

Excimer laser-induced microstructural changes of alumina and silicon carbide

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Surface treatments with a KrF excimer laser were applied on alumina and silicon carbide ceramic materials. Results on the surface modifications induced by laser were related to the processing parameters: laser fluence (1.8 and 7.5 J/cm²), number of laser pulses (1 to 500), frequency (1 to 120 Hz), pulse duration (25 ns), sample speed under the laser beam and working atmosphere. It was ascertained that alumina can be laser treated under air, while silicon carbide needs an inert atmosphere to avoid surface oxidation. Microstructural analyses of surface and cross section of the laser processed samples evidenced that at low fluence (1.8 J/cm²) the surface of both ceramics is covered by a scale due to melting/resolidification. At high fluence (7.5 J/cm²) there are no continuous scales on the surfaces; material is removed by decomposition/vaporisation and the depth of material removal is linearly dependent on the number of pulses. On alumina surface, a network of microcracks formed, while on silicon carbide different morphologies (flat and rugged areas, deposits of debris and discontinuous thin remelted scales) were detected. The evolution of surface morphology and roughness is discussed with reference to composition, microstructure and physical and optical properties of the two tested ceramics and to the laser processing parameters. © 2000 Kluwer Academic Publishers

1. Introduction

Laser surface processing of ceramics is an area of considerable technological importance for several structural, tribological, optical and electronic applications. For this reason, efforts have been made to alter the surface properties of ceramics using laser beams [1–9] and to test laser machining of ceramics [10–13]. Lasers, in fact, are ideal tools for fabricating small diameter high aspect ratio holes at designated locations, for obtaining ceramic alloys and coatings, for cutting, scribing, etc., thereby allowing flexible machining that can tailor surface properties of products and can heat treat or machine components when other methods cannot be employed. The possibility of controlling the technological parameters of radiation make it possible to obtain unique surface structures. The drawback is strength deterioration due to cracks formation caused by thermal shock [8, 12].

Excimer-laser irradiation, in particular, provides high peak powers, which strongly modifies the near-surface region of ceramics. The short wavelengths of excimer lasers (193–351 nm) correspond to high photon energies (3.5–6.4 eV) which are efficiently absorbed by a wide band gap materials as most of the ceramics; the energy of the laser photon is sufficient to break many of the ceramic atomic bonds. This is significant as to remove materials with light from longer wavelength lasers such as Nd : YAG and CO₂ requires great photon absorption

to break down constituent molecules: the high temperature so developed leads to undesirable effects such as combustion, melting, flow and boiling of the surrounding material. Light from pulsed excimer lasers rapidly heats the surface that remains at a temperature above the melting point for a period of 10–100 ns. After this time the surface rapidly cools through heat transfer into the bulk at rates of the order of 10⁸–10⁹ °C/s [1]: this allows shallow thermal penetration depths in the range 0.1 ÷ 10 μm [5]. The high temperature rise caused by absorption of a large number of laser photons in a short depth vaporises the top surface layers of ceramics. Moreover a plasma is generated by laser/material interaction which can absorb energy from the beam and transmit it to the sample through thermal conduction or direct emission of infrared radiation. This results in an increased absorption of beam energy and consequent decrease of the material breakdown threshold. Actually, when a material is exposed to a sufficiently intense laser beam, an irreversible alteration of the material occurs at atomic level and on a microscopic level.

All phenomena occurring, including energy absorption by solid, energy reflection from surface or transmission into the bulk etc., depend on processing parameters (energy, pulse duration, peak power, frequency and beam angle of incidence of the laser and working atmosphere) and on chemical, physical and optical properties of the material.

The considerable potentialities of laser techniques for ceramic treatments depend on optimization of processing conditions, which have to be based on knowledge of the phenomena occurring during laser beam/ceramic material interaction. In those systems for which excimer laser processing is an effective mean of surface modification, the process is rapid enough to be commercially viable.

The principal aim of this investigation is to study the effects of using a KrF excimer laser for surface treatment of alumina and silicon carbide materials. Several sets of experiments were conducted to investigate the surface microstructure modification depending on variables as laser energy, frequency, number of pulses, fluence, and environmental conditions.

2. Experimental

2.1. Starting materials

Two different technical grade ceramic materials were considered: alumina and silicon carbide. The main characteristics of these materials including roughness values of the surfaces (raw and polished) before laser treatments are resumed in Table I. Morphology characteristics are reported in Figs 1 and 2. The most relevant microstructural features of alumina (Fig. 1a, b) are: enhanced grain growth, presence of cracks, defects, large pores and voids. Secondary phases like aluminium silicate and aluminium titanate are due to the low purity level of the starting powders.

In Fig. 2a, b raw and polished surface of silicon carbide are shown: pores and voids up to 10 μm are distributed in the material. X-ray spectra showed polytypes of α -SiC, boron is present as it was added as sintering aid. The presence of silica derives from surface silica in the starting materials.

Surface laser treatments were carried out (at Centro Laser, Valenzano, Italy), using a KrF excimer laser (wavelength 248 nm, photon energy 5 eV). Several series of tests were done in order to investigate the effects upon surface microstructure of changing the following parameters: laser fluence (1.8 and 7.5 J/cm²), laser energy (0.4 to 1 J), frequency (1 to 120 Hz), number of pulses (1 to 500), sample speed under the beam (0 to 0.3 mm s⁻¹) and atmosphere (air or argon); fixed values of pulse duration (25 ns), spot size (1.8 \times 5.5 mm) and beam angle of incidence (90°) were selected.

The microstructure and microchemistry of the treated areas were analysed with scanning electron microscopy and microanalysis on surfaces and cross sections. Sur-

face roughness was also measured and related to the processing parameters. Material removal was estimated by the depth of treated areas.

3. Results

3.1. Microstructure variation on alumina

The microstructures developed on raw surfaces during tests conducted *under air* (fluence 1.8 J/cm²) evidenced the formation of a surface product that concentrated in areas with a higher amount of secondary phases. When the number of pulses was increased, the whole surface appeared coated with a progressively thicker layer resulting from melting/resolidification-recrystallization. Examples of microstructural evolution of alumina samples are shown in Fig. 3a–c: the material was kept still and exposed to an increasing number of laser pulses (10–200–500) with a fixed pulse energy and frequency. Other two sets of tests were done varying the pulse frequency (from 1 \div 120 Hz), with fixed pulse energy and number, and varying the pulse energy (0.4 \div 1 J) with fixed pulse frequency and number. Comparison of microstructural features revealed that the main parameter influencing surface evolution was the number of pulses, while less influence seemed associated with the variation of frequency and laser energy. After laser treatment, crystalline phases revealed by X-ray spectra were the same detected on the starting surfaces. On the other hand, EDS microanalysis revealed the following trend for impurity elements: when the number of pulses was rather limited (<50) there was a strong decrease of Ti, Si, Ca, Mg, and Na, while after a high number of laser pulses impurities like Na, Mg, Ca completely disappeared and Ti and Si showed a limited decrease.

After these preliminary results obtained in conditions of still sample and under air, another set of tests was carried out *under argon* and varying the speed of the sample under the beam, with fixed parameters of energy (0.5 J), frequency (10 Hz), laser spot (1.8 \times 5.5 mm²) and fluence 1.8 J/cm². The resulting surface morphology is shown in Fig. 4a–c. In samples treated with a high sample speed (1.8 mm s⁻¹) the surface starting morphology is still visible, but a partial melting, formed presumably on areas of secondary phase concentration, was also observed. Lowering the sample speed this phenomenon of melting and solidification became more and more evident until the whole surface was covered by a continuous layer. SEM micrographs of polished cross sections showed that layer thickness varied

TABLE I Characteristics of the materials used for laser treatment tests and values related to surface properties: Ra: roughness (cut-off 0.8 mm), Rt: maximum peak to valley heights

| Sample | Density % | Crystalline phases | Grain size (μm) | Impurities At% | Raw Surface roughness (μm) | | Polished Surface roughness (μm) | |
|-----------------|-----------|--|------------------------------|-------------------------------|---|---------------|--|---------------|
| | | | | | Ra | Rt | Ra | Rt |
| Alumina | ~95 | α -Al ₂ O ₃ , 10% Al ₆ Si ₂ O ₁₆ , traces Al ₂ TiO ₅ | 2–10 | Ti:~10, Ca~25, Si~7, Fe~1 | 0.8 \pm 0.1 | 9.3 \pm 2.9 | 0.3 \pm 0.1 | 5.9 \pm 1.5 |
| Silicon carbide | ~95 | α -SiC, traces SiO ₂ | 5–10 | B~5, Fe~0.1 traces: Na, Ca, K | 0.4 \pm 0.1 | 5.5 \pm 1.3 | 0.09 \pm 0.01 | 4.3 \pm 2.4 |

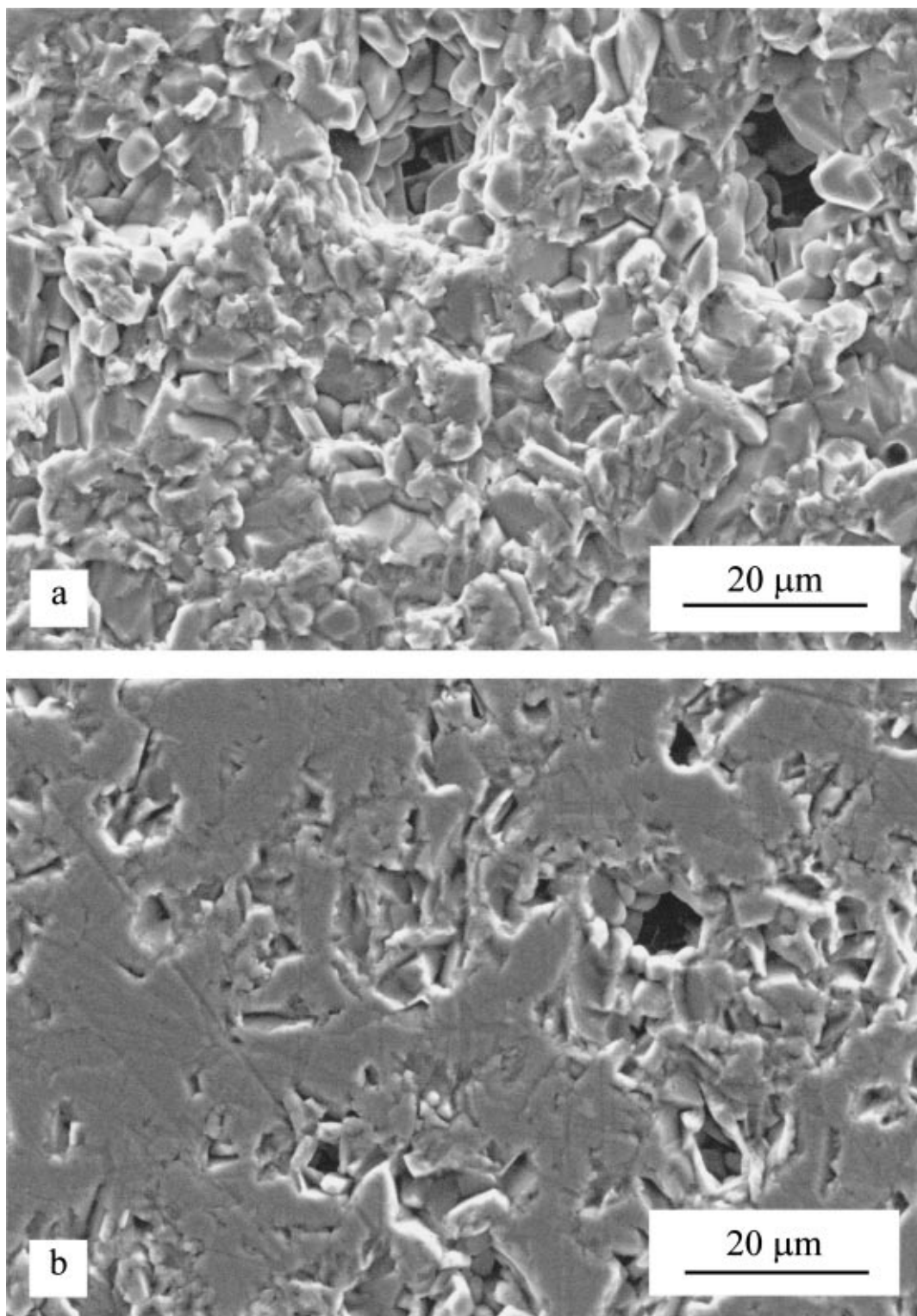


Figure 1 Morphology of raw (a) and polished (b) surfaces of alumina samples.

according to the initial surface roughness being higher in areas where the molten phase entered into surface voids or cracks (Fig. 5).

When laser fluence was raised to values of about 7.5 J/cm^2 , (Fig. 6a, b) surface material was removed by ablation, the original grain morphology disappeared and a network of microcracks appeared on a rather flat surface. Some melting occurred but the surface layer due to resolidification was very thin ($<1 \mu\text{m}$) and not continuous. EDS microanalysis and X-ray spectra showed a decrease of aluminium titanate, while alu-

mina and aluminium silicate were the same as in the starting samples.

3.2. Microstructure variation on silicon carbide

The laser treatment of silicon carbide surface *under air*, at various parameters of energy and number of pulses evidenced the formation of a surface scale, whose thickness increased with increasing number of pulses (Fig. 7a, b). This scale was mainly composed of silica, as evidenced by X-ray diffraction and EDS

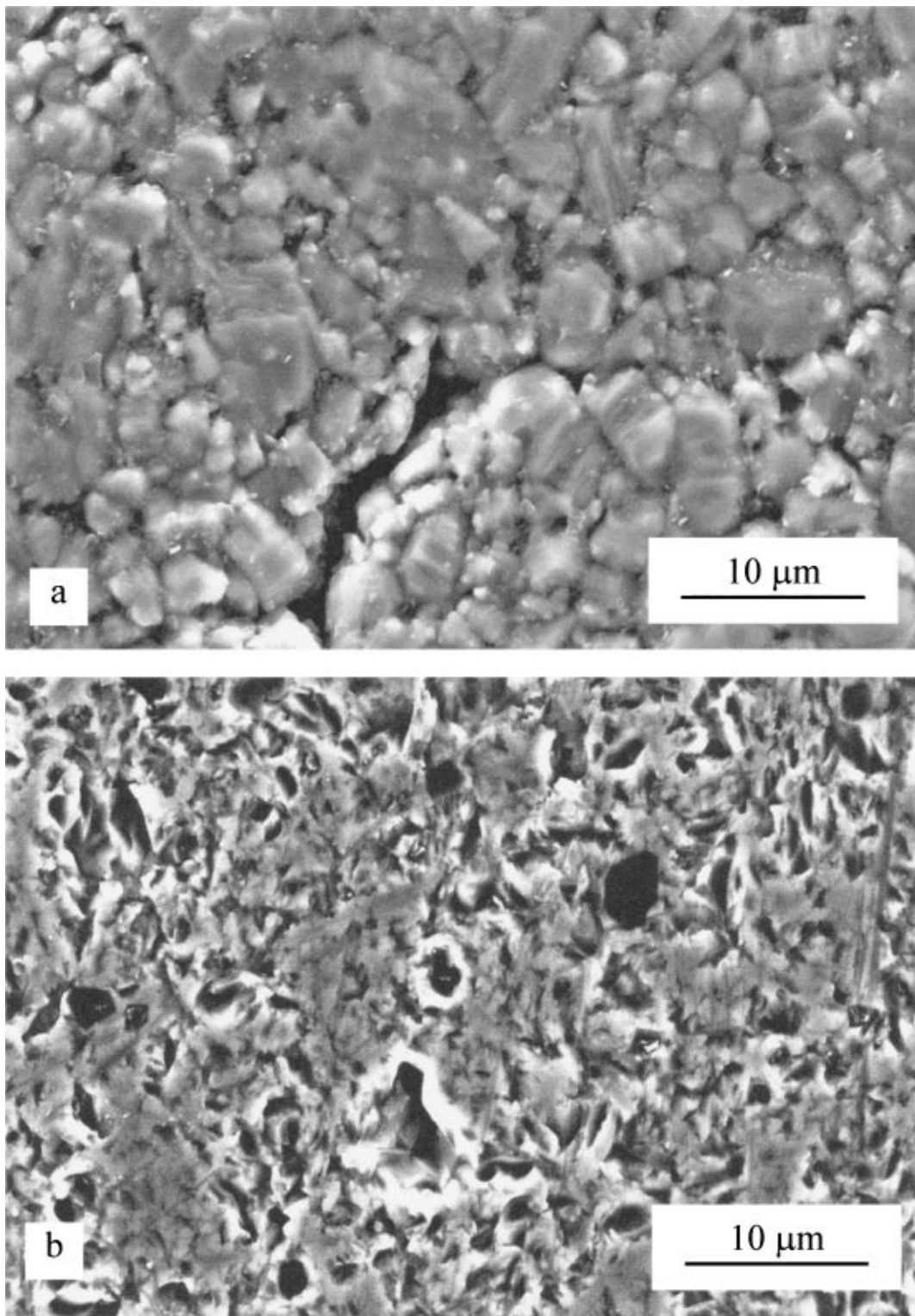


Figure 2 Morphology of raw (a) and polished (b) surfaces of silicon carbide samples.

microanalysis. The following reactions are likely to occur, as also previously observed [8]: $2\text{SiC} + \text{O}_2 (\text{g}) \rightarrow 2\text{SiO} (\text{g}) + 2\text{C} (\text{s})$; $2\text{SiO} (\text{g}) + \text{O}_2 \rightarrow 2\text{SiO}_2 (\text{s})$.

When the samples were treated *under argon*, at various sample speeds under the beam (energy 0.5 J, frequency 10 Hz, spot laser $1.8 \times 5.5 \text{ mm}^2$, fluence 1.8 J/cm^2), the reaction layer thickness increased with decreasing sample speed. In samples treated under a very low speed (0.09 mm s^{-1}) the surface was completely covered by this layer which appeared amor-

phous as it has solidified by a glassy melt. Cracks were also observed both on surface and polished sections under the amorphous layer (Fig. 8a, b). X-ray diffraction did not evidence new crystalline phases.

Samples treated with higher fluence laser pulses (7.5 J/cm^2) did not show continuous surface scales and cracks, but the morphology varied from flat to rugged (Fig. 9). Crystalline phases were the same of the starting material and microanalysis confirmed the absence of oxygen on sample surfaces.

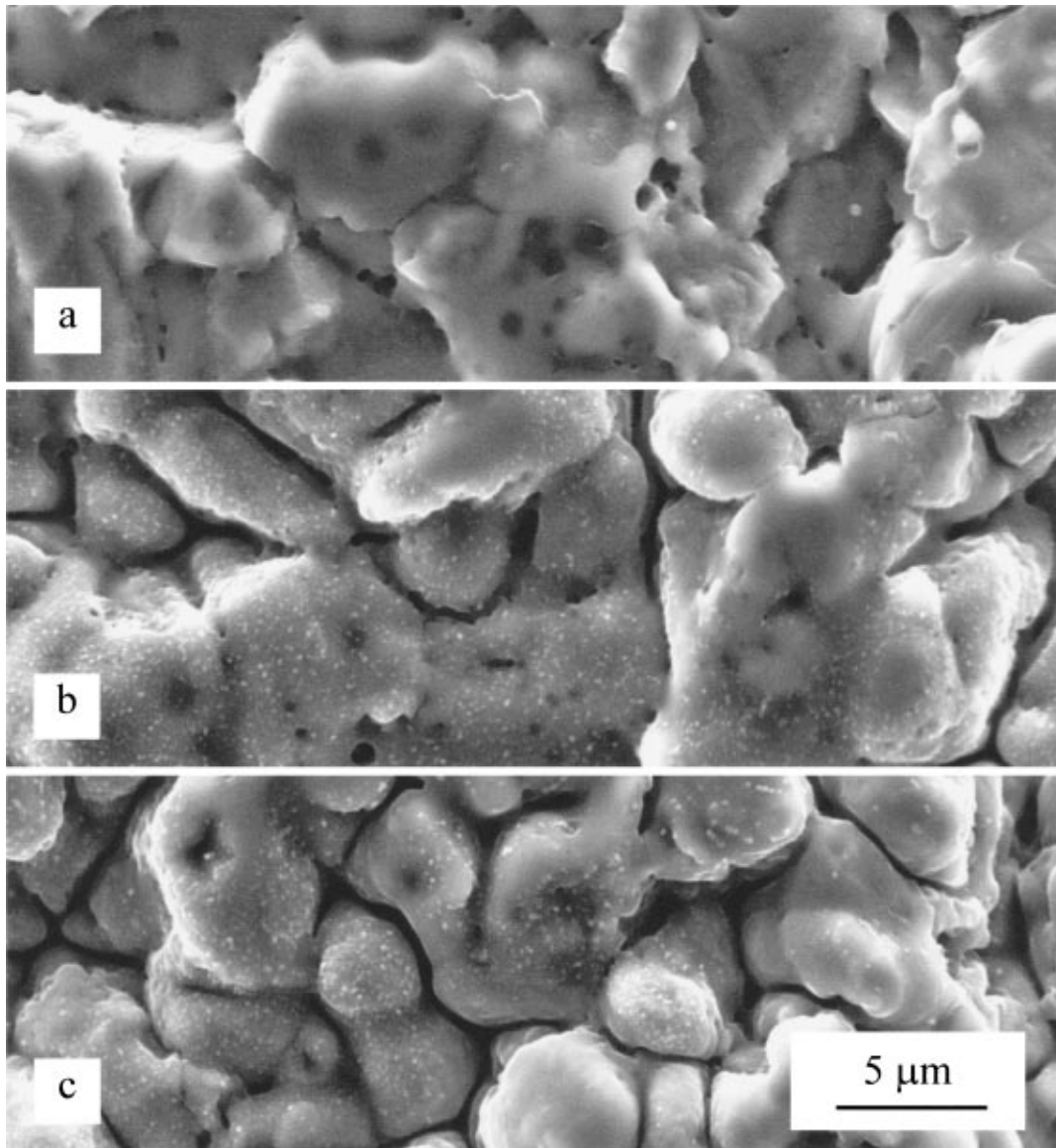


Figure 3 Surface modifications on raw alumina samples after (a) 10, (b) 200, (c) 500 laser pulses (with $E = 0.4$ J, $F = 10$ Hz, $fluence = 1.8$ J/cm²).

3.3. Surface roughness and material removal profiles

The values of surface roughness (Ra) and of peak-to-valley distance (Rt) (Fig. 10a, b relatively to treatment of raw surfaces at low fluence) slightly varied in comparison to the starting values, for both ceramics. Approximately all values fell in the range within the standard deviation of the starting ones. This is mainly due to the fact that starting roughness was rather low and laser treatment was probably not suitable to reduce it. In Fig. 11a, b, Ra and Rt values of polished surfaces laser treated under high fluence evidence that: i) on alumina, Ra slightly increased at low sample speed (partial overlapping of laser tracks), while Rt considerably lowered; ii) on silicon carbide, the values were the same as on the starting surface, except than at sample speed < 0.1 mm/sec, probably due to overlapping of tracks and presence of deposits at the track edges.

Plot in Fig. 12a, b showed the material removal at 7.5 J/cm² fluence for different pulse numbers in condition of steady sample. When the samples moved under the beam the pattern of groove and debris was repeated

resulting in a wavy morphology (Fig. 9a) dependent on grade of pulses overlapping (i.e. on sample speed). In Fig. 13 ablation depth in function of pulse number shows that material removal (depth of the tracks) has an approximately linear behaviour.

4. Discussion

Previous results suggest that, among the phenomena occurring during laser/material interaction, decomposition (vaporization) is responsible for material removal [13].

Generally, each combination of processing parameters for laser machining and material characteristics results in an interaction that can give rise to *surface melting* (on selected areas or on the whole surface) or *vaporization*. In both cases, threshold beam energies are required. Threshold energies are function of many factors such as: light wavelength, ceramic physical and optical properties, material impurities, energy absorption and re-emission by plasma, etc. As melting and vaporization are power-limited, laser effectiveness depends on the amount of incident power absorbed by the material.

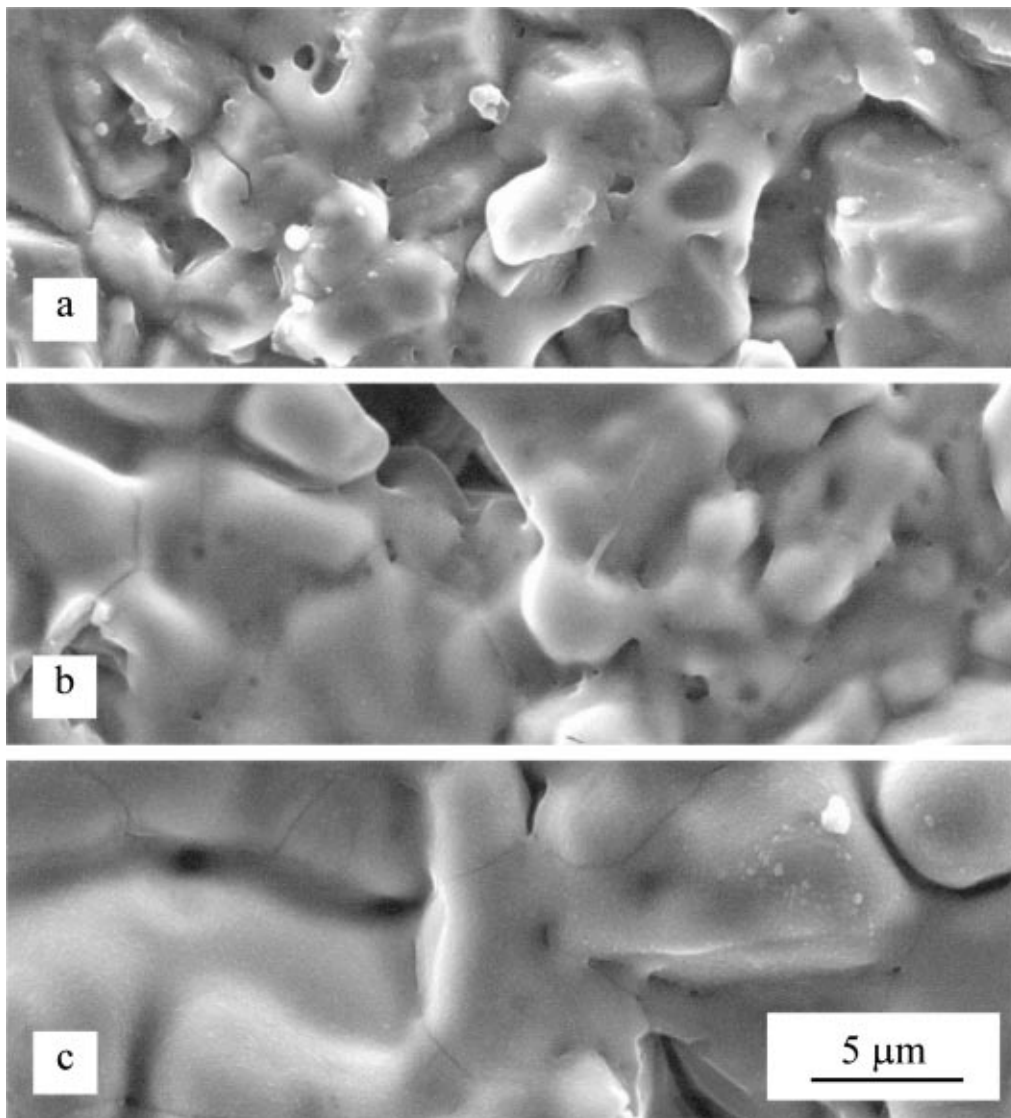


Figure 4 Surface modifications on raw alumina depending on sample speed under the beam of (a) 1.8, (b) 0.6, (c) 0.1 mm s^{-1} (with $E = 0.5 \text{ J}$, $F = 10 \text{ Hz}$, $\text{fluence} = 1.8 \text{ J/cm}^2$).

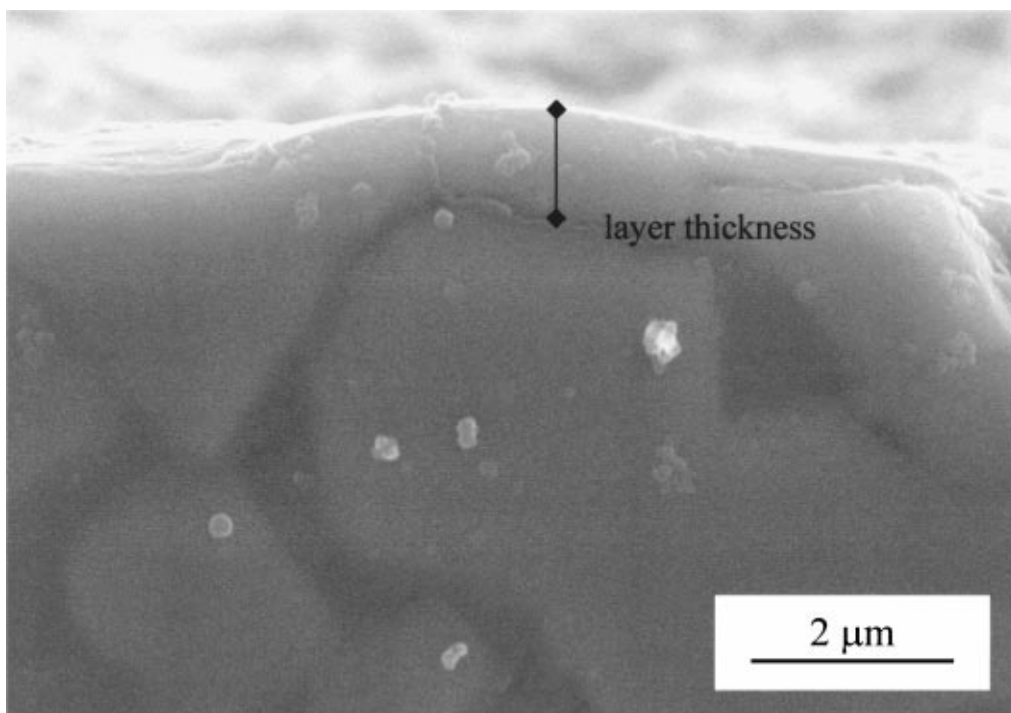


Figure 5 Cross section of raw alumina after treatment at $E = 0.5 \text{ J}$, $F = 10 \text{ Hz}$, $\text{fluence} = 1.8 \text{ J/cm}^2$, with sample speed 0.09 mm s^{-1} .

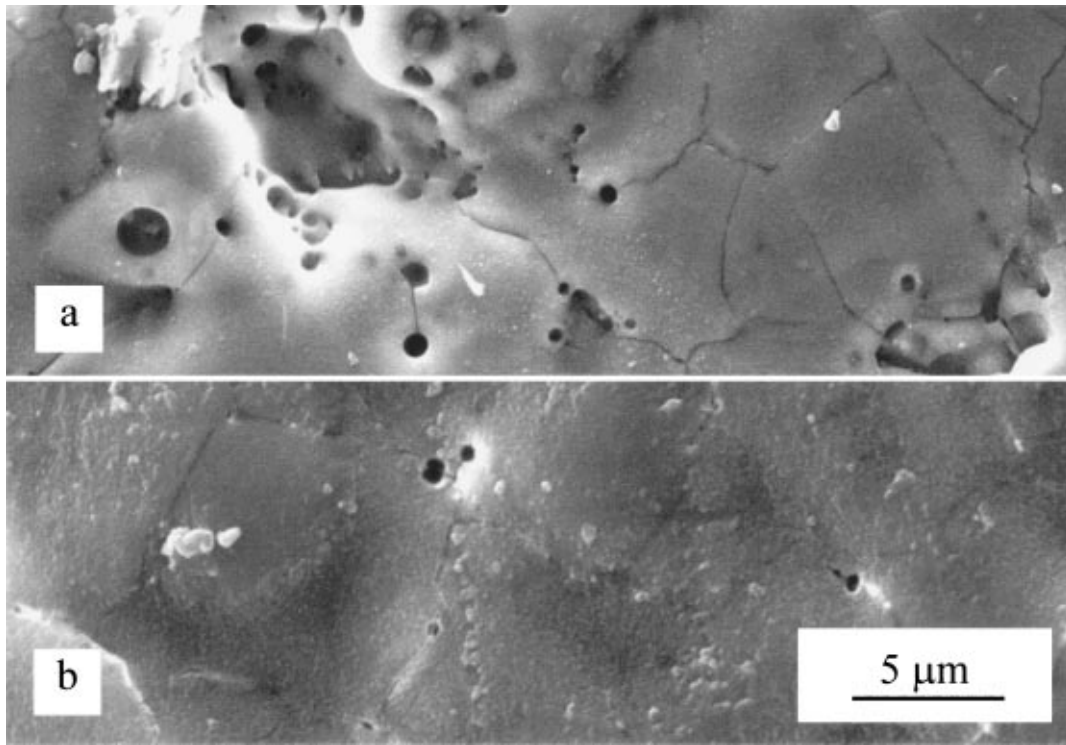


Figure 6 Laser induced surface modifications on polished alumina depending on sample speed: (a) 0.2, (b) 0.1 mm s⁻¹ ($E = 0.5$ J, $F = 10$ Hz, fluence = 1.8 J/cm²).

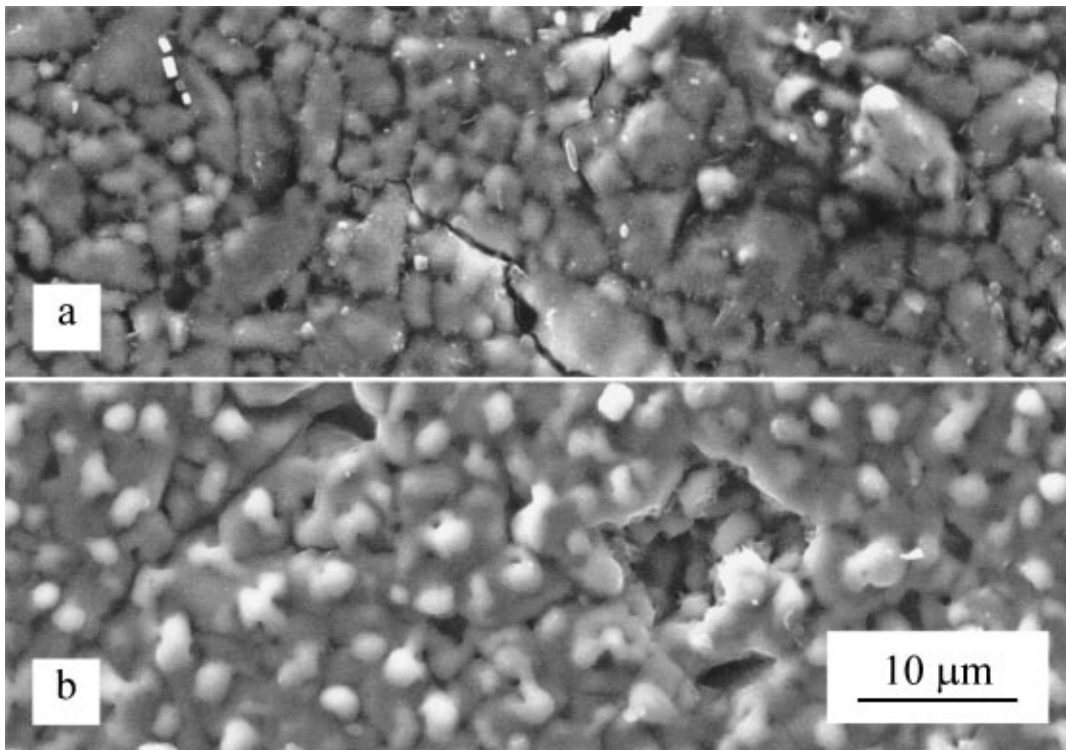


Figure 7 Surface modifications on raw silicon carbide samples depending on the number of laser pulses: (a) 10, (b) 100 laser pulses (with $E = 0.4$ J, $F = 5$ Hz, fluence = 1.8 J/cm²).

The short wavelength of KrF radiation (248 nm) corresponds to high photon energy (5.0 eV) which is well absorbed by SiC (band gap 1, 9 eV), while Al₂O₃ (band gap 6 eV) should be transparent to the 248 nm light. However polycrystalline sintered alumina has impurities such as grain boundary phases, inclusions, defects which absorb this radiation to some degree. On the other hand reflectance values (0.25 and 0.12 at 248 nm respectively for high purity sintered alumina and sintered

SiC) confirm that the main part of the energy supplied by the beam is absorbed.

No data on absorption depth was found for ceramics but, as in most metals is very low (7 nm in Al, 16 nm in Ti) it can be hypothesized that the absorbed energy is concentrated in a very thin layer, so that the light pulse acts essentially as a thermal pulse [1]. In this case, the effective pulse penetration depth can be calculated from the relationship $l = 2\sqrt{\tau D}$, where τ is the pulse length

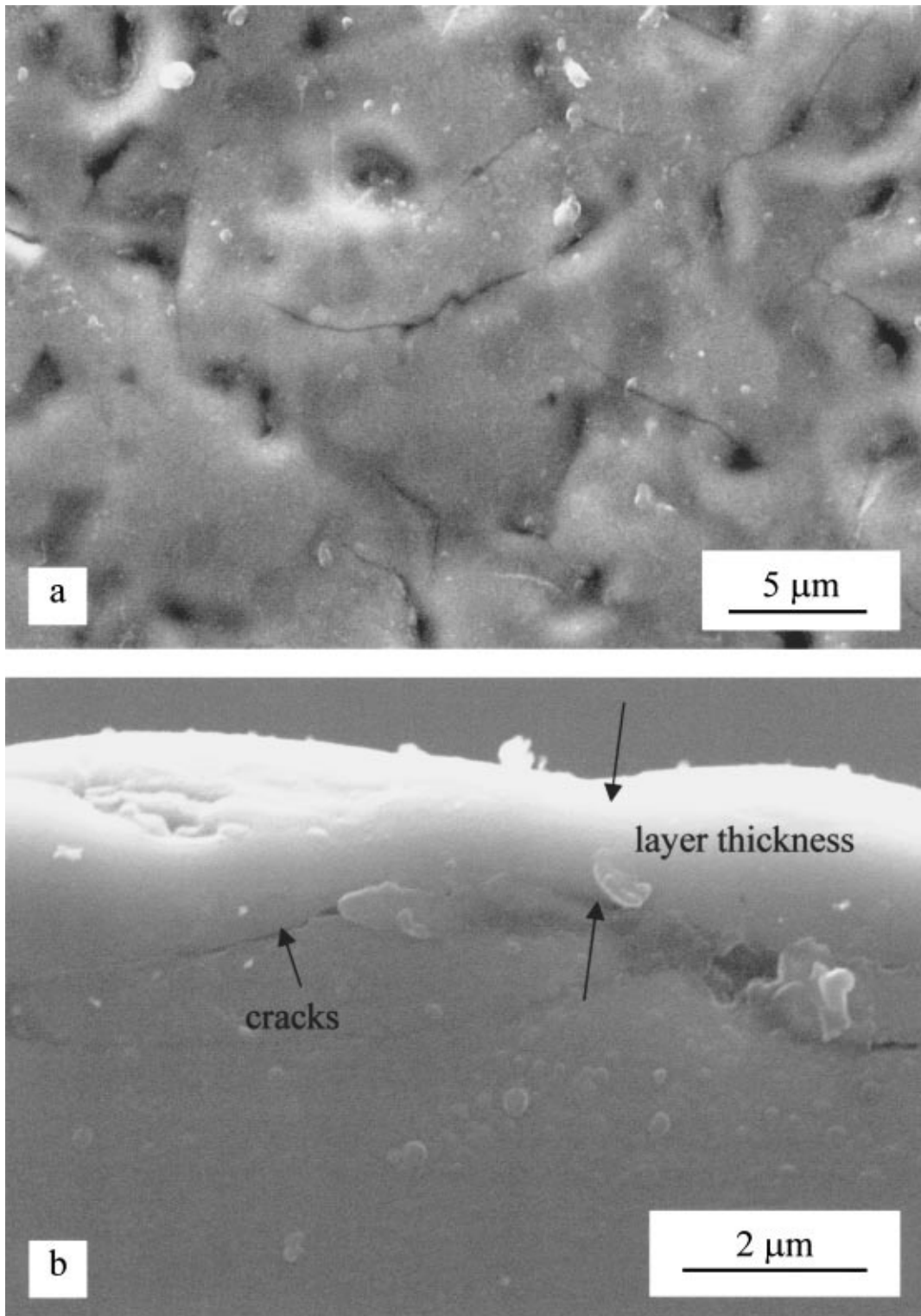


Figure 8 Surface (a) and cross section morphology (b) of raw SiC treated *under argon* (laser parameters: $E = 0.5 \text{ J}$, $F = 5 \text{ Hz}$, $\text{fluence} = 1.8 \text{ J/cm}^2$; sample speed: 0.09 mm s^{-1}).

and D the thermal diffusivity. Thermal diffusion distances depend on sample temperature, according to the decrease of thermal diffusivity with increasing temperature. As the absorbed energy is thermalized in a very short time compared to pulse length, it is assumed that very high temperatures are reached at the sample surface when it is exposed to the laser beam. Values of thermal diffusion distance l calculated at 1500°C were 150 nm for alumina 90% and $420\text{--}480 \text{ nm}$ for sintered silicon carbide. As l is so much larger than absorption depth, absorption processes do not affect the tempera-

ture distribution, so that the process can be considered as a simple heat pulse initially affecting the surface to the thermal depth l , and then being conducted into the bulk of the material [14]. The problem, then, is a one-dimensional heat flow from a surface source and it was calculated that temperatures well in excess the melting points can be obtained by laser with relatively modest laser pulse fluences [1].

In the reported SEM micrographs of the laser treated surfaces, irradiation of alumina and silicon carbide at fluence 1.8 J/cm^2 induced remelting, resulting in a

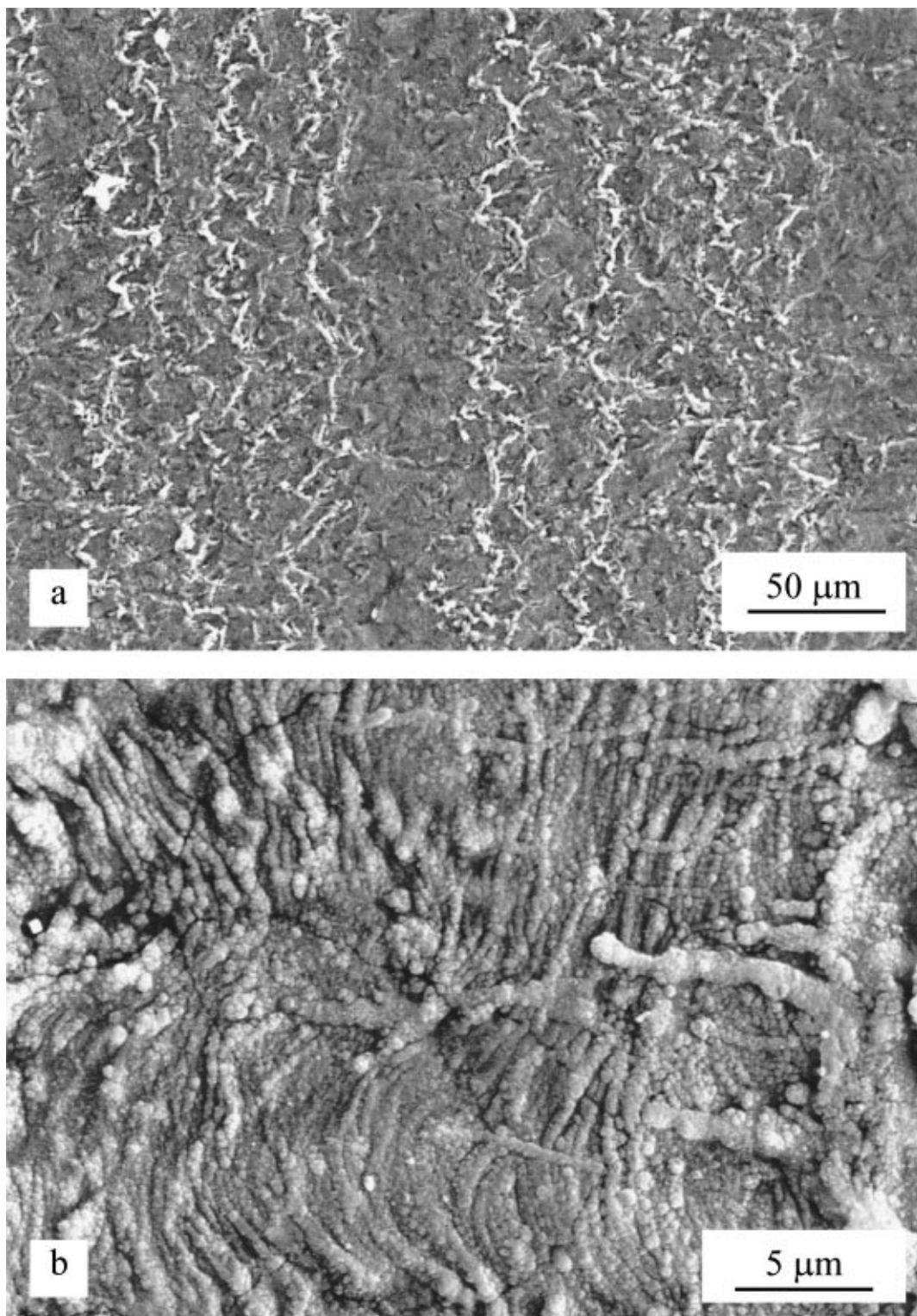
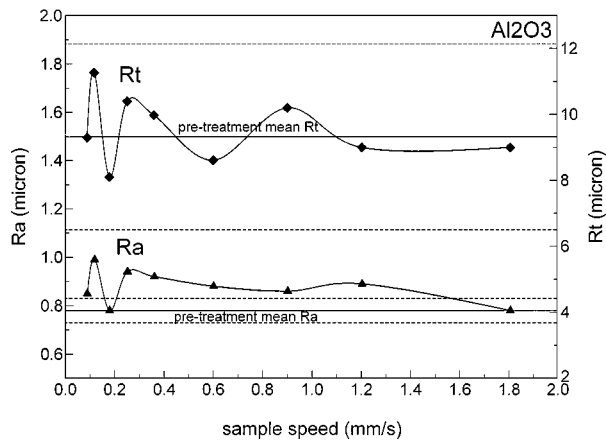


Figure 9 Surface morphology of polished SiC treated *under argon* (laser parameters: $E = 0.5 \text{ J}$, $F = 5 \text{ Hz}$, $\text{fluence} = 7.5 \text{ J/cm}^2$; sample speed (a) 0.2 , (b) 0.3 mm s^{-1}).

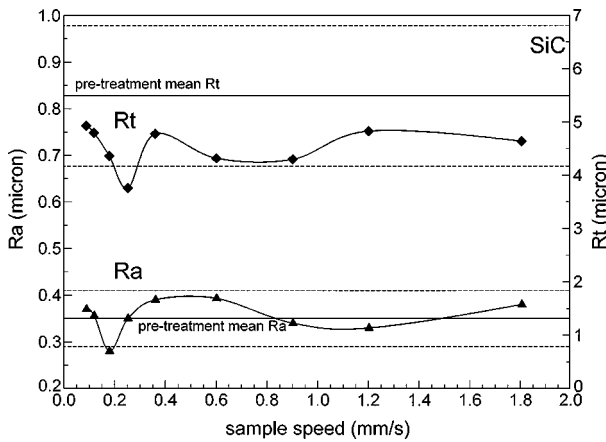
modification of porosity, grain size, secondary phases and flaws, and partial surface sealing of pores. The remelted layer thickness depended on laser pulse number and/or sample speed. In both materials a thickness of about $1.5 \mu\text{m}$ was observed, once the whole surface was completely covered by a remelt. Surface remelting of Al_2O_3 and SiC was accompanied by crack formation during cooling down from the melting temperature and crack density increased with the number of pulses. Laser remelting resulted also in reduction of

porosity. Moreover, in silicon carbide materials the surface composition was strongly related to the working atmosphere: when laser treatments were carried out in air, oxidation gave rise to a oxygen-rich, partially glassy surface scale.

In contrast on alumina samples, surface morphology and composition did not vary depending on the working gas (air or argon). Microanalysis of remelted zones in alumina indicates that impurity elements (Ca, Mg, Na) moved from bulk to surface and appeared more



(a)



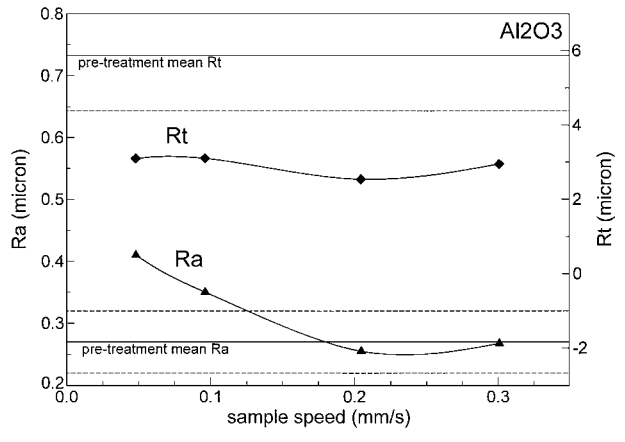
(b)

Figure 10 Raw Al_2O_3 (a) and SiC (b) surface roughness after laser treatment ($\text{fluence} = 1.8 \text{ J/cm}^2$) vs sample speed, compared to the range of values on untreated samples (area between dashed lines). Ra : mean roughness, Rt : peak to valley distance.

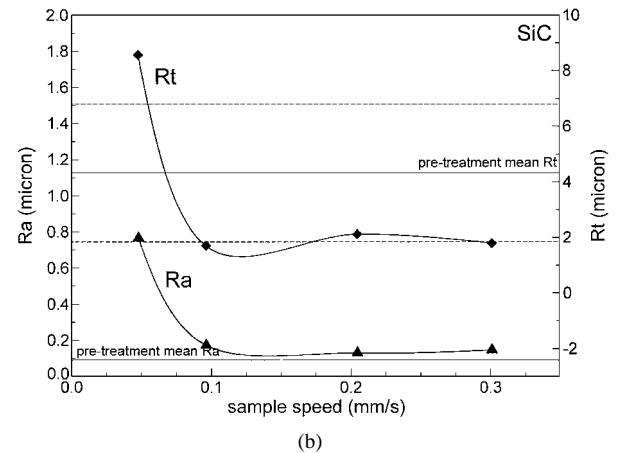
concentrated at the surface after low pulse number (<10) treatments. With increasing the pulse number, these elements progressively decreased up to a complete disappearance due to volatilization.

Melting phenomena similar to those observed in the present study were observed by other authors after irradiation of SiC and Al_2O_3 [1, 15] and a threshold laser fluence of 1.2 J/cm^2 for melting was reported [1]. For alumina, under energies $<1 \text{ J/cm}^2$ there was not a continuous coating by a melt layer [15].

At high laser fluence (7.5 J/cm^2), significant material removal occurred and the area around the laser spot evidenced fine debris deposit. After treatment alumina appeared brown and silicon carbide black. Generally physical ablation (vaporization) occurs behind threshold energy fluence: the irradiated material volume has to absorb enough energy to supply enthalpy for vaporization reaction. If the reaction is known, it is possible to calculate the power required to heat and decompose the material contained within the groove. The total enthalpy (ΔH) required to obtain decomposition is equal to the sum of enthalpy required to rise the temperature of the sample from room temperature to the critical temperature plus the enthalpy required to decompose the material [3]. The value of ΔH can be estimated using the equation $\Delta H = C_p \Delta T + \Delta H_R$, where C_p is the spe-



(a)



(b)

Figure 11 Polished Al_2O_3 (a) and SiC (b) surface roughness after laser treatment ($\text{fluence} = 7.5 \text{ J/cm}^2$) vs sample speed, compared to the range of values on untreated samples (area between dashed lines).

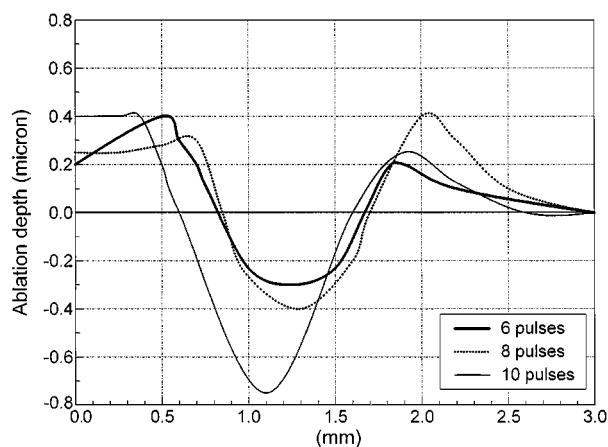
cific heat and ΔH_R is the heat of reaction and ΔT is the temperature increase.

Substituting the appropriate values in the above equation, the results are the followings:

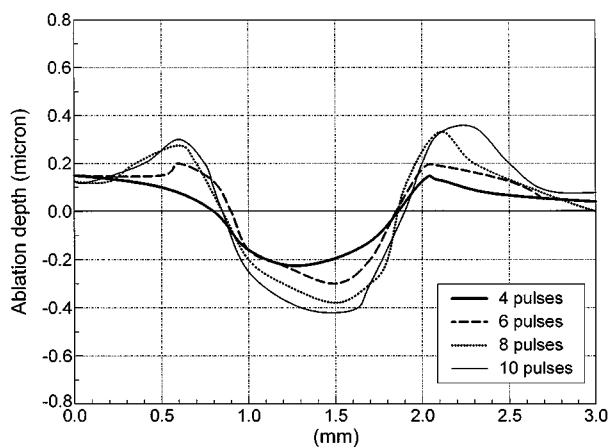
- in the case of alumina, assuming that it decomposes at 1950°C , ΔH results about $4 * 10^4 \text{ J/cm}^3$.
- in the case of silicon carbide, the estimation of ΔH is more uncertain as various values of its physical properties are found in literature. From these values, assuming that SiC decomposes to gaseous compounds at 2750°C , the value of ΔH results about $5.5 * 10^4 \text{ J/cm}^3$.

Under the hypothesis that laser beam energy is absorbed up to $1 \mu\text{m}$, the energy related to a unit volume of material is about $7.5 * 10^4 \text{ J/cm}^3$ for fluence 7.5 J/cm^2 i.e. high enough to decompose both alumina and silicon carbide. On the other hand for fluence 1.8 J/cm^2 , the energy supplied by laser is $1.8 * 10^4 \text{ J/cm}^3$, insufficient for both materials ablation.

Microstructure analysis confirmed that under beam fluence of 7.5 J/cm^2 in argon atmosphere, alumina underwent decomposition, leaving no surface remelted phase. Therefore, these experimental conditions were suitable for material removal by vaporization, even if remelting due to material redeposition from the plume or reaction between gas phase constituents and the hot



(a)



(b)

Figure 12 Surface profile on Al_2O_3 (a) and SiC (b) after treatment on still sample for different pulse number (laser parameters: $E = 0.5 \text{ J}$, $F = 5 \text{ Hz}$, $\text{fluence} = 7.5 \text{ J/cm}^2$).

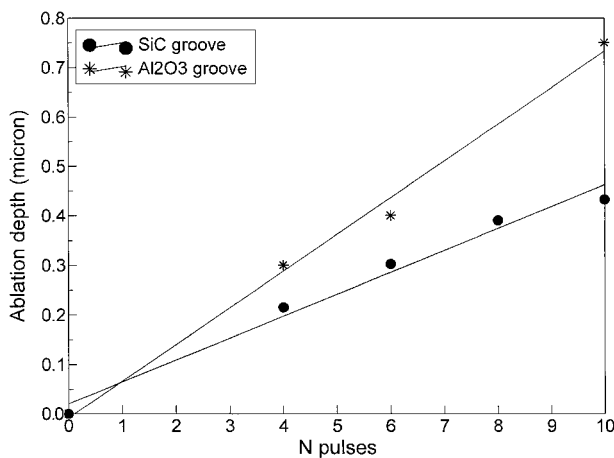


Figure 13 Ablation depth vs pulse number after treatment at fluence = 7.5 J/cm^2

surface can not be excluded. Another problem is the formation of a network of microcracks that can be related to the low thermal shock resistance of alumina.

In silicon carbide materials treated at 7.5 J/cm^2 , some remelting was still present, with a layer of about $1 \mu\text{m}$ thick. Across the laser track, morphology changed from smooth at the edges, to rugged in the center of the groove, according to pulse heat distribution. The irradiated area showed wave patterns normally deriving

from melting/resolidification. However, according to literature [15], after vaporization, the subsequent cooling down could have given rise to some silicon (with a lower melting point) covering resolidified SiC . If so, the Si layer should have been thin enough to allow elements detection (by microanalysis) as in the starting sample. Very few surface microcracks formed on surface.

On alumina and silicon carbide, at high laser fluence, reduction of surface roughness derived mainly from closure of surface pores. Material removal (provided that a sufficient energy is supplied for material vaporization) is directly related to pulse number (at still sample) or exposure time to the beam (i.e. the sample speed). Material removal is enhanced on alumina, probably owing to the absence of melting, in respect with silicon carbide, where a limited discontinuous scale of remelted phase was observed, under the experimental conditions.

5. Conclusion

The surface modification of alumina and silicon carbide components due to laser beam interaction evidenced the following aspects.

i) Silicon carbide has to be treated under inert atmosphere in order to avoid surface oxidation.

ii) At low fluences (1.8 J/cm^2), on both ceramics, surface melting and resolidification occurred. In conditions of steady sample the pulse number was the main factor influencing amount and thickness of the surface material interested in melting. Surface roughness did not improve after laser treatment, mainly because the starting roughness, particularly on polished surfaces, was very low.

iii) At high fluence (7.5 J/cm^2) material removal occurred by vaporization. A not continuous surface scale formed and in alumina local remelting was mainly associated with the presence of secondary phases in the starting material. The surface of alumina samples was cracked, while SiC surface showed a rugged morphology without cracks.

iv) Ablation depth was higher in alumina than in silicon carbide and approximately linear with increasing pulse number.

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