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EFFECT OF NITRIC HYDROFLUORIC ACID TREATMENT ON BRAZING OF ALUMINA CERAMICS AND PURE TITANIUM

M. Kinsho†, J. Kamiya, J-PARC, KEK&JAEA, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan
K. Abe, MARUWA CO., LTD. Kasugayama, Joetsu-shi, Niigata-ken, 943-0807
T. Nakamura, Asahi Kinzoku Kogyo Inc., Anpachi-gun, Gifu-ken, 503-0125

Abstract

Alumina ceramics vacuum chamber which is used for the 3GeV rapid-cycling synchrotron (RCS) in J-PARC is composed of alumina duct, titanium (Ti) flanges and Ti sleeves. Before brazing the alumina duct and the Ti sleeves, the Ti sleeves were treated with nitric hydrofluoric acid. The purpose of this study is to clear the effect of this treatment for titanium material. It was cleared by SEM observation that the roughness of the titanium material after the nitric hydrofluoric acid treatment becomes big. It was also measured that the thickness of oxide film on surface of the titanium material was 12.7 nm before treatment and 6.0 nm after treatment.

As a result of measuring the wettability of the brazing material which was silver brazing filler metal (Ag: 72%, Cu: 28%) on the Ti surface and the diffusion of the Ti material into the brazing material, it became clear that both the clearing of oxide layer on the alumina ceramics and the vacuum condition of the vacuum heating furnace were important for brazing between alumina ceramics and pure titanium.

INTRODUCTION

In the J-PARC 3 GeV synchrotron (RCS), about half of the vacuum chambers are using ceramics chambers[1]. These chambers consist of an alumina ceramics duct, and thin (about 1 mm) sleeves made of pure titanium (Ti-sleeve) and pure titanium flanges (Ti-flange) at both ends of the alumina ceramics duct. In manufacturing the vacuum chambers, the Ti- sleeves and alumina ceramics duct metallized by the Mo-Mn method were brazed with silver solder (BAg-8; 72% of Ag, 28% of Cu) [2]. These Ti-sleeves and Ti-flanges were TIG-welded at both ends of duct, and finished as a vacuum chamber. A nitric hydrofluoric acid treatment was performed as a pretreatment of the Ti-sleeve before brazing of alumina ceramics duct and the Ti-sleeve in the manufacturing process. The purpose of this pre-treatment was elimination of oxide layer on the surface of the Ti-sleeve. The effect of this treatment was enormous because vacuum leakage frequently occurred in the brazing process without this pretreatment but it has never occurred after adopting this treatment before brazing process in the manufacturing the alumina ceramics vacuum chambers. The purpose of this study is to clarify how this nitric hydrofluoric acid treatment affects the titanium material. Furthermore, the diffusion of silver brazing material with Ti material and wettability are measured, and the importance of the condition of vacuum heating furnace is also discussed in brazing alumina ceramics and pure titanium.

HYDROFLUORIC ACID TREATMENT OF PURE TITANIUM

In order to investigate the effect of nitric hydrofluoric acid treatment on the surface of pure titanium, surface observation by SEM (scanning electron microscope) and measurement of oxide film thickness by Auger Electron Spectroscopy (Auger electron spectroscopy) were carried out. The SEM photographs of pure titanium surface before and after hydrofluoric acid treatment are shown in Fig.1. It was confirmed that roughness of the surface which was treated with nitric hydrofluoric acid became apparent as compared with before the treatment.

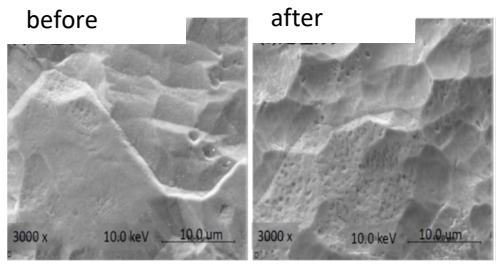

Figure 1: SEM Pictures of surface of the pure titanium before and after nitric hydrofluoric acid treatment.

The measurement results of thickness of the oxide film by AES are shown in Fig.2. An electron with an energy of 10 keV was irradiated to one place on the surface of pure titanium. The irradiation time was 1 minute and this corresponded to the electron beam reaching distance of 1 µm in the depth direction. When the point at which the signal of oxygen became half was defined as the thickness of the oxide film, it was found from this result that the thickness of the oxide film was about 8.5 µm before nitric hydrofluoric acid treatment and it became about 3.4 µm after that treatment. From these experimental results, it is presumed that the roughening of the titanium surface and removal of the oxide film on the titanium surface are main factors by the nitric hydrofluoric acid treatment for elimination of the vacuum leak in brazing between the titanium sleeve and the alumina ceramics

† kinsho.michikazu@jaea.go.jp.

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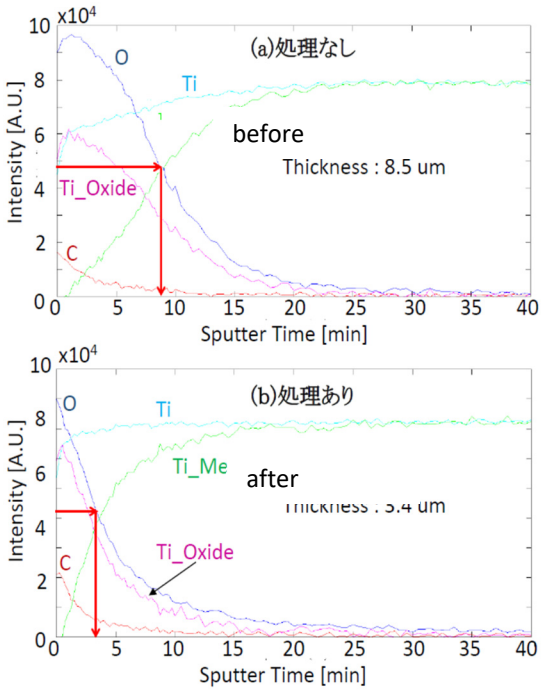

Figure 2: Measurements of the oxide film thickness before and after nitric hydrofluoric acid treatment measured by AES.

INFLUENCE OF HEAT TREATMENT IN VACUUM FURNACE

The condition of pure titanium and silver brazing filler metal (BAg - 8) by heat treatment in a vacuum heating furnace (brazing furnace) was investigated. The maximum heating temperature was 840 °C, and the pressure in the heating furnace at that temperature was 8.5×10^{-4} Pa. Wetting and spreading of silver solder were observed and typical results were shown in Fig.3. There was no significant difference in wetting and spreading of the brazing filler metal depending on the presence or absence of the surface treatment.

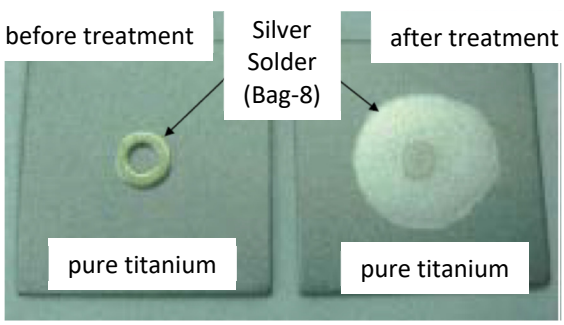

Figure 3: Pictures of the silver solder on the pure titanium surface before and after heat treatment. Outer diameter: 4.35φmm(before), ~11φmm(after), Inner diameter: 2.5φ mm(before), 0mm(after).

The diffused state of silver solder was observed from the cross-sectional photograph of the joining portion of silver solder and pure titanium. The cross-sectional photograph is shown in Fig. 4 and the diffusion depth of silver solder to pure titanium is summarized in Table 1. Only the silver solder diffusion layer was observed for silver solder on the titanium material which was not treated with nitric hydrofluoric acid. On the other hand, it was found that a titanium-copper rich layer (Ti-Cu rich layer) was formed between the silver braze diffusion layer and the silver braze layer when nitric hydrofluoric acid treatment was performed. Controlling this layer is important for brazing from experimental results of mechanical strength for several kinds of this Ti-Cu rich layer.

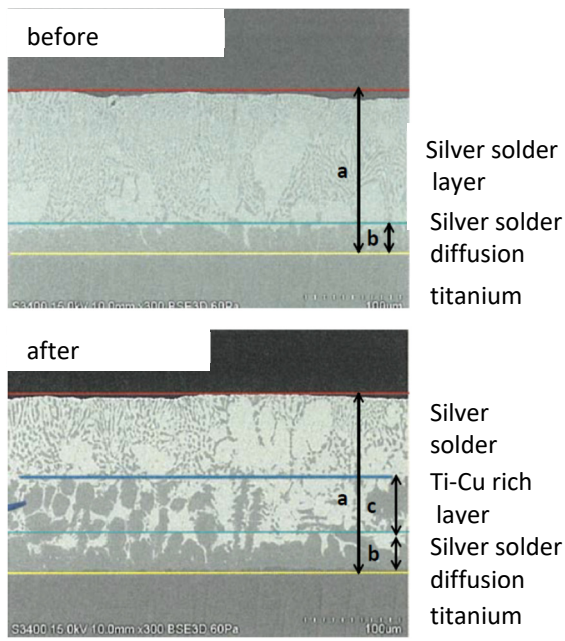

Figure 4: Cross section pictures of silver solder and pure titanium before and after heat treatment.

Table 1: Measurements of Diffusion Depth of Silver Solder on Pure Titanium After Heat Treatment.

	Without Treatment	After Treatment
a	135 μm	139 μm
b	31 μm	40 μm
c	0	53 μm

a : silver solder height from titanium surface
b : diffusion distance of silver solder into titanium
c : Ti-Cu rich layer thickness

Elemental analysis was carried out from Energy Dispersive X-ray spectrometry (EDX) in order to observe the brazing interface condition of pure titanium surface-

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treated with nitric hydrofluoric acid. Results are shown in Fig. 5 and Table 2. From these analysis results, the A and C areas (①) in Fig. 5 were the silver brazing component rich layer, and the titanium content was about 7.7 to 10.6%, respectively. The B, D, and E (②) areas were Ti-Cu rich layers. It is considered that the Cu in the silver solder diffused into the Ti base material and the Cu in the silver braze component reacted with the Ti base material. On the other hand, the Ag component was small as shown in Table 2. Although the F area (③) was the base material of pure titanium, it was obvious that the silver brazing component diffused also into the Ti base material, because the silver braze component (Cu or Ag) was detected. Oxygen was also detected, which was considered to be due to the oxide film remaining on the surface of the Ti base metal even after nitric hydrofluoric acid treatment.

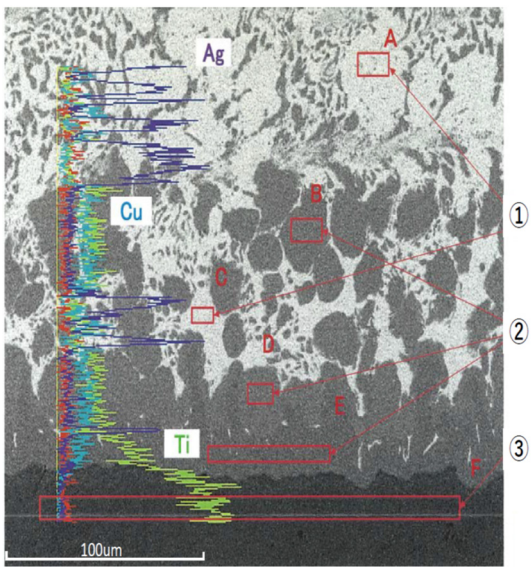

Figure 5: Elemental analysis of silver braze on pure titanium which was treated by nitric hydrofluoric acid after heat treatment measured by EDX.

Table 2: Elemental Analysis Data of Silver Solder on Pure Titanium Which is Treated by Nitric Hydrofluoric Acid After Heat Treatment Measured by EDX.

	Constitution element [%]			
	Ti	Cu	Ag	O
A	**7.7**	18.7	73.5	0.0
B	23.8	71.8	4.4	0.0
C	10.6	21.5	60.2	7.7
D	23.2	67.6	2.6	6.6
E	44.7	52.3	3.1	0.0
F	85.8	2.8	0.9	10.6

CONCLUSION AND FUTURE

From the results so far, it was found that the following was important for silver brazing of pure titanium and alumina ceramics.

- Roughen the pure titanium surface by hydrofluoric acid treatment or another method.
- Remove the oxide film on the surface of pure titanium by hydrofluoric acid treatment or another method.
- Do not allow silver braze to diffuse into pure titanium. Also, the thickness of the titanium-copper rich layer is controlled.

From these reasons, it important to control the pressure of the vacuum furnace used for brazing, especially the base pressure and temperature rise conditions. As a measure to solve these management, it is not necessary to pay particular attention as long as nickel can be plated on the surface of pure titanium. In order to clear these conditions, the nickel plating to pure titanium has been carried out, and we have obtained good nickel-plating layer on the titanium surface. We have started to conduct a brazing test with alumina ceramics and to evaluate mechanical strength such as brazing strength.

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[2] M. Kinsho et al., Titanium flanged alumina ceramics vacuum duct with low impedance, **Vacuum 81** (2007) 808-811