Journal of
MATERIALS RESEARCH

Species resolved analysis of the expansion of hydroxyapatite laser ablation plumes

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(Received 1 February 1996; accepted 25 June 1997)

The plume generated by ablation of hydroxyapatite targets under ArF excimer laser irradiation has been investigated by means of fast intensified charge coupled device (CCD) imaging and optical emission spectroscopy. Results have shown that the plume splits into two plasma clouds as it expands. Time and spatial resolved spectra have revealed that under the experiment conditions emission is mostly due to calcium neutral atoms and calcium oxide molecular radicals. Imaging of the plume with the aid of bandpass filters has demonstrated that the emissive species in the larger and faster plasma cloud are calcium neutral atoms whereas in the smaller and slower one are calcium oxide molecular radicals.

Pulsed laser deposition (PLD) is a good technique to deposit thin films of complex compounds, and many authors[1–6] have used it to obtain hydroxyapatite (HA) coatings for medical prostheses. This motivated us to study the HA laser ablation process through the characterization of the plume by fast intensified CCD imaging.[7,8] The resultant pictures of the plasma generated by ArF excimer laser irradiation of HA targets revealed the presence of two different emissive regions. Thus, in this paper we develop a more comprehensive analysis of the HA laser ablation plume by means of time and space resolved optical emission spectroscopy in addition to fast intensified CCD imaging in order to characterize better the ablation process and to identify the nature of both regions.

An ArF excimer laser (Lambda Physik LPX 205i) provides pulses at a wavelength of 193 nm, with duration of 23 ns, and energy of 300 mJ. The beam is limited by a 12×2 mm^2 mask and impinges at an angle of 45° onto a pellet made from HA powder pressed at 6×10^8 Pa at room temperature. The fluence on the target is about 1.5 J/cm^2. All the experiments are carried out in a high vacuum chamber evacuated to a base pressure of 5×10^{-5} mbar.

Images are taken with a gated CCD camera (ANIMATER-VI from ARP France), 288×384 pixels, 8 bits dynamic range, intensified by a microchannel plate (MCP) whose aperture is delayed by a pulse generator triggered by a fast photodiode that is activated by the laser pulse. Bandpass filters (MicroCoatings Inc.) centered at 520 and 600 nm with a FWHM of 10 nm are also used in some of the recorded images and, in these cases, accumulations of 20 shots are needed to acquire an image. Otherwise, pictures are taken in a single shot mode.

The optical emission spectra are acquired by means of a 0.5 m spectrometer (Chromex 500IS/SM). The laser-generated plume is imaged onto the entrance slit in such a way that the propagation axis of the plume remains parallel to this slit. This allows good spatial resolution (0.03 mm) to be obtained with the CCD camera, with no lens/mirror translation system needed. A 600 g/mm grating blazed at 400 nm provides a spectral resolution of 0.3 nm. Each spectrum consists of the accumulation of the light emitted by the plume after 20 laser shots. The synchronization system is the same as that described above. The spectral range of this setup covers the region from 320 to 750 nm.

Images of the HA ablation plume generated by ArF excimer laser irradiation [Fig. 1(a)] show the presence of two separate plasma clouds for delay times after the laser pulse of greater than or equal to 400 ns. For shorter delay times, only one very confined bright cloud is visible. This can also be seen from luminous intensity profiles displayed in Fig. 2(a) where both clouds appear as two local intensity maxima. The largest cloud shows a plume-like shape while the other one looks like a thin bright layer between the target and the former one. From simple inspection of the images as well as the profiles, it can be seen that the separation between them increases with time. Plots of their front position versus time show a linear dependence (Fig. 3). Then it can be inferred that plume expansion is at constant velocity, according to the free expansion of a plasma. The speeds of the clouds are found to be 1.27×10^4 m/s for the one further from the target and 3.2×10^3 m/s for the one closer to target.

This behavior was also found in our previous work[8] where HA laser ablation was carried out under identical conditions. Our purpose is now to identify the nature of the emitting species in the plume and, thus, to elucidate any compositional difference between both plasma clouds that could account for the observed splitting effect. In order to do this, the emission spectrum of

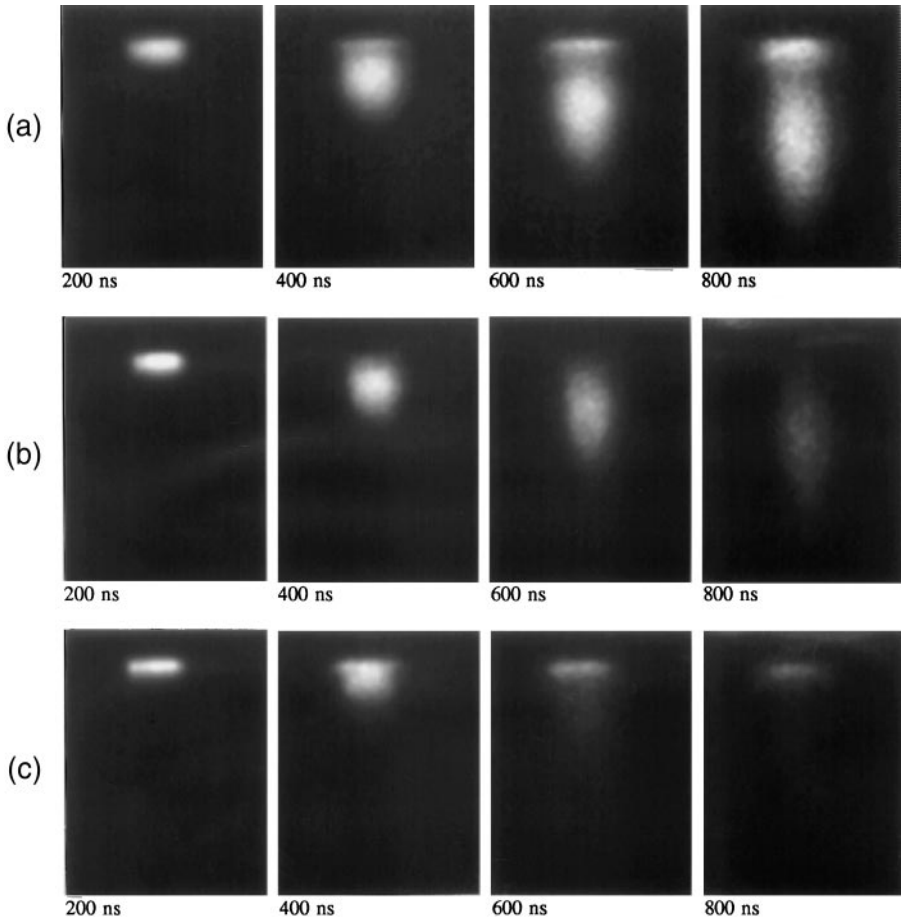

FIG. 1. Time evolution of HA laser ablation plumes after ArF laser irradiation imaged by means of a fast intensified CCD camera (a) without any filter, (b) with a bandpass filter centered at 520 nm, and (c) with a bandpass filter centered at 600 nm. The imaged region extends 1.3×1.0 cm^2.

the plume has been recorded at a delay time of 300 ns after the laser impingement with a MCP aperture time of 20 ns. This is the optimum delay to collect the best signal level because for instants of time previous to this the continuum emission due to a dense plasma does not allow identification of the species in it, and for longer times the signal level is not strong enough to be detected by the CCD camera. Under such conditions the cloud further from the target reaches distances up to 5 mm away from the target. The spectrum as obtained reveals that, in the spectral range from 320 to 750 nm and at any distance from the target, the emission is completely dominated by transitions involving neutral Ca atoms, that is, Ca I, in agreement with the work of Niemz on dental HA.[9] Only two low intensity lines correspond to ionic Ca emission (Ca II: 393.4 nm, 396.8 nm), and a little contribution from Na I is found at 589.0 and 589.6 nm, probably due to target contamination. Although phosphorus is one of the constituents of HA, no emission lines corresponding to this element have been found in the spectrum. This is likely due to the fact that the emission from phosphorus is very weak in the wavelength range under study. The identification of the spectral lines is made by means of standard tables.[10]

Whereas at long distances from the target (of the order of 2 mm) no more emissive species have been found, at short distances (of the order of 0.2 mm) two additional strong emission bands have been detected in the region 545–640 nm (Fig. 4). These bands are known to correspond to some kind of calcium polyatomic oxide, such as Ca_2O_2, but the right stoichiometry of the emissive molecular species is not described in the literature.[11] No other emission bands have been detected in this experiment. It must also be pointed out the absence of the Ca I line at 610.4 nm in Fig. 4(a), possibly shadowed by the calcium oxide band. It can be concluded, then, that the main compositional difference in the emissive species as a function of the distance to the target arises from the presence of calcium oxide molecular radicals close to the target. It clearly suggests that the presence of two plasma clouds observed in the images could be correlated with this compositional difference.

In order to clarify the role of the atomic and molecular species in the splitting phenomenon pointed out,

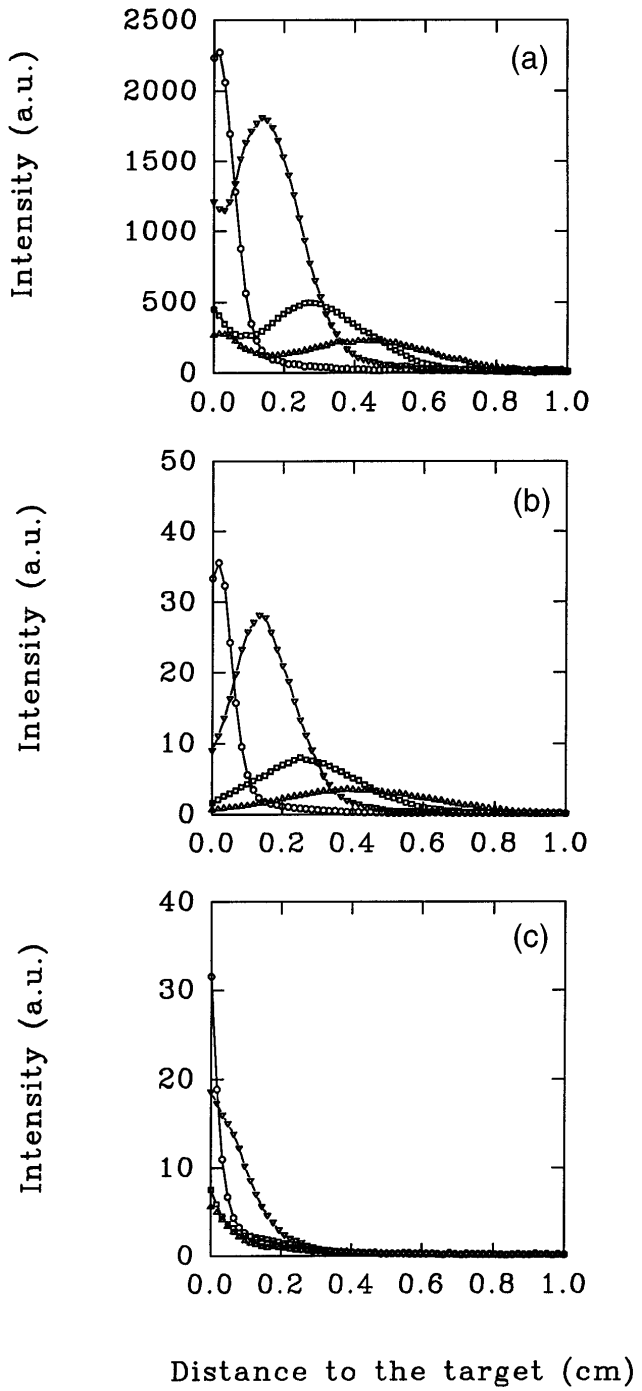

FIG. 2. Luminous intensity profiles corresponding to the respective images in Fig. 1. Each curve corresponds to a different delay time after the laser impingement: (○) 200 ns [intensity has been divided by 10 in (a) and (b), and by 5 in (c)], (▽) 400 ns, (□) 600 ns, and (△) 800 ns.

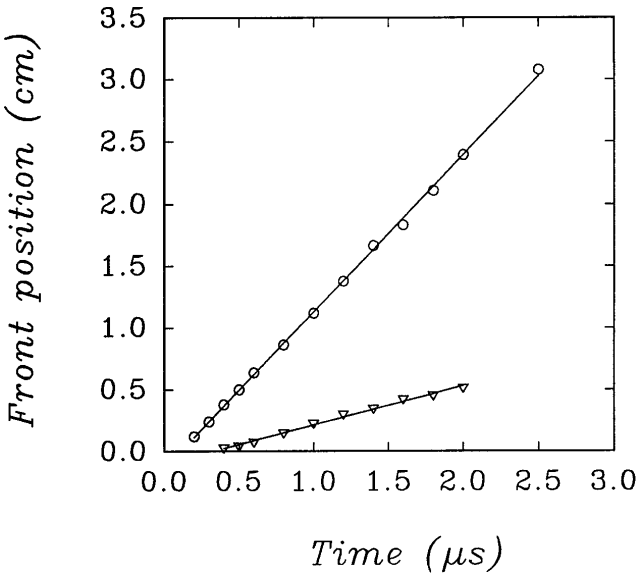

FIG. 3. Position of the front, measured from the target surface, versus time of the cloud further from (○) and closer to (▽) the target.

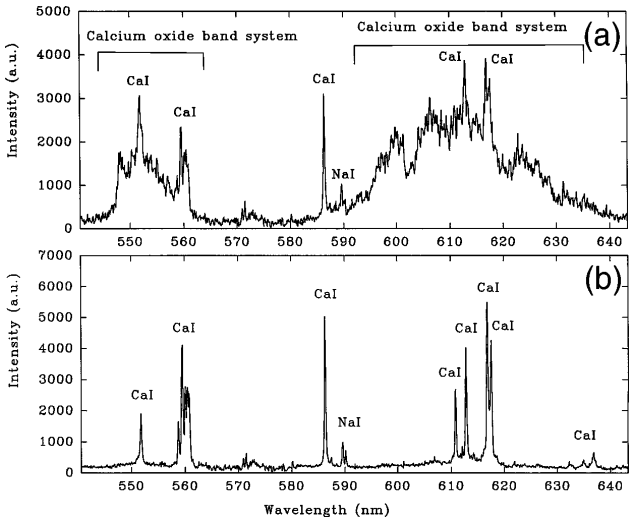

FIG. 4. A portion of the optical emission spectrum of the plume generated by ArF excimer laser irradiation of a HA target obtained after a delay time of 300 ns after the laser pulse at a distance from the target of (a) 0.2 mm and (b) 2 mm.

images have been taken with the aid of bandpass filters that can isolate one single species and allow us to analyze its expansion dynamics separately. Two filters have been chosen for this purpose: the first one, centered at 520 nm, intercepts only one emission line at 518.9 nm corresponding to the transition $4p^1\mathrm{P}–5d^1\mathrm{D}$ of Ca I whereas the second one, centered at 600 nm, intercepts a region of the largest calcium oxide band where no atomic lines are superimposed. Thus, images taken with the filter centered at 520 nm describe the dynamics of Ca neutral atoms whereas those taken with the filter at 600 nm account for the motion of calcium oxide molecular radicals. Results as obtained are presented in Figs. 1(b) and 1(c). These images, when compared to those of Fig. 1(a), clearly reveal the nature of the emissive species of the two different plasma clouds in the

plume. The expansion of calcium neutrals takes place in the same way as that of the largest plasma cloud, as does the molecular population with respect to the little cloud. It can be seen that for each time the superimposition of the plumes of Figs. 1(b) and 1(c) would result in a plume shape identical to that of Fig. 1(a) and the same applies for the profiles in Figs. 2(b) and 2(c) with respect to those of Fig. 2(a). Plots of the position front of the plume corresponding to Ca I and calcium oxide show that these species also expand at constant velocity and the calculated values are 1.20×10^4 m/s and 4.2×10^3 m/s, respectively, very similar to those found for the two plasma clouds present in the plume. All these results reveal the nature of the emissive species of the clouds: in the fastest and largest one are atomic species and in the slowest and smallest one molecular species. Then it can be said that the plasma generated by the laser segregates into two different populations, an atomic one and a molecular one. Under the conditions at which the experiment has been carried out, nothing can be concluded about the ionic population because, as it has been pointed out, its contribution to the light emitted by the plume is not significant.

Several hypotheses may be formulated to explain the segregation phenomenon observed in this experiment. One possibility is to suppose that molecules in the plume are not directly ejected from the target by the laser pulse but created by reactive processes in the dense plasma during the first instants of its expansion. It would result in a slow molecular population expanding near isotropically in contrast to a forward directed fast atomic plume, in good agreement with images shown in Fig. 1. This hypothesis was first formulated by Girault *et al.*[12] to explain a similar effect observed after laser ablation of $YBa_2Cu_3O_{7-x}$ targets. The other possible explanation is the segregation of the different species in the plasma phase due to their different masses, regardless of whether they are directly released from the target or created in the plume. Urbassek and Sibold[13] have elaborated a numerical model that explains such a segregation effect for a very simple two-component gas. Both hypotheses account for the phenomenon observed in this experiment. Only the elaboration of a more complex model will determine what is the dominant process, reactions in the dense plasma or mass segregation effects.

In conclusion, the plume generated by ArF excimer laser ablation of HA targets has been investigated in detail. Images of the plume obtained by means of fast intensified CCD imaging have revealed that it splits into two plasma clouds as it expands. Optical emission spectroscopy has shown that the main emissive species are neutral Ca atoms and calcium oxide radicals. Images obtained with the aid of filters have allowed us to investigate the dynamics of each one of these components separately. They have shown that each plasma cloud corresponds to a different emissive population. The fastest one is composed of atomic neutral Ca atoms and the slowest one of calcium oxide molecular radicals.

ACKNOWLEDGMENT

This work has been supported by CICYT of the Spanish Government (project MAT94-0264).

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