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High contrast laser marking of alumina

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ABSTRACT

Alumina serves as raw material for a broad range of advanced ceramic products. These elements should usually be identified by some characters or symbols printed directly on them. In this sense, laser marking is an efficient, reliable and widely implemented process in industry. However, laser marking of alumina still leads to poor results since the process is not able to produce a dark mark, yielding bad contrast.

In this paper, we present an experimental study on the process of marking alumina by three different lasers working in two wavelengths: 1064 nm (Near-infrared) and 532 nm (visible, green radiation). A colorimetric analysis has been carried out in order to compare the resulting marks and its contrast. The most suitable laser operating conditions were also defined and are reported here. Moreover, the physical process of marking by NIR lasers is discussed in detail. Field Emission Scanning Electron Microscopy, High Resolution Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy were also employed to analyze the results. Finally, we propose an explanation for the differences of the coloration induced under different atmospheres and laser parameters. We concluded that the atmosphere is the key parameter, being the inert one the best choice to produce the darkest marks.

1. Introduction

Aluminum oxide (alumina, Al_2O_3) is one of the most employed ceramic materials. It is used in many fields such as in medical industry, electronics or lab products. This is mainly because of its excellent combination of properties which make it a good electrical insulator, it is stable at high temperatures, with high wear and chemical resistance and is relatively economical.

Components for those industries should be commonly identified by a code, and it is useful to print this code right on its surface, so as to avoid any confusion. In this sense, laser marking is a widely implemented process in manufacturing industry for several reasons: it is a versatile process, suitable for marking different materials with complex geometries with a high processing speed. Furthermore, its automation is relatively easy, there is no need of using tools that can be wore and, of course, there is no need of using inks at all, which is very important for example in both medical and food processing industry. There are some different kinds of laser marking processes but all of them involve irradiating the surface of a material by a laser beam so it is chemically or physically changed.

Analysis on the influence of processing parameters leading to different marking width, depth and intensity has already been studied [1]. However, the physical mechanism that generates marks in alumina is not still clearly stated. The most supported mechanism for producing coloration in ceramics by lasers is the generation of oxygen vacancies. Oxygen vacancies are also known as color centers or F-centers (farbe center in German) because they produce electromagnetic radiation absorption bands in the spectrum region in which ceramics themselves (and particularly in alumina [2,3]) do not normally absorb, i.e. they produce coloration on ceramics. There are also some studies about F-centers in different ceramics: in silicate glass [4], in YAG crystals [5], in CaO [6], in crystalline metal oxides [7], etc. Laser treatment of alumina by ultraviolet (UV) lasers has already been studied by some authors. Pedraza et al. [8] tried with an excimer laser under inert atmosphere and demonstrated by XPS analysis the generation of oxygen vacancies on alumina owing to a preferential desorption of oxygen. Their conclusions agree with those obtained by Cappelli et al. [9]. They employed an ArF laser to irradiate alumina and found that produced coloration was also due to color centers. Notwithstanding, results of their XPS analyses do not agree since any traces of reduced alumina were found by the

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last one. Therefore, these analyses do not really seem to be definitive in order to confirm the existence of color centers. Cao et al. [10] demonstrated coloration on alumina by irradiating it with an excimer laser under a partially reducing atmosphere, while under air, alumina got a bright yellow color. This difference in the marking shade was attributed again to the quantity of oxygen vacancies produced. On the other hand, the possibility of generating oxygen vacancies by heating alumina at 2000 °C [11] and 1900 °C [12] under a strongly reducing atmosphere has been probed. Similarly, Zhou et al. [13] found that sapphire crystals generated by Czochralski method at 1800 °C has color centers and a characteristic red color.

Near-infrared (NIR) lasers are used for many different processes, among which marking treatment is one of the most typically implemented on industry because they can mark a great variety of materials, are reliable, durable and relatively economic. However, conventional marking process of alumina by NIR lasers produces light marks; therefore these marks exhibit low contrast, so they are hard to see and to read. It is already known that, at ambient temperature, alumina absorbs just a small part of NIR laser radiation [14]. Laser beam is only absorbed in alumina defects such as cracks, grain boundaries, impurities or oxygen vacancies [15]. In these singularities, laser radiation is absorbed and transformed into heat. However, there is a lack of any study on the process of coloration of alumina by NIR lasers.

Consequently, in this work we aimed to analyze the physical processes involved in marking alumina by NIR lasers, and especially by fiber lasers, in order to improve the marks by giving them higher contrast. Fiber lasers can be typically seen in marking industry because of its multiple advantages such as: energetic efficiency, even greater than 30%; high reliability; laser equipment are relatively small and light in weight; they can be guided by optic fiber; they emit high quality beams that can be focused in very small spots, providing high resolution marking, even while working with large working distances; and finally, they need less maintenance than other lasers. We have also carried out an experimental study on the marking process by green laser so that we can compare its results with those obtained by NIR lasers.

2. Materials and methods

2.1. Material

For the experimental study, we have employed several alumina plates of 25 mm × 25 mm × 1 mm of 97.5% purity (Good Fellow).

2.2. Experimental set-up

Three different lasers were used, two fiber lasers and a Nd:YVO_4 laser. Both kinds of lasers can be found in many industries carrying out the marking process of different materials.

First laser used is an Ytterbium-doped fiber laser (IPGYLR-3000) emitting up to 3 kW of continuous radiation at a wavelength of 1070 nm with a power up to 3 kW. This laser was used to carry out the experiments in stationary irradiation of the alumina samples. We focused it by a double focus lens (160 and 180 mm) in order to make the distribution of laser intensity in the cross-section of the beam more uniform. Treatments were made in continuous wave, with a laser power from 300 W to 3 kW (corresponding to irradiances of 1.69×10^4 and 1.69×10^5 W/cm^2, respectively) and exposition time from 5 ms to 1 s.

Second laser is a monomode Ytterbium-doped fiber laser (SPI, SP-200) emitting in continuous wave (CW, 1075 nm) mode with a power up to 200 W (3.5×10^6 W/cm^2). A processing head with galvanometric mirrors was used to scan the alumina surface.

Table 1
Laser operating conditions of the selected experiments analyzed in this work.

Trial name	Green	NIR Fib-1	NIR Fib-2	NIR Nd
Laser	Nd:YVO_4	Fiber laser (SPI)	Fiber laser (IPG)	Nd:YVO_4
Wavelength (nm)	532	1075	1070	1064
Focusing length (mm)	365	254	160 and 180	211
Working distance (mm)	365	254	210	211
Irradiance (×10^6 W/cm^2)	5800	3,5	0.169[b]	7200[b]
Fluency (J/cm^2)	81.2	–	–	144
Frequency (kHz)	20	CW	CW	10
Speed (mm/s)	25	300	0	25
Pulse time (ms)	0.014	–	20[a]	0.02
Number of laser passes	50	1	1	50

[a] Pulse time in the case of the fiber laser (IPG) refers to time of the sole pulse.
[b] Peak irradiance.

Last one, a diode end-pumped Nd:YVO_4 laser (Powerline E 20, Rofin-Sinar) running on its fundamental wavelength (1064 nm) and its second harmonic (532 nm) with a peak power of 140 and 120 kW respectively. Galvanometric mirrors were also used to scan the alumina surface. NIR laser treatments were made with a peak power from 20 kW (peak irradiance of 10^9 W/cm^2 or fluence of 20 J/cm^2) to 140 kW (7.2×10^9 W/cm^2 or 144 J/cm^2), frequency from 10 to 50 kHz, pulse time of 20 ns and speed of 25–1000 mm/s. On the other hand, green laser treatments were performed with a peak power of 42 kW (2×10^9 W/cm^2 or 28 J/cm^2) to 120 kW (5.8×10^9 W/cm^2 or 81.2 J/cm^2), 20 to 200 kHz, pulse time of 14 ns and speed from 25 to 1000 mm/s. We have carried out from 1 to 50 laser passes by both lasers in order to clearly see the difference between results, since average irradiance of these lasers is relatively lower.

The characteristics of these lasers as well as the operating conditions of the selected experiments discussed in this work are summarized in Table 1. For simplicity, we will refer to each experiment by its name in Table 1 (trial name).

All the experiments were carried out in a vacuum chamber in order to control the composition of the atmosphere. The experimental set-up is illustrated in Fig. 1. The experiments were performed under both inert (argon) and oxidizing atmosphere (air). We have previously made vacuum up to a pressure of 5×10^{-3} mbar. Then, with the vacuum pump still operating, we have injected a continuous flow of either argon or air directly on the surface of alumina where laser beam was going to irradiate.

2.3. Analysis

We have taken frontal and cross-section images by optical microscopy (Nikon, SZM-10) of the most important laser treated surfaces of alumina made in this work in order to clearly see the resulting colors of the marked areas and to compare them with the untreated alumina. To be precise, we show here optical images of treatments made by fiber laser (both SPI and IPG) and by Nd:YVO_4 laser on its fundamental wavelength (NIR) and its second harmonic (green laser). Samples of untreated alumina and alumina irradiated using both fiber lasers were also analyzed by Field Emission Scanning Electron Microscopy (FESEM JEOL JSM 6700F). High Resolution Transmission Electron Microscopy (HRTEM JEOL JEM 1010) was employed in order to characterize the microstructure of alumina irradiated by the fiber laser. With this aim, two lamellae were obtained by Focused Ion Beam (FIB HELIOS NANOLAB). This equipment employs a gallium ion beam to mill the surface of alumina with a sub-micrometer precision. As a result, thin slices of 5 × 10 μm can be taken from the samples. It allows us to study the microstructure of the cross-section of those lamellae. They must be thin enough so that they can be analyzed by HRTEM.

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