Supplementary Material

Visualizing oxygen transport pathways during intergranular oxidation in Ni-Cr

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Target preparation

Specimens of both Ni-5Cr and Ni-20Cr were exposed during two-stage tracer experiments at 600 °C. FIB/SEM inspection of the IG oxidation performed during sample preparation showed that the corrosion microstructure was well-suited for additional APT characterization with some limitations. Porosity, as evidenced in Figure 2b and Figure 3b, is a particular challenge as it degrades the mechanical stability of nanoscale APT specimens. Porous regions were largely avoided in APT sample preparation by targeting the oxide/metal interface beneath porous regions.

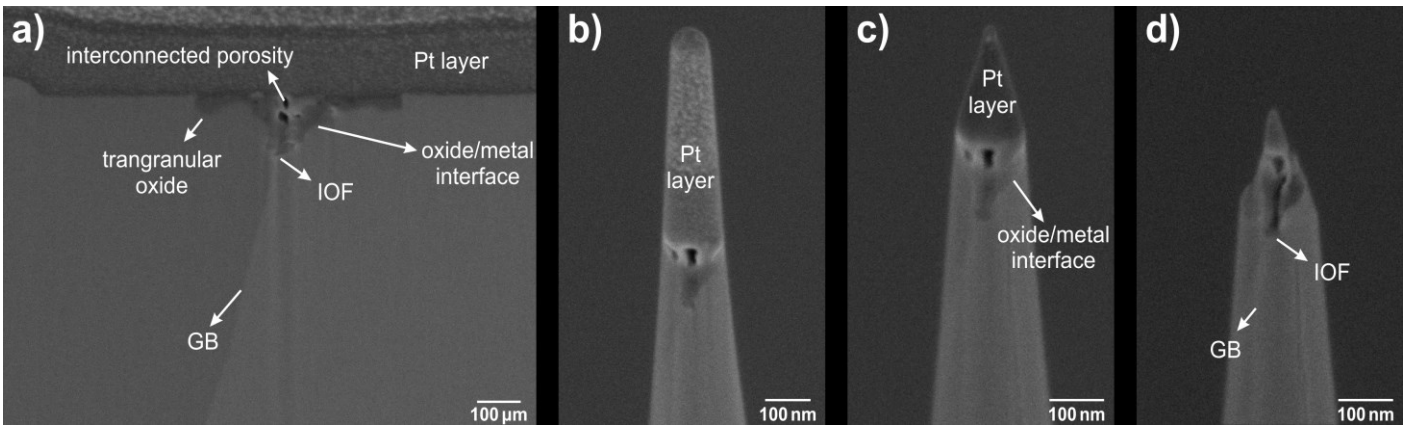

Figure S1: Electron micrographs documenting the FIB-based target preparation of IG oxide sections for APT analysis.

Figure S1 shows a representative sequence of SEM images from targeted APT specimen preparation of an oxidized GB in a Ni-5Cr specimen. After centering the tip on the oxide and reducing the cylinder diameter to ~200 nm via annular milling at 30 kV Ga^+, the terminating stage of FIB preparation proceeds at lower voltages (2 kV Ga^+). The final tip morphology, shown in Fig. S1d, is imperfect given the differential milling rates of the capping material, oxide, metal, and underlying grain boundary. Despite these limitations, high quality APT data can be collected as the field evaporation process will dictate the actual tip geometry subsequent to FIB milling. Close examination of this specimen shows that Cr_2O_3 penetrates along the GB, as indicated in Figure S1a.

APT allocation of ionic peaks

A custom treatment of the APT mass spectra was therefore needed. Figure S2 shows typical mass spectra that were collected from the IG oxide of Ni-5Cr specimens after 1 h in natural isotopic abundance CO-CO2 and then after tracer exchange experiments with CO-$C^{18}O_2$ environment during the second stage.

The naturally most abundant oxygen isotope was detected with the highest frequency between 16 and 18 Da. It is possible to calculate an expected peak height for the two remaining O isotopes in atmospheres with natural isotopic distribution. The peak at 18 Da is caused by the enrichment of ^{18}O tracers. The peak exceeds the hydroxide background $^{16}O^{1}H^{+}$ peak at 17 Da by two order of magnitude. This is an explicit indication for the presence of labeled oxygen in the data set. To verify the applied allocation of ions, peak ratio of the two most abundant Cr isotopes can be inspected in detail. Peak maxima at 26.0 and 26.5 Da for $^{52}Cr^{++}$ and $^{53}Cr^{++}$ appeared with a ratio of 8.7. Considering also the $^{52}Cr^{16}O^{++}$ and $^{53}Cr^{16}O^{++}$ peaks at 34.0 and 34.5 Da with a ratio of 8.4. Due to the enrichment of ^{18}O, combinations of most abundant Cr isotopes and ^{18}O have to be examined as well. The determined ratio ($^{52}Cr^{18}O^{++}$/ $^{53}Cr^{18}O^{++}$) from peak maxima at 35.0 and 35.5 Da is 7.8. Regarding the most abundant Cr and O isotopes, the peaks after allocation display the expected exclusive growth of Cr_2O_3 in the investigated APT data. The applied procedure for peak identification can therefore be considered to deliver relevant and accurate information about the distribution of natural and labeled contribution in the Cr_2O_3 region. Convolution of overlapping peaks was not conducted, since the exact isotopic ratio between ^{18}O and ^{16}O in the gas mixture during the second stage was not determined.

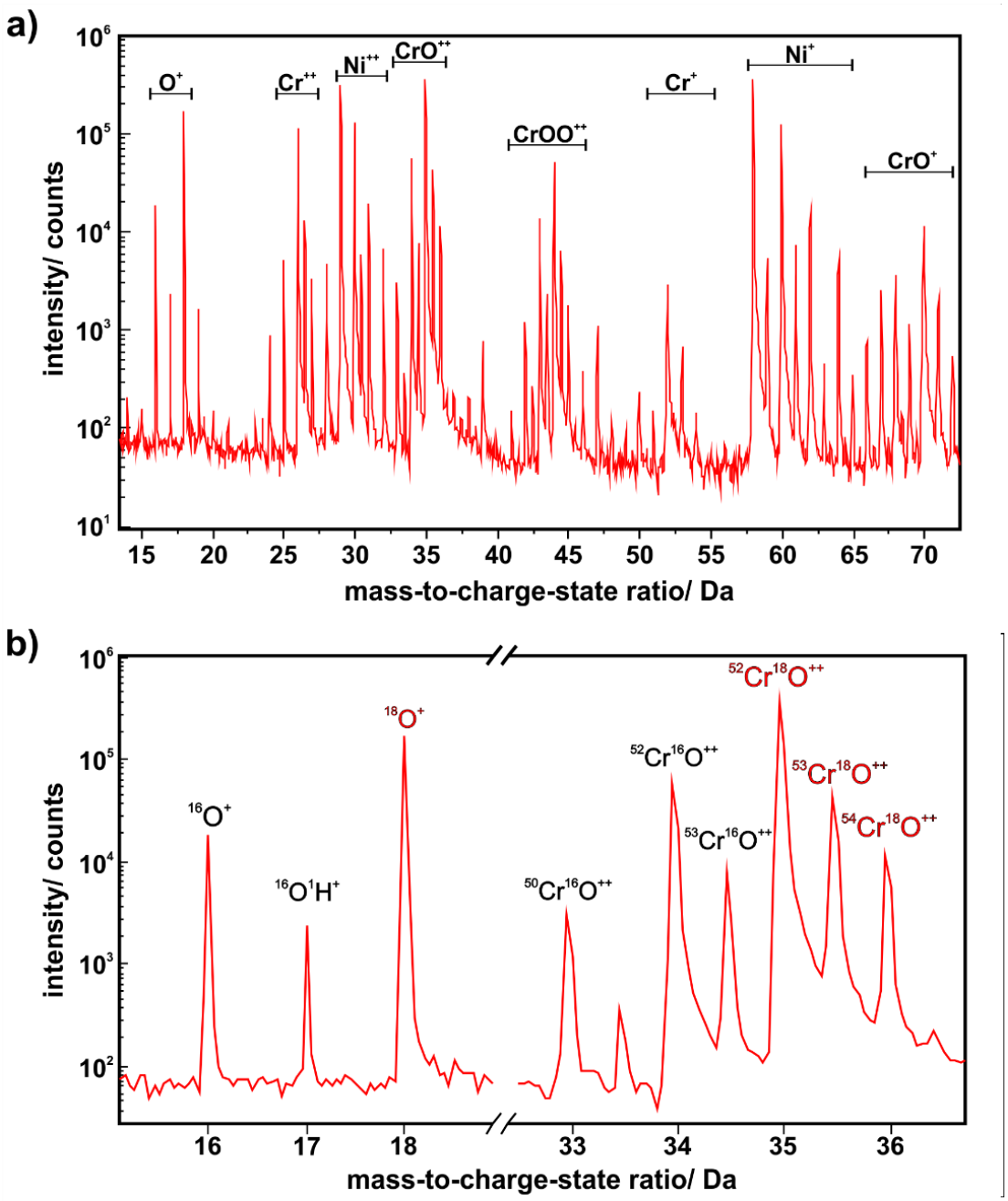

Figure S2: Mass spectra of Ni-5Cr after two-stage exposure (2 h total duration) of Ni-5Cr at 600 °C. The allocation of (a) important ranges and (b) more details on isotopic contributions between 16 and 18 Da (O^+) and 33 and 36 Da (CrO^{++}) are indicated.

Video S1: Tilt series (HAADF-STEM) of an internally attacked GB in Ni-5Cr (Fig. 2b)