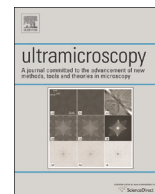




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Interpreting atom probe data from chromium oxide scales

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ABSTRACT

Picosecond-pulsed ultraviolet-laser (UV-355 nm) assisted atom probe tomography (APT) was used to analyze protective, thermally grown chromium oxides formed on stainless steel. The influence of analysis parameters on the thermal tail observed in the mass spectra and the chemical composition is investigated. A new parameter termed “laser sensitivity factor” is introduced in order to quantify the effect of laser energy on the extent of the thermal tail. This parameter is used to compare the effect of increasing laser energy on thermal tails in chromia and chromite samples. Also explored is the effect of increasing laser energy on the measured oxygen content and the effect of specimen base temperature and laser pulse frequency on the mass spectrum. Finally, we report a preliminary analysis of molecular ion dissociations in chromia.

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1. Introduction

Stainless steels have wide applications in new energy technologies thanks to a combination of high-temperature strength, corrosion resistance and affordability. However, they require improved high-temperature corrosion resistance for extreme conditions, such as within a concentrated solar power plant, where temperature cycles can range from room temperature up to 1000 °C in air or carbonaceous atmosphere. The protective oxide layer that forms on the stainless steels plays a major role in the performance of these components. Investigation of the structure of these oxide layers at the nano-scale is critical for the development of more stable protective layers.

While atom probe tomography (APT) [1] is an excellent technique to the study of the nano-structure of such oxides, the associated data analysis still presents many challenges. In the last ten years, there have been many studies of oxide materials by laser assisted APT [2–10]. However, it is only recently that laser-assisted APT has been used to study the corrosion of stainless steels, providing new insight into the microstructure of the passive oxide

layer that protects the alloy [11–13]. Thermally-assisted field evaporation of oxides leads to data that can be difficult to interpret [14–16]. With increasing interest in applying atom probe to the study of oxides, it is essential to assess the effect of analysis parameters on the data quality. Recent studies reported the influence of analysis parameters on the investigation of wüstite [16] by femtosecond laser assisted APT. The authors recommended that infra-red (IR) laser should be used to analyze wüstite as green and ultra-violet (UV) modes gave a measured oxygen content considerably below its expected value. They showed that an increase of IR-laser energy reduced the oxygen content measured. An increase of the thermal tail was also observed with increase of IR-laser energy.

Here, we aim to understand how atom probe data from thermally grown chromium oxides in stainless steels is affected by analysis conditions (laser pulse energy, laser pulse frequency and base temperature), specifically for data obtained by picosecond UV laser assisted APT. In particular, data from chromia (Cr_2O_3) was used to test the effect of different analysis parameters on the extent of the thermal tails that follow each peak in the mass-to-charge spectra and the measured composition that results. The results obtained from chromite-type spinel layers ($\text{Fe}(\text{FeCr})_2\text{O}_4$) are then compared to the chromia data.

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2. Experimental

Two chromium oxide scales were investigated, chromia (Cr_2O_3) and chromite ($\text{Fe}(\text{FeCr})_2\text{O}_4$). The chromia scale was thermally grown from a Fe–20Cr (wt%) model alloy. The alloy was exposed to Ar–20O₂ for 24 h and then to Ar–20CO₂ for 70 h at 650 °C. As a result, a protective scale of chromia was formed on the alloy surface. A more detailed description of the sample and how this data informs corrosion studies can be found in [13]. The chromite-type scale was formed in an intergranular corrosion region in a Sandvik 253MA austenitic stainless steel (ASS). The composition of the scale varies from Fe-rich chromite, $\text{Fe}(\text{Fe,Cr})_2\text{O}_4$, to near-stoichiometric chromite, FeCr_2O_4 . Details of the material and relevant corrosion studies can be found in [17]. APT samples were prepared using a Zeiss-Auriga focused ion beam (FIB) equipped with a Kleindiek micromanipulator system. Bars of oxide layers were lifted-out from milled cross sections using a micromanipulator. Samples were milled from these bars, attached to electropolished molybdenum grids and finally milled to form APT tips with a typical diameter of around 60 nm [18]. The APT experiments were conducted on a Cameca LEAP 4000 × SiTM atom probe equipped with a picosecond-pulse ultraviolet laser (355 nm, spot size < 4 μm). The data were reconstructed using Cameca IVASTM 3.6.6. EPOS files were generated using the same software and treated using custom-designed scripts in Matlab (TM, Mathworks), allowing access to the raw detector information collected for each ion, which enabled the study of singles and multiples ions events per pulses [19,20].

3. Results and discussion

In this section, we outline the methods used to range the mass spectra, since this is known to have a significant influence on the measured chemical composition [21]. We then focus on the influence of the laser pulse energy and repetition rate, as well as the base temperature, on the overall quality of the mass spectrum, with specific reference to the thermal tailing effect. Finally, we will investigate the influence of molecular ion dissociation events on the overall analysis.

3.1. Ion identification and ranging

Correct ion identification in the mass spectrum is critical for compositional accuracy and can be challenging for complex oxides. Two typical mass spectra from chromia and chromite are shown in Fig. 1a and b respectively. These two datasets were collected at a base temperature of 55 K and laser energy of 70 pJ with a laser pulse frequency of 500 kHz. For clarity, the spectra are shown in two parts, each with a different scale. Only minor peaks of Cr_3O^+ (173 Da) and Cr_2O_5^+ (185 Da) were detected above 105 Da for both oxides. Oxygen was evaporated either as an oxide-ion species or as O^+ and O_2^+ . Based on the work of Bachhav et al. [22] the peak at 16 Da was identified as O^+ , rather than O_2^{2+} . Chromium was evaporated as Cr^{2+} , CrO^{+2+} , CrO_2^{2+} , CrO_3^+ and Cr_2O_5^+ . Iron evaporated as Fe^{+2+} , FeO^+ and Fe_2O^{2+} .

We have investigated the influence of the ranging method for the chromia dataset used in Fig. 1a. There is still no agreement or standards on how mass ranges should be defined. Hudson et al.

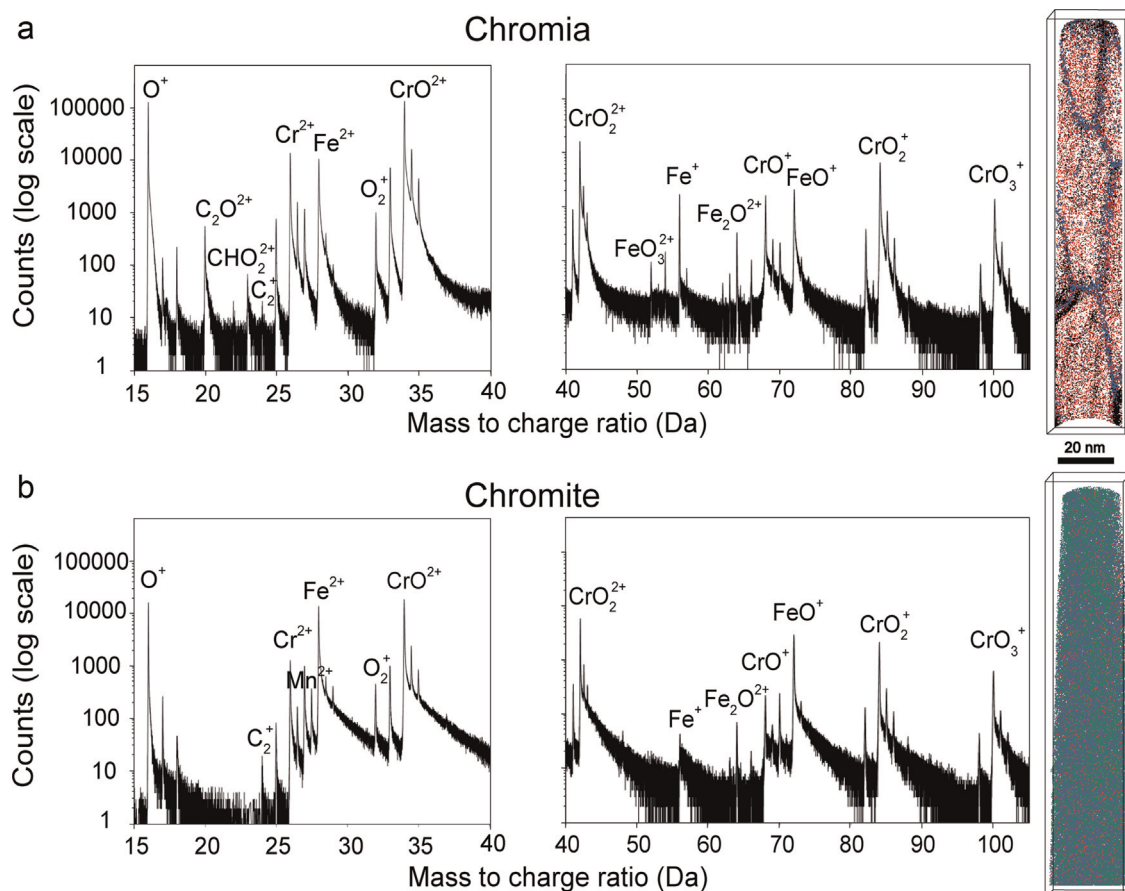


Fig. 1. Ion identification. (a) Mass spectrum of chromia (Cr_2O_3), and a corresponding 5 nm-thick atom probe volume (red: oxygen atoms, blue: carbon atoms and black: iron atoms), the specimen contains grain boundaries decorated with carbon and iron. (b) Mass spectrum of chromite ($\text{Fe}(\text{FeCr})_2\text{O}_4$) and a corresponding 3D atom probe volume (green: oxygen atoms, blue: iron atoms and red: chromium atoms). The chromite sample contains thin layers of Fe-rich chromite type spinels within near-stoichiometric chromite (FeCr_2O_4). (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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