CERAMIC TILE DECORATION BY LASER TECHNOLOGY

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ABSTRACT

There is great interest in the ceramic tile manufacturing sector in obtaining designs of enhanced sharpness and definition of line, and a polychrome range with more intense and stable colours at the high working temperatures used.

The innovations with rotary machines and the first steps in the field of ink jet injection have been interesting.

However the potential afforded by laser technology still remains largely untapped for achieving good definition of design (at a level close to that of a photograph), together with the heating power that is reached (at plasma level), which allows concurrently producing designs and reliefs, in addition to sintering colours "in situ" when making the rotogravure. The foregoing features, together with the use of the corresponding software and easy maintenance, open up new horizons in ceramic design.

The technology also enables shortening production lines, expediting changeovers in production models and provides savings in materials, minimising the wastes stemming from production rests, cleaning, etc., thus also leading to environmental benefits.

For this reason, ESMALTES S.A., in collaboration with specialised research centres (research group in inorganic chemistry from Universitat Jaume I, and the Instituto de Materiales of Aragon of the C.S.I.C. (Spanish High Council of Scientific Research), have set themselves the task of producing reliefs together with pigment synthesis "in situ" by laser technology, enabling ceramic tiles to be simultaneously decorated according to a pre-set design, directly transferring tile design from the computer to the actual tile.

This whole approach opens up a totally innovative field for the Spanish ceramic industry, which can be included within the Sixth Framework Programme of the European Union.

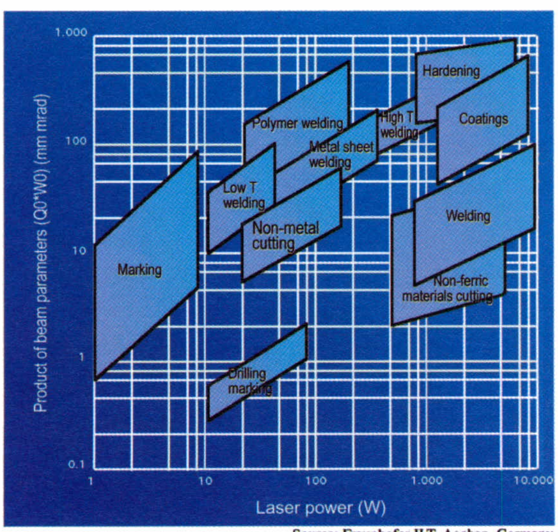
1. INTRODUCTION

There is currently great interest in the ceramic manufacturing industry for achieving designs that present greater sharpness and definition of line in decorations and gravures. This demand requires new techniques, which must also be capable of withstanding the very rapid, demanding and competitive manufacturing cycles used in this sector.

The present state of the art has reached a very interesting point, thanks to the innovations achieved through the application of rotary flexography and rotogravure machines. However, the constraints in the definition of designs and decorations, owing to the application technology itself, are evident. The reliefs produced in the traditional ceramic forming system (pressing and/or milling) are limited because they do not allow obtaining straight edge lines or tight angles, requiring the use of degraded edges and wide angles, since in the pressing process the punch would become clogged in a few pressing runs, and impair the design.

A field still unexploited until now has been the potential of laser technology, focused on achieving improvements in these types of applications, which include good design definitions (of photographic quality) and high heating power (at plasma level). Using laser technology could enable combining the execution of designs and reliefs of great quality, otherwise generally unattainable through conventional methods. This possibility, with the use of the appropriate software, as well as ease of maintenance and scarce environmental impact, allow this technology to open up new horizons for ceramic design. In addition, it also provides savings in the production line and versatility in the changeover of production models.

The following figure illustrates some industrial applications of lasers in other, non-ceramic fields, where they have already been used for several years with highly satisfactory results. The graph shows the applications in terms of laser power and product of beam parameters.



Source: Fraunhofer ILT, Aachen, Germany

Figure 1. Laser applications

Next, Figure 2 illustrates the possibilities afforded by laser technology based on three essential parameters: operating conditions (continuous or pulsed), pulse width (duration of the laser pulse), and energy density (energy applied per unit surface area treated material) or power density (power per unit surface area), a more widely used parameter in industry, particularly in fusion processes.

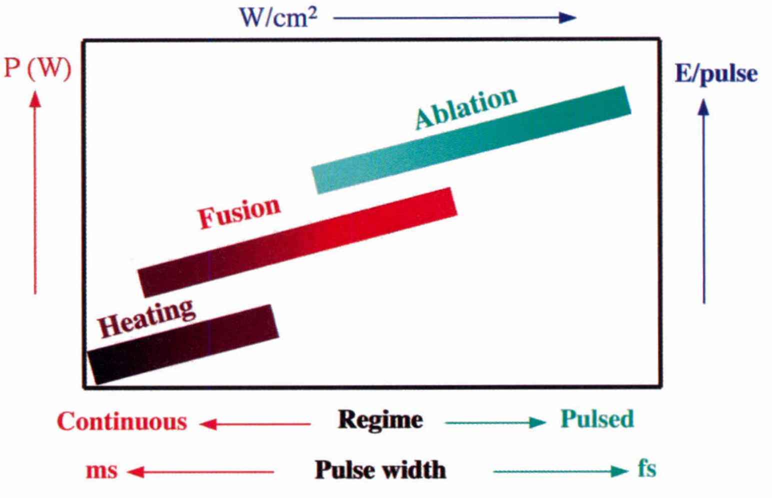


Figure 2. Laser-induced transformation processes on materials.

As may be observed, continuous operation, characterized by the continuous emission of a certain level of power, is widely used in applications of a thermal type, in which the heating power of laser radiation is used for fusion, cutting, welding and alloying processes, etc. There is further the pulsed mode, whose definition comprises the variables: time duration of the pulse, peak power, pulse energy and pulse repetition frequency. In this case, laser power undergoes periodic variations that are used particularly in applications requiring high peak powers, i.e., high energy densities concentrated in very short performance times, but with limited intermediate power values, which considerably reduce the very interesting heat transmission effects of the continuous mode. Thus, the pulsed mode is widely used in high-definition cutting applications, marking, drilling and machining or micromachining, which is the application that concerns us.

Therefore, in accordance with the requirements of this scoring application on ceramic materials, the pulsed mode of operation is the most appropriate, with short pulses of very high energy. That is to say, we need an ablative process that removes material by mechanisms involving fusion, evaporation and/or direct sublimation, in such a way as to minimize the damage caused by thermal interaction. Up till now, the scientific literature has focused on the ablative process in purely technical ceramics of technologically very interesting applications [1],[2],[3] but of much less complex behaviour than the heterogeneous ceramic materials used in the floor and wall tile industry. On the other hand, laser systems are used in the ultraviolet wavelength range [4],[5] which, though they allow an eminently cold ablation mechanism, are very complicated to implement in an industrial process, because they need a very demanding technical and environmental infrastructure. And finally, note that most of the work published focuses on the study of the effect of a single laser pulse on the surface of the material, and not on the possibility that the laser offers of performing in-line treatment that enables surface scanning.

The present study intends to demonstrate that the power lasers of wavelengths close to the near infrared (1064 nm) are highly effective in the ablation process and simultaneously very versatile and appropriate for the industrial environment. For this, a study has been conducted of the optimization of ablation ratios for making reliefs and rotogravures by applying laser technology, so that the decoration of the ceramic material is made through a pre-established design, going directly from the design of the piece on the computer to the surface to be treated. Designs have been developed with edges having a straight finish, tight angles, high reliefs in the bas-reliefs themselves, all with adjustable depth according to process conditions. These types of reliefs are impossible to achieve with the traditional ceramic forming method by pressing.

The present study also presents an application of this technology in "in situ" ceramic pigment synthesis, i.e. on the ceramic body itself, using the high-temperature and high-definition production characteristics of the application for ceramic design and decoration.

2. EXPERIMENTAL DEVELOPMENT

2.1. LASER ABLATION: CREATION OF RELIEFS

The technique used in this process is laser ablation. A Nd:YAG (Q-switched) laser was used with a wavelength of 1064 nm and 65 W power. In these instruments, the pulsed mode is obtained through the Q-switch mechanism, achieved by introducing in the laser cavity a device that inhibits laser action in a controlled way. While this device is active, the pumping in the active medium causes a greater than usual population inversion. If the Q-switch is then opened, feedback occurs between the mirrors and all the accumulated energy in the active medium leaves in the form of a very intense laser pulse. With this pulsing technique, the system produces pulses of 0.4 μs with peak powers up to 10^6 W. This type of pulsed system is very common in laser marking equipment, which is the industrial operating mode closest to the work to be performed. This laser provides a good quality beam, of a similar mode to that of the TEM_{00}, which means that it has a Gaussian energy distribution (Figure 3), which is the one that enables focusing on a spot with a minimum diameter.

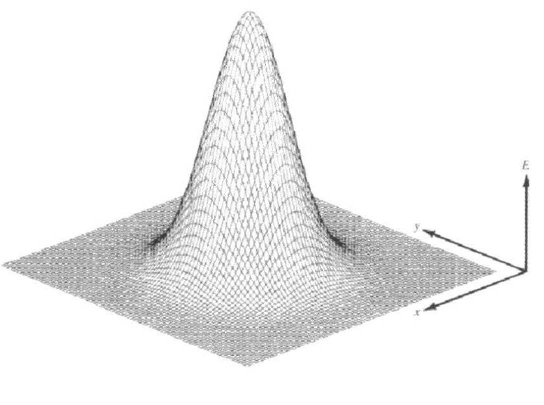


Figure 3. Energy distribution of a TEM00 mode.

Coupled to the described laser, the experimental system used in this study contains a head with galvanometric mirrors that allow precise movement in the X-Y axis of the laser beam. The presence of a flat focal lens at the head output allows focusing the laser beam with constant quality on a spot of approximately 20 μm with a maximum angle of deviation of 24.5º. Thus, with this lens, a working circle of 160 mm diameter is obtained. The system is schematically illustrated in Figure 4.

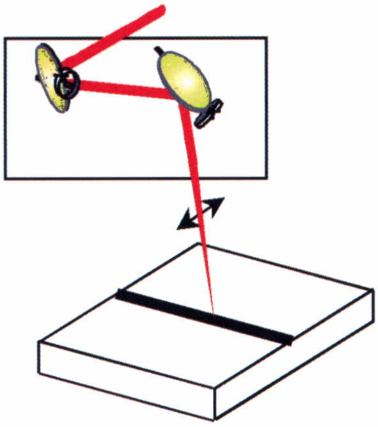


Figure 4. Scheme of the experimental system used.

The basic interaction mechanisms between laser radiation and material may be photothermal and/or photochemical [1]. Laser ablation occurs when the laser beam energy that is absorbed by the material is sufficiently intense for it to evaporate and be expelled. The arising vapour cloud is mainly made up of excited and ionized electrons and atoms. This mechanism depends on many parameters, such as the physico-chemical nature of the material and its surface state, parameters of the laser radiation itself (power density, wavelength, pulse width), and the atmosphere surrounding the process. In order to obtain evaporation, power density must be higher than the ablation threshold of the radiated material. As a general rule, the greater the power density, the greater will also be the level of damage caused in the surface of the sample.

When ablation is eminently thermal, the material undergoes a process of fusion and evaporation or direct sublimation. This happens because the pulses used have a duration ranging from 100 ns to 100 ms (in this case 0.4 μs), which is why the laser-material interaction is sufficiently long to enable heat transfer phenomena to take place. The substrate is heated and the thermally affected zone is larger than the laser beam. If the instrument produced shorter pulses (between 100 ps and 100 ns), the process would be non-steady and would only permit photomechanical and photochemical processes, resulting in machining by high-resolution ablation (micro and nanomachining).

The effect of power density on the ablation process can be described in the following way: when the values of power density are moderate (<10^8 W/cm^2), the bulk of the material is observed to be barely affected by the laser radiation. All the process then takes place at the sample surface, which is why only low-energy ionization species are observed in the vapour cloud. At higher energy density values (>10^9 W/cm^2), the laser transfers much more energy to the sample surface, where a plasma plume is created with severe gradients of very high temperature and pressure (Figure 5), generating a typical crater and, in this case, the bulk of the solid is indeed affected. The removed species of the material produce a springback pressure that expels the induced molten surface layer, while simultaneously generating a mechanical shock wave that also favours the expulsion process.

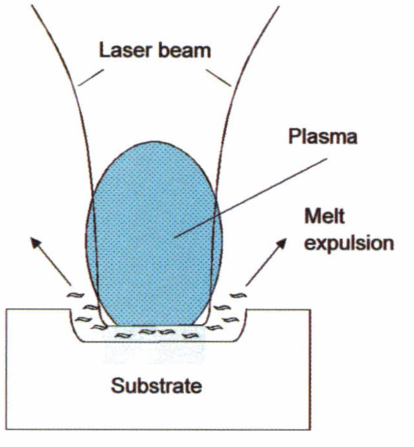


Figure 5. Scheme of the ablative process

Now that we have defined our ablation process, the most important variable to be characterized and optimized is undoubtedly the scoring depth obtained with the laser interaction. This entails making a systematic study of all the parameters involved in the ablative process. With regard to the relation technological interaction-equipment, these parameters are: parameters relative to energy output (excitation intensity), scanning speeds (surface treated per unit time) and repetition frequencies (pulsed mode frequency).

The material used was a high-strength porcelain tile, made up of a mixture of clays (aluminosilicates), quartz and feldspars, as well as organic additives, and zircon ($ZrSiO_4$) as a whitening agent.

The laser modified products have been studied by optical and scanning electron microscopy to observe the effectiveness of the process.

2.2. SELECTIVE LASER SINTERING: "IN SITU" PIGMENT SYNTHESIS AND DECORATION

Extremely high and very localized temperatures, combined with minimum or even zero damage or undesired transformation of the material, as well as the obtainment of thermodynamically metastable phases, frozen by fast cooling, are some of the more interesting advantages that laser technology can offer the field of ceramic surface modification. To date, most of the published work has related to ceramic materials that use lasers, either in a pulsed regime to perform surface ablation processes [6],[7],[8] or in a continuous regime for surface recrystallisation treatments or classic cutting by fusion and expulsion of the melt, using a gas jet at high pressure. [9],[10] The following figure schematically illustrates temperature distribution in surface treatments with laser, in which we can observe the variation of temperature with the depth or distance from the point of application of the radiation.

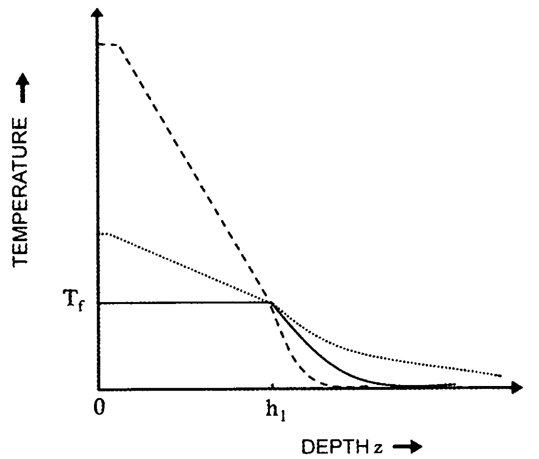


Figure 6. Temperature distribution based on depth

In this plot, T_f is melting temperature, z the distance from the surface and h_l the depth of the melt. The solid curve plots the temperature distribution in the presence of strong convection. The dotted curve refers to prolonged laser pulses, and the dashed curve to short pulses of high intensity, which cause strong overheating.

To be noted is a fundamental difference between laser fusion and ablation transformation processes [11],[12],[13],[14],[15]. In the former case, in a continuous wave (cw) regime with a lower power density by several kW/cm^2, temperatures up to 3000°C can be achieved in small volumes of inorganic solids whose melting temperatures approach these values, such as for example ZrO_2 and $BaZrO_3$[16]. In the latter case, in a pulsed emission regime, nanoparticulates can be obtained that detach from the surface of the substrate during the ablation process and whose size is determined by the width of the laser pulse [17]. A relief is left at the surface of the substrate whose physico-chemical characteristics depend not only on the width of the laser pulse, but also on other experimental parameters, such as pulse intensity (E_{pulse}) and repetition frequency (pulses/s), as well as the physical properties and chemical composition of the substrate. Depending on pulse width, which usually ranges between values of μs (10^{-6} s) to fs (10^{-15} s), processes can be run in which the surface is transformed in fusion-evaporation stages, a typical process when the width is of the order of µs, or in direct sublimation, when the pulse width approaches fs. The instantaneous power of the pulse is usually of the order of kW to MW, and the typical power density approaches values of GW/cm^2. The different laser actuation regimes are thus delimited, which enable inferring the potentiality of the technique with regard to the design of different chemical-physical transformation procedures for any ceramic material, which is the objective of the present project.

The laser-solid interaction occurs at the surface in such a way that the appropriate design of any ceramic transformation process requires considering the optical and surface properties of the ceramic materials. [18],[19],[20],[21]

In previous studies, various ceramic materials were selected, which were synthesized by Selective Laser Sintering-SLS [22],[23]. The refractory properties of these materials, their high hardness and potential for inducing colour by an electronic mechanism, acting as inorganic pigments of interest for the ceramic industry, were the preferentially used selection criteria.

The good results obtained were confirmed with the award by the *Spanish Society of Ceramics and Glass* of the Alfa de Oro Prize to *Esmaltes* S.A., for this development, at the CEVISAMA 2003 trade fair.

Figure 7 presents 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 certain pigment with an aerosol, so that that when the laser strikes, this pigment sinters. Thanks to the small focus of the laser, lines could be drawn of thickness below 100 μm (please see Figure 7). The fact that the pigment layer bonds well to the body allows recovering the non-reacted precursor by blowing, with the ensuing reduction in materials cost and minimization of environmental impact. All the pigments obtained consist of grains smaller than 200 nm in larger-sized agglomerates, so that this grain size favours the possibility of making decorative patterns of reduced thickness.

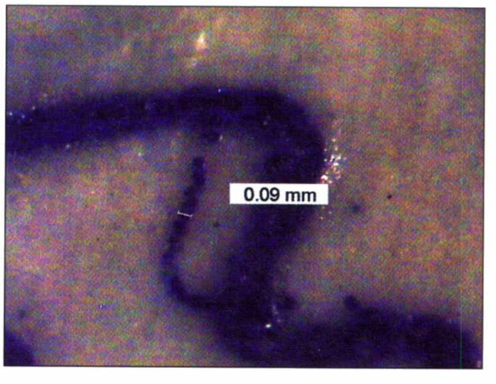


Figure 7. Lines on porcelain tile body obtained by means of laser technology (Pigment: $CoAl_2O_4$, laser: YAG:Nd)

3. RESULTS

The following sets out some of the results obtained both in the laser ablation process for the creation of reliefs and for "in situ" decoration with ceramic pigments by Selective Laser Sintering.

3.1. LASER ABLATION

This part has focused on two objectives:

A) Scoring by means of laser ablation with a view to obtaining relief decorations.

B) Effects by ablation to obtain decorations from designs that produce different optical effects.

Samples of the results for both objectives are shown in Figures 8a and 8b.

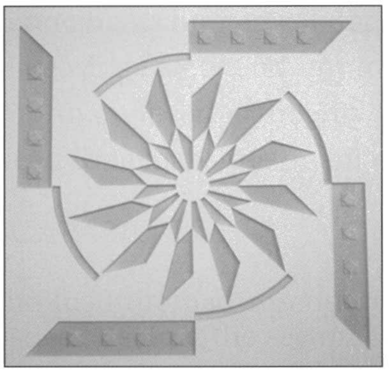


Figure 8a.

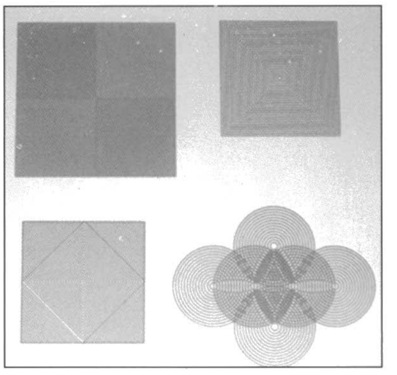


Figure 8b.

Figure 8*a* shows the definition possibilities offered using scoring by laser ablation. This technique enables effecting a procedure similar to that of rotogravure, with the depth that we desire. A scoring efficiency can be defined for this application based on material removal volume per unit time.

Figure 8*b* illustrates a second possible case, with other ablation effects, combining the design and effect of the laser. In this case, scoring depth is not so important and, therefore, the material removal efficiency is not so relevant. What is interesting in this case is the scanning or design efficiency, i.e., an efficiency that values the surface treatment speed.

Figure 9 shows a scanning electron microscopy (SEM) image displaying a cross section of one of the scored designs, with a scoring depth of approximately 1 mm.

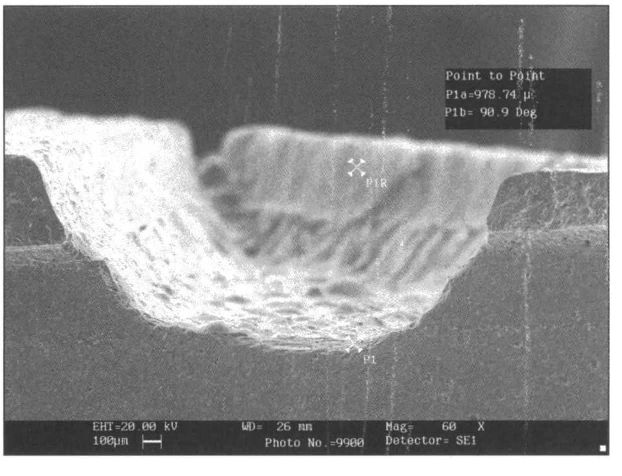


Figure 9. SEM micrograph. Measurement of relief depth, magnification 60x.

SEM was also used to study the effect on the body of the action of the laser in scoring. SEM photographs have been taken of the body without any laser action, and of the bottom part of the resulting relief. The micrographs in Figures 10a and 10b show that there is no appreciable difference between the two surfaces after treatment. Only a light surface densification of the material is observed.

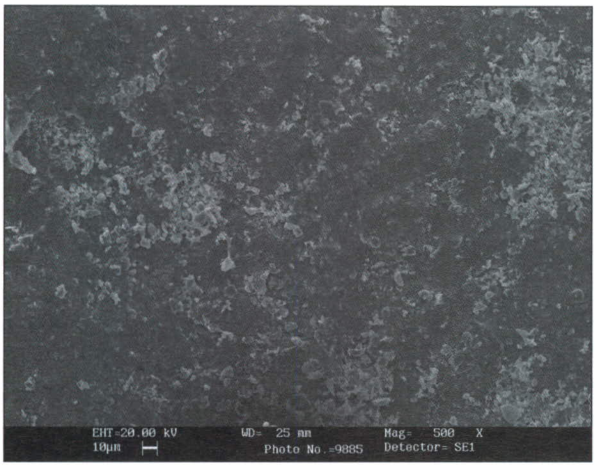


Figure 10a. Surface of the body non-reacted with the laser, magnification 500x.

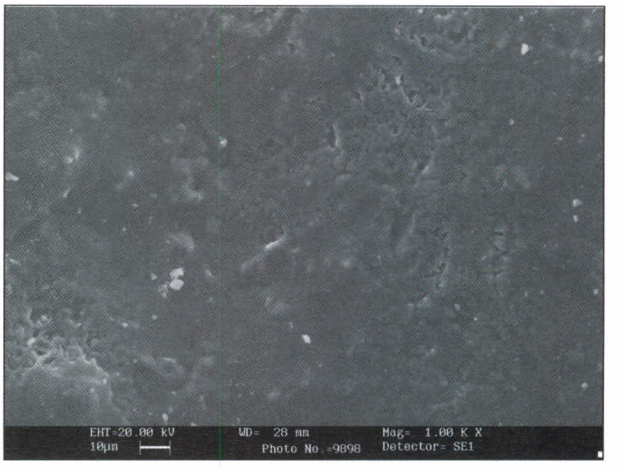


Figure 10b. Surface of the bottom of the relief scored with the laser, magnification 1000x.

The main parameter to be noted in the production of reliefs on ceramic bodies is the high quality of definition obtained with this method, unattainable with traditional techniques.

The following figures (Figures 11, 12 and 13) display cross sections of high definition, in a green, fired, and fired glazed sample. This material should preferably be worked in the green state, to avoid problems of cracks or failure by heat transmission, since firing produces a very highly densified state with practically no porosity. For this reason, it is necessary to carefully study the influence of the final firing process on the result of the ablative process. Nevertheless, the most recent experiences in the process are already revealing the possibility of applying laser ablation on fully finished ceramic materials, without requiring any subsequent heat treatment.

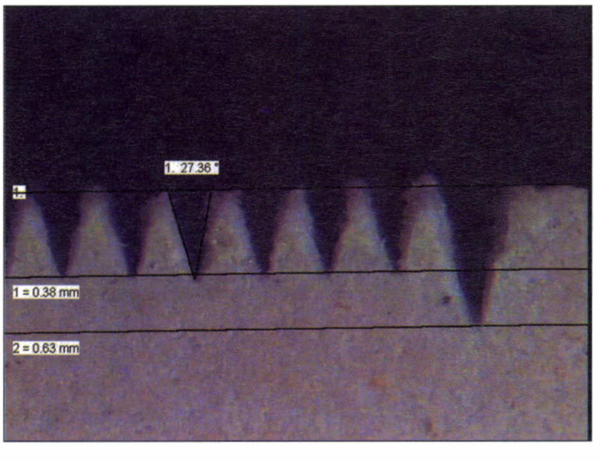


Figure 11. Depth of scoring on the green porcelain body.

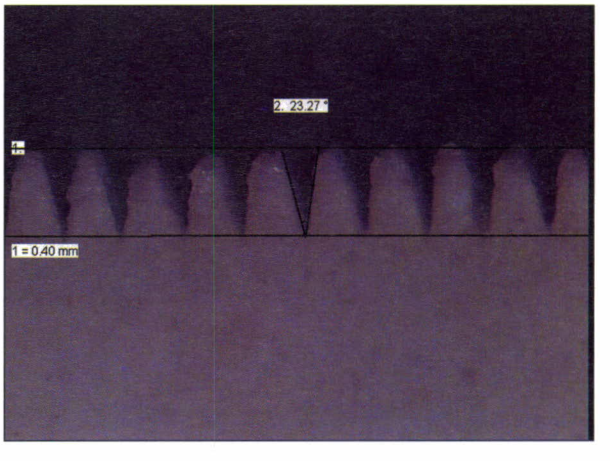


Figure 12.- Depth of scoring after firing.

The track left by the ablation process has the shape of an inverted cone, which is qualitatively explained as the result of the ablation process with a beam having the power curve already depicted in Figure 5. As power increases, the size of the track

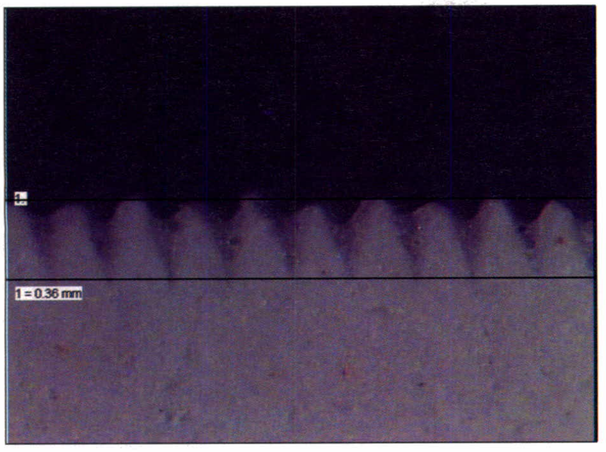


Figure 13.- Depth of scoring after firing with glaze

rises, and the cone becomes wider. This is characteristic of all ablative processes of a thermal type, in which, as already set out before, a phenomenon of molten material expulsion occurs, generating a cross section in the form of a *crater*, whose shape (width and depth) depends directly on process parameters (energy density and pulse repetition frequency).

The definition of the design is very good and hardly any dimensional changes are observed as a result of shrinkage after the firing process of the piece, which means that the process exhibits very good dimensional stability with thermal changes.

On the other hand, the glaze is clearly observed to wet the decorated surface perfectly, penetrating inside the design without producing air bubbles or other types of defects, while also conserving the laser-induced relief.

Finally, the ablation ratio also depends on the size of the laser beam. The size of the beam is going to determine the dimensions of the track and the characteristics of the plasma. The ablation ratios will be larger as beam size decreases, since the same nominal power is concentrated in a smaller area, notably increasing the density of the supplied energy.

Trials have been conducted with industrial laser systems to compare these results and thus determine which type of laser is most appropriate for this process. For this, a 65W lamp-pumped system was tested, and two diode-pumped systems, one of 50 and the other of 100W, which had a beam of smaller size and better quality.

The resulting efficiencies are set out in the following table (Table I):

	Scanning efficiency (cm^2/h)	**Scoring efficiency (cm^3/h)**
65W Lamps	288	6,05
50 W Diodes	1080	8,316
100 W Diodes	2160	10,8

Table I. Working efficiencies.

The table presents two types of efficiencies. First, there is what has been termed the Scanning Efficiency, which refers to the speed at which the laser covers the whole surface with the optimum ablation conditions selected. Secondly, there is the Scoring Efficiency, in terms of material volume removal per unit time.

The diode-pumped systems are observed to provide much better performances, with significantly superior efficiencies, particularly evident in the case of scanning output. This is mainly due to the quality of the beams, their much smaller size and the high scanning speeds that they provide owing to their greater power. The quality of the beam also provides a cleaner and more uniform scoring process, with a better quality at edges and corners, unattainable with lamp-pumped systems.

Since design and aesthetic quality are important factors in the ceramic industry, a diode-pumped laser provides greater potential for working possibilities.

3.2. SELECTIVE LASER SINTERING

As remarked previously, besides synthesis, this treatment also allows fixing the synthesized pigment on the tile surface, enabling recovery of the non-reacted material for later reuse, which increases the profitability of ceramic pigment use in decorations.

The degree of pigment sintering observed by SEM is appreciable, indicating the effectiveness of the "in situ" pigment synthesis process by laser heat treatment. A detail of the result obtained can be observed in Figure 14.

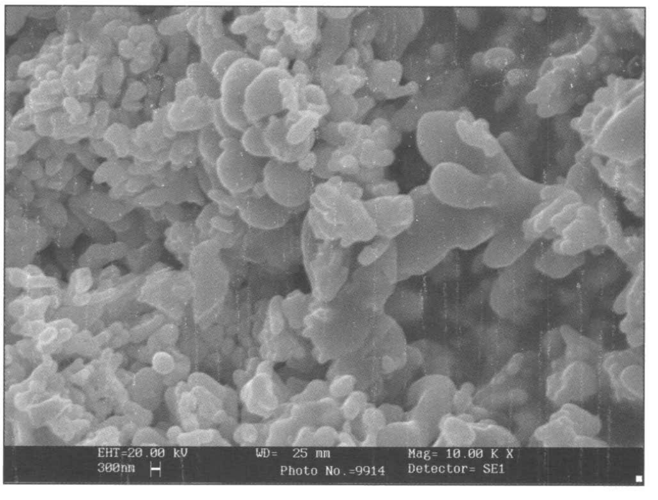


Figure 14. SEM micrograph of the synthesized pigment surface magnification 10000x.

The degree of pigment sintering is also evidenced by X-ray diffraction (XRD), as shown in Figures 15 and 16.

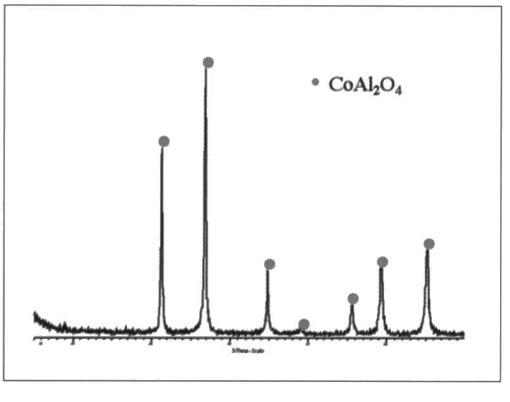


Figure 15. XRD of the "in situ" sintered pigment of composition $CoAl_2O_4$.

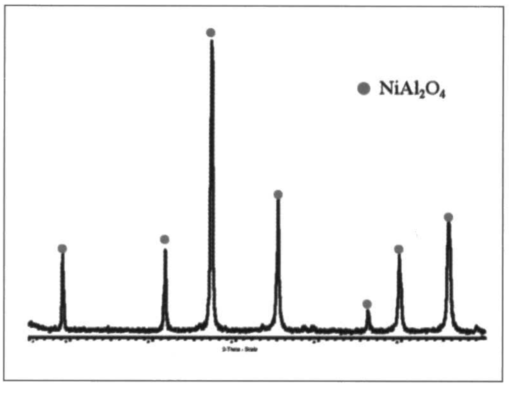


Figure 16. XRD of the "in situ" sintered pigment of composition $NiAl_2O_4$.

As the X-ray diffractograms show (Figures 15 and 16), a high degree of crystallinity is obtained with this new pigment synthesis method, producing as sole product the desired pigment.

A wide range of colours has been developed by this methodology. Some of the prepared pigments are listed below in Table II, together with their objective colour data, i.e., their CIE Lab chromatic coordinates.

	Chromatic Coordinates			
Composition	**L***	**a***	**b***	**Colour**
Sn-V	71,22	-1,64	25,60	Yellow
Zr-V	73,50	4,73	30,09	Orange
Al-Cr	41,97	-10,67	11,30	Green
Al-Mn	63,54	8,17	9,34	Brown
Al-Co	45,65	3,20	-39,39	Blue
Al-Ni	54,97	3,56	7,51	Green
Cr-Co-Fe-Mn	31,03	1,31	1,80	Black

Table II CIE Lab chromatic coordinates of some of the laser-synthesized pigments.

4. CONCLUSIONS

4.1. The present study has demonstrated that it is possible to successfully apply laser ablation with a view to scoring heterogeneous ceramic materials; to date the literature had reported no results of ablation on this type of material. The efficiency of the switched Nd:YAG lasers has also been shown, in the pulsed mode, for application to commercial ceramic surfaces.

4.2. Among the many possible applications in the use of lasers for decoration, this study has specifically highlighted two objectives: scoring by laser ablation to obtain relief decorations, and scoring by ablation to obtain decorations from designs that produce different optical effects, using the high resolution provided by narrow focal spots of the laser used.

4.3. This technology allows shortening the line of decorating applications with the ensuing savings in facilities and infrastructures in production plants.

4.4. The application of laser technology has been confirmed to produce ceramic pigment synthesis, and the corresponding pigmenting structures have been characterized.

4.5. There are environmental and economic connotations, as a colour palette can be obtained, without requiring ceramic pigment deposition, since these are sintered "in situ", thus also minimising the wastes generated by production rests and the use of screen printing vehicles, etc.

5. ACKNOWLEDGEMENTS

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