SIMS Depth Profiling of Characteristic Thin Surface Layers Formed in Titanium by Mechanical Abrasion and Annealing

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SIMS depth profiling was applied for characterizing the distributions of elements in a surface layer of titanium, which are formed by mechanical abrasion followed by annealing at low temperatures under air or ozone. The SIMS depth profiles showed that enrichment of carbon and hydrogen were found in the surface layer of mechanical abraded titanium, and they were likely to penetrate into the titanium sample from the surface during abrasion. Annealing up to about 150°C under air was shown to reduce the amounts of carbon and hydrogen in the surface layer. Exposure of the sample to a low partial pressure of ozone at about 150°C was also found to reduce the amount of carbon and hydrogen in the surface layer. These phenomena are discussed in conjunction with the diffusivities of carbon and hydrogen in bulk titanium.

INTRODUCTION

As titanium demonstrates a strong affinity with oxygen [1], and its surface is reacted with oxygen to form a stable oxide layer [2,3]. As related to such a property, titanium is a promising material used for an ozone reservoir, in which the lifetime of ozone is kept to be long [4]. In addition, light elements such as carbon and hydrogen are also likely to be easily reacted with titanium [5-7], e.g. during sample treatment hydrogen and carbon. However, characteristic features of those elements in a surface layer of titanium are unclear yet.

In this work, SIMS depth profiling has been applied for characterizing distributions of such light elements in a surface layer, which are formed by mechanical abrasion and annealing at low temperatures under air or ozone. SIMS depth profiles were utilized for evaluating enrichment of carbon and hydrogen in surface layers. In order to study an influence of annealing on the distribution of elements in the surface layer, samples were annealed at different temperatures under air or a low partial pressure of ozone. The characteristic SIMS depth profiles obtain in this work were discussed in conjunction with the diffusivities of carbon and hydrogen in bulk titanium.

EXPERIMENTAL

Titanium plates were cut from a block of commercial grade pure titanium. They were mechanically abraded to obtain flat surfaces, which were adequate to gas reaction and surface analysis.

Samples were annealed at 100, 150 and 200°C for 1800 s, in order to study an influence of annealing temperature on compositional changes in the surface layer. Under these annealing conditions, any clear oxide layer did not appear to be observed.

The ozone exposure of samples was also done at 150°C±2°C for 1800 s. The pressure of ozone was 200 torr, and the gas flow was 50 sccm, and the content of ozone was 600 g/m^3.

SIMS measurements were carried out using PHI-6600 with quadrupole-type mass analyzer. An incident beam of 5.0keV Cs^+ ions was irradiated to the sample surface at an incident angle of 45 degree, and the beam current was 50 nA. Mainly positive

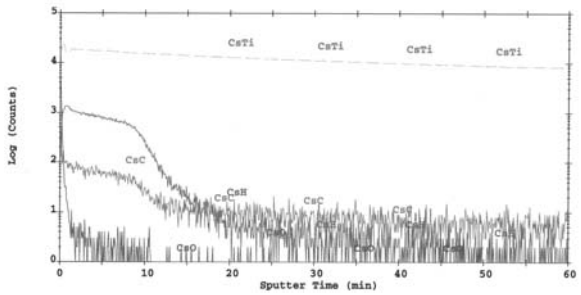

Fig.1 Depth profile of a surface layer in titanium as abraded.

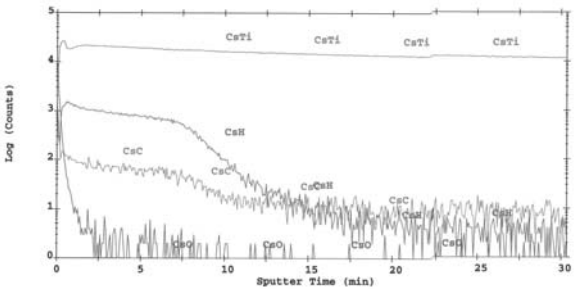

Fig.2 Depth profiles of surface annealed at 100 ℃.

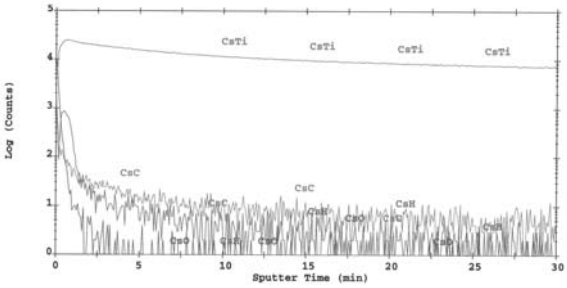

Fig.3 Depth profiles of surface annealed at 150℃.

secondary ions, $CsTi^+$, CsO^+, CsC^+, CsH^+, sputtered from the sample surface were analyzed, in order to avoid the interference effect of mass [8]. The sputtering rate of titanium was estimated to be about 0.167 μm/min by depth measurements of sputter craters.

RESULTS AND DISCUSSION

Depth profiles of a surface layer as abraded

Figure 1 show a typical depth profile of a surface layer in titanium as abraded. Enrichment of carbon and hydrogen is found in the surface layer, of which the thickness is estimated to about 1.5 μm from the sputtering rate, although the thickness is not always constant. The surface layer containing carbon and hydrogen is considered to form by penetration of these elements during abrasion, because carbon and hydrogen from the atmosphere are absorbed on the titanium surface and reactive to titanium.

DEPTH PROFILES OF SURFACE LAYERS ANNEALED IN AIR

Figures 2 and 3 show depth profiles of surface layers in titanium annealed at 100 and 150°C for 1800 s in air, respectively. Enrichment of carbon and hydrogen in the surface layer of about 1.5 μm in thickness is still observed in the sample annealed at 100°C. On the other hand, in the sample annealed at 150°C, the amounts of carbon and hydrogen in the surface layer decreased, although a very thin layer of adventitious carbon and hydrogen is still detected. These results indicates that there is a critical temperature between 100 and 150°C, at which a surface layer containing carbon and hydrogen disappears. Therefore, carbon and hydrogen are considered to diffuse out above the critical temperature, and they may be mainly emitted from the surface by reaction with oxygen in air.

DEPTH PROFILES OF SURFACE EXPOSURE TO OZONE AT 150°C

An influence of ozone exposure on the surface layer containing carbon and hydrogen was also investigated. The carbon and hydrogen in the surface layer were not changed by ozone exposure at room temperature. Therefore, influences of annealing on ozone exposure of the surface layer were analyzed by SIMS depth profiling.

Figures 4 and 5 show depth profiles for surface layers of samples annealed at 100 and 150°C in air, which were exposed to a ozone 150°C, respectively. Although carbon and hydrogen still remain in a surface layer of the sample exposed to ozone at 100°C, as shown in Fig. 2, the amounts of carbon and hydrogen decreased by ozone exposure at 150°C. Also, the carbon and hydrogen in the surface layer is low in the sample annealed at 150°C in air, followed by ozone exposure. These results indicate that a partial pressure of oxygen in an annealing atmosphere play an important role in distribution of carbon and hydrogen in the surface layer, and the occurrence of

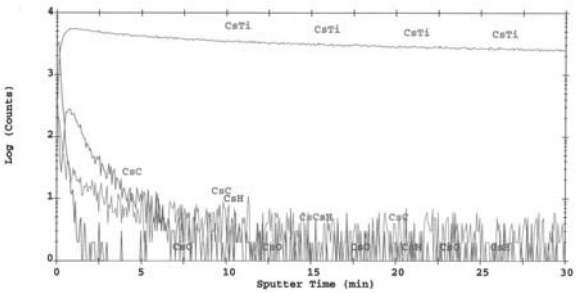

Fig.4 Depth profiles of surface annealed at 100°C in air, followed by exposure to ozone at 150°C.

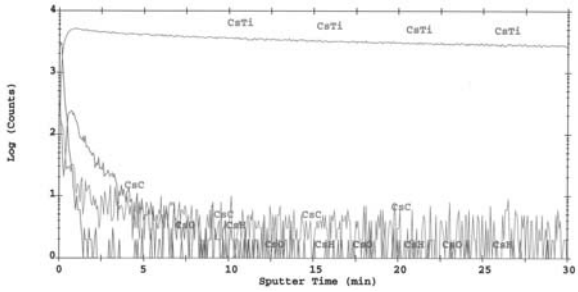

Fig.5 Depth profiles of surface annealed at 150°C in air, followed by exposure to ozone at 150°C.

this phenomenon strongly depends on annealing temperature.

MOBILITY OF CARBON AND HYDROGEN IN TITANIUM

Carbon and hydrogen in titanium is practically immobile at about room temperature. With increasing annealing temperature, these elements become mobile. They may be reacted with oxygen to form as carbon oxides and water, and released from the surface of titanium. The present work has shown that the amounts of carbon and hydrogen in the surface layer decreased by annealing above about 150°C. This characteristic feature should be discussed in conjunction with the bulk diffusion of carbon and hydrogen in titanium, of which diffusion data are available, as listed in **Table 1**. It lists the pre-exponential factors and activation enthalpies estimated from temperature dependence of diffusion coefficients of carbon and hydrogen in bulk titanium [9].

Table 1 Pre-exponential factors and activation enthalpies in Arrhenius relations of diffusion coefficients of carbon and hydrogen in titanium.

	Pre-exponential factor (m^2/s)	Activation enthalpy (kJ/mol)	Temp. (K)
C	7.9×10^{-8}	128	873-1073
H	5.8×10^{-6}	30.9	293-353

Table 2 Diffusivities of carbon and hydrogen at 100 and 150°C.

	100°C（373K）	150°C（423K）
C	9.37×10^{-26} (m^2/s)	1.23×10^{-23} (m^2/s)
H	2.73×10^{-10} (m^2/s)	8.86×10^{-10} (m^2/s)

Table 3 Mean diffusion distance of carbon and hydrogen at 100 and 150°C.

	100°C（373K）	150°C（423K）
C	1.30×10^{-11} (m)	1.49×10^{-10} (m)
H	$7{,}01\times10^{-3}$ (m)	1.26×10^{-3} (m)

As the above diffusion parameter were measured at high temperatures, diffusion coefficients of carbon and hydrogen in titanium at 100 and 150°C are estimated from the temperature dependence of the diffusion coefficients, as shown in **Table 2**.

Using the above diffusion coefficients, the order of magnitude the mean diffusion distances ($\sqrt{Dt}$) of carbon and hydrogen in titanium at 100 and 150°C can be calculated, although the temperature dependence is not strictly so simple. Then, as diffusion time was 1800 s, the diffusion distances are given in Table 3.

Thus, the diffusion distances estimated are compared with the thickness of the surface layer containing with carbon and hydrogen, 1.5 μm. The thickness of the surface layer is considerably larger than the diffusion distance of carbon in titanium estimated above. This indicates that the decrease in the amount of carbon by annealing is not dominated by simple bulk diffusion of carbon in titanium. Rather, the decrease in the amount of carbon in the surface layer may be enhanced by crystalline defects in the surface layer (i.e. short circuit diffusion), such as dislocations. This is because the dislocations are easily introduced during mechanical abrasion. On the other hand, the thickness of the surface layer is shorter than the diffusion distance of hydrogen in titanium. This may be associated with crystalline

defects introduced in the surface layer, to which hydrogen are easily trapped. Thus, the dispersion of carbon and hydrogen in the surface layer by annealing is not simply explained by bulk diffusion of carbon and hydrogen in titanium, but some kinds of defects are likely to significantly influence the reduction process of carbon and hydrogen.

CONCLUDING REMARKS

SIMS depth profiling was applied for characterizing the distributions of elements in a surface layer of titanium, which are formed by mechanical abrasion followed by annealing at low temperatures under air or ozone.

1) A surface layer containing enriched carbon and hydrogen was found in mechanical abraded titanium.
2) Annealing up to about 150°C under air was shown to decrease the amounts of carbon and hydrogen in the surface layer.
3) Exposure of the sample to a low partial pressure of ozone was at about 150°C also found to reduce the amount of carbon and hydrogen in the surface layer.
4) The reduction of the amounts of carbon and hydrogen in the surface layer by annealing is not simply explained by bulk diffusion of carbon and hydrogen in titanium, but some kinds of defects are likely to influence the reduction process of carbon and hydrogen.

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