STUDY OF THE LUSTRE EFFECT IN GLAZES

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1. ABSTRACT

A study was undertaken of the transformations that arise during the heat treatment of an industrial frit containing cerium and zirconium oxides, used to produce the so-called "lustre effect" in glaze surfaces.

Tests were conducted with the frit by itself (using a standard industrial particle-size distribution) in the form of cylindrical test specimens or applied as a coating onto a fired body, and by screen printing the frit as a fine sheet onto a layer of unfired, transparent-firing glaze particles.

In both cases, the influence of the firing cycle was studied on the characteristics of the end glaze (gloss, colour, etc.) and on the content and grain size of the crystalline phases present, which at around 1100°C were zircon and a solid solution of ZrO_2 in CeO_2 ($Ce_xZr_yO_2$), with a CaF_2 type structure.

2. INTRODUCTION

One of the optical effects usually produced for decorative purposes in ceramic tile glaze surfaces is the so-called "lustre effect". This involves providing the glaze surface with a metallic gloss that changes colour slightly on modifying the angle of incident light. These changes of colour, with a beam of white incident light at a given angle, are possibly due to the constructive interference between the light rays reflected at the top and bottom interfaces of a thin sheet, when this has a different refractive index from the medium where the light beam comes from. For this interference to arise for a given wavelength, the difference between the optical path travelled by the reflected rays at each of the two interfaces, needs to be a whole multiple of incident light wavelength. As white light is a mixture of radiation of different wavelengths, for each of these, the constructive interference condition occurs at a different layer thickness [1].

The lustre effect can be achieved by screen printing a fine sheet of frit with an appropriate composition, containing Ce and Zr, onto a consolidated layer of unfired glaze particles on a ceramic body, subsequently firing the whole piece according to the usual conditions (thermal cycle) used in industry for single-fire ceramic wall tile manufacture.

The purpose of this study has been to: a) attempt to determine the cause of the lustre effect and the most appropriate firing conditions for encouraging it; b) attempt to establish why the glaze surfaces in which lustre is produced sometimes exhibit a bluish and sometimes a yellowish hue, when using the same frit and base glaze.

3. EXPERIMENTAL

A frit containing CeO_2 and ZrO_2 in its composition was used. This was wet milled until obtaining a particle-size distribution leaving a reject of 2 wt% on a 40-μm-mesh screen.

Experiments were conducted with three types of samples prepared from the milled frit containing Ce and Zr:

a) Cylinders shaped by casting a suspension of the frit.
b) Consolidated layers of frit particles applied by the wet method onto a fired ceramic wall tile body.
c) Fine sheets obtained by screen printing a suspension of the frit particles in an organic liquid onto an unfired, consolidated layer of transparent-firing frit particles.

Different heat treatments were performed under identical conditions for the three types of prepared samples, with a view to studying the influence of heating rate, peak heat-treatment temperature and residence time at peak firing temperature on the characteristics of the resulting products (glazes).

XRD scans were run on the fired cylindrical specimens to determine the devitrifying crystalline phases, integrated peak intensity of the strongest line of these phases (after

[1]. NASSAU, K. *The physics and chemistry of color: The fifteen causes of color.* New York: John Wiley, 1983.

verifying there was no overlapping) and crystallite size from the XRD peak amplitude, using the SCHERRER equation [2]. The integrated peak intensity of the strongest line corresponding to each crystalline phase present is proportional to the content of this phase in the studied specimen.

In the glazes made by firing the samples described in points (b) and (c), gloss was determined at an incident angle of 60°, together with the chromatic coordinates on a diffuse reflectance spectrophotometer, including the specular component, using a standard CIE 2° observer and standard CIE C illuminant [3].

4. RESULTS

4.1.- IDENTIFICATION OF THE DEVITRIFYING CRYSTALLINE PHASES

Figure 1 depicts the diffraction patterns obtained after heating cylindrical specimens of the type described in point 3(a) at a heating rate of 25°C/min to different peak temperatures. Only three crystalline phases were detected, corresponding to a cerianite, zircon and petedunite structure. The figure shows that the peak of the cerianite structure already appears clearly defined in the experiment conducted at a maximum temperature of 900°C, shifting to lower angles (higher values of the d_{111} interplanar spacing) as T_{max} rises, with a progressive increase of d_{200} zircon peak intensity above T_{max} 1000°C, which practically stabilises at 1100°C. Table 1 shows that the interplanar spacing of the phase crystallising with a cerianite structure (d_{111}), which for pure CeO_2 is 3.124(, shifts from 3.07Å to 3.09Å on raising T_{max} above 1000°C. It is to be noted that petedunite is no longer detected above 1050°C.

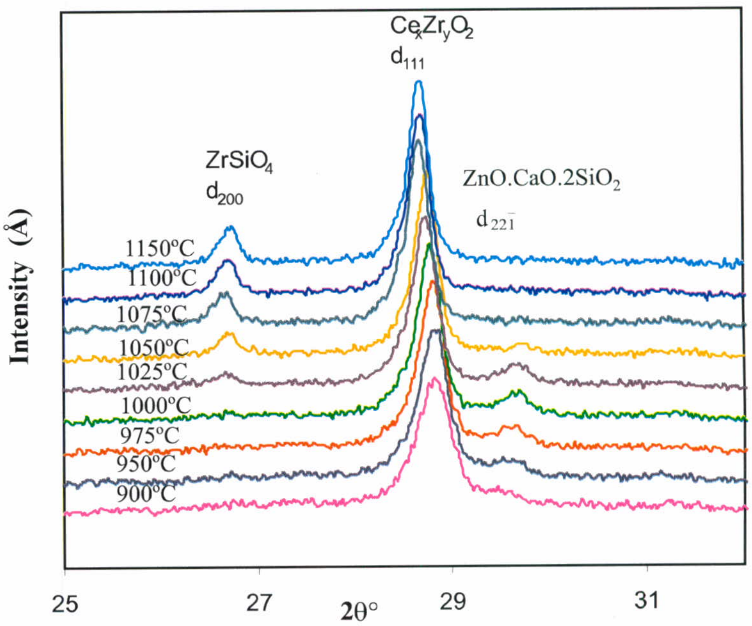

Figure 1. Diffraction patterns obtained on heating the specimens at 25°C/min to different peak temperatures.

These results indicate that the peak corresponding to the cerianite structure appearing in the 2θ range of values plotted in Figure 1 is due to a solid solution of ZrO_2 in CeO_2, with the characteristic cubic crystalline structure of the latter oxide. In the literature surveyed [4] the value d_{111}=3.07Å, which is the mean value of this parameter for

[2]. KLUG, H.P.; Alexander, L.E. *X-ray diffraction procedures for polycrystalline and amorphous materials.* 2nd ed. New York: John Wiley, 1974.
[3]. HUNTER, R.S.; HAROLD, R.W. *The measurement of appearence.* New York: John Wiley, 1987.
[4]. DUWEZ, P.; ODELL, F. *Phase relationships in the system zirconia-ceria.* J. Am. Ceram. Soc., 33 (9), 274-283, 1950.

the crystalline species with a cerianite structure obtained in the experiments in which the specimens were heated to $T_{max} \leq 1000°C$ (Table 1), corresponds to a solid solution of ceria and zirconia that crystallises in the cubic system, with molecular formula $Ce_{0.5}Zr_{0.5}O_2$. This solid solution progressively expels ZrO_2 above T_{max}=1000°C as T_{max} rises, reflected in the progressive rise of d_{111}, which reaches 3.09Å at 1150°C, corresponding to a solid solution of molecular formula $Ce_{0.75}Zr_{0.25}O_2$. The exsolving ZrO_2 crystallises and subsequently interacts with silica in the glassy phase, forming zircon [5].

Tmax (°C)	Cerianite structure d_{111} (Å)	Other crystalline phases	
		Zircon	Petedunite
900	3.07	No	No
950	3.07	No	Yes
975	3.06	No	Yes
1000	3.07	No	Yes
1025	3.08	Yes	Yes
1050	3.08	Yes	Yes
1075	3.09	Yes	No
1100	3.09	Yes	No
1150	3.09	Yes	No

Table 1. *Variation of the interplanar spacing of crystals with a cerianite structure on raising T_{max}.*

The presence in the end glaze of considerable proportions of $Ce_xZr_yO_2$ and zircon crystals in the specimens heat treated at T_{max} between 1100°C and 1150°C, must be the cause of the lustre effect produced industrially from the studied frit. Thus, in almost all the firing cycles used industrially to produce glazed wall tiles, the stretch of constant peak temperature, in which, according to Figure 1, considerable quantities of zircon and the solid solution of empirical formula $Ce_xZr_yO_2$ (where x + y = 1) with a cerianite cubic structure (of the CaF_2 type) devitrify, ranges from 1075°C to 1140°C.

4.2.- POSSIBLE EXISTENCE OF A HOMOGENEOUS NUCLEATING STEP

In oxide glasses containing zirconium and cerium in proportions similar to those found in the frit being studied, crystallisation nuclei of these oxides can form by homogeneous nucleation. The literature mentions their capacity to act as nucleating agents in glasses [6,7].

If, in the studied frit, the zircon and/or $Ce_xZr_yO_2$ solid solution crystal growth step were preceded by a homogeneous nucleation step at a temperature below T_{max} of the standard firing cycle used for firing glazed tile (1075-1140°C), the quantity of crystals present in the end glaze could be affected by the rate at which the preheating stage is run in the corresponding firing cycle. This might affect the intensity or characteristics of the lustre effect in the resulting glaze.

4.2.1.- Preliminary experiments

To study the possibility of homogeneous nucleation occurring prior to crystal growth, a series of experiments was conducted with cylindrical specimens made from the

[5]. ESCARDINO, A.; MORENO, A.; AMORÓS, J.L.; GOZALBO, A.; Aparici, J.; Sánchez, L.F. *Study of crystalline-phase formation in white zirconium glazes.* Cerám. Acta, 8 (6), 21-34, 1996.

[6]. KINGERY, W. D.; BOWEN, H.K.; UHLMANN, D. R. *Introduction to Ceramics.* 2nd ed. New York: John Wiley, 1976. Chap. 8, pag. 368.

[7]. MCMILLAN, P.W. *Glass ceramics.* London: Academic Press, 1979.

studied frit particles at a constant temperature (600 or 700°C), for a set time (20 or 180 min), in an attempt to produce eventual nucleation. The specimens were subsequently heat treated at 1000°C for 20 min to try and produce crystal growth. Table 2 reports the findings.

Experiment no.	Nucleation step		Crystal growth step		XRD information		
	T (°C)	t (min)	T (°C)	t (min)	$Ce_xZr_yO_2$ crystallite size (Å)	$CexZryO_2$, d_{111} peak intensity (c.p.s.)	Zircon, d_{200} peak intensity (c.p.s.)
1	600	20	1000	20	606	761	125
2	600	180	1000	20	750	1147	77
3	700	20	1000	20	581	754	91
4	700	180	1000	20	740	1671	67

Table 2. *Results of the preliminary experiments.*

The table shows that at the two temperatures tested in attempting to produce homogeneous nucleation, raising residence time increased the relative size of the crystallite slightly and considerably raised the $Ce_xZr_yO_2$ content in the glaze, apparently without affecting the zircon content in the same way, which decreased.

The duration of the nucleation period did not greatly affect mean crystallite size, as this depends on the duration and temperature of the crystallisation period, which were held steady in the four experiments run.

Analysis of these values suggests that ZrO_2 acts together with CeO_2 as a co-nucleating agent, both oxides forming part of the stable nuclei at which $Ce_xZr_yO_2$ crystals grow. Thus, as the $Ce_xZr_yO_2$ solid solution content rises, the zirconium available in the system for forming zircon crystals decreases, as the latter is produced as a result of the interaction between free ZrO_2, which crystallises directly by heterogeneous nucleation, and the silica present in the glassy phase [8].

4.2.2.- Influence of heating rate on the development of the nucleation step

As the length of frit specimen residence time at 600 or 700°C considerably affected the $Ce_xZr_yO_2$ crystal content present in the glaze obtained by the heat treatment, this content was thought to be also possibly affected by the rate at which the preheating stage developed in the industrial heat-treatment cycle. A longer dwell in the temperature range at which nucleation occurred might produce a larger quantity of cerianite crystals in the end glaze, owing to the formation beforehand of a greater number of stable crystallisation nuclei. Therefore, at higher heating rates, a smaller quantity of cerianite crystals would be produced as a result of the specimens being held for a shorter time at the temperature range that favoured homogeneous nucleation.

Table 3 lists the data obtained for different heating rates and different residence times at three peak heat-treatment temperatures (T_{max}) of 1000°C, 1075°C and 1100°C.

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[8]. AMORÓS, J.L.; ESCARDINO, A.; ORTS, M.J.; MORENO, A. *Zirconium glazes used in fast single fired wall tile manufacture: Part 1. Crystallisation mechanism.* Br. Ceram. Trans., 93 (6), 224-228, 1994.

Experiment no.	Heating rate (°C/min)	Tmax (°C)	t_{max} (min)	XRD information $Ce_xZr_yO_2$ d_{111} (Å)	Crystallite size (Å)	$Ce_xZr_yO_2$, d_{111} peak intensity (c.p.s.)	Zircon, d_{200} peak intensity (c.p.s.)
5	1	1000	20	3.103	698	1813	297
6	5	1000	20	3.088	692	1428	154
7	10	1000	20	3.085	693	1253	126
8	25	1000	20	3.087	661	918	142
9	50	1000	20	3.081	607	750	54
10	10	1000	6	3.083	602	1285	47
11	25	1000	6	3.080	605	943	32
12	50	1000	6	3.079	553	721	--
13	10	1075	6	3.091	944	1143	191
14	25	1075	6	3.089	896	959	146
15	50	1075	6	3.087	881	699	128
16	10	1100	6	3.096	1112	1160	199
17	25	1100	6	3.092	1024	940	157
18	50	1100	6	3.091	1245	713	141
19	50	1100	4	3.088	1042	766	93

Table 3. *Influence of heating rate.*

These findings confirm that the homogenous nucleation step plays a very important role in the devitrification process being studied. At a given T_{max}, as heating rate rises (which is equivalent to reducing the time during which the specimen remains in the 500-800°C range), the $Ce_xZr_yO_2$ crystal content drops and the mean crystallite size decreases slightly. The decrease in crystallite size can be explained by considering that solid solution crystallisation initiates at temperatures around 900°C (Figure 1). Hence, at the same specimen residence time at T_{max}, raising the heating rate progressively reduces the specimen residence time at 900°C < T < T_{max}, and therefore total time for crystal growth. This effect is more pronounced at a heating rate of 50°C/min.

The decrease in the number of stable crystallisation nuclei together with the drop in arising crystal size yielded a reduction in $Ce_xZr_yO_2$ content on raising heating rate.

The micrographs in Figures 2 and 3 allow comparing the size of the crystals produced at a heating rate of 1°C/min and 50°C/min up to 1000°C. No significant qualitative difference can be observed between the crystal sizes, as they only differ by 13% according to the diffractogram measurements (last column in Table 3)

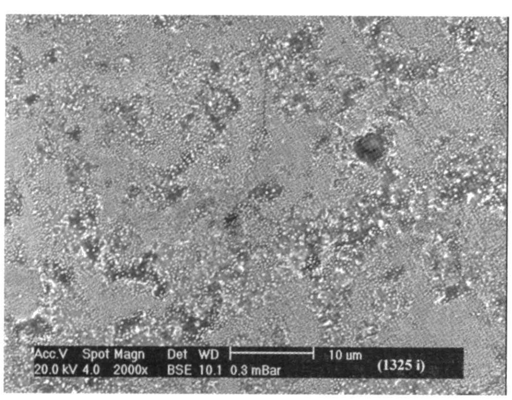

Figure 2. *Heating rate = 1°C/min.*

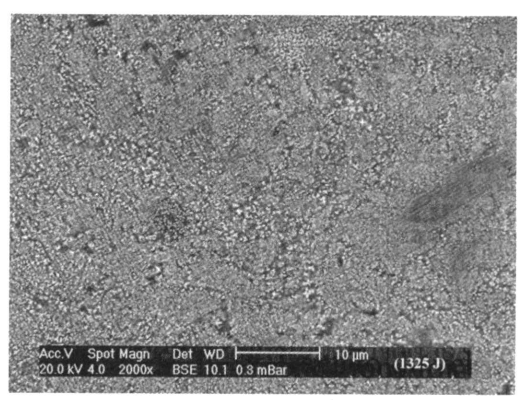

Figure 3. *Heating rate= 50°C.*

The fact that the d_{111} interplanar spacing values corresponding to the $Ce_xZr_yO_2$ solid solution in the diffraction pattern approach the pure cerianite value (d_{111} = 3.124Å) more closely as the quantity of zircon crystals present in the glaze rises matches the conclusion set out above, according to which the crystalline phase with a cerianite structure is a solid solution of empirical formula $Ce_xZr_yO_2$, which as more ZrO_2 exsolves, more closely approaches a pure CeO_2 structure, as this oxide content rises.

Shortening the crystal growth period from 20 to 6 minutes at T_{max} = 1000°C hardly affected the $Ce_xZr_yO_2$ content at heating rates of 10, 25 and 50°C/min. However, the crystallite size in the end glaze decreased a little, as expected. Therefore, starting with the same number of nuclei, the shorter the crystal growth period, the less will the $Ce_xZr_yO_2$ crystals grow.

On raising T_{max} to 1075 and 1100°C, the $Ce_xZr_yO_2$ content remained practically steady at each tested heating rate, though the crystallite size increased. This can be explained by assuming that equilibrium has been reached in the crystal growth step, and under these circumstances, the smallest crystals can dissolve by growth of the largest crystals, holding a steady total quantity of crystalline phase. This fact was observed on studying zircon crystal growth in a different frit under non-isothermal conditions [9,10].

With regard to the zircon content in the fired specimens, zircon content dropped at the three tested peak temperatures on raising the heating rate used.

At heating rates of 10, 25 and 50°C/min and a residence time (t_{max}) of 6 min, an important rise was found in zircon content on going from T_{max} = 1000°C to T_{max} = 1075°C, while the rise was much less on going to T_{max} = 1100°C, probably as a result of ZrO_2 exsolution from the solid solution ceasing.

4.3.- CRYSTAL GROWTH STEP

To confirm the influence of the peak heat-treatment temperature at which the crystal growth step largely develops, on the characteristics and content of the crystalline phases present in the resulting glaze, various experiments were carried out in an electric laboratory kiln, in which cylindrical specimens made with the studied frit particles were heat treated according to the thermal schedule set out below (Figure 4):

From $T_{ambient}$ to 500°C heating at maximum possible rate.
From 500 to 825°C heating at 25°C/min.
From 825 to 900°C heating at 7.5°C/min.
From 900 to T_{max} heating at 25°C/min.
6-min residence at constant T_{max}.

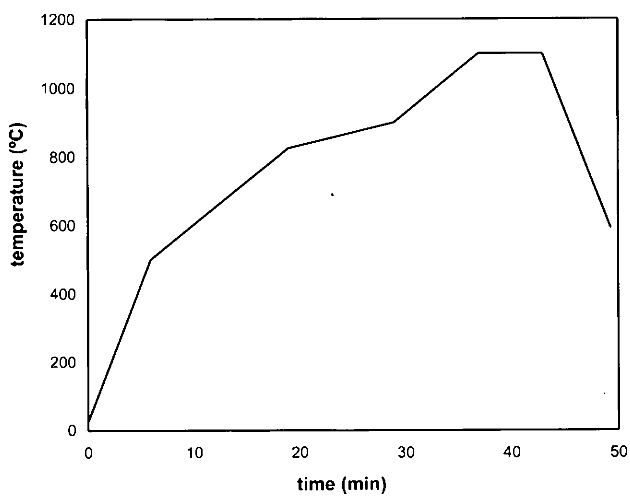

Figure 4. *Heat-treatment cycle used (variable T_{max}).*

[9]. ORTS, M.J.; GOZALBO, A.; LEMUS, R.; CANTAVELLA, V. *Estudio de la desvitrificación en una frita de circonio, por difracción de rayos X a alta temperatura.* Técnicas de laboratorio, 239, 132-133, 1999.
[10]. ESCARDINO, A.; MORENO, A.; AMORÓS, J.L.; ORTS, M.J.; BARBA, A. *Zirconium glazes used in fast single-fired wall tile manufacture: Part 2. Empirical model for fitting experimental data from the devitrification process.* (Accepted for publication in Br. Ceram. Trans.).

The table shows that for the heat-treatment cycle used, as peak firing temperature is raised (at steady t_{max}), the $Ce_xZr_yO_2$ content in the T_{max} range from 1000°C to 1100°C slowly decreased, with a gradually increase in corresponding crystallite size. The zircon content rose. These outcomes match the findings in the foregoing section.

Experiment. no.	Tmax (°C)	$Ce_xZr_yO_2$ d_{111} (Å)	Crystallite size (Å)	$Ce_xZr_yO_2$, d_{111} peak intensity (c.p.s.)	Zircon, d_{200} peak intensity (c.p.s.)	Petedunite, $d_{22\bar{1}}$ peak intensity (c.p.s.)
20	950	3.074	467	1048	0	98
21	975	3.075	550	1066	0	127
22	1000	3.085	627	1027	33	141
23	1025	3.083	670	1012	69	121
24	1050	3.086	789	1025	103	39
25	1075	3.087	894	1002	153	0
26	1100	3.088	1045	958	159	0
27	1125	3.091	1253	926	165	0

Table 4. *Influence of firing cycle T_{max}.*

Raising firing T_{max} increased zircon crystal content as a result of a higher ZrO_2 crystallisation and reaction rate with silica to form zircon [5,10] in this temperature range. It has been observed elsewhere [8] that zircon crystal content starts decreasing beyond 1150°C, because crystallisation equilibrium is achieved under less favourable conditions as crystallisation temperature rises above 1150°C [8].

Figures 5, 6 y 7 present the SEM micrographs of the glazes obtained in experiments no. 22 (T_{max}: 1000°C), 25 (T_{max}: 1075°C) and 27 (T_{max}: 1125°C). It can be qualitatively observed that mean crystal size rises on raising temperature in the studied range, in accordance with the values calculated by XRD from the corresponding $Ce_xZr_yO_2$ peak (Table 4).

With a view to confirming the effect of specimen residence time at peak firing temperature in the proposed thermal cycle on the crystal growth step, a peak temperature of 1075°C was chosen, and several tests were performed modifying the dwell at this temperature (t_{max}). Table 5 presents the results.

Exp. no.	Tmax °C	t_{max} (min)	Crystallite size (Å)	$Ce_xZr_yO_2$, d_{111} intensity peak (c.p.s.)	Zircon, d_{200} intensity peak (c.p.s.)
28	1075	5	1100	617	60
29	1075	10	1252	666	141
30	1075	20	1288	676	234
31	1075	60	1326	704	309

Table 5. *Influence of residence time at heat-treatment cycle T_{max}.*

It can be observed (figures 5, 6 and 7) that as residence time increases at peak temperature, the glaze zircon and cerianite content grows, with a rise in estimated mean cerianite crystal size. These results agree with the foregoing findings. Thus, raising crystal growth time should increase glaze crystalline phase content, provided values close to equilibrium values are not reached, under the operating conditions.

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[5]. ESCARDINO, A.; MORENO, A.; AMORÓS, J.L.; GOZALBO, A.; Aparici, J.; Sánchez, L.F. *Study of crystalline-phase formation in white zirconium glazes.* Cerám. Acta, 8 (6), 21-34, 1996.

[10]. ESCARDINO, A.; MORENO, A.; AMORÓS, J.L.; ORTS, M.J.; BARBA, A. *Zirconium glazes used in fast single-fired wall tile manufacture: Part 2. Empirical model for fitting experimental data from the devitrification process.* (Accepted for publication in Br. Ceram. Trans.).

[8]. AMORÓS, J.L.; ESCARDINO, A.; ORTS, M.J.; MORENO, A. *Zirconium glazes used in fast single fired wall tile manufacture: Part 1. Crystallisation mechanism.* Br. Ceram. Trans., 93 (6), 224-228, 1994.

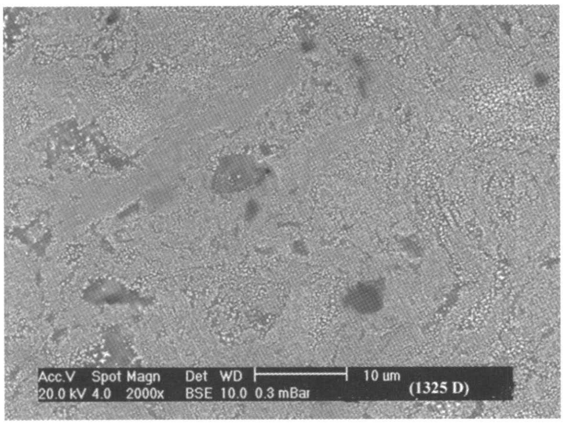

Figure 5. Surface appearance of the glaze obtained in experiment no. 22.

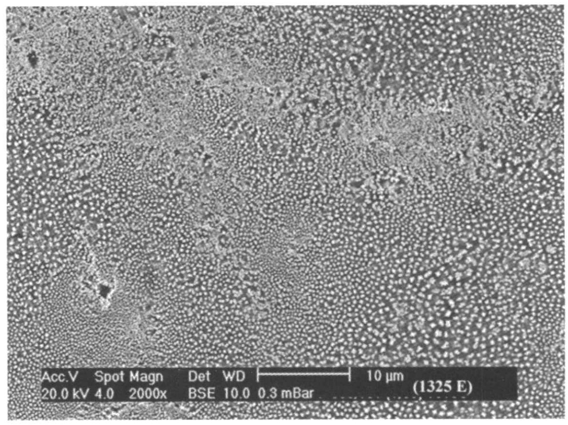

Figure 6. Surface appearance of the glaze obtained in experiment no 25.

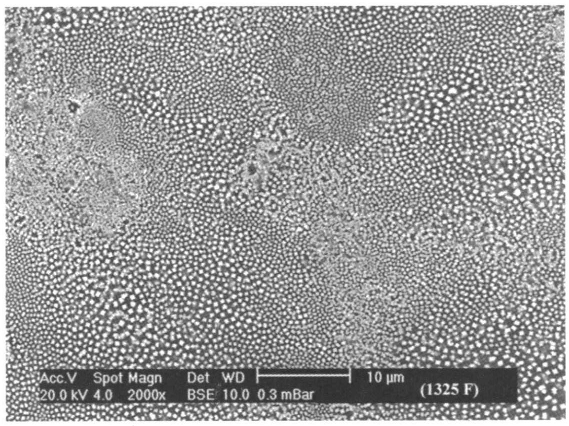

Figure 7. Surface appearance of the glaze obtained in experiment no. 27.

4.4.- VARIATION OF GLAZE GLOSS AND COLOUR WITH OPERATING CONDITIONS

The size and shape of the cylindrical specimens made with the milled frit, which were used to identify the crystalline phases and to study the nucleation and crystal growth steps, did not allow using them to adequately measure end glaze gloss and chromatic coordinates.

It was therefore decided to apply a suspension of frit particles (with the same particle-size distribution as the one used to form the above specimens) as a layer onto a fired ceramic body, and proceed to heat treat the whole piece, thus obtaining glazed specimens whose surface would enable measuring gloss and chromatic coordinates.

4.4.1 Influence of heating rate

Table 6 presents the values found for gloss (β), and the chromatic coordinates: L* (white-black) and b* (yellow-blue) of the glazes obtained on subjecting the pieces glazed with the consolidated layer of frit to the same heat treatments as those of the specimens listed in Table 3 (experiments 5 to 19).

The data in Table 6 show that for each pair of values of T_{max} and t_{max}, gloss decreased or remained steady on raising the heating rate. The same occurred with coordinate b*. The greater blueness corresponded to experiments 36 to 38. On shortening the crystal growth period (T_{max}) from 20 to 6 min, glaze gloss rose. Gloss remained practically steady on shortening t_{max} to 4 min at T_{max} 1100°C. These findings are very interesting, as tile dwell at T_{max} is of the same order in industrial firing cycles.

The fact that the glazes obtained at T_{max} = 1000°C and T_{max} = 1100°C, at t_{max} = 6 min presented slightly higher gloss values than those found at T_{max} = 1075°C, could be because these last glazes exhibited pinholing, which lowers the gloss value measured with the usual equipment.

Experiment no.	Heating rate (°C/min)	T_{max} (°C)	t_{max} (min)	β (‰)	L*	b*
32	1	1000	20	104.5	92.2	-1.07
33	10	1000	20	100.4	88.0	-2.09
34	25	1000	20	94.7	85.1	-1.43
35	50	1000	20	94.1	82.3	-0.84
36	10	1000	6	110.4	84.4	-4.41
37	25	1000	6	106.8	80.5	-3.75
38	50	1000	6	107.1	75.0	-2.92
39	10	1075	6	103.5(*)	88.7	-2.04
40	25	1075	6	103.5(*)	86.6	-2.03
41	50	1075	6	97.3(*)	85.0	-2.00
42	10	1100	6	107.8(*)	88.9	-1.78
43	25	1100	6	102.7(*)	87.2	-1.80
44	50	1100	6	103.2(*)	86.1	-1.60
45	50	1100	4	102.8(*)	85.5	-1.83

(*) PINHOLING

Table 6. *Effect of heating rate on end glaze surface characteristics.*

Coordinate L* values dropped very slightly on raising the heating rate of the pieces, and in each series of experiments at the same T_{max}, the greatest lightness (largest value of L*) corresponded to the glazes containing the greatest quantity of crystallised zircon (Tables 3 and 6).

The data obtained in the range of tested operating conditions indicate that using a heating rate of 25°C/min from 500°C on (below this temperature the process hardly develops) up to a peak temperature of 1100°C, with a 6-min hold at this temperature followed by cooling, yields a glaze with a sufficiently high gloss (β≅103), value for L*≅87 which involves high lightness, and value for b* between -2.03 and -1.80, which corresponds to a slightly bluish hue that favourably affects the whiteness index (W≅90).

4.4.2 Influence of peak firing temperature

Table 7 details the values for gloss (β) and the chromatic coordinates L* and b* of the glazes obtained on heat treating the bodies covered with a consolidated layer of frit according to the heat-treatment cycle in Figure 5, modifying cycle T_{max}, while trying to exactly reproduce the specimen treatment conditions of experiments 20 to 27 (Table 4).

Experiment no.	T_{max} (°C)	β (‰)	L*	b*
46	950	82.2	72.5	-3.56
47	975	92.9	78.2	-3.51
48	1000	95.1	84.2	-3.59
49	1025	96.1	87.0	-2.61
50	1050	98.9	88.2	-2.04
51	1075	99.1(*)	88.7	-2.01
52	1100	105.7(*)	89.4	-1.52
53	1125	108.2(*)	89.4	-1.10

(*) PINHOLING

Table 7. *Influence of firing cycle T_{max} on end glaze surface characteristics.*

The values of the three studied properties listed in the table indicate that raising peak temperature of the chosen firing cycle increased the values for gloss (b) and chromatic coordinate L*, and made the value of coordinate b* less negative (less blueness), while still keeping below zero. Specifically, for T_{max} 1100-1125°C, values were found for b between 105.7 and 108.2 (very high), L* = 89.4 (very white) and the value for b* ranged from–1.52 to –1.1 which means still keeping in the blue zone, though very close to the yellow zone (b* > 0). At these two peak temperatures, the corresponding whiteness index is W =91.1 (at 1100°C) and W = 90.0 (at 1125°C), frankly good values.

These conclusions match those drawn at the end of point 4.4.1, except that in this case, a T_{max} between 1100 and 1125°C is proposed, owing to the greater T_{max} range studied, having obtained better results, and an almost identical preheating stage is suggested, except for the intermediate period at 7.5°C/min.

On the other hand, peak temperature in the standard heat-treatment cycles used in industry to fire wall tile lies between 1080 and 1140°C, a range in which optimum properties were found in the resulting glazes. Moreover, the heating rate in these industrial firing cycles does not differ substantially from the one tested in this study (cycle in Figure 4).

4.5 TESTS OF THE SCREEN PRINTING APPLICATION OF A FINE SHEET OF FRIT ON A CONSOLIDATED LAYER OF UNFIRED GLAZE

4.5.1 Crystal growth step

After studying the behaviour of the frit by itself with regard to heat treatment, agglomerating the particles in cylindrical specimens in one case, and applying a consolidated layer of frit particles onto a fired ceramic body in the other, the study was completed by conducting a series of experiments in which the frit under study was screen printed as a fine sheet onto an unfired layer of glaze, firing the multi-layer piece immediately afterwards. Gloss and chromatic coordinates L* and b* were then determined on the end glaze.

The same firing cycle was used as in the tests set out in point 4.3, depicted in Figure 4.

Two sets of tests were performed: i) The pieces were held for 6-min at peak temperature, modifying T_{max} in different tests; ii) T_{max} was held at 1075°C, modifying the residence time at peak temperature in different tests.

4.5.1.1 Effect of peak firing cycle temperature

The data are presented in Table 8.

Exp. no.	T_{max} (ºC)	t_{max} (min)	β (‰)	L*	b*
54	1050	6	170	85.0	4.1
55	1075	6	190	83.6	1.2
56	1100	6	182	83.0	-0.7
57	1125	6	126	84.2	1.4
58	1150	6	104	84.4	4.0

Table 8. *Influence of firing cycle T_{max} on end glaze surface characteristics.*

Comparison of these data with those of Table 6 shows that the values for gloss (b) were in some cases about 90% higher (at T_{max} 1075 and 1100°C) than when the frit was applied by itself. It is very important to note that at temperatures of around 1125°C, gloss decreased without any pinholing being observed in the glaze surface. This phenomenon occurs because above 1100°C, crystal size, which rises with T_{max} (see Table 4), can exceed the optimum value and lower gloss. This phenomenon had already been observed on studying thin layer crystallisation of $CaWO_4$ [11]. Therefore, the optimum temperature for producing the lustre effect in industrial firing cycles with the studied frit ranges from 1075°C to 1125°C.

With regard to the chromatic coordinates, L* remains practically steady on raising peak heat-treatment temperature, and b* varies little in the range T_{max} 1075-1125°C, going through a minimum value (-0.7) in the blue region at T_{max} = 1100°C. Variations in temperature of 25°C above and below 1100°C make the colour tend to become slightly more yellowish, according to the data presented in Table 8.

4.5.1.2 Effect of specimen residence time at firing cycle T_{max}

Table 9 gives the values for β, L* and b* found on firing the specimens at different holding times at peak firing temperature.

Exp. no.	T_{max} (ºC)	t_{max} (min)	β (‰)	L*	b*
59	1075	5	181	83.8	4.1
60	1075	10	178	84.0	1.3
61	1075	20	149	85.6	1.8
62	1075	60	111	86.4	3.0

Table 9. *Influence of residence time at T_{max} on end glaze surface characteristics.*

In this case as well, higher gloss values were found compared to when the frit was applied by itself as a thick layer on the body. It should be noted that at values of t_{max}>10 min, glaze gloss decreased considerably.

This conclusion is not too serious, in the sense that in standard firing cycles in industrial kilns for wall tile manufacture, the dwell at T_{max} is usually about 5-8 min. Chromatic coordinate L* rose very little on raising t_{max} and b* little at minimum value (less yellowness) for t_{max} = 10 min.

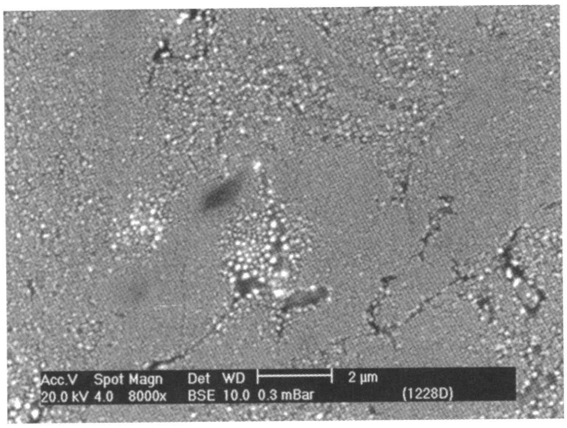

Figure 8. *Surface appearance of the glaze obtained in experiment no. 59.*

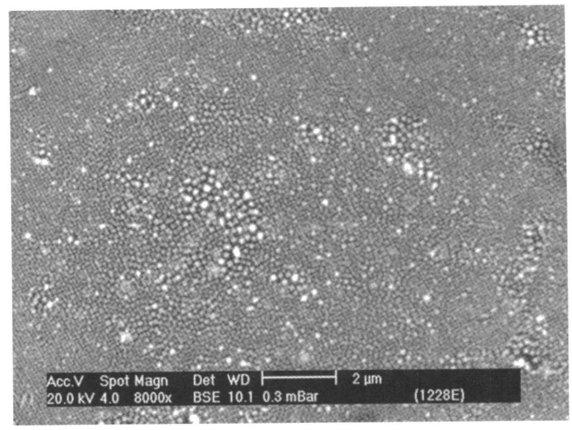

Figure 9. *Surface appearance of the glaze obtained in experiment no. 61.*

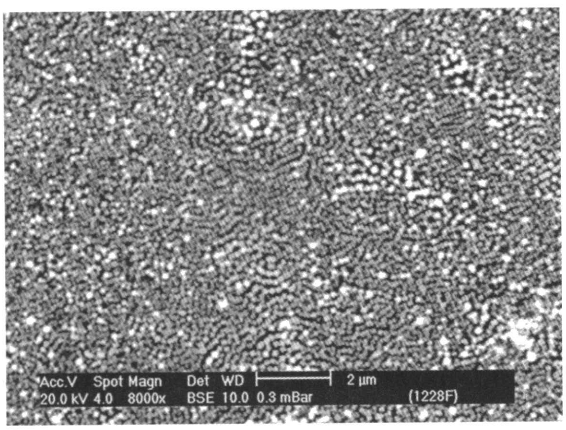

Figure 10. *Surface appearance of the glaze obtained in experiment no. 62.*

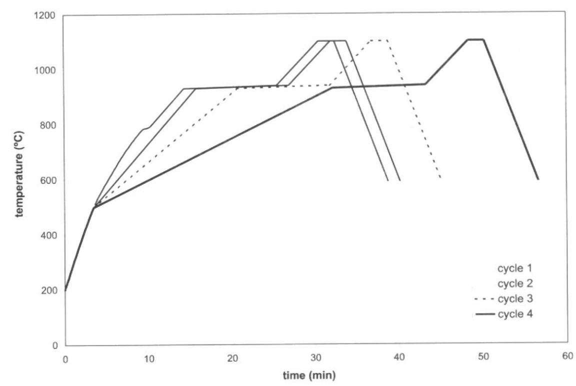

Figure 11. *Tested heat-treatment cycles to study the effect of heating rate up to the carbonate decomposition segment, on end glaze gloss.*

Figures 8, 9 and 10 present the micrographs of experiments no. 59, 61 and 62. It can be qualitatively observed that when the frit applied to a layer of unfired glaze was involved, mean $Ce_xZr_yO_2$ and zircon crystal size in the end glaze also rose with residence time at T_{max}. There was thus a parallelism with regard to the behaviour of the studied frit during firing with its behaviour on being applied by itself, in a layer about 0.8 mm thick on a fired body (see Table 5).

The reduction in gloss after a 10-min dwell at peak temperature could be due, as suggested above, to there being an optimum crystal size, beyond which gloss starts decreasing.

After firing, the fine layer of studied frit contained $Ce_xZr_yO_2$ and zircon crystals with quite a higher refractive index than the underlying transparent glaze. Therefore, at a certain crystal size, the constructive interference of light mentioned in the introduction could be reinforced, while enhancing gloss in respect of the glaze obtained on applying the frit by itself.

4.5.1.3 Effect of heating rate

Four heating rates were tested in the firing cycle stretch between 500°C and 930°C, keeping this variable constant between 930°C and T_{max}, as well as holding the duration of this last period (Figure 11), with a view to studying the influence of the heating rate, in the temperature range in which homogeneous nucleation arises, on the characteristics of the end glaze.

Table 10 presents the resulting data.

Exp. no.	Heating rate segment 500-930°C (°C/min)	Heating rate segment 930°C-Tmax (°C/min)	T_{max} (°C)	t_{max} (min)	β (‰)	L*	b*
63	15	31.6	1100	2	118	86.5	3.8
64	25	31.6	1100	2	126	86.1	3.2
65	35	31.6	1100	2	147	86.0	3.6
66	40	31.6	1100	2	154	85.6	2.9

Table 10. *Glazes obtained with the heat-treatment cycles of Figure 11.*

The data show that gloss rose when the heating rate increased in the indicated temperature range, peaking at 40°C/min. This result is analogous, though the differences are greater, to the findings in experiments no. 43 and 44 (Table 6), on firing a layer of the studied frit by itself, at heating rates of 25 and 50°C/min, where β rose from 102.7 to 103.2, but with pinholing reducing the measured gloss value.

On the other hand, L* remained virtually steady and b* hardly varied. Between 25 and 40°C/min, the heating rate barely affected the chromatic coordinates of the resulting glaze. In this case as well, the result coincides with that of experiments no. 43 and 44 (Table 6), even when the values of b* differ a little, probably as a result of the influence of the presence of the base glaze.

4.5.1.4 Pilot roller kiln

Two firings were run using the heat-treatment schedules shown in Figure 12. In this case, as the base glaze and the fine layer of studied frit were applied onto a fired body, the stretch of almost constant temperature between 900-930°C, whose purpose is to produce carbonate breakdown, was suppressed. The data are presented in Table 11.

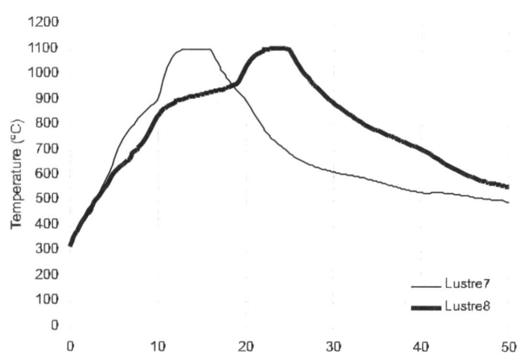

Figure 12. *Firing cycle used in the pilot kiln.*

Exp. no.	Heating rate (°C/min)	T_{max} (°C)	β (‰)	L*	b*
67	60	1100	213	81.7	2.8
68	50	1100	202	83.1	4.4

Table 11. *Glazes obtained with the firing cycles of figure 12.*

The outcome agrees with the findings set out in the foregoing section, where the maximum gloss value was found in the specimen fired at peak firing rate, although in this case, the gloss values were considerably higher, possibly owing to a slightly longer dwell at peak temperature ($t_{max} \cong 5$ min.) than in experiment no. 66 (heating rate 40°C/min), where this was 2 min. Slightly higher heating rates were also used.

Coordinate L* was a little lower (less lightness), while coordinate b* was of the same order as in experiments no. 65 and 66.

4.5.1.5 Tests in industrial kilns

Two pairs of specimens were fired in four different industrial kilns, in which the glazes obtained by screen-printing the studied frit as described in point 4.5 had sometimes been observed to exhibit a yellowish and bluish colour respectively. These pieces were prepared in such a way that half the specimen was only covered by the transparent base glaze, whereas the other half was covered by a screen-printing application of the studied frit. The characteristics of both halves of the fired piece could thus be compared.

Table 12 presents the results.

Figures 13 and 14 show the relative size of the devitrifying crystals in the glaze surfaces obtained in experiments 69 and 72. It can be observed in these figures, that the crystals in the glaze obtained in experiment no. 69 were larger than those of the glaze produced in experiment no. 72. The colour of the glaze surface obtained in experiment no. 69 is visually observed to be more bluish than the glaze surface in experiment no. 72, which is even slightly yellowish. This result appears to contradict the findings on studying the behaviour of the tested frit when it was applied by itself. Thus, raising the crystallite size was found to make the glaze surface exhibit less blueness (see Tables 4 and 7 and Figures 6, 7 and 8).

Exp. no.	Kiln no.	Half glazed with the base glaze			Half glazed with lustre effect		
		β (‰)	L*	b*	β (‰)	L*	b*
69	1	123	86.8	3.8	195	88.0	2.8
70	2	121	88.4	4.5	235	89.1	3.2
71	3	123	88.3	4.6	223	89.0	3.4
72	4	120	93.0	6.2	240	92.7	5.0

Table 12. *Glazes produced in industrial kilns.*

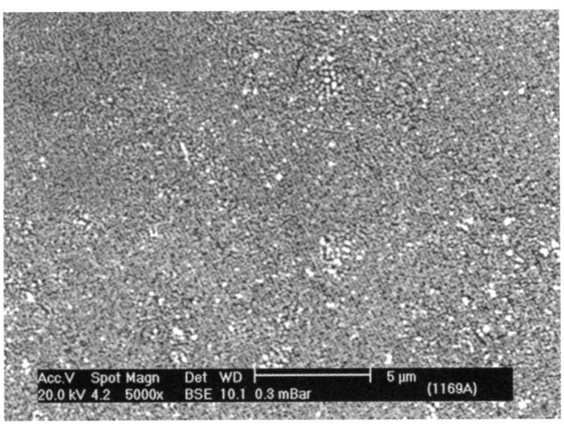

Figure 13. *Surface appearance of the glaze obtained in experiment no. 69.*

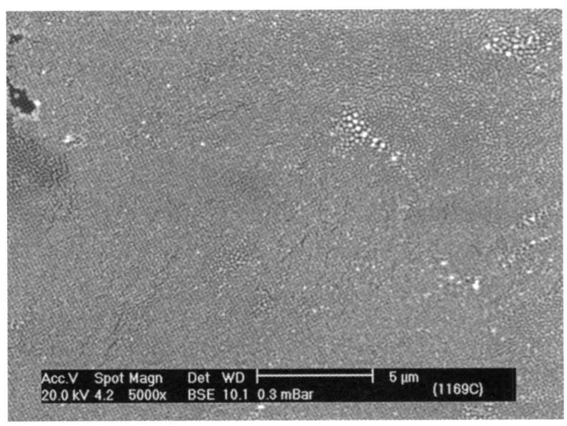

Figure 14. *Surface appearance of the glaze obtained in experiment no. 72.*

However, a comparison of the chromatic coordinates of the two specimen halves, one with just the base glaze, and the other with an application of the studied frit on this glaze (using the same base glaze in the four experiments), explains the apparent contradiction. The fine sheet of studied frit has a certain transparency, and the chromatic coordinates of the glaze produced on firing the base glaze have a decisive effect on the chromatic coordinates of the glaze that arises on applying the frit coat over the base glaze. These findings highlight the enormous influence of base glaze behaviour in firing on the characteristics of the end glaze, with the ensuing lustre effect.

It is clear that the heat-treatment cycles and firing conditions used were different in the four industrial kilns used to run the trials (kilns 2 and 3 appeared to operate under quite similar conditions), as the glaze surfaces produced with just the base glaze exhibited appreciable variations of L* and b* amongst the kilns.

5. CONCLUSIONS

The study of the process yielding the so-called lustre effect in ceramic glazes has allowed drawing the following conclusions:

i) The devitrifying crystalline phases in the studied frit, during heat treatment, were: petedunite, zircon and a cubic structure (of the CaF_2 type), which was identified as a ZrO_2 solid solution in CeO_2.

ii) The firing conditions yielding the best results as far as surface gloss and chromatic coordinates were concerned, when the glaze was produced only with the studied frit, were:

Heating rate from 500 to 900°C: 25-50°C/min (higher heating rates were not tested).

Peak firing temperature: about 1100°C.

Residence time at T_{max}: 5-6 min.

Under these operating conditions, the following values were found for gloss and the chromatic coordinates: β= 106 (with a slightly pinholed surface), L* = 89.4 and b* = -1.52 which involves a whiteness index of W=91.1.

iii) When the studied frit was applied as a fine sheet (by screen printing) onto an unfired glaze layer, the heat-treatment cycle yielding the most interesting gloss and chromatic coordinate values was:

Heating rate from 500 to 900°C: 45-60°C/min.

Peak firing temperature: about 1100°C.

Residence time at T_{max}: 5-8 min.

Under these conditions, the following values were found for gloss and the chromatic coordinates: β = 182 (surface without pinholing), L* = 83 and b* = -0.7

iv) The bluish or yellowish colour of the glaze surface depended on devitrifying crystal size when a layer of frit was applied by itself. When a fine sheet of the studied frit was applied to a layer of base glaze, the colour of the fired glaze was mainly determined by the colouring acquired by the base, which was closely related to the thermal cycle and firing conditions.

REFERENCES

[11]. RODRIGO, J.L.; SANMIGUEL, E.; GOZALBO, A.; ORTS, M.J.; AMORÓS, J.L.; BELDA, A. *Studio su alcune variabili che influenzano la brillantezza degli smalti ottenuti da miscele di fritte e di ossido di tungsteno.* Ceram.Informazione, 335, 613-620, 1995.