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SCIENCE & METROLOGY SOLUTIONS / AMETEK

NanoSIMS

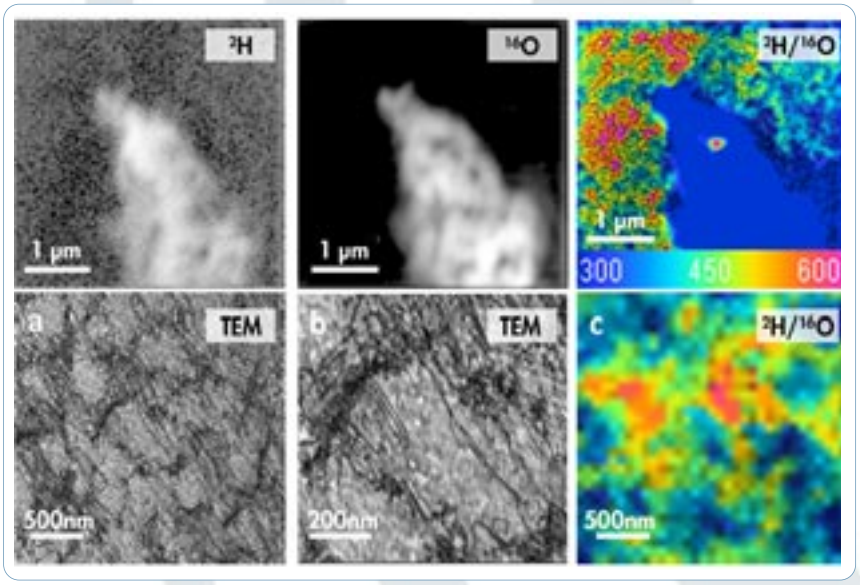
MATERIALS

Secondary Ion Mass Spectrometry for Hydrogen & Deuterium Analysis

Two- and three-dimensional hydrogen imaging with 50nm lateral resolution

Hydrogen depth profiles from areas of few microns





Top: ^{2}H distributions in 316 stainless steel after fatigue testing in high pressure deuterium environment. High resolution NanoSIMS images and derived ratio images at crack tip (sample heat AS198).

Bottom: Dislocation structure at crack tip (sample heat AS192).
a: TEM image in crack wake region ~ 4–5 µm from crack.
b: same region at higher mag. showing dislocations clusters are responsible for forming the cellular network observed in (a).
c: $^{2}H/^{16}O$ image in the crack wake region 4–5 µm from crack, with magnification as in (a). Note areas of high and low deuterium also display cellular-like structure with cell sizes very similar to those observed in (a).

From G. McMahon et al. High resolution NanoSIMS imaging of deuterium distributions in 316 stainless steel specimens after fatigue testing in high pressure deuterium environment. npl Materials Degradation (2018).



NanoSIMS 50L

Introduction to the SIMS technique

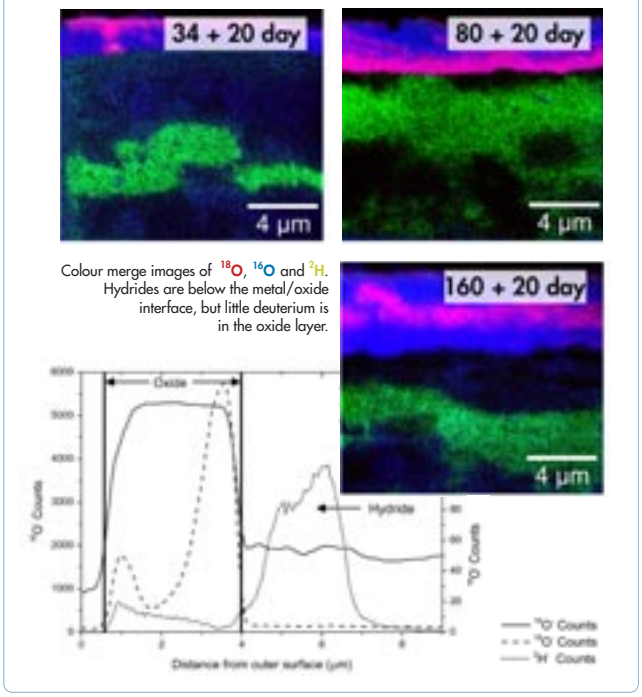
Secondary Ion Mass Spectrometry (SIMS) is based upon the sputtering of a few atomic layers from the surface of a sample, induced by a "primary ion" bombardment. Molecules are broken, atoms and atomic clusters are ejected, some of them being spontaneously ionized. These "secondary ions" are a characteristic of the composition of the analyzed area. They are separated according to their mass, and an image containing quantitative information is formed for a selected mass.

The **NanoSIMS 50L** is a totally unique analytical instrument offering **high spatial resolution** (50nm) together with **ultra-high sensitivity** for localized isotope ratio or trace element analysis.

Zirconium alloy oxidation using ^{2}H and ^{18}O tracers

Zr alloys were oxidized for various times (34, 80, 114 or 160 days) in an autoclave (360°C and 18 Mpa) to simulate pressurized-water nuclear reactor conditions and produce specimens before, around and after the first kinetic transition. Subsequently all these samples were oxidized for 20 days in a similar autoclave but containing water doped with ^{18}O and ^{2}H. ^{18}O and ^{2}H signals can be used to track the location at which new oxide is grown at different stages of the oxidation process.

NanoSIMS was used to map on cross-sections near the surface the enrichment of the rare isotopes used as tracers. Hydrides were present in all samples, even those with short oxidation times. Porosity development in the oxide allows the corroding medium to penetrate locally to the metal/oxide interface. Porosity mediated transitions between corrosion regimes occur at critical oxide thicknesses.



Colour merge images of ^{18}O, ^{16}O and ^{2}H. Hydrides are below the metal/oxide interface, but little deuterium is in the oxide layer.

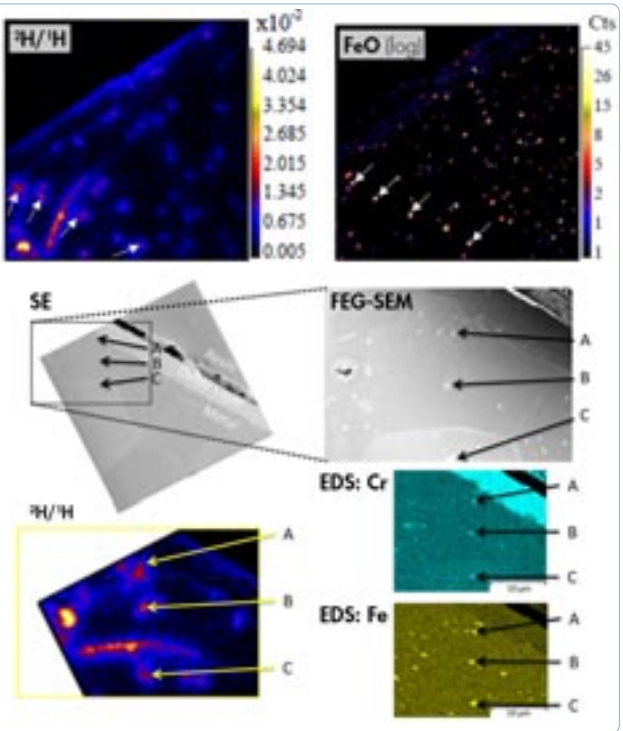
Line scan of ^{16}O, ^{18}O and ^{2}H across the oxide and into the metal for an 80 + 20 days low tin ZIRLO sample. ^{18}O is located at the metal/oxide interface while the hydride is located approximately a micron below the surface.

From S. Yardley et al., J. Nucl. Mater. 443, (2013).

Hydrogen trapping at second phase particles in Zr alloys

Zirconium alloys are used in safety–critical roles in the nuclear industry and their degradation due to ingress of hydrogen in service is a concern. In this work experimental evidence, supported by density functional theory modelling, shows that the α-Zr matrix surrounding second phase particles (SPPs) acts as a trapping site for hydrogen, which has not been previously reported in zirconium.

Zircaloy-2 and Zircaloy-4 samples were corroded at 350 °C in simulated Pressurized Water Reactor coolant before being isotopically spiked with $^{2}H_2O$ in a second autoclave step. The distribution of ^{2}H, Fe and Cr was characterized using correlative NanoSIMS and FEG-SEM EDS mapping.



Top row: NanoSIMS $^{2}H/^{1}H$ ratio and FeO images. (FOV: 50x50µm).
Bottom: Correlative imaging between the NanoSIMS and EDS from the Zy-4 sample. NanoSIMS SE and $^{2}H/^{1}H$ images, rotated and cropped, marked to line up exactly with the SE, Cr and Fe EDS images from FEG-SEM. Three SPPs (A–C) are indicated showing deuterium concentrated around.

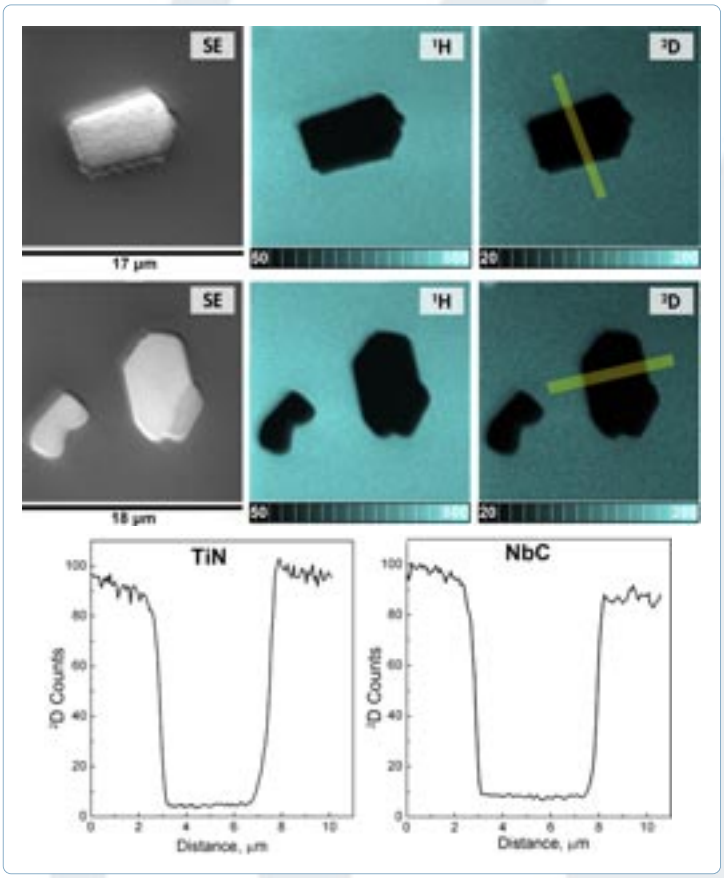
From C. Jones et al. Evidence of hydrogen trapping at second phase particles in zirconium alloys. Scientific Reports 11 (2021).

The role of precipitates in hydrogen trapping and hydrogen embrittlement of a nickel-based superalloy

NanoSIMS was employed to directly visualize the hydrogen and deuterium distribution related to specific precipitates, namely δ phase and carbonitrides, in cathodically charged Alloy 718 (in a mixture of NaCl, H_2O and D_2O).

Concurrent failure mechanisms associated with the potential hydrogen trapping behavior of these precipitates was investigated using slow strain rate tensioning to failure.

Remarkable differences in hydrogen and deuterium adsorption between the precipitates and the matrix were visualized by **NanoSIMS.** The work provides new insight into the role of δ phase and carbonitrides in hydrogen embrittlement of Alloy 718. The higher vulnerability of δ in H induced cracking is attributed to its higher capacity in H adsorption, and vice versa for carbonitrides.



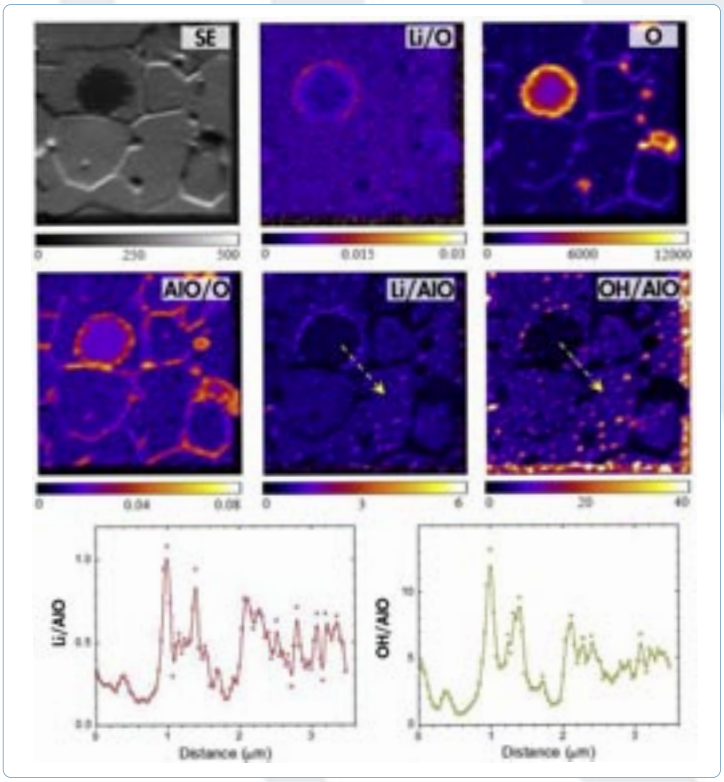
SE, ^1H and ^2D NanoSIMS maps and extracted line-scans from nickel-based superalloy areas containing TiN (a)-(c) and NbC (d)-(f) particles. The particles adsorb much less hydrogen than the γ matrix enriched by the cathodic charging, and no hydrogen segregation is observed at the interfaces.

From Z. Zhang et al. On the role of precipitates in hydrogen trapping and hydrogen embrittlement of a nickel-based superalloy. Corrosion Science Vol.146 (2019).

Lithium and hydrogen in lithium aluminate

Tritium must be replenished for strategic stockpile and fusion reactors. ^6Li-enriched g-$LiAlO_2$ pellets have been used for ^3H production by thermal neutron irradiation. A fundamental study of ^3H and ^6Li diffusion processes in irradiated g-$LiAlO_2$ pellets is needed to assess and predict the long-term material performance. This study focuses on identifying the trapping sites and diffusion pathways of ^1H (a surrogate for ^3H) and Li atoms in polycrystalline g-$LiAlO_2$ pellets irradiated with both $^4He^+$ and $^1H_2^+$ ions.

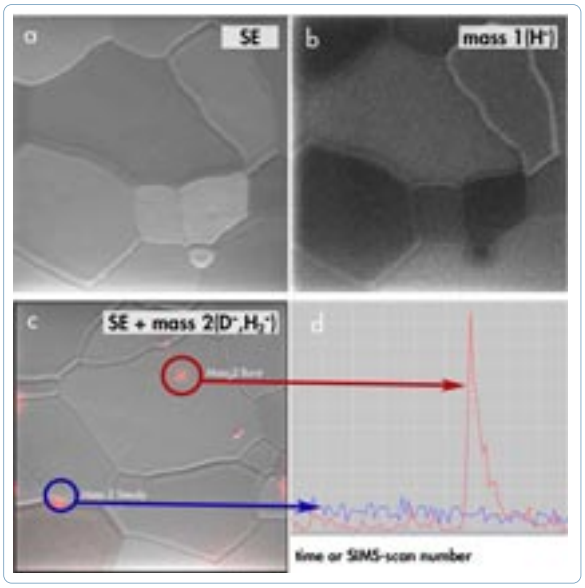
A combination of STEM-EELS, NanoSIMS and APT is employed in this study. The **NanoSIMS** is used on the images on the right to map simultaneously SE, Li^-, O^-, AlO^-, and OH^- as a substitute for H signal. Possible lithium hydrides and/or hydrates are precipitated on the surface of the irradiated pellets as indicated by the coincidence of OH/AlO and Li/AlO images and extracted line-scans.



Secondary electron and ion maps of Li, O, OH and AlO normalized or not by O or AlO in a g-$LiAlO_2$ pellet irradiated with both He^+ and H_2^+ ions. **Field of view:** 10 x 10 µm. **Below:** Normalized line-scans (Li/AlO and OH/AlO) extracted from the images. The two line-scans show a good correlation between Li and H with each peak representing a precipitate.

From W. Jiang et al. Chemical imaging and diffusion of hydrogen and lithium in lithium aluminate. Journal of Nucl. Mater. 511 (2018).

The NanoSIMS: a unique instrument for high resolution analysis of hydrogen and light elements, supporting fundamental materials research and the development of advanced technologies.



Hydrogen in plasma-facing materials for fusion reactors

Recrystallized tungsten was exposed to deuterium plasma at 370K. **NanoSIMS** maps reveal hydrogen enrichment at grain boundaries.

a: Sec. electron (SE) induced by primary ions
b: Hydrogen map
c: In situ SE image superimposed to D image in red
d: In blue: spots at grain boundaries showing continuous D– emission. In red: intra-grain spots showing time-limited gas bursts with decay, as is typical for the opening of gas-filled pores.

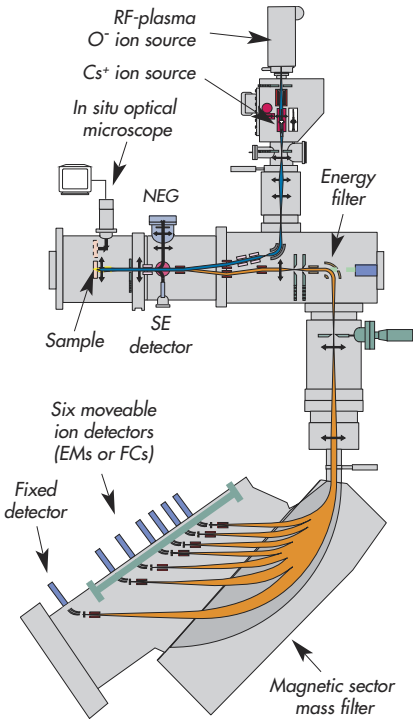
From S. Lindig et al. Sub-surface structures of ITER-grade W (Japan) and re-crystallized W after ITER-similar low-energy and high-flux D plasma loadings. Physica Scripta T145 (2011).

In addition to fundamental academic research, the NanoSIMS is also used in the display industry for small area depth profiling and 3D imaging (e.g. H and F) of individual transparent transistors (TFTs) in failure analysis & development.

NanoSIMS: a unique design

The NanoSIMS is based on an original design by Pr. Slodzian, University of Paris Sud, France. Cs^+ or O^- primary ions are focused and rastered on the surface of the sample, at normal incidence. The ions sputtered by this primary beam are collected, and the secondary ion beam is shaped in order to be mass analyzed. Seven detectors are available at the exit of the mass analyzer, six of them being moveable. Up to seven ionic species can be simultaneously recorded, originating from the exact same sputtered volume, ensuring reliable isotopic or elemental ratio and excellent distribution comparison.

Synopsis of a CAMECA NanoSIMS 50L



CAMECA is the world premier provider of microanalytical instrumentation. We deliver cutting-edge science and metrology solutions, and offer our customers unparalleled support and maintenance service through the comprehensive AMECARE program.

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