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Determination of spatial distribution of alloying and impurity elements in zircaloy using imaging secondary ion mass spectrometry and principal component analysis

V. Karki*, R. Agarwal, D. Alamelu

Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India

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ABSTRACT

SIMS (Secondary Ion Mass Spectrometry) was successfully utilized for investigating the surface microstructure and depth distribution analysis of alloying and impurity elements in unirradiated zirconium alloy, Zr X-868 sample. Oxygen (O_2^+) and Cesium (Cs^+) primary ion beams with positive and negative secondary ions detection mode respectively was selected for the present analyses. It was concluded from the surface ion distribution images that the elements O, Zr, Nb, Sn, Hf and Ta were homogenously distributed while C, Na, Mg, Si, Ca, V, Cr, Fe, Co and Cu were non homogenously distributed laterally. Multivariate technique called Principal Component Analysis (PCA) was selected for studying the correlation between surface distribution pattern of different elements. The scores plot between PC2 and PC1 showed that the groups of elements (Mg, Si, Fe), (Ca, Co, Cu) and (V, Cr) have similar distribution patterns while C and Na which doesn't belong to any of the groups, showed unique distribution patterns. Depth distribution analyses were also carried out which revealed uniform depth distribution of all the elements within the analysis area of 250 × 250 μm^2.

1. Introduction

SIMS is a highly sensitive detection technique (detection limits in the range of ppm to ppb and for some elements even in the range of ppt), commonly employed for surface imaging (2-Dimensional (2D) imaging) and depth distribution analysis of elements and molecular ions in the sample [1]. Unlike other surface analysis techniques, SIMS is also capable of detecting low atomic number elements including hydrogen [1]. SIMS offers various advantages over other techniques (XPS (X-ray Photo electron Spectroscopy), AES (Auger Electron Spectroscopy), RBS (Rutherford Backscattering Spectrometry) etc.) such as ability to analyze full mass spectrum, very low detection limits, 2D and 3D (3-Dimensional) distribution analysis of elemental and molecular ions, high mass resolution, direct solid sample analysis, large dynamic range, rapid acquisition of data, good lateral resolution (μm) for surface imaging and excellent depth resolution (nm) for depth distribution analysis [2–4]. As a consequence of these inherent advantages, SIMS has been widely used for various applications in different fields of science and technology such as semiconductor [5], thin films [6], biomedical [7–9], geological [10] and nuclear [11–15].

SIMS has been effectively utilized over the last few decades for investigating 2D and 3D distributions of elemental and molecular ions in various types of samples such as semiconductors, organic molecules, inorganic materials (metals, alloys, metal oxides and others), fibers, particles, contaminants, composites and catalysts [16]. Investigation of these distributions help in understanding various phenomenon such as microstructural changes due to corrosion process, effects on the grain boundaries, grain boundary diffusion and phase determination. An enormous amount of work has been reported for studying the surface microstructure, grain boundary diffusion, corrosion process, grain boundary and phase determination in various alloy samples including zirconium alloys using SIMS [11–13,17–21]. For instance, Grams et al. utilized TOF-SIMS technique for obtaining high resolution surface ion images of elements as well as molecular secondary ions from support catalyst [22]. They have investigated the influence of catalyst preparation conditions on the distribution and composition of active phase using SIMS [22]. Krecar et al. investigated 2D and 3D distribution of the sintering activator of phosphorus and carbon in steel by means of SIMS [23]. They have concluded from the

* Corresponding author.
E-mail address: vijaykarki.karki@gmail.com (V. Karki).

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distribution patterns that with increase in phosphorous concentration in steel, phosphorous gets precipitated in the grain boundary region, especially at higher sintering temperatures [23]. Shankar et al. utilized SIMS in depth profile mode and XPS for understanding the corrosion behavior of Zircaloy-4 in comparison with other candidate materials like commercially pure Titanium, Ti-5%Ta and Ti-5%Ta-2%Nb [11]. They have concluded from SIMS depth profile and XPS analysis of Zircaloy-4 sample which was exposed to nitric acid (11.5M HNO_3) solution that Zircaloy-4 exhibited superior corrosion resistance in both wrought and welded condition in comparison to other materials [11]. Matsuda et al. utilized depth profiling and imaging mode of SIMS for understanding the mechanism of corrosion in Zircaloy-4 sample annealed at temperature range from 640 to 780 °C followed by two stage oxidation method using oxygen isotope ^{18}O as a tracer [12]. They have concluded that the oxidation rates are linearly proportional to the concentration of Fe and Cr precipitates in a particular region and also these precipitates enhance the grain boundary diffusion of oxygen [12]. Gebhardt investigated the depth and surface distribution of reactor water components Li and B in the oxide layer of in-reactor corroded zircaloy fuel rod cladding specimens using SIMS [13]. The analyses results showed that Li and B were not homogenously distributed in the oxide layer [13].

Zirconium based alloys are very promising structural materials for nuclear industry and power engineering applications [24]. Zirconium based alloys Zircaloy-1, Zircaloy-2, Zircaloy-4, ZIRLO, Zr-2.5%Nb etc. are widely used in cladding, calandria tubes, pressure tubes and structural materials in nuclear power reactors because of their adequate aqueous corrosion resistance, low neutron absorption cross-section and good mechanical properties at elevated temperatures [25,26]. Alloying elements such as Fe, Cr, Nb, Sn and Ni as well as impurity elements such as C, Na, Mg, Co, Cu, V, Ca, Si, O, Ta and Hf alters the physical, mechanical and chemical properties of the alloy. For example Sn improves the corrosion resistance without seriously affecting the neutron economy while Fe, Cr and Ni provide high temperature corrosion resistance to the alloy [26]. Nb has a beneficial effect on hydrogen embrittlement phenomenon, and significantly decreases the hydrogen pickup during reactor operation conditions [26]. Hf has high thermal neutron absorption cross-section and hence affects the neutron economy in a reactor and hence there is stringent specification limit for Hf as well as other neutron poisons B, Sm, Gd, Eu etc. [26]. Small differences in the distribution of the alloying as well as impurity elements within the Zr matrix can cause significant differences in physical, mechanical and chemical properties of the alloy such as high temperature corrosion resistance, radiation damage effects and hydrogen embrittlement [12,26,27]. In addition, during long term exposure to reactor core environments of high temperature, corrosion, radiation etc. leads to significant changes in the material properties arising from microstructural changes [28]. Hence, the studies of microstructure of the surface as well as depth distribution of constituent elements in these alloys are necessary both in production stages and during reactor operation for monitoring the degradation in their properties. SIMS has already been used for studying the surface and depth distribution of hydrogen in zirconium alloy [14,15,29]. Therefore, it is considered worthwhile to investigate and characterize the microscopic distribution of impurity and alloying elements in zircaloy sample using a suitable analytical technique as these elements significantly influence the properties of the alloy.

The present work describes the combined effects of both, micron lateral resolution advantage of SIMS technique for surface imaging and multivariate data reduction technique using PCA as an analytical tool to identify the microstructural distribution of different elements in zirconium alloy, Zr X-868 sample. O_2^+ primary ion beam with positive secondary ion detection mode was selected to investigate the surface distribution pattern and depth distribution analysis of major alloying elements (Fe, Cr, Nb and Sn) and impurity elements (C, Na, Mg, Co, Cu, V, Ca, Si, O, Ta and Hf) in the sample. In order to recheck the surface ion distribution of these elements, all the analyses were also carried out using Cs^+ primary ion beam with negative secondary ion detection mode. Line scan analysis constructed from the surface ion distribution images of elemental ions were used as an input data to PCA program for studying the correlations between the distribution patterns of these elements.

2. Experimental

Surface and depth distribution analyses were carried out using double focussing, magnetic sector, Cameca ion microprobe-7f SIMS instrument equipped with oxygen (O_2^+, O^-) and cesium (Cs^+) primary ion beams. Certified reference material Zr alloy sample, Zr X-868 was used for the present analyses as it contains all the important elements commonly present in the nuclear reactor grade Zr alloy sample. The elemental composition of various elements C, Ca, Co, Cr, Cu, Fe, Hf, Mg, Na, Nb, O, Si, V and Ta in the Zr alloy sample are 340, 10, 39, 580, 78, 2950, 180, 5, 10, 620, 1940, 180, 87 and 710 ppm respectively while Sn was present in 1.25 wt%. All the analyses were carried out using O_2^+ primary ion beam with positive secondary ion detection mode. The lateral resolution primarily depends upon the spot size of the primary ion beam, hence O_2^+ beam was finely focused to a spot size of diameter ~1 μm by suitably adjusting primary beam apertures, stigmators and quadrupole lenses etc. The primary beam was raster over an area of 250 × 250 μm^2. High lateral resolution (~1 μm) secondary ion images of dimension 250 × 250 μm^2 were obtained from electron multiplier detector having pixel density of 1024 × 1024. To remove the isobaric mass interferences arising from the sample as well as from the background gases present in the analysis chamber, all the analysis were carried out at UHV of ~4 × 10^{-9} mbar (pressure in analysis chamber) with a mass resolution (m/dm) of 4000. For understanding the correlations between the distribution patterns of different impurity and alloying elements, analyses were carried out at a specific location for all the elements. All the analyses were also carried out using Cs^+ primary ion beam with negative secondary ion detection mode in order to confirm the surface and depth distribution of these elements in the sample. Investigation of surface microstructure of zircaloy sample Zr X-868 sample was also carried out using Energy Dispersive X ray Spectroscopy (EDS) technique. The EDS spectrum was recorded on Bruker Nano GmbH XFlash detector 410-M (Berlin, Germany) and spectrum was analyzed using Quantax Esprit 2.0 Bruker microanalysis software.

SIMS spectra are enriched with information and for static SIMS, the 2D distribution images contains intensity of the secondary ions at each pixel. For instance, in our case the electron multiplier detector contains pixel density of 1024 × 1024, hence contains huge amount of data for each element. Investigation of 2D distribution pattern using univariate technique is therefore not effective. Hence, multivariate analysis technique known as PCA was employed for classification of surface ion distribution images into groups (elements having similar distribution patterns) and to identify similarities and differences in the distribution patterns of all the elements. Multivariate technique, PCA is a standard, unsupervised technique which reduces a large data matrix to a few manageable variables called principal components (PCs) such that the first few PCs contains maximum variability (information) of the data set. The relationship between samples and variables can be easily visualized and interpreted by plotting of the resulting 'scores' plot. PCA were carried out using XLSTAT (adds on for Microsoft Excel) version 2014.5.03 software. Line scan data constructed from the surface ion