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Characterization of a Fe/Y$_2$O$_3$ metal/oxide interface using neutron and x-ray scattering

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The structure of metal/oxide interfaces is important to the radiation resistance of oxide dispersion-strengthened steels. We find evidence of gradual variations in stoichiometry and magnetization across a Fe/Y$_2$O$_3$ metal/oxide heterophase interface using neutron and x-ray reflectometry. These findings suggest that the Fe/Y$_2$O$_3$ interface is a transitional zone approximately ~64 Å-thick containing mixtures or compounds of Fe, Y, and O. Our results illustrate the complex chemical and magnetic nature of Fe/oxide interfaces and demonstrate the utility of combined neutron and x-ray techniques as tools for characterizing them. © 2014 AIP Publishing LLC.

Nanoscale Y-Ti-O oxide precipitates are thought to play a major role in the radiation resistance of oxide dispersion-strengthened (ODS) steels.$^1$ In particular, the interfaces between these particles and the ferritic matrix are presumed to be excellent sinks for impurities created during nuclear reactions, such as helium (He$^{2+}$).$^2$ Improved models of the structure of these interfaces would be helpful in understanding and, eventually, improving the radiation resistance of ODS steels. However, due to the mixed ionic/covalent/metallic bonding present at metal/oxide interfaces, their structure is generally much more complex and difficult to investigate than that of metal/metal$^1$ or even oxide/oxide$^4$ interfaces. Moreover, according to Gibbs’ phase rule, equilibrium phases absent from phase diagrams of bulk materials may, nevertheless, be found at metal/oxide interfaces, given the number of chemical species that meet there.$^5,6$

We present an experimental investigation of the local structure of a Fe/Y$_2$O$_3$ metal/oxide heterophase interface using a combination of neutron (NR) and x-ray (XR) reflectometry as well as x-ray diffraction (XRD). This interface involves only three elements and its oxide component has a well-defined stoichiometry. Fe/Y$_2$O$_3$ is therefore easier to investigate than the more complex Fe/Y-Ti-O interfaces found in ODS steels,$^{1,2}$ and can serve as a useful model system for understanding the influence of interfacial bonding on local interface structure. Our investigation reveals gradual variations in stoichiometry and magnetization across a ~64 Å-thick transition zone at this interface, demonstrating that its structure differs markedly from the neighboring bulk phases.

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Complementary NR and XR techniques may be used to study the structure of thin films as a function of depth with near Å-level resolution.$^7$ NR is sensitive to density, chemical composition, and magnetization. XR is also sensitive to density and composition, but with different scattering contrast than NR (electronic vs. nuclear), and is almost insensitive to magnetic structure. Unlike analytical transmission electron microscopy (TEM)$^8$ or atom probe tomography (APT),$^9$ which are also capable of Å-level characterization of interface composition, NR and XR are non-destructive and do not suffer from artifacts that may arise from the proximity of free surfaces or sample preparation. However, they require flat samples of relatively large surface area (~50–500 mm$^2$) and high-perfection, i.e., uniform layer thickness, density, and composition as well as low surface roughness.

We use room temperature RF magnetron sputtering to grow high-quality α-Fe and Y$_2$O$_3$ films on Si (100) substrates with a 1 μm-thick SiO$_2$ surface oxide. For Fe deposition, using 2 mTorr, 400 watt DC, and 30 SCCM of Ar flow results in a growth rate of 0.37 nm/s. To grow Y$_2$O$_3$, we use a Y$_2$O$_3$ target at a process pressure of 5 mTorr, RF power of 200 watt, and an Ar flow of 30 SCCM, yielding a deposition rate of 0.012 nm/s. The base pressure of the deposition chamber is <5.0 × 10$^{-8}$ Torr. Two samples are synthesized: A nominally 40 nm-thick layer of monolithic Y$_2$O$_3$ and a bilayer of Fe and Y$_2$O$_3$, each layer being nominally 20 nm thick with the Fe layer adjacent to the SiO$_2$ surface. The latter sample contains one Fe/Y$_2$O$_3$ interface.

We perform NR measurements using the Surface Profile Analysis Reflectometer (SPEAR) at the Lujan Neutron Scattering Center at Los Alamos National Laboratory.$^{10}$ The neutron beam is obtained from a spallation source and modulated by liquid H$_2$. In the experiment, neutrons impinge on a sample at a small angle, $θ$, and the ratio of elastically scattered to incident neutrons is measured. This ratio is defined
as the reflectivity, \( R \), and measured as a function of the momentum transfer vector, \( Q_z \), where \( Q_z = 4\pi\sin(\theta)/\lambda \). In a time-of-flight (ToF) instrument such as SPEAR, neutron momentum—and therefore wavelength, \( \lambda \)—may be determined by measuring the angle of scattered neutrons and the time it takes the neutrons to travel the length of the instrument. Neutron wavelengths at SPEAR range from 4.5 to 16 \( \text{Å} \). To cover the range \( 0.001 < Q_z < 0.25 \text{ Å}^{-1} \), measurements are performed at three different incident angles: \( \theta = \sim 0.5, \sim 1.0, \sim 2.6 \) degrees. XR and XRD are performed using a \( \theta-2\theta \) Rigaku Ultima III x-ray diffractometer with Goebel mirror and a set of footprint limiting slits and in Bragg-Brentano geometry, respectively. We used a 2kW linear x-ray source with Cu K\( _{\alpha} \) radiation (\( \lambda = 1.5418 \text{ Å} \)) and a curved graphite monochromator.

Analysis of specular NR data provides information on the coherent nuclear scattering length density (n-SLD) and the magnetic component of the scattering length density (m-SLD)\(^{11} \) as a function of depth normal to the sample surface. The n-SLD depth profile is uniquely determined by the composition and density of the sample and m-SLD by the magnetic properties of the film. Because the SPEAR neutron beam is not polarized, reflectivities for spin-up and spin-down polarizations in magnetic films are added incoherently to simulate the measured reflectivity curve. This procedure assumes that magnetic domains are larger than the coherence of the neutron beam (\( \sim \mu \text{m} \)). XR provides information on the x-ray scattering length densities (x-SLD), which are generally complex to account for x-ray absorption.

The \( \text{Y}_2\text{O}_3 \) monolayer and Fe/\( \text{Y}_2\text{O}_3 \) bilayer are approximated by layered slab models parameterized by layer thickness, n-SLD, m-SLD (in the case of Fe), x-SLD, and interface roughness. The models consist of oxide and metal layers sandwiched between a super-phase (air) and a sub-phase (\( \text{SiO}_2 \)). We use tabulated bound coherent scattering length (BCSL) values\(^{12} \) for Si, Y, O, and Fe in the model. Given a trial SLD profile, the Abeles matrix method\(^{13} \) as implemented in Motofit\(^{14} \) and the Parratt formalism employed in locally developed fitting programs\(^{15} \) are used to calculate the corresponding reflectivity curves. The model is then refined to optimize the \( \chi^2 \) goodness of fit\(^{16} \) between the calculated and measured reflectivity curves by changing the parameters describing each layer. To avoid over-parameterization, structural models employing the minimum number of layers to yield satisfactory fits are used.\(^{15} \)

NR curves for the \( \text{Y}_2\text{O}_3 \) monolayer are shown in Fig. 1(\textit{left}) and the model parameters for the best-fit SLD profile, plotted in Fig. 1(\textit{right}), are given in Table I. There is good agreement between the measured and calculated NR corresponding to the fitted n-SLD profile. The fitted SLD is constant throughout the depth of the layer, consistent with stoichiometric \( \text{Y}_2\text{O}_3 \) of uniform density. The increased roughness of the \( \text{Y}_2\text{O}_3 \) free surface compared to the interface with the \( \text{SiO}_2 \) substrate is likely due to the columnar microstructure of the \( \text{Y}_2\text{O}_3 \), which has lower overall thickness near column boundaries than in column centers due to grain boundary grooving at the surface. This result confirms that the \( \text{Y}_2\text{O}_3 \) depositions, NR measurements, and reflectivity modeling methods are reliable.

NR curves for the Fe/\( \text{Y}_2\text{O}_3 \) bilayer are shown in Fig. 2(\textit{left}), and the model parameters for the best-fit SLD profile, plotted in Fig. 2(\textit{right}), are given in Table II. Agreement between the NR measurement and calculated reflectivity from the best-fit SLD profile is very good. The NR data may only be fitted if neutron scattering due to spontaneous magnetization of the Fe layer is taken into account. The combined (nuclear and magnetic) SLD profiles obtained from the NR fit are shown in Fig. 2(\textit{right}). The red and blue solid curves represent the SLD profiles obtained for incoming neutrons in spin-up and spin-down states, respectively. In the first case, the m-SLD of \( 5.3 \times 10^{-6} \text{ Å}^{-2} \) is added to the n-SLD while in the second case it is subtracted. Reflectivities for spin-up and spin-down neutron polarizations as well as their equally weighted average are shown in Fig. 2(\textit{left}). The XR fit is shown in Fig. 3, and the associated model parameters are presented in Table III.

### Table I. Model parameters used to fit NR data for \( \text{Y}_2\text{O}_3 \) on a \( \text{SiO}_2 \) substrate.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (Å)</th>
<th>n-SLD ( (10^{-6} \text{ Å}^{-2}) )</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiO}_2 )</td>
<td>...</td>
<td>3.47(^{a} )</td>
<td>2</td>
</tr>
<tr>
<td>( \text{Y}_2\text{O}_3 )</td>
<td>382.1 ± 2</td>
<td>4.48</td>
<td>7.6</td>
</tr>
</tbody>
</table>

\(^{a}\)parameters constrained to the theoretical values.
Aside from the Fe/Y₂O₃ interface, both the n-SLD and m-SLD distributions in Fig. 2 (right) as well as the x-SLD in Fig. 3 (right) match the expected values for Fe and fully dense, stoichiometric Y₂O₃. However, n-SLDs and x-SLDs immediately adjacent to the Fe/Y₂O₃ interface deviate markedly from those of Y₂O₃ and Fe. Adjacent to the 155.4 Å thick Fe layer (measured from the SiO₂ interface), there is a 22.8 Å non-magnetic layer, labeled X. This region is especially visible in the spin-down (blue) SLD curve. Layer X is followed by a region 41 Å thick labeled (Y₂O₃)ₙ with SLDs just below that of fully dense, stoichiometric Y₂O₃.

The lower than bulk Y₂O₃ SLD of the (Y₂O₃)ₙ layer cannot be explained by Fe substitution of the Y sites because BCsL values of the elements at this interface increase as O < Y < Fe. Furthermore, because of the high formation energies of antisite defects in Y₂O₃, it is not likely that the SLD is due to Y substitution on O sites. The SLD of (Y₂O₃)ₙ layer may be explained by Y or O vacancies or by lowered density compared to the bulk material, possibly due to porosity. For example, the difference in n-SLD between (Y₂O₃)ₙ and Y₂O₃ may be accounted for by a ~15% decrease in the density of this layer or similar deficiency of the number of either Y or O atoms. Layer X has an n-SLD close to that of Fe, but is not magnetic. Meanwhile, its x-SLD is close to that of Y₂O₃. One possible interpretation of these results is to identify layer X as consisting of FeO, with n-SLD of 7.2 × 10⁻⁶ Å⁻² and x-SLD of 4.1 × 10⁻⁵ Å⁻². FeO₂ exhibits several phases with different magnetic properties.

FIG. 2. (left) NR data (circles) from the Fe/Y₂O₃ bilayer, fitted total reflectivity (solid green line), and fitted partial reflectivities for spin-up and spin-down beam polarizations (dashed red and blue lines, respectively). Error bars in the data show the statistical uncertainty of the measurement. (right) n-SLD profile from which the NR fit is obtained. The SLD of the Fe layer has different m-SLD contributions for the spin-up and spin-down components of the beam (red and blue lines, respectively). The interface with the SiO₂ substrate is at z = 0.

FIG. 3. (left) XR data (circles) from the Fe/Y₂O₃ bilayer and fitted reflectivity (solid red line). Error bars in the data show the statistical uncertainty of the measurement. (right) x-SLD profile from which the XR fit is obtained. The interface with the SiO₂ substrate is at z = 0.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness (Å)</th>
<th>n-SLD (10⁻⁶ Å⁻²)</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>...</td>
<td>3.47ᵃ</td>
<td>2 ± 0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>155.4 ± 2</td>
<td>8.02ᵇ</td>
<td>8.8 ± 0.5ᵇ</td>
</tr>
<tr>
<td>X</td>
<td>22.8 ± 2</td>
<td>8.02 ± 0.2</td>
<td>8.8 ± 0.5ᵇ</td>
</tr>
<tr>
<td>(Y₂O₃)ₚ</td>
<td>41.0 ± 2</td>
<td>3.70 ± 0.2</td>
<td>8.8 ± 0.5ᵇ</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>129.7 ± 2</td>
<td>4.40ᵇ</td>
<td>8.8 ± 0.5ᵇ</td>
</tr>
</tbody>
</table>

ᵃParameters constrained to the theoretical values.
bParameters constrained to be equal.
bulk thermodynamics... on metal/oxide interfaces may be driven by environment. It may play a role in explaining the local enhancement of Ti, particles and the ferritic matrix in ODS steels. Such changes may also be expected at interfaces between Y-Ti-O oxide particles and Fe in composition, density, and magnetization. By contrast, previous NR investigations allowed to vary ±5% from their theoretical values. Parameters fixed to the values obtained from NR fits (Table II).

Our study reveals a 63.8 Å-thick (41 Å + 22.8 Å) region at the Fe/Y2O3 interface that differs from Y2O3 and Fe in composition, density, and magnetization. Given that interfacial regions with altered stoichiometry, density, and magnetization may be as thick as ~64 Å, oxide particles with diameters below ~10 nm in ODS steels may be expected to exhibit markedly different structure and properties from bulk Y-Ti-O.

Our work demonstrates the utility of combining NR, XR, and XRD for investigating buried metal/oxide interfaces, similar to those found in ODS steels. NR investigations of Fe/Y-Ti-O metal/oxide interfaces with compositions closer to those in ODS steels may be performed in the future, provided that high-perfection samples of sufficiently large area may be synthesized. By combining NR with TEM and APT characterization, a more complete understanding of metal/oxide interfaces may be obtained.

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15See supplementary material at http://dx.doi.org/10.1063/1.4891432 for a description of how the magnetic component of the SLD was fitted as well as of how the number of layers in the model was selected.