Preventing hydrolysis of BaTiO₃ powders during aqueous processing and of bulk ceramics after sintering

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Abstract

This present article addresses the reactive behaviour of barium titanate (BaTiO₃, hereafter referred to as BT) with water either in powder form or as bulk ceramics. Chemisorbing a suitable phosphate-based protective agent at the surface of BT particles prevented hydrolysis reactions and made aqueous processing of BT a safe and viable route. Highly concentrated (50 vol.%) fluid and long term stable suspensions could be easily prepared from surface treated BT particles, contrasting with the poor stability and high viscosity of slurries derived from the as received powders. For aqueous suspensions, the course of hydrolysis reactions was monitored through changes in pH and concentrations of leached ionic species along aging time. For bulk ceramics, the extent of hydrolysis reactions was assessed through the microstructural changes occurred at polished surfaces without and with surface treatment, which have been kept in contact with water for a certain time period.

Key words: Barium titanate, ferroelectrics, aqueous colloidal processing, surface treatment.

1. Introduction

Barium titanate is a ferroelectric material commonly used in microelectronic discrete components such as multilayer ceramic capacitors (MLCCs), thermistors and piezoelectric sensors.¹ The fabrication of BaTiO₃ ceramics for these commercial applications often involves the dispersion of BT powders in a suitable organic or water medium so as to shape or cast the material into suitable geometrical shapes, followed by drying and sintering steps for achieving the desired final properties. For this purpose, the preparation of well dispersed and stable suspensions, which can be consolidated through various ceramic powder forming processes such as tape casting, injection moulding, slip casting, is essential for obtaining green compacts with uniform particle-packing.² Concentrated stable suspensions of enough repulsive and well dispersed particles facilitate their homogeneous packing, enhance the sintering behaviour of the components and are beneficial to the dielectric properties of the materials.^{3,4} To achieve stable suspensions in an appropriate processing media, the powder particles dispersed in the suspending medium must exhibit sufficient repulsive forces to offset van der Waals attraction. Currently, the production of BT MLCCs involves the dispersion of BT powder in organic solvents (n-hexane, acetone, ethanol, etc...) rather than in water as dispersing media, which increase the cost of final product and also require proper safety precautions to avoid long term health issues.

Processing difficulties of BT in aqueous media have been disclosed in a significant number of studies.⁵⁻¹¹ The main drawbacks included: (i) thermodynamic instability of BT in water;^{5,7,11} (ii) leaching of Ba²⁺ ions from the powder;^{8,9} (iii) adsorption (and/or redeposition upon drying) of the leached Ba²⁺ ions onto the BT surfaces, which, in turn, may lead to deviations from the desired stoichiometry, exaggerated grain growth,

inhomogeneous microstructure, and degradation of the dielectric properties of the final products.^{10,11} Much research efforts have been put forward, aiming at understanding the solid/liquid interfacial reactions between BT and water and to find out the proper aqueous processing conditions.¹²⁻²⁰ Some of these studies tested the efficiency of various polymers and polyelectrolytes as dispersants for BT–water systems, including ammonium salts of polyacrylic acid (PAANH₄)¹⁶ and of polymethacrylic acid (PMAANH₄)¹⁷, PVA-b-COOH¹⁸, ammonium polyacrylate (PAANH₄)¹⁹ and polyaspartic acid (PAPa-Na).²⁰ The adsorption of anionic species derived from the dissociation of polyelectrolytes onto the surface of BT particles enabled both electrostatic and/or steric stabilization mechanisms to cooperate. Thermodynamic calculations showed that BaTiO₃ is unstable in aqueous solutions and that substantial amounts of Ba²⁺ ions are leached from BaTiO₃ before chemical equilibrium, described by the following chemical reaction is achieved (Eq. 1)²¹:

This non-stoichiometric dissolution reaction that involves a cationic exchange process between the hydronium ions from the solution and the Ba²⁺ ions from the solid has obviously a faster kinetics under low pH values. This explains why high pH environments are consensually preferred to prepare BT suspensions as a way to decrease the leaching extent of Ba²⁺.¹² But the aqueous processing difficulties of BT powders persist even under alkaline environments. The poor dispersion ability of BT powders in aqueous media has been attributed by several authors to the ubiquitous presence of barium carbonate (BC) in BT powders. The BC impurities could either result from unreacted remnants of solid state reaction or derive from the CO₂ naturally dissolved in the water.^{5, 9, 22, 23} According to this view, the dissolution of BC in BT powders is the main source of Ba²⁺ ions released into the aqueous dispersing media, and

would tend to hinder the preparation of aqueous BC suspensions with high solid loadings. But this assumption was contradicted by our experimental evidences²⁴ revealing that very high solid loadings up to 60 vol.% could be achieved and kept stable for long periods by just dispersion a BC powder in water in the presence of a suitable dispersing agent. This view also neglects the solid/liquid interactions occurring at the surface of BT particles described by Eq. 1, and is not supported by the most recent experimental evidences reported elsewhere.²⁵ As a matter of fact, it was demonstrated by Ferreira et al.²⁵ that the deleterious effect of BC on the dispersing ability of BT in water was completely speculative and based on wrong assumptions. Oppositely, it was further proved that the presence of 2–5 wt.% BC deliberately added to BT enhanced the dispersing ability of the mixed BT–BC systems in water.

Several research works on aqueous processing of BT have reported suspensions with solid loadings up to 40 vol.% with dispersion of powders being achieved via pH variations or by adding dispersing agents.¹²⁻²⁰ But suspensions containing > 40 vol.% solids that are stable over the whole processing time and not undergoing hydrolysis degradation have not been reported so far for barium titanate. Similar problems have been already identified for other water sensitive powders such as AlN²⁶, MgAl₂O₄ spinel,²⁷ barium-strontium titanate (BST),²⁸ and a lead-free alkaline earth zirconate-titanate (0.5Ba(Zr_{0.2}Ti_{0.8})O₃–0.5(Ba_{0.7}Ca_{0.3})TiO₃, BZT–BCT) piezoelectric compound.^{29,30} Such processing difficulties were successfully overcome through a suitable thermochemical surface treatment given to the powder particles to prevent hydrolysis, improve their dispersion ability in water, increase the solid loadings and enhance colloidal stability, without damaging final properties of the sintered material. The earlier findings²⁵⁻³⁰ stimulated us undertaking further research aiming at preparing high concentrated and stable aqueous suspensions of pure BT by means of a similar

thermochemical surface treatment. The efficacy of this approach in protecting BT from hydrolysis was further proved upon immersing in water for different time periods (1, 3 and 7 days) non-thermochemically treated polished surfaces of BT ceramics sintered for 2 h at 1250 °C. For **comparison** purposes, thermochemically treated polished surfaces were also immersed in water for 7 days. In both cases, half of each polished surface was coated with an adhesive tape, letting the other part exposed to water.

2. Experimental Procedure

2.1 Synthesis and characterisation of powders

The barium titanate (BT) powder was synthesized by conventional solid state reaction process. A stoichiometric mixture of BaCO₃ (Barium Carbonate, Sigma-Aldrich, Steinheim, Germany, purity > 99% specific weight = 4430 kg m⁻³) and TiO₂ (Titanium IV Oxide, Riedel-de Haen, Sietze, Germany, purity > 99% specific weight = 4260 kg m⁻³) powders were chosen as starting precursor materials. 400 g batch size was prepared.

The calculated stoichiometric mixture of precursor powders was homogenised by dry ball-milling for 2 h followed by calcination at 800 °C for 4 h. The calcined powder was then dry ball-milled for 2 h and submitted to a second heat treatment step for further 4 h at 1200 °C. In order to destroy the agglomerates formed during heat treatments and suitably reduce the size of the particles to improve the rheological behaviour of BT suspensions, the as-obtained BT powder was attrition milled for 10 h in ethanol medium. The particle size distributions were monitored by a light scattering particle size analyser (Coulter LS 230, Buckinghamshire, UK, Fraunhofer optical model). **For that, dilute aqueous suspensions (1 wt.% solids with added 0.5 wt.% Targon 1128) were**

prepared from dry milled BT and AM BT powders and ultrasonicated for 15 minutes to de-agglomerate the BT particles, followed by particle size distribution measurements. The resultant BT powder obtained after attrition milling was dried at 100 °C and characterized for further studies. Part of this hereafter referred to as non-treated (BT–NT) powder was submitted to a thermochemical surface treatment against hydrolysis to obtain the surface treated (BT–ST) counterpart. The details of surface treatment method have been described elsewhere.²⁶⁻³⁰ It consisted of adding 100 g of the attrition milled BT–NT powder into 200 cm³ of 2 wt% aqueous solutions of aluminium di-hydrogen phosphate, Al(H₂PO₄)₃, (Bindal A, TKI, Hrastnik, Slovenia). The mixture was then kept at 60 °C under magnetic stirring for 30 minutes, followed by centrifugation. The settled cake was removed dried at 80 °C for 12 h to obtain the surface treated powders. The orientation and crystallinity of the BT powder was studied using a Rigaku X-ray diffractometer in 2θ range 20° to 70°. The BET method (Gemini, Micromeritics, Norcross, GA) was used to determine the specific surface area of BT-NT powder.

2.2 Reactivity of powders in aqueous media

To assess the reactivity of BT powders in aqueous media several complementary approaches were applied. Firstly, the aging effects on pH variations and ionic leaching was evaluated by using relatively low concentrated (10 wt.% solid loading) BT suspensions of both non-treated (BT–NT) and surface treated (BT–ST) powders in the presence and in the absence of Targon 1128 used as dispersant (BK, Ladenburg, F.R. Germany). The pH evolution was monitored along a maximum period of 5 days. The aged suspensions were then ultra-centrifuged (10,000 rpm, 20 min) to obtain clear supernatant liquids. The supernatants were filtrated (0.2 µm) and the concentrations of leached Ba²⁺ ions were analysed by Inductively Coupled Plasma – Optical Emission

1 Spectroscopy analysis (ICP) (ICPOES, Jobin, Yvon, JY 70 plus, France). Three
2 measurements per sample were made and the average plus standard deviation (SD)
3 values were taken.
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6 In order to further elucidate about the reactivity of BT towards water, the water
7 corrosion effects on polished surfaces of well sintered (1250 °C, 2 h) samples were also
8 analysed by scanning electron microscopy (SEM, Hitachi S-4100, Tokyo, Japan). BT
9 ceramics prepared from the unprotected powder were immersed in water for different
10 time periods up to 7 days and the water corrosion effects were then analysed by
11 scanning electron microscopy (SEM, Hitachi S-4100, Tokyo, Japan). For this, disc-
12 shaped pellets (20 mm diameter, 3–5 mm thickness) were consolidated by uniaxial
13 pressing BT powders (treated and non-treated), under a pressure of 60 MPa, followed
14 by isostatic pressing at 200 MPa. The green samples were then sintered at 1250 °C for 4
15 h with a heating rate of 5 °C/ min. The ceramic samples were embedded in resin
16 supports and then properly surface polished using diamond suspensions (9, 6 and 1 µm)
17 by polishing unit (Rotoforce 4, Struers, Spain). The polished samples still embedded in
18 the resin supports were immersed in water for 1, 3 and 7 days. For comparison
19 purposes, polished and thermochemically treated surfaces (against hydrolysis with
20 aluminium di-hydrogen-phosphate) were immersed in water for 7 days. In both cases,
21 half of each polished surface was coated with an adhesive tape, letting the other part
22 exposed to water. Both parts (covered, or in contact with water) were examined by
23 SEM.
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51 **2.3. Preparation of high concentrated suspensions and their stability with time**

52 Zeta-potential measurements for both non-treated (BT–NT) and surface treated
53 (BT–ST) powders were performed in Coulter equipment (Delsa 440 Sx, Coulter,
54 Buckinghamshire, UK) by using dilute suspensions in the absence and in the presence
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of dispersant. For this, the powders were suspended into a background electrolyte solution of 1 mM KCl to insure a constant ionic strength. Each suspension was divided in two equal parts to analyse for both increasing and decreasing pH runs. The pH values were adjusted by using 0.1 M solutions of either NH₃ or HNO₃.

The effects of aging time (5 h, 1 day, 4 days and 1 week) on the rheological behaviour were evaluated by rheological measurements of both BT–NT and BT–ST powder aqueous suspensions with 35 vol.% solid loadings in presence of 0.5 wt% Targon 1128 as dispersant (BK, Ladenburg, F.R. Germany). Viscosity of the prepared suspensions was measured using a rotational Rheometer (Bohlin C–VOR Instruments, Worcestershire, UK) at shear rates up to 500 s⁻¹ with a cone and plate (4°, 40 mm, 150 µm gap) measuring configuration. High concentrated aqueous suspensions with 50 vol% solid loadings of BT–NT and BT–ST powders, in presence of the same amount of Targon 1128 were also prepared and analysed. Flow behaviour of the suspensions after de-agglomeration and 5 days aging time was also evaluated.

3. Results and Discussion

3.1 Preparation and characterization of barium titanate powder

Considering that the high temperature heat treatment (1200 °C, 4 h) used to synthesize the BT powder promotes the formation of hard agglomerates and that well de-agglomerated powders are required to prepare homogeneous and concentrated suspensions, attrition milling for 10 h was carried out in ethanol. The particle size distributions of BT powders as synthesized and after attrition milling are shown in Figure 1. The as synthesized powder shows an average particle size of 0.9 µm and

exhibits a trimodal distribution with populations centred at 0.5 μm , 2.2 μm and 3.7 μm . Attrition milling revealed to be effective in destroying agglomerates and resulted in a final unimodal particle size distribution with an average particle size of $\sim 0.09 \mu\text{m}$. For a uniform sized powder with a theoretical density of 5.99 g cm^{-3} , this would correspond to an estimate specific surface area of $\sim 11 \text{ m}^2 \text{ g}^{-1}$. However, the measured BET specific surface area of the AM milled BT powder was only $8.2 \text{ m}^2 \text{ g}^{-1}$, corresponding to a slightly larger estimated particle size of $\sim 0.12 \mu\text{m}$. This apparent lack of consistency can be attributed to deviations from the ideally assumed particle size distribution.

The selection of ethanol for wet milling was intended to avoid early exposing the surface of the particles to water, thus preventing them from undergoing non-controlled hydrolysis reactions. The XRD patterns of both BT-NT and BT-ST powders displayed in Figure 2 reveal that all the diffraction peaks correspond to tetragonal phase of BT, matching well the corresponding standard diffraction peaks (JCPDS # 01-074-4540). This means that the surface treatment performed in aqueous environment did not alter the purity of the BT phase, within the detection levels of the XRD technique used to characterize the powders. The chemisorption of phosphate species onto the surface of other ceramic powders (AlN , MgAl_2O_4) was already proved.^{27, 31, 32} The same kind of chemical interactions is assumed to occur in the case of BT powders.

3.2 Reactivity of barium titanate in aqueous media

The evolution of pH along aging time of aqueous suspensions containing 10 wt.% of BT-NT and BT-ST powders in the absence (BT-NT; BT-ST) and in the presence of dispersant (BT-NT-D; BT-ST-D) are presented in Figure 3. A starting pH value of $\sim \text{pH } 8.6$ was registered for the BT-ST powder system, which was kept essentially unchanged along the entire aging period irrespective of the presence or absence of

dispersant. For the BT-NT powder in absence of dispersant the starting pH value increased to about 3 pH units (~pH 11.4) when compared to BT-ST, while the difference has increased about ~2 pH units in the presence of dispersant (BT-NT-D). Although the starting pH values of BT-NT-D (pH 10.3) and BT-NT (pH 11.4) suspensions differ for about 1 pH unit, both attained a final pH of ~12 after aging for 5 days. The lower value measured for the BT-NT-D system is probably due to the neutralization of some OH⁻ groups by the hydronium ions released upon dissociation of the dispersant's functional groups. But the more accentuated pH variations registered for the BT-NT suspension with added dispersant means that the polyelectrolyte species do not hinder the hydrolysis/dissolution reactions predicted by Eq. 1. This drastically contrasts with the stable behaviour observed for the BT-ST suspensions, suggesting that the surface treatment was effective in preventing hydrolysis/dissolution reactions at the solid-liquid interfaces.

According to Eq. 1, the pH variations occur concomitantly with ionic leaching of Ba²⁺ from BT into the solution and the leached amounts are expected to be higher for the non-treated powder. This hypothesis is confirmed by the data of ICP analysis performed for the centrifuged supernatants derived from all aqueous 10 wt.% solid loaded suspensions (BT-NT, BT-NT-D, BT-ST and BT-ST-D) aged for 5 days as shown in [Figure 4](#). The ICP measurements reveal that the extent of Ba²⁺ ion leaching was 4 times higher for the non-treated powder in the absence of dispersant and that the leaching process was somewhat enhanced in the presence of dispersant. The less extended leaching observed for the surface treated powder confirms the efficiency of the surface protection method against hydrolysis of BT, in good agreement with similar observations already reported for other water sensitive powders such as BST²⁸ and BZT-BCT.^{29,30} It is suggested that chemisorption of Al(HPO₄)₃⁻ or Al(PO₄)₃²⁻ species

1 onto the surface of the particles hinders its direct contact with water molecules, reducing
2 hydrolysis and preferential ionic leaching. On the other hand, the enhanced leaching
3 process in the presence of dispersant suggests that the poly-anionic species of
4 ammonium polycarbonate dispersant (hereafter designated as D^-) are “sequestering”
5 some Ba^{2+} cations from the solution, probably through the formation of monovalent (D^-
6 $-Ba^{2+}$)⁺ or neutral ($D^- - Ba^{2+} - D^-$) complexes.²⁵ This will decrease the chemical potential
7 of Ba^{2+} cations in the solution, shifting the chemical equilibrium of Eq. 1, to the right.
8 This explains why the leaching process was somewhat enhanced in the presence of
9 dispersant as shown in Figure 4.

3.3 Preparation and characterization of barium titanate suspensions

10 Zeta potential gives a measure of the magnitude of the electrostatic repulsive or
11 attractive interactions at the solid/liquid interface, being one of the fundamental
12 parameters known to affect colloidal stability. Its measurement brings detailed insight
13 into the causes that promote particles’ dispersion or aggregation and can be used to
14 improve the formulation and concentration of suspensions. Sorption effects of the
15 surface treating agents and dispersant species at the surface of BT particles can also be
16 evaluated by the solid/liquid interface potential. Figure 5 presents zeta potential *versus*
17 pH variation of the BT particles treated and non-treated in the absence and in the
18 presence of dispersant. The BT–NT powder system shows an isoelectric point (IEP) at
19 around pH 3 in the absence of dispersant. The addition of dispersant shifted the
20 electrophoresis curve to the more acidic region with a new IEP appearing at pH ~2,
21 while significantly increasing the absolute values of zeta potential. This shift confirms
22 the anionic character of Targon 1128. The BT–ST powder system in the absence of
23 dispersant exhibits the highest values of IEP at pH ~4, suggesting that the di-hydrogen

aluminium phosphate species from the surface treating agent have been adsorbed at the surface of BT particles. The cationic character of these species in comparison to the surface of naked BT particles surface enhanced the positive charge of BT–ST particles. This is expected to stimulate a more extensive adsorption of anionic species in the presence of dispersant. This hypothesis is confirmed by the largest difference between the IEPs measured before and after adding the dispersant, as well as by the highest absolute zeta potential values measured for the BT–ST–D system. The differences in zeta potential between BT–NT and BT–ST within the basic pH region are small in the absence of dispersant. At the natural pH of the BT suspensions ($\text{pH} \approx 8.5\text{--}9.5$), the dissociated polyanionic groups will strongly adsorb at the surface of the BT–ST particles enhancing the negative zeta potential values and consequently contributing for a good dispersion, essential for achieving high solids loading.

A moderate solids loading of 35 vol.% was firstly used to enable comparing the effects of aging time and surface treatment given to BT particles on the rheological behaviour of the suspensions. The attrition milled powders were dispersed in a 0.5 wt.% Targon 1128 solution and the suspensions were let to deagglomerate by ball milling in polypropylene bottles using alumina balls (the charge to balls ratio was 1:3) by 1 day. The viscosity of the suspensions was measured after ball milling for 5 h and 1 day, and after 4 days and 1 week with constant rotation in the polypropylene bottles without milling bodies. Figure 6 (a) and (b) shows the corresponding suspension viscosity (η_s) — shear rate ($\dot{\gamma}$) curves within the shear rate range from $\dot{\gamma} = 0 - 500 \text{ s}^{-1}$ for the BT–NT–D and BT–ST–D suspensions, respectively, after different aging time periods. All the suspensions exhibit shear thinning behaviour at this moderate solids loading. However, the evolution of viscosity with aging time shows opposite trends. In case of BT–NT–D system, the viscosity increases with aging time increasing, emphasizing the

1 lack of colloidal stability. These changes derive from the occurrence of hydrolysis/non-
2 stoichiometric dissolution reactions predicted by Eq. 1 with the associated release of
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4 Ba^{2+} ions into the aqueous suspending media, thus increasing the ionic strength. In the
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6 case of BT–ST–D systems, the viscosity decreases with increase in aging time from 5 h
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8 to 1 day (24 h) and thereafter remains essentially constant with further increase in aging
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10 time from 4 days and 1 week.
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15 The above results further confirm the efficacy of the surface treatment given to the BT
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17 powder particles in preventing their reactivity with water, and in the preparation of long
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19 term (at least up to one week) stable suspensions for colloidal processing. Based on
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21 these results, the preparation of aqueous suspension with 50 vol.% solids loading was
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23 attempted from both BT–NT–D and BT–ST–D systems using the same dispersing
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25 conditions (0.5 wt.% Targon 1128). [Figure 7](#) shows the flow curves for the suspensions
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27 after ball milling for 5 h (deagglomeration time) and suspension kept for 5 days of aging
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29 time under constant rotation. It can be clearly seen that the BT–NT–D suspension was
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31 already too viscous after deagglomeration for 5 h and presented an irregular behaviour
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33 that denotes lack of homogeneity. Such behaviour significantly worsened after aging for
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35 5 days as a consequence of the undergoing hydrolysis/non-stoichiometric dissolution
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37 reactions predicted by Eq. 1. In contrast, the BT–ST–D system exhibits smooth shear
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39 thinning behaviour after deagglomeration for 5 h and the viscosity values slightly
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41 decreased along the 5 days of aging period. These results definitely confirm the efficacy
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43 of the thermochemical surface treatment given to the BT powder particles in preventing
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45 hydrolysis. This makes aqueous colloidal processing a viable approach for micro
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47 fabrication of BT ferroelectric components for microelectronic applications through
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49 different advanced replication methods.³³
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As stated above, it was hypothesized that di-hydrogen aluminium phosphate species would equally be effective in preventing hydrolysis of bulk ceramics surfaces exposed to water molecules. This hypothesis was tested by immersing mirror polished surfaces of bulk BT ceramics (sintered for 2 h at 1250 °C) in liquid water under both non-treated and surface treated conditions as described in section 2.2. SEM observations enabled gathering complementary evidences about the effects of BT-H₂O reactivity by observing the water corrosion effects after different immersion times (1–7 days) for non-treated and surfaces (Figure 8), and about the efficacy of the thermochemical surface treatment after 7 days of immersion (Figure 9). The left side SEM images of Figure 8 and Figure 9 were taken from the half part of the samples covered with the adhesive tape, while the right side ones correspond to the areas exposed to water. The gradual corrosion effects of water are clearly shown in the right side SEM images of Figure 8 through an apparent increase of porosity with aging time increasing. This constitutes an irrefutable evidence of the occurrence of hydrolysis/dissolution reactions especially at microstructural point defects derived from small pores or pull-out grains during polishing. On the other hand, not noticeable morphological changes along the immersion time could be detected in the left side SEM images of Figure 8, suggesting that covering with an adhesive tape was effective in hindering the direct contact of the polished surfaces with water. The observed small differences derive more from the fact that the SEM images have been collected from different areas/samples. Oppositely, polished surfaces that have been thermochemical treated and kept in contact with water show fewer/smaller differences between the parts uncovered and covered with adhesive tape even after the longer immersion period of 7 days (Figure 9). These results confirm the efficacy of the thermochemical surface treatment in preventing hydrolysis of different kinds of particulate materials.²⁸⁻³⁰ They also provide further visual evidences

1 about the effects of hydrolysis/dissolution reactions in sintered ceramics exposed to
2 water, meaning that bulk ceramics are likely to undergo degradation when in contact
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4 with water molecules. Moreover, such degradation could be avoided by applying the
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6 same thermochemical surface treatment to bulk BT-based ceramics.
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10 11 12 **4. Conclusions**

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15 The results presented and discussed along this work demonstrated that only moderately
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17 concentrated suspensions, but of poor stability could be prepared from the starting BT-
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19 NT powder, making aqueous processing a non-viable route. In contrast, high
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21 concentrated (50 vol.%) and colloidally stable (up to at least 7 days) suspensions could
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23 be easily prepared from the BT-ST powder. This enhanced stability makes aqueous
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25 processing of functional ceramics viable by preventing hydrolysis/dissolution reactions
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27 that degrade the material. This surface treatment process is also effective in preventing
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29 bulk ceramics from undergoing degradation when in contact with water molecules.
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39 **Acknowledgments**

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42 The authors S.M. Olhero and Ajay Kaushal are thankful to the Foundation for Science and
43
44 Technology of Portugal (FCT) for the postdoc fellowship grants SFRH/BPD/87486/2012 and
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46 SFRH/BPD/77598/2011, respectively. The financial support from FCT under the project
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48 PTDC/CTM/099489/2008, and the facilities from CICECO are also gratefully acknowledged.
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Figure 1. Particle size distribution of barium titanate powders as obtained (BT) and after attrition milling for 10 h (BT-AM).

Figure 2. XRD patterns of barium titanate obtained by solid state reaction at 1200°C for 2 h before (BT-NT) and after surface treatment (BT-ST).

Figure 3. Evolution of pH *versus* time for suspensions containing 10 wt.% of barium titanate powders non-treated (BT-NT) and surface treated (BT-ST) in the absence and in the presence of dispersant (-D).

Figure 4. Barium ion concentration in the centrifuged supernatant solutions derived from the 10 wt.% BT-NT and BT-ST aqueous suspensions aged for 5 days in the absence or in the presence of dispersant.

Figure 5. Zeta potential of barium titanate powders non-treated and surface treated in the absence (BT-NT, BT-ST) and in the presence (BT-NT-D, BT-ST-D) of dispersant.

(a)

(b)

Figure 6. The effects of aging time on the flow behaviour of aqueous suspensions containing 35 vol.% of barium titanate powders (a) non-treated (BT-NT) and (b) surface treated (BT-ST) dispersed with 0.5 wt.% Targon 1128.

Figure 7. The effects of surface treatment given to barium titanate powder and of aging for 5 days on the flow behaviour of aqueous suspensions containing 50 vol.% solids dispersed with 0.5 wt.% Targon 1128.

Figure 8. SEM micrographs of sintered (1250°C, 2 h) polished and non-treated barium titanate (BT-NT) surfaces after different time periods (1, 3 and 7 days) of immersion in water: (left) covered with adhesive tape; (right) exposed to water.

Figure 9. SEM micrographs of sintered (1250°C, 2 h) polished treated barium titanate (BT–ST) surfaces after 7 days of immersion in water: (left) covered with adhesive tape; (right) exposed to water.

Figure Captions

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