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Direct visualization of chemical transport in solid-state chemical reactions by time-of-flight secondary ion mass spectrometry

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Background incl. aims

Systematic control and design of solid-state chemical reactions are essential for modifying material properties and pioneering novel synthesis techniques. Enhanced chemical transport and accelerated kinetics of active elements and compounds across interfaces are known to drive solid-state chemical reactions [1]. Monitoring temperature-dependent chemical dynamics at micro- to nanometer length scales in real-time is crucial for providing valuable feedback to tailor the properties, performance, and stability of multi-material structures. Conventional methods for studying solid-state reactions, such as in-situ TEM heating, can identify formed phases and their relative weights but may overlook transient and minor phases [2, 3]. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) at nanometer resolution offers a solution to these challenges. This technique provides information about element distribution and bonding encoded in multiatom ions from the near-surface region of solids [4], making it ideal for studying complex chemical processes in energy storage and hot corrosion. In this study, we combine focused ion beam–scanning electron microscopy (FIB-SEM) and TOF-SIMS to track the migration of active chemical elements from a glass coating to the oxide scale during in-situ hot corrosion experiments. Our findings demonstrate the distinct potential of TOF-SIMS in exploring nano-scale chemical dynamics of materials in response to temperature, optical, or electromagnetic stimulations.

Methods

TOF-SIMS analysis was performed using a Ga primary ion beam at an accelerating voltage of 30 kV and a current of 0.23 nA, scanned continuously across the sample surface throughout in-situ heating using MEMS heating chip. The lateral resolution of the resulting images was estimated as better than 290 nm at an abrupt step in the 23Na+ signal (20%–80% of the maximum intensity). Isochronal heating was applied from 50 to 850 °C (1 °C/s), producing a Z-direction (direction of successive two-dimensional scans) that directly tracks the temperature. Each frame's acquisition time was 1.4 s, allowing for real-time observation of chemical dynamics. The examined sample comprises a sodium borate coating as the uppermost layer, followed by the intermediate oxide layers with the dendritic iron oxide grown above the continuous iron–chromium oxide layer. The sample was cross-sectioned using FIB, and the cross-sectioned specimen was lifted out and deposited on a MEMS heating chip (flat on the chip, perpendicular to the ion beam).

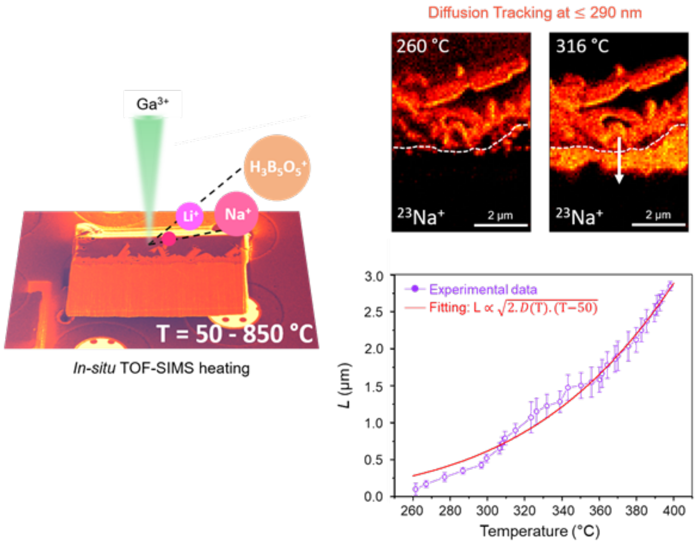
Results

This advance in nanoscale chemical analysis with TOF-SIMS reveals corrosion induced by sodium diffusion below the coating's glass transition. These findings unveil sodium diffusion decoupled from boron at much lower temperatures than previously known. Moreover, selective dissolution of iron oxides in solid-state corrosion was observed, with iron moving into the borate coating while chromium remains in the steel oxide, elucidating a part of the nanoscale electrochemical mechanism. Additionally, this technique enables the detection of transient phases and impurities during hot corrosion reactions between sodium ion and oxide layers, allowing us to track the formation of early-stage corrosion reaction products and lithium impurities in the oxide layers. Ultimately, we can employ image-based determination of the sodium diffusion coefficient by combining our established Fickian diffusion model with microscopic measurements of the moving sodium front, extracting the activation energy for diffusion and the temperature-dependent diffusion coefficient through FIB-based TOF-SIMS analysis.

Conclusion

In summary, the developed in-situ TOF-SIMS experiments provide valuable inputs for the study of chemical dynamics occurring in the hot corrosion processes of inorganic glasses with complex compositions, offering insights for mitigating corrosion reactivity at high temperatures. More widely, the developed TOF-SIMS techniques open the exploration of chemical dynamics at high temperatures in applications from metal-forming and engine lubricants to nuclear reactor components to advance the understanding of performance degradation through to new materials synthesis routes.

Graphic:



Keywords:

Coatings, TOF-SIMS, Sodium, Borate, Corrosion

Reference:

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