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Technical Report

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and External Surfaces

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HYDROGEN SEGREGATION TO GRAIN BOUNDARIES AND EXTERNAL SURFACES

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Segregation of hydrogen to grain boundaries, surfaces and defects has been studied in Nb, Nb - V alloys, and Ni using Secondary Ion Mass Spectrometry. This technique has been shown capable of determining the distribution of hydrogen at interfaces under suitable experimental conditions. Very large segregation enhancements are shown for surfaces and grain boundaries. The enhanced concentrations extend for significant distances from the surfaces.

Introduction

Secondary Ion Mass Spectrometry (SIMS) is one of the very few techniques capable of determining the distribution of hydrogen and its isotopes on a microscopic scale /1,2,3,4/. Due to the complexity of the instrumentation and the experimental variables care must be taken to ensure that measurement artifacts do not interfere with the determinations. Generally, only qualitative analysis can be carried out unless internal standards are available; as is the case in many hydride forming systems. In the present paper a review of some of the necessary experimental conditions will be presented /1/ and the results of applying the technique to hydrogen distributions in Nb - V alloys and Ni will be presented. *JR/6*

Experimental Procedures

A number of reviews of SIMS techniques are available /1,5,6/ and the present discussion will focus on those aspects which are particular to the determination of hydrogen distributions. Many of the precautions which must be taken for H analysis result from the very high mobility of H in metals and the concomitant possibility of redistribution of the H during the SIMS measurement. This difficulty may not be present during measurements in other materials. The Cameca IM3 measurements were carried out using a primary sputtering ion beam of 17 keV Cs⁺. While measurements were carried out with an O⁺ or Ar⁺ ion beam, it was generally observed that the ion yield was greatest for the Cs beam. The ion yields for H or its isotopes have been measured only in a few cases. Most of the sputtered species are neutrals and as a practical matter the sensitivities for H in various materials studied at Illinois are 8×10^{17} H atoms/cm³ for Si, 10^{18} - 10^{19} H atoms/cm³ for Ni and 10^{19} - 10^{20} H atoms/cm³ for Nb. These detection limits are expected to decrease as the techniques improve.

One factor which provides a background against which measurements must discriminate is contaminants from the vacuum system; residual H₂O, hydrocarbons, H₂, etc. Although the instruments typically operate at vacuums of 10^{-7} or 10^{-8} torr adsorption of these species on sputtered surfaces is generally a source of difficulty and sets a lower limit to the measurement of ¹H. A straightforward method of avoiding this difficulty and of greatly decreasing the concentrations at which useful measurements can be made is to use ²H (D) as the alloying element to be studied. In the case of a Cs⁺ ion beam the greatest ion yield is generally for ²H⁻ although strong signals are often observed for M²H⁻ (where M denotes a metal species). An additional advantage of this choice is the signal from the adsorbed H can also be monitored as a measure of the effects of other factors, such as the effects of crystal orientation on ion yield.

Ion yields are sensitive to many variables such as the surface orientation from which the sputtering is done; in many cases the D signal may vary by an order of magnitude between adjacent grains. To some extent this effect can be minimized by monitoring the M⁻ signal and using the ratio D/M to characterize the D distribution. The D yield is strongly enhanced by O on the surface or in the alloy. This effect can be minimized by normalizing the ²H yield with the ¹⁶O yield.

Hydrogen Segregation

The high mobility of H in many solids requires that it be immobilized during any measurement. We have accomplished this using of a low temperature stage which can achieve about 100 K at the specimen surface during sputtering. There are three primary factors to be considered /3/; a) diffusion to the surface as a result of the tendency for segregation, b) diffusion to the ion damaged region beneath the sputtered surface due to trapping, and c) diffusion from the sputtered surface which is heated slightly by the sputtering process due to thermomigration. An estimate for the temperature rise beneath the sputtering beam is about 20 K for a typical 3 micrometer beam rastered over a 250×250 micrometer² area with a 100 nA beam current and a sputtering voltage of 20 keV. Thermomigration of H in Nb /7/ results in a $dC/C \approx -0.4$ during the sputtering process. In a Nb - V alloy containing 0.2 at% D the $^2\text{H}/^{93}\text{Nb}$ signals were ≈ 50 at 298 K, ≈ 8 at 215 K, and ≈ 0.8 at 110 K with the variation being due to the three factors discussed above.

The spatial resolution of the SIMS technique in depth profiling is limited by ion beam mixing, which for the Cs ion beam at 17 keV appears to be about 5 nm. In order to avoid edge effects in depth profiling a large area (250×250 micrometer²) is generally sputtered but the signal is taken from the central part (10×10 micrometer²). Sputtering rates are measured using profilometer determinations of the depth of the sputtered pits and the uniformity of sputtering is determined using the SEM. Lateral resolution of the Cameca is limited by the smallest field aperture available for reasonable signal strength, about 3×3 micrometers. (Better lateral resolution is available using micro-ion sources but at the expense of signal.) This aperture limited resolution also is the resolution of a line scan across a feature such as a grain boundary. Imaging of particular species is available by means of the channel plate detectors. We have found that video taping the images followed by image enhancement and/or line scans in the video images has the advantage of being able to analyze the time evolution of the signals and to attain a somewhat better lateral resolution (approaching that of the channel plate).

Experimental Results and Discussion

Depth profiling of the D distribution in specimens which have been thermally charged to a uniform distribution of D in solid solution have consistently shown very significant surface segregation during low temperature anneals /1,2,3,8/. An example of the results obtained is shown in Fig. 1 where the dependence of the normalized D signal is shown

as a function of depth beneath the surface. These results are the consequence of diffusion controlled segregation to the external surface; in the as quenched condition the D distribution is constant and only after low temperature anneals does the segregation manifest itself. The enhancement factor (maximum D concentration/bulk solute concentration) is a factor of about 100 in Ni annealed at 295 K and about a factor of 15 for Nb-V annealed at 110 K.

One striking aspects of these results is the enhanced solute distribution behind the surface which extends for about 100 nm. This may be contrasted with the segregation distribution of other species measured simultaneously with the D measurements, eg. S segregated in Ni or O in Nb-V which show only a surface distribution. Surface segregation of the classical type is difficult to measure with the SIMS technique but can be established using Auger Electron Spectroscopy on the same specimens. An example of the differences is shown in Fig. 2 which shows the segregation of D to and the adsorption of O on a previously sputtered surface of Nb-V. The D segregation extends for about 50 nm while the O distribution extends for only 5 nm; about the expected extent of the ion beam mixing.

Due to the difficulty of measuring H distributions there have been few comparable determinations. Nuclear reaction profiling has been applied to Zr alloys /9/ in which segregation over distances similar to those reported in this paper were obtained. X-ray studies /10,11/ of Nb - Ta modulated layer structures have shown that the solubility of H in these structures is increased by the compositional modulation and that the Nb-Ta composition modulation imposes H modulations whose fundamental Fourier component equals that of the composition modulation. The physics of this H modulation was interpreted as being caused by the lattice gas properties of H in the bcc lattice.

This lattice gas nature of H in solids is believed to be responsible for the extended segregation profiles shown above. The H-H interactions are attractive at greater than third nearest neighbors and repulsive at closer distances. As a result, the chemical potential of hydrogen can be written

$$\mu_s = \mu_1 - \mu_{seg}$$

$$\mu_i = \mu_1 - \sum_j P_j (u / |r_i - r_j|^3)$$

Hydrogen Segregation

where μ_s , μ_l , and μ_i are the chemical potentials of H on the surface, in the lattice far from the surface, and in the i^{th} interstitial position in the vicinity of the surface, m_{seg} is the chemical potential difference between H on the surface and in the lattice, u is the mean field H-H interaction energy and P_j is the occupation probability of the j^{th} site. As a result of this long range interaction the chemical potential for H near the surface is decreased by H segregation at the surface leading to a H concentration which decays slowly in from the surface as observed experimentally.

Attempts to establish the segregation of H at or near internal surfaces such as grain boundaries have met with only limited success. SIMS techniques presently do not have the sensitivity to determine such segregation by linear scans across grain boundaries if the H has a monolayer distribution. Nonetheless, grain boundary segregation has been reported by linear scans across grain boundaries /1/ using 3 micrometer field apertures and 15 micrometer ion beams in two separate systems and has been confirmed by a second investigator /12/. In these studies, only a small minority of grain boundaries studied showed D segregation peaks suggesting that only "special" boundaries show the effect. A study of the nature of these "special" boundaries did not reveal any particular character which would account for the large D signals /12/.

Studies of the equilibrium of Ni with hydrogen plasmas /13/ indicate that D segregation can occur in specimens having D concentrations of the order of 1000 to 2000 appm. An example of an ion image formed with ^2H is shown in Fig. 3 where every grain boundary, with the exception of a twin boundary, is decorated with D. This image was obtained in 1/60 sec. and the ^2H signals appear as bright spots, each of which appeared only on a single field of the video output corresponding to a depth average of 0.02 nm, ie each recorded event corresponds to a single ^2H ion. Since the ^2H yield is about 1/400, it is most likely that each of the recorded event corresponds to a small cluster of ^2H rather than isolated ^2H atoms. The distribution of D is clearly associated with the grain boundaries which are seen in the ^{58}Ni ion image (Fig. 4) as a result of orientation differences in the ion yields. Integration of the images over a number of frames results in a D distribution which is continuous along the grain boundaries. The distribution along the grain boundaries is clearly not a classical monolayer distribution. Identical specimens of Ni were thermally charged with 560 appm D by equilibration with D_2 gas at elevated temperatures followed by quenching into oil. SIMS studies of these specimens did not show any segregation to the grain boundaries. The reasons for the differences between

these two types of D charging are not known, nor is the role of point defects introduced by the plasma charging completely understood.

Conclusions

It has been shown that when carefully applied, the Secondary Ion Mass Spectrometry is capable of determining the distribution of deuterium near surfaces and grain boundaries in a variety of metallic systems. The surface segregation observed is highly non-classical and extends for appreciable distances behind the surfaces. This can be accounted for qualitatively in terms of the H-H interactions characteristic of metal-H systems. Segregation of H at internal surfaces is not as well established except for Ni containing very high supersaturations of H introduced by equilibration with H plasmas.

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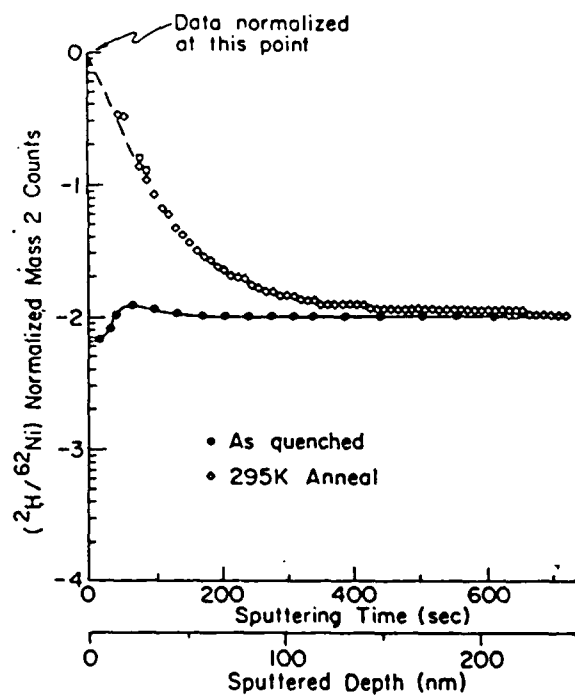


Fig. 1. SIMS depth profile of Ni-300 appm ^2H . ●—● As quenched; ○—○ Annealed at 295 K.

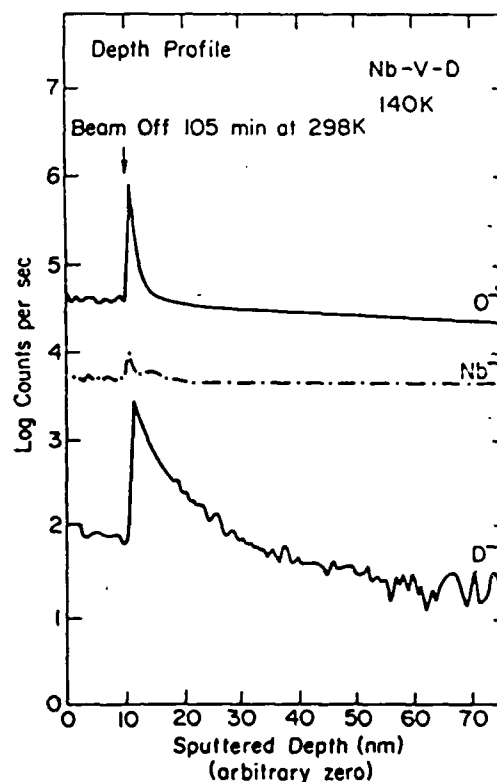
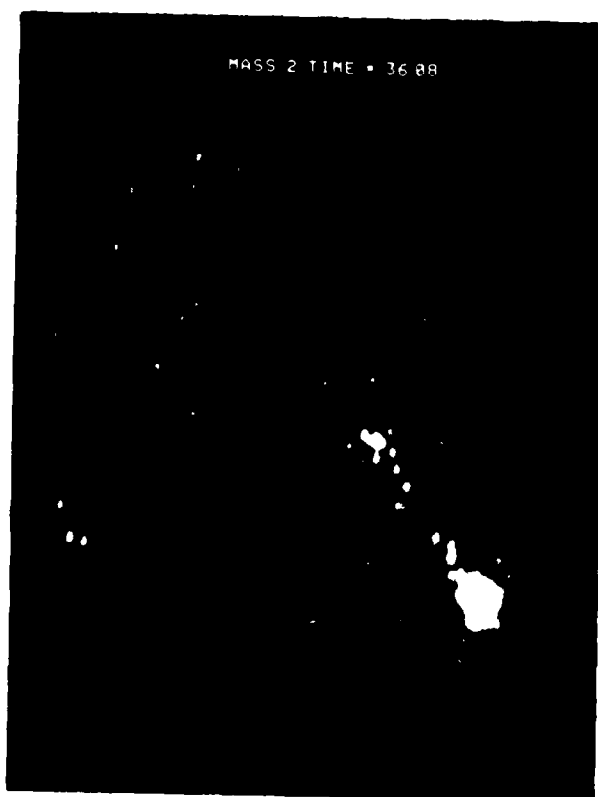


Fig. 2. SIMS profile of Nb-V-O alloy at 140 K. The sputtered depth has an arbitrary zero. At the indicated point the sputtering was stopped for 105 minutes to allow diffusion of ^2H to the surface and adsorption of ^{16}O on the surface.



(a)



(b)

Fig. 3. SIMS images of the grain boundaries in Ni which was equilibrated with ^2H plasmas. (a) shows the image formed with ^{58}Ni and (b) is the image formed with ^2H . Grain boundary segregation of ^2H is shown except at the twin boundary.

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