porosity and, consequently, low water absorption and good mechanical strength. Currently, there are two typologies of porcelain stoneware, glazed or unglazed porcelain tiles (the latter also known as technical porcelain tiles). Glazed porcelain tiles receive a vitreous coating on the surface while technical porcelain tiles are composed only by the support layer. A support layer is formulated from clays, fluxing agents (usually feldspar) and inert raw materials (usually quartz). Porcelain tile is a fully vitrified tile with water absorption $\leq 0.5\%$, belonging to groups AIa and BIa according to ISO 13,006 standard [1].

Ceramic tiles are currently being marketed with features that make them products whose applications go far beyond traditional tile uses. In these new tile applications, the functionalities involved are mainly related to surface modifications or coatings in order to promote photocatalysis [2], hydrophobicity [3], photovoltaics [3] and antibacterial activity [4]. On the other hand, surface modifications have also been employed to increase hardness, abrasion resistance and bending strength particularly of porcelain tiles [5]. Those enhanced mechanical properties make porcelain stoneware the first choice for high traffic and industrial areas, as well as for environments where resistance to chemical and cleaning agents is of prime importance. Finally, if a surface modification may improve functional and structural performance, the development of innovative tiles may be directed towards a decrease in the thickness of tiles. Instead of making thicker tiles to increase mechanical strength, thinner tiles with a surface modification could bring similar results with a lower amount of raw materials and energy during manufacturing, as well as lower costs during transportation and final application due to lower product volumes or weights [6].

The mechanical resistance of ceramic materials can be increased by several methods. First, one can change the composition of the ceramic support and some process variables, such as the compaction pressure and the firing temperature [7,8]. On the other hand, the mechanical strength may be enhanced through surface treatments, such as tempering.

Usually two types of tempering processes may be applied. Thermal tempering is a process in which the material is subjected to a temperature quenching on its surface [9], while chemical tempering involves replacing ions present on the surface material [10,11]. Both processes have the purpose of incorporating surface compressive residual stresses. Those compressive stresses promote an extra gain in mechanical resistance. In this way, the treated material becomes tougher, since it is necessary to overcome firstly the compressive stresses on the surface, to later

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[*] Corresponding author.
E-mail address: marcelodalbo@hotmail.com (M. Dal Bó).

http://dx.doi.org/10.1016/j.ceramint.2016.06.138
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overcome the fracture strength of the material [12].

Thermal tempering is a standard procedure employed in the manufacture of metals and alloys [13,14] and flat glasses [15], but also has been applied to dental porcelain [16], porcelain stoneware [17], and glass matrix composites [18]. In this case, the compressive stresses on surface material are generated after a quenching from firing to room temperature. De Noni et al. studied the development of macroscopic residual stresses for porcelain tile, and observed that the mechanical strength increased less than theoretically expected, owing to deterioration of the sintered tile microstructure [17]. A major contributing factor was the presence of large quartz particles within the glassy matrix, which is typical of porcelain stoneware tiles. On the other hand, chemical tempering is commonly used in glasses for special applications [15,19]. This process is characterized by ion exchange between cations of molten salt bath (of larger ionic radius) by constituent cations of the material (of smaller ionic radius). This cationic substitution causes compressive residual stresses on surface material, thus increasing its mechanical strength.

Previous studies have shown that chemical tempering can generate compressive residual stresses around 750 MPa in soda-lime glasses, whereas this increase typically does not exceed 75 MPa in thermal tempering [11,20]. Another drawback of thermal tempering is related to the thermal shock resistance, remembering that porcelains are glassy materials with insertions of crystalline quartz, what makes this material unsuitable for rapid quenching. Porcelain microstructure may deteriorate during rapid cooling due to subcritical growth of the cracks that form in the material in the presence of thermal tensile stresses at the surface during cooling [17].

Thus, this work aims to study the application of the chemical tempering as an original and innovative approach for strengthening porcelain tiles. In addition, this process can enable a significant reduction of thickness in ceramic tiles. This in turn may decrease the consumption of raw materials as well as the demand of energy during processing.

2. Experimental

2.1. Design of experiments

Considering the dependence of the chemical tempering process with temperature and time, a 2^2 factorial experiment with one central point was designed (Table 1). For each point of the design of experiments, 10 specimens were prepared.

2.2. Specimen preparation

Porcelain spray-dried powder – produced from sodium feldspar, clays and some inert materials – was used for preparing samples. Humidity of the ceramic powder was controlled at 8 wt%, and the forming process was carried out in a semiautomatic uniaxial press (Mawil). Specimens with dimensions of 70 × 30 × 6 mm³ were pressed at 21 MPa to produce samples of ~2000 kg/m³ of green density, measured by the Archimedes method.

Table 1
Factors and levels studied during the chemical tempering process.

Variable/factor	Level		
	−1	0	+1
Tempering temperature (°C)	360	420	480
Tempering time (h)	1	5.5	10

Samples were dried at 110 °C for 24 h. The sintering was performed in a muffle furnace at a heating rate of 20 °C/min and a hold of 18 min at the maximum temperature of 1200 °C. After sintering, the specimens were slowly cooled in the oven to room temperature (4 °C/min). The water absorption tests followed the ISO 10,545-3:1995, within the standards set for porcelain tiles [21].

2.3. Chemical tempering

For the chemical tempering process, anhydrous potassium nitrate (KNO_3, > 99% PA, melting point 334 °C, Química Moderna, Brazil) was used. The salt was molten in a muffle furnace and held at temperatures specified in the factorial design (Table 1). Then, the porcelain specimens were immersed into molten KNO_3 with the aid of a support and kept during the respective time slots. After chemical tempering, the samples were removed and cleaned under running water. Subsequently, the specimens were dried in an oven for 1 h to remove the surface moisture.

2.4. Mechanical and chemical characterization

The flexural strength was measuring using a fleximeter (BIV Pavitest) at 44 N/s. The results were analyzed statistically (Statistica 7.0, Statsoft).

In addition, a chemical and microstructural characterization of the samples was performed. The porcelain microstructure was analyzed using scanning electron microscopy (SEM, Jeol JSM 6390) with secondary electrons (SE) mode, potential of 15 kV, and magnification between 20 to 150 ×. Additionally, an energy dispersive X-ray spectroscope (EDS, Thermo 6733-A) attached to the microscope was employed to perform a semiquantitative compositional analysis. Finally, a concentration profile of Na and K elements was built with the aid of an image analysis software (ImageJ, INH).

3. Results and discussion

3.1. Chemical tempering

According to the chemical composition in Table 2, porcelain is constituted by alkaline (Na, K) and alkaline earth (Mg, Ca) elements. Those elements act as a flux during sintering, aiding densification and consequently reducing the porosity of the final product. The higher concentration of Na_2O in relation to K_2O suggests the use of larger amounts of sodic feldspar (albite) in this porcelain composition.

Chemical tempering process is characterized by the substitution of smaller ions by larger ions. In this case, the aim of chemical tempering is the replacement of sodium cations (Na^+, ionic radius 116 pm), present on the surface of porcelain, by potassium cations (K^+, 152 pm) that are available in the molten KNO_3 bath [22].

Table 2
Chemical composition of porcelain powder.

Oxides	Weight percentage (wt%)
SiO_2	67.01
Al_2O_3	19.42
Na_2O	2.34
K_2O	1.03
MgO	1.03
CaO	1.73
Fe_2O_3	0.88
TiO_2	0.17
Loss on Ignition at 900 °C (LoI)	6.45