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Study of zircon or zirconia crystals addition in ceramic glazes by impedance spectroscopy

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Abstract

The addition of fine-grained polycrystalline tetragonal (3%Y_2O_3–TZP) zirconia, monoclinic zirconia, or zircon to conventional, single-firing, ceramic glazes with the aim of enhancing their hardness, fracture toughness and wear resistance for floor tile applications was studied by impedance spectroscopy (IS). This technique proved to be useful to monitor several interfacial phenomena, since the response of sintered bodies revealed interesting microstructure-electrical relationships. As a consequence, it might be used as a complementary technique to evaluate different opacity levels of glazes.

Keywords: D. Zirconia; Zircon; Ceramic glazes; Gloss; Impedance spectroscopy

1. Introduction

Formulations of ceramic glazes, composed of a mixture of a wide number of acid (SiO_2, B_2O_3, ZrO_2, TiO_2), basic (Na_2O, K_2O, MgO, CaO, BaO, ZnO, PbO) and amphotere (Al_2O_3) oxides, are carefully developed or tailor-made to satisfy both aesthetical (gloss, transparency or opacity, and colour) and technical requirements (compatibility with the clay tile and with the firing schedule, chemical resistance, and good mechanical properties to withstand severe wear, stress and/or impact conditions derived from use). Usually, reinforcement of ceramic glazes is obtained either with the addition of highly refractory crystalline phases of high hardness and/or strength values (corundum, mullite, zircon, rutile, β-spodumene, andalucite) which remain insoluble and stable in the glassy matrix, or with the in situ devitrification of the reinforcement phase (zircon, diopside, β-spodumene) during glaze annealing [1,2].

Monoclinic zirconia (m-ZrO_2, or baddeleyite) might be used in complex ceramic glaze formulations as a nucleation agent [3], with the aim to promote zircon devitrification, which confers opacity and/or an improvement of mechanical properties. However, the direct incorporation of zircon crystals ($SiZrO_4$) in the glassy matrix is much more common, due to economic reasons. The use of yttrium-stabilized polycrystalline tetragonal zirconia (3Y-TZP) as a mechanically reinforcing additive was attempted, with the main effects previously reported [4–6].

In previous works [7–10], we have shown that impedance spectroscopy (IS) can be a useful technique to monitor the YSZ or TZP electrolyte degradation process. In fact, after attack by the glassy phase, new interfaces develop inside the electrolyte (YSZ/glass), with specific electrical responses. IS measurements evidenced a large increase in the intermediate frequency arc (usually ascribed to the grain boundary or interfacial contribution) and a shift in the relaxation frequency of this arc to lower values. Impedance spectroscopy has been used as an important tool in several other different situations: (i) sintering and characterisation of clay-based dry-pressed bodies [11,12]; (ii) crack formation in different

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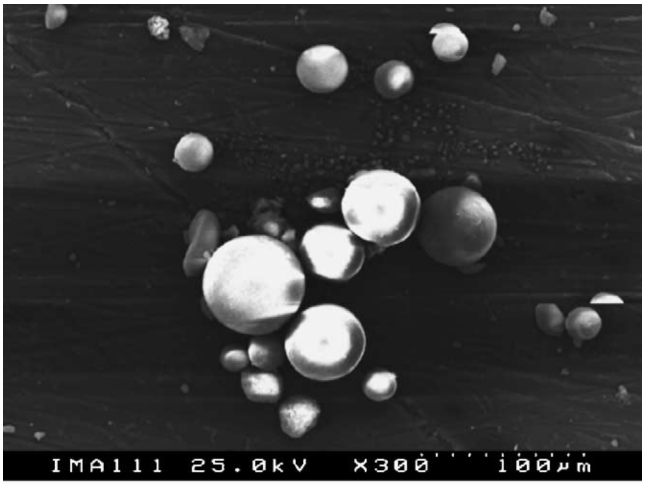
materials (e.g., TZP) [13,14]; (iii) setting/curing processes of cements [15,16]; and (iv) devitrification of glazes [17].

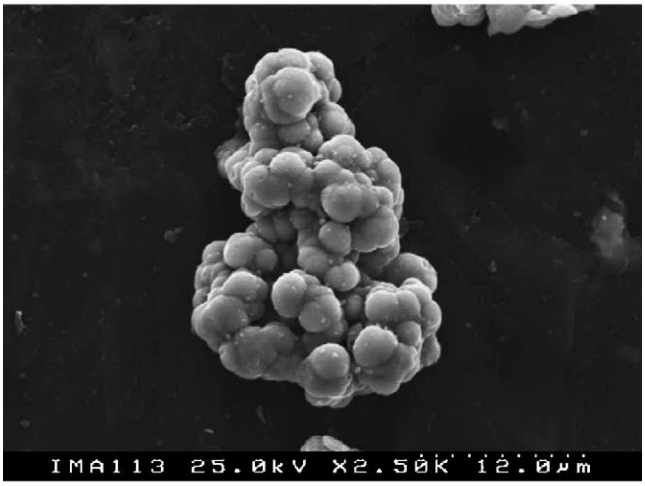
2. Experimental

2.1. Raw materials

A commercial polycrystalline tetragonal zirconia stabilized with 3 mol% of yttrium (3Y-TZP, hereby named TZP) supplied by Tosoh Co. (Japan) was selected to be added to conventional single-firing ceramic glaze formulations. This powder consists of spherical agglomerates (granules) of sizes under 50 μm (see Fig. 1A). The typical crystallite size is about 25 nm, and the specific surface area (estimated by BET analysis) is 16 m^2/g. XRD analysis of TZP powder indicated the presence of a minor quantity of monoclinic zirconia in addition to the tetragonal grains (the approximate monoclinic phase content was estimated around 8 wt.%).



(A)



(B)

Fig. 1. SEM views of (A) TZP and (B) M powders.

A monoclinic zirconia powder (from Riedel-de Haen, Germany), hereby named M, was also added to glazes in order to compare with *t*-ZrO_2 induced effects. It is made of agglomerates of irregular size (from 10 to 30 μm) involving single particles of about 2 μm (Fig. 1B).

Finally, two zircon powders ($ZrSiO_4$), given by Esmalglass Portugal S.A., which are currently used as opacifying agents of glazes were also tested. Their commercial designation is ZS300 or ZS5 derived from their grain size distributions. The first is made of coarse particles whose mean size is about 9 μm (90 wt.% under 30 μm, and only 10 wt.% under 1 μm). The wet milling of this powder for 1 h 30 min with zirconia balls was conducted to obtain a finer powder (hereby named ZS5, since 90 wt.% of particles are under 5 μm). Its mean grain size is about 1 μm.

Two representative formulations of conventional single-firing transparent ceramic glazes, also supplied by Esmalglass Portugal S.A., and referenced as L and H, were selected for the present study. These glazes were used as frit (previously melted at higher temperatures and quenched in water to room temperature to obtain an amorphous glass). Their approximate oxide compositions (wt.%) can be seen in Table 1 and the corresponding melting temperature is about 1150 and 1240 °C, for glazes L and H, respectively.

2.2. Sample preparation

Cylindrical pellets (2 cm of diameter) were obtained by uniaxial pressing of dry powders (4 g/pellet). To obtain a homogeneous distribution of all the raw material components, the frits were previously milled in an agate mortar and the fraction below 45 μm was mixed with the corresponding quantity of TZP, M, ZS300, or ZS5 (up to 30 wt.% in excess to the glaze). This operation was carried out in dry conditions and without grinding media to prevent changes in size and morphology of tetragonal zirconia grains, and also to avoid transformation to the monoclinic form, generally induced by grinding [18].

For the common complementary characterization (mechanical and optical) another set of samples was prepared from mixtures of glaze L with different quantities (10, 20 and 30 wt.%) of TZP and ZS300. Its fully description is given elsewhere [4].

2.3. Firing schedules

Pellet samples were fired in laboratory electrical kilns following two different firing schedules: (i) a slow firing cycle consisting of a 2 h 45 min heating ramp up to 1200 °C,

Table 1
Approximate oxide composition (wt.%) of the transparent ceramic glazes employed in the study

Frit or glaze	$Na_2O + K_2O$	$CaO + MgO$	ZnO	B_2O_3	Al_2O_3	SiO_2
L	6	15	10	3	8	58
H	6	14	9	–	6	65

a soaking time of 1h at this temperature, and a slow cooling down of 4–5 h to room temperature, and (ii) a 51 min fast-firing cycle (industrial schedule) with a 20 min heating ramp up to 1200 °C, a 5 min soaking time at this temperature, and a 19 min cooling down to room temperature.

2.4. Characterisation techniques

X-ray diffraction (XRD) of the fired pellets was carried out with a Rigaku diffractometer using Ni filtered Cu Kα radiation, in order to assess the stability of the tetragonal zirconia towards dissolution in the glaze and/or the zircon devitrification processes. Further information was obtained by scanning electron microscopy (SEM) characterization of the samples, performed with a Hitachi S4100 electron microscope equipped with EDX analysis. Pellet samples were cut in thin layers, polished with diamond paste and C-graphite sputtered prior to SEM observation.

Samples were electroded with porous Pt and their electrical behaviour was studied by impedance spectroscopy. Measurements were conducted in air and in the range 400–800 °C, by using the experimental setup represented in Fig. 2. An Hewlett-Packard 4284A bridge was used in the frequency range between 20 and 10^6 Hz. Fitting and interpretation of curves was done by using a specific routine program [19].

Relevant optical and mechanical properties are detailed elsewhere [4] and are now referred to for comparison.

3. Results

3.1. Behaviour of different glazes and effect of additives

To analyze the effect of glaze composition on zircon, M or TZP stability, several pellets of both glazes (L and H) were prepared, containing or not 10 wt.% of zircon-based powders. These pellets were fired at 1200 °C following the cycle (i). Fig. 3 shows the XRD patterns corresponding to doped and undoped glazes (L and H) after the firing treatment. As previously mentioned [4], TZP stability was found much higher in glaze H. In fact, the reaction between TZP and glaze L (more fusible) was almost complete. In this sample, martensitic-type transformation to the monoclinic structure should occur followed by the formation of zircon. In glaze H, however, XRD characterisation still shows the presence of a large amount of unreacted (stabilized) TZP, despite the appearance of zircon and the presence of small amounts of monoclinic ZrO_2 [4]. These observations clearly denote an incomplete reaction between TZP and H glaze phases.

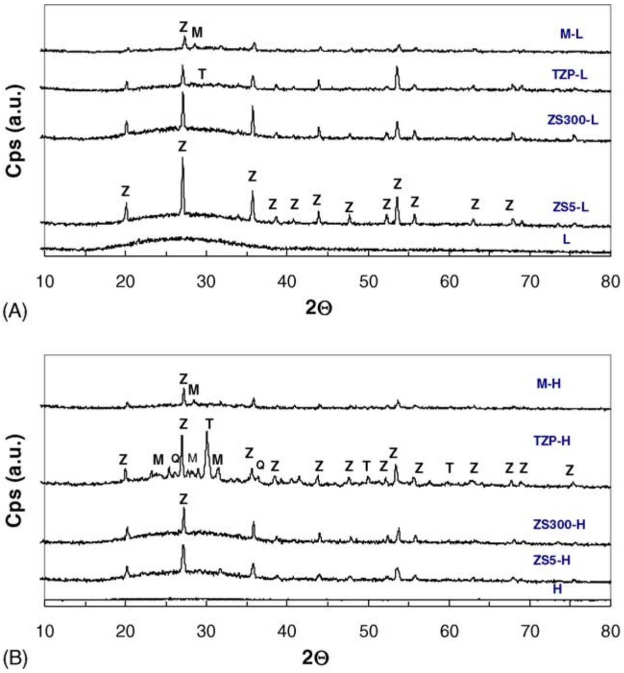


Fig. 3. XRD patterns of pellets made from mixtures of glaze and TZP, M, ZS, or ZS300 (10 wt.%) powders, after sintering at 1200 °C using a slow-fired cycle (8–9 h): (A) glaze L; (B) glaze H (Z = zircon, T = tetragonal ZrO_2, M = monoclinic ZrO_2, Y = Y_2O_3).

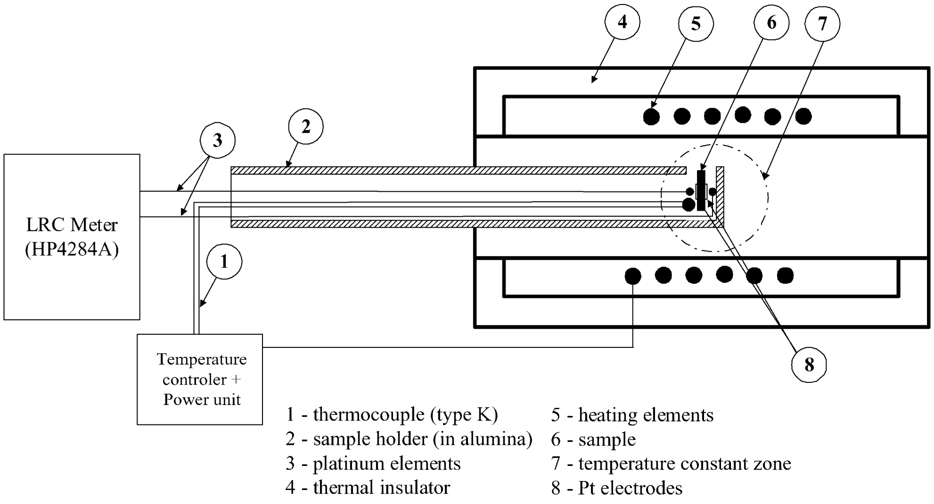


Fig. 2. Schematic view of impedance spectroscopy apparatus.

M-based materials show a similar behaviour [4]: monoclinic zirconia has reacted almost completely in both glazes and some zircon devitrification has occurred. In ZS-materials, the presence of more intense zircon peaks may be observed by XRD (especially in glaze L), which can arise both from unsolved and also from devitrified crystals. By comparing the width of the XRD peaks, the particle size of zircon crystals must be considerably higher in glaze L than in glaze H (with less intense and broader peaks). Therefore, differences in composition of the ceramic glaze (higher silica content and absence of boron oxide in glaze H, etc.) and in the melting temperature (glaze H shows higher refractoriness) cause important effects on the stabilisation of polycrystalline tetragonal or monoclinic zirconia and also on zircon dissolution and/or devitrification.

Undoped glazes also denote significant differences, as shown in Fig. 4. Glaze H tends to devitrify upon long annealing treatment, with formation of Ca/Si rich zones [4]. In that sense, we would expect higher resistivity values for this glaze than for pure L glaze, but differences are not clear and an inversion seems to occur (see Fig. 5). Differences in porosity level, detailed below, might explain this behaviour. Impedance spectra of both undoped glazes are basically made of one single arc, more depressed for the H sample by the reasons previously mentioned.

All doped samples show stronger complex impedance responses (Fig. 5), denoted by the higher depression angle of the corresponding arc ($n < 0.8$, while a centred semicircle shows $n = 1$ generally ascribed to a single contributor). The possible appearance of a second arc at intermediate/low frequency region, which deconvolution might be done by using mathematical tools such as NLLS, is generally governed by interfacial effects. The dispersion of less conductive opacifying particles in the glaze matrix (like ZS or M powders) acts as local electrical insulating barriers to the transport of conducting species, resulting in higher resistivity values. The complexity/dispersion of the IS response is also predicted. In the case of M-doped materials, for instance, the presence of zircon particles with a relatively small size (small and broad peaks) strongly increases the electrical resistivity. In the case of TZP-samples, moreover, the impedance spectra seem to be sensitive to the different stabilisation degree of the more conductive t-ZrO_2: in glaze H a considerable amount of t-ZrO_2 remains stabilised in the glaze matrix, while in glaze L only traces of this phase are present. The higher resistivity of the second would account therefore for the lower stabilisation of t-ZrO_2.

The electrical response seems to be also sensitive to differences in particle size, which may be well illustrated by the differential behaviour of ZS-doped L and H glazes. As may be appreciated in Fig. 5, the electrical resistivity is much higher in glaze H than in glaze L. In the later, XRD (Fig. 3) evidenced more intense and sharper zircon peaks, associated to zircon particles of a higher particle size, and this was also responsible for the loss of gloss of the corresponding layers [4]. In glaze H, however, the dispersion

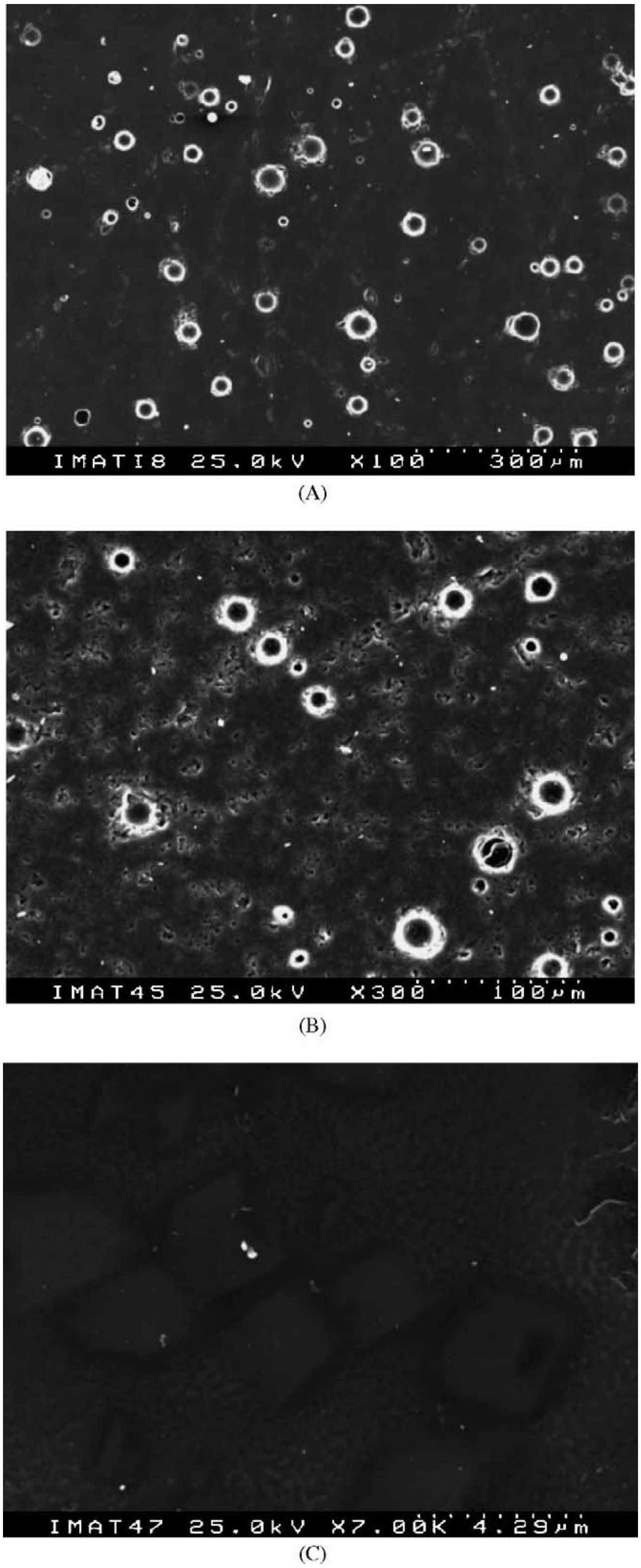


Fig. 4. SEM views of pure glaze pellets sintered at 1200 °C using a slow-fired cycle (8–9 h): (A) low magnification of glaze L; (B) low magnification of glaze H; (C) high magnification of glaze H, showing devitrification zones (Ca/Si-rich).

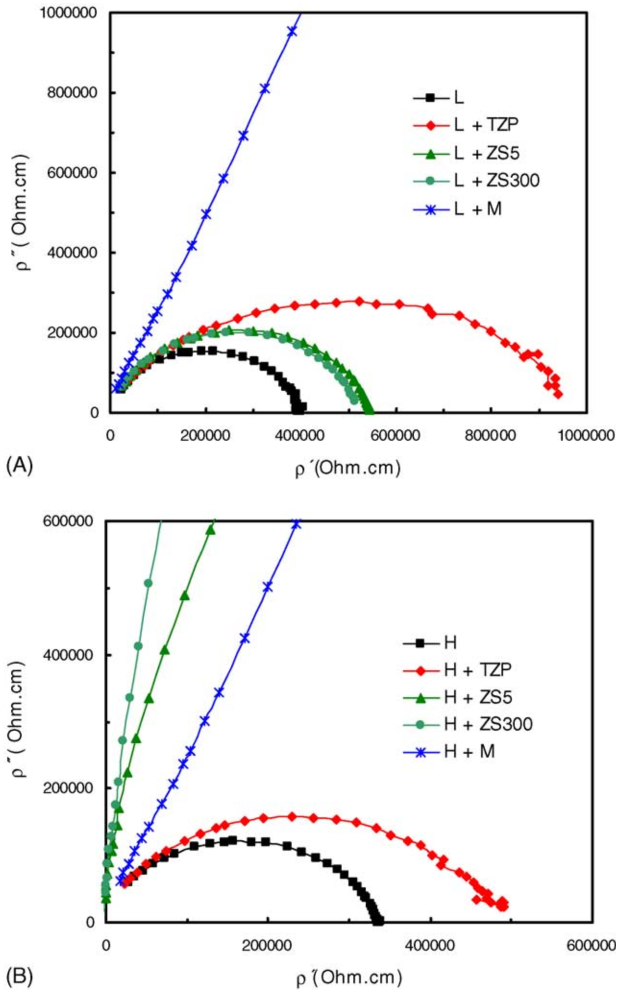


Fig. 5. Representative impedance spectra obtained at 500 °C for undoped or doped (10 wt.%) pellets fired at 1200 °C using a slow-fired cycle (8–9 h): (A) glaze L; (B) glaze H.

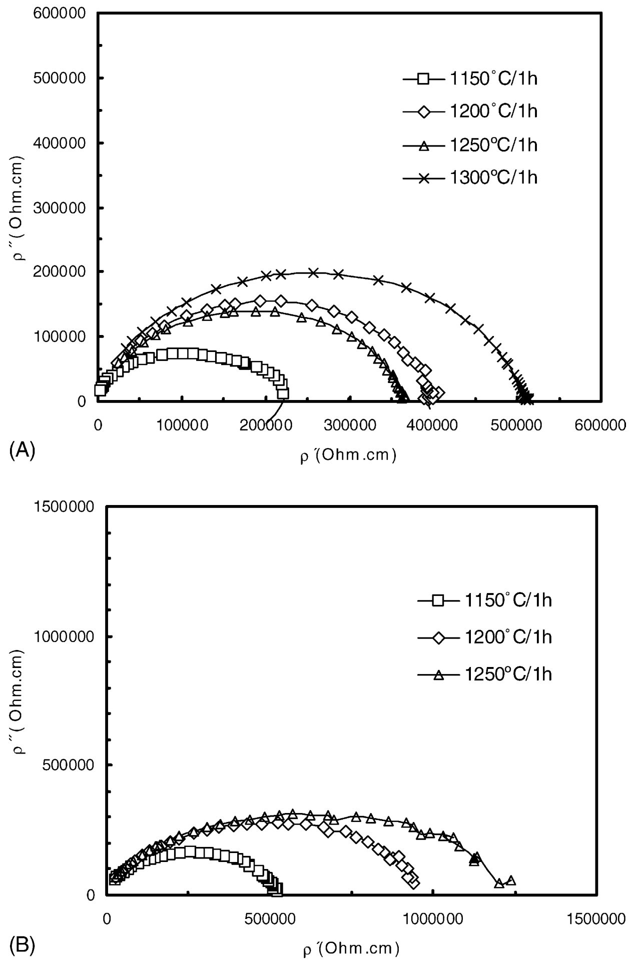


Fig. 6. Impedance spectra obtained at 500 °C for L pellets slowly fired at different temperatures: (A) undoped; (B) doped (10 wt.% TZP).

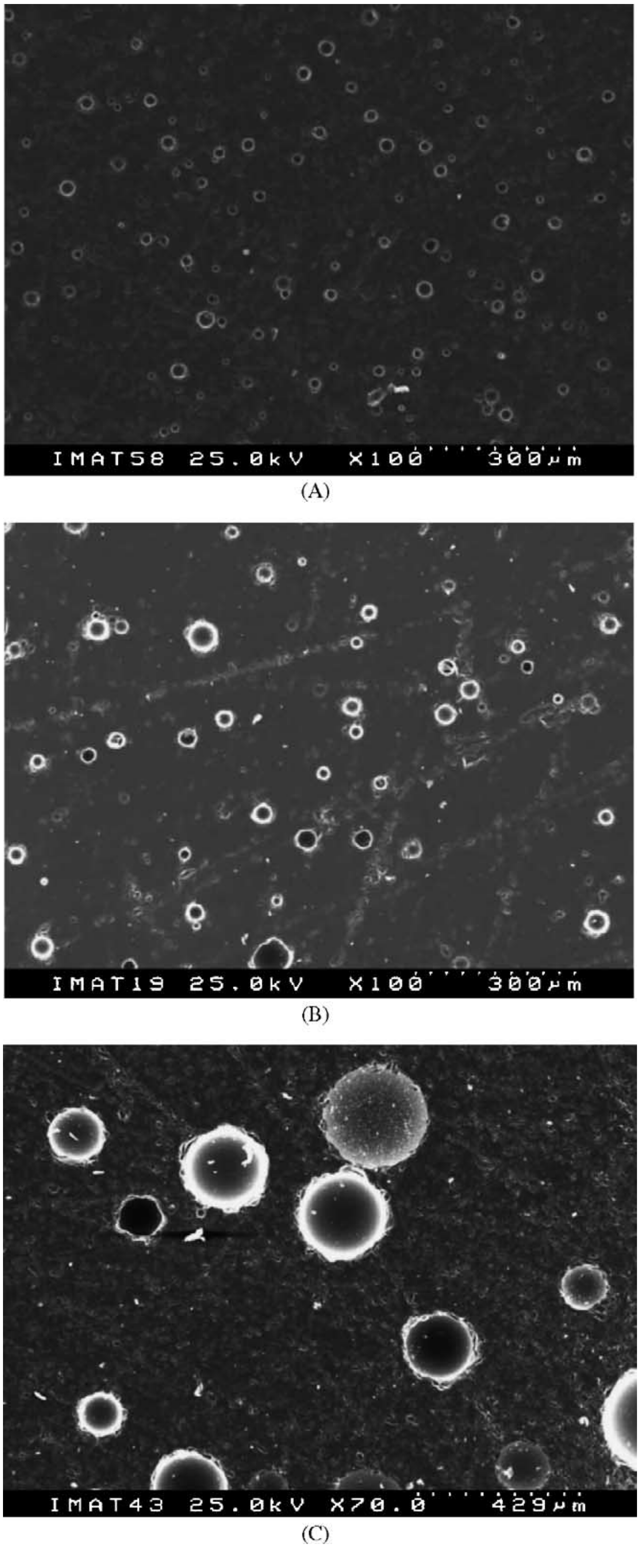
of smaller zircon particles (zircon dissolution and devitrification processes take place more slowly, due to the higher refractoriness of this glaze) could result in a higher grain boundary contribution (electrical barriers) and thus contributing to the higher resistivity. In both glazes, the solution of zircon is faster when finer powders (ZS5) are used. However, the use of long firing cycles tends to mask these differences and, as a consequence, the electrical response is almost independent of the initial average grain size (Fig. 5). A compromise between size and amount seems responsible for this similitude.

Since glaze L is (more) frequently used in monoporosa formulations, the further study of the influence of parameters was only conducted with this material. However, relevant effects might be extrapolated for other glazes (including H).

3.2. *Effect of the firing cycle*

The effect of peak temperature in firing cycle (i), was evaluated on pure glaze L and TZP doped (10 wt.%) slowly fired pellets. Fig. 6 shows that the behaviour is similar, irrespective of the presence of opacifying additives. All samples tend to be more resistive with increasing peak firing temperature, despite the predictable higher dissolution of crystalline additives. However, SEM pictures (Fig. 7) reveal strong changes in the porosity of samples that might explain the electrical behaviour. Coalescence of pores tends to occur as the temperature rises (typical pore size between 15 and 30 μm and 50 and 180 μm at 1150 and 1300 °C, respectively) and its blocking effect to the electrical transport becomes more effective. We should also mention that this phenomenon causes deleterious effects on both transparency and mechanical resistance levels of the glaze layer and the careful choice of the firing temperature is essential to obtain desirable properties. Even so, differences are expectably less pronounced for fast-fired samples.

To analyse the effect of firing treatment duration, pellets made of pure glaze L and TZP doped (10 wt.%) were also fast-fired up to 1200 °C during only 51 min. In such rapid thermal cycles, it is expected that TZP particles remains stable and less formation of zircon would be formed. Effectively, XRD characterization (Fig. 8) confirms that



(A)

(B)

(C)

Fig. 7. Typical microstructure (SEM) of L-glaze pellets slowly fired at different temperatures: (A) 1150 °C; (B) 1200 °C; (C) 1300 °C.

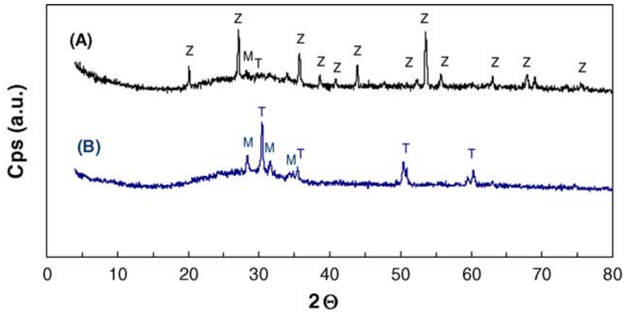


Fig. 8. XRD patterns of 10 wt.% TZP-doped L samples fired at 1200 °C following: (A) a slow-fired cycle (8–9 h); (B) a fast-fired cycle (51 min).

almost all of tetragonal zirconia remains in the pellet after this firing, without the occurrence of either martensitic-type transformation to monoclinic zirconia (a similar m-ZrO_2 content to that of the TZP raw material was observed) or zircon crystallization. The absence of zircon crystals was also confirmed by SEM, since only spherical TZP aggregates made of fine (0.3 μm) rounded-shaped grains were reported [4]. Therefore, even in those ceramic glazes in which the tetragonal zirconia phase is less stable (glaze L), the use of rapid firing schedules made it possible to obtain

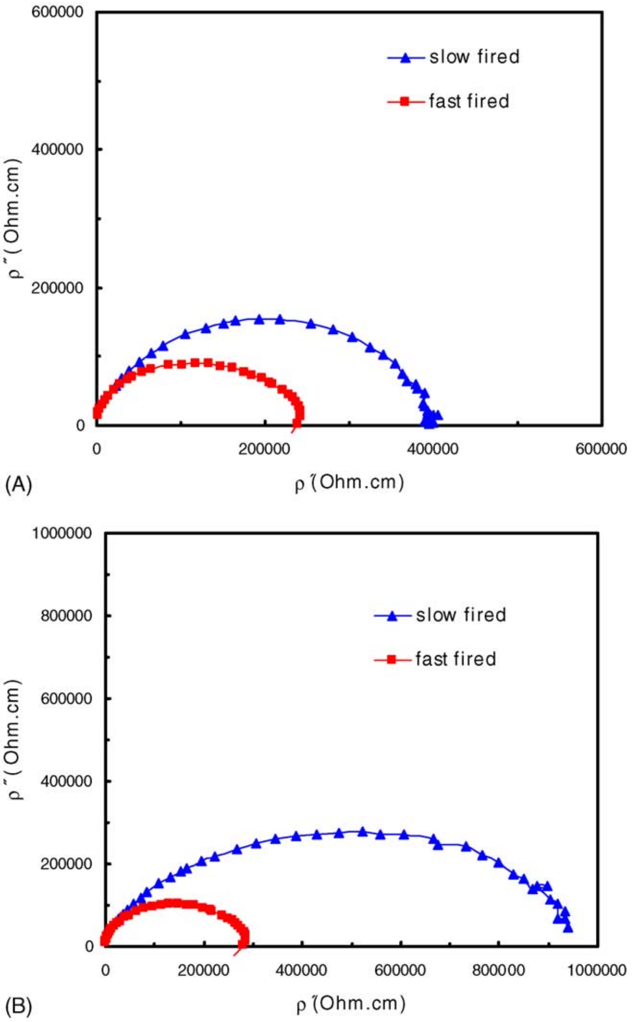


Fig. 9. Impedance spectra obtained at 500 °C for L pellets fired at 1200 °C following a slow-fired cycle (8–9 h) and a fast-fired cycle (51 min): (A) undoped; (B) doped (10 wt.% TZP).

vitro-crystalline glazes mostly consisting of fine-grained and stabilized (unsolved) tetragonal zirconia. As may be seen in Fig. 9, the electrical resistivity is clearly lower for fast-firing samples, where the dispersed phase is the more conductive TZP and remains stable, instead of devitrified zircon.

3.3. *Effect of the amount of additives*

Pellets with increasing amounts (10, 20 and 30 wt.%) of TZP or zircon (ZS300) were prepared and fired in a laboratory-scale electrical furnace following the same rapid cycle (51 min). These tests served as comparison between pellet samples and industrially prepared coatings, since the stability of the added tetragonal zirconia grains is expected to be rather different in both cases, due to differences in diffusion processes, exposure to kiln atmosphere, and interfacial contact between grains and glaze. XRD patterns of the fast-fired pellets shows that both TZP and zircon phases remain stable, irrespective of the addition level [4]. Moreover, the XRD peaks area of added crystalline phases (t-ZrO_2 and $ZrSiO_4$) is observed to rise in correlation with their amounts. Interestingly, the electrical response also follows this tendency (Fig. 10). In this sense, it might be used as a complementary non-destructive technique to predict desirable opacity/whiteness levels, but experimental difficulties in measuring glazed layers on the top of ceramic tiles should be overcome. Measurements on the glaze surface are now underway.

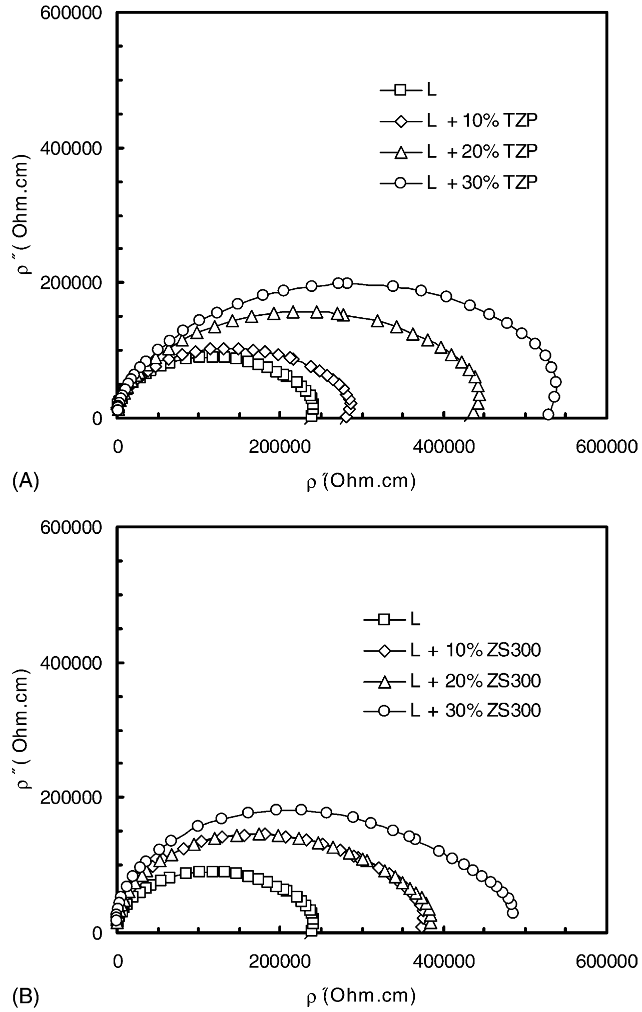


Fig. 10. Impedance spectra obtained at 500 °C for L pellets fired at 1200 °C following a fast-fired cycle (51 min) containing several amounts of: (A) TZP; (B) ZS300.

4. Conclusions

The impedance spectroscopy proved to be a useful auxiliary technique to study the electrical behaviour of glazes. Changes of the nature and amount of opacifying crystalline phases, in the nature of glaze matrix, and in firing conditions were found to be the relevant morphological parameters that affect the ultimate electrical behaviour of the samples. Since impedance spectroscopy enables the separation of lattice from intergranular/interfacial contributions, it can be used for this purpose. Since glazes are very complex systems, made of very thin layers covering insulating and thicker ceramic bodies, further measuring experimental details should be studied. In particular, measurements on the glaze surface should be made and correlations with functional characteristics might be established.

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