The Ceramic Industry in Spain: Challenges and Opportunities in Times of Crisis

J. Llop, T. Stoyanova Lyubenova, E. Barrachina,
M. D. Notari, I. Nebot, J. B. Carda

In the last few years, the Spanish ceramic industry has gone through a severe crisis, which has led to great market loss and reduction in profits. Nevertheless, the ceramic industries in Spain have always characterised themselves as an innovative sector, highly predisposed to changes. It is precisely in times of crisis that the industries most seek to break new ground in their quest for new innovations that will give them an edge over competitors.

This study provides an overview of the advances that have recently materialised in the ceramic tile industry. Various technological issues are thus highlighted, such as tile decoration by inkjet printing, laser technology, physical vapour deposition (PVD) technology, firing using laser technology (laser-firing project), etc. These techniques are being used to develop innovative products, thus obtaining tiles with bactericidal capability, conductive glazes, anti-electrostatic tiles, etc.

Introduction

More than 90 % of Spanish ceramic tile is produced in the *Castellón Cluster,* which is made up of 223 companies, accounting for 81 % of Spanish ceramic companies, 85 % of these being SMEs (i.e. having fewer than 250 workers in their workforce). With regard to the situation of the Spanish ceramic sector in the world, in 2007, Spain was the top European ceramic tile producer, ahead of Italy, with a 38 % share of EU-27 tile production and 17,4 % share of world trade in ceramic tile. In addition, in the global export ranking, Spain occupied 3rd place. However, the situation has changed since 2007. In the period from 2007 to 2010, world ceramic tile production increased by 11,7 %, China and Brazil being the world's top producers and accounting for 52 % of global production. On the other hand, emerging countries such as India, Iran, and Vietnam have become producers with an important market share (Tab. 1). In 2010, in the domestic market, Spanish ceramic tile sector turnover as a whole fell by 1,7 % with respect to the previous year. To be noted was the positive export performance, which partly offset the drop in the domestic market. In contrast, Italian ceramic tile sector turnover grew, though sales were also impacted by the negative performance of their domestic market. In Italy, exports accounted for 73,7 % of total tile sales in 2010, whereas that figure was a little lower (68,6 %) in Spain.

As mentioned, the Spanish tile manufacturing industry has shrunk considerably these last few years. Particularly to be noted among the proposed solutions, some of which have already been implemented, are

Tab. 1 Ceramic tile production by countries and years (Source: Ceramic World Review)

Country	2008 $[Mm^2]$	2009 $[Mm^2]$	2010 $[Mm^2]$	World Production in 2010 [%]	Variation 2009/10 [%]
1 CHINA	3400	3600	4200	44,1	16,7
2 BRAZIL	713	715	753	7,9	5,3
3 INDIA	390	490	550	5,8	12,2
4 IRAN	320	350	400	4,2	14,3
5 **ITALY**	513	368	387	**4,1**	5,2
6 VIETNAM	270	295	375	3,9	27,1
7 **SPAIN**	495	324	366	**3,8**	13,0
8 REST OF THE WORLD	2343	2366	2435	25,6	2,9
TOTAL WORLD	**8520**	**8515**	**9515**	**100**	**11,7**

J. Llop, M. D. Notari, I. Nebot, J. B. Carda
Escuela Superior de Cerámica de l'Alcora
12110 Alcora
Spain

T. Stoyanova Lyubenova, E. Barrachina
Dept. of Inorganic and Organic Chemistry
Universitat Jaume I
12071 Castellón
Spain

Keywords: laser application for tiles, bactericidal tiles, thermal tiles, anti-slip tiles, photoluminiscent tiles, anti-electrostatic tiles, photovoltaic tiles

Paper held at the 13th Qualicer,
17–18 February 2014, Castellón, Spain

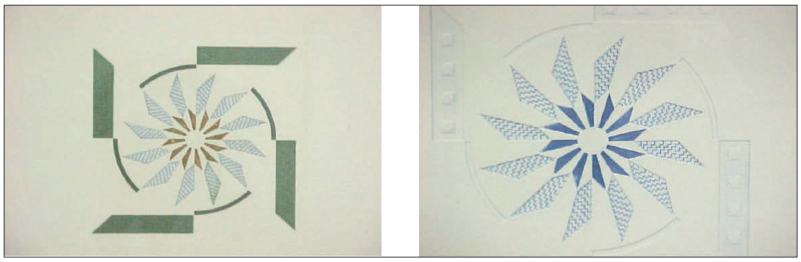

Fig. 1 Photographs of tiles decorated by in situ pigment synthesis and laser ablation

important structural adjustments and improved management in order to address the new situation, as well as the need for greater flexibility in adapting to the changes in the economic circumstances.

Of vital importance is a commitment to innovation and added value, which allows a different product to be offered, in which the quality and exclusiveness perceived by the client are determining factors. In addition, export leadership is required, opening up new markets and consolidation in natural, albeit mature markets, such as the European Union. To achieve these objectives, the collaboration between ceramic sector companies is an indispensable prerequisite. In regard to the products obtained, in recent years ceramic innovation has focused on new functional properties of ceramics: decoration, mechanical features, health and hygiene, air cleaning, visual and smart signalling, heating, and energy saving.

Innovations in the ceramic sector

Decoration

Since the first inkjet machines for decorating ceramic tiles appeared at the CEVISAMA trade show in the year 2000, their mechanics, electronics, inks, and pigments etc. have evolved constantly [1–4]. The enormous competition to develop new machines and inks for tile decoration has led to the emergence of inkjet technology, which consists of printing by dropwise ink deposition, enabling full-colour personalisation, with photographic resolution, of any desired design (murals, columns, etc.).

There are two different techniques for this purpose, namely continuous inkjet technology and drop on demand (DOD) inkjet technology. There is great competition in the development of new machines and inks that are able to decorate ceramic tiles based on digital printing. Inkjet machines are perfectly fitted into the glazing lines for decoration, to enhance efficiency. Some of the advantages of these decoration systems are as follows:

- no direct contact with the work piece (possibility of decorating low reliefs)
- elimination of intermediate tools (screens, rollers, etc.)
- drastic reduction in pigment consumption
- high-resolution printing: greater realism of the design or photograph
- high printing speeds
- applicable on a multitude of materials
- reduction in the time required to change designs and colours
- decoration of 100 % of the design surface.

Laser

Laser ablation has emerged as a valid process for obtaining profiles or embossings on ceramic bodies. It allows ceramic pigment synthesis on tile bodies, enabling the pattern established by the ceramic design to be followed. This provides savings in pigment consumption and suppresses the need to use mineralisers in pigment synthesis, as very high temperatures can be reached on the surface with the ensuing environmental benefits. This technology allows the line of decorative applications in the production process to be shortened [5–8].

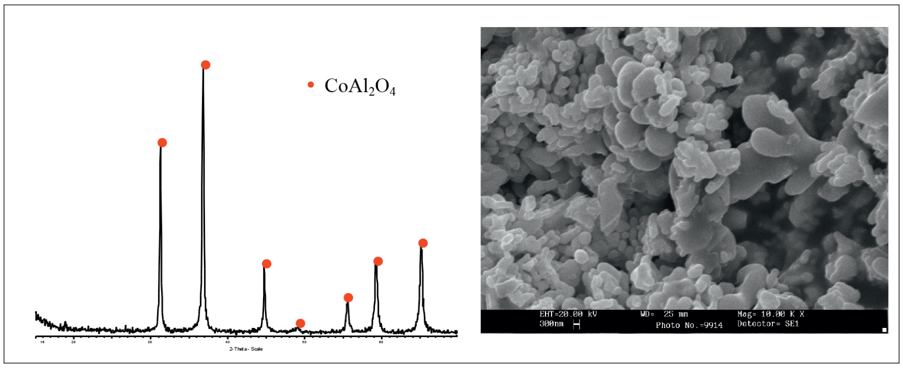

Fig. 2 Diffractogram and micrograph of a pigment sintered in situ by laser technology

Thus, when a laser beam impinges on a surface, an energy transfer takes place that only implicates one surface region of the ceramic tile. The energy transfer involves excitation and de-excitation processes at electronic level of the atoms and/or molecules of the material during an extremely short time, which can generate extreme heating and cooling rates in surface regions without significantly affecting the temperature of the rest of the material. This allows only very thin thicknesses to be processed under extreme conditions, with a minimum effect on the properties of the rest of the work piece. Depending on the irradiation conditions and the surface, optical, and thermal characteristics of the material, changes of phase and/or state will take place in the area subject to irradiation, related to heating, melting, and/or evaporation processes [9–11].

Fig. 1 shows an example of the high definition that can be attained with in situ decoration. This type of decoration is obtained by applying the precursors of a given pigment with an aerosol, so that when a laser impinges on them, the pigment sinters. The fact that the pigment layer remains well-bonded to the body allows the non-reacted precursor to be recovered by blowing, with the ensuing reduction in materials costs and minimisation of the environmental impact.

The high degree of pigment sintering has been evidenced by X-ray diffraction (XRD) analysis and has been observed by scanning electron microscopy (SEM) (Fig. 2).

Laser application for thermal treatment of ceramic tiles

The *Institute of Materials Science of Aragón (ICMA)*, a mixed centre of the *University of Zaragoza*, and the *Spanish National Research Council (CSIC)*, together with a company from the Castellón frit and glaze sector, have developed the application of a new technology that reduces energy consumption in ceramic firing by incorporating a laser inside a tile firing kiln.

Thus, irradiating the ceramic tiles in the kiln produces a significant increase in ceramic tile surface temperature, with an important reduction in stresses. At the temperatures at which the energy beam is applied, the atoms and molecules have greater mobility than at room temperature because the thermal energy is transformed into the kinetic energy of molecules [12]. In this fashion, the laser concentrates the heat at the tile surface, enabling temperatures close to 2000 °C to be reached in a surface area without damaging the material.

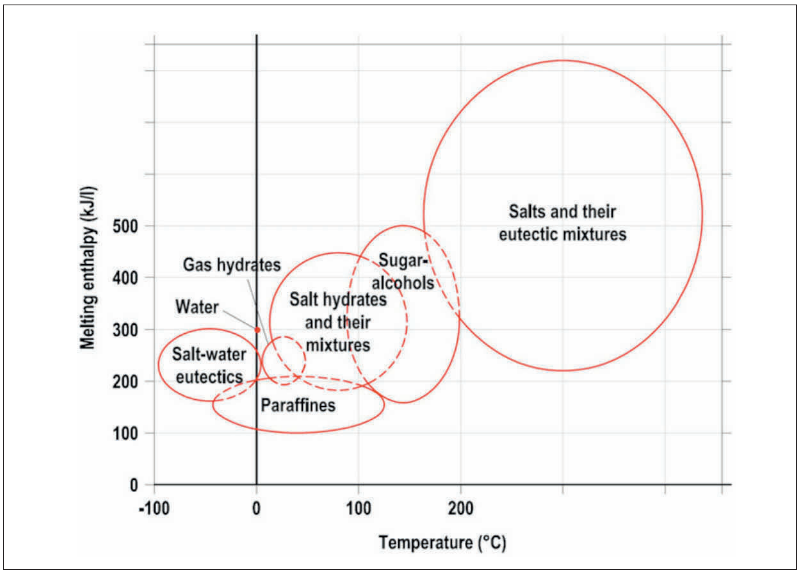

Fig. 3 Melting enthalpy as a function of the temperature range, different groups of phase change materials (PCM) [Dieckmann, J.: Latent heat storage in concrete]

Bactericidal tile

Titanium dioxide is an n-type semiconductor that features, as particularly interesting property for environmental applications, a photocatalysing action that can degrade organic compounds. The sequence of the arising heterogeneous photocatalysis mechanism consists of the absorption of ultraviolet or visible radiation, the generation of the electron-hole pair in the semiconductor by the transition of electrons from the valence band (VB) to the conduction band (CB), and the participation of the photogenerated species in redox reactions in which the hole in the VB opening is strongly oxidising and the electron in the CB is moderately reducing.

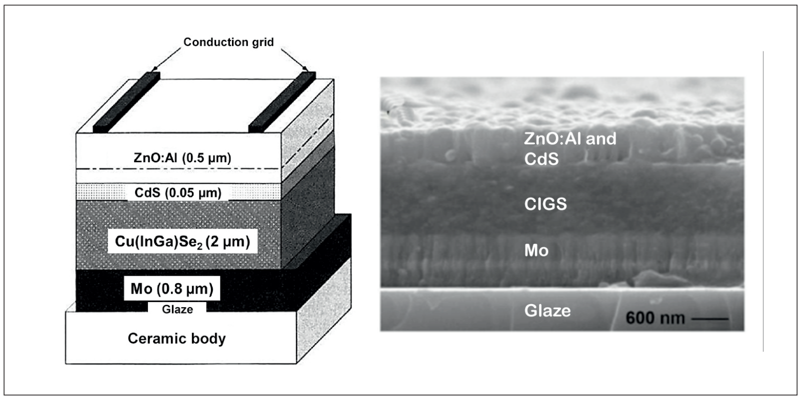

Fig. 4 **Photovoltaic solar cell of chalcopyrite (CIGS) and its corresponding cross-sectional SEM micrograph**

The interaction with the adsorbed water and oxygen molecules at the surface of the particle generates superoxide ions (O^{2-}) and hydroxyl radicals (OH’) that are short-lived and highly reactive in the medium, which react with the external tissues of microorganisms such as bacteria [13–17].

Air cleaning

A further functionality that has also been developed in ceramic tiles is air purification. In this line, to be noted are tiles that are capable of transforming pollutant particles in the environment into harmless substances for human health by means of photocatalysis, thanks to the UV rays in solar radiation and to ambient humidity. To do this, an appropriate tile glaze composition encourages the photocatalysis reaction, enabling NO_x (nitrogen oxides) to be eliminated, reducing nitric acid by 75 % and tropospheric ozone by more than 10 %. A tile functionality is involved that does not harm the environment and whose effect persists on the tiles throughout their life cycle [18].

Bioclimatic architecture

A ceramic tile is involved that accumulates energy, in the form of heat, and returns this to the environment when this is needed, providing important savings and optimising energy use in new sustainable construction. The main property of these materials, known as phase change materials (PCM), is thermal energy storage in latent form, increasing the heat storage capacity by unit volume with respect to that of conventional construction materials. Thus, when ambient temperature increases excessively, the chemical bonds in the materials break, causing the material to change from a solid to a liquid. As this phase change is an endothermic process, it absorbs heat from the environment, reducing the temperature. On the other hand, when the ambient temperature drops again, the PCM returns to the solid state, releasing the absorbed heat.

Some of the desirable characteristics in this type of product are as follows:

- From a chemical viewpoint, it must have high stability and very low or zero reactivity with the ceramic material.
- From a thermal viewpoint, these materials must have an appropriate phase change range under the conditions of their intended installation location.
- From a physical viewpoint, these products must have high density, together with a low coefficient of volume change (ongoing from a solid to a liquid state and vice versa) and a high latent heat of phase change.

At present, various (organic and nonorganic) materials are being studied that could be introduced into these types of products with a view to achieving this objective (Fig. 3). One of the issues to be solved at present in this technology is identifying the types of products that could be introduced into the substrate (tile body) and meet the requirements indicated previously [19–23].

Thermal tiles

A type of tile is involved that is designed to generate heat, in contrast to the coolness that standard tiles usually display. For this, a voltage difference is applied to a conductive glaze, generating heat by the *Joule* effect and obtaining warm tiles. In this case, the tile body, unlike the glaze, must behave as thermal insulation so that there are no power losses and all the applied current is transformed into heat. In addition, the insulating nature of the body also provides an additional safety measure, insulating the conductive surface [24].

Independently of this characteristics, this type of ceramic keeps its characteristic properties, such as durability, cleanability, watertightness, etc.

Smart surface systems

Tiles are involved with surface coating systems that detect the presence of humans, and they activate devices that regulate traffic lights at pedestrian crossings, serve as interactive games for children, improve accessibility and safety in given spaces, etc. It is estimated that in the year 2050, 70 % of the population will live in urban contexts, thus requiring the development of smart materials that can provide solutions, starting right now, to future citizen demands [25–27].

Photoluminescent tiles

This type of tile is based on the development of a fluorescent pigment that, when it is incorporated into a glaze composition and applied on ceramic bodies, produces a tile that can accumulate energy to release it later into the environment, without altering tile properties in the course of time. Thus, new ceramic functionalities are emerging that can also open up new decorative possibilities, such as signalling escape routes when there is no light, or the presence of luminous signs to provide a suitable setting for given building areas. Smart photoluminescent ceramic materials are involved that also exhibit high resistance and strength for use in architecture and urban development. They withstand wear by pedestrian traffic or atmospheric agents, are easy to clean, and require no special upkeep. Thus, this type of ceramic product fosters energy efficiency, as the possibility of accumulating energy in order subsequently to release it into the ambient during certain periods of time entails an important energy saving, and it can also help avoid distressing situations in public places stemming from darkness and people's loss of their bearings [28–30].

Anti-electrostatic tiles

This type of tile has been manufactured using a glaze composition that is able to generate surface electric conduction, adapted to stoneware and porcelain tile bodies. It is used in locations where a charge build-up may be dangerous, in explosives stores, hospitals, or areas with high electric activity [31].

Anti-slip tiles

Anti-slip tiles have a rough surface texture, which is obtained using appropriate glaze compositions and grits. These tiles enable safe and stable pedestrian traffic and are therefore used in public spaces, pavements, hospitals, ramps, and gymnasiums, as well as in private homes. The installation of anti-slip tile is very useful and prevents accidents. From an aesthetic viewpoint, anti-slip tile use entails no particular problem, as colour and texture can be readily adapted to the home. The tiles also prevent slip-falls because they have a particular profile or groove that enables liquids to evaporate or flow away. The technology in this type of product has evolved greatly in recent years. The technology started by simply applying a grit that produced a very rough surface, while at present, glass-ceramic glaze compositions are used that devitrify small crystals at the surface of glaze [32].

Ecological tiles

This term refers more to a way of processing the product than to an innovation in resulting tile properties. With a view to optimising natural resources, and in consideration of future generations, the ceramic sector is actively engaged in this sustainability initiative. Tiles are involved with raw materials compositions that are respectful of the environment because they incorporate ceramic sector waste and by-products (unfired tile scrap, fired tile scrap (known in the sector as chamotte), wastewater from glazing line cleaning or from glaze grinding, etc.), as well as waste from other sectors, such as recycled glass waste or cellulose fibres from the paper sector. In this case, it is important for there to be a sufficient abundance of the waste raw materials, in addition for the waste to have a consistent, homogeneous composition and particle size.

For many years, the ceramic sector has thus been introducing such unfired suspended solids and liquid waste as raw material in formulating both red-body and white-body tiles, reducing ceramic sector waste by recycling this as raw material [33–48].

Photovoltaic tile

Photovoltaic cells are also being developed for application as thin films integrated into the ceramic tile itself, which allow solar energy to be transformed into electricity. These devices are intended to replace conventional construction materials with new architectural elements that, in addition, are a main source of power and energy saving. The photovoltaic modules, based on thin-film technology, stand out as interesting routes for drastically cutting down production costs, by reducing the quantity of material used. In addition, their uniform, elegant appearance, as well as the freedom of possible shapes and designs that they afford, make them particularly appealing for architectural integration into buildings.

The structure of the photovoltaic cell incorporated into the ceramic tile is detailed in Fig. 4. It is made up of a substrate, covered by a conductive film, followed by another film of a p-type semiconductor (called absorber), in which the electron-hole pairs are generated. The most widely used absorber materials are mainly made up of chalcogen compounds, such as CdTe [49], $Cu(In,Ga)Se_2$ (CIGS) [50], and Cu_2ZnSnS_4 (CZTS) [51, 52], owing to their high coefficient of absorption ($\sim 10^5$ cm^{-1}). Among these, the compound $Cu(In,Ga)Se_2$, which crystallises in the chalcopyrite structure, has achieved the highest photovoltaic efficiencies (20 %) [53]. The device further features a buffer film (CdS) that generates the p–n bond with the absorber film and finishes with transparent coatings that act as a window and allow the light to directly reach the active part of the cell.

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