OBTAINMENT OF GLAZES WITH A METALLIC APPEARANCE IN SINGLE-FIRED TILES

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ABSTRACT

A product range has been developed for providing ceramic tiles with a metallised decoration, containing no noble metals in its composition, adapted to the usual single-fire tile manufacturing techniques.

The present study analyses the state of the technique, indicates the benefits contributed and characterises in depth the crystalline phases responsible for the metallised effect, as well as for their evolution with the different parameters of the firing cycles.

1. INTRODUCTION

In the present study, a line of products has been developed for the decoration of ceramic materials, which combine the aesthetics of metals in regard to their gloss, metallic reflection and colorations, with all the advantages of ceramic products in relation to their ease of installation, replacement, transport, thermal and acoustic insulating capacity, etc., as well as the advantages in respect to the technical characteristics of the pieces – far superior to those of metal sheets or plates – and considerable aesthetic advantages, with countless decorating possibilities for ceramic tiles.

This product range, whose study and development began in 2000 and is still being extended and improved, displays many innovations for the decoration of single-fire ceramic tiles, compared with the decorations made by adding noble metals, using formulations containing lead, reduction techniques or specific firings at lower temperature (third fire), etc.

On the other hand, the disadvantages regarding the corrosion of metal sheets, worn by weathering, will not occur in ceramic pieces, since these, as they display practically zero porosity, are completely inert to weathering agents (air, water, ice, vapours, etc.) and, therefore, will not change in time.

The developed product range, devoid of noble metals in their formulation, has a chemical composition whose major oxides are: SiO_2, Al_2O_3, Fe_2O_3 and P_2O_5. The formulations have been modified to obtain the desired colouring and look, and have been adapted to the aesthetic needs of the pieces.

Using and firing the relevant raw materials mixtures causes an iron phosphate crystalline phase with a modified structure and a highly pronounced preferential orientation to develop at the surface of the piece, which provides the tiles with the effects mentioned. Given the little information available in the literature on this crystalline phase, extensive study has been required of its formation, microstructure, etc.

On the other hand, a profound study of the firing cycles has been necessary, paying special attention to the cooling stage in which the iron phosphate crystallises, and adapting the formulations to the typical firing cycles used in the ceramic sector.

In addition, a series of products have been developed (engobes, glazes, grits, screen printing inks) to complement this range of metallic glazes, performing studies of different compositions in order to obtain the most appropriate compositions for providing the final pieces with the desired textures, gloss, appearance and colouring.

Furthermore, studies have been conducted on different metallic glaze application techniques (bell, airless, disks), as well as on different screen printing techniques (flat screens, decorations with rotating machines in different roller pressure conditions, types of laser incisions, and studies on the density and viscosity of own ink formulations, etc. The foregoing, supported by studies of the most innovative designs and appropriate sizes, has enabled obtaining a broad range of models.

2. BACKGROUND

The fabrication of ceramics with a metallic appearance, featuring golden, chrome and silver highlights has a long, unbroken tradition, in which these special effects have been used in the aesthetic development of borders, listels, trims and small-sized tiles.

These types of effects were mainly made in two ways:

- By applying a solution of noble metals (gold, silver, platinum) to the finished tile and then refiring this at low temperature (third-fire technique), with the high ensuing cost involved in terms of raw materials and production processes.
- Using ceramic kilns with a reducing atmosphere (traditional method) with a high degree of instability in the resulting effects, as well as the generation of undesirable gases from the reduction.

The compositions typically used to obtain a metallic appearance consist of noble metals in the form of glossy preparations, preparations for burnishing, such as lacquers or pastes, or powdered substances. Most of these preparations contain sulphur and organic substances (oil-sulphide-resinous solutions), which may often contain mercury; on the other hand, all the silver compounds are also toxic. This involves a great environmental impact, in the handling of the products and in the wastes originating in the production process. Nor should one forget the poor technical characteristics and instability in appearance and colouring of ceramic tiles with metallised effects obtained with these types of products.

3. OBJECTIVE OF THE STUDY

The main objective of the studies carried out has been the development of a line of products for the decoration of ceramic materials, with similar effects to those produced by metals as far as gloss, metallic highlights and colourings are concerned, with a view to being able to compete with these types of materials, and to broaden the offer in ceramic tiles.

This objective has been addressed on the basis of four premises:

- Not to use noble metals in the formulation of the products to be developed.
- To obtain products that are suited to present single-fire manufacturing technologies for ceramic floor and wall tiles, avoiding the use of additional firing techniques, and adapting these products to the customary glazing and decoration techniques used in the sector.
- To provide the resulting products with the appropriate technical characteristics.
- To reduce the costs in raw materials and in the fabrication process, thus enhancing the competitiveness of these products.

4. MATERIALS AND CHARACTERISATION

4.1. MATERIALS

This product range has been developed without using any noble metals in their formulation. The compositional range of the mixture of oxides that make up the product chemically, expressed in percentages, is detailed in the following table:

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	P_2O_5 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	Li_2O (%)	ZrO_2 (%)	ZnO (%)
24-51	7-21	10-30	7-27	0-7	0-6	0-8	0-8	0-6	0-10	0-10

Applying the appropriate treatments to the raw materials mixtures, an entire range of products has been obtained: frits, glazes (liquid, spray-dried, granulates), screen printing and granular materials.

The resulting products, depending on the design to be made, have been applied by the techniques typically used in the ceramic tile manufacturing sector:

- Wet applications: for glazing by bell, disk or airbrushing.
- Dry applications: as grits, spray-dried material or granulates.
- Screen printing applications: by flat screens and rotating machines.

These products have been adapted to the firing temperatures of the clients, from fast double-firing temperatures and cycles to porcelain temperatures and cycles, using the appropriate bodies for each firing cycle.

4.2. CHARACTERISATION

The following equipment has been used for the characterisation of the different tested compositions:

- Philips Magi-X, X-ray fluorescence spectrophotometer for chemical characterisation of the samples, raw materials and impurities present.
- X-ray diffraction for identification of the crystalline structures.
- Scanning electron microscope (SEM), connected to an energy-dispersive X-ray microanalysis (EDX) instrument, for sample observation and microanalysis.

In addition, the different tiles made were subjected to the usual studies that are performed on finished products, following the methods established by the relevant standards.

To evaluate the resistance to corrosion the following tests were conducted:

- Test in salt chamber, at 35ºC and NaCl saturation, with pH between 6.5 and 7.2
- Test in humidostatic chamber at 30ºC with saturation of 100 % humidity and dwell time of 1008 hours.
- Accelerated corrosion test in acetic salt mist. UNE-112-017, ISO 9227.

Corrosion was quantified according to the ISO-4540 standard, analysing the samples by optical microscopy (OM).

5. RESULTS

5.1. GLAZE CHARACTERISATION

With a view to determining which crystalline phases were responsible for the metallised effect, the following characterisations were performed:

5.1.1. Identification, by X-ray diffraction (XRD), of the crystalline components in the unfired glaze.

The crystalline components identified in the unfired glaze are shown in Figure A1:

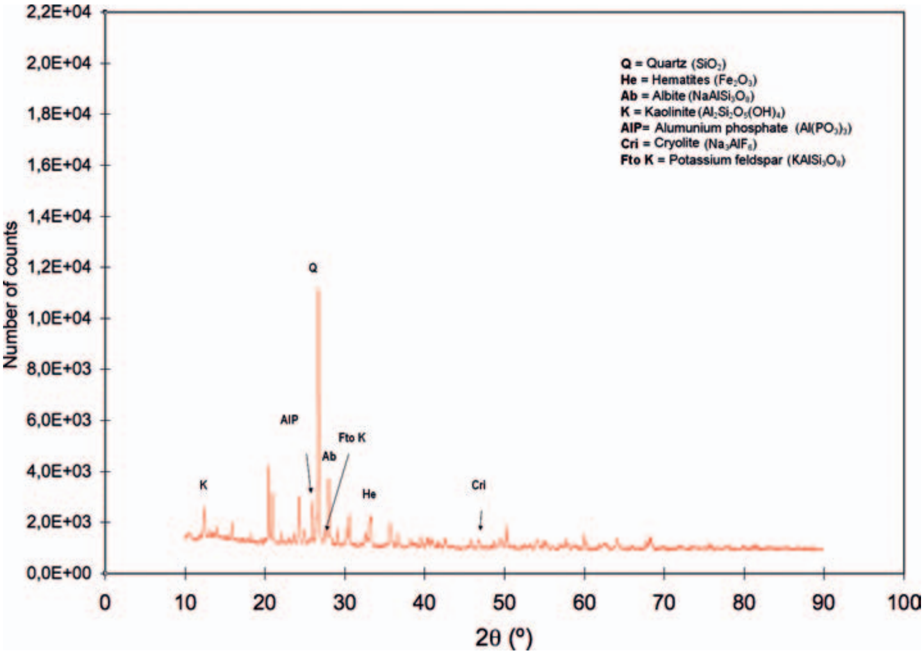


Figure A1. Unfired glaze.

5.1.2. Identification, by X-ray diffraction (XRD), of the crystalline components in the fired glaze.

The identification was made by two XRD analyses, one at the surface of the fired piece and another of the glaze layer, fired in the form of powder; it was this latter XRD analysis that enabled identifying the most intense peak as the iron phosphate peak.

The fact that the diffractogram corresponding to the surface of the fired piece displayed much greater peak intensity is because very superficial and simultaneously highly oriented crystallisation is involved.

It should be noted that although the most intense peak in the diffractogram corresponds to the iron phosphate crystalline phase with structure ($Fe_2Fe(P_2O_7)_2$), two other peaks appear, related to this peak and following the same tendency, but whose identification has been impossible according to the crystallographic tables. This suggests that the structure of this phase is not exactly ($Fe_2Fe(P_2O_7)_2$), so that an iron phosphate with a modified structure and different iron oxidation states would likely be involved, a structure that has not been envisaged with such modifications in the crystallographic tables. This is also why there is little available information in the literature and few studies on this phase.

Figure A2 presents a comparison of the diffractograms obtained:

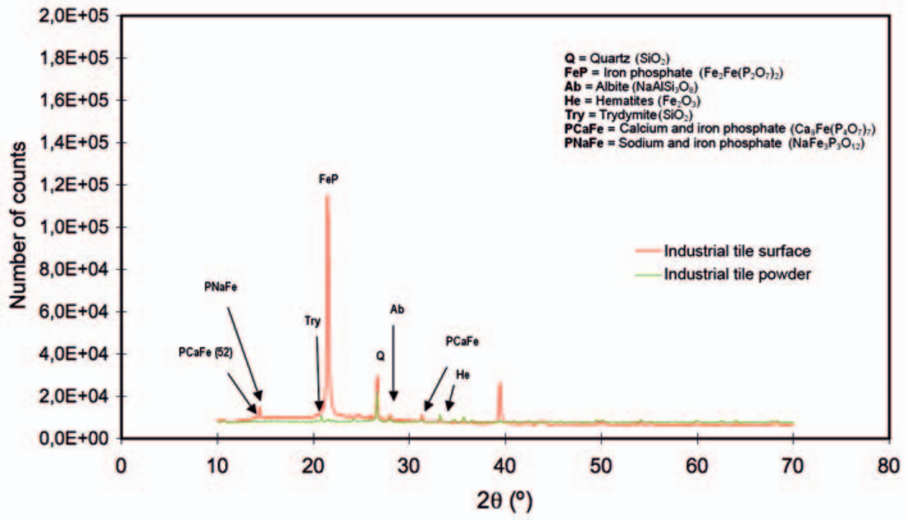


Figure A2. Industrial tile surface - Industrial tile powder.

5.1.3. Observation of the glaze surface by scanning electron microscope (SEM).

The observation was conducted on industrial tiles. Figures 1 and 2 show two photographs of different surface regions of a tile.

Figure 1 shows the existence of lighter-coloured regions (A and B), in which phosphorus, calcium and iron are mainly concentrated. The lighter the area, the greater the iron content; therefore, the B-type areas contain less iron than the A-type areas. The continuous glassy matrix, C, in which these drops are immersed is mainly made up of silica.

The shape of the lightest-coloured regions suggests a phase separation (type D), although if some of these shapes are closely observed (for example E), the existence of an ordering can be appreciated. Taking into account the XRD results and the EDX analysis of the light and dark areas, it may be concluded that the A-type areas could contain the crystalline species corresponding to the iron phosphate phase with a modified structure.

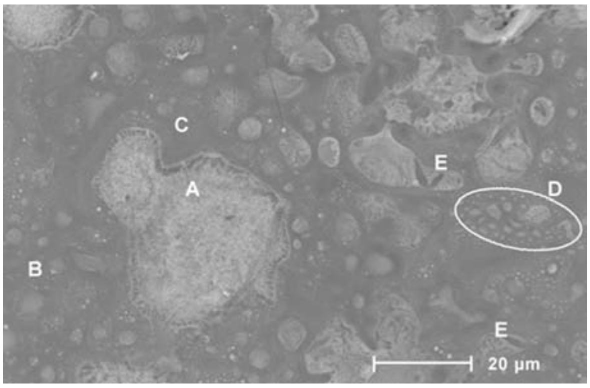


Figure 1. Surface of an industrial tile.

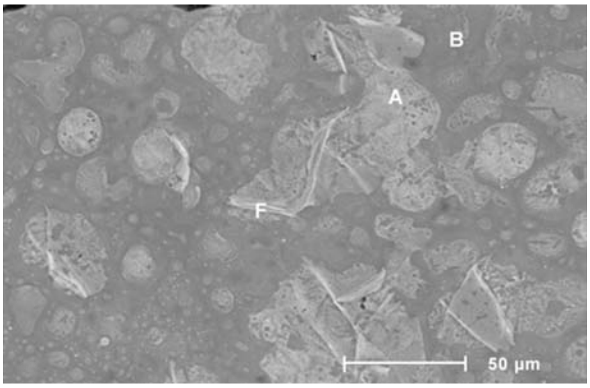


Figure 2. Surface of an industrial tile.

Figure 2 shows another surface image in which it can be observed that the lighter regions (A) contain acicular crystals (F) with an even lighter colour, whose analysis reveals they contain a greater amount of sodium than the rest of the light area, indicating that these crystals must correspond to the iron and sodium phosphate identified by XRD. These crystals appear in the areas with the greatest iron concentration and where it was concluded that the iron phosphate crystalline species with a modified structure was found.

In order to pursue further the study of the formation of this crystalline phase, a photograph was taken of a chip at the edge of the tile, which then underwent surface observation (Figure 3). The bottom right of the photograph corresponds to the tile surface, while the top left corresponds to the inner part of the glaze. It shows that the lighter areas (A) are at the surface of the glaze and they seem to be floating, as if they had migrated to the surface by a difference in density.

The glaze surface contains a greater amount of phosphorus, calcium and iron, while the inner part of the glaze is richer in silica. The white points (G), observed inside the glaze, correspond to hematites that have not managed to dissolve. These hematites do not lie in the areas near the surface, which indicates that they have dissolved in those areas to give rise to the phase rich in phosphorus, calcium and iron.

Figure 4 displays the bevelled cross-section of the glaze layer. It shows the existence of hematite (G) and quartz particles (H), in the bottom part of the glaze layer. Regions can also be observed where phosphorus, calcium and iron (A) are concentrated, this last element coming from hematite dissolution. These areas lie both inside the glaze and floating in the surface; on top of these latter areas (area in contact with the air) the crystalline phase has formed which causes the metallised effect, involving crystals of a very light colour, which are highly oriented.

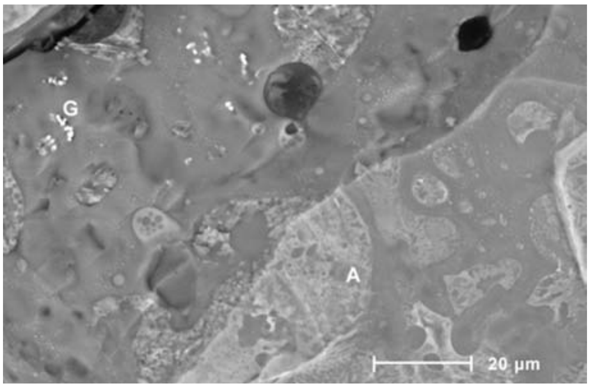


Figure 3. Observation of a chip produced at the edge of the industrial tile.

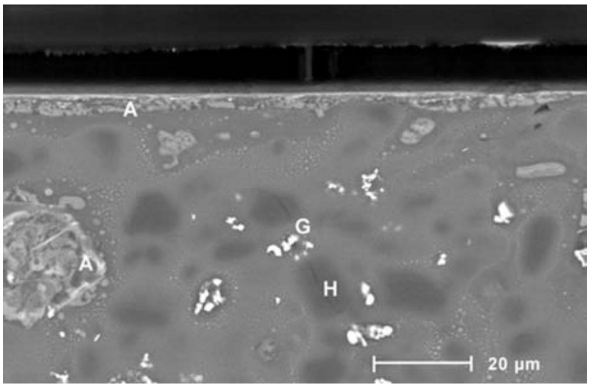


Figure 4. Observation of the (bevelled) cross-section of the glaze layer on the industrial tile.

5.1.4. Influence of the cooling stage of the firing cycle

To determine the influence of the cooling stage, glazed tiles were fired in a laboratory muffle kiln at a peak temperature 1190ºC, and 8 min. dwell time at this temperature, after which two types of cooling were applied: normal cooling in the kiln, and quenching in air (extraction of the piece after the dwell time at peak temperature had elapsed, and cooling at ambient temperature).

The pieces obtained by cooling inside the kiln displayed a metallic appearance; however, the pieces obtained by quenching exhibited a dark colour without a metallic appearance.

The pieces obtained were examined by SEM, and X-ray diffraction analysis of the surface (Figure A3), which showed that the species responsible for the metallic appearance was the iron phosphate phase with a modified structure, which displayed considerably greater intensity with the normal cooling.

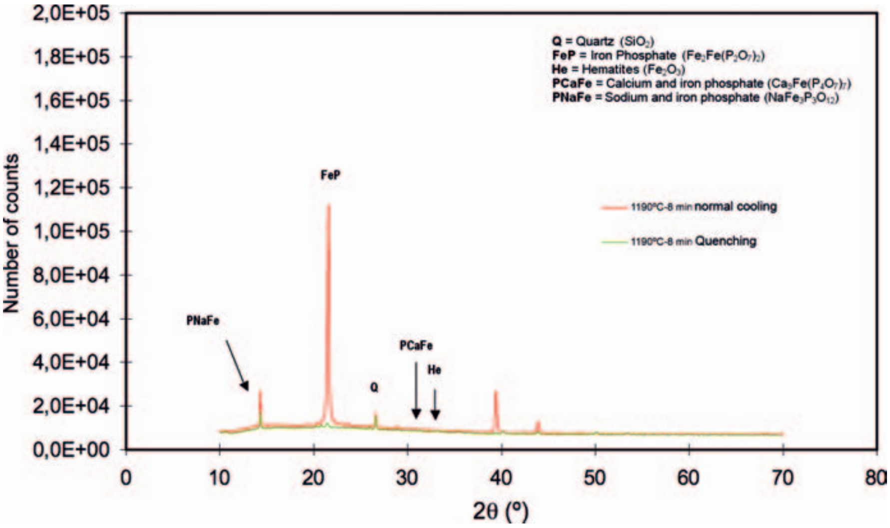
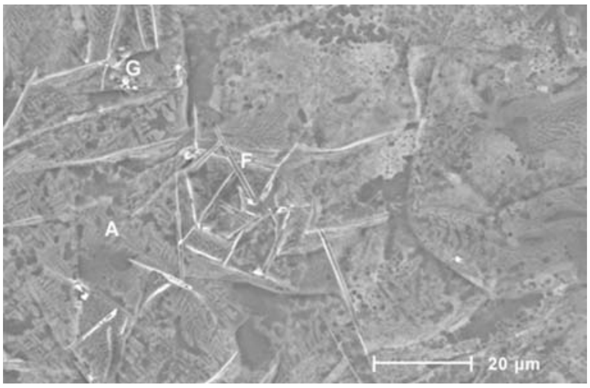
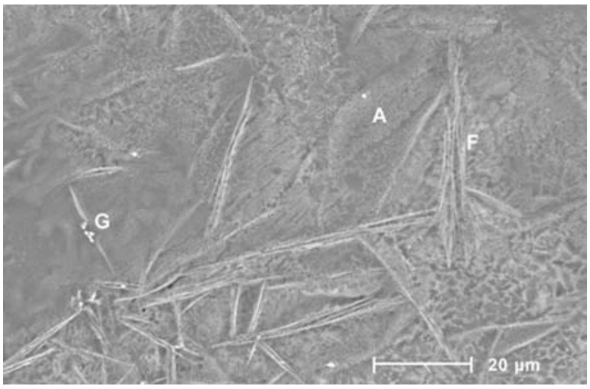


Figure A3. Comparison of cooling cycles at 1190ºC

The photographs taken show that the entire surface is practically covered with the observed lightest-coloured phase in the industrial piece (A). In the piece with normal cooling, this phase evidences a dendritic type of crystallisation, which corresponds to the iron phosphate phase with a modified structure (Figure 5) that is not observed in the surface of the piece obtained by quenching.



Normal cooling.
Figure 5. Tile surface 1190 ºC – 8′.



Quenching.
Figure 6. Tile surface 1190 ºC – 8′.

5.1.5. Effect of phosphorus on the development of the effect. Evolution of the phases with firing temperature.

Glazed pieces were fired in a laboratory muffle kiln at different firing temperatures, stopping the thermal cycle when the programmed temperature was reached, followed by normal cooling in the kiln. The test temperatures were: 1000, 1100, 1140, 1170, 1190 and 1220ºC.

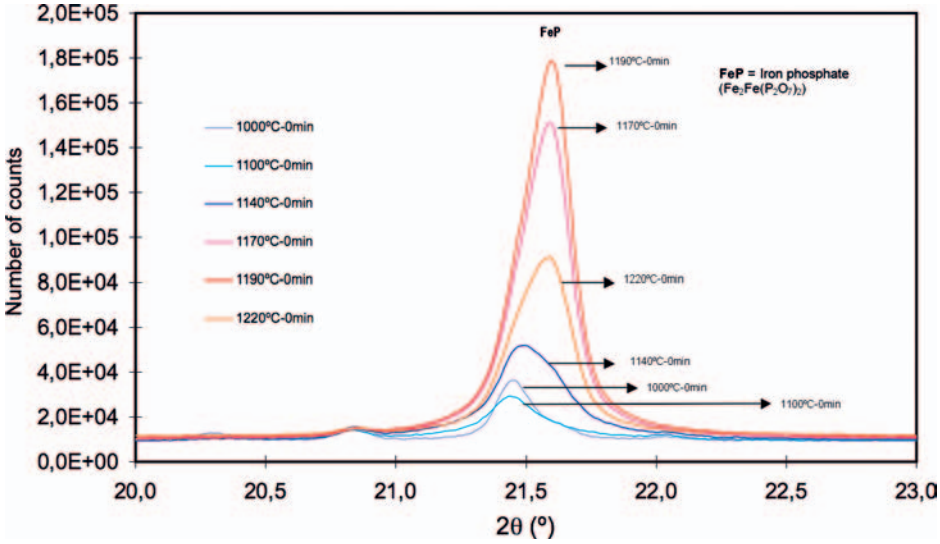


Figure A4. Comparison of series 1000 to 1220ºC. Normal cooling.

The pieces have been referenced with the firing temperature and 0′. The resulting XRD analyses of these samples are shown in Figure A4, displaying the evolution of the iron phosphate crystalline phase peak, which is related to the look of the piece (the higher the peak, the more metallic the look).

The SEM observations of the samples show that the piece obtained at 1000ºC, Figure 7, contains hematites (G) and acicular crystals (F), which correspond to sodium and iron phosphate. The acicular crystals appear to form from hematite particles, probably due to their dissolution. The clearest areas (I) correspond to calcium and iron phosphate.

At a temperature of 1100ºC (Figure 8), the hematites are observed to have dissolved in the surface to give rise to the phase rich in phosphorus, calcium and iron, covering the surface of the piece, in which phases already appear in the form of dendrites. Acicular crystals can also be observed of sodium and iron phosphate, which appear to come from the zones in which the hematites were found.

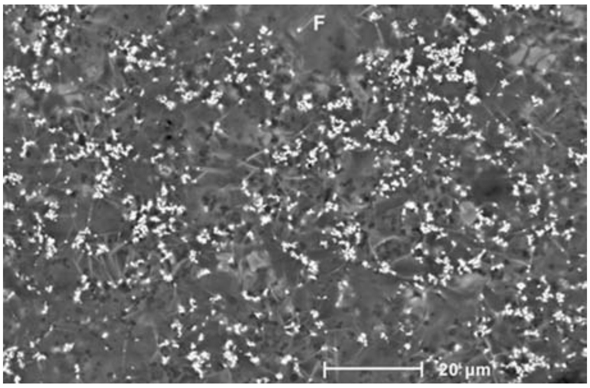


Figure 7. Surface of the piece at 1000ºC-0′. Normal cooling.

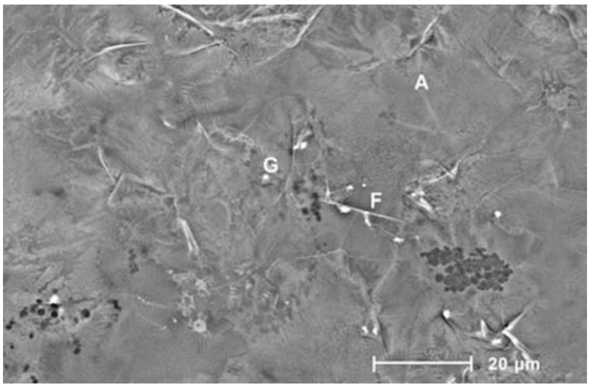


Figure 8. Surface of the piece at 1100ºC-0′.Normal cooling.

As the firing temperature increases (Figure 9) hematites dissolve, and the phase rich in phosphorus, calcium and iron groups together to cover practically the entire surface with the iron phosphate phase with a modified structure.

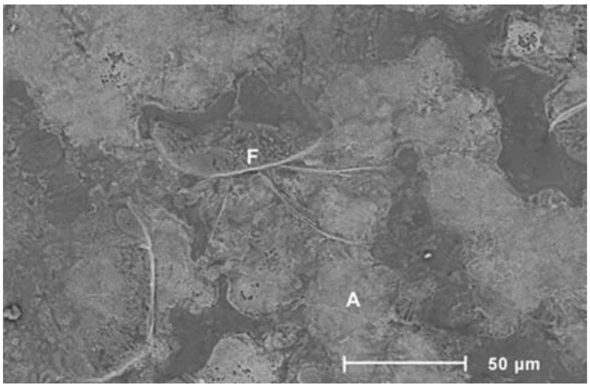


Figure 9. Surface of the piece 1190 ºC–0'. Normal cooling.

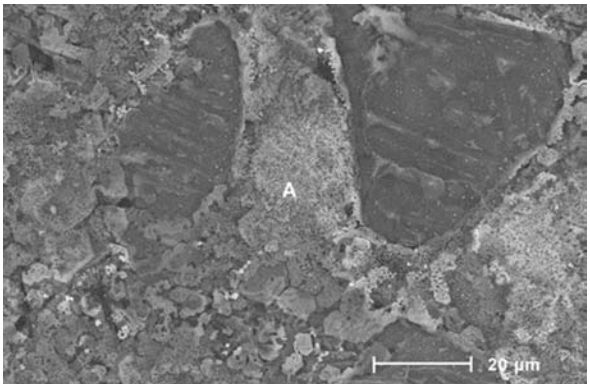


Figure 10. Surface of the piece 1220 ºC–0'. Normal cooling.

When the temperature is raised further (Figure 10) the phase coalesces, revealing the inside of the glaze layer. This causes dark-coloured areas to appear at the surface of the piece at very high temperatures, which break the continuity of the metallic effect.

On the other hand, in the overall EDX analysis of the samples obtained at different temperatures, the evolution of the quantity of Fe, Ca and P in the surface of the pieces was observed, which increased as the temperature rose.

5.2. STUDY OF THE TECHNICAL CHARACTERISTICS OF THE RESULTING PIECES

The following sets out the results with relation to the technical characteristics of the pieces obtained with these products, although these pieces depend to a large extent on the design involved:

Test in salt chamber at 35º C and NaCl saturation	After 1008 h exposure, no significant changes were observed in the surface.
Test in humidostatic chamber at 30ºC with 100 % humidity saturation	After 1008 h exposure, no significant changes were observed in the surface.
Accelerated corrosion test in acetic salt mist	After 1008 h exposure, no significant changes were observed in the surface.

Chemical resistance UNE-EN-ISO 10545-13	Minimum GLB/GHB
Stain resistance UNE-EN-ISO 10545-14	Class 5
Resistance to surface abrasion UNE-EN-ISO 10545-7	Minimum PEI III
Scratch hardness Mohs scale UNE-67101	Minimum Mohs 7

6. CONCLUSIONS

An entire line of products has been developed that produce a metallised appearance on single-fire ceramic tiles, reproducing the gloss, metallic reflection and colouring of metals.

In the formulations of these products (Formulations and Procedures for the obtainment of metallic effects on ceramic tiles and their applications. Patent of Spanish Invention No. 200000799, and International Patent PCT/ES 00/00498), noble metals have not been used, nor have additional firing techniques been used; the products developed have been adapted to the standard manufacturing lines of the single-fire ceramic tile manufacturing sector.

The crystalline phase responsible for the effect is iron phosphate with a modified structure, which forms at the surface of the piece, with a highly pronounced preferential orientation.

This phase develops during the cooling process of the firing cycle, and appears to come from a phase separation in which phosphorus, calcium and iron are concentrated. The phase separation is located in the surface of the piece, and the iron phosphate, responsible for the effect, forms during the cooling process. When the firing temperature is raised, maintaining the cooling cycle, the separated phase progressively coalesces, forming large drops of a phase with a high iron concentration, from which iron phosphate forms.

With respect to the previous state of the art for obtaining metallic appearances on tiles, a series of advantages has been achieved, such as the reduction in cost, elimination of environmental problems, and improvement of the technical characteristics, in addition to the noteworthy stability and reproducibility of the products.

The present work has contributed a new range of differentiating products to the ceramic sector, with which to continue competing with other building materials.

By way of example of an industrial application of these products, the **'Corten' project** may be mentioned, aimed at manufacturing ceramic tiles for both floorings and wall claddings, and in particular for exterior claddings in the form of self-ventilated types of facades, with the modern aesthetic of 'corten' steel, a product currently in rapid expansion, whose use is becoming widespread among architects seeking an 'industrialist', avant-garde aesthetic.

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