

Effect of Electrospun Alumina Nanofibers Incorporation in Ceramic Glaze

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Abstract

Al₂O₃ nanofibers were produced with the electrospinning technique based on a precursor solution of PVP with aluminum 2,4-pentanedionate. After fiber deposition onto ceramic specimens, specimens were calcinated at a maximum temperature of 1400 °C, similar to the manufacturing temperature of commercially available whitewares. Structural and morphological characterization of the produced alumina nanofibers was performed as well as a vast mechanical characterization of ceramic glazed specimens with incorporated nanofibers. Without any significant alteration in the aesthetics properties of the glaze, a 10-% increase in the maximum allowable loads before break was noted.

Keywords: Electrospinning, nanofibers, alumina, ceramic, glaze.

I. Introduction

Over the last few decades, interest has been growing in electrospinning technology, noticeable mainly from the new possibilities and applications opened up by this nanofiber fabrication technique^{1–3}. One of the key factors that has boosted the interest of researchers around the world is the fact that, with relatively uncomplicated assemblies⁴, it is possible to obtain nanofibers of the desired material at very low costs⁵. With a use of a syringe pump (that feeds a solution through a spinneret), a high-power voltage supply and some basic electrically conductive collector (metal sheet or aluminum foil) it is possible to build a typical electrospinning set-up. When a high voltage is applied to the solution, a Taylor cone is formed at the tip of the spinneret. Thus, when the surface tension is overcome by the applied electrical force, a jet of the solution is ejected from the tip of the spinneret. A random stream is then deposited in the collector while the solvent used to obtain the solution is evaporated^{2,3,4,6,7}.

Various nanostructures have drawn much attention to themselves in the last couple of decades since they can fulfill the technological requirements of a broad range of applications^{16–19}. The nanofiber structures are unique when compared to other bulk materials, mainly owing to their high surface-to-volume ratio, interconnectivity between fibers, micrometer-sized interstitial space and high porosity. In particular, alumina (Al₂O₃) is one of the most interesting ceramic oxides studied, mainly owing to its po-

tential application in absorbents, catalysts and reinforcement for composite materials. Alumina is also used for the adsorption of toxic heavy metal ions such as arsenic and arsenate⁸.

In 2003, Z.-M. Huang *et al.*¹ reviewed the state of the art on polymer electrospinning. According to them, until then only a handful of researchers had worked on electrospun nanocomposites. A method to prepare alumina-borate/PVA nanofibers is also described in which after calcination an ultrafine alumina-borate ceramic material is obtained. In the same year, interesting work involving α -Al₂O₃ fibers produced with diameters below 200 nm was reported⁹; these were made from aged sols of aluminum di-sec-butoxide ethylacetate in acidic H₂O/EtOH media with a method involving electrohydrodynamics apparatus. This apparatus is in fact electrospinning equipment.

Later in 2007, R. Ramaseshan *et al.*¹⁰ compiled in their work the developments in the field of nanostructured ceramics. By then the number of publications regarding electrospun fibers had shown a sharp rise. Among the dozens of papers referred to in R. Ramaseshan work, it is important to highlight the use of aluminum 2,4-pentanedionate as alumina precursor by A. Azad¹¹. This author used a solution of polyvinyl pyrrolidone (PVP) to prepare inorganic-organic composite fibers, obtaining a transparent α -alumina crystal of high purity after calcination at high temperature. Around the same time, P.K. Panda and S. Ramakrishna¹² were working with different polymers, namely Polyvinyl Alcohol (PVA) and Poly Ethylene Oxide

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(PEO) mixed with aluminum nitrate or aluminum acetate as precursors, concluding that the latter allows smoother production of better fibers. Maneeratana and Sigmund have reported direct synthesis of continuous hollow alumina fibers via sol-gel, by means of electrospinning, using aluminum tri sec butoxide as alkoxide precursor¹³. More recently W. Kang *et al.*¹⁴ produced nanofibers by electrospinning of an AlCl_3/PVP solution, followed by calcination at high temperature. In 2011, A. Mahapatra *et al.*⁸ reported a method for producing α -alumina nanofibers by means of electrospinning, using organometallic aluminum acetate as precursor with a solution of PVP in ethanol. The preparation of aqueous aluminum acetate was made by coprecipitation and used for the production of fibers. Pei-Ching Yu *et al.*¹⁵ went further in trying to understand the growth-related microstructures formed during the synthesis of alumina nanofibers, inspired by A. Azad's work. They theorized a smallest potential diameter for the fibers to be 17 nm. However, as many others, the fibers produced had diameters ranging from 50 nm to 100 nm. Despite previous nanosized alumina addition in porcelain²², the incorporation of electrospun alumina structures allowing the localized functionalization of the ceramic surface, in this particular case a ceramic glaze, is an innovation only possible through the use of electrospinning technology.

In this work, Al_2O_3 nanofibers were produced with the electrospinning technique; they were prepared from a solution of polyvinylpyrrolidone (PVP) with aluminum 2,4-pentanedionate (AP). After deposition, the specimens underwent a calcination process in an industrial porcelain tableware manufacturing plant. Electrospun alumina nanofibers were incorporated into the glaze of commercial whitewares for enhancement of ceramic surfaces, by reducing the number of defects on the surface, while at the same time keeping other surface properties unchanged, such as color and roughness.

II. Material and Methods

(1) Fiber preparation

The precursor solution for electrospinning was prepared by dissolving aluminum 2,4-pentanedionate (Alfa-Aesar) in acetone^{8,11,15}. The subsequent solution was mixed with a solution of polyvinylpyrrolidone (PVP, average molecular weight $\sim 1.3 \times 10^6$) in ethanol in equal volume, totaling 10 ml.

Previously, different concentrations of the precursor were prepared in order to obtain an optimum proportion between both solutions. Here, 0.5 g precursor was dissolved in 5 ml acetone.

In this study the concentration of polymer in ethanol remained constant at 0.1 g/ml. This proportion diminishes the defects in the produced fibers. By increasing the viscosity to a certain optimum value, the occurrence of fiber breakage or solution drops is minimized.

The solution for the polymer matrix was prepared by dissolving PVP in 5 ml ethanol under constant stirring, at approx. 50 °C, for better dissolution of polymer and homogeneity of the solution. Concluding this process, the precursor/polymer solutions were mixed for a period of one to two hours.

Immediately, after the solution was made, it was placed in the electrospinning system with the preparation conditions detailed in Table 1. For posterior characterization the fibers were collected in an aluminum foil covered in parchment paper. This method has many advantages, the most important being the easy removal of the nanofibers after deposition. The deposited specimens were dried at 60 °C for 1 h in order to remove the remaining solvent. Thereafter, the nanofibers were calcinated at 1200 °C since this temperature should be equal to or greater than the decomposition temperature of the final compound and its transformation into respective oxide (Al_2O_3). The firing rate was 5 °C/min.

Table 1: Characteristics of preparation for electrospinning experiments.

Voltage (kV)	8
Flow rate (ml/h)	0.9
Needle distance to collector (cm)	11.5
Humidity (%)	33
Temperature (°C)	~24
Deposition time (min)	15 to 30

(2) Fiber incorporation

To proceed to the incorporation of nanofibers in glaze, ceramic specimens made of porcelain were produced. These were processed in accordance with the established commercial standards. The process used was slip casting, in which the slurry (porcelain suspension) was poured into a mold containing the shape of the test piece and allowed to dry for 24 hours in order to remove it. After being dried, the specimens underwent thermal treatment at 980 °C, and then glazed. The specimens were dipped in a suspension of glaze composed mainly of alumina, silica and potassium oxide and then placed into the electrospinning apparatus (immediately above the collector). The dimensions of the specimens allowed direct deposition of the nanofibers, successfully obtaining similar fiber mats such as the ones previously obtained in paper. The specimens with alumina nanofibers were taken to a second firing at a maximum temperature of 1400 °C in a thermal cycle of 6 h with a reducing atmosphere.

The dimensions of the specimens (175 mm in length, 21 mm in width and 6 mm in thickness) were designed to be involved in all tests related to further validation, thus taking into account the 3-point-bending test which required a larger operating area. We followed the specifications in ISO 178: 2001 (E).

(3) Characterization

The crystalline phase was identified by means of X-ray diffraction (XRD; Bruker D8 Discover) using $\text{CuK}\alpha 1$ radiation with 1.5406 Å wavelength and 2θ ranging from 20° to 80°.

The morphology of the as-spun and incorporated fibers were studied by means of scanning electron microscopy (NanoSEM – FEI Nova 200), and energy dispersive spectroscopy (EDAX – Pegasus X4M). Differential scanning calorimetry in an argon atmosphere (SDT 2960 Simultaneous TGA, DSC) was performed to assess the thermal behavior of as-spun nanofibers.

The last stage of the present work consisted in the validation of use of nanofibers in the desired final application. The primary goal of the characterization was the study of the effect of the incorporation of the alumina nanofibers, in the overall characteristics of the ceramic glaze.

One can assume the possibility of changes in color and brightness after incorporation of nanofibers. The color characterization was performed in two sets of specimens with and without nanofibers using a portable spectrophotometer, Minolta CM-2600d. Quantification of color of the specimens was prepared using the CIELAB system.

It is important that this procedure does not change surface roughness. Average roughness and roughness depth were measured with a HOMMEL ETAMIC-T500 mobile roughness measuring instrument.

Knoop hardness test, essentially required for brittle materials and ceramics, was performed according to the ASTM C849 norm. The equipment used was a hardness tester Model HVS-1000 Micro Knoop, applying a load of 2.98 N for 30 s.

Mechanical properties of a ceramic material were determined with a three-point bending test, enabling determination of the maximum bending load to which the specimen can be subjected. The equipment used was a Shimadzu Model: AG – X50 kN, and the guidelines of ISO 178:2010 for determination of flexural properties in plastic materials were followed.

III. Results and Discussion

(1) Scanning electron microscopy

Fig. 1 shows the as-prepared fibers. They were smooth, without marked variation in diameter. After calcination, the fibers remained smooth, without drops or breakage, and the average diameter was 179 nm. No significant variation in the morphology of the fibers was induced with variation of the concentrations of the precursor solution. The main difference lay in the surface area of the specimen after calcination. The nanofiber diameter shrinkage after heat treatment is inversely proportional to the quantity of alumina precursor. Indeed the specimen with largest area after calcination was the specimen produced with a higher concentration of alumina precursor. Since the purpose of this work was the future incorporation into ceramic glaze, a bigger area is preferable.

EDS was used to perform a qualitative and quantitative analysis. The presence of aluminum (23.81 at%) and oxygen (76.19 at%) is revealed, indicating the formation of alumina as envisaged.

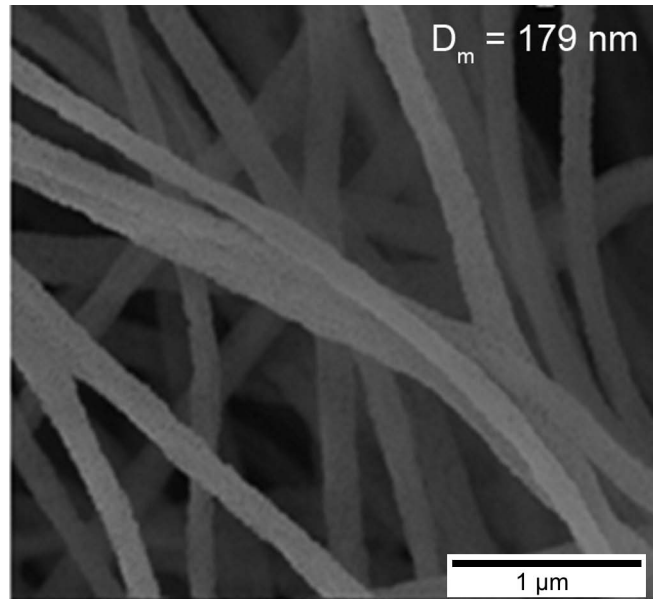


Fig. 1: As-prepared fibers submitted to calcination at 1400 °C.

(2) Differential scanning calorimetry and thermogravimetric analysis

The DSC heat flow curve (red line) illustrated in Fig. 2 shows two main transformations owing to heating. The first one, which occurs at 487.43 °C, possibly indicates a gamma phase alumina ($\gamma\text{-Al}_2\text{O}_3$), which normally occurs at low temperatures. Then the second one would refer to the alumina delta phase ($\delta\text{-Al}_2\text{O}_3$) established between 700 °C and 800°C. The obtained TGA curve (black line) shows three major weight losses. The first, of 11.62 % at 84.75 °C, is related to the evaporation of the residual moisture and ethanol molecules and also impurities present in the nanofibers, originating from the electrospinning process. The second weight loss at 222.38 °C, with a value of 27.07 %, results from the decomposition and combustion of PVP. Finally, the last weight loss, of 53.64 %, observed at 465.04 °C corresponds to the combustion of the fibers. When the temperature exceeds 600 °C, the curve is nearly flat, which indicates the complete burning of the polymer and organic materials resulting from the formation of aluminum oxide nanofibers 8, 15, 20.

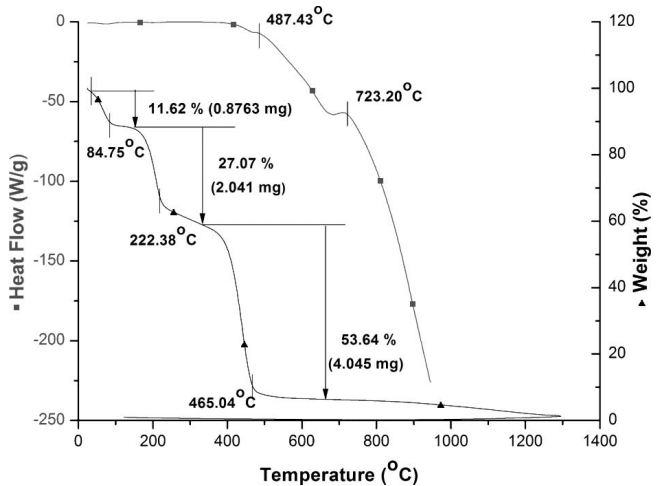


Fig. 2: DSC/TGA of the electrospun nanofibers.

(3) X-ray diffraction

In order to have a complete structural characterization and taking into account the final application, thermal annealing was performed and XRD was subsequently measured. Fig. 3 shows well-defined XRD patterns of the nanofibers. As expected at 1050 °C, the peaks reveal the presence of γ -Al₂O₃ (ICDD - 01-088-1609). This phase is anticipated above 1000 °C and should start disappearing beyond 1100 °C. At 1300 °C, the phase α -Al₂O₃ (ICDD - 00-046-1212) coexists with the θ -Al₂O₃ phase (ICDD-01-086-1410) until the latter gradually disappears. From 1400 °C and beyond, the main phase α -Al₂O₃ is observed. The normal route of transformation of amorphous phase / boehmite \rightarrow γ -Al₂O₃ \rightarrow δ -Al₂O₃ \rightarrow θ -Al₂O₃ \rightarrow α -Al₂O₃ usually originates the presence of the alpha phase above 1200 °C and there should not be any other phase simultaneously. In this case there were still traces of the θ -Al₂O₃ phase in quantities that may be considered negligible. After incorporation and calcination at 1400 °C, one should expect the presence of only α -Al₂O₃.

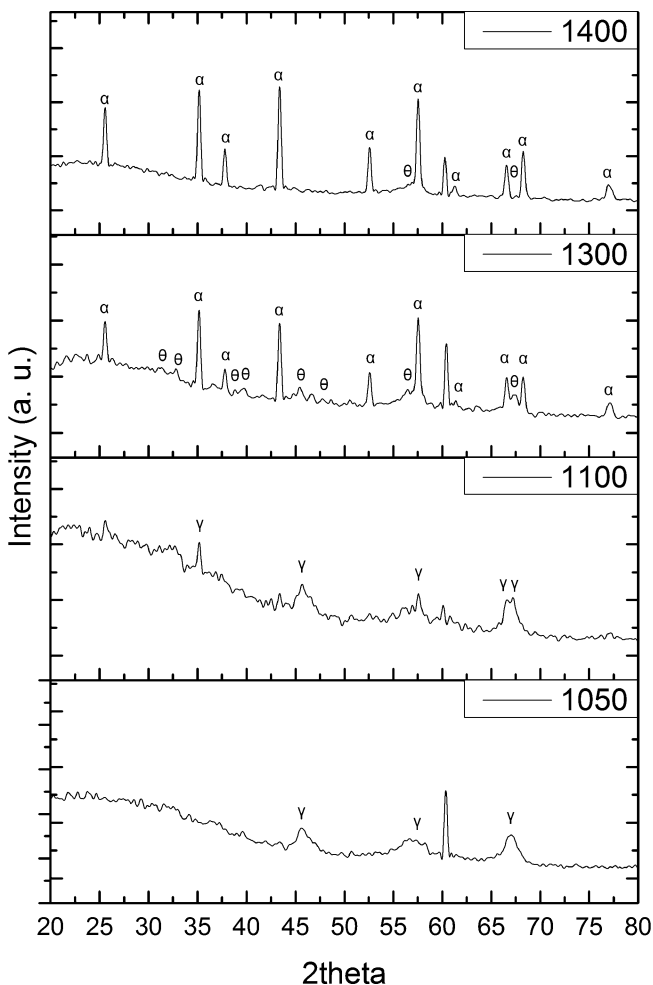


Fig. 3: XRD spectra of nanofibers calcinated at temperatures of 1050–1400 °C.

(4) Raman spectroscopy

It is natural to speculate about the presence of carbon as an impurity resulting from the degradation process, since it is highly active. After calcination, Raman spectroscopy (Fig. 4) was performed on the heat-treated fibers.

With this technique it is possible to detect the presence of the vibrational modes from carbon bonds. To study these active modes, measurements were performed from 0 to 700 cm⁻¹ and 1000 cm⁻¹ to 1700 cm⁻¹. Typically active carbon modes (D and G) appear between 1300 and 1600 cm⁻¹²¹. No presence of carbon-active modes was found, either at lower wavelengths or at higher ones, meaning the complete elimination of organic compounds in the resulting nanofibers. The slight slope of the curves outlined in Fig. 4 can be related to the morphology of the specimen. The surface of the deposited nanofibers is rather irregular, diffusing light, and so creating a background approximately linear signal.

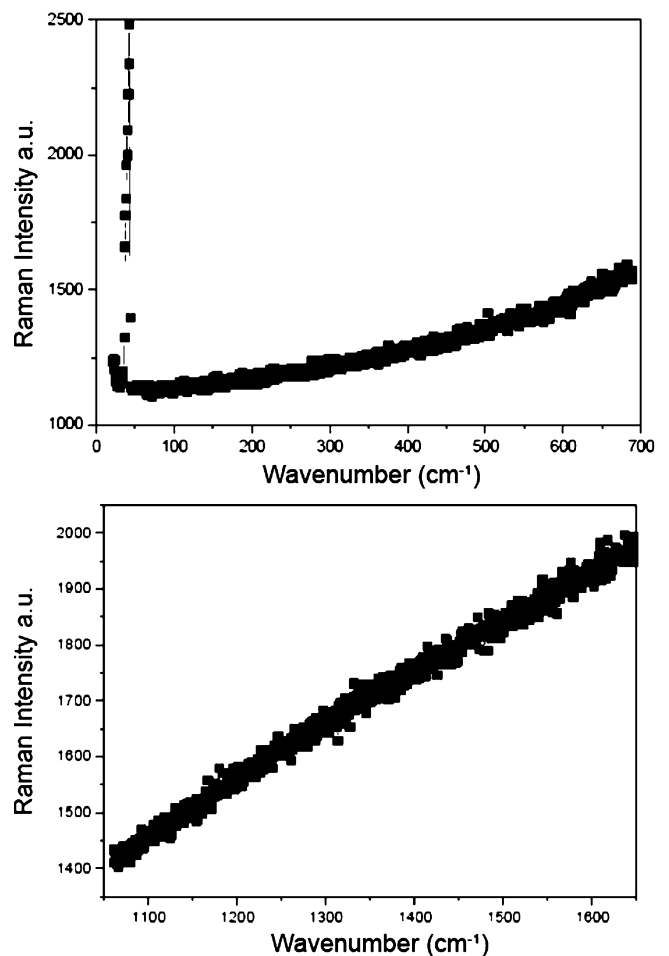


Fig. 4: Raman spectrum of Al₂O₃ nanofiber mat calcination.

(5) Validation after incorporation

After firing at 1400 °C, standard ceramic glaze and nanofibers-incorporated glaze were analyzed to determine their surface and mechanical properties (Table 2).

The white color from the ceramic glaze remains mostly unaffected after incorporation of the nanofibers, which is quite satisfactory as a required parameter.

Concerning surface roughness, no significant differences were observed on the glassy surfaces with and without nanofibers.

There is also no noteworthy increase in Knoop hardness by incorporating the nanofibers. However, the results of three-point-bending test suggest that incorporation of nanofibers in ceramic glaze produces a 10-% increase in

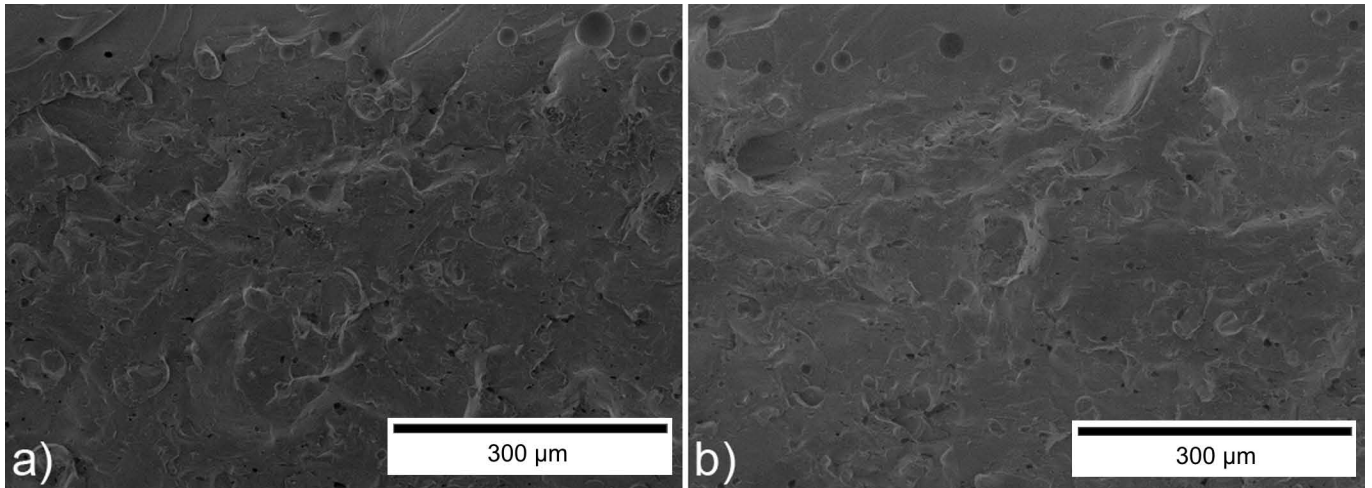


Fig. 5: SEM micrographs of the ceramic glaze in sectional cut: a) standard; b) with nanofibers incorporation. A white line, positioned at the same parallel distance to the surface of each individual specimen was drawn for reference.

the maximum allowable loads before break. Thus, incorporation of aluminum oxide nanofibers in the glaze seems to lead to a clearly positive result.

Table 2: Surface and mechanical properties of standard glaze and glaze with alumina nanofibers incorporated, both after firing at 1400 °C.

		Standard	With nanofibers
Color	L*	86.59 ± 0.35	86.88 ± 0.21
	a*	-1.31 ± 0.07	-1.43 ± 0.11
	b*	0.51 ± 0.08	0.35 ± 0.18
Roughness	Ra (μm)	0.07 ± 0.02	0.06 ± 0.01
	Rz (μm)	0.33 ± 0.03	0.33 ± 0.04
Hardness	(HK)	525.58 ± 18.26	526.02 ± 16.55
Maximum Load	(N/mm ²)	62.2 ± 2.70	70.6 ± 2.90

During firing, with the increase in the temperature, gases are released from the porcelain body towards the surface and across the glaze. This causes the formation of irregularities in the glaze surface. To prevent this, mildly rapid cooling is necessary during processing. This allows bubbles to be trapped inside the glaze in a rather homogeneous manner. SEM micrographs (Fig. 5) showed a clear difference in the glaze fired with the deposited nanofibers (Fig. 5b) and the standard ceramic glaze (Fig. 5a). Thickness remains at approximately 160 μm for both specimens. The nanofibers act as a barrier to the bubbles from the calcination process. It can be said that the incorporation of nanofibers trapped the bubbles in the glaze slightly below the surface of the glaze when compared with the standard specimens, improving mechanical properties, by decreasing the defects in the bulk.

IV. Conclusions

Stable continuous alumina nanofibers were successfully produced with the electrospinning technique, as proven

by SEM and X-ray diffraction. The phase evolution from amorphous to α-Al₂O₃ was thoroughly investigated in order to understand the composition of the incorporated nanomaterial at the final temperature of 1400 °C. The incorporation of nanofibers in the ceramic glaze allows an improvement in the mechanical behavior without affecting other surface properties of the glaze. For the intended final application, in ceramic glazes, maintaining these aspects is absolutely mandatory, and was satisfactorily achieved.

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