

Effect of Chemical Polishing in Titanium Materials for Low Outgassing

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Dear Author,

I am pleased to inform you that your paper no. 663938, titled "Effect of Chemical Polishing in Titanium Materials for Low Outgassing", has been accepted for publication in the proceedings of the IVC-17/ICSS-13 and ICN+T2007 Congress. The proceedings will be published in Journal of Physics: Conference Series.

Yours sincerely,

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Effect of Chemical Polishing in Titanium Materials for Low Outgassing

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Abstract. A chemical polishing using a nitric acid solution was found to be the most suitable for the titanium materials. 1.8 nm of small surface roughness was observed in a microscopic range in 1 μm square, and 7 nm of a thin oxide layer was shown to exist for the chemically polished titanium. The surface processing for the titanium was developed combining the chemical polishing and the precision cleaning. The chemically polished pure titanium of JIS grade 2 showed extremely low outgassing rate below 10^{-12} Pams⁻¹ after baking process, which is two orders of magnitude smaller than that for standard vacuum materials under the same baking condition. Outgassing rates of the titanium is about 1/5 of that for a stainless steel without baking process.

1. Introduction

Recent years, titanium has been paid attention as a high vacuum material because of lightweight, non-magnetism, a low Yong's modulus, and a small thermal expansion coefficient. The vacuum characteristics for some kinds of titanium materials, pure titanium of JIS grade 2, Ti-3Al-2.5V and Ti-0.35Fe-0.35O, have been investigated and their outgassing rates are clarified to be lower than that for the standard materials.[1-3]

The surface polishing process, which improves smoothness, cleanness and passivation layer at the material surface, is necessary to obtain the low outgassing property. For the stainless steels and aluminum alloys, various surface polishing processes have been developed, and the electrolytic polishing [4-8], the chemical polishing [9,10] and the electro-chemical buffing [5,7,11] are clarified to be suitable for reduction in the outgassing rate. However the surface polishing for titanium materials were hardly discussed, although the mechano-chemical polishing was found to be effective to improve the outgassing rate.[2]

In this paper a newly developed chemical polishing method for titanium materials is described. The outgassing properties and surface conditions of chemically polished titanium materials were examined, and the excellent outgassing properties have been obtained.

2. Chemical Polishing

In generally, mechanical polishing, wet polishing and the wet polishing combined with mechanical polishing are applied for the surface treatment of the vacuum materials. The chemical polishing and the electrolytic polishing give a smooth surface, thin and uniform surface layer and non-residual impurities, and these polishing methods have advantages for a complex shaped samples and a cost. Therefore, these polishing processes were applied to the pure titanium of JIS grade 2 and the effects were discussed in this study. The electrolytic polishing was difficult, since some electrolytic solutions were insufficient to improve surface conditions, and other solutions are chemically unstable.

Figure 1 shows the mechanism of a chemical polishing. A surface of the metal immersed in chemical polishing solution dissolves into metal ions and the ions diffuse in the polishing solution. In the case that the metal dissolves faster than the ion diffusion, the metal ions concentrate at the concave, and a density of cations, mainly hydrogen ions (H^+), in polishing solution decreases at the concave as shown in Fig. 1 (a). This gives smooth surface, because an etching rate at the convex is larger than that at the concave as shown Fig. 1 (b) and (c). In addition, substances un-removed by a precision cleaning can be removable by the chemical polishing as shown in Fig. 1 (a) and (b). Where un-removable substances are sticking impurities such as powders produced in cutting or polishing process, the stain due to osmosis and diffusion of atoms and ions into vacuum materials, and chemically modified surface layer such as an oxidation scale formed in welding process as shown in Fig. 1 (a) – α , β and γ .

The effects of chemical polishing for the three kinds of the solutions, a sulfuric acid bath, a hydrochloric acid bath and a nitric acid bath, were evaluated. The process conditions, such as chemical composition of the polishing solutions, temperature and process time, were optimized. The chemical polishing with a nitric acid bath, which is stable and workable, was found to be the most suitable for the titanium materials.

Figure 2 shows the flow chart of the developed chemical polishing process using the nitric acid bath and precision cleaning, named “precision chemical polishing”. Here, the process 2 is the chemical polishing and the other processes are precision cleaning. In the precision cleaning, the process 1 removes organic materials such as oil. Process 3 removes metallic salts and heavy metals after the polishing process. The process 4 is the wet wiping. The removal effects of impurities can be further improved by adding the physical cleaning process between the chemical cleaning processes. Processes 5 and 6 remove particles and the inorganic salts. Moreover, in order to protect the contamination, the materials are treated in a clean room for the process 5. The materials are dried out by nitrogen gas, inspected and packed in clean atmosphere in processes 7 and 8.

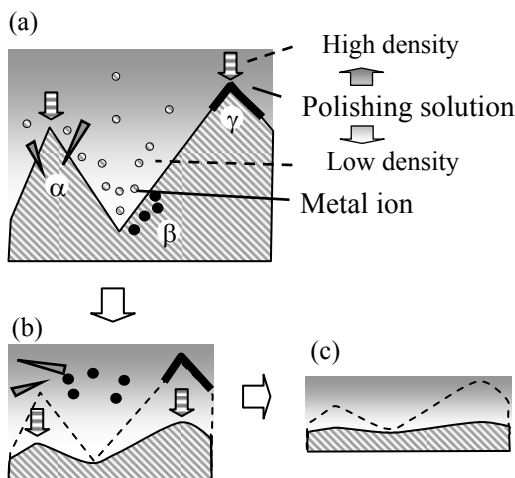


Fig. 1 Mechanism of a chemical polishing.

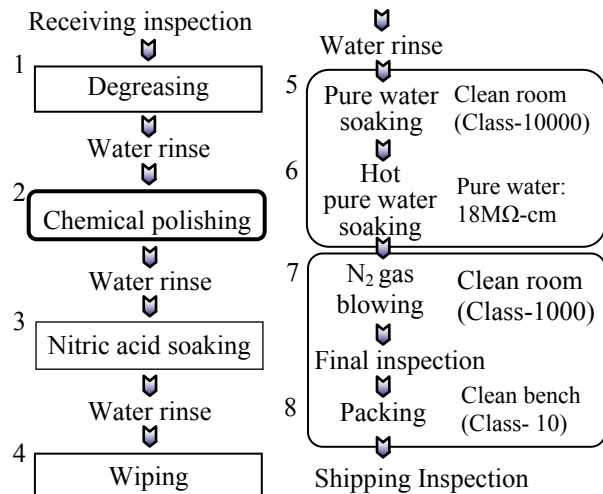


Fig. 2 Flow chart of developed chemical polishing and precision cleaning process.

3. Experimental Procedure

1-mm-thick plates of pure titanium, JIS grade 2, were employed as sample materials. Unpolished basis metal Ti ($Ti_{(BM)}$), buffed Ti ($Ti_{(BP)}$), mechano-chemically polished Ti ($Ti_{(MCP)}$) and chemically polished Ti ($Ti_{(CP)}$) were prepared. Here alumina abrasive grains (#400) were used for the buffing, and the mechano-chemically polishing consists of the wet chemical polishing combined with the mechanical polishing. The values of surface roughness (R_a) of the samples were estimated by an atomic force microscopy (AFM) in $10 \mu m^2$ and $1 \mu m^2$ area. In order to measure the surface oxide layer thickness, depth profiles were analyzed by an auger electron spectrometer (AES) with Ar etching gas, and transmission electron microscope (TEM) images were observed. The distribution of hydrogen atoms around the surface layer was analyzed by a time of flight - secondary ion mass spectrometry (TOF-SIMS) with Ar etching gas.

The outgassing rates were estimated by a modified orifice method, switching between two pumping paths[12]. The detection limit of the system was 7×10^{-13} Pams $^{-1}$ since the upstream and downstream pressures attained to 10^{-9} Pa and below, the orifice conductance C_0 was set to 6.1×10^{-3} m $^3 \cdot s^{-1}$ and the sample area was 8.9×10^{-1} m 2 [3]. The outgassing rate was measured at room temperature under non-baking and after baking process. Here the baking condition was 393K for 20 hours and 48 hours natural cooling process.

4. Results and Discussions

Table 1 shows the R_a and thickness of surface oxide layer for polished pure titanium samples. In the macroscopic area of $10 \mu m^2$, R_a for $Ti_{(CP)}$ is smaller than those for $Ti_{(BM)}$ and $Ti_{(BP)}$, and 10 times larger than that of $Ti_{(MCP)}$. However, the surface of $Ti_{(CP)}$ in microscopic area of $1 \mu m^2$ is as smooth as that of $Ti_{(MCP)}$, and the difference in R_a is considered due to the macroscopic undulation. R_a for $Ti_{(CP)}$ is smaller than twice the R_a for $Ti_{(MCP)}$ in microscopic area of $1 \mu m^2$. Since the amount of the adsorption gas is influenced by the surface roughness in a microscopic area, the surface of $Ti_{(CP)}$ is considered to be smooth enough.

The thickness of the surface oxide layer in $Ti_{(CP)}$ is smaller than those of the other polished samples as seen in Table 1, where the thickness was estimated by the half maximum value of the AES depth profile of oxygen (O). The surface oxide layer is confirmed to be an amorphous by the cross sectional TEM observation. The thin oxide surface layer is considered to act as barrier for bulk gas, mainly hydrogen, diffusion, resulting in low outgassing.

Table 2 shows the outgassing rates of the samples measured at 5 and 50 hours after the pumping without the baking process, and those rates with the baking process. Outgassing rates for $Ti_{(CP)}$ and $Ti_{(MCP)}$ without baking are 1/5 of that for $SUS_{(CP)}$, and the outgassing rate of $Ti_{(BP)}$ is comparable to that

Table 1 Surface roughness and thickness of surface oxide layer of various polished pure titanium samples

	Surface Roughness (R_a)		Thickness of Surface Oxide Layer (nm)
	$10 \mu m^2$ range (nm)	$1.0 \mu m^2$ range (nm)	
$Ti_{(BM)}$	108	-	13
$Ti_{(BP)}$	44	-	10
$Ti_{(MCP)}$	2.5	1.03	11
$Ti_{(CP)}$	25	1.80	8

Table 2 Outgassing rates for various polished titanium samples and chemical polished stainless steel

	Non-Baking (Pams $^{-1}$)		With Baking (Pams $^{-1}$)
	5 h	50 h	
$Ti_{(BP)}$	3.3×10^{-8}	2.8×10^{-9}	-
$Ti_{(MCP)}$	9.3×10^{-9}	4.6×10^{-10}	7×10^{-13}
$Ti_{(CP)}$	7.0×10^{-9}	5.1×10^{-10}	7×10^{-13}
$SUS_{(CP)}$	4.7×10^{-8}	3.1×10^{-9}	1.0×10^{-10}

for SUS_(CP). The outgassing rates for Ti_(CP) and Ti_(MCP) with baking process reach to 7×10^{-13} Pams⁻¹, which is two orders magnitude smaller than that of SUS_(CP) under the same pre-baking process. This means that chemical polishing is also suitable as the surface treatment for titanium materials.

In order to discuss the mechanism for the low outgassing property in the titanium material, the TOF-SIMS depth profiles were measured for Ti_(CP) and Ti_(MCP). The depth profile of hydrogen ions showed the peak at the boundary between the surface oxide layer and the bulk titanium. This result suggests that the hydrogen atoms localize at the boundary region as schematically shown in Fig. 3. This boundary region is considered to prevent the bulk hydrogen diffusion. And also the smooth surface and the thin oxide surface layer are considered to be important for the lower outgassing property because the rough surface has many adsorbed sites for gases and the thick oxide layer has many defects and dislocations which adsorb and dissolve gasses. Consequently smooth surface, thin oxide surface layer and barrier region preventing the bulk hydrogen diffusion give the extremely low outgassing rate for the titanium materials.

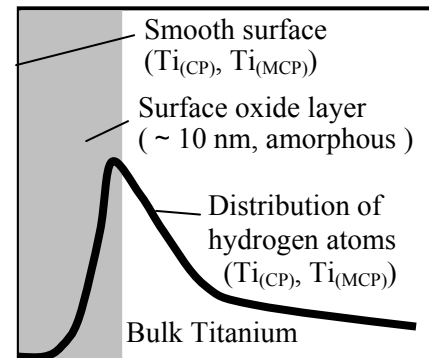


Fig. 3 Schematic diagram for the low outgassing titanium material.

5. Summary

The chemical polishing of the pure titanium of JIS grade 2 for UHV systems were discussed in this study. The chemical polishing using a nitric acid is clarified to be stable, and the chemically polished titanium showed smooth surface in a microscopic area, thin oxide surface layer and formation of barrier region preventing the bulk hydrogen diffusion, resulting in low outgassing property (see Fig. 3). The surface processing composed of the chemical polishing and the precision cleaning, named “precision chemical polishing”, was developed for the titanium material.

The outgassing property of the chemically polished titanium is excellent, and the outgassing rate without or with the baking process is smaller than that of standard vacuum materials, and comparable to that of mechano-chemically polished titanium with a mirror surface.

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