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Surface analysis with a position-sensitive atom probe

A Cerezo, T J Godfrey, C R M Grovenor and G D W Smith

Department of Metallurgy and Science of Materials, Parks Road, Oxford OX1 3PH, UK

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Abstract. A position-sensitive detector has been combined with time-of-flight mass spectrometry in a short-flight-path atom probe, to yield an instrument in which both the chemical identity *and* surface position are obtained for individual atoms removed by field evaporation from the surface of a field-ion specimen. This enables thin films and surface layers to be analysed, not only with atomic-layer depth resolution, but also with sub-nanometre lateral resolution. The new instrument is described, and examples are presented showing the application of the technique to the study of the oxidation of metal surfaces, and surface segregation in an yttrium barium cuprate ceramic-oxide superconductor.

1. Introduction

A time-of-flight atom probe [1] combines a field-ion microscope, which can yield atomic-resolution images of the surface of a wide range of materials, with a sensitive time-of-flight (TOF) mass spectrometer capable of determining the chemical identity of atoms removed from the specimen surface by field evaporation. Typically, a hole in the imaging screen of the field-ion microscope (FIM) section acts as an aperture to the mass spectrometer, selecting ions from a region 0.5–5 nm in diameter on the specimen surface. This is combined with a depth resolution for composition profiling of one atom layer, determined by the strong surface sensitivity of field evaporation. As such, the atom probe provides the highest spatial resolution of any microanalysis technique. Over the past fifteen years, this has been used to study fine-scale compositional effects in a variety of metallurgical alloys [2, 3] and more recently has been extended for use in the analysis of advanced semiconductor materials [4]. The technique has also been used to study a variety of surface chemical effects, such as surface segregation in metallic alloys [5], native oxidation of silicon and GaAs [6], and the reaction between semiconductor surfaces and thin metal overlayers [7, 8].

Due to the very high lateral resolution of the atom-probe technique, the volume of material analysed can be extremely small. This is a particular disadvantage in surface studies, where the total material analysed from the 1–2 monolayers of interest may be no more than 50–100 atoms. (In the case of the surface segregation studies of Tsong and co-workers [5], several analyses were performed for each heat treatment in order to improve the statistics of composition measurements.) Larger volumes of material may be analysed by using the imaging atom probe (IAP) [9, 10], in which a double channel-plate assembly is used for imaging and as a single-ion detector. This enables a semi-quantitative mass spectrum to be obtained from the whole of the imaged area, although

with lower mass resolution. This has been used to study a variety of surface chemical reactions, such as the oxidation of platinum alloy catalysts [11] and the interaction of carbon monoxide with rhodium [12]. In addition, the spatial distribution of ions having a given mass-to-charge value can be determined by a time-gating technique. However, since only one mass-to-charge peak may be selected at any time, only a small proportion of the material contributes to each image, and it is not possible to obtain spatial and compositional information simultaneously (with one exception [13]). This makes it impossible to distinguish between diffuse interfaces, and those which are *chemically* abrupt, but rough over the area of analysis—a problem suffered by conventional large-area depth-profiling techniques to a greater extent.

In the position-sensitive atom probe (POSAP) [14], the aperture and single-ion detector of the conventional atom probe are replaced by a position-sensitive detector with a larger acceptance angle. This not only produces a chemical analysis from a greater area on the specimen surface (currently 10–20 nm), but also enables the position of impact of each field-evaporated ion to be determined. With these data, the original distribution of *all* the elements present on the sample surface can be mapped out. Since atom probe analysis is a depth-profiling technique, successive atomic layers removed from the specimen are analysed, allowing the variations in composition present in the surface layers of the sample to be reconstructed in three dimensions. The increase in data available from the larger analysis area in the POSAP permits a more accurate analysis of thin films to be undertaken, whilst still retaining the spatial information which allows the morphology of an interface to be observed.

2. Experimental details

Figure 1 shows a schematic of the POSAP instrument, which is actually mounted on a conventional atom probe FIM, allowing both conventional atom-probe and POSAP analysis of the same specimen. Field-ion specimens are formed initially by conventional techniques of electro-polishing to give an end radius of around 100 nm. The specimens are then field evaporated in the microscope to a smooth, approximately hemispherical end-form consistent with an aberration-free image. After a surface treatment (vacuum annealing, air oxidation etc), either in a separate vacuum chamber or outside the instrument, the specimens are returned to the microscope for POSAP analysis. Single atoms of material are field evaporated by a combination of DC voltage (about 10 kV) and nanosecond risetime high-voltage pulses of 1–2 kV amplitude. For each ion detected, the flight time is measured to an accuracy of 1 ns, and the charges derived from the position-sensitive anode are used to calculate the position of impact.

3. Surface segregation in ceramic-oxide superconductors

Since the discovery of ‘warm’ ceramic-oxide superconductors [15], a wide range of techniques has been used to investigate the stoichiometry of bulk and thin film samples. One aspect of particular interest is the study of the surface chemistry of these materials. It is known that atmospheric exposure, and especially humidity, results in the formation of insulating surface layers, and can lead to an apparent loss of superconducting properties by preventing the preparation of low-resistance contacts. The high resolution of the atom probe technique, together with its ability to determine accurately the local oxygen

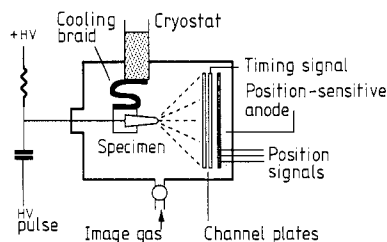


Figure 1. Schematic diagram showing the design of the position-sensitive atom probe (POSAP).

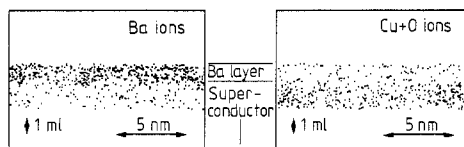


Figure 2. Barium and copper+oxygen distributions (cross sectional view) from the POSAP analysis of a yttrium barium cuprate ceramic-oxide superconductor after annealing for 2 h at 500 °C. The formation of a monolayer of almost pure barium at the surface is clearly visible.

concentration in the ceramic superconductor materials, makes it a powerful tool in studies of bulk stoichiometries and surface reaction phenomena [16]. Figure 2 shows the Ba and O element distributions, seen in cross section, from the analysis of an yttrium barium cuprate ceramic-oxide superconductor surface after vacuum annealing for 2 h at 500 °C. The treatment is seen to form a monolayer-thick barium-rich layer, which is found to have a composition of Ba–15 at. % O and only low levels of yttrium and copper. A number of analyses, using both POSAP and conventional atom probe techniques, have shown similar Ba layers, with oxygen concentrations of 10–50 at. % in the first monolayer.

4. Oxidation of stainless steel

The formation of protective oxides on a variety of materials is well known, and is very important in the generation of corrosion-resistant properties in, for example, stainless steels. In this case, it is the presence of chromium in the steel that gives corrosion protection resulting from the growth of a stable chromium-rich oxide layer. Figures 3 and 4 show the POSAP analysis of such an oxide grown on the surface of a CF3 duplex stainless steel (Fe–21wt% Cr–9wt% Ni–0.4wt% Mn–0.7wt% Si) by air oxidation at room temperature for 200 h. The cross sectional view (figure 3) shows an oxide layer approximately 1 nm thick, with the substrate interface running at an angle to the plane of analysis. It should be noted that an imaging atom probe analysis of such an interface would have indicated a far more diffuse interface than is actually present. The steel used here had previously been thermally aged for 10 000 h at 400 °C, resulting in a spinodal-type decomposition process and forming a strong variation in chromium concentration throughout the bulk. This variation is not, however, visible in the image of the oxide layer (figure 4), although the Cr composition fluctuations are seen in the bulk metal immediately below the oxide film.

5. Surface segregation on a platinum–rhodium catalyst

The surface composition of Pt–Rh alloy catalysts is known to be sensitive to prior thermal treatments and exposure to oxidation–reduction cycles at elevated temperatures [17].

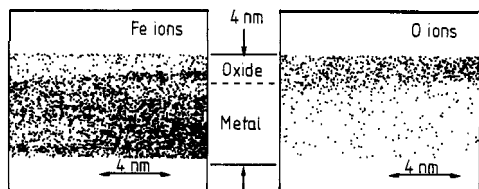


Figure 3. POSAP cross section showing the iron and oxygen distribution in the surface region of a CF3 stainless-steel specimen oxidised for 200 h in air at room temperature. The 1 nm thick oxide is seen to contain very little iron (about 10 at. %), being primarily a chromium oxide.

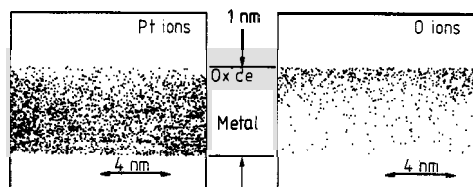


Figure 5. Cross sectional view from the POSAP analysis of a Pt-10 wt% Rh alloy catalyst after exposure to air at room temperature. A single monolayer of oxide is formed, with some oxygen penetrating into the second monolayer.

With the aid of the POSAP, it is possible to demonstrate that even room-temperature exposure to air produces changes in the Rh/Pt ratio of the topmost atom layer of such materials. Figure 5 shows the composition variations in the surface region of a Pt-10wt% Rh (17at.%Rh) specimen which has been exposed to air at room temperature. Viewed in cross section, the analysis shows the formation of a monolayer of oxide, with some oxygen in the second layer. The Rh/Pt ratio in the topmost (oxide) layer is found to be above 1:2, as compared with 1:5 in the bulk material (figure 6). Such composition changes may have significant effects on the catalytic properties of the materials.

6. Conclusions

The POSAP is a new tool for surface characterisation, having uniquely high spatial resolution both laterally and normal to the specimen surface. Some initial applications to the study of oxidation and surface segregation processes have been described in this paper, showing the power of the new technique. Many other applications can be envisaged, especially in the study of catalyst surfaces, their response to thermal and chemical processing, and the atomic-level effects of promoters and poisons on their behaviour.

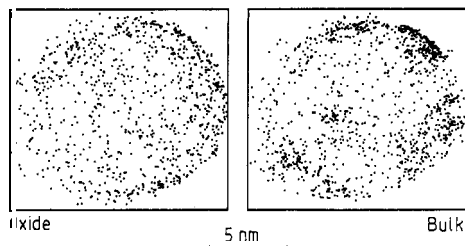


Figure 4. POSAP images of the chromium distribution within the oxide layer, and immediately below the oxide, from the specimen of figure 3. Whilst the Cr is distributed randomly in the oxide, the image obtained from just below the oxide already shows the variations resulting from a spinodal decomposition produced in the bulk material by an earlier heat treatment.

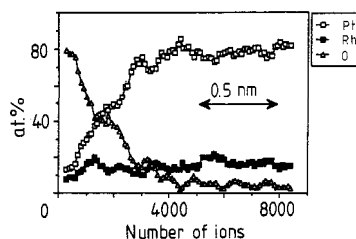


Figure 6. Smoothed composition-depth profiles from the analysis of the specimen of figure 5. Note that the surface Rh/Pt ratio is above 1:2 in the first monolayer, whereas it is less than 1:5 in the bulk alloy.

Acknowledgments

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