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Analysis of Titanium Microalloying in As-Received and Oxidized Crofer® 22 APU

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The addition of titanium to ferritic stainless steel alloys has been shown to benefit the high temperature characteristics of these alloys for use in solid oxide fuel cell (SOFC) interconnects. TiN precipitates can reduce the fractional softening of interconnects at high temperatures by preventing recrystallization and recovery of the cold-worked alloy [1]. TiN has a lower solubility in austenite than ferrite [2]. During solidification of molten steel, TiN precipitates in the austenitic region and is then annealed in the ferritic region [2]. During long term SOFC operation, titanium oxide forms and provides a keying effect at the interface of the alloy and chromia scale [3]. Titanium oxide also forms at the surface of the chromia scale to reduce chromium volatilization [4]. Analysis of an interconnect alloy, Crofer® 22 APU, before and after oxidation was performed to show the initial development of titanium precipitate morphology, structure, and diffusion.

Titanium within as-received Crofer® 22 APU: The alloy with 0.2 wt% Ti was received as a sheet, 0.21 mm in thickness, after a commercial finishing process of cold rolling, solution annealing, and bright annealing. Samples for SEM were produced by polishing electrolytically to remove a ≈50 μm thick metallic layer from the surface, leaving Ti-rich particles in relief. Such particles were found in stringers lying parallel to the sheet surface as shown in Figures 1a and 1b. These precipitates adopt a cubic morphology as shown in Figure 1c with edge lengths of 1.0 - 2.4 μm. X-ray spectrometry and electron diffraction data obtained from such particles using TEM (Figure 2) confirmed that these were TiN particles with the NaCl structure (a_0 = 4.23 Å).

Titanium within oxidized Crofer® 22 APU: The distribution of titanium precipitates along the interface of the alloy and its oxide scale was studied using STEM on a FIB-cut cross-section as shown in Figure 3 [5]. A chromia scale with 0.5 wt% Ti developed after a 750 h heat treatment at 800 °C. There were also fine TiOx particles up to 50 nm in diameter lying underneath the oxide scale. Like the TiN particles in the initial alloy, these internal oxides were arranged in stringers parallel to the sheet surface.

The complex multicomponent diffusion of Cr, Mn, and Ti is partly responsible for the excellent high-temperature oxidation resistance of Crofer® 22 APU. Our observations demonstrate that there is a transfer of titanium from the initial TiN precipitates to the fine sub-scale TiO_x particles and to the chromia scale during oxidation at 800 °C. The formation of a primary titanium oxide phase on the scale surface is prevented due to the size of the TiN precipitates. The large precipitates have a small surface area to volume ratio, limiting dissolution and diffusion of titanium to the scale surface. The TiO_x phase forms instead, as sub-scale internal oxides on the dislocations formed during cold rolling, rather than on the grain boundaries. This is significant because grain boundary titanium oxides could lead to spallation of the chromia scale [3].

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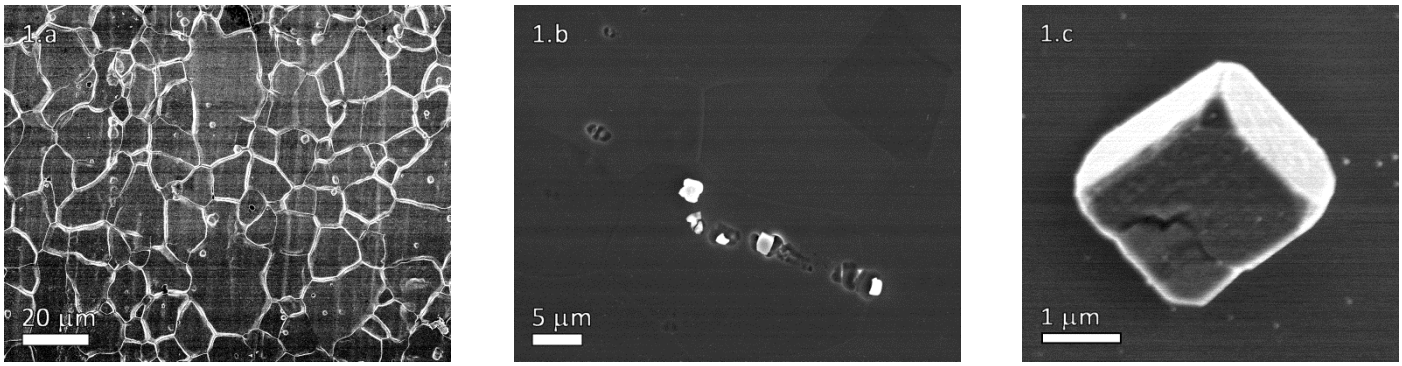

Figure 1. SEM images of TiN precipitates on etched surfaces of as-received Crofer® 22 APU: (a) no decoration of alloy grain boundaries; (b) precipitates lie in stringers; (c) cubic particle morphology.

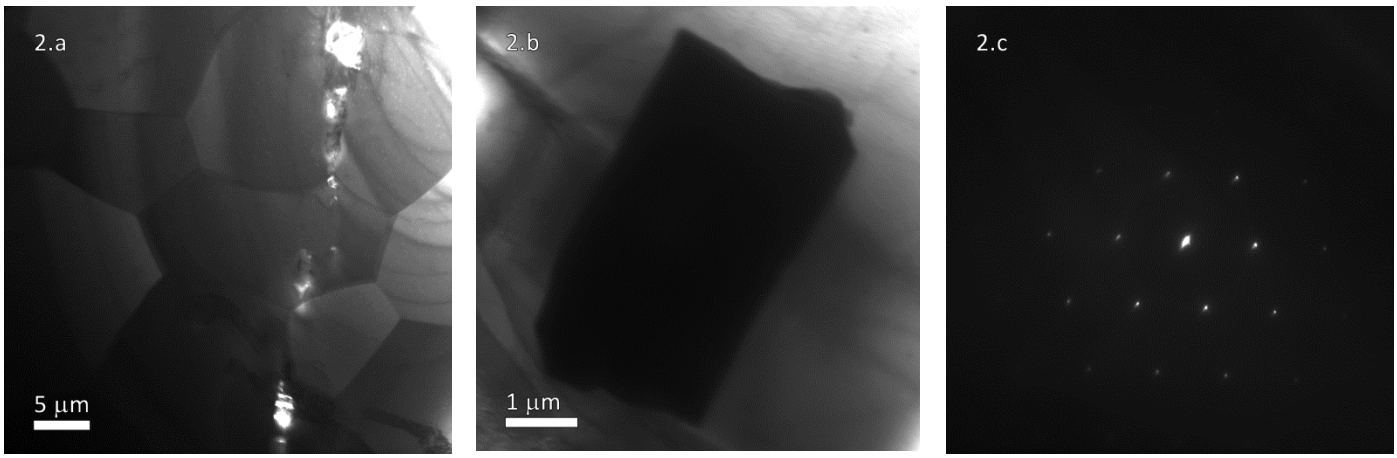

Figure 2. TEM data from as-received Crofer® 22 APU. (a) TiN stringers in the alloy; (b) cuboidal morphology of a TiN particle; (c) 011 zone axis pattern from a TiN precipitate.

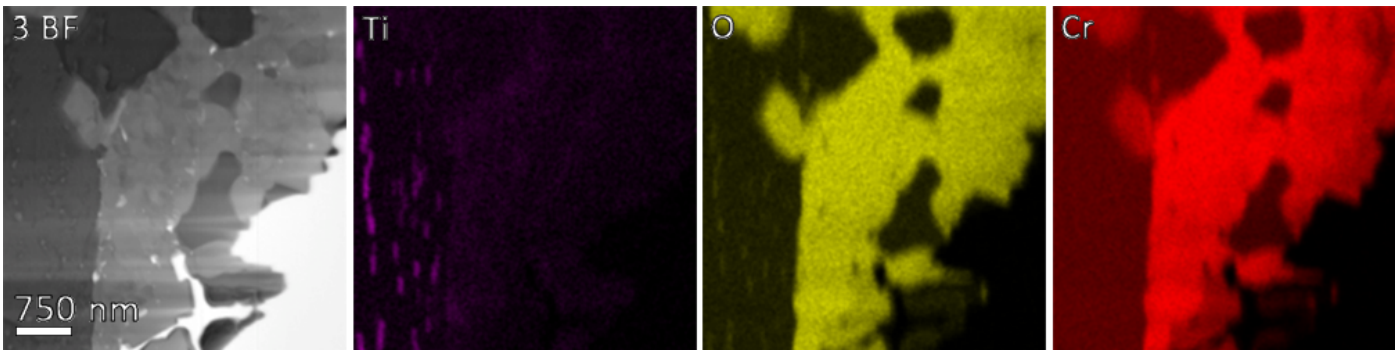

Figure 3. BF STEM image with EDXS maps from a cross-section through the scale on Crofer® 22 APU oxidized at 800°C. The maps show TiO_x internal oxides below the chromia scale.

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