Simplifying elemental mapping, from lithium to uranium

The challenge

As today's industries strive to improve efficiency and performance while reducing costs, innovative new materials are being tested, developed, and brought to market. From raw material quality control to failure analysis, elemental characterization is a critical part of this lifecycle. Despite its importance, performing elemental characterization is difficult and time-consuming, requiring multiple analytical instruments, complicated operational and calibration procedures, and trained chemists. Traditional mass spectrometry and spectroscopy techniques involve digesting solid material with acid for the most accurate elemental analyses. This results in a bulk composition of the material only and fails to identify how elements change spatially or in depth. Investigating elements' spatial distributions is especially critical for diagnosing failures in the manufacturing process or after use.

To access spatial elemental data, some users combine mass spectrometry techniques with laser ablation instruments. Due to the complexity of each part of the combined laser ablation and spectroscopy system and lack of continuity between different configurations and vendor combinations, there are still numerous challenges in data collection and processing. Another approach is to apply scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX). This can be easier to use than other spectroscopy tools that require liquid sample introduction, but it does not provide high-sensitivity elemental results. Because the detection limits of SEM-EDX are typically in the weight percent or high thousands of parts per million, its elemental mapping is limited to major elements only. Elements in the low parts-per-million (ppm) range are not detected.

MASSBOX LALI-TOF-MS

The EXUM™ MASSBOX™ Laser Ablation Laser Ionization Time of Flight Mass Spectrometer (LALI-TOF-MS) addresses many challenges associated with other analytical techniques to offer rapid, high-sensitivity quantification of nearly the entire periodic table. The ionization source, LALI, uses two lasers to first ablate, or release, material from a solid sample's surface and then ionize neutrals present in the ablated material. The laser ablation process allows direct analysis of solid materials, from raw material to final product, without the complicated sample preparation procedures of other techniques that require liquid sample introduction. The ionization laser targets the neutral particles created by ablation, which are more representative of the sample's constituents than plasma-generated ions. Overall, LALI results in more reliable elemental verification and reduces sample matrix effects. After ionization, the TOF mass analyzer creates a full mass spectrum at each laser spot. Based on the naturally occurring isotope patterns, the software verifies each detected element.

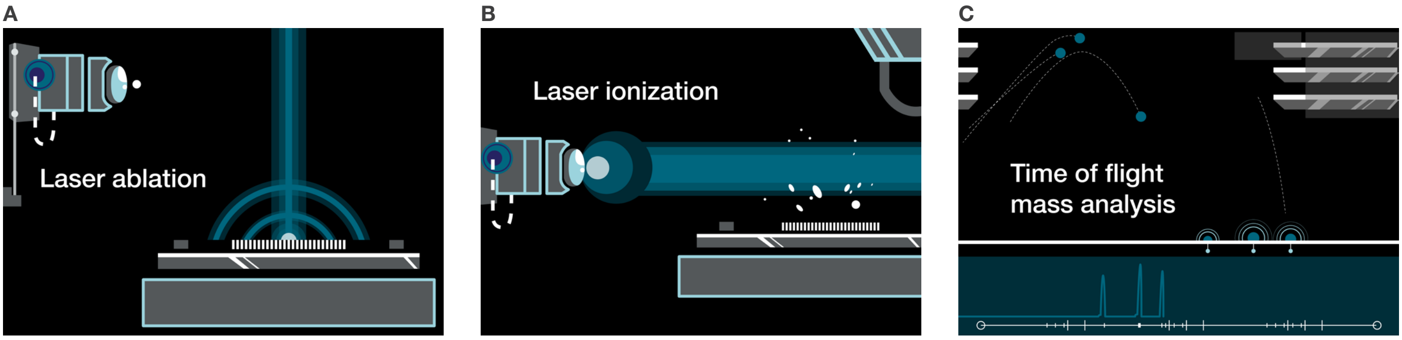

Figure 1. A) Ablation laser fires perpendicular to the sample's surface. The laser spot size is adjustable from 5-200 micron.
B) Secondary laser performs multiphoton ionization of neutral particles created by ablation process.
C) Ions are separated by Time-of-Flight mass spectrometry and detected with a multichannel plate (MCP).

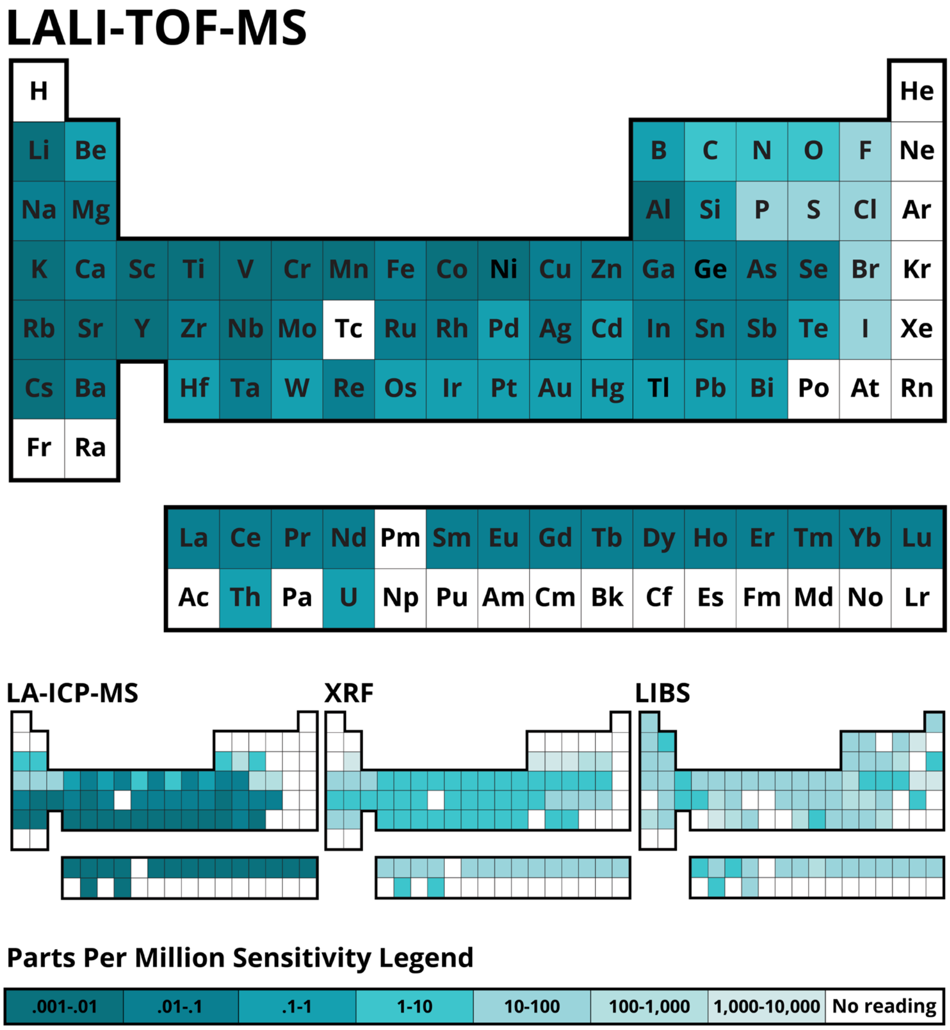

Figure 2. Detection limits for MASSBOX LALI-TOF-MS, LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry), XRF (X-Ray Fluorescence), and LIBS (Laser Induced Breakdown Spectroscopy). Each element is colored by its respective limit of detection. Darker colors represent lower detection limits.

Elemental mapping

In addition to bulk elemental characterization, the MASSBOX LALI-TOF-MS performs elemental mapping. In each analytical session, it can analyze an area up to 83 mm by 83 mm. The resulting map's spatial resolution is determined by the ablation laser's spot size, which is adjustable from 5-150 microns. Each laser spot contains a full mass spectrum of data, and the resulting map reveals the variation of any element of interest. Figure 3 shows an example set of maps from analyzing a LLZO solid- state electrolyte sample. On the map, each pixel is a 50-micron laser spot, and the color scale indicates the relative concentration of the elements. Brighter blues are higher concentrations and darker blues are lower. Figure 3 shows the maps of two major matrix elements, zirconium (Zr) and La. Within the wedge shape of the sample, these elements have generally high concentrations, with the exception of several defects with lower concentrations.

Figure 3 shows the resulting maps from analyzing a 25-mm-by-5-mm area with a 120-micron laser spot size. This relatively large laser spot size creates a coarse map to identify where the transition between the nickel alloy and stainless-steel occurs on the tensile bar specimen. Once the area of interest has been identified, the user can then perform a higher-resolution map with a smaller laser spot size, as shown in Figure 5. The higher resolution map allows enhanced characterization of the interface.

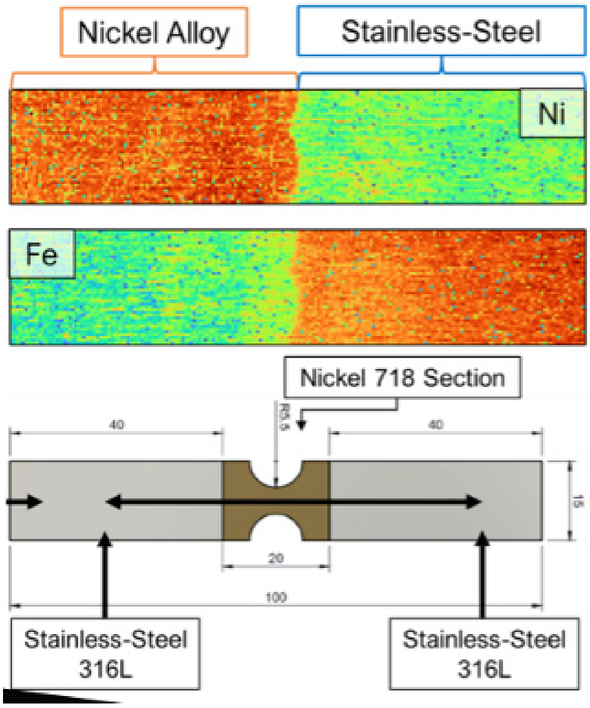

Figure 3. : Mapping results acquired by the MASSBOX LALI-TOF-MS. on a multi-material additive manufacturing sample, a tensile bar built from Stainless-Steel 316L transitioning to nickel alloy, Inconel 718. The 25-mm-by-5-mm maps have spatial resolutions of 120 microns. The top map shows the distribution of nickel (Ni) and the bottom map shows the distribution of iron (Fe). Mapping results clearly demonstrate the nickel alloy with relatively high Ni concentrations on the left and stainless steel with relatively high Fe concentrations on the right.

High-resolution interface mapping

To further characterize the interface, the MASSBOX LALI-TOF-MS performed a higherresolution elemental map with a 25-micron laser spot across a 7.5-mm-by-6-mm area. These results reveal a distinct area of mixed chemistry between the two materials. The size of mixed chemistry interface matched the laser diameter used in the DED (direct energy deposition) 3D-printing process, and the curved pattern indicates the melt pool. Such insights are critical for understanding melt pool mixing and improving process control in multi-material additive manufacturing.

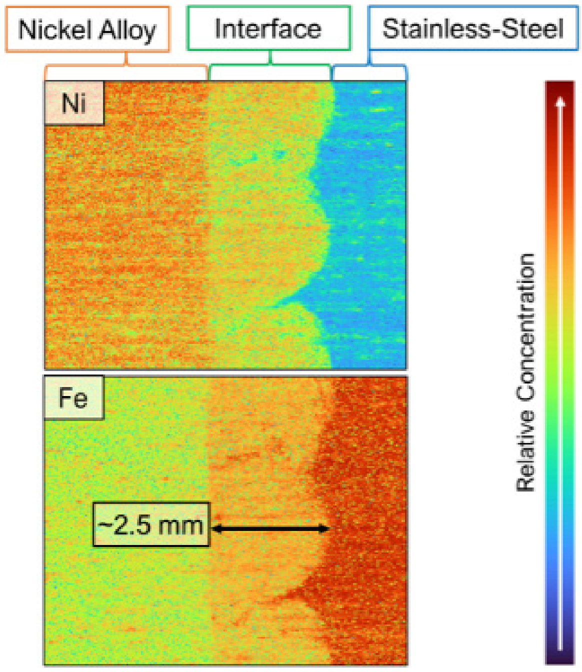

Figure 4. Elemental mapping results from a multi-material additive manufacturing specimen of Stainless-Steel 316L and nickel alloy, Inconel 718. The color scale indicates relative concentrations of Ni (top map) and Fe (bottom map) with warmer colors (e.g., red) indicating higher concentrations. The area analyzed is 7.5 mm by 6 mm with a mapping resolution of 25 microns.

3D elemental mapping

In addition to the 2D elemental maps presented in this study, the MASSBOX LALI-TOF-MS provides unprecedented 3D characterization. Because the MASSBOX instrument's LALI technique involves ablating and removing material, repeating the mapping process allows users to analyze multiple layers of material.

Repeat elemental maps result in 3D reconstructions of any solid material. Each pulse of the ablation laser removes 10s-100s of nanometers of material, allowing high-resolution depth profiles. The amount of material removed per layer can be controlled by adjusting the ablation laser's power and overlap of pixels. To probe through hundreds of microns of material, the user chooses a high laser power and large overlap of laser spots. Each voxel contains a full mass spectrum, allowing users to understand the 3D distribution of any element of interest. Such insights are important for complex multi-layered materials, including coatings, oxide layers, and surface contaminants. The MASSBOX LALI-TOF-MS has the unique ability to combine nanometer-scale resolution with profiles extending through hundreds of microns of material, ensuring its depth profiling abilities are impactful for a variety of applications.

Summary

This study demonstrates how the MASSBOX LALI-TOF-MS can help in developing and manufacturing innovative materials and products. Characterizing the interface between two materials is critical for improving the novel multimaterial additive manufacturing process. A 3D-printed tensile bar specimen was loaded into the MASSBOX LALI-TOF-MS with no sample preparation required. The MASSBOX LALI-TOF-MS performed a quick scan with a relatively large laser spot size (120 microns) to identify the location of the stainless-steel-to-nickel-alloy interface. A higher-resolution (25-micron) elemental map revealed a distinct area of mixed chemistry, corresponding with the melt pool created during the Directed Energy Deposition process. These insights will inform the next iteration of functionally graded material development.

In addition to the elemental mapping results presented here, the MASSBOX LALI-TOF-MS provides quantitative analysis of the full periodic table of elements, rapid screening of unknown materials, and depth profiling. Combining these powerful modalities into a single desktop package, the MASSBOX LALI-TOF-MS accelerates development and discovery. Instead of combining results from several instruments and different test methods, users acquire full chemical characterization in a single analytical session with the MASSBOX LALI-TOF-MS. Furthermore, because the entire analytical process is conducted under vacuum, it is an ideal tool for analyzing air- and moisture-sensitive materials.

Elemental mapping | **Depth profiling** | **Rapid screening** | **Quantitative analysis**

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