# Minimally Destructive Analysis of Aluminum Alloys by Resonance-Enhanced Laser-Induced Plasma Spectroscopy 

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## Supplementary Information

The experimental setup is shown schematically in Figure S-1.


Figure S-1. Schematics of the two pulse RELIPS setup for the analysis of aluminum alloys.

The extent of sample destruction was also measured with a scanning profilometer. Four crater profiles were shown in Figure S-2. They were produced by
single pulses of Nd:YAG laser ( 532 nm ) at 5 mJ per pulse. As can be seen, crater morphology was reasonably reproducible.


Figure S-2. Crater profiles measured with a scanning profilometer. Each crater was produced by a single pulse of Nd :YAG laser ( 532 nm ) at 5 mJ per pulse.

The RELIPS advantage was found to diminish when the analysis became more destructive. This could be understood in terms of plume expansion. Plume dispersion effect is shown in Figure S-3 where the Na LIPS signal off 6061 alloy was plotted against spectrometer slit-width, for two laser energies. At the lower energy of 0.8 mJ per pulse, $t_{d}$ of the ICCD was set to 60 ns for best signal. The corresponding plume
size could be deduced from the leveling of the signal to be about 1 mm . At the higher energy of 5 mJ per pulse, $t_{d}$ had to be increased to 185 ns to avoid the initial continuum emissions. The plume size now grew to more than 2 mm . In analytical runs, the slit-width was set to $300 \mu \mathrm{~m}$ for spectral capture, and the emissions from oversized plumes were therefore attenuated more. Because the size of the luminous RELIPS plume was still bigger than that of the LIBS plume, it was affected still more.


Figure S-3. Na LIPS signal off 6061 alloys was plotted against spectrometer slit width, at two Nd:YAG laser energy of 0.8 and 5 mJ per pulse. The maximum analyte signal was normalized to one.

The reproducibility of single-shot RELIPS analysis was investigated. The shot-to-shot fluctuation of Mg signal off 6061 alloy is shown in Figure S-4. The laser energy was 0.2 mJ per pulse. The standard deviation was about $49.8 \%$. If the
analyte signal was normalized by the intensity of the background continuum, the fluctuation was reduced to about $30.8 \%$. Given a Nd:YAG laser energy instability of about $7 \%$ and a dye laser instability of about $18 \%$, the observed signal fluctuation was larger than expected. Whether it was due to sample inhomogeneity or instrumental limitations such as poor beam profile remained to be investigated.


Figure S-4. Single-shot analysis of Al 6061 for Mg at a Nd:YAG laser energy of 0.2 mJ per pulse. The net $285.2-\mathrm{nm}$ signal (open circles, left axis) and background normalized signal (open triangles, right axis) were plotted against event number. For both axes, the vertical scale ranged from zero to $3.5 \times$ the average value.

The z-profiles of the analytes were very reproducible. Figure S-5 shows two LIPS profiles (open circles and open triangles) of Mg in 1130 alloy at a laser energy of 5 mJ per pulse. The target was rotating while the LIPS spectra were captured.

Each data point was the average signal of 200 shots.


Figure S-5. Depth profile of Mg in aluminum 1130 alloy, as measured by LIPS on a rotating target at a Nd:YAG energy of 5 mJ per pulse. Two profiles (open circles and triangles) are shown to illustrate the reproducibility.

