SURFACE MODIFICATION OF ORGANIC COMPOSITE AFTER LASER ABLATION

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SUMMARY : Pulsed laser, such as the second harmonic emission of a Nd^+:YAG laser at 532 nm, is used for surface modification of composite material consisting of elastomer and carbon black. Morphology and chemical compositions of the composite were probed by scanning electron microscopy (SEM). Microstructures such as conical, flat conical and dome-like structures were produced on the ablated surface at a pulse energy of 23 mJ/pulse and pulse width of 10 ns. For each of these microstructures, the origin of the ablated process is particularly addressed and a model describing their nucleation and growth process is proposed.

KEYWORDS : Nd^+:YAG laser, composite polymer, carbon black, ablation, surface microstructure

INTRODUCTION

In these two decades, numerous papers have reported the formation of microstructures on the polymer surface after laser ablation since an unusual roughness was noted in the first paper of polymer ablation by Srinivasan and Maye-Barton [1]. Nowadays, it is well-known that excimer laser ablation of polymers can produce a variety of morphological changes such as conical, granular, ripple, cone-like structures, and so on [2 - 7]. These morphological changes are growing in importance as surface modification of materials in industrial uses. The ablated surface with microstructures plays an important role, for instance, for improving adhesive bonding, controlling friction and wear, fabricating filtration, or aligning liquid crystal [8 - 11]. In particular, we are interested in surface modification of elastic composite materials by laser ablation, because the control of tribological properties such as friction and wear is directly correlated with microstructures on the surface as one of the most important factors. At present, mechanical processing has been a primary tool for the fabrication of microstructures. However, in the case of

elastic materials, the mechanical method is limited to sub-millimetre feature size because of difficulty in fabricating micro-structures on the visco-elastic surfaces of elastomers. Therefore, excimer laser ablation can be expected to be especially useful for surface modification of elastic composite materials. In the preceding paper [12, 13], we have reported the surface modification of elastic materials consisting of acrylate polymer and carbon black, as the results of the formation of cone-like microstructures by KrF excimer ablation at the fluence of 500 mJ/cm^2. In this paper, we report the formation of conical structures using the second harmonic of Nd$^+$:YAG laser, and discuss comparatively the mechanisms for the formation of different microstructure shapes between the Nd$^+$:YAG and KrF excimer lasers.

EXPERIMENTAL

Material

The samples of elastomer and carbon black composite were prepared by mixing 100 parts of acrylate co-polymer (-(CH_2-CH(CO-O-R)-)-, R = C_4H_9 and $C_2H_4OCH_3$) (PMA) (Nippon Mektron, PA404K) and 50 parts of carbon black (ISAF grade, particle size 18 - 30 nm) [12]. Composite samples (PMA/C) are kneaded with rolls, vulcanised after addition of the vulcanising agent and accelerator, and compressed into sheets under 100 kgf/cm^2 by precuring at 195°C for 3 minutes and postcuring at 165°C for 6 hours.

Irradiation procedure

Irradiation was performed at normal incidence angle using a Nd$^+$:YAG (LOTIS LS-2125) laser operated with a fluence of 250 mJ/cm^2 at 10 Hz. Each irradiation was performed in air.

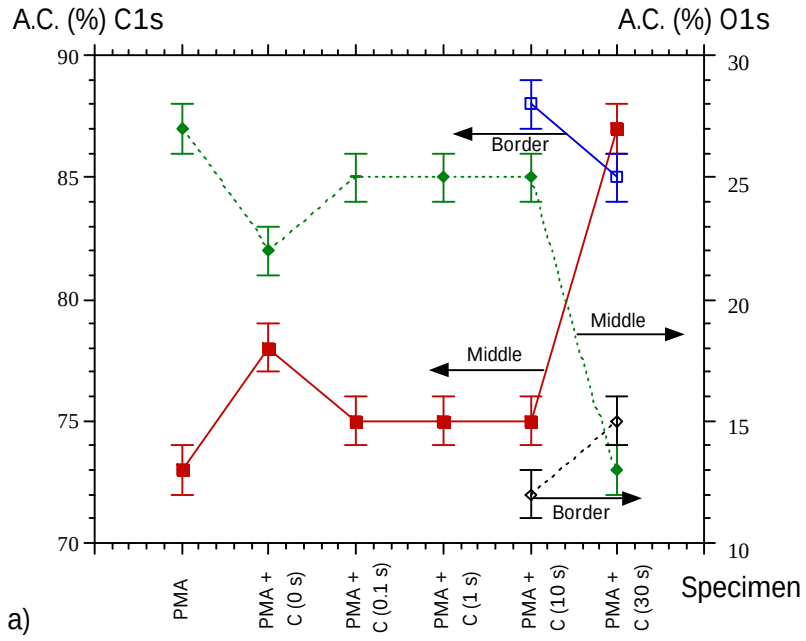
Methods

Ablated and non-ablated composite samples were analysed by scanning electron microscopy (SEM) using a Topcon JSM-6300F instrument. Plane view micrographs, normal incidence observation, and cross section micrographs, 80° tilted angle observation, were performed. Because of their rather good electrical surface conductivity, these samples were not coated with additional gold or carbon before SEM observation. XPS measurements were undertaken using a Perkin Elmer PHI 5600 instrument, using a monochromated Al Kα radiation sourcewithout charge compensation because of the rather good surface electroconductivities of all tested samples. In all the cases spectra (analysis size, 200 mm spot) were referenced to C1s peak of carbonyl group (C=O) at a binding energy (BE) of 289.1 eV. Data were acquired for the O1s (522-542 eV) and C1s (276-294 eV) regions. Deconvolution of the XPS spectra was achieved by fitting the data with a Gaussian/Lorentzian combination of peak shapes with variation in peak full width at half maximum (FWHM), energy position and height determined by an iterative program. The peak identification was determined by reference to an XPS data base or from compounds analysed in the same apparatus.

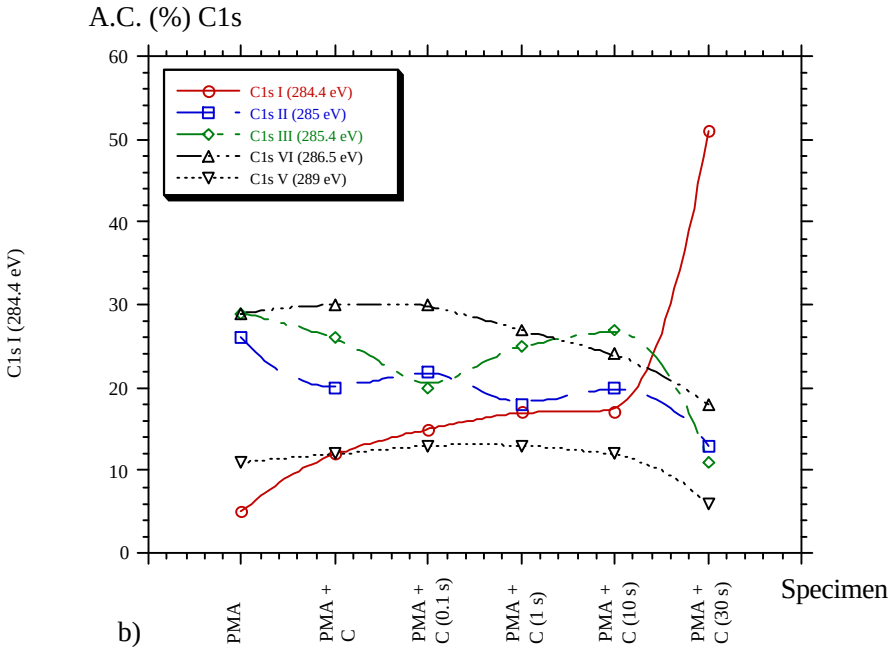
RESULTS

Chemical surface modification

As XPS by its nature is a surface sensitive technique even for organic materials, XPS always shows surface composition. It has to be noticed that the binding energy and the FWHM of the four carbons C1s and the two oxygen O1s are identical for the ablated and non ablated polymer.



a)



b)

Fig. 1 : Evolution with the laser fluence of a) the C1s and O1s atomic concentrations before deconvolution, and b) the five C1s atomic concentrations after deconvolution.

The evolution of the carbon C1s and oxygen O1s atomic concentration of ablated and non ablated composite surface, before deconvolution, is summarised in Fig. 1(a). For the laser treated samples the laser fluence is equal to 270 mJ/cm^2. Fig. 1(a) shows that, for the pure PMA, non-ablated PMA/C composite and ablated composite (ablation time smaller than 10 s), no significant carbon and oxygen concentration change can be observed whereas, for an ablation time greater than 10 s, a huge increase of the carbon concentration, in correlation with the decrease of oxygen concentration, is observed. In Fig. 1(b) the evolution of the five carbons C1s components is presented. As for Fig. 1(a), two identical regimes are observed depending on the material and the laser ablation conditions. It has to be noticed that the increase of the carbon C1s peak observed in Fig. 1(a) can be correlated with the increase of the carbon-graphite C1s peak (C1s I) and the general decrease of the four other carbons components. This carbon concentration evolution has to be associated with the evolution of the density of the microstructure induced after laser treatment. Indeed, the coverage of the ablated composite surface is smaller than 50% for ablation times smaller than 10 s and rapidly close to 100% for longer ablation time. The increase of the carbon-graphite C1s peak will be discussed, further on, on the base of the nucleation of the microstructure observed after laser ablation.

Scanning electron microscopic studies

Fig. 2 shows SEM micrographs, at low and high magnifications, for the evolution of the surface microstructure with the increase of number of laser pulses. In these laser ablation experiments, cross section micrographs, 80° tilted angle observation, were performed in order to clearly observe each microstructure shape. Sharp conical microstructures start to grow since the first laser ablation pulse. No shape evolution (except the microstructure growth) can be observed during the further irradiation pulses. The microstructure density and the growth kinetics can easily been observed with the SEM micrographs of Fig. 2(e) to 2(h). Conical microstructures, with diameter ranging from 20 to 30 mm, are formed.

DISCUSSION

Carbon cluster formation inside the laser plume

SEM micrographs (cf. Fig. 2) show that, for the samples ablated with a Nd^+:YAG laser, most of the microstructures are topped with spherical particles with diameter of 2 to 6 mm range.

The analysis of the ejected species from the ablated composite shows two types of debris: non spherical debris which can be associated with polymer and carbon fragments and spherical one associated with pure carbon fragments. The SEM observation of these debris and of the spherical carbon particles topped on conical microstructures leads to answer two questions : (1) How are such particles formed? (2) How can these particles recondense, after each laser shot, on the ablated surface? In order to give an answer to these two questions, assumption based on previous works will be made.

Rohlfing [14] shows that the vaporisation of carbon rod, with a second harmonic of a Q-switched Nd^+:YAG laser, leads to the formation of particles grown from smaller species in a gas phase. In

that way, carbon vapour is trapped, cooled by the carrier gas and simply condensed to form the most thermodynamic stable product, particle of bulk carbon. In this experiment, particle size ranging from a few nanometer to thousand of nanometer is formed. He also shows that, for his experimental conditions (which are similar to our conditions), power density of 10^7 to 10^8 W/cm^2 yields a hot surface in excess of 5000K, and that the melting temperature for carbon at low pressures lies within the range of 4100 - 4800K. Considering the above explanations, during laser ablation of PMA/C composite materials, high temperature nanometer carbon particles can be ejected from the composite surface and then agglomerate inside the laser plume to form spherical and non spherical carbon particles on micrometer sizes. In order to explain recondensation behaviour of these large particles, the work made by Kelly et al [15] is considered. Indeed, they show that laser sputtering of polymethylmetacrylate causes two groups of particles , light and heavy, to be emitted from the surface.

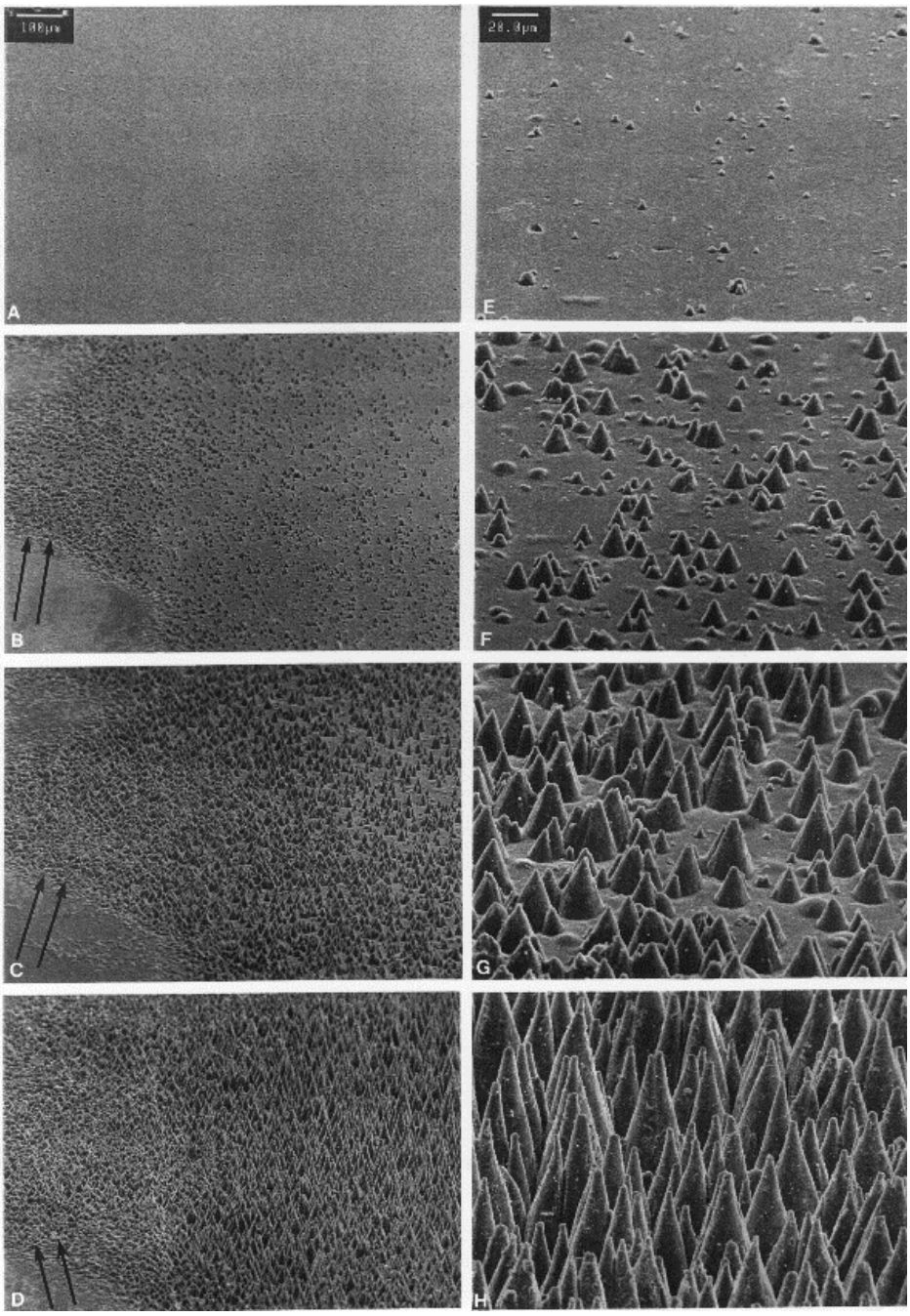


Fig. 2 : SEM micrographs (80° incidence) showing the evolution of the surface microstructure for a Nd^+:YAG laser fluence equal to 250 mJ/cm^2 : (a), (e) 10 shots; (b), (f) 50 shots; (c), (g) 100 shots and (d), (h) 200 shots

Light particles are emitted more rapidly and escape to form a shock wave. On the other hand, heavy particles are emitted more slowly and can recondense inside and outside of the ablated area. If we now consider that the micrometer particles observed during our laser experiments belong to the low speed particles, recondensation of these particles can occur, after each laser

shot, on the ablated surface on further on stick on the molten surface layer (see Fig. 3 (a) and 3(b), first laser shot, at time t and t + Dt).

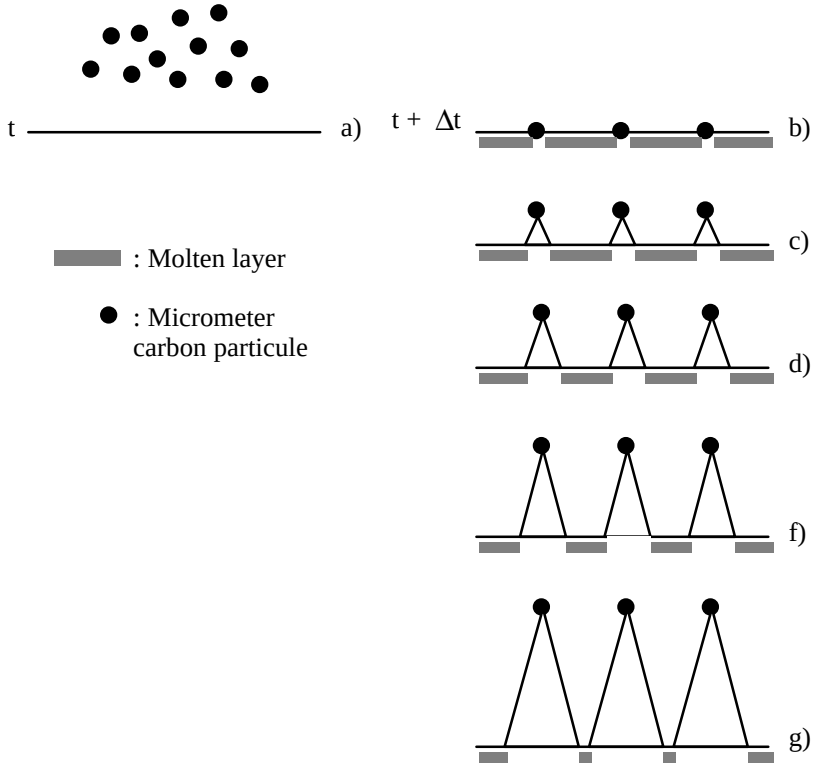


Fig. 3 : Schematic picture of conical microstructures induced by Nd^+:YAG laser irradiation of composite materials

Conical microstructure growth : Nd^+:YAG laser ablation

In order to explain the mechanism for microstructure growth induced on composite surfaces after Nd^+:YAG laser irradiation, the absorption behaviour of PMA polymer and of carbon particles and the creation of molten layer have been schematically described in Fig. 4. In this figure, a homogeneous distribution of square area of alternative carbon and PMA regions is drawn to tentatively represent a model composite which has a volume fraction of carbon particles equal to 50%. This volume fraction of carbon has been chosen arbitrary and obviously does not match with the real volume fraction of the ablated composite. However, this schematic representation is just shown to explain how the photons of the Nd^+:YAG and of the KrF excimer lasers interact with the composite surface and near surface and in that way can be associated with a wide range of carbon volume fraction.

Fig. 4(a) and 4(b) show two representations of the square distribution of dissociate nanometer carbon particles and PMA polymer, respectively, and the penetration profile of Nd^+:YAG laser photon after one laser shot. The penetration depth of the photons through the carbon layers is quite small because of the high absorption of the Nd^+:YAG laser photons by carbon particles whereas the Nd^+:YAG laser photons go all through the PMA layers because of its quasi transparency at that wavelength. Taking into account these considerations, Fig. 4(c) shows how

the heat transfer from the hot carbon particles towards the cold surrounding polymer occurs and allows heat up and thermal ejection of PMA fragments; the ejection of carbon particles obviously occurs at the same time. The molten layer induced after each laser shot is considered to be quite small (cf. Fig. 4(d)); its thickness is correlated with the penetration depth of the photons shown in Fig 4(a) and the vertical heat transfer from the nanometer carbon particles towards the underneath PMA polymer (cf. Fig. 4(c)). Therefore, rapid solidification of this molten layer leads to the absence of motion of the carbon cluster on the laser induced surface. In this way, a carbon cluster which sticks on the top of this surface (see Fig. 3(b)) will remain at that position on consecutive laser shots.

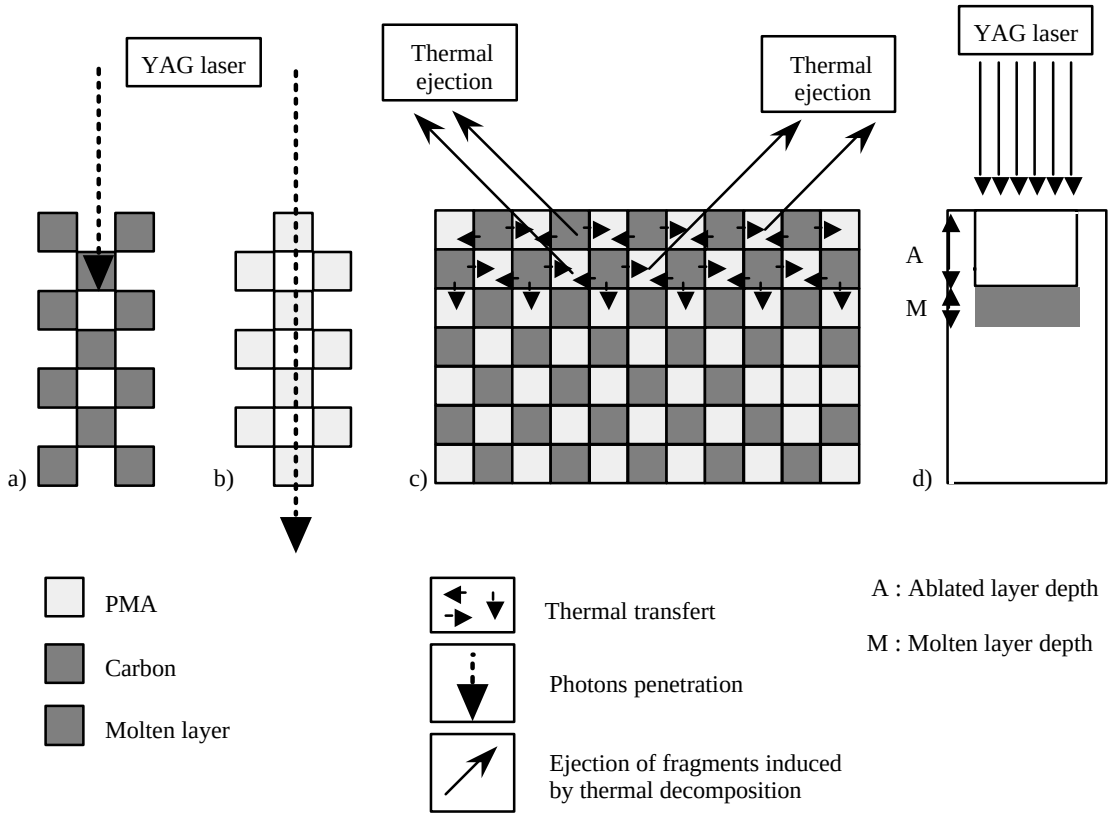


Fig. 4 : Schematic picture of the interaction between the photons of a Nd^{+}:YAG laser and the PMA/C composite material. a) photon penetration inside the nanometer carbon particles, b) photon penetration inside the PMA polymer, c) thermal (through heat transfer) desorption of fragments, and d) ablated and molten layers induced after one laser shot

The properties of carbon clusters play an important part on all microstructure growth. Therefore, thermal and ablation properties of these carbon particles are predominant. High thermal conductivity (100 to 800 W/mK depending on the graphitization degree of the carbon) allowed high temperature of the carbon cluster inside the plume and explains that nearly all the energy of incident laser pulse is absorbed into a thin layer near the surface. It can also be shown that the ablation rate of carbon is nearly 10 times higher than common polymers [3] and that the absorption efficiency of carbon particles increases and ablation decreases when particle size increases.

Taking into account these findings, beneath this hot surface, carbon particles can act as a temperature regulator and lower the temperature of the surrounding polymer and indeed explains why the sputtering rate slows down in the immediate vicinity of the particle. Once the cone starts to grow, the conical structure tends to propagate on its own, because the surface temperature is lower on the edge of the microstructure than in the surrounding flat areas (see Fig. 3(c) to 3(g)), and finally the ablated surface can be completely covered with that kind of conical microstructure (Fig. 3(g)). It has to be mentioned that, during the polymer ablation, the composite structure (nanometer carbon density and spatial distribution) of the conical microstructure remains almost unchanged and close to the structure of the non ablated composite.
Consequently, from the above mentioned considerations, the conical microstructures are produced as a result that the microstructure shape will not be affected from the quasi absence of molten layer but be determined by shield effect of irradiation beam.

CONCLUSIONS

In conclusion, we proposed simple model for the nucleation and growth of microstructure as the results of laser ablation of PMA/C composite.

Two points will be summarised in this study of the formation of surface microstructures after irradiation of PMA/C composite surfaces performed at normal incidence and 60° angle incidence using a Nd^{+}:YAG (532 nm) laser operated at 10 Hz:

a) The carbon concentration increases and oxygen concentration decrease with the increases of laser fluence. This increase of carbon concentration on the ablated surface can be associated (i) with the redeposition of large carbon cluster inside the laser plume and (ii) with the diffusion and segregation of small carbon clusters in the surface layer.

b) Conical microstructure formation during laser ablation is associated with the formation of large carbon particles inside ablation plume. After being redeposed on the molten composite surface, the shielding effect associated with the thermal properties of the micrometer carbon particles leads to the formation of sharp or flat conical microstructures depending on the particle shape and adhesion strength with the composite surface.

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