**2.4 EFFECTS OF SUBSTRATE ETCHING ON Fe - {110} $Y_2Ti_2O_7$ INTERFACES; IMPLICATIONS FOR NANOSTRUCTURED FERRITIC ALLOYS** - T. Stan, Y. Wu, S. Kraemer, and G.R. Odette (University of California Santa Barbara)

## OBJECTIVE

The objective of this work is to create surrogate bulk Fe – $Y_2Ti_2O_7$ interfaces, with similar characteristics to those found in Nanostructured Ferritic Alloys, which are amenable to conventional characterization techniques and irradiation experiments.

## SUMMARY

Nanostructured Ferritic Alloys (NFAs) have a Fe-Cr matrix and are dispersion strengthened by <5 nm Y-Ti-O phases. The interfaces between these Y-Ti-O nanofeatures (NFs), such as $Y_2Ti_2O_7$ (YTO), and the surrounding matrix provide many favorable properties pertinent to fusion environments, such as trapping He in fine scale bubbles. As a supplement to current characterization efforts of the NFs themselves, surrogate bulk Fe-YTO interfaces have been fabricated by electron beam Fe deposition onto un-etched and etched {110}YTO substrates. The observed Fe-{110}YTO orientation relationships (ORs) and interface characteristics are reported. Etching the substrate prior to Fe deposition has yielded interface structures and ORs that are believed to be similar to those found in embedded NFs. These bulk samples are more amenable to conventional characterization techniques and irradiation experiments. The results also support the development of computational models to predict NFA behavior.

## PROGRESS AND STATUS

### Introduction

The smallest <5 nm features in Nanostructured Ferritic Alloys (NFAs) are composed of the $Y_2Ti_2O_7$ (YTO) complex oxide, fcc pyrochlore phase. The interface between the bcc Fe-Cr matrix and the fcc YTO plays a critical role in the stability, strength and damage tolerance of NFAs [1,2]. In particular, NFAs may turn He from a liability to an asset. For example, He bubbles at Fe-YTO interfaces act as recombination sites for vacancies and interstitials, thus promoting self-healing. The high density of matrix-NF interface traps prevent He from gathering at grain boundaries which would otherwise degrade creep and fracture properties as well as preventing the nucleation of voids.

There is ongoing research to determine NF compositions, structures, and matrix-NF orientation relationships (ORs). A summary of these studies and other NFA properties was recently published by Odette [1]. Determination of the matrix-YTO orientation relationship (ORs) is of interest because they affect characteristics like misfit strains and interface energies, as well as the critical functional properties of NFs. Cube-on-cube[3] and edge-on-cube[4] bulk ORs have been reported for embedded NFs. For example, Dawson et al.[3] observed the following interfacial OR for embedded NFs: $\{110\}_{Fe}||\{110\}_{YTO}$ and $<100>_{Fe}||<100>_{YTO}$. Ciston et al.[4] observed the following interfacial OR for an annealed NF: $\{100\}_{Fe}||\{110\}_{YTO}$ and $<100>_{Fe}||<100>_{YTO}$. These ORs both have {110}YTO planes matching with {110}Fe and {100}Fe, respectively. Other ORs were also observed [3-5].

The experimental approach in this study is to deposit Fe on oriented {110}YTO single crystal substrates to create surrogate mesoscopic-scale interfaces. We recognize that these bilayers may not have the same interfacial characteristics as those found for embedded NFs. A similar characterization of Fe-{111}YTO interfaces was published by T. Stan [6] and some preliminary results from of this Fe-{110}YTO study were mentioned in a previous fusion semiannual report [7]. Even if the mesoscopic interfaces are not the same as the embedded ones, the study will further the general understanding of metal-oxide interfaces. These surrogate interfaces will also be more amenable to irradiation studies such as interactions with point defects and He. Characterization and analysis of Fe-YTO interfaces will help develop and improve current first principles and atomic interface models, and help predict NFA performance in fusion reactor conditions.

## Experimental Procedure

The details of how samples were fabricated and what instruments were used for characterization are covered in a previous publication [6]. In summary, a two pure YTO single crystals were {110} oriented and a 2 mm thick wafer was cut using a wire saw. An Allied Multiprep instrument was used to polish the wafers using a sequence of diamond lapping films, followed by a final 15 minute polishing step using a 0.02 µm non-crystallizing silica suspension. One wafer was etched with Aqua Regia for 5 minutes, then annealed in air for 1 hour at 800 °C. The other wafer remained un-etched and un-annealed. An electron beam system was used to deposit Fe on the {110}YTO crystals at $6.2 \times 10^{-6}$ torr and 800 °C. The deposition rate was 8 nm/s for 250 s, producing Fe layer thicknesses of ≈ 2 µm. The samples were then cooled to room temperature at a rate of ≈ 0.16°C/s.

## Results

### Fe on Un-etched {110}YTO

Scanning Electron Microscope (SEM) and Electron Backscatter Diffraction (EBSD) results for Fe on un-etched {110}YTO were previously reported [7]. In summary, three Fe grain orientations were found. A flat area with a rippled surface was {110}Fe textured. Both pointed and sharp {112}Fe grains were also observed. Neither of these types of grains had an OR with the {110}YTO substrate that is found in embedded NFs. A single large 10 µm grain was found which had the $\{100\}_{Fe}||\{100\}_{YTO}$ and $<100>_{Fe}||<100>_{YTO}$ OR, same as reported for some embedded NFs [6]. This grain is of interest and has been further analyzed.

Scanning Transmission Electron Microscopy (STEM) was carried out on a Focused Ion Beam (FIB) lift-out cross section of the 10 µm grain to observe the interface. The scan is shown in the middle of Figure 1. The orange and blue/white sketches indicate the Fe and YTO orientations, respectively. The black and white STEM image shows the Fe layer in light gray at the top, and the YTO substrate at the bottom. Fe strain in the first deposited layers and/or a thin metallic oxide interlayer is visible in the dark area at the interface (marked with a red bracket). CrystalMaker was used to recreate the interface by matching the oriented Fe and YTO lattices. The results are shown in the right side of Figure 1. Fe, Ti, Y, and O are represented as orange, blue, green and red spheres, respectively. The light blue and dark green circles indicate Ti and Y atomic columns which run through the page, respectively. The purple circles indicate columns of mixed Y and Ti. The contrast in the STEM image allows for column identification, where the brighter substrate spots are indicative of Y columns, the darker spots are Ti columns, and the medium intensity spots are indicative of mixed Y and Ti columns. Note that STEM cannot detect O and thus the YTO chemistry at the interface is not clear.

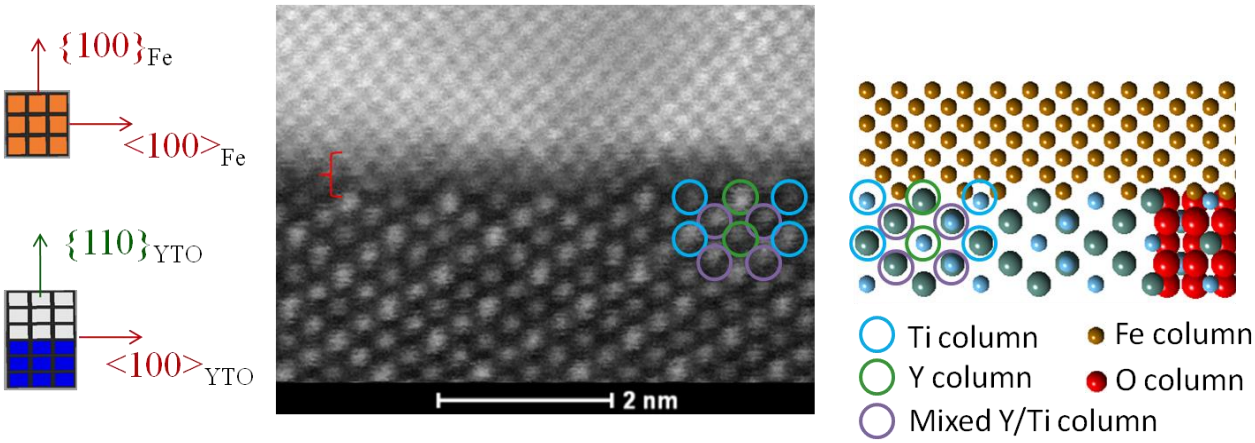


**Figure 1**. STEM image from the large {100}Fe grain observed on the un-etched {110}YTO substrate. A sketch of the Fe and YTO orientations are shown on the left. A CrystalMaker rendering of the interface is shown on the right.

**Fe on Etched {110}YTO**

A second {110}YTO substrate was etched with Aqua Regia for five minutes, then annealed for one hour in air at 800 ºC prior to Fe deposition. The EBSD map and associated legend are shown in Figure 2. The Fe film has two types of morphologies. The ~1 micron grains on the left have strong {100}Fe texturing and are shown in red. Pole figures (not shown) indicate that this film has one of the same ORs found in embedded NFs. The right side of the sample shows a polycrystalline film with many grain orientations such as {111}Fe shown in blue and {112}Fe shown in purple. The grains on the right are 1 – 5 microns in size, slightly larger than those on the left. Pole figures from this film (not shown) indicate that the grains have an axiotaxial OR with the substrate. The {100}YTO substrate planes (which are not normal to the sample surface) are parallel to the {100}Fe planes (not normal to the interface plane). These results are relevant since the observed axiotaxial OR for these grains was also reported observed for embedded NFs [4]. Clearly, etching the substrate led to Fe-YTO ORs that are observed in NFAs.

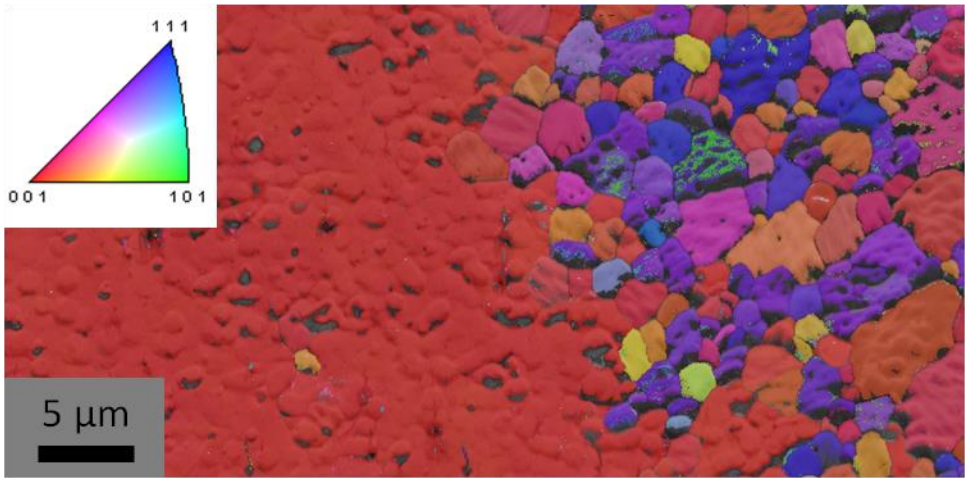


**Figure 2**. EBSD map of Fe film on etched {110}YTO substrate. The left side of the sample has a continuous {100}Fe oriented film. The right side has a polycrystalline layer with many orientations.

## Discussion and Conclusions

Fe deposition on un-etched {110}YTO substrates yielded flat {110}Fe areas with a rippled surfaces, and pointed {112}Fe grains. There was a single 10 micron {100}Fe grain with an OR reported in embedded NFs. Fe deposition on etched {110}YTO led to two types of films. The continuous film on the left side of the sample was {100}Fe textured and had the same OR as the 10 micron grain in the un-etched sample. The polycrystalline side had many Fe orientations including {111}Fe and {112}Fe which are in fact axiotaxially oriented with the substrate to have a different OR found in embedded NFs. Clearly, etching the substrate yielded ORs reported for NFAs.

First principles calculations by Y. Jiang et al.[8] suggest that the deposition conditions used in this experiment should yield O-rich YTO terminations which would promote the growth of an oxidized surface. This was previously shown with depositions on {111}YTO [6] and expected for depositions on the unetched {110}YTO surface used in this experiment. Preliminary TEM and STEM show that the Fe-YTO interface may have strain in the Fe layer and/or a metallic oxide interlayer. These interfaces are still being analyzed.

Future studies include Fe depositions on {110}YTO in a system capable of ultra high vacuum conditions and Reflective High Energy Electron Diffraction (RHEED) monitoring. If the cleaner deposition conditions yield cleaner interfaces, then the work will be extended to Fe depositions on {100}YTO and {111}YTO.

These samples are being prepared for eventual He implantation and dual-beam irradiation studies. The results will help inform first principle models of metallic oxide interfaces, as well as reaction-rate theory models for predicting NFA behavior.

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