

CHEMICAL REACTIONS IN LASER PRODUCED PLASMA

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In the present paper the laser-induced fluorescence method (LIF) combined with the time resolved emission spectroscopy was adopted to measure the spatial and temporal distributions of ions, atoms, and molecules, electron temperature and density in the laser ablation plasmas. Based on the results of quantitative LIF diagnostics chemical dynamics in the laser-produced plasmas of metallic, and graphite samples were examined. The main attention was focused on the LIF detection of reagents and reaction products, their spatial and temporal distributions as well as on the elucidation of the pathways for oxide and dimer formations in the ablation plumes.

The chemical kinetics of ablated species, both in vacuum and gas environments is complex mainly because of wide range of the variation of the thermodynamic conditions (from high pressure and temperature at the time of ablation to a rarefied gas at times long after the ablation event). Besides, there exist many possible reaction pathways and reaction rates are available only for the limited pressure and temperature regimes.

Plasma was produced by focusing of a Nd:YAG laser radiation (1064nm, 10ns, 10^8 - 10^9 W/cm²) or XeCl (308nm, 10ns, 10^8 - 10^9 W/cm²) on the surface of the metallic (Al, Ti) and graphite samples in the helium (air) atmosphere at pressures of 10^{-3} -500 Torr. The details about the densities, temperatures, time-space distributions of various ablated species (Al, Al⁺, Ti, Ti⁺, AlO, TiO, C₂) were obtained. The quantitative interpretation of LIF measurements was performed by using the three-level atomic and four-level molecular approximations, the measured collisional quenching rates of the excited states as well as taking into account the shape of the excitation laser pulse and the temporal variation of the absorption linewidth (Burakov *et al.*, 1992).

The temporal profiles of atoms and ions in the plume were in the form of curves with maxima whose value and position were dependent on the conditions of focusing of radiation onto the target. The range of the concentrations of Ti atoms of $2 \cdot 10^{13}$ - $1.1 \cdot 10^{15}$ cm⁻³ and ions of $2.5 \cdot 10^{12}$ - $4.5 \cdot 10^{13}$ cm⁻³ was recorded in the titanium/air plasma. TiO molecules were detected at the stages of plasma expansion and afterglow in the time interval of 5-60 μ s after ablation laser pulse and up to 3 mm from the target surface. With the plasma evolution the density decreases up to $1 \cdot 10^{13}$ cm⁻³ (60 μ s) as well as with increasing of a distance from a target (Burakov *et al.*, 1995).

The energy distributions of the TiO molecules over the vibrational-rotational states were used to determine the mechanisms of their formation. An analysis of the populations of the rotational levels shows that only for the groups of levels ($J' \leq 60$, $J'' \leq 50$) the rotational distribution may be considered as Boltzmannian with a temperature varying from 800 to 450 K for the lower state ($v''=0$, $a^1\Delta$) and from 2100 to 1400 K for the upper state ($v'=0$, $c^1\Phi$) over a time interval of 5-30 μ s. Measured temperatures differ from the surface temperature attainable at the values of the radiation power density on the target that were used in our experiment. The maximum vibrational temperature is attained in the time interval within which the density of Ti atoms in the ground state and the intensity of luminescence of TiO molecules reach their maximum values ($t = 15-20 \mu$ s). The results obtained indicate that the most probable reason for the formation of electronically excited titanium oxide molecules is the gas-phase reaction proceeding between titanium atoms and oxygen inside the plume. Comparison of the spatial-temporal distributions of the TiO atoms and excited molecules allowed us to find a correlation in their change, which testifies that electronically excited titanium oxides most probably are formed from oxidation of atoms in the ground and low lying metastable states (Burakov *et al.*, 1999).

The formation of C_2 and C_3 molecules in laser ablation carbon plasma was investigated by LIF monitoring of the time-space distributions of these molecules in the plasma. Estimates of vibrational temperatures of C_2 species under various helium pressure support that, the recombination of free carbon atoms is the most likely mechanism for the production of C_2 molecules.

So, the experiments performed demonstrate the great diagnostic capabilities of the LIF combined with the time resolved emission spectroscopy for the analysis of chemical dynamics during the laser induced ablation of solid samples. Based on the quantitative data provided by LIF measurements the details about the densities, temperatures and kinetic energies of various ablated species were obtained. These results permitted to elucidate the pathways of oxidation reactions and dimer (cluster) formation and their influences on the relative concentrations of various species in ablation plasmas. The role of excited and metastable reagents in oxidation kinetics has also been established.

References

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