THERMAL DESORPTION OF GASES FROM ALUMINUM ALLOY Al 6061
THEIR RATES AND ACTIVATION ENERGIES*

H. J. Halama and J. C. Herrera

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Brookhaven National Laboratory
Associated Universities, Inc.
Upton, New York 11973

ABSTRACT

The use of aluminum in the construction of the vacuum chamber of intersecting proton storage rings has several advantages over the use of stainless steel. We have, therefore, undertaken ultrahigh vacuum studies on long pipes made of aluminum alloy 6061 to see whether this material could be used in the proposed proton intersecting storage accelerator facility, ISABELLE, at Brookhaven. The outgassing rates, measured by two different methods, are compared for several surface treatments and three bake-out temperatures. The lowest outgassing rate of less than 1×10^{-14} Torr liter $\text{cm}^{-2} \text{sec}^{-1}$ was obtained with argon and oxygen discharge cleaning. The residual gas in the pipe contained more than 99% H_2 with traces of CO and CO_2 . By observing the temperature dependence of the desorption of these gases, we have measured the heat of diffusion of H_2 ($E_{\text{H}_2} = 10.5 \pm 1.0 \text{ kcal/mol}$) and the thermal activation energies of CO ($E_{\text{CO}} = 20 \pm 2 \text{ kcal/mol}$) and CO_2 ($E_{\text{CO}_2} = 25 \pm 2 \text{ kcal/mol}$). Argon, with a peak desorption at 280 to 300° C, also appears to be embedded in the metal. Since all commercially available UHV equipment uses stainless steel flanges, we have investigated the behavior of stainless steel to aluminum transitions up to 350° C.

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1. Introduction

In large intersecting proton storage rings, tubular vacuum chambers several kilometers long must be maintained at a pressure of less than 10^{-11} Torr. In addition the residual gas molecules should have a low ionization cross section, i.e. their atomic number should be low. The pressure, in such a long tube, depends on the distance between pumps, the gas conductance, and the outgassing rate. Since the lengths and apertures are, in general, governed by other requirements such as magnet construction and cost, the outgassing rate of the metal from which the chamber is fabricated is the principal vacuum parameter and should, therefore, be as low as possible. Furthermore, the surface of the chamber should be free of adsorbed gas which will desorb when ionized residual gas molecules formed by the circulating beam bombard the wall of the vacuum envelope.¹

The above conditions were satisfied at the CERN ISR by using a special stainless steel vacuum chamber² pumped by a large number of sputter ion and titanium sublimation pumps.³ Because aluminum has several interesting properties such as a low outgassing rate^{4,5} and good electrical and thermal conductivity, we have undertaken studies on long pipes made of the common aluminum alloy Al 6061 to see whether this material could be used for the vacuum chamber of the proposed proton storage accelerator facility, ISABELLE, at Brookhaven.⁶ In this case the high electrical conductivity of the wall is an asset as far as beam stability is concerned, while the good thermal conductivity and lower cost of the aluminum decrease the price of the vacuum envelope and associated equipment. The smaller atomic number also reduces the radiation background in the experimental straight sections.

The measurements reported were performed on commercially available 2.6 m

long aluminum tubes such as might be used in storage rings rather than small carefully prepared samples. Effective outgassing rates of 1×10^{-14} Torr liters/s cm^2 at room temperature were obtained in tubes with two transitions. Hydrogen which diffuses from the bulk of the metal constituted 99% of the residual gas present in the chamber.

Since all commercially available UHV equipment uses stainless steel flanges we have also investigated the behavior of stainless steel to aluminum transitions up to 350°C and have found them reliable. On the basis of these measurements, we have concluded that aluminum is well suited for the construction of a UHV system for storage rings.

II. Experimental Considerations

The gas coverage of a metal surface depends not only on the previous history but also on the residual pressure and the sticking coefficient. It is, therefore, important that low outgassing measurements be carried out at the lowest pressures attainable. Opening and closing of valves should be avoided. If valves are used, a long time should be allowed to reach equilibrium. The pumping speed of various components such as gauges should be determined and their contribution taken into account. In the measurements to be described, the above guidelines were followed. Both the gauge pumping and/or outgassing were measured in separate experiments. Two experimental setups yielding comparable results were used to obtain the data.

1. Pressure Gradient Method

This method is based on the solution of the equation

$$C \frac{d^2 P}{dx^2} = -Q$$

and the apparatus is shown in Fig. 1. The effective outgassing rate Q [$\text{Torr } \text{ts}^{-1} \text{ cm}^{-2}$] for a given gas conductance per unit length $C[\text{ts}^{-1}]$ is then calculated to be

$$Q = \frac{2C (P_1 - P_0 - P_G)}{LA}$$

where $A \text{ (cm}^2\text{)}$ is the total area and $L \text{ (m)}$ is the length of the tube. Pressures P_1 and P_0 are read directly on the calibrated gauges G_1 and G_0 as shown in Fig. 1. The pressure correction, P_G , is calculated from the outgassing of the Helmer gauge G_1 . This outgassing was determined in a separate experiment to be $\leq 1 \times 10^{-11}$ Torr liters s^{-1} . It is significant only in measurements where $Q < 3 \times 10^{-14}$ Torr $\text{l s}^{-1} \text{ cm}^{-2}$. The mass spectrometer, MS, in this setup indicates only the relative abundance of various residual gas species in the tube.

2. Calibrated Conductance Method

This method (Fig. 2) is used most commonly in thermal desorption studies.⁷

The effective outgassing rate Q

$$Q = \frac{C_0 (P_1 - P_2)}{A}$$

where $C_0 \text{ [l s}^{-1}\text{]}$, is the conductance of a calibrated orifice (diameter = 6.38 mm), P_1 and P_2 are the pressures read on the Helmer gauge G with the valve V_1 open and closed respectively. The conductance C_0 in these measurements was about 100 times smaller than the pumping speed S .

The pumps employed in both experimental setups were either an Ultec 400 l/s sputter ion pump with a residual pressure of $\sim 1 \times 10^{-11}$ Torr or an 1000 l/s Excalibur liquid helium cryosorption pump capable of operating in 10^{-12} Torr range. Partial pressures were measured by 2 quadrupole mass spectrometers (Extranuclear and UTI). The apparatus was initially glow-discharged in argon and oxygen and baked-out to 300°C . Then after every exposure to atmospheric pressure it was rebaked to 250°C . The gauges and mass spectrometers were rigorously outgassed.

3. Calibration

The correctness of the data presented depends on the accuracy with which we can determine both total and partial pressures. The gauges and the mass spectrometers were therefore calibrated⁸ using a leak with a known accuracy of $\pm 10\%$ traceable to an NBS standard. In addition, the cracking patterns for CO and CO₂ were determined. During the measurements the gain of the multiplier in the UTI mass spectrometer was often checked and adjusted. The calibration of the UTI Quadrupole yielded the following sensitivities with the multiplier gain set to 10^5 :

H ₂	104	A Torr ⁻¹ ,
N ₂	73	" ,
CO	70	" ,
CO ₂	49	" .

It must be stressed that most of the measurements were carried out in 10^{-11} Torr range where even with the greatest care and rigorous gauge outgassing the accuracy was estimated to be not better than $\pm 30\%$. Furthermore, since the accuracy decreases with the measured pressure, we quote a value of $\pm 50\%$ on outgassing rates less than 5×10^{-14} Torr ℓ/s cm². The values, however, are likely to be too high rather than too low since the detection capability is around 5×10^{-15} Torr liters s⁻¹ cm⁻².

III. Measurements

The measurements were performed on 260 cm long tubes with a 7.2 cm diameter, manufactured from an aluminum alloy Al 6061-T4. These tubes were terminated on both ends by stainless steel to aluminum (Al 5083) transitions so that they could be attached to the stainless steel chamber and accept a vacuum gauge. The total area of ~ 6000 cm² thus included about 150 cm² of stainless steel surface for which no correction was made. The tubes were

subjected to the following surface treatments:

- A Degreasing in acetone with a methanol rinse,
- B Chemical polishing in a solution of 805 ml ortho-phosphoric acid, 35 ml nitric acid and 160 ml water at 80° C. This solution was pumped through the tube for five minutes and followed by a water rinse and cleaning with a soft brush. Finally, it was rinsed with methanol.
- C Glow discharge¹⁰ in pure argon at a pressure $2-3 \times 10^{-2}$ Torr for 30 minutes with a current density $5-10 \times 10^{-5}$ A/cm² and $T = 20^{\circ}$ C.
- C' Same as C but $T = 120^{\circ}$ C.
- D Glow discharge in pure oxygen for 3 minutes, $T = 20^{\circ}$ C.
- D' Same as D but $T = 120^{\circ}$ C.
- E Firing at 340° C for 4 hours in a vacuum furnace $P = 5-10 \times 10^{-4}$ Torr.

Both dc and ac glow discharge cleaning resulted in the same final outgassing. After each treatment the tubes were exposed to the lab atmosphere for a day before they were incorporated into the measuring apparatus in order to approximate the condition which will exist during the assembly of ISABELLE. After the tubes had reached room temperature and pressure equilibrium the outgassing rates were measured for three 24-hour bake-outs at 100° C, 150° C and 200° C. Total outgassing rates Q_t in nitrogen equivalent and the relative abundance of H₂, CO and CO₂ corrected for mass spectrometer sensitivity and pumping speeds are tabulated in Table I.

In addition to the outgassing rates at 20° C, the activation energies of the residual gases were obtained from their temperature dependence listed in Table II. When these values are plotted versus T^{-1} (T being absolute temperature) the activation energy E can be calculated from the slope of the curve according to

$$Q = Q_0 e^{-E/RT}$$

where R is the gas constant. In Fig. 3 a straight line fitted to experimental points by the least square method yields $E_{H_2} = 10.5 \pm 1.0$ kcal mole⁻¹ which is in good agreement with the heat of diffusion for H₂ in pure aluminum¹¹ ($E_{H_2} = 9780$ cal/mole).

Though only 3 points are available for CO and CO₂ the binding energy can also be obtained but with less accuracy. In these cases the least square fits yield

$$E_{CO} = 29 \pm 2 \text{ kcal mole}^{-1}$$

$$E_{CO_2} = 25 \pm 2 \text{ kcal mole}^{-1}$$

It should be pointed out that the tube had been baked-out at 200° C for approximately 30 hours before the data in Table II were taken. Inspection of Table II shows that as this temperature (200° C) is approached, gases adsorbed on the surface with activation energies larger than 25 kcal/mole begin to appear in appreciable quantities. Following the experiment detailed in Table II, the tube was heated to 320° C and the release of argon, implanted in the surface during the glow discharge cleaning, was monitored on the mass spectrometer. Maximum rate of release appeared at temperatures between 280 and 300° C. This can be compared with argon implanted in nickel.¹² Subsequent measurement at 235° C gave argon outgassing rate of 3×10^{-13} as

compared with 7×10^{-12} Torr liters $\text{cm}^{-2} \text{s}^{-1}$ at that temperature in Table II.

1. Transitions

The aluminum vacuum chamber in ISABELLE will be connected to stainless steel pumping stations through an aluminum to stainless steel transition. In addition to sputter ion and sublimation pumps the pumping stations will contain vacuum diagnostic equipment and valves. They will be bakeable to 300°C and the transitions must therefore withstand these temperatures. There are two types of transitions suitable for UHV applications, namely explosively bonded (Du Pont) and friction welded (Japanese Oxygen Company). Because of the excellent performance they showed at SLAC¹³ only the former was tested.

The transitions were subjected to the following tabulated tests:

<u>Heat Cycle $^{\circ}\text{C}$</u>	<u>Times</u>	<u>Hours at High Temperature</u>
20 - 200 - 20	10	100
20 - 250 - 20	3	10
20 - 300 - 20	4	24
20 - 350 - 20	1	2

Mass spectrometric measurements revealed no surprises and the transitions remained leak tight within the accuracy of our instrumentation which is better than $\sim 5 \times 10^{-13}$ Torr liter s^{-1} . The aluminum alloy Al-5083 used in these transitions contains two high vapor pressure elements, i.e. 4 - 5% Mg and 0.25% Zn. A magnesium peak starts appearing in the spectrum at $T > 180^{\circ} \text{C}$ while zinc, $M = 65$, appears at $T > 270$. No aluminum peak was observed during this test. In the ISA the transitions will be made of the same alloy as the vacuum chamber, i.e. Al 6061 which contains only 1% of Mg.

IV. Conclusions

Based on the results of our investigation, we can draw the following conclusions:

1. Effective outgassing rates of 1×10^{-14} Torr liters $s^{-1} cm^{-2}$ can be achieved in vacuum systems using commercially available alloy 6061 with a rather simple surface treatment.
2. The most abundant residual gas in a baked-out Al system is hydrogen which diffuses from the metal. This is consistent with the fact that H_2 is the only gas known to be appreciably soluble in either solid or molten aluminum.¹⁴ Due to the insufficient sensitivity of the apparatus¹⁵ which was $5 \times 10^{-3} cm^3 (STP) g^{-1}$ for $S/N = 1$, no H_2 was detected in samples cut from the measured tubes. Because of the low permeation of H_2 in Al,¹⁶ outgassing rates below our measuring capability (5×10^{-15} Torr liters $s^{-1} cm^{-2}$) can be achieved in Al vacuum systems using the surface treatment described.
3. Other gases such as H_2O , CO, CO_2 and hydrocarbons commonly found in vacuum systems seem to be adsorbed on the surface with a continuous spectrum of binding energies. After a $200^\circ C$ bake-out the binding energies of these gases are above 25 kcal/mol and their outgassing rates are negligible at room temperature.
4. Argon is implanted in the metal during glow discharge cleaning. Its release rate is negligible at room temperature and reaches a maximum between 280 and $300^\circ C$. The implanted argon can be rapidly depleted by heating to this temperature.
5. During the oxygen glow discharge the oxygen combines with aluminum to form aluminum oxides. Besides its cleaning effects, oxygen also probably removes carbon from the surface by forming CO and CO_2 .

6. Aluminum to stainless steel transitions can be heated safely up to 300° C.

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TABLE I

Outgassing Rates Q_t in Torr liters $s^{-1} cm^{-2}$ and residual gas composition in % at 20°C after 100, 150 and 200°C bake-outs.

Bake-out °C	100	150				200			
Treatment	Q_t	Q_t	H ₂	CO	CO ₂	Q_t	H ₂	CO	CO ₂
A	6×10^{-12}	1×10^{-12}				6×10^{-13}			
A,B	3×10^{-12}	7×10^{-13}	89	5	6	2×10^{-13}	92	4	4
A,B,C	5×10^{-13}	2×10^{-13}	97	1.5	1.5	6×10^{-14}	98	1	1
A,B,C,C',	5×10^{-13}	6×10^{-14}	98	1	1	3×10^{-14}	99		
D'	4×10^{-13}	5×10^{-14}	99			1×10^{-14}	> 99		
	+ 8 hrs at 250°C					$< 1 \times 10^{-14}$	> 99		
B,E,C	8×10^{-13}	1×10^{-13}	97	1.5	1.5	5×10^{-14}	98	1	1
B,E,C,C',	4×10^{-13}	7×10^{-14}	98	1	1	2×10^{-14}	> 99		
D'	4×10^{-13}	4×10^{-14}	99			$< 1 \times 10^{-14}$	> 99		

TABLE II

Thermal desorption rate Q_p in Torr liters $s^{-1} cm^{-2}$ corrected for individual gases at various temperatures. (Surface treatment: last entry in Table I)

Mass		Temperature °C				
No.		55	95	150	195	235
2	H ₂	8×10^{-13}	2.5×10^{-12}	1.3×10^{-11}	5.5×10^{-11}	2.7×10^{-10}
14					7×10^{-14}	8×10^{-13}
15					2×10^{-13}	2×10^{-12}
16					3×10^{-13}	5×10^{-12}
18	H ₂ O				1.1×10^{-13}	3.9×10^{-11}
28	CO			6.8×10^{-14}	1.1×10^{-12}	2.3×10^{-11}
40	Ar				4×10^{-13}	7×10^{-12}
44	CO ₂				6.5×10^{-13}	8×10^{-12}

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FIGURE CAPTIONS

- Fig. 1 Pressure gradient measuring setup. G_1 - Helmer gauge, G_o - modulated BA gauge; MS-mass spectrometer; S-pump, V_2 -bakeable valve; TC-thermo-couples; A-S-aluminum to stainless steel transitions. Neg. #6-1066-75
- Fig. 2 Calibrated conductance set-up. G-Helmer gauge; MS-mass spectrometer; Co-orifice; S-pump; V_1 , V_2 -bakeable valves, V_3 -variable bleed valve. Neg. #6-1065-75
- Fig. 3 Outgassing rate as a function of temperature.
Neg. 6-1064-75