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Short communication

Mass spectral analysis and quantification of Secondary Ion Mass Spectrometry data

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ABSTRACT

This work highlights the possibility of improving the quantification aspect of Cs-complex ions in SIMS (Secondary Ion Mass Spectrometry), by combining the intensities of all possible Cs complexes. Identification of all possible Cs complexes requires quantitative analysis of mass spectrum from the material of interest. The important steps of this mass spectral analysis include constructing fingerprint mass spectra of the constituent species from the table of isotopic abundances of elements, constructing the system(s) of linear equations to get the intensities of those species, solving them, evaluating the solutions and implementing a regularization procedure when required. These steps are comprehensively described and the results of their application on a SIMS mass spectrum obtained from D9 steel are presented. It is demonstrated that results from the summation procedure, which covers entire range of sputtered clusters, are superior to results from single Cs-complex per element. The result of operating a regularization process in solving a mass spectrum from an SS316LN steel specimen is provided to demonstrate the necessity of regularization.

1. Introduction

Knowledge of chemical composition is an important aspect in the study of materials. As a surface analytical technique, Secondary Ion Mass Spectrometry (SIMS) is employed for composition profiling of materials in widely varying fields like semiconductor industry [1] and nuclear technology [2,3]. This technique has high sensitivity, surface specificity, and high dynamic range. However, it lacks quantification because of the dependence of yield of secondary ions on the composition (matrix) of the surface from which it is ejected [4,5]. This artefact of the technique is called as matrix effect. In semiconductor industry, the number of commonly analyzed semiconductor materials is limited. Hence, semiconductor research uses matrix-matched standards to quantify SIMS measurements [6]. However, in a general case, like a compound multilayer or an alloy with oxidized surface, the composition is likely to vary over a vast range in the volume being analyzed. Such specimens would require a very large number of standards matching each of those compositions to quantify the data. Hence, employing matrix-matched standards in such cases is near to impossible. The matrix effect in the intensities of XCs_n^+ secondary ions measured with Cs^+ primary ions (where X stands for an atom from the specimen and n is equal to 1 or 2) was shown by Gao [7,8] to be much lower (in some cases, even by orders of magnitude) than that in secondary elemental ions. However, there is still considerable deviation of the composition computed from these XCs_n signals from the actual composition. In spite of developments in understanding the formation process of these species (for example, Refs. [9–17]), a gap remains in this approach in reaching complete quantification. The current work provides an incremental step in filling this gap.

2. Theory

The XCs^+ secondary ions are understood to be formed by the combination of a resputtered Cs^+ ion with a sputtered neutral atom from the specimen [9–17]. Since secondary neutrals are formed as different atomic clusters [17–20], the intensities of the Cs complexes of all these clusters should be combined to enhance the quantitativeness of XCs SIMS. This was earlier verified with a limited number of Cs complexes [21]. However, testing this with all the Cs complexes involves quantitative measurement of the intensities of the species constituting a mass spectrum and then computing the composition from those intensities.

3. Material and methods

In this report, the details of this process are presented by analyzing a mass spectrum obtained from a sample of D9 steel, produced

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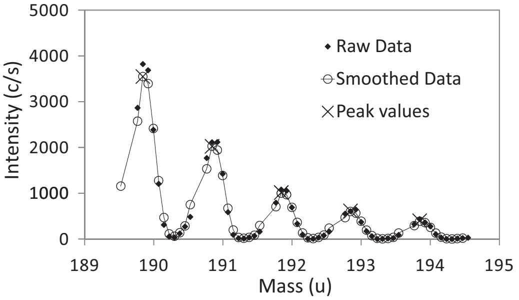

Fig. 1. A portion of mass spectrum from D9 steel depicting estimation of peak values.

by M/s. Valinox, France. D9 is the steel used in fast reactors as a construction material of core components because of its resistance to void swelling [3]. It was selected as a material for test in this report, because it is a multi-component alloy with known composition. The implementation of the above theory involves setting up and solving systems of linear equations to know the composition of the mass spectrum. A mass spectrum is analyzed completely by considering its peaks one after another. With a peak chosen for analysis, a probable species with its mono-isotopic mass equal to the mass of that peak is first identified. This species could be mono-atomic or a poly-atomic cluster. Its fingerprint mass spectrum has to be constructed and matched with the experimental mass spectrum. If this species contains n number of elements, the number N of different isotopic combinations forming this species is given by $N = \prod_{i=1}^{n} \frac{(r_i+s_i-1)!}{r_i!(s_i-1)!}$ where r_i is the number of atoms of the ith element in the species and s_i is the number of isotopes of the ith element. Those isotopic combinations with differences in mass, which are not discernible by the resolving power of the mass analyzer, appear as a single peak in the mass spectrum. (For example, in the cluster species CrFe, the combinations, ^{54}Cr^{54}Fe and ^{52}Cr^{56}Fe, differ by a mass of 0.003 u. A typical mass spectrometer with mass resolving power (MRP) of 500 cannot resolve these two combinations since the MRP required to resolve these species is 35,428.) Hence, generally in a mass spectrum, the number of peaks corresponding to a cluster species is fewer than N. This group of peaks from the mass spectrometer forms the fingerprint spectrum of the species after normalizing the sum of their intensities to unity.

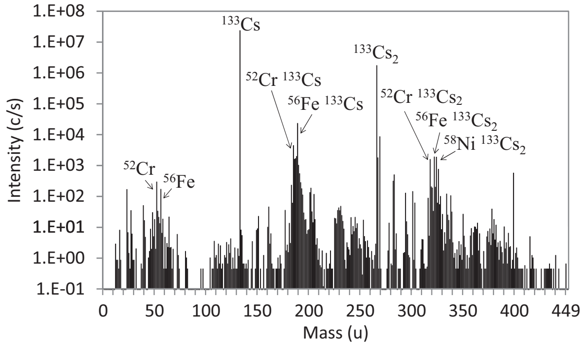

Fig. 2. Mass spectrum from D9 steel over the complete mass range: This bar spectrum was constructed using the peak values obtained as depicted in Fig. 1. A few of the prominent species are labeled to the corresponding peaks.

The fingerprint spectra of many species are likely to overlap with each other. The difficulty of identifying and measuring the intensities of such species in the measured spectrum depends on the number and complexity of their fingerprint spectra. The overlapping fingerprint spectra in the measured spectrum are mathematically represented by a system of linear equations. This system of equations contains one equation for every peak in the spectrum that is the resultant of overlap. For q number of species, overlapping with each other, constituting p number of peaks, the system of equations is

$$\sum_{j=1}^{q} a_{ij}s_j + \delta_i = m_i \tag{1}$$

where i runs from 1 to p representing the p number of equations and m_i is the measured intensity of the ith peak. s_j is the intensity of the jth species, for which the equations are to be solved. If the fingerprint mass spectrum of the jth species has a peak at the mass of the ith peak, a_{ij} is the intensity of that peak of the fingerprint mass spectrum. Otherwise, a_{ij} is zero. δ_i is the noise that occurred while measuring m_i, which is unknown. Although this term was added for completeness of mathematical description, the above set of equations has to be solved without the knowledge of this term.

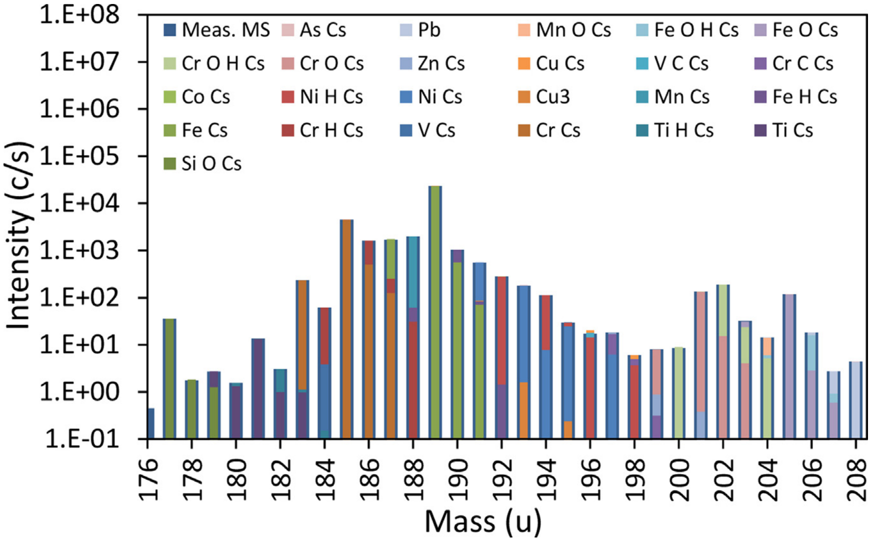

Fig. 3. Decomposing (a portion of) measured mass spectrum shown in Fig. 2 into fingerprint spectra of constituent species. The measured spectrum is labeled as "Meas. MS" (Measured Mass Spectrum) and shown a little wider behind the fingerprint spectra whose intensities were computed using Eq. (3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)