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Temperature dependence of oxide decomposition on titanium surfaces in UHV*

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It is well known that the titanium surface forms stable oxides of Ti₂O, TiO, Ti₂O₃, Ti₃O₅, Ti_nO_{2n-1} (4 < n < 38) and TiO₂ and, as a result, exhibits a high degree of immunity against attack by acids and chlorides. However, titanium is also a very active getter. In the gettering characterizing the process, we have investigated the temperature dependence of stable titanium oxides on titanium in ultra-high vacuum (UHV) using Auger electron spectroscopy (AES), quadrupole mass spectrometry (QMS) and x-ray photoelectron spectroscopy (XPS) in the temperature range RT- 600 °C. Surfaces of titanium specimens were prepared by electropolishing (EP) and a thin titanium oxide layer was formed on the surface, principally TiO₂. On increasing the temperature to above 300°C, the O_{KLL} Auger intensity began to decrease in a drastic way while, in contrast, the Ti_{LMM} Auger intensity was increased. Above 450 °C, no oxygen was detected on the titanium surface in UHV. However, the outgassing rates of H₂O, O₂, CO, and CO₂ from the surface did not show any changes in QMS measurements below 450°C. This behavior is explained as gettering, which is an enhancement of diffusion of oxygen from the surface into the bulk. To investigate the temperature dependence of the chemical states of titanium oxides on an EP surface, XPS analysis was also performed in the range 200 - 450°C in the same way. The results showed drastic changes of the titanium oxide core levels such that the TiO₂ decomposed to suboxides at 180°C, and even the remaining TiO₂ was still decreasing on heating up to 420°C. The titanium surface has a very sensitive oxide composition, depending on temperature.

I. INTRODUCTION

Titanium is reported as a corrosion-resistant metal¹ with the potential applications in a wide variety of technologies, e.g., aerospace, chemical industries, and biomedical.² The corrosion-resistance of titanium is provided by a passive film, which means that the surface is

covered with stable compact titanium oxides. A variety of surface analysis techniques have been devoted to the study of such properties, exact structures and composition of the oxides on titanium surface.³⁻⁶ The oxidation mechanisms on the titanium surface were also studied extensively for the past half-century from the points of view of the preparation, stoichiometry of oxides, layer structures and growth kinetics.⁷⁻⁹ As is well known, the material most widely used as a getter in ultra high vacuum (UHV) is also titanium, though a few other metals (Zr, Mo and Nb) are occasionally used. On titanium, oxygen, nitrogen and carbon dioxide are rapidly sorbed above about 670°C.¹⁰

The adsorption, oxide processes, stable oxides and gettering properties on titanium surface have been studied by many investigators with several models reported concerning mechanisms for forming a stable oxide surface.^{11,12} However, these models do not cover the dissolution mechanism of how established stable oxides are sorbed into the bulk at such low temperatures, although Gibbons and Stout have reported that alloys of titanium and zirconium are capable of dissolving any oxide film at temperatures below 400°C.¹³ That is because the stable oxides, TiO, Ti₂O₃, Ti₃O₅ and TiO₂, have high melting points above 1700°C, and does titanium itself. Generally, a phase diagram of the Ti-O system¹⁴ is not enough to explain the behavior of titanium oxides on titanium surface in UHV, because phase equilibrium properties of oxides on a titanium surface are different from the bulk ones.

Recently, Vaquila et al¹⁵ have reported that no oxygen is detected on a titanium surface in UHV when the substrate temperature is increased over 400°C. In addition, the titanium oxide stability is dependent on the surface temperature, i.e. below 200°C, TiO₂, between 200 and 350° C, TiO₂ and Ti₂O₃, and above 400°C TiO or Ti+O.

As discussed below, the focus of studies presented here is to clarify the behaviors of stable titanium oxides on a metal titanium surface in UHV below the sorbing temperature. To investigate these processes, the titanium surface with an EP treatment was analyzed *in situ* by

using Auger electron spectroscopy (AES), with a quadrupole mass spectrometer (QMS) and with x-ray photoelectron spectroscopy (XPS) during specimen heating. The behavior of oxygen was characterized by AES and QMS, and the changes of chemical states of titanium oxides in the near surface region were characterized with XPS curve fitting results for $Ti2p_{3/2}$ cores with Ti, TiO, Ti_2O_3 , Ti_3O_5 and TiO_2 reference spectra.

II. EXPERIMENTAL

A. Preparation of specimens

Two kinds of titanium specimens were prepared; one of them was commercially pure titanium of Japanese industrial standards Grade 2 (JIS2; purity > 99.5%), and the other was a high purity titanium (purity > 99.99%) single crystal. The single crystal specimen was made using the strain-anneal technique.¹⁶ The chemical compositions of the specimens are listed in Table I. The surfaces were polished using silicon carbide abrasive papers (#400-2000), and ultrasonically-rinsed with distilled water. Then, electrolytic polishing (EP) was applied to the samples in a non-aqueous electrolyte solution, which consists of 175 ml ethyl alcohol, 75 ml isopropyl alcohol, 15 g aluminum chloride and 62.5 g zinc-chloride under electrolytic conditions of 25 V and 0.14 A/cm² for 30 minutes at room temperature. The characteristics of EP-treated titanium surfaces were previously studied with surface analysis^{17,18} and the surface morphologies imaged by scanning electron microscopy (SEM) are summarized in Table II and Figure 1. Oxide growth was measured on the single crystal surface with AES and reflection high energy electron diffraction (RHEED). XPS studies were done on the polycrystalline sample in a separate system. The oxides on single crystal or polycrystal surfaces with EP treatment did not show observable differences.

Figure 2 shows a schematic configuration of the surface analysis systems.

B1. Auger electron spectroscopy (AES) with quadrupole mass spectrometer (QMS)

The single crystal specimen geometry was a slab strip of $5\times5\times2$ mm, baked for 24 hours at 150 °C in a loadlock chamber, and transferred into the measurement chamber, where it was flashed at 600 °C and, finally, dosed with oxygen at 1.3×10^{-5} Pa for one hour at RT. The base UHV pressure was 6.7×10^{-9} Pa and the pressure rose to 9.3×10^{-9} Pa during heating. The temperature was measured using an alumel/chromel thermocouple spotwelded to the specimen surface. In the AES analysis system,¹⁹ Auger electrons were excited by a 10 keV grazing-incidence electron beam and measured with a hemispherical electron energy analyzer with the input lens of the analyzer oriented about 80 degrees with respective to the incident electron beam. The energy resolution of the analyzer is about 1.0 eV. The residual gas in measurement chamber was monitored with QMS (RGA; Leybold, TRANSPECTOR).

B2. X-ray photoelectron spectroscopy (XPS)

The chemical states on a titanium specimen surface were measured with a PHI model ESCA1600 spectrometer using 300 watts of Al K α x-ray 1486.6 eV radiation. The analyzer was operated at a pass energy of 11.75 eV with an energy step size of 0.1 eV for survey spectra. The reference used for binding energy calibration was the Au 4f_{7/2} line at Eb = 83.9 eV.

The polycrystalline EP treatment JIS2 sample had dimensions of $10 \times 10 \times 1$ mm in a plate form and was measured with XPS before baking. Then the XPS system was baked at a temperature of 180° C for 24 hours after exchanging a special sample holder with a resistively heated platinum filament. A base pressure of 10^{-8} Pa was achieved the bakeout. Again, the substrate temperature was monitored by a chromel/alumel thermocouple spotwelded on the specimen while varying temperatures RT- 450° C. The vacuum pressure remained below 2.7×10^{-6} Pa during sample heating. In all data analysis and curve-fitting routines with Gaussian, Lorentzian and Doniach-Sunjic (D-S) line shapes, the X-ray satellite lines were subtracted from each spectrum, prior to fitting. The chemical species of titanium oxides in the near surface region were identified by the curve fittings of the Ti2p_{3/2} peaks with using five contributions of Ti, TiO, Ti₂O₃, Ti₃O₅ and TiO₂ reference data.²⁰

III. RESULTS and DISCUSSION.

The EP surface of titanium was analyzed with several sensitive techniques in previous works^{17, 18} and, basically, the mirror-finished surface was covered with a thin oxide layer and carbon contamination. The topographies of both surfaces are shown in Figure 1, with an average roughness of 100 nm for the polycrystalline titanium surface. The curve-fit are presented in Figures 3 and 4. The C1s peak is attributed to a contamination layer, but not titanium carbide. The O1s peak also appears on the titanium EP surface. On the high resolution analysis of the Ti2p region, the XP spectrum from EP titanium surface was decomposed into several contributions (Figure 4). The main spin-orbit-split doublet is attributed to Ti⁺⁴, mainly due to TiO₂. The Ti⁰ peaks are also observed on the EP surface, because the oxide layer is very thin. These results are similar to those in Pouilleau's report.²¹

A. AES observation

With respect to AES measurements, the titanium single crystal sample was exposured to oxygen immediately following heating and cooling to RT. Then, the surface was AES-measured from RT - 600°C. Figure 5 shows the changes of the O_{KLL} AES intensities and the QMS ion current intensities for H₂O, O₂, CO and CO₂ desorbed from the surface during increasing temperature. The O_{KLL} Auger decreases above 400°C, and the intensity saturates

background signal level above 520°C in Figure 5(a). The desorbed gases H₂O, O₂, CO and CO₂ are emitted above 550°C in Figures 5(b) and (c). The titanium oxides on the surface sorb to bulk of titanium without evaporation initially, due to enhanced diffusion, followed by oxygen desorption at higher temperature. These observations agree with Vaquila's results.¹⁵ In UHV, a low flux of oxygen molecules are striking the surface at ~ 10^{10} molec/cm²·sec (~ 10^{-8} Pa), and the oxygen is immediately diffusing into the bulk without being detected by AES (analysis depth of a few nm) above 400°C.

Throughout these experiments, the measuring AES electron beam did not interfere with the titanium oxides on a specimen surface, i.e., "radiation effect", because there were no differences to the intensities of O_{KLL} with or without prolonged electron beam exposure.

B. XPS observation

The next focus of this work is identifying the chemical states of the titanium oxides in the surface region during heating. To analyze these oxides, XPS measurements were used. First, the specimen was measured with the conventional sample holder of the XPS system, shown in Figure 3. Next, the sample holder was changed to the special sample holder which had a heating platinum filament and then the XPS system was baked at a temperature of 180°C for 24 hours. The vacuum pressure before baking was 2.7×10^{-4} Pa, and the maximum vacuum pressure was 1.3×10^{-3} Pa during baking, and finally, the base vacuum pressure was 8.0×10^{-8} Pa. Figure 6 shows the RT XPS spectra of the titanium surface with EP treatment, after baking. There were no differences in surface contamination between before and after baking, except for small peaks of Ag and Al.

During measurement, the vacuum pressure was kept under 2.7×10^{-6} Pa to avoid contamination to the titanium surface in the range between RT and 450°C. Figure 7 shows the RT Ti2p core levels after the bakeout. The broad Ti2p_{3/2} peak is decomposed into several

contributions, obtained after heating at 180°C for 24 hours. The contributions represent compounds of Ti: TiO, Ti₃O₅, Ti₂O₃ and TiO₂. The Ti2p_{3/2} of TiO₂ is reduced, compared to Figure 4, but the peaks of TiO, Ti_2O_3 and Ti_3O_5 increased with the 180°C heating. The spectra, after heating at temperatures of 330°C and 450°C are presented in Figure 8. Figure 9 shows the dynamic changes of Ti2p and O1s between RT and 450°C while Figure 10 presents the changes of intensities for Ti2p_{3/2} of Ti, TiO, Ti₂O₃, Ti₃O₅ and TiO₂ depending on each temperature, respectively. Ti2p_{3/2} shows increasing intensities for Ti and TiO, and decreasing intensity for TiO₂ when heated up to 400°C. Ti₃O₅ exists stably between 200 and 330°C, and Ti₂O₃ from 200 to 400°C. The titanium oxides remain on the surface below 330°C; however, the oxide layer is reduced above 330°C as shown by the rapidly-increasing intensity of Ti° for metallic titanium. Above 400°C, TiO, Ti₂O₃, Ti₃O₅ and TiO₂ each begins to decompose with the component diffusing into the titanium bulk from the surface region. In Figure 8(b), TiC is observed because C1s peak energy 284.5 eV is shifts to 281.6 eV as TiC, which means that the surface carbon contamination has reacted with the metallic titanium. However, even the titanium carbide decomposes above 420°C.

The normally-protective and stable RT TiO₂ layer decomposes, upon heating in UHV, to TiO, Ti₂O₃, Ti₃O₅ and TiO₂. This complex oxide layer remains up to 400°C, although the TiO₂ fraction decreases, TiO increases, and Ti₃O₅ decreases over 330°C. Above 400°C, the oxide layer is disappears from the surface and the freed oxygen quickly dissolves into the bulk. The diffusion mechanism is expected to be mainly bulk diffusion, not to be short circuit diffusion, because there are not large differences between the diffusion behavior of the polycrystal and single crystal specimens in the present measurements.

IV. CONCLUSION

In present work, the changes of titanium oxides in the near surface region have investigated in UHV between RT and 600° C. The TiO₂ phase is stable at RT, however the TiO₂ decomposes to other titanium oxides which are TiO, Ti₂O₃ and Ti₃O₅, above 180°C. The titanium oxides remain on the surface between 200 and 330°C. Between 330 and 400°C, TiO is a stable oxide in comparison with Ti₃O₅ and TiO₂, however, all the oxides decompose above 400°C and the oxygen is diffused into the bulk.

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Fig. 1. Surface morphologies on EP titanium surfaces with SEM images. Polycrystal titanium in (a) and single crystal titanium in (b).



Fig. 2. Schematic illustration of AES, QMS and XPS surface analysis *in situ* system.



Binding Energy [eV]

Fig. 3. XP spectrum from titanium surface with EP treatment.



Intensity [cps]

Fig. 4. XP spectrum of Ti2p

region for EP titanium surface at RT.







Binding Energy [eV]

Fig. 6. XP spectrum from titanium surface with EP treatment after 180°C baking.



Fig. 7. XP spectrum of Ti2p region for EP titanium surface after baking with 180°C.



Fig. 8. XP spectra of Ti2p region for EP titanium surface with temperatures of 330°C in (a) and 450°C in (b).



Fig.9. Changes of XP spectra of Ti2p and O1s from titanium surface of EP treatment with temperature from RT to 450oC. Ti2p range in (a) and O1s range in (b).



Fig. 10. Changes of Ti $2p_{3/2}$ peaks for Ti, TiO, Ti₂O₃, Ti₃O₅ and TiO₂ depending on temperatures.

*The measurements were performed at RT after 180°C baking.

			A	I C	a	Cr	Cu	Fe	Н	Mg	Mn	
	JIS G	rade 2	-	-	1	-	-	0.25	0.013	-	-	
4N		<0.6	6 0.	6	0.3	<0.1	2.4	-	<0.1	<0.1		
	Ni	Si	Na	K	0	Ν	С					
	-	-	-	-	0.20	0.05	-	(%))			
	<0.2	<10	<0.05	<0.05	140	10	10	(pp	m)			

Table I. Chemical compositions of titanium specimens.

		Thickness	[nm]		Roughness Ra(mean value)	Mirror finishing	
TiO ₂ layer	O-layer	C-layer	H-layer	Modified layer	[nm]		
3	30	10	65	< 10	100	Yes	

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Table II. Characteristics of EP titanium surface.