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Viewpoint set

Viewpoint: Nanoscale chemistry and crystallography are both the obstacle and pathway to advanced radiation-tolerant materials☆

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ABSTRACT

New candidate materials for GenIV or fusion nuclear energy systems, e.g., nanostructured ferritic alloys, are distinguished from older-generation nuclear materials by much smaller feature sizes and complex local nanochemistry and crystallography. Established and perspective nuclear materials, e.g. reactor pressure vessel steels or plasma-facing tungsten, also form small nanoscale structures under in-reactor service. Here, we discuss recent advances in materials characterization – high-efficiency X-ray mapping combined with datamining; transmission Kikuchi diffraction; and atom probe tomography – that make it possible to quantitatively characterize these nanoscale structures in unprecedented detail, which enables advances in understanding and modelling of radiation service and degradation.

1. Introduction

Materials long have been, and remain, the main obstacle to advanced reactor concepts [1]. Only with new more-radiation-tolerant materials can nuclear energy move on from the 1960s technology dominating the present fleet into true a 21st-century technology. Three broad methods have been proposed to improve the radiation tolerance of materials [2]: (1) chose or design a material with an intrinsically radiation-tolerant matrix phase. (2) Chose or design a material in which vacancies or interstitials are immobile at the service temperature. (3) Choose or design a material with engineered high sink strength, which is to say, a nanoengineered material. Broadly speaking, strategy (3) is under the most research in the modern nuclear materials community, and even approaches emphasizing strategies (1) or (2) will often incorporate nanostructuring.

Nanoengineering and nanostructuring, then, are the main pathway forward to advanced nuclear materials that can withstand the conditions envisioned for future reactors. However, nanostructuring poses distinct obstacles to experimental characterization, making it difficult to identify in sufficient quantitative detail microstructural processes that are occurring under irradiation. What new tricks and tools, available to the microscopist, will help us move the radiation-tolerant materials community forward? We attempt to provide our viewpoint to that question in this article.

As an example, compare and contrast 316 stainless steel (SS), the archetypical example of Generation-II (GenII) in-core reactor structural materials, to nanostructured ferritic alloy (NFA) 14YWT [3,4], the archetypical example candidate material for GenIV or fusion systems. First, the ferritic (BCC) 14YWT matrix is more inherently radiation-resistant in contrast to the austenitic (FCC) 316SS matrix [2]. Second, the contrast *is in size scale*: 316SS has grain sizes of tens to hundreds of microns, and large precipitates (100 s of nm or more). In 14YWT, grain sizes are a small fraction of a micron, with nano-scale precipitates (certainly $\ll$10 nanometers) that serve to pin the grain boundaries and act as strong sinks for migrating point defects and He produced by transmutation [5]. Which is to say, the materials of interest for future reactors have nanostructure sizes at least three orders of magnitude smaller than those of current-generation reactors.

As feature sizes shrink, characterization of the features becomes progressively more difficult. Nuclear materials, in particular, undergo multiple simultaneous modes of microstructural evolution under irradiation, and quantifying the microstructure under radiation damage is an absolute necessity to model and predict the changes in physical properties, such as fracture toughness, vital for regulatory approval and safe operation of future-generation reactors.

So, our thesis for this Viewpoint: *although the traditional methods of electron microscopy developed in the early days of radiation materials science [6,7] are well-suited to the materials studied in the early days of*

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radiation materials science, modern nanostructured materials must be analyzed with modern nanocharacterization methods. Perhaps this is tautological, and we've made some of these arguments already [8–10], but here we expand upon these thoughts. Specifically, we (1) describe how applications of the new analytical hardware and software available to materials scientists makes unprecedented levels of detail available at nanometer-level size scales, and (2) try to speculate upon how these techniques might lead to breakthroughs in radiation materials science in the near future.

Electron microscopy is thriving currently, thanks to ever-improving computers and related improvements such as analytical detectors and electron-optical aberration correctors. We will emphasize only three methods in order to keep this Viewpoint short, but these are the three methods we think are most likely to drive near-term advances in radiation materials science understanding and attendant materials design. These three methods are: scanning transmission electron microscopy X-ray mapping (STEM-EDS); transmission Kikuchi diffraction (tKD); and atom probe tomography (APT).

These three methods, in their latest incarnations, are illustrated in Fig. 1. The various vendors' latest generation analytical electron microscopes [11–13] (in the case of Fig. 1a–c, the FEI Talos F200X STEM) incorporate bright electron optics and multiple large X-ray detectors, which provide improvements of around 100× in terms of X-ray collection compared to instruments available a few years ago. Fig. 1c illustrates the importance of advanced data analysis: correlations unexpected by the analyst, or too small to see using standard analysis techniques, are discovered by computational datamining. Both advanced X-ray mapping (Fig. 1a) and computational data analysis (Fig. 1c) will be discussed below. The next of the three techniques we wish to discuss, tKD [14–16], is illustrated in Fig. 1d. Here, the highly nanocrystalline grain size of 14YWT is seen in the crystallographic map. Combining STEM-EDS and all its modern capabilities with tKD allows a tremendously comprehensive and quantitative analysis of the specimens. In terms of radiation materials science, local chemistry, grain boundary character, and precipitate character all link to the ability of a material to retain its properties and survive radiation service. APT complements both tKD and STEM-EDS by combining a higher quantification precision, and finer spatial resolution, and some crystallographic capabilities [17].

Briefly, let's illustrate our thesis using Fig. 1. A focused-ion-beam (FIB) prepared thin foil of 14YWT NFA (ORNL heat SM10) was analyzed in the Talos F200X STEM [18] by X-ray spectrum imaging. This sample was Pt-ion irradiated to ~160 dpa at −100 °C [19,20], and the EDS map is from below the irradiated region. From the spectrum image, the X-ray counts for W-Lα, Ti-Kα, and Y-Lα were extracted, false colored, and presented as Fig. 1a. This shows a complex array of microstructural features: W grain boundary segregation (as well as Cr, not shown for easier readability), and Y-Ti-rich and Ti-rich precipitates, in different sizes. The accompanying HAADF-STEM image is Fig. 1b. A multivariate statistical analysis (MVSA) decomposition of the EDS SI, using the Sandia National Laboratories AXSIA code [21], separates Cr-W segregation, Ti precipitate component, and Y-O precipitate components very clearly. This statistical decomposition denoises the data, finds the correlations (such as Cr-W at the grain boundaries and Ti-Y-O in the precipitates), providing a tremendously improved qualitative analysis of the elemental signals. MVSA also finds components the human analyst might not have looked for: aluminum is not deliberately added to the alloy, but Al-Ti-O precipitates appear in the MVSA map. In Fig. 1d, tKD is taken using the same TEM foil and a standard EBSD system. The foil is held in a special holder and raised until it nearly touches the SEM objective lens, and then maps are acquired using the EBSD hardware and software, but capturing the transmitted patterns that have passed through the foil. This provides an EBSD-like crystallographic map, but with tremendously improved spatial resolution. In Fig. 1c, pixels are 5 nm, and features down to <40 nm are easily seen. APT is a technique capable of providing highly spatially and chemically resolved three-dimensional atom-by-atom rendering of a materials specimen, with a unique ability to resolve the chemical identities of atoms, even at extremely dilute concentrations or very light species that are not easily distinguishable via electron microscopy based techniques. A

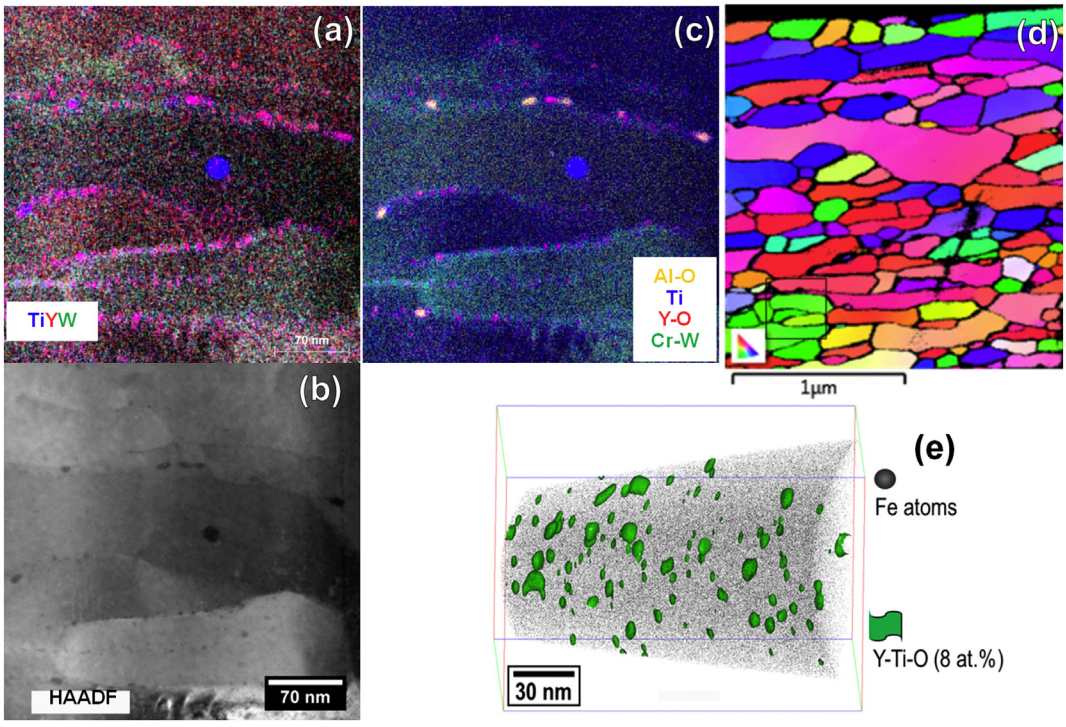

Fig. 1. (a) Colored X-ray maps (Ti, Y, W) of 14YWT alloy. (b) HAADF image of the same region. (c) Colored score images from multivariate statistical analysis of the same dataset as (a); an unexpected Al-O rich phase is discovered via this datamining. (d) tKD map, colored on the out-of-page direction; the black box denotes the region of (a)–(c). (e) APT image of 14YWT alloy (see online Supplementary information Fig. S1 for details). (a) has a 3 × 3 pixel smoothing filter applied. (c) is binned 4 × 4 pixels, from 1024^2 to 256^2 pixels. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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