Space integrated, time resolved studies of the formation of aluminium (II) oxide in laser produced plasmas

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Abstract. We present time resolved, spatially integrated spectra of aluminium II oxide formed from the condensation of an aluminium laser plasma in air. The spectra show a revival of the emission from aluminium oxide molecules at 35 µs after the plasma ignition. Thermodynamic calculations, together with temperature measurements, indicates that as the plasma cools, the aluminium oxide molecule forms through two different channels, explaining its increased presence.

1. Introduction

When a high-powered laser is focused onto a solid target, the plasma formation occurs in the following way: First, the rapid absorption of energy from the laser by the electrons in the solid results in the target being heated through energy transfer to the ions. The heated target releases hot electrons and ions in the form of a plasma. As the laser continues to heat the target, the electron density increases to the critical density – where the laser stops being absorbed and starts being reflected. Thus, the plasma expands and cools, lowering the electron density such that the laser starts to be absorbed again. This cyclical process occurs many times over the laser pulse duration. After the laser pulse terminates, the plasma consists of free electrons, excited atoms, and excited ions. The radiative losses in the plasma generally occur through de-excitation of the atoms and ions to form a characteristic emission spectrum of atomic, ionic line emission. This spectrum can be used to characterize the plasma which, in the case of composite target materials, is known as Laser Induced Breakdown Spectroscopy (LIBS). Long after the laser pulse has terminated (say ~10µs after ignition), the plasma cools to reach a temperature where molecular formation with the background is possible. Species of this kind tend to emit light in the form of molecular emission spectra and such the emission spectrum contains electronic, vibrational, and rotational components.

In a previous study [1], it was pointed out that the effect of oxidation may significantly alter the stoichiometry of the plasma and thus affect any quantitative analysis thereof. The article argues, then, that consideration of the molecular emission is an important part of the study of LIBS. In this paper, the authors determine a temperature range, identified by a post-pulse-delay time, during which the molecular emission can be studied without significant modification to the stoichiometry. Another previous study [3] showed how the plasma temperature can be calculated from the molecular spectrum using a computational algorithm indicating that the plasma can still be diagnosed in the late stages when
atomic emission has disappeared and traditional methods such as line-to-continuum and Boltzmann plots are unavailable. However, detailed studies and explorations of the AlO emission remain relatively unexplored compared to the atomic counterparts. One such unexplored area is the affect of double-pulse reheating on the AlO species within the plasma. This is potentially useful at correcting and stoichiometric changes from the oxidation process and extending the range over which the AlO spectrum can be used in plasma diagnosis for LIBS purposes. It is this area that this article explores.

The articles is arranged as follows: in section 2 the experimental setup is described as well as our experimental methodology and discussion of how the double pulse arrangement was setup. Section 3 then outlines the results of emission spectroscopy in the late phase of the plasma lifetime (some 10μs after plasma ignition). The freely available computational package discussed in [3] is used to extract plasma temperatures. Section 4 then discusses the results in a thermodynamical framework. Finally, we conclude the article with some perspectives on the meaning behind the data.

2. Experiment

Figure 1 shows the experimental setup used to measure emission spectra. The arrangement uses an orthogonal configuration to ignite and reheat a laser plasma from an aluminium target.

Figure 1. Experimental configuration for measuring emission spectroscopy from an aluminium plasma in air.

The aluminium target (99.99% pure aluminium) was housed inside a quartz cuvette cube of size 50mm x 50mm x 50mm. The environment around the target was regular air, not treated in any way. Within the cuvette was a Teflon base on which the aluminium target set and was fixed with nylon screws. The Teflon base fit snugly into the bottom of the cuvette. This was to prevent any movement of the aluminium or damage to the cuvette through shock from the force of the laser beam. The Teflon acted as a shock absorber. The entire cuvette-target arrangement sat on a precision hand-held x-z translation stage such that the target could be moved after every laser shot in order to provide a fresh surface for each plasma. Plasma was ignited using an Nd:YAG laser of 30mJ pulse energy, 6ns duration, focussed to a spot size of 100μm duration. The plasma was imaged using a 3:1 lens relay system onto the entrance of a fibre-optic coupled 0.1m focal-length spectrometer that used an ICCD camera as a detector. The mean spectral resolution of the system was 0.17nm and the mean temporal resolution of the camera was 10ns. The size of the plasma image, together with the acceptance angle of the fibre optic meant that for all intents and purposes, the system could be considered as spatially integrating.
For the single pulse experiments, only the pump pulse was used to create the plasma, and the emission spectrum was recorded with a 500ns ICCD gate width at times ranging from 1μs - 50μs after plasma ignition. The timings of ICCD camera gate was controlled by having the pump laser flash lamps acting as the master clock and using a TTL pulse generator to trigger the Q-switch, and camera gate by external software.

3. Results

1μs - 6μs after ignition, in the window of 460nm – 520nm, the emission spectrum was dominated by Hydrogen-β line emission, presumably from the water vapour in the surrounding air. Stark broadening analysis was used to estimate the electron density as exponentially decaying from $8 \times 10^{17} \text{cm}^{-3}$ at 0.5μs to $2 \times 10^{17} \text{cm}^{-3}$ at 6μs. The Hydrogen-β line is a common line of choice for Stark analysis in this region of time [2].

Single pulse measurements.

The growth of the AlO emission signal is evident from Figure 2. The distinctive sharp edge of the ∆ν=0 transition of the Χ^2Σ^+ → Β^2Σ^2 emission band of aluminium monoxide can be seen from 7μs. The gas temperature can be calculated from these data using a freely available computational method which uses known line strengths to compute theoretical spectra and then fits to experimental data by folding in the experimental resolution of the spectrometer [4]. The temperature evolution is shown in Figure 3.

![Figure 2](https://example.com/fig2.png)

**Figure 2.** Emission spectra from aluminium plasma in ambient air at different times. In all cases, the pulse energy was 30mJ and the ICCD gate width was 500ns.

The data in Figure 3 show two distinct regions, t<10μs and t>20μs with a plateau region in the times in between. The rate of cooling below 10μs, where the temperature decreases from 0.69eV to 0.42eV, is greater than that above 20μs where the decay rate is slower: from 0.42eV to 0.40eV.

The integrated intensity is measured and plotted in Figure 4.
Figure 3. Temporal evolution of the gas temperature of the plasma in the region 5-50μs. Inset shows an example of the temperature fitting routine.

While the temperature of the gas seems to fall monotonically over time, the integrated intensity undergoes oscillations over time as shown by Figure 4.

Figure 4. Integrated intensity of the entire AlO spectrum as a function of time. All data was taken with a gate width of 500ns, and a laser energy of 30mJ.

The data seem to show repeated recovery of the AlO signal most predominantly at \(~13\mu s\) and \(~25\mu s\).

4. Discussion
We take a thermodynamic view of the results, similar to previous studies [1]. The two main pathways of AlO formation are [5]:

\[
\begin{align*}
Al + O_2 &\rightleftharpoons AlO + O \text{ (Channel 1)} \\
Al + O &\rightleftharpoons AlO \text{ (Channel 2)}
\end{align*}
\]

Both of these compete with molecular oxygen formation through recombination of atomic species

\[
O + O \rightleftharpoons O_2
\]
The dominant direction of these reversible reactions is determined by the Gibbs free energies of the reactions which are temperature dependent. The change in the Gibbs free energy of a reaction is given by the difference between the sum of the Gibbs energies of the products and the reactants. The sign of the total change indicates the energetically favored direction of the reactions. Using ideal gas thermodynamics tables [6], the Gibbs free energy of the above reactions can be evaluated in the temperature range 0-0.52eV.

![Figure 5](image-url)  
**Figure 5.** Calculations of the change in the Gibbs Free energy of the AlO formation/dissociation and related molecular oxygen reactions as a function of temperature.

The delay in the onset of dominant AlO emission observable in Figure 4 is explained by Figure 5. As the temperature cools to below 0.44eV at ca. 25μs formation via Channel 1 occurs at a greater rate than dissociation via Channel 2, as indicated by Figure 5. At 0.38eV, Channel 2 can be considered at equilibrium as the change in Gibbs energies is zero. Thus, as the plasma cools below this, AlO formation is expected to occur through both channels. This explains the increase in emission intensity as the plasma cools below to 0.4eV.

**Conclusion**

To conclude, we measured the formation of the AlO spectrum using time resolved spectroscopy and found that the onset in the delay of formation can be explained using thermodynamics.

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