ION MICROPROBE ANALYSIS OF HYDROGEN AND OXYGEN IN TITANIUM

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Introduction

It is well known that metallurgical properties of titanium are severely influenced by trace elements. The quantities of those elements are usually determined as average composition by means of chemical analysis method. However, the trace elements are often localized during heat treatments and deformations. The electron probe microanalyser (EPMA) is very useful instrument for micro-analysis of elements and many metallurgical problem has been revealed. Recently, ion microprobe mass analysers (IMMA) have been developed and the IMMA is applied to hydrogen and oxygen analysis in titanium. Hydrogen in titanium hydride (TiH) can be directly observed and also quantitative analysis of hydrogen in titanium is developed. The IMMA was also applied to surface analysis of oxide layer on titanium and depth-profile of oxygen was obtained.

Ion Microprobe Mass Analyser (IMMA)

The IMMA have a few unique features as follows:

1. High sensitive microanalysis of 1 μm order
2. High sensitive surface analysis and also in-depth analysis
3. Microanalysis of hydrogen

In Fig.1, a schematic diagram of the IMMA is shown. Primary ion beam through an energy separating sector is focussed on a specimen and secondary ions are sputtered from the specimen. These secondary ions are analysed by double focusing mass spectrometer and intensity of the secondary ions are recording as digital count or ion beam scanning image mapping. In the case of in-depth analysis, the secondary ion intensity of analysed element is memorized by a multi-channel scaler. In the present paper, representative application results of IMMA to titanium are mentioned.

Hydrogen Analysis

Titanium hydride has been identified from relationship between the quantity of precipitation in metallurgical micrograph and hydrogen composition.
In the present work, hydrogen in the hydride can be directly determined by the IMMA. In the IMMA analysis, primary ion beam ($O_2^+$) bombards on sample surface, and the sample is sputtered and the secondary ions is emitted. During the primary beam scans on the sample, a point in the analysed area is momentarily bombarded and repeated. Fig.2 shows that the secondary ion ($H^+$) intensity relating to time from titanium containing 32 ppm (wt.) hydrogen when the primary ion beam is fixed at a point. The beginning peak of $H^+$ intensity is thought to be sputtering of adsorbed hydrogen and the $H^+$ ion intensity decreases to constant value. After cut off period, the phenomena is repeated.

Fig.2 Hydrogen ion intensity from Ti (32 ppm H), repeating of primary ion bombarding and cutting off.

$O_2^+$, 20KV-lnA (1000 x 800)
In the sample chamber of IMMA, vacuum condition is $10^{-8}$ torr order and it is not enough to avoid adsorption of $H_2O$ which is source of $H^+$ secondary ion, as shown in Table 1.

It is necessary that the adsorbed $H_2O$ is decreased in the case of hydrogen analysis, and a cold-plate cooled to liquid nitrogen temperature is used.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Fresh</th>
<th>300 sec Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1H^+$</td>
<td>0.76 K</td>
<td>+180 K</td>
</tr>
<tr>
<td>$^{12}C^+$</td>
<td>0.036 K</td>
<td>+ 04 K</td>
</tr>
<tr>
<td>$^{13}C^+$</td>
<td>0.04 K</td>
<td>+ 02 K</td>
</tr>
<tr>
<td>$^{17}OH^+$</td>
<td>0.167 K</td>
<td>+255 K</td>
</tr>
</tbody>
</table>

Table 1 Relative intensity of ion from Zirconium surface before and after adsorption

$O_2^+$, 20KV-2mA ($100\mu m \times 100\mu m$)

In Fig.3, influences of adsorption are shown using titanium, zirconium and iron. Effectiveness of cold plate (C.P.) using liquid nitrogen are also recognized in Fig.3.
Fig. 4 shows the relation between $H^+$ intensity from titanium containing 32 ppm (wt.) hydrogen and current density of primary ion beam, which is beam current divided by analysed area. The normalized $H$ intensity decreases with average current density and reaches to a constant level.

This fact means that higher primary ion intensity decreases the adsorbed hydrogen (=vapor), and the relation may be expressed by the following equation.

$$I = I_b + K_i$$  \hspace{1cm} (1)

Where $I$ is the secondary $H^+$ ion intensity, $I_b$ is the background $H^+$ intensity caused by adsorbed hydrogen (vapor), $i$ is current density, and $K$ is a parameter to hydrogen content. From eq.(1),

$$\frac{I}{i} = \frac{I_b}{i} + K$$  \hspace{1cm} (2)

The hydrogen content $C_H$ is given by the following equation.

$$C_H = \frac{I - I_b}{1 - k}$$  \hspace{1cm} (3)

In Fig. 4, effects of the cold-plate (C.P.) and current density upon $H^+$ intensity are generalized.
1. Titanium hydride (TiH)

Fig. 5(a) is optical microphotograph of titanium hydride (TiH) in titanium containing 950 ppm (wt.) hydrogen. Fig. 5(b) is the step-scan analysis results of $H^+$ intensity. Fig. 5(c) shows the $H^+$ ion image. The hydrogen in titanium hydride precipitate is directly determined by the IMMA.

![Microphotograph of TiH](image1)

![Step-scan analysis of H+](image2)

![H+ ion image](image3)

Fig. 5 Hydrogen analysis of TiH in Ti ($H = 950$ ppm)

$O_2^+$, 20KV-3.5nA, 1sec/1 step

2. Zirconium hydride (ZrH)

Similar experiment is applied to zirconium hydride and hydrogen is determined as shown in Fig. 6.

![Microphotograph of ZrH](image4)

![Step-scan analysis of H+](image5)

Fig. 6 Step-scan analysis of $H^+$ from ZrH in Zr ($H = 100$ ppm)

$O_2^+$, 20KV-3.5nA, 1sec/1 step
3. Quantitative analysis of hydrogen in titanium

Intensities of secondary hydrogen ion H⁺ are shown in Fig. 7 using NBS Ti-H series, in which there is no segregation of hydrogen. In Fig. 8, the working curve of hydrogen in titanium and the influence of adsorbed vapor are shown.

![Fig. 7 Hydrogen analysis of NBS Ti-H series](image1)

**Fig. 8 Calibration curve of H**

Analysis of Surface Oxide Layer

When titanium is heated in air, surface of the titanium is oxidized and colored, it is important to know the relationship between the oxide layer thickness and the color. The oxide layer is analysed by the IMMA with the mode of in-depth analysis. Using N₂⁺ primary ion beam, secondary ion O⁻ intensity indicates the thickness of oxide layer as shown Fig. 9. In Fig. 10, relation between the thickness of oxide layers and the heating conditions are shown. However, the IMMA is time-consuming instruments to analyse, then electron microprobe analysis is developed for routine analysis. Intensity of O(Kα) obtained by the EPMA gives the finite thickness of oxide layer as shown in Fig. 11.

In the case of high temperature and long time heating of titanium, thick oxide layer is formed and diffusion of oxygen can be observed by metallographic microphotograph as shown in Fig. 12(a). Structures of heated titanium are identified by X-ray diffraction, IMMA, EPMA and Vickers microhardness test. These results are shown in Fig. 12 (b) and Fig. 12 (c).
Fig. 9 Measurements of oxide layer thickness on titanium by IMMA (Pri. ion; \( N_2^+ \))

Fig. 10 Relationship between Ti-oxide layer thickness by IMMA and heat temperature

Fig. 11 Relationship between Ti-oxide layer thickness and O\( K\alpha \) intensity by EPMA
Fig. 12 Metallographic microphotograph, EPMA analysis and Vickers microhardness measurement of titanium oxide layer for high temperature and long time heating in air.

a ; Cross-section microphotograph of titanium oxide
b ; EPMA line analysis
c ; Vickers microhardness measurement
Conclusion

For local analysis of hydrogen in titanium, ion microprobe analysis was applied. Hydrogen in titanium hydride was directly determined by the IMMA and zirconium hydride in zirconium was also detected. Quantitative analysis of hydrogen in titanium was developed and a practical working curve was obtained. In-depth analysis using IMMA was applied to decide the relationship between the absolute thickness and heating conditions for thin oxide layer and color on titanium surface. Based on the absolute thickness, practical working curve for thickness was obtained from O_K intensity using EPMA.

References

2) T. Shiraiwa et al., Sumitomo Metal, 26, 470 (1974)
4) N. Fujino et al., Titanium-Zirconium, 27, 74 (1979)
5) ibid., 26, 198 (1978)