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TIME-RESOLVED SPECTROSCOPIC STUDY OF A PULSED ELECTRON BEAM ABLATION PLASMA

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The plasma plume produced at the interaction of a pulsed, intense electron beam with a hydroxyapatite target was investigated by time-resolved optical emission spectroscopy and fast imaging. It has been found that at earlier times (<1 μs) the plume expansion take place in the ionized Ar gas, while at later times (>1 μs) the expansion of the HA plasma plume is dominated by the calcium atoms and ions. For determining the plasma parameters a Monte-Carlo simulation-fit code was used. The excitation temperatures of the argon ions and calcium atoms become comparable in the interval 600 ns – 1000 ns after the beginning of the electron beam current. The electron density is of the order of 10^{17} cm^{-3}, the electron temperature is about 1.4 eV and both decrease after about 1300 ns.

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1. Introduction

Hydroxyapatite $Ca_{10}(PO_4)(OH)_2$ (HA) is a well-known material with biocompatible properties for biomedical applications. Due to its excellent biocompatibility HA is highly recommendable for coatings of orthopaedic and dental implants, and in the last years it became subject of extensive reasearch in the field of material science. Different plasma-based techniques are applied to biomedical materials research, such as plasma sputtering and etching, plasma implantation, plasma deposition, plasma polymerization, laser plasma deposition, plasma spraying, and so on. Plasma sprayed HA coatings of 50-200 μm thickness are already used in medical applications for metallic joint prosthesis [1]. HA thin films are produced by nanosecond pulsed laser deposition (PLD) with the advantage of stoichiometric deposition [2]. As an alternative to PLD, pulsed electron deposition (PED) with an electron beam produced in a channel-spark discharge is a novel growth technique, in particulary for HA thin films [3,4].

The plasma plume produced during PLD or PED may be critical for the deposition of thin films. The understading of the composition, density and temperature distributions in the plasma plume will be helpful for control and optimisation of the thin film growth.

The aim of this paper was to investigate the properties and dynamic evolution of the plasma plume produced at the pulsed electron beam interaction with a HA target in Ar ambient gas, under similar conditions as for thin film growth experiments.

2. Experimental set-up

The plasma was generated by ablation of a HA target with a pulsed electron beam produced in a channel spark-type discharge. The pulsed electron beam parameters used in experiments were: pulse width (FWHM) 100 ns, beam current ~400 A and energy distribution (polyenergetic) from 0 to

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16 keV. The repetition rate was 1 Hz and the working gas was argon at a pressure of 10^{-3}-10^{-2} mbar [5-7].

The HA target was mounted on a rotating holder in order to get uniform erosion of the surface. The incidence angle of the electron beam on the target was 45°. The fluence was estimated to 2.8 J cm^{-2}.

The plasma emission spectrum was analyzed with a Czerny-Turner spectrograph (Acton SpectraPro-750I – 750 mm focal length), with an intensified charge-coupled device Princeton Instruments PI-Max 512 as detector. Two gratings were used: 300 lines/mm and 1200 lines/mm, with a blaze wavelength of 500 nm, and 350 nm, respectively. The investigated spectral range was between 350 nm and 750 nm. The plasma was observed perpendicularly on the target-substrate axis and was imaged on the entrance slit of the spectrograph by using an optical fiber. The ICCD detector was operated in an externally gated mode, synchronized to the beam current pulse. The measurements were performed with 100 ns exposure time, with trigger delays varying in steps of 100 ns. All spectra were averaged over 100 discharges. The plasma plume was photographed side-on with the gated, intensified ICCD camera. Two-dimensional images of the overall visible emission from the plasma were recorded with 10 ns acquisition gate time and delay times varying in steps of 100 ns.

3. Spectra processing

We have performed time-resolved investigation of the HA plasma plume for the analysis of the plume composition over a broad spectral range (350 nm and 750 nm). A Monte-Carlo simulation-fit code SimSpec [8] was used for determining the plasma parameters for a large number of spectra recorded. SimSpec, written in C++ language, was initially developed for the calculation of species densities, temperatures and equillibrium deviation in the non-LTE plasma of the Cu-Cr vacuum arc, but it is also capable of using PLTE approximation.

The simulation code assumes Boltzmann-like plasma with a volume emissivity of the transition *u-l* given by:

$$I_{ul} = \frac{h \cdot c}{\lambda} \cdot \frac{g_u \cdot A_{ul}}{U_z(T)} \cdot n_z \cdot \exp\left(-\frac{E_u}{k \cdot T}\right) \quad (1)$$

with A_{ul} the transition probability, E_u the upper level energy of the transition, g_u the statistical weight, T the excitation temperature, n_z the species density.
$U_z(T)$ is the partition function for the species *z:*

$$U_z(T) = \sum_{u=1}^{u=u\max} g_u \cdot \exp\left(-\frac{E_u}{k \cdot T}\right) \quad (2)$$

where u_{max} is the last excited energy level with an energy lower than the ionisation potential, which depends on the ionization potential lowering ΔE ($E_{umax}<E_i-\Delta E$).

For computing the partition functions we included into the SimSpec sources a C++ program sequence inspired from the COSSAM [9] code of the University of Vienna, usually the reference code for computing partition functions.

As one can see from (1) and (2), the program requires absolute intensity calibration and a good knowledge of the plasma volume to determine the densities. New code sequences introduced in SimSpec made possible to use the electron density and temperature as additional simulation parameters.

The program determines the best approximation for the measured spectrum using simulated densities and temperatures for all species in an optically thin plasma. The simulation is performed in a multi-threaded way in order to resolve superposed lines emited by different species. Spectra simulated simmultaneously with random densities and temperatures for all species in the plasma construct a global spectrum, which is compared with the measured spectrum. The simulation stops if the global error reaches a minimum in the limits of a given convergence parameters. The program automatically identifies the spectral lines in the spectroscopy tables.

4. Results and discussions

The evolution of the species of the HA plasma plume was analysed by time-resolved optical emission spectroscopy.

Emission spectra of ablation plasma in the wavelength range from 442 to 498 nm, recorded for two different trigger delays (300 ns, 1000 ns) are presented in figure 1. The delay time "zero" corresponds to the beginning of the electron beam current. The spectrum recorded at 300 ns is dominated by Ar II lines, while in the spectrum recorded at 1000 ns we notice an important decrease of the Ar II lines and the presence of neutral Ca lines.

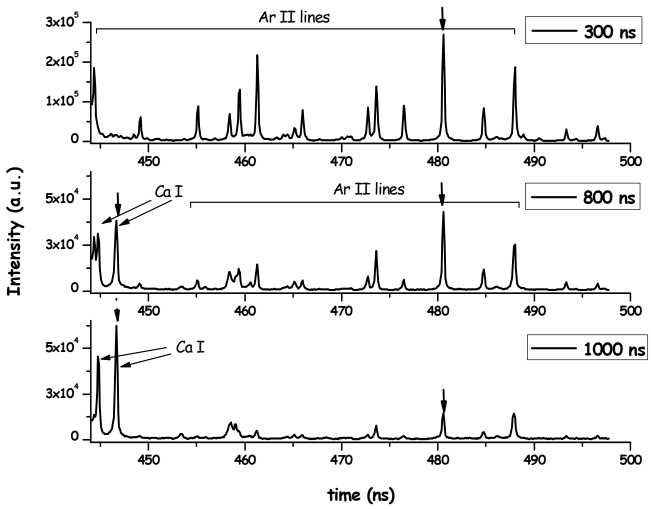


Fig. 1. Spectra recorded at 300 ns, 800 ns and 1000 ns.

The emission intensity temporal profile obtained from the singly ionized argon line at 480.6 nm (with energies transitions of 19.2 - 16.6 eV) and calcium atom line at 445.47 nm (with energies transitions of 1.9- 4.7 eV) respectively, is presented in figure 2. We notice the appearance of a Ca I delayed maximum intensity (~1500 ns) in the emission intensity distribution with respect to the Ar II maximum intensity (~300 ns). The Ar II emission tail extends up to 1000 ns, while a long tail for Ca atoms at longer times (up to few μs) is observed.

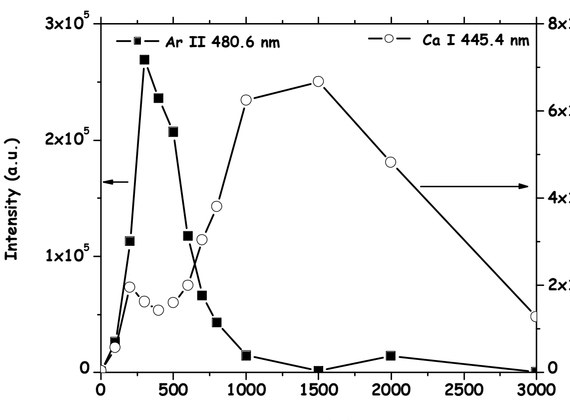


Fig. 2. Temporal evolution of Ar II (480.6 nm) and Ca I lines (445.47 nm).

The temporal features of the singly ionized calcium lines 393.33 nm (with energies transitions of 3.15 -0 eV) and 396.81 nm (with energies transitions of 3.12 - 0 eV) are quite similar to that observed for above calcium neutral lines and are given in figure 3. For comparison, a singly ionized argon line at 385.05 nm (with energies transitions of 19.9 - 16.7 eV) is presented on the same figure.

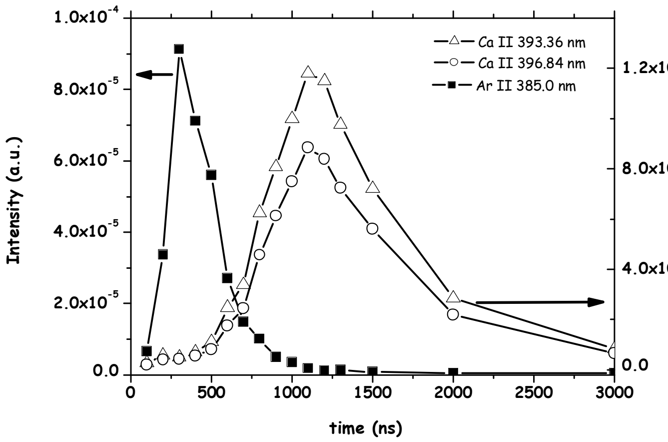


Fig. 3. Temporal evolution of ArII and Ca II lines.

As mentioned in section 3, for determining the plasma parameters, we used the Monte-Carlo simulation-fit code SimSpec. The program determines the best approach for the measured spectrum using simulated densities and temperatures for all species in an optically thin plasma, in PLTE approximation. For all emission spectra of HA ablation plasma recorded in the wavelength range from 442 to 498 nm and for trigger delays from 0 to 1500 ns, the temporal evolution of Ar II and Ca I excitation temperatures obtained from the code are presented in figure 4.

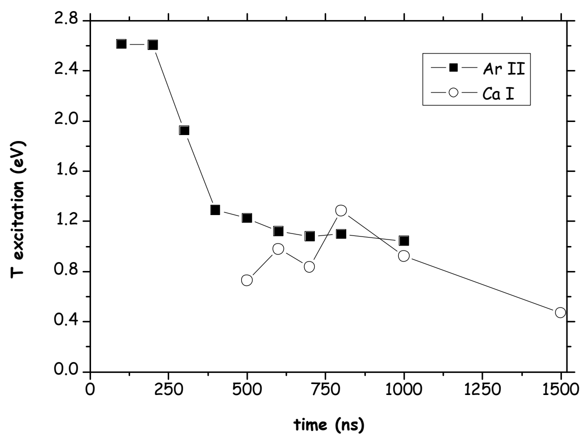


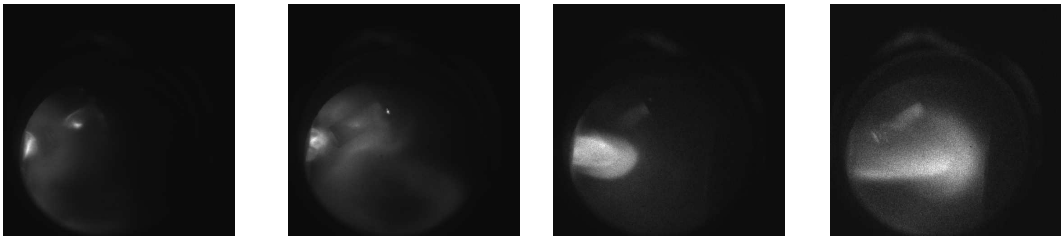
Fig. 4. Temporal evolution of the Ar II and Ca I excitation temperatures.

It is noted that in the early stages of the plasma evolution the Ar II excitation temperature is high and it varies rapidly. The high value of the Ar II temperature within 200 ns after the beam pulse is most likely due to the low energy electrons of the tail of the electron beam current. When the time is greater than 500 ns, the Ar II excitation temperature is reduced to about ~ 1.2 eV and is comparable with that of the calcium atoms. The simulation showed that the total number of argon ions decreases after 800 ns while the total number of calcium atoms increases after 1000 ns. The electron temperature obtained from the code is about 1.4 eV. The electron density is of the order of 10^{17} cm^{-3} and decreases after 1300 ns, most likely due to recombination.

Our results are in agreement with other spectroscopic studies on plume plasmas generated by different pulsed electron beams on targets [10,11]. In the case of channel spark ablation of TiN, Si and fused silica targets the excitation temperature was estimated to 1.1 eV from Si lines and an electron density of 1.6 to 3.7×10^{17} cm^{-3} was measured by nonresonant interferometry [10].

The composition of the HA ablation plasma, obtained in our measurements, is similar to that obtained in the case of pulsed laser ablation [12,13] for comparable fluences. In the case of PED, the ablation is made in argon background gas at a pressure of 6×10^{-3} mbar, and the ionization of argon is evidenced. In the case of the KrF excimer laser [12] the HA ablation was made at a pressure of 5×10^{-5} mbar.

Images of the overall visible emission of the HA plasma plume at different delays from 0 to 4000 ns and 10 ns acquisition gate time, following the electron beam pulse in Ar at 6×10^{-3} mbar, are given in Fig. 5. At earlier times (<1000 ns) the plume expansion take place in the ionized Ar gas, as observed in previous optical emission measurements (Figs. 2 and 3). At later times (>1000 ns) the expansion of the HA plasma plume is dominated by the calcium atoms and ions. The plasma plume reaches the substrate at ~ 3500 ns. We notice that the plasma expansion is similar to that observed for nanosecond PLD induced HA plumes [12].



a) b) c) d)

Fig. 5. Images of the visibile emission of the HA plasma plume induced by the pulsed electron beam ablation in Ar background gas at time delays of a) 200 ns; b) 500 ns; c) 1400 ns and d) 3500 ns. The exposure time was 10 ns.

The observed increase of optical emission intensity of the calcium atoms and ions after the decrease of the Ar II intensity, as observed in optical emission measurements (Figs. 2 and 3), could be due to a shock wave formation and thus plasma heating occuring during plume expansion into a backround gas as in nanosecond pulsed laser deposition experiments [14,15].

5. Conclusions

In this study the HA plasma induced during pulsed electron beam ablation in Ar background gas was investigated by time-resolved optical emission spectroscopy and fast imaging. It has been found that at earlier times (<1000 ns) the plume expansion take place in the ionized Ar gas, while at later times (>1000 ns) the expansion of the HA plasma plume is dominated by the calcium atoms and ions. The excitation temperature of the calcium atoms is comparable with that of argon ions (1.1eV) in the interval 600 ns - 1000 ns. The electron temperature is about 1.4 eV and the electron density is of the order of 10^{17} cm^{-3}. From both techniques employed, the Ar background gas strongly affects the population kinetics of Ca atoms and ions in the region between the target and substrate.

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