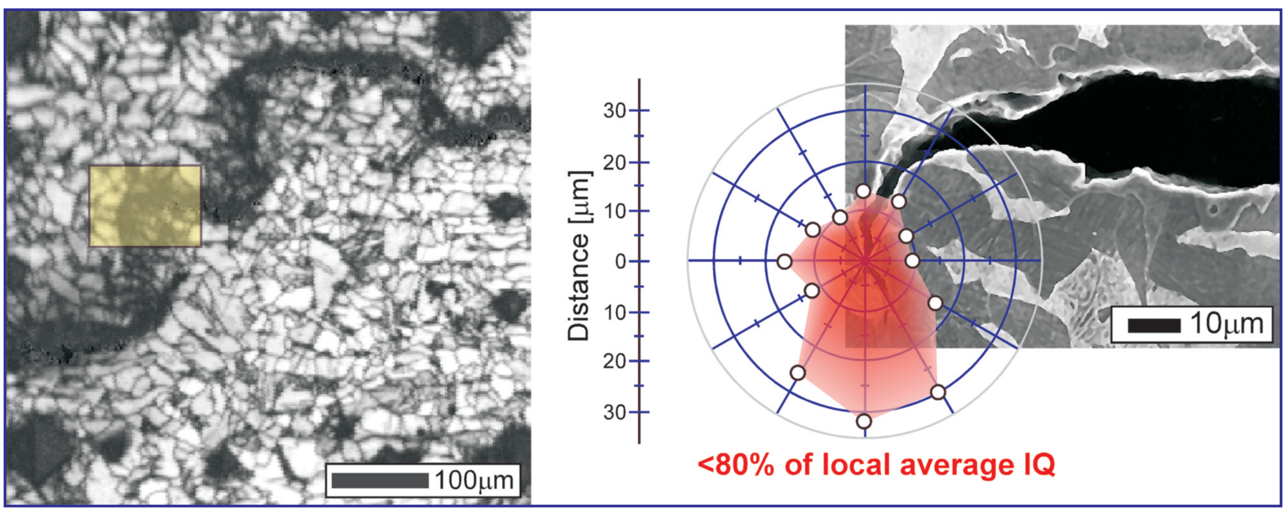
Deployment of EDAX Tools in Support of Materials Problems Associated with the Hydrogen Economy

Introduction

In a recent issue of JOM, Jones and Thomas gave an overview of materials issues associated with the Hydrogen Economy [1]. They point out that while there are economic and societal issues associated with moving to a hydrogen economy, ultimately the successful transition may hinge upon technological issues such as hydrogen production, distribution, storage and propulsion which in turn depend on advancements in key materials technologies. EDAX provides a suite of characterization tools needed by materials scientists to support research in these key enabling technologies. This brief note explores several arenas in which EDAX tools have been used in support of advancing enabling technologies towards a viable hydrogen economy.

Hydrogen Distribution

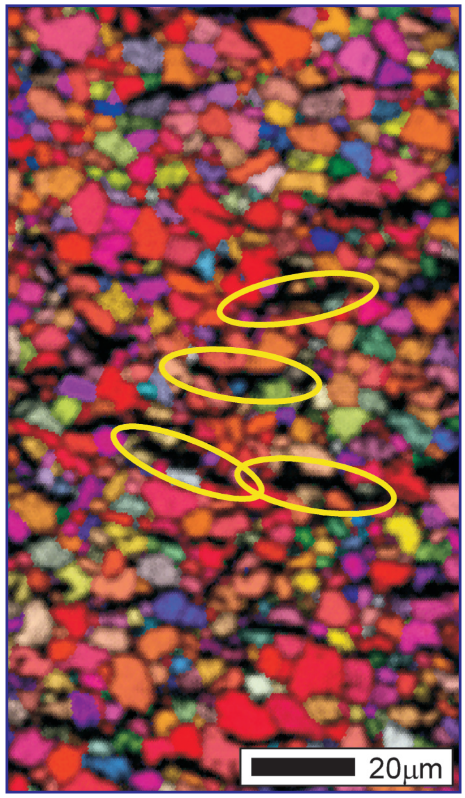
H_2 has been effectively stored in steel vessels and transported in steel pipelines; however, at the gas pressures needed for commercial distribution of hydrogen in support of the hydrogen economy, steels become more susceptible to hydrogen-induced crack growth and embrittlement. Changing the gas composition and/or the steel composition are two approaches that have been employed to reduce the susceptibility. However, changing the thermomechanical treatment of the steel may also improve its performance. Grain boundary engineering (GBE) has been shown to be effective in improving a materials resistance to stress corrosion cracking [2]. The same ideas can be employed for steel intended for hydrogen transportation and storage as shown in a recent example by Venegas et al. [3,4] Using EBSD the authors were able to determine that intergranular crack propagation mainly follows high angle grain boundaries while transgranular propagation occurs by cleavage along the {001} planes and slip on specific slip systems. In addition the authors found that the EBSD pattern quality parameter was effective for characterizing the spatial distribution of plastic deformation fields surrounding hydrogen induced cracks. Intense strain regions associated with plastic zones left in the wake of a propagating crack were observed. The largest and most intense plastic zones were observed to develop between approaching cracks. Mani Krishna studied hydride formation in Zircaloy tubes. While Zircaloy is not likely to be used as a pipeline material for hydrogen transport, hydride formation is a common problem in many materials associated with the hydrogen economy. In this study, the authors found that hydrides show preferential formation in grain boundaries of specific crystallographic character. In this paper EBSD was shown to be an ideal tool for studying grain boundary character, particularly if a statistical approach is used.



EBSD Image Quality (IQ) map of a secondary electron image of the highlighted area. Diagram of the low IQ area surrounding the crack tip, which is indicative of the local strain field. [4]

Hydrogen Fuel Cells

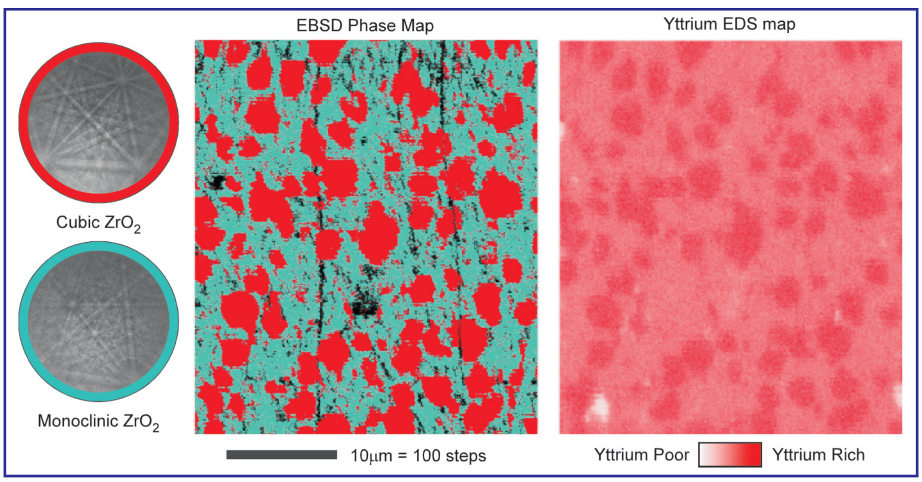
Solid-oxide fuel cells (SOFCs) are being developed for distributed power production units and even being considered for transportation. SOFCs are composed of a solid electrolyte separating a cathode and node. In addition to the electrochemical cell, there are other components as interconnect materials and sealants. As the cells are made up of many different layers of materials, there are many materials issues related to the interaction of the different layers and its impact on cell performance. A few examples of these challenges are presented here along with the application of EDAX characterization tools to help the materials scientist find solutions to these challenges. Combining EBSD and EDS is particularly useful with many of these challenges as it helps identify various phases from the various chemical species present at the interfaces between the different material layers.



EBSD map of Zircaloy tube. Hydrides appear dark in the map - a few are highlighted.

Electrolyte

The electrolyte should have good ionic conductivity and low electronic conductivity. Good control of the electrolyte composition and structure is required to optimize these properties. Yttriastabilized zirconia (YSZ) is the most commonly used electrolyte in SOFCs. As the YSZ electrolyte is in contact with both the anode and cathode, interdiffusion of the chemical species must be considered. It has been found that small additions of NiO help to stabilize the cubic phase in YSZ at high temperatures. However, the prolonged aging of these samples results in the decomposition of part of the cubic phase to produce a cubic and tetragonal phase composition. As migration is pertinent to the use ofNiO in an SOFC, Delaforce et al used a combination of EBSD, EDS, and XRD analysis to examine the effect of NiO on the microstructure and phase stability of dense pre-fired YSZ substrates. [5]

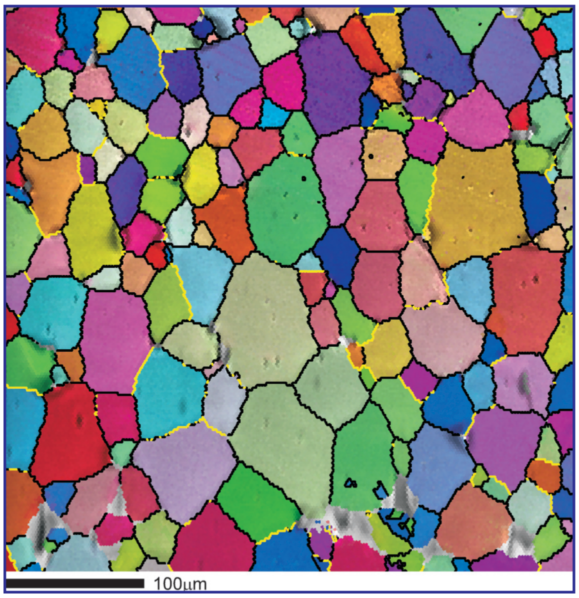


EBSD phase map and an EDS elemental map for Yttrium obtained simultaneously showing the correlation between phase and Yttrium content. [5]

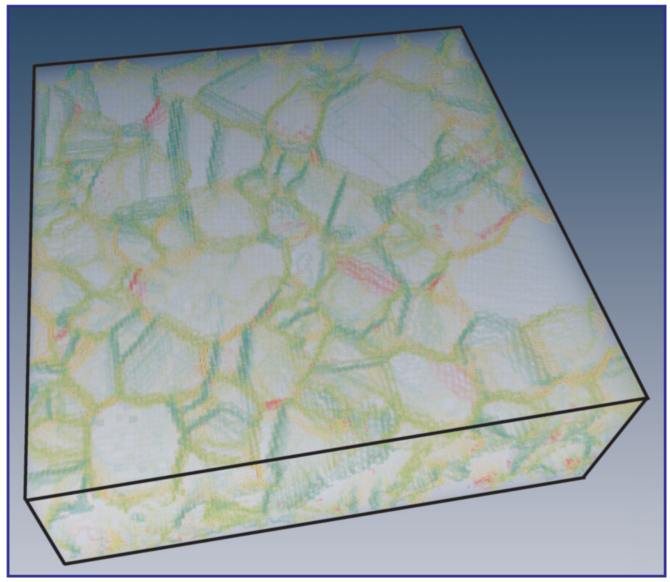
They found the effect of NiO to be dependent on the Yttria content of the substrate. With 3 mol% YSZ, NiO promotes the formation of large cubic phase grains with lower yttria concentrations compared to those doped with yttria only. The grain growth of both the cubic and tetragonal grains increased. Greater numbers of the tetragonal grains were found to exceed the critical size, i.e the size at which they transform to the monoclinic phase during cooling. At 8 mol% YSZ, the addition of NiO does not alter the phase composition remains although large grains are formed beneath the printed NiO layer. Additionally, nickel was found to migrate through the thickness to a distance of approximately 200 mm with 3 mol% YSZ and is confined to the depth of the large grains with 8 mol% YSZ.

Anode

$SrTiO_3$ is a candidate material for SOFC anodes due to its chemical stability at high temperatures under oxidizing and reducing atmospheres. However, the electrical properties of this material are sensitive to the existence of defects and interfaces. Horikiri et al. used EBSD to study the sensitivity of the electrical properties to grain boundaries in Nb–$SrTiO_3$. [6] They examined grain boundary distribution in polycrystalline samples and compared conductivity results against bicrystals and single crystals. Their results suggest that conduction is neither through the grains nor across the grain boundaries; but rather, through the three dimensional network of grain boundaries. 3D EBSD [7] may yet play a role in understanding the effect of grain boundaries on conductivity.

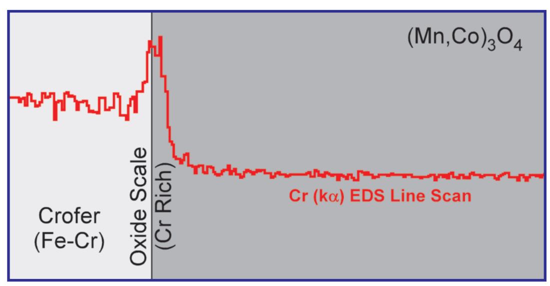


OIM™ orientation map overlaid over a secondary electron image $SrTiO_3$ with special boundaries highlighted in yellow.



3D visualization of the grain boundary network in a nickel alloy measured by EBSD on a series of 2D sections. Grain boundaries are colored according to misorientation: from blue (low angle) to red (high angle).

Interconnect

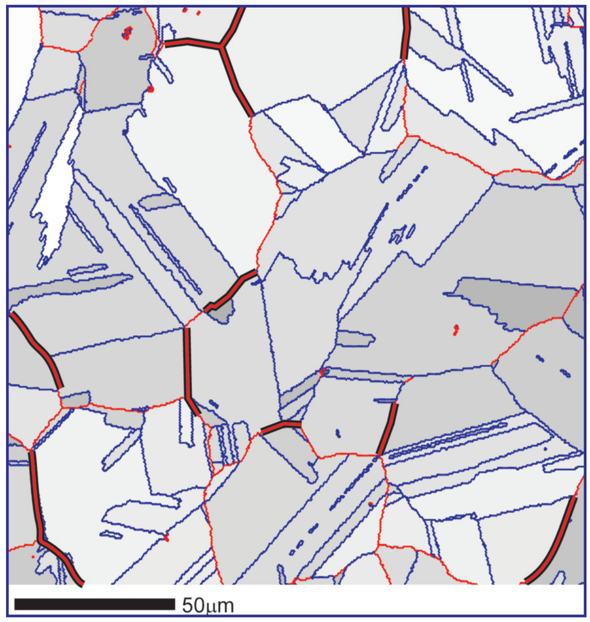


Schematic of a chromium EDS line scan of a post-tested SOFC showing minimal chromium migration from the stainless steel interconnect into the $Mn_{1.5}Co_{1.5}O_4$ barrier coating. [8]

Some SOFC designs suggest using thin-film (<20µm) YSZ electrolyte membranes with anode substrate supports. This combination decreases ohmic losses across the electrolyte; enabling reduced operating temperatures and the potential use of lower cost metals for the interconnects. One candidate metal would be ferritic stainless steel due to its thermal expansion match and oxide scale conductivity. However, this material suffers in performance due to the formation of a Cr containing oxide scale, which poisons the cathode. One approach to minimizing Cr volatilization is to coat the stainless steel. $(Mn,Co)_3O_4$ spinel is one promising coating. A study by Simner et al. was undertaken using EDS as a characterization tool. [8] These results showed that coating a ferritic stainless steel interconnect with $Mn_{1.5}Co_{1.5}O_4$ effectively mitigates Cr volatilization even at temperatures of 800°C over long time periods.

Hydrogen Production

Hydrogen for refining petroleum and producing ammonia is generally produced by steam methane reforming. As this process does not reduce greenhouse gas emission and generally requires fossil fuels, other processes are being considered. These include electrol sis, solar and photo-electrochemical processes and thermo-chemical processes. The source of energy for these processes underlies whether the Hydrogen economy can successfully reduce greenhouse gasses and dependence of fossil fuels. There are several different aterials challenges associated with these different processes. One issue common to most of these processes is the creep of corrosion-resistant materials at high temperatures. An example of this type of research is that performed by Boehlert and co-workers on Udimet, a cobalt based alloy with good creep strength and oxidation resistance. [9] They studied the effect of grain boundary character on creep using in-situ EBSD. They found that surface cracking initiated and propagated preferentially at high angle grain boundaries. Again, the principles of grain boundary engineering could be applied to potentially improve the creep performance of this material.



EBSD grain averaged image quality map of a crept sample overlaid with grain boundaries. Boundaries shaded red are random high angle boundaries (>10°) and blue are coincident site lattice boundaries. Thick black lines denote cracked boundaries.

Conclusion

The successful transition to a hydrogen economy hinges on advances in key materials technologies. EDS and EBSD are important characterization tools needed by materials scientists to support research in these key enabling technologies.

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