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Chemical Polishing on Titanium Materials for UHV Systems

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The surface treatment, which improves outgassing property for the titanium materials, was examined in this paper. A chemical polishing using a nitric acid solution was found to be the most suitable for the titanium materials, because the polished titanium has a surface roughness of 1.80 nm in a microscopic range of 1 μm and thin oxide surface layer thickness of 7 nm, and the polishing solution has stability and workability. And the surface processing for the titanium was developed by the combination of the chemical polishing and the precision cleaning. The chemically polished pure titanium of JIS grade 2 showed excellent 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 1/6 of that for a stainless steel without baking process.
Key words: chemical polishing, titanium, outgassing rate, ultrahigh vacuum system

1. INTRODUCTION

The development of the processing technology for the super minute electronic device is important, because the sizes of the thin film processing and the micro-fabrication already moved to nano-meter scales. The vacuum equipments for the fabrication of these devices are required to realize the ultrahigh vacuum (UHV) and the extremely high vacuum (XHV) in a short time. This implies the very low outgassing property is required for the vacuum materials.

In order to obtain low outgassing rate, a smooth surface and a thin passive surface layer are necessary. For the standard vacuum materials such as stainless steels and aluminum alloys, various surface polishing processes have been developed, and the electrolytic polishing [1-5], the chemical polishing [6,7] and the electro-chemical buffing [2,4,8] are clarified to be suitable for reduction in the outgassing property. However, the decrease in the outgassing rates of these materials is already facing the limit.

Recent years, titanium has been paid attention as a high vacuum material because of lightweight, non-magnetic material, 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.[9-11] The mechano-chemical polishing was found to be effective to improve the outgassing rate for titanium, while other polishing processes were hardly discussed so far. 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 proved.

2. POLISHING METHODS

In the production of the vacuum equipments, vacuum materials undergo machining and welding processes. The vacuum equipments after the production have various residual impurities on the surface, such as machine oil, inorganic salts, and particles, and chemically modified surface layer, which is an oxidation scale by welding. These impurities are the source of outgassing, and can be somewhat removed by a precision cleaning. However, the following substances cannot be removed by the cleaning as shown in Fig. 1.

① Sticking impurities such as powders produced in cutting or polishing process.
② Stain due to osmosis and diffusion of atoms and ions into vacuum materials
③ Chemically modified surface layer such as an oxidation scale produced in welding process.

These impurities, stains and modified layers are removable by the wet polishing which dissolves metal surface layer by a several micrometers in depth.

In generally, five kinds of wet polishing processes are employed for the surface treatment of the vacuum materials, which are an acid pickling, an electrolytic polishing, a chemical polishing, an electro-chemical buffing and a mechano-chemical polishing. Table 1 shows the evaluations of the wet polishing processes in terms of the specifications of vacuum equipments with low outgassing property. Here, three specifications, smooth surface, thin and uniform surface layer and non-residual impurities, are important for the reduction in outgassing. The applicability to a complicated shape and low cost

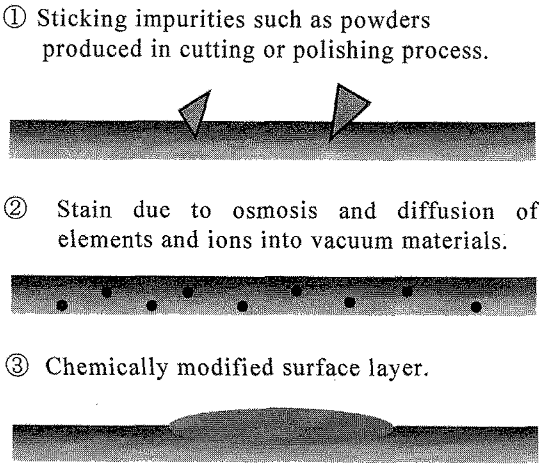

Fig.1 Un-removable impurities, stains and modified surface by a precision cleaning.

Table I Evaluations of the wet polishing processes in terms of the specifications of vacuum equipments with low outgassing property

	CP	EP	MCP	ECB	AP
Smooth surface	○	○	◎	◎	×
Thin and uniform surface layer	◎	◎	◎	◎	◎
Non-residual impurities	◎	◎	△	△	◎
Applicability to compicated shape	◎	○	×	×	◎
Cost	◎	○	×	×	◎

◎ : Better, ○ : Good, △ : Fair, × : No good

CP : Chemical polishing
EP : Electrolytic polishing
MCP : Mechano-chemical polishing
ECB : Electro-chemical buffing
AP : Acid picking

are also necessary from the viewpoint of practical use.

From Table I, the acid pickling is insufficient to obtain smooth surface, although the acid pickling fulfills the other specifications. The electro-chemical buffing and the mechano-chemical polishing processes combine the wet polishing with the mechanical polishing. Therefore, the polishing tools are complicated, and they are not easily applied to complicated shaped chambers and components, and their costs are high. The problem of remaining powder produced in polishing process is also considerable. On the other hand, the chemical polishing and the electrolytic polishing fulfill all the specifications in Table I with low outgassing properties. Therefore these polishing

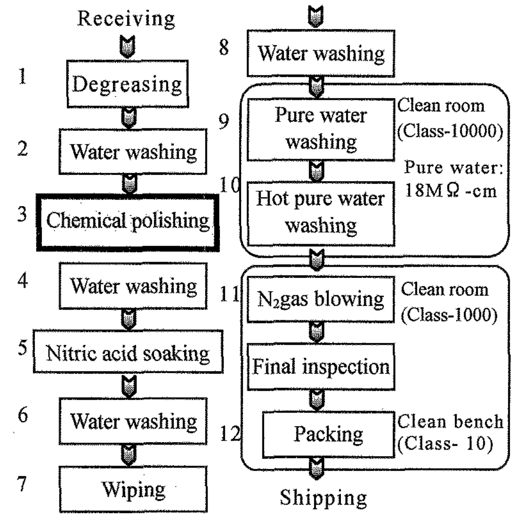

Fig.2 Flow chart of developed chemical polishing and precision cleaning process.

processes were applied to the pure titanium of JIS grade 2 and the effects were discussed in this study.

Two kinds of electrolytic solutions were examined for electrolytic polishing treatment. These are a phosphoric acid bath and a mixture electro-bath of phosphoric acid with sulfuric acid, which are used for the treatment of stainless steels and the aluminum alloys. However, the smooth surface and the thin oxide surface layer for the titanium were not obtained, although the electrolytic solutions were stable in the processes. Moreover, three kinds of electrolytic solutions that had been developed recently were evaluated in terms of polishing effects, which are a alcoholic bath, a perchloric acid bath, and a hydrogen peroxide-sulfuric acid bath.[12] These electrolytic solutions were chemically unstable, because the chemical composition for the solutions easily changes and the range of proper current density for the electrolytic process tends to be narrow. Consequently, the electrolytic polishing for the titanium was found to be difficult.

The effects of the three kinds of the solutions, a sulfuric acid bath, a chloride bath, and a nitric acid bath, were also evaluated for chemical polishing treatment. 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 is found to be the most suitable for the titanium materials, since the polished titanium fulfills the following specifications, i.e., smooth surface and thin oxide surface layer, low outgassing property. In addition, the chemical polishing solution has good stability and workability.

Figure 2 shows the flow chart of the developed chemical polishing process using a nitric acid bath, and precision cleaning, named as "precision chemical polishing". Here, the process 3 is chemical polishing and the other processes are precision cleaning. In the precision cleaning, the process 1 and process 2 remove organic materials, such as oil. Process 5 removes metallic salts and heavy metals after the polishing process. The process 7 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 9 and 10 remove particles and the inorganic salts. Moreover, in order to protect the contamination in air, the materials are treated in a clean room for the process 9. The materials are dried out by nitrogen gas, inspected and packed in clean atmosphere in processes 11 and 12.

3. EXPERIMENTAL PROCEDURES

Unpolished basis metal (BM), buff polished (BP), mechano-chemical polished (MCP) and developed precision chemical polished (CP) pure titanium materials, JIS grade 2, were prepared as reference. The values of surface roughness (Ra) of the samples were estimated by a stylus-type profilometer in a 1.25 mm range and an atomic force microscopy (AFM) in a 1 μm^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 transmitting electron microscope (TEM) images were observed.

The total amount of outgassing from the sample was measured by a thermal desorption spectroscopy (TDS), and the outgassing rates were estimated by a modified orifice method, switching between two pumping paths (SPP), of which detection limit for the outgassing rate is 7×10^{-13} $Pams^{-1}$ [13]. The total amount of outgassing and outgassing rate were measured for the samples with or without a baking process. The baking process for TDS measurement was made at 180℃ for 24 h, and that for SPP measurement was at 120℃ for 20 h.

4. RESULTS AND DISCUSSIONS

Table II shows the Ra and thickness of surface oxide layer for polished pure titanium samples, BM, BP, MCP and CP. In the macroscopic range of 1.5mm, Ra for CP is smaller than those for BM and BP, and 10 times larger than that of MCP. However, the surface of CP in microscopic range is as smooth as that of MCP, and the difference in Ra is considered to originate in a macroscopic undulation as seen in Fig. 3 (a) and (b). Surface morphology for CP is comparable to that for MCP as seen in Fig. 3 (c) and (d). Ra for CP is smaller than twice the Ra for MCP in microscopic range of 1 μm. Since the amount of the adsorption gas is influenced by the surface roughness in a microscopic range, the surface of CP is considered to be smooth enough.

The thickness of the surface oxide layer in CP sample is smaller than those of the other polished samples as seen in Table II, where the thickness was estimated from 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

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

	Surface Roughness (Ra)		Thickness of Surface Oxide Layer (nm)
	1.25 mm range (μm)	1.0 μm range (nm)	
BM	0.61	–	13
BP	0.34	–	10
MCP	0.024	1.03	11
CP	0.26	1.80	8

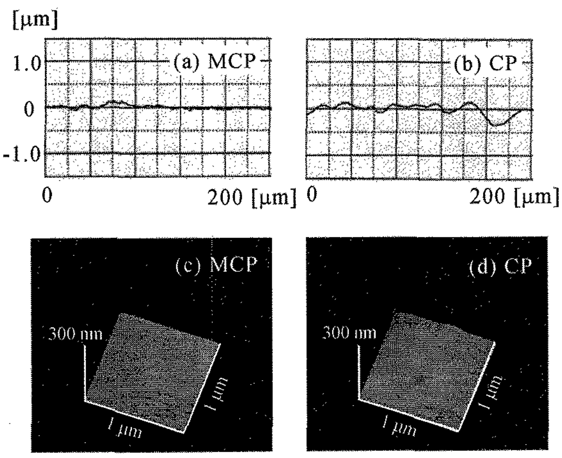

Fig. 3 Surface profiles of the pure titanium samples, (a) MCP and (b) CP, and AFM images of the samples, (c) MCP and (d) CP.

surface layer is considered to act as barrier for bulk gas, mainly hydrogen, diffusion, resulting in low outgassing.

Table III shows the total amount of outgassing from samples, BM, BP, MCP and CP, and chemical polished stainless steel, SUS(CP), estimated by TDS measurements from room temperature (RT) to 200 ℃ without baking and from RT to 400 ℃ with baking process. The reference sample SUS(CP) has reported to show low outgassing properties.[6] Without the baking process, The total amounts of outgassing from CP and MCP samples are about 1/3 of that from SUS(CP) and 1/2 of those for BM and BP samples. After the baking process, total amount of outgassing from CP and MCP samples are two order magnitude smaller than that from SUS(CP), and one order magnitude smaller than those of BM and BP samples.

Table IV shows the outgassing rates of the samples at 10 and 50 hours after the pumping without the baking process, and those rates with the baking process. Without the baking process, CP

Table III Total amount outgassing from polished titanium samples (BM, BP, MCP, CP) and chemically polished stainless steel (SUS(CP)) measured by TDS

	Total amount outgassing (arb. u.)	
	Witout Baking (RT～200℃)	With Baking (RT～400℃)
BM	0.61	3.18×10^{-2}
BP	0.552	1.40×10^{-1}
MCP	0.290	4.40×10^{-3}
CP	0.291	2.87×10^{-3}
SUS(CP)	1.00	1.00

Table IV Outgassing rates for polished titanium samples (BP, MCP, CP) and chemically polished stainless steel (SUS(CP)) measured by SPP method

	Without Baking ($Pams^{-1}$)		With Baking ($Pams^{-1}$)
	10 h	50 h	
BP	1.6×10^{-8}	2.8×10^{-9}	—
MCP	4.3×10^{-9}	4.6×10^{-10}	7×10^{-13}
CP	3.3×10^{-9}	5.1×10^{-10}	7×10^{-13}
SUS(CP)	2.4×10^{-8}	3.1×10^{-9}	1.0×10^{-10}

and MCP showed 1/6 of the outgassing rate comparing to SUS(CP), and the outgassing rate of BP is comparable to that for SUS(CP). With the baking process, the outgassing rates for CP and MCP 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, which brings the excellent low outgassing property to the titanium materials.

5. SUMMARY

The chemical polishing and the electrolytic polishing of the pure titanium of JIS grade 2 for UHV systems were discussed in this study. The electrolytic polishing for the titanium is estimated to be difficult, since some electrolytic solutions are insufficient to obtain smooth surface and the thin oxide surface layer, and the other solutions are unstable during the processing. On the other hand, the chemical polishing using a nitric acid is clarified to be stable, and the chemically polished titanium also showed smooth surface in a microscopic range and thin oxide surface layer, resulting in low outgassing property. And the surface processing for the titanium, named "precision chemical polishing", composed of the chemical polishing and the precision cleaning was developed.

The outgassing property of the chemically polished titanium is excellent, the outgassing rate under 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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