Mapping interfacial excess in atom probe data

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ABSTRACT

Using modern wide-angle atom probes, it is possible to acquire atomic scale 3D data containing 1000 s of nm^2 of interfaces. It is therefore possible to probe the distribution of segregated species across these interfaces. Here, we present techniques that allow the production of models for interfacial excess (IE) mapping and discuss the underlying considerations and sampling statistics. We also show, how the same principles can be used to achieve thickness mapping of thin films. We demonstrate the effectiveness on example applications, including the analysis of segregation to a phase boundary in stainless steel, segregation to a metal–ceramic interface and the assessment of thickness variations of the gate oxide in a fin-FET.

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1. Introduction

In recent years, atom probe tomography (APT) has proven to be a valuable tool for the analysis of interfaces in materials, thin film structures and micro-electronic devices [1,2]. The field of view of modern atom probes allows the capture of several 1000 s of nm^2 of interfacial area within single datasets. This has increased the need for data analysis methods that enable the extraction of quantitative values from interfaces.

The analysis of interfaces in APT data was so far largely limited to the analysis of concentration values towards an interface. This was facilitated by either manual cropping of the data to small box or cylinder shaped volumes [3], effectively reducing the analysis to a 1D problem, or the use of iso-surfaces [4]. These objects acted as reference coordinate systems for 1D concentration profiles, cumulative plots for the determination of interfacial excess [5,6] or concentration vs. distance plots ('proximity histograms' [7]). These methods are very useful for the analysis of phenomena where the distribution of certain species towards an interface is of interest, such as precipitation in metals [8–10]. However, for interfaces, surfaces and thin films (thickness < 10 nm) the distribution of the

elements in the plane of the interface or the thin film is of great interest.

This demands the mapping of the distribution of the elements or chemical species across the feature, which can achieved by mapping either the concentration of the species, or it is interfacial excess. In most cases, the use of the interfacial excess is preferred, since it is much less sensitive to artefacts such as local magnification [11] and preferential retention [12] and can easily be applied to interfaces and thin films with varying thickness.

The interfacial excess Γ_i of a species i describes the excess number of atoms per unit area that are caused by the presence of an interface [13]. In atom probe data, this is approximated by counting the number of atoms of a certain species in the vicinity of the interface, minus the extrapolated number of atoms that would be present without the segregation contribution of the interface. The interfacial excess was introduced by Gibbs [14], who defined it relative to a surface (Gibbs dividing surface), at which the interfacial excess Γ_k^k of a species k with respect to itself as the reference species is 0 (the subscript denotes the species of interest, the superscript is the reference species). It entails that the excess Γ_i^k of species i is in reference to a selected species k and therefore not unique. Guggenheim [15] later showed that the interfacial excess for a given species is unique and therefore a thermodynamic quantity, if the dividing surface is replaced by an interfacial layer that is thick enough to incorporate any volume that is influenced

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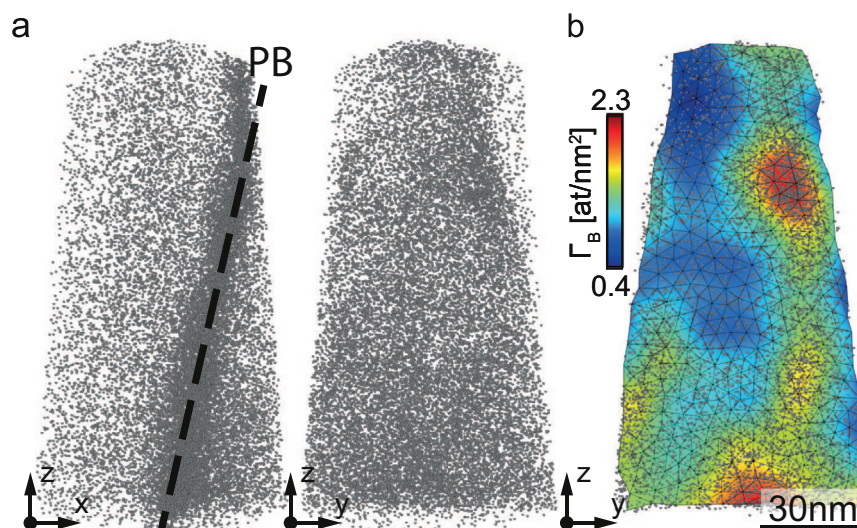   E-mail address: peter.felfer@sydney.edu.au (P. Felfer).

Fig. 1. IE mapping of B at a phase boundary (marked PB) in a super duplex stainless steel [16] with B atom positions overlayed. While he variation in IE is not obvious from visual inspection of the atomic position data shown in two perpendicular views in (a), the formation of enriched zones becomes apparent when overlaying the IE map (b).

by the presence of the interface. This ambiguity is small in data commonly encountered in APT analysis, where thicknesses of interfaces are often 10 nm and below, with a pronounced maximum. We will therefore use the Gibbs definition throughout.

IE mapping provides both a quantification of the distribution of a selected species as well as a method for the detection of variations that are not apparent by simple visual inspection of the data. How large such variations can be is illustrated in Fig. 1. In this figure, we show the distribution of B at a curved phase boundary in nano-crystalline super-duplex stainless steel [16], together with the IE map. Although the variation in the atomic density of the B is significant (∼80%), it is not easily seen by a visual analysis of the atomic distribution (the phase boundary is shown in two perpendicular orientations in Fig. 1a). The IE map (Fig. 1b) however, picks these variations up and corresponds well with the distribution of the atoms close to the grain boundary (in Fig. 1b, only B atoms closer than 5 nm to the interface are displayed).

In an earlier paper [17], we introduced a framework, based on computational geometry, to delineate features in atom probe data and then to use these features as a basis to partition the data by using a Voronoi decomposition [18]. This forms the basis of our analysis techniques. In the current paper, we focus on the specific technique of interfacial excess (IE) mapping. We show how the delineation of the dividing surfaces in atom probe data can be optimised and largely automated. This plays a central role in IE mapping, since the analysis statistics are dependent on the triangulated mesh that represents the interface. These analysis models can also be used to facilitate established analysis techniques such as proximity histograms [7]. We then show examples of how IE mapping can be applied to the analysis of various problem sets in interface and thin film analysis.

2. Experimental methods

The data from the metal–ceramic interface was acquired using a Cameca LEAP 4000 × Si instrument operated in pulsed laser mode at a temperature of 60 K, a pulse energy of 90 pJ and an evaporation rate of 1%. The fin-FET data was acquired on a Cameca LAWATAP in pulsed laser mode. The instrument is equipped with an S-pulse laser from Amplitude Systems, delivering 400 fs laser pulses at 10 kHz (spot size > 100 μm). The APT analysis was conducted using varying pulse energies (0.19, 0.24, 0.31 and 0.40 μJ) at

a wavelength of 515 nm, a base temperature of 80 K and an evaporation rate of 2%.

3. Data treatment

3.1. The principle of IE mapping and surface concentration mapping

IE mapping is based on the determination of interfacial excess values in small, elongated volumes along their long axis, as defined by the surface normals of the interface. These volumes are produced if the Voronoi cells of the vertices of a suitable, triangulated mesh are determined.

In Fig. 2, the process of IE mapping is shown for an interface between Ni and yttria-doped zirconia (YDZ) in a nanostructured Ni–YDZ anode for a solid oxide fuel cell (SOFC). At the anodes of SOFCs, H is oxidised to form water and the released electrons can be used to power an electrical device. The nanostructured interface was generated via an *in operando* reverse-current treatment described elsewhere [19]. This is reported to reduce the polarisation resistance of the electrochemical reaction at the anode by 40% at 700 °C compared to the same anode before reverse current treatment. This is attributed to the properties of the interface between metal and ceramic [20]. Atom probe experiments have revealed that O is present in the Ni at the interface between metal and oxide, observed as NiO ions, raising the question of the influence of the O on the properties of the interface. Indeed, O in the metallic Ni phase was almost exclusively observed as NiO, making it possible to separate it from the O in the YDZ, detected as ZrO_x.

While some aspects of the NiO segregation, such as the large agglomeration of NiO in the top left corner, are immediately apparent in the atom map, smaller variations easily go overlooked. In Fig. 2a, a Voronoi filter [21] was applied to the data for visual clarity. The algorithm calculates the volume of the Voronoi cell of each atom of one or more species that are associated with the feature (Fig. 3 a). Atoms of these species that belong to high-density regions in the vicinity of the feature are separated from the 'bulk' atoms by picking a threshold for the volume of the Voronoi cell of each atom. This threshold can automatically be determined by comparing a histogram of the individual volumes to a histogram of volumes from spatially random data. For a comparison of filtered and unfiltered data see supplementary movie. The IE map (Fig. 2b, included as a *.ply file in the