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Optimized method of producing washers of titanium hydride for plasma gun using occluded hydrogen gas

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An optimized way of producing washers of titanium hydride for the application to a plasma gun using the occluded gas is presented. The amount of H_2 gas (equivalently, gas pressure p) is entirely preadjusted in a gas reservoir of a simple instrument. The temperature T of a furnace is completely feedback controlled. Data show that when p is the order of 1 atm, T needs to be higher than about 450 °C in order to successfully produce washers of titanium hydride. Results on compressive strength of the loaded washers suggest that an appropriate ratio of atoms of hydrogen to titanium is less than $\mathrm{H}:\mathrm{Ti} \sim 0.85:1$. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2227648]

I. INTRODUCTION

There is long history about research on basic properties of metal-hydrogen systems.[1,2] Even recently, it has attracted great interest in relation to the possibility of hydrogen in future energy technology. Efforts to develop new hydrogen-storage materials[2] and their application to rechargeable batteries and fuel cells[3] have continued in many countries.

The hydrogen-storage material has been applied also in the field of plasma science. The most known use is an *occluded gas source*[4] that has been widely employed for five decades.[5–9] Significantly, the occluded gas source can produce a plasma in one place without any filling gas and, moreover, eject the plasma into another region. This actually provides great flexibility of the location of plasma source. In fact, it is possible to produce plasmas locally even inside the closed magnetic surfaces of toroidal fusion plasmas.[8]

Generally, the occluded gas source contains several washers of titanium hydride,[4] one of nonmagnetic materials. Therefore, it is also called a *titanium washer stack source* (or *gun*)[4] (henceforth, called Ti gun). If the number of hydrogen atoms occluded in titanium washers is enough, a hydrogen plasma can be formed by releasing the trapped hydrogen through the high voltage applied across the source. Then, the formed plasma is accelerated out from the source through the center hole of washers. Because no H_2 gas is supplied during the discharge process, only a small amount of residual neutral particles is being carried along with the formed plasma. Therefore, the Ti gun has the advantage of doing experiments which require high vacuum conditions. With regard to disadvantage, on the other hand, plasma parameters of the Ti gun such as plasma density n_0 have changed considerably in the wide range from 10^{11} (Ref. 8) to $10^{14}\ \mathrm{cm}^{-3}$.[5,6] Moreover, the value of n_0 is often unsteady even in a series of several plasma shots.[10] This poor reproducibility should be improved, especially for basic plasma research such as non-neutral plasma experiments[11] where a small change in n_0 may affect much on the self-electric field of the plasmas.

Apparently, n_0 of the formed plasma depends on the number of hydrogen atoms released from the loaded titanium washers and therefore on the amount of hydrogen occluded in titanium washer and perhaps the process of hydrogen occlusion. In past experiments using Ti guns, diverse ways of producing titanium hydride had been applied. Asano *et al.* heated up the titanium washers with radio frequency until the introduced H_2 gas was absorbed in them, but without measuring the temperature T.[12] Takeda used an electric furnace to heat up titanium washers and succeeded in the occlusion of hydrogen when a valve for introducing H_2 gas was opened at $T \sim 700$ °C, which, however, had been entirely determined by empirical cut-and-try experiments as well.[10] Contrary to such high temperature, successful occlusion at considerably lower T has been also reported, where $T \sim 320$ °C.[5] For these reasons, it is quite puzzling what T and how much H_2 gas should be set in order to make washers of titanium hydride, although many articles on experiments using Ti guns have been published.[4–9] In fact, in the previous works, attention has been paid mainly to what plasma parameters are attained in plasma confinement regions. No instructive work on how washers of titanium hydride should be produced has thus been reported yet.

This article presents an optimized way of producing washers of titanium hydride, especially for the application to Ti guns. The method employs a simple instrument that can exactly control the amount of hydrogen and operate in ultrahigh vacuum condition. In order to heat up the titanium washers, a cylindrical electric furnace is used where T is entirely feedback controlled. In experiments, we have tested two kinds of titanium washers and investigated the condition of successful occlusion systematically. Data show that in order to produce washers of titanium hydride in which the

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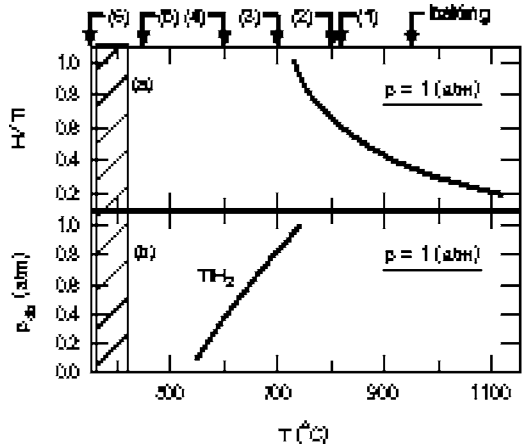

FIG. 1. Temperature dependence of (a) the solubility of hydrogen in titanium and (b) the equilibrium pressure p_{dis} of hydrogen dissolved from titanium hydride (TiH_2), when the surrounding pressure of hydrogen gas p is 1 atm. The solubility is expressed using the ratio of the number of H atoms to the number of Ti atoms. It can be seen that full occlusion/dissociation of hydrogen in/from titanium happens at $T \sim 730$ °C. This means that prior to hydrogen occlusion, titanium washers must be heated up at least above $T \sim 730$ °C for degassing and then cooled down in an atmosphere of hydrogen.

concentration of hydrogen into the titanium washers is relatively high ($H/Ti \sim 1$), T needs to be higher at least ~ 450 °C. Besides, in this research, we have examined for the first time the mechanical strength of the loaded titanium washer. Results on compressive strength suggest that an appropriate ratio of atoms of hydrogen to titanium is less than $H:Ti \sim 0.85:1$.

The remainder of this article is organized as follows. In Sec. II, the process of occlusion of hydrogen into titanium is briefly reviewed. Details of the constructed instrument are presented in Sec. III. In Sec. IV, the procedure for operating the instrument is explained. Then, we show experimental results on occlusion of hydrogen in titanium washers and the mechanical strength of the loaded titanium washers. Finally, summary is given in Sec. V.

II. OCCLUSION OF HYDROGEN INTO TITANIUM WASHER

It is known that at a given high temperature, solubility of hydrogen into a metal increases with increasing surrounding pressure p of H_2 gas.[1] Moreover, when the concentration of hydrogen in a metal is relatively low, the relation of $H/M \propto \sqrt{p}[\Leftrightarrow H/M = (1/K_s)\sqrt{p}]$ is satisfied, where H/M is the ratio of the number of H atoms to the number of M atoms and K_s is the Sieverts constant. The temperature dependence of K_s is approximately written as $\ln K_s = -\Delta S_S/R + \Delta H_s/RT$, where ΔS_s and ΔH_s are called the entropy and enthalpy (heat) of solution, respectively, and R is the gas constant. Since the value of ΔH_s for titanium is negative (about -53 to -60 kJ/mol), thus the solubility of hydrogen into titanium becomes relatively large. Figure 1(a) shows the temperature dependence of H/Ti for the case of $p = 1$ atm.[2] As recognized, at $T \sim 730$ °C, the value of H/Ti reaches almost unity.

The temperature of $T \sim 730$ °C corresponds also to the critical value at which titanium hydride (TiH_2) is fully dissociated. As seen from Fig. 1(b), at $T \sim 730$ °C, the equilibrium pressure p_{dis} of hydrogen dissolved from TiH_2 reaches unity, which is equal to $p(=1$ atm). This indicates $T \sim 730$ °C as the lowest temperature for degassing. Below $T \sim 730$ °C, a part of hydrogen is thus trapped in titanium and then forms a titanium hydride, which results in decreasing the value of p_{dis}. And finally, at room temperature (RT), the value of p_{dis} becomes negligible small. It is noted that despite finite p_{dis} at RT theoretically, no hydrogen can indeed come out from titanium. This attributes to the existence of potential barriers on the surface of titanium so that the occluded hydrogen is completely blocked.[1]

III. APPARATUS

As explained, titanium metal must at first be heated up above 730 °C if it needs to be degassed. Also, the amount of hydrogen occluded in titanium washers should be controlled correctly, which calls for an ultrahigh vacuum condition. In order to answer these requirements, we have constructed a simple instrument adequate for the occlusion of hydrogen into titanium washers.

Figure 2 shows a schematic diagram of the device which operates in a controlled high-temperature furnace with ultrahigh vacuum environment. The instrument consists of mainly four parts: (A) the cylindrical electric furnace for heating, (B) the container tube made of quartz, (C) the gas reservoir, and (D) the vacuum generator. Figure 3 shows a schematic

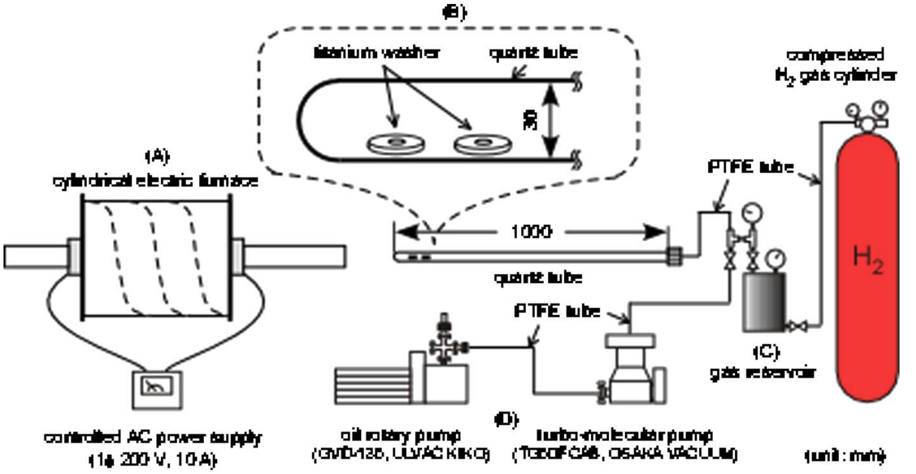

FIG. 2. A schematic diagram of the instrument for hydrogen occlusion. It operates in controlled high-temperature furnace with ultrahigh vacuum condition. The instrument consists of mainly four parts: (A) the cylindrical electric furnace for heating, (B) the container tube made of quartz, (C) the gas reservoir, and (D) the vacuum generator.

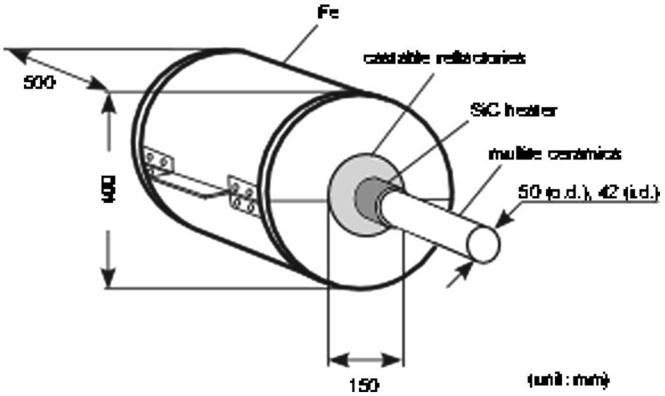

FIG. 3. A schematic drawing of the cylindrical electric furnace. A SiC heater is used as a heating element which can generate $T \sim 1600\ ^\circ\mathrm{C}$ as the maximum temperature.

drawing of the cylindrical electric furnace that is energized with an ac (~ 10 A, 1ϕ, 200 V) flowing through the SiC heater, a heating element. This element can generate high temperature up to a maximum of $T \sim 1600\ ^\circ\mathrm{C}$ on its surface. Around the SiC heater, castable reflactories are placed, which act as heat shields to prevent thermodiffusion. Inside the SiC heater, a mullite ceramic tube is placed, in which the container tube having titanium washers will be inserted. All of these components are wholly held in an iron vessel. Regarding the value of T, it is measured with a thermocouple temperature probe and entirely feedback controlled. The measured gradient of T inside the furnace is about $\pm 0.5\ ^\circ\mathrm{C/cm}$. Therefore, T can be considered to be uniform for the purpose of this research.

As for the container tube, it is made of quartz that can resist heat up to $T \sim 1100\ ^\circ\mathrm{C}$. The length of the tube is 1 m, and the both inner and outer diameters are 30 and 35 mm, respectively. While the front-end side of the quartz tube is vacuum sealed, the other side is completely open ended at which to be connected with the gas reservoir through a polytetrafluoroethylene (PTFE) tube. The inner diameter of the PTFE tube is 4 mm. Through the open-ended side of the quartz tube, titanium washers are taken in/out before and after the occlusion of hydrogen.

In order to control the amount of hydrogen occluded into titanium washers, we have applied the gas reservoir in which a prescribed amount of H_2 gas is preintroduced. The gas reservoir is made of stainless steel (SUS304) and the shape of it is cylindrical whose inner diameter and height are 10 and 14 cm, respectively. Thus, we can exactly calculate the number of hydrogen atoms from the pressure of H_2 gas p_{fil} filled into the gas reservoir. The value of p_{fil} is completely limited never to excess ~ 5.5 atm so that the preintroduced gas can be regarded as ideal gas with an error of $\sim 0.5\%$ at $T \sim 25\ ^\circ\mathrm{C}$.

Another key point to successful occlusion is that little impurity (such as N_2 or O_2) must be left in both the quartz tube and the gas reservoir. In fact, those residual molecules immediately form thin-film nitride (or oxide) on the surface of titanium washer, which prevents hydrogen from dissolving into the titanium washers. Thus, a turbo molecular pump with 50 l is used to pump the device down to ultrahigh vacuum.

IV. RESULTS AND DISCUSSION

In this research, two different washers of pure titanium have been tested. The one is a conventional commercial hollow washer. Its bore and the outer diameters are 10.5 and 22.0 mm, respectively, and the thickness of the washer is 1.5 mm. The other one is a custom-made washer which is thicker than the commercial washer; its thickness is 5 mm and the diameter of the center hole is 3.2 mm, although having the same outer diameter (21.5 mm) as that of the commercial one. Using those washers, we have made six sets of titanium washers. Each set is a mixture of various washers that are composed of the two kinds of washers explained above. On the other hand, the total weight of each set is arranged in approximately the same weight of ~ 30 g.

A. Sequence of operation

The process of hydrogen occlusion had been induced as follows. First of all, all titanium washers of each set are cleaned for 15 min in an ultrasonic bath with ethanol in order to remove grease from surfaces of titanium washers. After finishing the cleaning, the washers are installed into the container tube and placed in a line at intervals of about 5 mm. Here it should be noted that in every experiment, one of handmade washers is always placed at the nearest to the open-ended side of the container tube as the front washer. This is because if a vacuum leak should happen, the influent air is blocked to some extent by being absorbed in the *fat* washer, which consequently minimizes the damage on the rest of washers lined behind it.

Secondly, the container tube having titanium washers is vacuum sealed with an o ring and pumped down to $\sim 10^{-7}$ Torr. Subsequently, the tube is inserted into the furnace and T rises gradually to $\sim 950\ ^\circ\mathrm{C}$ in 2.5 h. After reaching $T \sim 950\ ^\circ\mathrm{C}$, T is maintained for 30 min for degasification and then cooled down by reducing the heating current of furnace. Figure 4 shows the time histories for each set. As recognized, no difference among the six cases is found until $t \sim 3.5$ h. On the other hand, the time when H_2 gas begins to be introduced T_{in} is different from each other. For example, the value of T_{in} is $810\ ^\circ\mathrm{C}$ for the case of (1), while $T_{\mathrm{in}} = 350\ ^\circ\mathrm{C}$ for the (6) case. All values of T_{in} are described in Table I along with p_{fil} in the gas reservoir. Also, in Fig. 1, those are indicated with arrows.

As recognized from Fig. 4, after H_2 gas goes in the container tube, T_{in} is kept for a certain time dt in order to diffuse hydrogen in titanium washers: $dt=1$ h for cases of (1)–(5) and 2 h only for the case of (6). In fact, the diffusion coefficient D of hydrogen into titanium is approximately written as $D = D_0 \exp(-E_a/kT)$ where $D_0 = 1.5 \times 10^{-6}\ \mathrm{m^2/s}$, $E_a = 0.54$ eV, and k is Boltzmann's constant, although D is usually anisotropic in hcp metals.[1] This indicates that the value of D is in the range between 10^{-9} and $10^{-11}\ \mathrm{m^2/s}$ in this research ($350\ ^\circ\mathrm{C} < T < 810\ ^\circ\mathrm{C}$). Assuming $\delta = \sqrt{Ddt}$ as the penetration depth δ into titanium, δ are then calculated to be

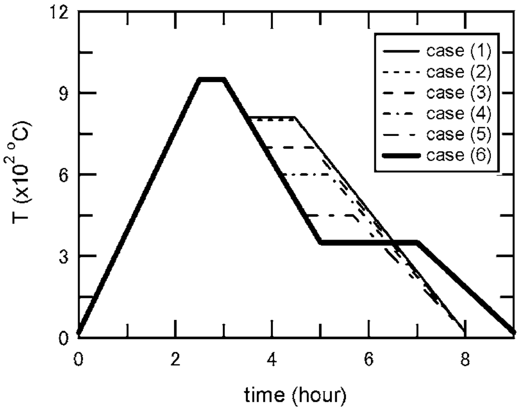

FIG. 4. Time histories of temperature T for each set of titanium washers listed in Table I. At first, T rises gradually to ~950 °C in 2.5 h. After reaching ~950 °C, T is maintained for 30 min for degasification. Subsequently, T decreases programmatically. When H_2 gas is introduced at $T=T_{\text{in}}$, T is retained at the temperature for $dt=60$ min [for cases of (1)—(5)] and $dt=120$ min [for the case of (6)].

$\sim 0.5-4$ mm for $dt=1$ h. This value of δ is almost the same as the scale length of the titanium washers employed.

B. Hydrogen absorption versus T_{in}

The mass of H_2 gas ω, which is preintroduced in the gas reservoir, can be calculated from the equation of $\omega = p_{\text{fil}}VM/RT(\propto p)$, where V, M, and R are the volume of the gas reservoir, the mass number, and the gas constant, respectively. It is noted here that T is assumed to be RT and the purity of H_2 gas is four nines (99.99%). If completing the occlusion process, each set of titanium washers increases in weight due to the occluded H_2 gas. Meanwhile, no change happens in weight, if nothing is occluded in them. Based on this fact, we can investigate the dependence of H_2 occlusion on T_{in}.

Using a conventional weigh scales, we have measured the change in weight dm and compared it with ω for the six cases. Figure 5(a) shows the ratio of dm to ω. As seen from the plotted data, all values of dm/ω are ~1 except in the case of lowest temperature ($T_{\text{in}}=350$ °C). This means that as long as $T_{\text{in}}>450$ °C, the prereserved H_2 gas is fully occluded into titanium washers. On the other hand, for the case of (6) where $T_{\text{in}}=350$ °C, little hydrogen is absorbed into titanium washers, regardless of the longer time of dt [equivalently, $T_{\text{in}}dt=700$ °C/h, as shown in Fig. 5(b)]. This result seems to be consistent with the consequence deduced from the theoretical curve of p_{dis} [see also Fig. 1(b)]. That is to say, p_{dis} is negligibly small at $T\sim 350$ °C so that TiH_2 structure could form considerably. Therefore, no occlusion of hydrogen may be observed at the temperature.

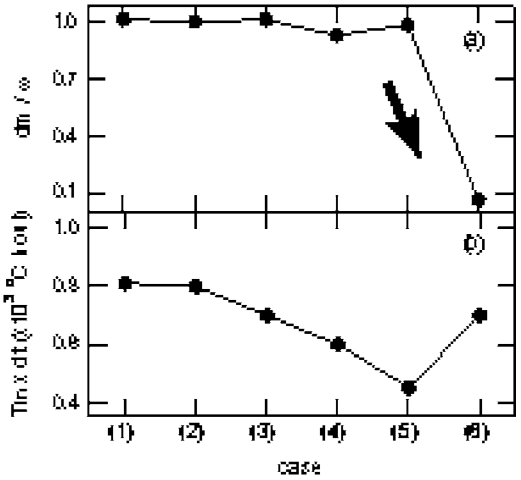

FIG. 5. Values of (a) the ratio of dm to ω and (b) the product of T_{in} and dt for each set of titanium washers listed in Table I. Here, dm and ω are the change in weight of titanium washers before and after occlusion of hydrogen and the amount of hydrogen prereserved in the gas reservoir, respectively. Also, T_{in} is the temperature at the time when H_2 gas begins to be introduced and dt is the duration of T_{in} maintained at the temperature.

The above result is also inferred from the dependence of solubility (H/Ti) on T shown in Fig. 6. Since the surrounding pressure p in the quartz tube is monitored, with one of vacuum gauges on the gas reservoir (see also Fig. 2), all the time during the occlusion process, values of H/Ti can be calculated on the assumption that the rest of p is fully absorbed into titanium washers. As seen from the data plotted at $T\sim 800$ °C (black circles), H/Ti ranges approximately from 0.2 to 0.4. This value of H/Ti increases gradually, as T drops. This result can be understood from the theory explained in Sec. II (see also Fig. 1). And finally, H/Ti reaches its prescribed value and simultaneously, p is seen to approach zero at $T\sim 400$ °C (within the measurement sensitivity of the vacuum gauge). This means that all hydrogen are completely absorbed and blocked in titanium washers at $T \sim 400$ °C and, therefore, it is concluded that the value of $T_{\text{in}}=350$ °C is hardly suitable to cause an efficient occlusion of hydrogen into titanium washers. The threshold temperature would exist in the shaded area drawn in Fig. 1.

As explained in Fig. 4, when H_2 gas was introduced in the container tube from the gas reservoir, we had kept T for $dt(=1-2$ h). This is probably inessential for well-controlled occlusion of hydrogen. In fact, despite larger value of dt for the lowest T_{in} case [the case of (6)], no occlusion of hydrogen was occurred (see also Fig. 5). The dt would be related directly to diffusion of hydrogen in titanium washers. Thus, properties of produced plasmas might be influenced, which will be studied in the next series of experiments and reported elsewhere.

TABLE I. Values of temperature T_{in} when H_2 gas begins to be introduced and the filling pressure P_{fil} of hydrogen in the gas reservoir for six sets of titanium washers.

	(1)	(2)	(3)	(4)	(5)	(6)
T_{in} (°C)	810	800	700	600	450	350
P_{fil} (atm)	2.7	5.6	2.7	5.7	3.1	3.6

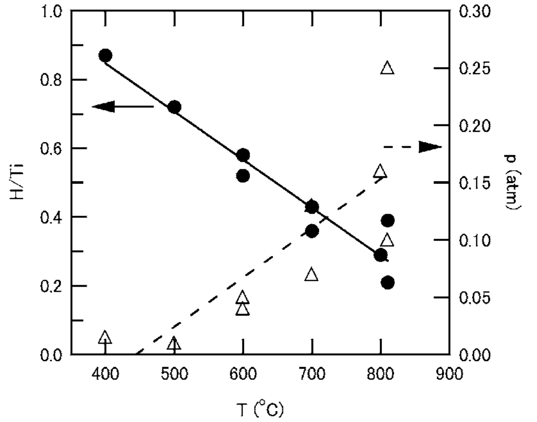

FIG. 6. The dependence of solubility (H/Ti) on T along with pressure p in the quartz tube. At $T \sim 800$ °C, H/Ti (black circles) ranges approximately from 0.2 to 0.4. As T drops, H/Ti increases and finally reaches its prescribed value at $T \sim 400$ °C. Simultaneously, p is seen to approach zero at the temperature. This means that at $T \sim 400$ °C all hydrogen are completely absorbed and blocked in titanium washers, suggesting that no occlusion of hydrogen can appear at $T_{\mathrm{in}} = 350$ °C.

C. Strength property of loaded titanium washer

As one of noteworthy properties, titanium becomes structurally weak and eventually crumbles as it absorbs hydrogen, which is so called hydrogen embrittlement. As mentioned, several loaded washers are usually mounted inside the barrel of a Ti gun and fastened together tightly. This calls for sufficient mechanical strength of them, which, for instance, exceeds the fastening strength of tie bolts. In order to examine it experimentally, we have measured the compressive strength of the loaded washers with a compression machine.

Between a pair of weights of the machine, a loaded washer is set up vertically and compressed gradually until it crumbles. Figure 7 shows a typical time history of the compression pressure F imposed on a loaded washer. As recognized, when cracking appears on the washer at $t \sim 12$ s, F decreases rapidly from ~ 110 to ~ 40 kgw. We define the value of ~ 110 kgw as the maximum tolerable pressure $F_{\max}$. As seen from the data plotted in Fig. 7, $F_{\max}$ is ~ 110 kgw for H/Ti ~ 0.5. And, as H/Ti increases to ~ 0.85, the value of $F_{\max}$ decreases significantly to ~ 70 kgw. This value is approximately equal to the recommended strength for fastening a flange of ICF70 with a gasket made of copper. Although more data are required, the result suggests that the appropriate value of H/Ti is hardly unity for the application to a Ti gun.

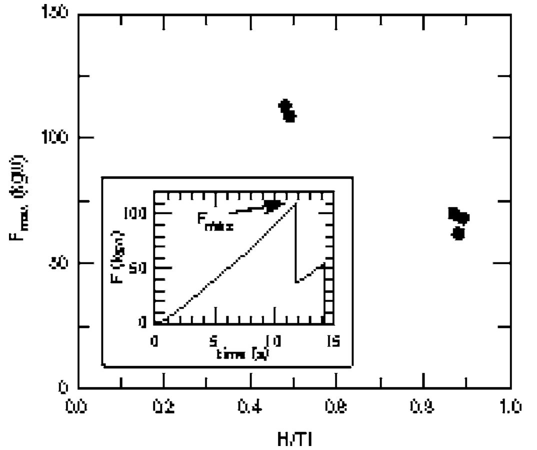

FIG. 7. A typical time history of the compression pressure F imposed on the loaded titanium washer and the dependence of the maximum tolerable pressure $F_{\max}$ on H/Ti. As H/Ti increases, $F_{\max}$ decreases significantly. Data suggest that the appropriate value of H/Ti is less than unity for the application to the Ti gun.

V. SUMMARY

In order to produce washers of titanium hydride systematically, we have constructed a simple instrument and examined an optimized procedure of occlusion of hydrogen into titanium washers experimentally. On the device, the hydrogen occlusion proceeds with ultrahigh vacuum condition and the amount of hydrogen occluded in titanium washers can be exactly controlled by changing p_{fil} of H_2 gas in the gas reservoir. Data show that when p_{fil} is the order of 1 atm, T needs to be higher than ~ 450 °C for providing successful occlusion of hydrogen. A test on mechanical strength on the loaded titanium washer has been conducted for the first time. Preliminary results from a compression test imply that the ratio of atoms of hydrogen to titanium should be less than H:Ti $\sim 0.85:1$ for the application to a Ti gun.

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