Outgassing properties of a Carbon-doped Titanium Oxide Film on a Titanium Material Surface

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The paper addresses the vacuum performance of a carbon-doped titanium oxide film on a titanium material and applicability of the surface modification of vacuum flange to ultrahigh vacuum systems. The total amount of desorption gases of this material is almost the same as that of chemically-polished stainless steel with very low outgassing under non-vacuum baking conditions. Its total amount is half of that of stainless steel after the vacuum baking process. These results indicate that the carbon-doped titanium oxide film has very low outgassing properties. The surface modification was also applied to knife edge of a titanium vacuum-flange. The carbon-doped titanium oxide film exhibits sufficient durability so that after being tightened 40 times the knife edge was not worn out. It was found that Conflat flange made of this material can be utilized for practical vacuum systems.

Key words: Carbon-doped titanium oxide, Vacuum performance, Vacuum flange

1. INTRODUCTION

Titanium has very low outgassing rate compared with conventional materials such as stainless steels and aluminum alloys[1,2]. Titanium and its alloys, therefore, are used for ultra high vacuum components. On the other hand, titanium is susceptible to wearing and scratching, which poses durability issues in the use of a contact surface such as a knife edge of flange.

The authors propose surface modification of titanium to gain the durability of titanium components. The applied surface modification technology is so-called Fresh Green technology developed by Central Research Institute of Electric Power Industry (CRIEPI) [3]. The titanium surface is modified to a carbon-doped titanium oxide layer by oxidizing and carbonizing a titanium surface. This is free from binders and the concentration of oxygen and carbon is gradually changing within the boundary layer between the film and base metal. The crystal structure of the film is the rutile-type titanium dioxide structure, which was confirmed by an X-ray diffraction analysis [3]. Some of the oxygen atoms in a rutile-type titanium dioxide crystal are replaced by carbon atoms, this fact was analyzed by an X-ray photoelectron spectroscopy [3].

The carbon-doped titanium oxide film has a high hardness (e.g. 1600 Hv), a superior adhesion, a good sliding property and a high heat resistance up to 500°C [3]. These properties are attractive for vacuum applications, such as a vacuum flange with a knife edge for ultrahigh vacuum (UHV)
and driving parts in transfer systems.

This paper addresses the vacuum performance of the carbon-doped titanium oxide film with a thermal desorption spectroscopy (TDS) and the applicability of surface modification of vacuum flange to UHV system.

2. VACUUM PERFORMANCE

2.1 Experimental Procedures

The 10-µm-thick carbon-doped titanium oxide film on the pure titanium (JIS grade 2) was used as the sample. The unpolished bases metal was used, and then the surface roughness, Ra, of this material was about 100 nm. For a comparison, a chemically-polished stainless steel with the Ra of 20 nm was prepared, which has low outgassing and is already widely applied to UHV systems. [4]

The vacuum performances of the samples were evaluated by the TDS. Figure 1 shows the schematic illustration of the apparatus for TDS measurement and its specification. The pressure of this apparatus is achieved to $1 \times 10^{-8}$ Pa by using a titanium alloy with very low outgassing as the vacuum chamber material and serially-concatenated the two turbo-molecular pumps. Then the resolution of ion current of $10^{-14}$ A for the quadrupole mass spectrometer can be detected in this system.

The TDS measurements were done according to the following procedures. The sample tube of the size of 35 mm $\times$ 250 mm was installed in the measurement system. As an initializing treatment, the sample was baked at 150°C for 18 hrs, cooled down in a vacuum, and exposed to the air with 50 % relative humidity for 30 min. Afterwards, for the case of the non-baking process, pump down was done at the UHV of $10^{-9}$ Pa under room temperature for 48 hrs. For the case of the vacuum baking process, pump down was done for 4 hrs and the sample was baked at 150°C for 18 hrs and cooled down for 26 hrs in a vacuum. Then thermal desorption spectra for the sample was measured up to 720°C at a rate of 12°C/min. The elements of the thermal desorption gas were analyzed by a quadrupole mass spectrometer (QMS). In the measurement, mass-to-charge ratios were set to m/e=2 ($H_2$), m/e=18 ($H_2O$), 28 ($N_2$, $CO$), 32 ($O_2$) and 44 ($CO_2$).

2.2 Results and Discussion

Figs. 2 (a) and (b) show the thermal desorption spectra for the carbon-doped titanium oxide film and the chemically-polished stainless steel,

![Fig. 2 Thermal desorption spectra without the vacuum baking process for the carbon-doped titanium oxide (a) and the chemically polished stainless steel (b), respectively.](image)

![Fig. 3 Total amount of the each desorption gas from the room temperature to 200°C in carbon-doped titanium oxide ( ■ ) and chemically polished stainless steel ( ■ ) without baking process.](image)
respectively. Below 300°C H₂O is the primary contributor of adsorption gas in these samples. Above 300°C the amount of H₂ desorption increased in the stainless steel, while the increase in H₂ desorption for the surface-modified titanium is relatively small. This suggests that the carbon-doped titanium oxide film acts as the diffusion barrier for dissolved H₂ gas in bulk titanium.

The adsorption gases on the material surface govern the vacuum performance of vacuum systems. These gases are almost desorbed up to 200°C. Fig. 3 shows the amount of the desorption gas from room temperature to 200°C in each molecule for two sample materials under the non-baking condition. The amounts of primary desorbed H₂O gas are approximately the same as to each other sample. In the remaining molecules, the amounts of desorption gases of the surface-modified titanium sample are larger than those of the stainless steel sample. However, those differences between the amounts remained less than several times. Thus, the total amount of desorption gases of carbon-doped titanium oxide is almost the same as that of the chemically-polished stainless steel under non-baking conditions, though the surface of the modified titanium sample is rougher than that of the polished stainless steel.

Fig.4 shows the amount of the desorption gas from room temperature to 200°C in each molecule for two sample materials after baking process at 150°C for 18 hrs.

surface-modified titanium sample is one order smaller than those of the stainless steel sample, this is because the adsorbed H₂ gas on the titanium oxide surface and dissolved H₂ gas in that film are considered to be quickly evacuated by the vacuum baking. The amounts of the remaining desorption gases of the surface-modified titanium sample are slightly larger than those of the stainless steel sample. Thus, the total amount of desorbed gases for the carbon-doped titanium oxide is half of those for the chemically-polished stainless steel.

The chemically-polished stainless steel has very low outgassing properties, whose rates are 10⁻⁸ Pa m s⁻¹ without a baking process and 10⁻¹⁰ Pa m s⁻¹ after a conventional baking process.[3] Thus TDS results in this study indicate that the carbon-doped titanium oxide film has very low outgassing properties.

3. DEVELOPMENT OF VACUUM FLANGE
3.1 Development of ConFlat flange

A vacuum flange with knife edge, named ConFlat (CF) flange, is applied to UHV system as shown in Fig. 5 (a). In this flange, the vacuum seal is done by placing a Cu-gasket between two CF flanges and tightening as shown in Fig. 5 (b). The CF flange made of the titanium (JIS grade 2) with the carbon-doped titanium oxide film after 40 times tightening (c).

Fig. 4 Total amount of the each desorption gas from the room temperature to 200°C in carbon-doped titanium oxide (■) and chemically polished stainless steel (■) after baking process at 150°C for 18 hrs.

Table 1 Results of vacuum leak tests of CF flanges to tightening times.

<table>
<thead>
<tr>
<th>Operation cycles</th>
<th>1</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
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<tr>
<td>Titanium Oxide</td>
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<tr>
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of the carbon-doped titanium oxide is above 500 Hv and that of the titanium of JIS grade 2 is 150 Hv. A durability of the knife edge for the CF flange made of the surface-modified titanium material was evaluated by the vacuum leak test.

3.2 Durability of ConFlat flange

Table 1 shows the results of vacuum leak tests of the CF flanges to tightening times. Vacuum leak occurred in CF flange made of the titanium material after tightening more than 10 times, because the knife edge was worn out. On the other hand, the knife edge made of the surface-modified titanium showed a durable property. In fact, the knife edge was not worn out as shown in Fig. 5 (c), vacuum leak did not occur after tightening 40 times. Therefore, the titanium material with carbon-doped titanium oxide film (Vickers hardness > 300 Hv) is considered to be suitable for CF flange.

4. CONCLUSION

This paper describes the vacuum performance of a carbon-doped titanium oxide film on titanium material and development of the vacuum flange for ultrahigh vacuum systems made of this material. The vacuum performance of the sample was evaluated by the thermal desorption spectroscopy. The total amount of desorption gases of the carbon-doped titanium oxide film is almost the same as that of the chemically-polished stainless steel without vacuum baking process, though the surface of the modified titanium sample is rougher than that of the polished stainless steel. In addition, its total amount is half of that for the stainless steel after the baking process at 150°C for 18 hrs. Since the used chemically-polished stainless steel has the very low outgassing properties, the carbon-doped titanium oxide film has very low outgassing properties as well.

Conflat flange made of the surface-modified titanium was fabricated and its durability was examined. It showed a durable property after being tightened up to 40 times. Hard carbon-doped titanium oxide film was found to be promising for the knife edge of the CF flange.

References


(Received December 26, 2008; Accepted June 22, 2009)