Quantitative Analysis of Hydrogen in Titanium with an Ion Microanalyzer

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Quantitative analysis of hydrogen in titanium was investigated with an ion microanalyzer. Argon ions as primaries were accelerated at a voltage of 10 kV. The diameter and the current of the beam were 1 mm and 2 μA, respectively. A mass spectrum was measured at 2×10^{-7} Torr. It was found that the intensity ratio of $m/e=49$(^{48}TiH$^+$) and 46(^{46}Ti$^+$) can be used for the determination of hydrogen in titanium. A linear relation was obtained between the intensity ratio and hydrogen concentration determined by the standard vacuum fusion method. The present method was applied to determine the hydrogen concentration in the surface layer of a sample treated by cathodic polarization. It was observed that hydrogen concentrations in the surface layer were much higher than those in the bulk of the sample.

It is well known that titanium is embrittled by the presence of small amounts of hydrogen. Phillips *et al.* investigated the kinetics of embrittlement by observing a sample cross section with an optical microscope, determining the hydrogen concentration by the vaccum fusion method.[1] In order to investigate the mechanism of embrittlement, it is necessary to determine hydrogen concentrations on a microscopic scale. The vacuum fusion method, however, cannot be applied to determination of hydrogen concentration in a microscopically thin layer.

An ion microanalyser (IMA) enables us to carry out analyses of the impurities contained in a small selected volume and in very thin layers. Gray[2] and Someno *et al.*[3] reported on the application of IMA to the determination of hydrogen in titanium. Gray used the intensity ratio of titanium ($m/e=48$) to hydrogen ($m/e=1$). However, Gray's method cannot be applied with sufficient reproducibility, due to a trace amount of contaminants containing hydrogen compounds in the sample chamber. Someno *et al.* used deuterium instead of hydrogen.

The present paper describes an IMA method which can be applied to the determination of hydrogen in titanium with good reproducibility.

Experimental

Materials. The titanium specimens used were 1 mm thick and 5×5 mm in size. Table 1 gives the composition obtained by chemical analysis. In order to obtain specimens with high concentrations of hydrogen, hydrogen was diffused in the specimen by cathodic polarization. Specimens were ultrasonically cleaned in acetone and methyl alcohol. The hydrogen concentration was analyzed by the standard vacuum fusion method.

Argon gas, used as a source of primary ions, was purified by passing through CuO particles heated to 500 °C, $Mg(ClO_4)_2$ particles and a liquid oxygen trap.

TABLE 1. CHEMICAL ANALYSIS OF TITANIUM SPECIMEN

Specimen	Concentration (%)				
	N	O	H	Fe	C
1	0.003	0.059	0.0012	—	—
2	0.008	0.057	0.0020	0.002	0.005
3	0.009	0.070	0.0020	0.030	0.007

Experimental Procedure. A Hitachi type IMA-2 ion microanalyzer was used. Argon ionized by a duoplasmatron was accelerated from 6 to 15 kV and struck the sample mounted with silver paste on a holder. The beam diameter was focused to about 1 mm. The primary ion current at the sample was 0.5 to 5 μA. The pressure in the sample chamber was 4×10^{-6}—8×10^{-8} Torr. Secondary ions sputtering from the sample surface were accelerated at a voltage of 3 kV and analyzed with a mass spectrometer.

Results

Principle of Quantitative Analysis. The secondary ion current I_X of an element X with one isotope only is given by

$$I_X = I_p S_X{}^+ C_X \eta_X, \tag{1}$$

where I_p is primary ion current, $S_X{}^+$ the yield of ions of element X, C_X the concentration of element X, and η_X the transmission of the instrument between sample and collector. Thus the ratio of the secondary ion current of an element X to a reference element (matrix) R is given by[4]

$$I_X/I_R = S(\mathrm{rel})^+ C_X/C_R, \tag{2}$$

where I_R is the secondary ion current of a reference element R, C_R the concentration of a reference element R, and $S(\mathrm{rel})^+$ the ratio of the yield of ions of an element X to a reference element R. When the analysis is carried out by means of Eq. 2, it is necessary to select the peak of the element to be analyzed and that of a reference element.

Selection of Peak. Figure 1 shows the mass spectra of samples of different hydrogen concentrations. The hydrogen concentrations of samples A and B analyzed by the vacuum fusion method are 12 and 3800 ppm, respectively. The heights of the peaks of hydrogen ($m/e=1$) do not show any appreciable difference. On the other hand, the peak height difference of $m/e=49$ between A and B is very large. The peak at $m/e=49$ contains both ^{49}Ti$^+$ and ^{48}TiH$^+$ ions. Hydrogen sources of the ion TiH$^+$ seem to be the hydrogen in the titanium sample and impurities such as water and hydrocarbons in the sample chamber. In order to determine the hydrogen in titanium using the peak at $m/e=49$, the impurities in the system should be minimized.

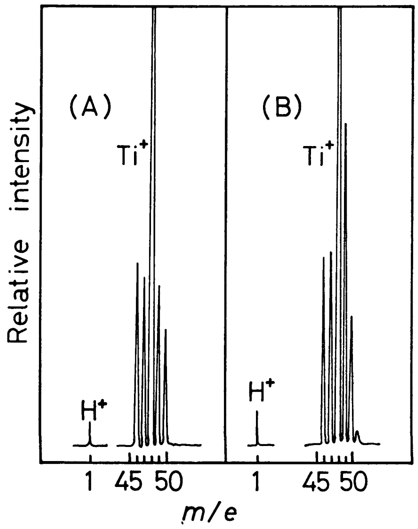

Fig. 1. Mass spectra of titanium before and after hydrogen absorption.

(A): Before absorption(12 ppm H), (B): after absorption (3800 ppm H).

In the present work, argon gas was purified by passing through CuO particles heated to 500 °C, $Mg(ClO_4)_2$ particles and a liquid oxygen trap. The impurities in the sample chamber were minimized by cooling with liquid nitrogen. Since the impurities adsorbed on the sample surface also give a TiH^+, they should be separated from other secondary ions using a high accelerating voltage.

Table 2. Peak height ratio for titanium

m/e	Peak height ratios (%)				
	46	47	48	49	50
Sample A	8.06	7.20	73.94	5.83	4.97
Sample B	6.94	7.82	66.67	13.47	5.10

Isotopic ratio of m/e=46, 47, 48, 49, and 50 is 7.93, 7.20, 73.94, 5.51, and 5.34, respectively.

Table 2 gives the peak height ratios for samples A and B, as compared to the isotopic ratio of titanium. The values at $m/e=49$ are greater than the isotopic ratio. The high value at $m/e=49$ for sample B indicates a high concentration of hydrogen. Thus the peak at $m/e=49$ can be used for the determination of the concentration of hydrogen.

It is preferable to select the peak at $m/e=46$ as a reference, since titanium of $m/e=45$ is not detected and the TiH^+ gives no signal at $m/e=46$. Since the intensities at $m/e=46$ and 49 are comparable, errors can be minimized.

Effect of Primary Ion Current on I_{49}/I_{46}. The temperature of the sample surface and the sputtering rate[5] are influenced by the primary ion corrent. When the sample is heated by primary ions, the absorbed hydrogen in titanium might be released. Figure 2 shows the relation between the intensity ratio of $m/e=49$ to $46(I_{49}/I_{46})$ and to the primary ion current. I_{49}/I_{46} is constant in the range 0.5—5 μA. The results show that no thermal release of hydrogen occurs by the present method.

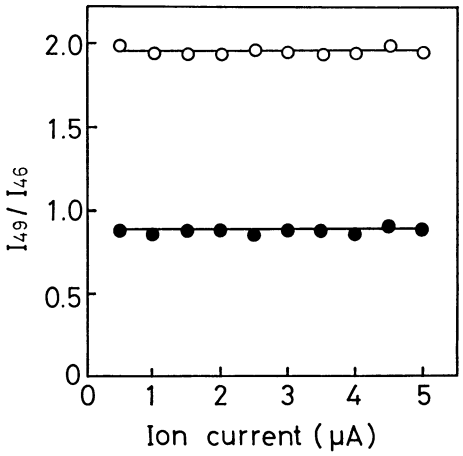

Fig. 2. Relation between I_{49}/I_{46} and primary ion current.

●: Before absorption (12 ppm H), ○: after absorption (3800 ppm H). Primary ion accelerating voltage :10kV.

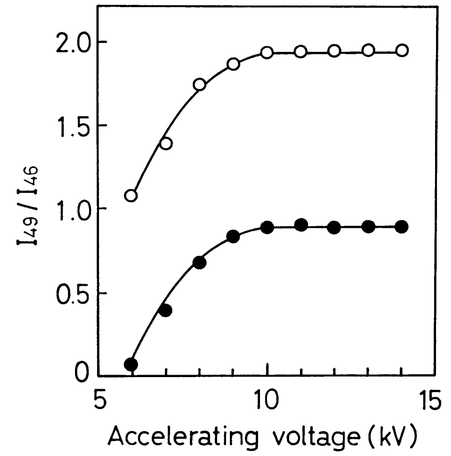

Fig. 3. Relation between I_{49}/I_{46} and primary ion accelerating voltage.

●: Before absorption(12 ppm H), ○: after absorption (3800 ppm H). Primary ion current: 2 μA.

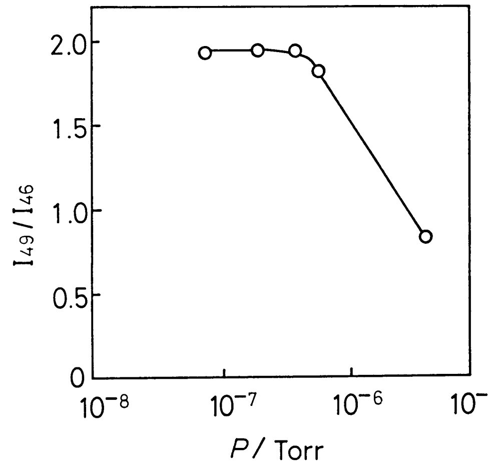

Fig. 4. Relation between I_{49}/I_{46} and pressure in sample chamber at primary ion current of 2 μA and primary ion accelerating voltage of 10 kV.

Effect of Primary Ion Accelerating Voltage on I_{49}/I_{46}. The measurements were carried out at a primary ion current of 2 µA. Figure 3 shows the relation between I_{49}/I_{46} and the primary ion accelerating voltage. I_{49}/I_{46} increases with the accelerating voltage and becomes constant at voltages above 10 kV.

Effect of Pressure in Sample Chamber on I_{49}/I_{46}. Figure 4 shows the relation between I_{49}/I_{46} and pressure. I_{49}/I_{46} decreases at pressure above 4×10^{-7} Torr. Decrease in I_{49}/I_{46} with pressure seems to be due to the increase of oxygen present in the sample chamber.[6]

Effect of Surface Layer on I_{49}/I_{46}. The sample surface is contaminated with impurities such as oxygen, water and hydrocarbons which generate secondary ions, making the quantitative analysis of hydrogen difficult. Surface sputtering is effective in removing the impurities on the surface. In the early stages of bombardment, the peak intensity changes widely. However, a stable signal can be obtained after bombardment for *ca.* 10 min. It was confirmed by surface roughness measurement that 2 µm or less had been sputtered by 10 min bombardment.

TABLE 3. WORKING CONDITIONS FOR QUANTITATIVE ANALYSIS

Ionic species	Argon(Ar^+)
Primary ion accelerating voltage	10 kV
Primary ion current	2 µA
Primary ion beam diameter	1 mm
Pressure in sample chamber	2×10^{-7} Torr
Preliminary sputtering time	10 min
Secondary ion accelerating voltage	3 kV

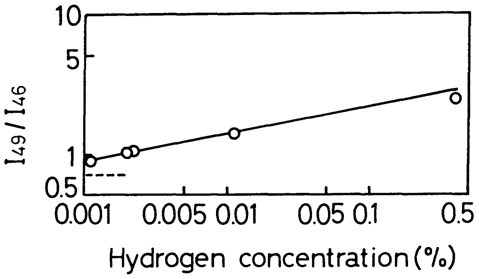

Fig. 5. Calibration curve.
----: Isotopic ratio($^{49}Ti/^{46}Ti$).

Calibration Curve. The working conditions for the IMA method are summarized in Table 3. Under these conditions, I_{49}/I_{46} was plotted as a function of hydrogen concentrations, which were determined by the vacuum fusion method. A linear relation was obtained between I_{49}/I_{46} and hydrogen concentration as shown in Fig. 5.

Hydrogen Concentration in Surface Layer. The present method has been applied to determine hydrogen concentration in the surface layer of a sample treated by cathodic polarization. The hydrogen concentration decreases with increase in depth (Fig. 6).

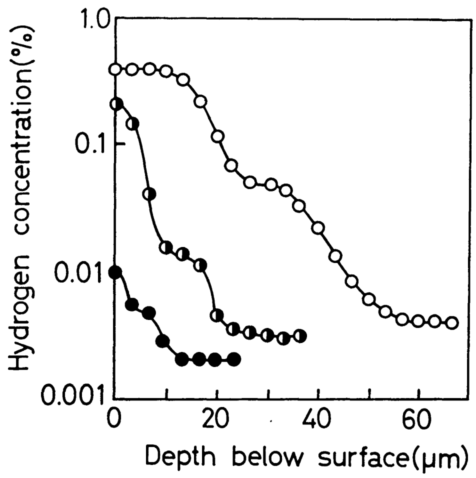

Fig. 6. In depth concentration profiles for titanium treated by cathodic polarization.
○: −5 V *vs.* SCE, 10 h, ◑: −1.5 V *vs.* SCE, 4940 h, ●: −0.5 V *vs.* SCE, 4940 h.

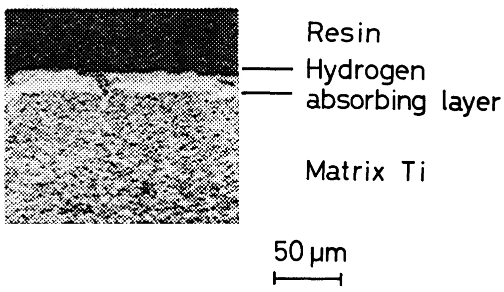

Fig. 7. Cross section of titanium treated by cathodic polarization at a potential of −5 V *vs.* SCE for 10 h.

Figure 7 shows a cross section of the sample treated for 10 h at a potential of −5 V *vs.* SCE. The 20 µm layer in the photograph corresponds to the layer in which the hydrogen concentration is higher than 0.05%.

References

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