Formation of nanocrystalline foamy coatings by laser irradiation of glass-ceramic substrates in the nanosecond regime

Substrate temperature and wavelength dependence

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ABSTRACT

In this paper a study of the formation mechanisms of foamy coatings on the surface of glass-ceramic substrates produced by laser ablation is presented. Three laser systems emitting at 1064, 532 and 355 nm with pulse-widths in the nanosecond range were used. In the NIR range the formation of the coating is only possible when the temperature of the surface is higher than 300 °C. In this case, the generation is related to an increase of the layer in liquid phase produced in the interaction zone. However, when the sample is machined at 532 or 355 nm the local temperature and the pressure exerted over the interaction zone produce the generation of this coating, obtaining the layer at room temperature. Furthermore, in this case it is possible to reduce the energetic cost improving the efficiency of the process. Morphology, composition, microstructure and thermal properties of the layer are described.

1. Introduction

Laser processing is of great interest in the field of optics, electronics, microelectronics, aerospace and medicine. This technique is cost-effective compared to traditional methods and it may be applied to a wide range of substrates, such as metals, ceramics and semiconductors [1]. In the field of materials processing by laser several methods such as laser machining, micromachining, marking, drilling and pulsed laser deposition, have been developed in the last two decades [2,3].

The appearance of techniques for generating short and ultrashort laser pulses, ranging from tens of nanoseconds to a few femtoseconds, has allowed the availability of more powerful systems, with power densities that can reach TW/cm². These laser systems, with better features and lower prices, offer a high-speed/high-quality tool for laser machining, which is of great interest in both basic and applied research for scientific and technological purposes [3,4].

However, the foundations of the mechanisms involved in laser ablation are far from being well established. It is known that laser ablation depends on laser wavelength, optical features of laser beam, pulse-width regime and optical-thermal-mechanical properties of the substrate. Some theoretical descriptions have been developed by many authors to generalize the stages of the ablation process: laser

radiation absorption, heat transfer to the target, evaporation and gas-dynamic of the vapor [4–19].

Glass and glass ceramic substrates are commonly used in a variety of applications such as lasing systems, opto-informatic devices, microoptical components, mirrors and waveguides, the optical properties of which are of great interest [20–23].

Table 1
Thermo-physical properties of the glass-ceramic substrate.

Ceran Suprema	
Density (g/cm ³) ^(a)	2.5
Bending strength (MPa) ^(a)	110
Modulus of elasticity (×10 ³ MPa) ^(a)	95
Hardness Vickers	800
Thermal conductivity (W/mK) _{100 °C} ^(a)	1.7
Thermal diffusivity (m ² /s ×10 ^{−6}) _{25 °C}	0.85
Melting temperature (°K) ^(a)	1473
Optical absorption α _{1064 nm} (cm ^{−1})	3.52
Optical absorption α _{532 nm} (cm ^{−1})	28.37
Optical absorption α _{355 nm} (cm ^{−1})	62.15
Absorption length L _α = α ^{−1} _{1064 nm} (μm)	2840
Absorption length L _α = α ^{−1} _{532 nm} (μm)	352
Absorption length L _α = α ^{−1} _{355 nm} (μm)	161
Thermal diffusion length L _{th} 10 ns (μm)	0.18
Diffuse reflectance (1064 nm)	0.94
Diffuse reflectance (532 nm)	0.96
Diffuse reflectance (355 nm)	0.87

^(a) Schott technical data.

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Fig. 1. Laser processing arrangement for heating the sample from room temperature until 600 °C.

Furthermore, the aim of surface modification of these materials is very interesting for industrial applications, mainly for functional purposes. Modification in the mechanical properties can be applied to improve the wear resistance or the variations in the thermal properties can be used like thermal-barriers, heat-conductor tracks and so on.

In a previous work, we presented the influence of the substrate temperature in the generation of a foamy coating when a glass-ceramic is machined by laser ablation in the NIR range [24].

In this work we present the different formation mechanisms of this coating in function of the wavelength of the laser beam.

2. Experimental

2.1. Laser processing

To study and compare the machining process under different wavelengths three commercial laser systems were used:

- A diode-pumped Q-Switch Nd:YAG laser system (E-line 20, Rofin-Sinar). This system operates at its fundamental wavelength, 1064 nm, in Gaussian mode with a beam quality factor $M^2 < 1.3$ and a maximum mean power of 11 W. A beam expander 5× before the galvanometric mirrors and an optical lens with focal length of 100 mm placed at the output was used.
- A diode-pumped Q-Switch Nd:YVO₄ laser system (TruMark 6230, Trumpf). This system operates at a wavelength of 532 nm, Gaussian mode TEM₀₀ with a beam quality factor $M^2 < 1.2$ and a mean power of 7.2 W. An optical lens with focal distance of 160 mm was used.
- A diode-pumped Q-Switch Nd:YVO₄ laser system (PowerLine E20 THG, Rofin-Sinar). This system operates at a wavelength of 355 nm, Gaussian mode TEM₀₀ with a beam quality factor $M^2 < 1.3$ and a mean power of 2 W with an optical lens with focal distance of 160 mm placed at the output of the system.

The three laser systems are equipped with a programmable galvanometer at the output of the cavity controlled by CAD software. In this way, the beam can be deflected making a bidirectional

Fig. 2. Topographies and profiles of the machined areas. (a) At room temperature and (b) 600 °C.

movement in such a way that any predefined pattern and processing procedure can be performed. The machining process is controlled by the diode pump current I_p (in relation to peak power), pulse frequency f , linear speed V and distance between adjacent lines Δ .

As material, a glass-ceramic substrate, Ceran Suprema®, manufactured by Schott was used. Its properties are shown in Table 1.

The sample was placed at focal distance and the laser processing was carried out as follows:

When it was processed at 1064 nm, the substrate temperature was modified and controlled from room temperature up to 600 °C placing the sample at the focus point of an elliptical mirror with a halogen lamp at the other focus point, Fig. 1. A 250 W lamp allows an increase of the surface temperature above 700 °C in a working area of 1 cm². A thermocouple was used to check the temperature of the substrate. The sample was processed with pulses of 2.45 mJ, irradiance I of 83 GW/cm², frequency of 2 kHz, a linear speed of 1 mm/s with a distance between adjacent lines of 10 μm.

When it was machined at 532 and 355 nm, the processing was carried out at room temperature. For 532 nm the processing was performed with pulses of 0.27 mJ, an irradiance of 28 GW/cm², using a working frequency of 20 kHz, a linear speed of 25 mm/s and a distance between adjacent lines of 10 μm.

For 355 nm the sample was processed with pulses of 130 μJ, an irradiance of 8.5 GW/cm², a working frequency of 15 kHz, a linear speed of 60 mm/s and a distance between adjacent lines of 10 μm.

2.2. Characterization techniques

The microstructure and composition has been determined by means of scanning electron microscopy (SEM) using a JEOL JSM6400

with EDS analysis. Superficial topography, profile measurements and photography have been carried out with an optical confocal microscope Nikon Sensofar Plμ2300 and a stereoscope microscope. Transmission electron microscopy (TEM) images and electron diffraction patterns were obtained using a JEOL 2000 FXII microscope.

Diffusivity measurements have been determined between room temperature and 500 °C using a Holometrix ThermoFlash 2200 laser system. Crystalline phases were determined by XRD analyses with a Bruker D8 Advance diffractometer. Absorbance spectrum and diffuse reflectance were measured using a double beam spectrophotometer UV–Vis–IR Cary 500 Varian.

3. Results and discussion

It is possible to produce foamy coatings on the surface of glass-ceramic substrates when they are machined by means of pulsed lasers in the nanosecond range [25]. Depending on the working parameters of the laser system, on the optical properties of the laser beam and on the temperature of the substrate, a porous and crystalline coating can be generated on the surface during the ablation process.

3.1. Substrate temperature dependence

When the laser wavelength is on the NIR range, the coating formation depends on the temperature of the substrate [24]. The topography of Fig. 2-(a) depicts how, at room temperature, laser machining generates a groove on the surface. With these working conditions the depth reached is around 300 μm. However, with the same working conditions, when the temperature of the surface is higher than 300 °C a foamy coating that protrudes from the surface

Fig. 3. Frontal (a) and cross-section view (b) of the foamy layer generated at 600 °C.

Fig. 4. Micrographs of the particles removed at room temperature (a) and 600 °C (b).

approximately 100 μm is produced. Fig. 2-(b) shows the topography and the profile obtained by machining at 600 $^{\circ}\text{C}$. In Fig. 3-(a) and -(b) frontal and cross-section views of this coating can be observed. The white color of the coating, produced by the crystallization process carried out during the laser processing, gives a high contrast if compared to the black color of the former. Furthermore, the surface of the coating is very irregular, with a mean roughness R_a of 7.04 μm , and the inside is porous with a thickness that can reach about 500 μm .

During the laser ablation process at room temperature the material is removed by the thermal mechanisms activated by the laser beam. They essentially consist in the absorption of the laser energy and subsequent evaporation and ejection of the material. Fig. 4-(a) shows the particles ejected at room temperature. However, when the temperature of the substrate is increased and the foamy coating is generated, the size of the particles ejected increase. Fig. 4-(b) shows the size of the particles produced during the laser processing at 600 $^{\circ}\text{C}$. The angular morphology of the particles points out that they are caused by a fracture process. During the laser processing, the laser pulses are overlapped. The linear distance between consecutive pulses is obtained by the quotient V/f , where V is the scanning speed and f is the frequency. The lateral overlap is the distance between adjacent lines, Δ . Thus, during the coating formation the pulses overlapping generate the particles by fracture of the new coating, being ejected from the interaction zone.

During the ablation process, a thin layer of material in liquid phase is formed in the interaction zone [2], Fig. 5-(a). The recoil pressure produced in the process squeezes the liquid out from the interaction zone and the material is removed from the surface via evaporation and liquid phase expulsion. The thickness of liquid phase, h_l , and recoil pressure, P_{rec} , can be expressed as [2]

$$h_l \propto (D)^{1/2} \left(\frac{\Delta H_v}{I_a} \right)^{1/4} \quad (1)$$

$$P_{rec} \approx 10^{-5} I_a \quad (2)$$

where D is the thermal diffusivity, ΔH_v the enthalpy of vaporization, and I_a the absorbed laser intensity.

Since the variations of thermal diffusivity and enthalpy of vaporization with temperature are negligible, the thickness of the molten layer and the recoil pressure depend mainly on the absorbed irradiance.

Fig. 5. Scheme of ablation process and molten layer of thickness h_l formed in the interaction zone (a). The thickness increases when the surface temperature of the glass-ceramic substrate is heated while machined using a laser system emitting at 1064 nm.

Fig. 6. Absorption spectrum of the glass-ceramic substrate.

Taking into account the working conditions and the laser features, in this case the ablation process is a photothermal–mechanical one. Since the melting temperature of the glass ceramic is approximately 1200 $^{\circ}\text{C}$, by increasing the temperature the vibrations of the ions in the lattice increase and the material acquires a pseudo-plastic character. This fact together with the larger size of the particles ejected which shield the incoming irradiation produce a diminution in the effective irradiance and so, in the recoil pressure produced, resulting in an increase of the thickness of the layer in liquid phase present in the interaction zone, Fig. 5-(b), generating the foamy coating.

3.2. Wavelength dependence

The formation of the foamy coating is also possible when the wavelength of the laser beam is in the green or in the UV range. Furthermore, it is produced at room temperature, reducing the energetic cost of heating the sample.

In this case, the formation of the foamy coating is in relation with the variation of the absorbance of the glass-ceramic substrate with the wavelength. Fig. 6 shows how the absorbance of the material decreases with the wavelength, in such a way that the optical absorption α for 355 nm is 17 times greater than for 1064 nm, Table 1.

Fig. 7. Plain view of the foamy layer obtained machining with a laser system emitting at 532 nm.

As the absorption coefficient increases the absorbed irradiance and the absorbed power per unit of volume $(1-R) \cdot \alpha \cdot I$ will be higher. Taking into account the values of diffuse reflection R and the optical absorption in Table 1, this power density is about 17.52, 31.77 and 68.67 GW/cm³ for 1064, 532 and 355 nm respectively. According to the Eqs. (1) and (2), when the substrate processing is carried out with a lower wavelength the pressure increases and a diminution in the thickness of the layer in liquid phase is produced. Furthermore, the temperature on the surface can be expressed as [6]

$$\bar{T}_n \approx 2T_m(\tau_L f)^{1/2} \quad (3)$$

where $T_m \propto (I_a(D\tau_L)^{1/2})/k$, τ_L is the pulse width, f the working frequency, D the thermal diffusivity and y k the thermal conductivity.

Thus, an increase in the absorbed irradiance produces a higher temperature on the surface of the substrate, $\bar{T}_n$.

In this way, laser processing at 532 nm or 355 nm produces a local increase in the temperature of the substrate and in the recoil pressure exerted over the substrate, inducing a growth of the crystalline phase of the glass-ceramic substrate and generating the foamy layer. In these cases, the size of the particles ejected during the process is negligible if compared to the ones ejected at 1064 nm and high temperature.

Fig. 7 depicts a plain view image of the foamy coating produced using a laser system emitting at 532 nm. The coating produced by this laser is different than the one produced at 1064 nm. Local heating produces a texture on the surface of the coating that cannot be obtained using the NIR laser beam, the heating of which is produced in the whole surface. The micrograph in Fig. 8-(a) shows a detail of the texture produced by scanning direction, indicated by an arrow, of the laser beam during the processing. In the micrograph of Fig. 8-(b), it can be observed that the thickness of the layer is around 300 μ m and, as in the previous case, presents high porosity.

In order to compare the energetic yield needed in the formation of the coating, the energy delivered per square millimeter was calculated by means of the pulse energy and the dynamic parameters of the process, i.e., frequency, linear speed and distance between adjacent lines resulting in 29.4, 0.86 and 0.42 J/mm² for 1064, 532 and 355 nm respectively.

Table 2

Composition of the glass-ceramic substrate and foamy coating in wt.%.

	O	Mg	Al	Si	Ti	Zn	Zr
Ceran Suprema	65.82 $\pm$ 0.12	0.52 $\pm$ 0.15	7.58 $\pm$ 0.23	24.47 $\pm$ 0.40	0.87 $\pm$ 0.16	0.56 $\pm$ 0.31	0.19 $\pm$ 0.39
Foamy coating	65.74 $\pm$ 0.20	0.58 $\pm$ 0.25	7.37 $\pm$ 0.22	24.74 $\pm$ 0.39	0.82 $\pm$ 0.16	0.43 $\pm$ 0.30	0.32 $\pm$ 0.23

Fig. 8. Frontal (a) and cross-section micrographs (b) of the foamy coating produced with a laser system emitting at 532 nm.

Thus, as the processing is carried out at lower wavelength, the absorption of the laser radiation is favored, obtaining a foamy coating without the requirement of heating the whole sample and being possible to process at higher speed and entailing a lower energetic cost.

3.3. Compositional and micro-structural characterization

The elemental composition of the layer was analyzed by semi-quantitative EDS microanalysis, concluding that the composition of the foamy coating is the same of the former, Table 2.

A glass-ceramic substrate consists of a crystalline phase in a vitreous phase. To check possible variations induced in the crystalline phase by the laser processing, a sample of the foamy coating was analyzed by XRD and compared with the glass-ceramic one. The diffractograms obtained, Fig. 9, show that in both cases the crystalline phase is the same and is composed by crystals of $\text{MgAl}_2\text{Si}_4\text{O}_{12}$, the size of which is slightly larger in the foamy coating.

Samples of this coating were observed using transmission electron microscope TEM. As Fig. 10 shows, this layer is formed by crystals, pointed out with arrows, embedded into an amorphous matrix. In Fig. 11-(a) is presented one of these crystals, the diffraction pattern of

Fig. 9. Diffractograms of the glass-ceramic substrate former, Ceran Suprema, compared with the one obtained for the foamy coating.

which shows its crystalline nature and corroborates the phase obtained by XRD, Fig. 11-(b). The dimensions of these crystals can vary between 30 and 76 nm.

Finally, the thermal properties of the layer were analyzed comparing the thermal diffusivity of the glass-ceramic with respect to the processed sample. As Fig. 12 shows, the diffusivity was tested

Fig. 11. Detail of one crystal (a). The diffractogram shows its crystalline nature (b).

between room temperature and 500 °C. The presence of the crystalline phase favors the heat conduction and furthermore, predominates over the pores present in the layer. In this way, the diffusivity of the processed sample is higher than the glass-ceramic one in the whole range of temperatures.

Fig. 10. TEM micrograph of a fragment of the foamy coating. The crystals, pointed out by arrows, are embedded in an amorphous matrix.

Fig. 12. Thermal diffusivity of the foamy coating compared with the glass-ceramic former.

4. Conclusions

The formation of foamy coating as a function of the wavelength of the laser beam has been investigated.

The formation mechanism of this layer is different depending on whether the sample is processed with laser beams emitting at 1064 nm or at 532 and 355 nm. In the NIR range the formation of the foamy coating takes place only if the surface of the sample has been heated beyond 300 °C. In this case, a decrease in the recoil pressure leads to an increase in the thickness of the layer in liquid phase present in the interaction zone generating the foamy coating.

When the sample is processed at 532 or 355 nm, the formation is related to the increase in the absorbance of the glass-ceramic substrate at these wavelengths. In these cases, the better absorption produces a local increase in the recoil pressure and in the temperature of the sample, inducing a growth of the crystalline phase of the glass-ceramic substrate and generating the foamy layer. Furthermore, this process is carried out at room temperature, avoiding the heating of the whole sample and thus, reducing the energetic cost.

The processing at these wavelengths allows the formation of the coating to be produced at a higher linear speed. At 355 nm the layer can be obtained at 60 mm/s while at 1064 nm it is produced at 1 mm/s. The efficiency of the process is also improved machining with lower wavelengths. The formation of the layer requires 29.4 J/mm² for 1064 nm and only 0.42 J/mm² for 355 nm.

The composition of the layer is the same as the former and is made up of the same crystalline phase of the glass-ceramic substrate, MgAl₂Si₄O₁₂, immersed in amorphous material, the size of which is slightly larger than in the glass-ceramic.

Despite the presence of pores inside the layer, thermal diffusivity test showed that the crystalline phase favors the heat conduction between room temperature and 500 °C.

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