2.

CONF-881002--14

Proc. 35th National Symposium & Topical Conf. of the American Vac. Soc., Atlanta, GA, 10/3-7/88.

BNL-41181

OUTGASSING AND DESORPTION OF THE STAINLESS STEEL BEAM TUBES AFTER DIFFERENT DEGASSING TREATMENTS*

OCT 28 1988

BNL--41181

DE89 001268

H.C. HSEUH & XIUHUA CUI**
Brookhaven National Laboratory
Upton, New York 11973

Abstract

Chemical cleaning, vacuum firing, glow discharge cleaning and insitu bakeout have become standard practice for lowering the outgassing rate and removing surface contaminants in the ultra high vacuum systems of particle accelerators and storage rings. This paper presents the work done with the thermal outgassing of several long stainless steel (304LN and 316L) beam chambers with areas of more than 1×10^4 cm^2. They were measured between 20° C and 500° C after vacuum firing, glow discharge cleaning or reactive gas (nitric oxide) cleaning. Outgassing rates of low 10^{-13} and low 10^{-14} Torr .l/s.cm^2 were achieved for H_2 and CO, respectively, with vacuum firing alone. The outgassing of H_2 in this temperature range is consistent with that due to bulk diffusion with an enthalpy of 9 ± 1 Kcal/mole. The photon stimulated desorption of the chamber surface after the above treatments were also studied by exposure to an intense photon beam at the National Synchotron Light Source. The effectiveness and merits of reactive gas cleaning in removing the surface contaminants in large vacuum systems are compared to those of vacuum firing and glow discharge cleaning.

---

*Work performed under the auspices of the U.S. Department of Energy.

** Permanent address: Department of Electronic Engineering, Southest University, Nanjing, China.

I. INTRODUCTION

The vacuum systems of particle accelerators and storage rings range from hundreds of meters to tens kilometers. However, the cross sections of the vacuum chambers are usually small as imposed by the more costly magnet apertures. This leads to a low linear conductance typically in low 10^2 l.m/sec range. Therefore, the need to reduce the outgassing of the vacuum chamber becomes crucial in order to achieve the desired vacuum.

The vacuum requirement of these machines is dependent on the degree of tolerable beam degradation (beam loss and beam blowup) caused by the beam-residual gas interaction. Except for heavy ion machines, the vacuum required for accelerators is relatively relaxed in comparison with that of the storage rings (1). In heavy ion accelerators, the charge exchange cross sections between beam and the residual gases are rather large, especially for low beta, high Z, partially stripped ions. To ensure the survival of these heaviest ions during the acceleration cycles, ultra high vacuum is required

At Brookhaven, a rapid cycling synchrotron for the acceleration of both heavy ions and protons is under construction(2). The vacuum is required to be 3×10^{-11} Torr (N_2 equivalent) or less. To achieve this vacuum level, careful attention must be given to the proper selection of materials, the UHV compatible processing and the degassing of the vacuum chambers and other beam components located inside the vacuum chamber.

Stainless steel and inconel are commonly seleted as synchrotron chamber material for their excellent mechanical, magnetic, and vacuum properties. The purpose of this work is to evaluate and compare the effect of different degassing treatments on the outgassing of the actual synchrotron vacuum chambers. These chambers were made of either 304LN or 316L stainless steel 1.9 mm thick, 2-5 m long, 30-50 cm in perimeter and having an inner surface area of more than 1×10^4 cm^2. The evaluation was carried out by measuring the thermal outgassing and the photon stimulated desorption (PSD) after different treatments. The thermal outgassing is mainly composed of the desorption of weakly bonded molecules, while the PSD desorbs the tightly bonded species under the bombardment of energetic photons. The thermal outgassing of hydrogen which is the predominant outgassed species in our test chambers is also interpreted within the scope of bulk diffusion.

II. DEGASSING TREATMENTS

The following degassing treatments were used to treat the test chambers (or samples of the chambers in the case of PSD) at different stages of the evaluation. All the chambers were subjected to a thorough chemical cleaning before the evaluation began. This was followed by degassing in a vacuum furnace before the next measurement. Either glow discharge cleaning or reactive gas cleaning was then applied to the vacuum fired chambers. Between the degassing treatment and the measurement, the chambers were usually exposed to ambient air for several days followed by an insitu bakeout at 200° C for 48 hours.

A. CHEMICAL CLEANING

We have adopted the following cleaning process developed at CERN(3) as our standard chemical cleaning proedure.

1. Degreasing in hot trichloroethane with ultrasonic agitation.
2. Washing in hot (60°C) non-etch alkaline (pH = 11) detergent with air agitation.
3. Rinsing in cold tap water.
4. Rinsing in deionized water with air agitation.
5. Drying in hot air oven.

B. VACUUM FIRING

Predegassing the chambers in a vacuum furnace has been found to drastically reduce the hydrogen content and therefore, the hydrogen outgassing in the stainless steel (4-7). The test chambers were subjected to the following firing conditions: ramped to 950° C in 4 hours; soaked at 950° C and low 10^{-5} Toor for 2 hours; cooled down to below 500° C in one hour or less.

C. GLOW DISCHARGE CLEANING (GDC)

DC glow discharge with Ar/10% O_2 mixture as plasma was used to clean the inner surface of the test chambers. The principle of GDC can be found in Ref. 8. The setup and procedure for GDC has been described fully in a previous publication (9). Only a brief outline will be given here. A long tungsten wire was inserted into the center of the test chamber as the discharge anode. The entire fixture was insitu baked at 200° C for 24 hours before the flow started.

The Ar/O_2 mixture was continuously fed into the chamber during the discharge. A pressure of approximately 2×10^{-2} Torr was maintained during the treatment. The bias voltage is pressure dependent and was approximately 400 V. We have found that glow discharge with argon alone is not effective in removing the carbonic species from the surface (9). With the presence of oxygen, the sputtered species would chemically react with oxygen to form stable compounds which were then removed by the pumping system. The GDC process was terminated when the yields of carbon oxides (CO and CO_2, would not decrease further. A typical treatment took 6 to 20 hours. A discharge dosage in the mid 10^{18} ions/cm^2 level was usually accumulated.

D. NITRIC OXICE (NO) CLEANING

Reactive gas cleaning (RGC) has been widely used to remove contaminants and to give atomically clean metal surface in surface science studies (10). It typically involves either oxidation or reduction cycles by reactive gases such as O_2, NO, H_2 and NH_3. It has advantages over sputtering or GDC. No electrodes are required and the cleaning is uniform with no risk of surface damage caused by excessive sputtering. The best choice of the reactive gas for stainless steel was found to be nitric oxide (11). Because of its reactivity at relatively low temperature (200° C), it can be easily incorporated in a large system like our vacuum chambers.

The setup for NO treatment consisted of a gas inlet valve, an RGA, an ion gauge and a high vacuum pumping system. NO gas detectors with sensitivity down to ppm level were also required to monitor and warn of any minor NO leaks to the ambient. After an insitu bake at 200° C for 24 hours, pressure of mid 10^{-7} Torr level was usually attained inside the test chamber. NO gas (99% pure from Matheson Gas Products) was then fed into the chamber through the variable leak valve. A pressure of between 10 and 100 times the background pressure was maintained during the NO treatment. The partial pressure inside the chamber was monitored with the RGA during the treatment.

The changes in residual gas composition of a typical NO run on a chemical cleaned then vacuum fired chamber are plotted against treatment time in Fig. 1. The peak heights of the carbonic peaks such as m/e = 28, 41, 78 increased by one decade or more immediately after the admission of NO; then gradually decreased with the treatment time. This is due to the breakdown, and removal of the surface carbon and hydrocarbon by NO. The NO peak (m/e = 30) at the beginning was relatively small compared with that of CO/N_2.
The gradual increase in the NO peak and the decrease in the CO peak indicate the reduction of the contamination level. The sharp increase in the CO_2 peak and the large decrease in the hydrogen peak with increased NO flow suggest an ample supply of NO, which combines with CO and H_2 to form CO_2 and water.

The cleaning was terminated when either no detectable hydrocarbon was present or the ratio of NO peak to CO peak was 3 or larger. A typical cleaning run would last several hours with the accumulated NO dosage in the mid 10^{-4} Torr. hour range.

E. NITRIC OXIDE TREATMENT OF A CONTAMINATED CHAMBER

To evaluate the effectiveness of the RGC in removing heavy contaminant, a test chamber was treated with NO, coated with a thin layer of mechanical pump oil, then treated with NO again. This chamber was insitu baked several times before the NO treatments. The peak heights of the residual gas (taken at ambient temperature) are compared in Fig. 2; with A and B being before coating with oil; C and D after coating with oil; A and C before NO treatment; and B and D after NO treatment. Up to one decade decrease in some of the carbonic peaks was observed between A and B. However, the biggest improvement was observed between C and D with some hydrocarbon peaks decreased by 5 to 6 decades. This test shows the possibility of using NO to remove heavy hydrocarbon contamination in vacuum system with limited access such as the vacuum chambers in accelerators.

III. MEASUREMENT OF THEMAL OUTGASSING

The thermal outgassing of the test chambers was measured using the throughput method. After the degassing treatments, the test chambers were usually exposed to the ambient air for several days before the measurement began.

The setup is shown schematically in Fig. 3. The test chambers were flanged to the UHV pump body through a removable orifice with a calculated conductance of 2.4 l/s for hydrogen. The total and partial pressures were monitored by calibrated Bayard Alpert gauges (IG) and RGA (12). The system was roughed by a turbo pump and insitu baked at 200° C for 48 hours before the titanium sublimation pump and the ion pump were activated. The outgassing rate at the selected temperature was then measured by bringing the test chamber from ambient to the desired temperature and held for 24 hours or longer (until the system reached steady pressure). The background pressure of the UHV pump was typically in the 10^{-12} or low 10^{-11} Torr range. This limited the accuracy of the measured outgassing rate to the low 10^{-14} Torr.l/sec. cm^2 level.

After the insitu bakeout, hydrogen usually made up more than 90% of the desorbed gas with CO, $CO_2$and CH_4 in descending order made up the balance. At ambient temperature, little difference in the outgassing rates of CO, CO_2 and CH_4 was observed among the unfired, the vacuum fired, the GDC and the NO treated chambers. At 100° C or higher, the unfired chamber liberated 3-5 times more CO and CH_4 than those by other treatments. Some hydrocarbon peaks appeared in the unfired and the fired chambers when the temperature reached beyond 200° C, but not in the GDC and NO treated chambers.

This shows the effectiveness of GDC and the RGC in removing the surface contaminants. Sufficient data was not gathered in our measurement to give a correlation between the temperature and the outgassing of CO, CO_2 and CH_4.

The outgassing rate of hydrogen is plotted against 1/T in Fig.4 with T the absolute temperature in Kelvin. Little difference was observed among the vacuum fired chambers whether with or without GDC and RGC. The outgassing of the unfired chambers was usually one decade higher than that of the fired ones. Before vacuum firing, the chambers made of 316L had outgassing rates slightly higher than that of 304LN; and lower after firing. After vacuum firing, both had an ambient hydrogen outgassing rate of approximately 1×10^{-13} Torr .l/s. cm^2. The least square fit of the outgassing data to $Q = Qo \exp(^{-}\Delta E/RT)$ gives an enthalpy ΔE of 8 to 10 Kcal/mole as represented by the slopes in Fig. 4. The similarity in the enthalpy of outgassing between the unfired chambers and the fired chambers, and between 316L and 304LN suggests that the rate determining step for the outgassing of hydrogen in stainless steel is the diffusion from the bulk instead of the desorption from the surface. The amount of outgassing was proportional to the hydrogen content in the metal, which was greatly reduced after vacuum firing (5,6).

IV. MEASUREMENT OF PHOTON STIMULATE DESORPTION (PSD)

We have used the PSD to assess the cleanliness of the chamber surface after these degassing treatments. Photons from the Vacuum Ultra Violet (VUV) ring in the National Synchrotron light Source were used in this measurement. The VUV ring is an electron storage ring operating at 750 MeV with beam intensity up to 1 Ampere. The photon flux emitted by the electrons has a critical energy of 486 eV. The number of photons emitted is proportional to the stored beam current.

The experimental setup and procedure has been described in detail in Ref. 13 and 14. In short, samples of the test chambers, after different degassing treatment were inserted at one of the beam lines in the VUV ring. Only samples made of the 316L stainless steel were investigated. After insitu bake at 200° C for 48 hours, the samples were bombarded with photons. The specific increase in total and partial pressures due to PSD was measured by the calibrated ion gauges and the RGA(13). The background pressure inside the sample chamber was in the low 10^{-9} Torr range and the PSD induced pressure at beam current around 300 mA was usually in the 10^{-7} Torr range. With the known pumping speed (14), the molecular desorption yields per incident photon could be derived through the specific pressure rise.

The molecular desorption yields for samples of different treatments are summarized in Fig. 5 as a function of accumulated photon dosage. Curve A is that of vacuum fired then GDC, curve B of vacuum fired then NO treated, curve C vacuum fired and curve D the chemical cleaned only.

The yields for each gas species as measured by the RGA have been corrected for the pumping speeds and gauge sensitivities. The total molecular yields are the N_2 equivalent yields as derived from the increase in total pressure. In all four cases, the yields of hydrogen were approximately one decade higher than those of CO and the yields of CO were several times higher than those of CO_2. The yields of CH_4 were about a factor of two smaller than those of CO_2 and are not plotted.

Among the different treatments, the yields of the GDC (A) and RGC (B) were significantly lower than those of the vacuum fired (C) and the chemical cleaned (D) indicating the effectiveness of GDC and RGC in removing the tightly bonded surface contaminant. The yields of the RGC were comparable with those of the GDC which gives further evidence of the effectiveness of NO treatment. The total molecules desorbed from each sample can be estimated by integrating the "total" yields over the photon flux. At an accumulated photon dosage of 1 x 10^{21} photons, approximately 0.1 Torr.l molecules were desorbed from the vacuum fired sample and the chemical cleaned sample, and only 0.02 Torr.l from the GDC sample and the RGC sample. The total area exposed to photons is approximately 20 cm^2 therefore, the total molecules desorbed correspond to hundreds of monolayers.

V. CONCLUSION

From the result of our evaluation, we have come to the following conclusions:

A. The hydrogen outgassing of stainless steel could be reduced to 1×10^{-13} Torr. l/s. cm^2 by degassing at 950° C in a vacuum furnace. The enthalpy of outgassing is approximately 9 kcal/mole for both 3041N and 316 L stainless steel; and is similar between the unfired chambers and the fired chambers. The rate determining step of the outgassing is probably the diffusion from the stainless steel bulk.

B. The thermal outgassing of the carbonic species after insitu bake is approximately 1×10^{-14} Torr. l/sec. cm^2 with or without vacuum firing, GDC or RGC.

C. RGC with nitric oxide is very effective in removing the loosely bonded surface contaminant and can be applied to clean vacuum chambers which have limited access.

D. The NO treatment is comparable to GDC in removing the tightly bonded contaminant from the surface, which might be desorbed under the bombardment of energetic particles as in the case for storage rings (1).

ACKNOWLEDGMENTS

We wish to thank J. Slavik and C. Lanni for their excellent technical support in setting up and carrying out some of the measurements. The permission by H.J. Halama to use his PSD setup at the NSLS is also appreciated.

FIGURE CAPTIONS

1. Typical residual gas composition during nitric oxide treatment of a test chamber which were chemical cleaned and vacuum fired. The chamber was maintained at 200° C. The NO pressure was either 10 or 100 times of the background pressure. The lines are for guiding the eyes.

2. The variation in residual gas composition before and after NO treatment. A and B are those of a clean chamber before and after the treatment, respectively; C and D are those of contaminated chamber before and after NO treatment.

3. Experimental setup for measuring the thermal outgassing rate of the long vacuum chambers.

4. The outgassing rates of hydrogen for the 304LN and 316L stainless steel vacuum chambers at different temperatures. The enthalpy ΔE is the least square fit of the data to $Q = Qo \exp(-\Delta E/RT)$.

5. Photodesorption yields of the samples after different degassing treatments; A. chemical cleaned, vacuum fired and GDC; B. chemical cleaned, vacuum fired and NO treated; C. chemical cleaned and vacuum fired; and D. chemical cleaned. The accumlated photons are those over an area of approximately 20 cm^2.

1. C. Benvenuti, R. Calder and O. Grobner, Vacuum 37 699 (1987).

2. "AGS Booster Conceptual Design Report", BNL 34989, April,1985.

3. A.G. Mathewson, Xth Italian Nat'l Congr. Vac. Sci. Technol., Stresa, Italy 12-17 Oct. 1987, CERN-LEP-VA/87-63 (unpublished).

4. H.C. Hseuh and E.F. Gaudet, IEEE Trans. Nucl. Sci. NS28, No 3, 3295, 1981.

5. R. Calder and G. Lewin, Brit. J. Appl. Phys., 18 1459 (1967).

6. G. Lewin , J. Vac. Sci. Technol., 6, 420(1969).

7. R. Nuvolone, J. Vac. Sci. Technol., 14, 1210 (1977).

8. H.F. Dylla, J. Vac. Sci. Technol., A6, 1276 (1988).

9. H.C. Hseuh, T.S. Chou and C.A. Christenson, J. Vac. Sci. Technol. A3, 518 (1985).

10. R.G. Musket, W. McLean, C.A. Colmenares, D.M. Makonieky and W.J. Siekhaus, Appl. Surf. Sci., 10, 143(1982).

11. M. Grunze, H. Ruppender and O. Elshazly, J. Vac. Sci. Technol., A6 1266 (1988).

12. H.C. Hseuh and C. Lanni, J. Vac. Sci. Technol., A5, 3244(1987).

13. T. Kobari and H.J. Halama, J. Vac. Sci. Technol.,A5, 2355(1987).

14. T.S. Chou, C.L. Foerster, H.J. Halama, and C. Lanni, (to be published).

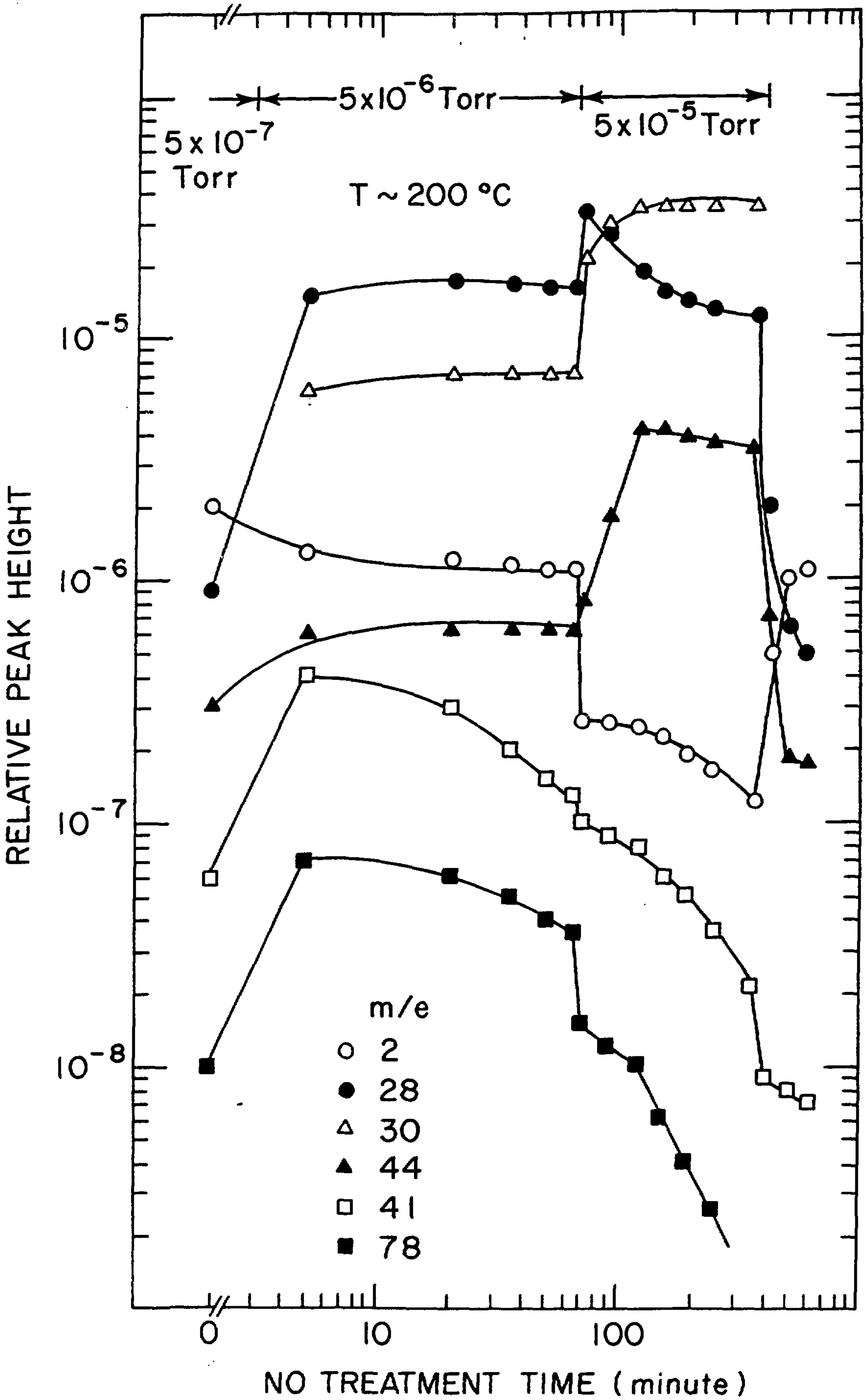
5 x 10^-7 Torr
5x10^-6 Torr
5x10^-5 Torr
T ~ 200 °C
RELATIVE PEAK HEIGHT
10^-5
10^-6
10^-7
10^-8
0
10
100
NO TREATMENT TIME (minute)
m/e
○ 2
● 28
△ 30
▲ 44
□ 41
■ 78

FIGURE 1

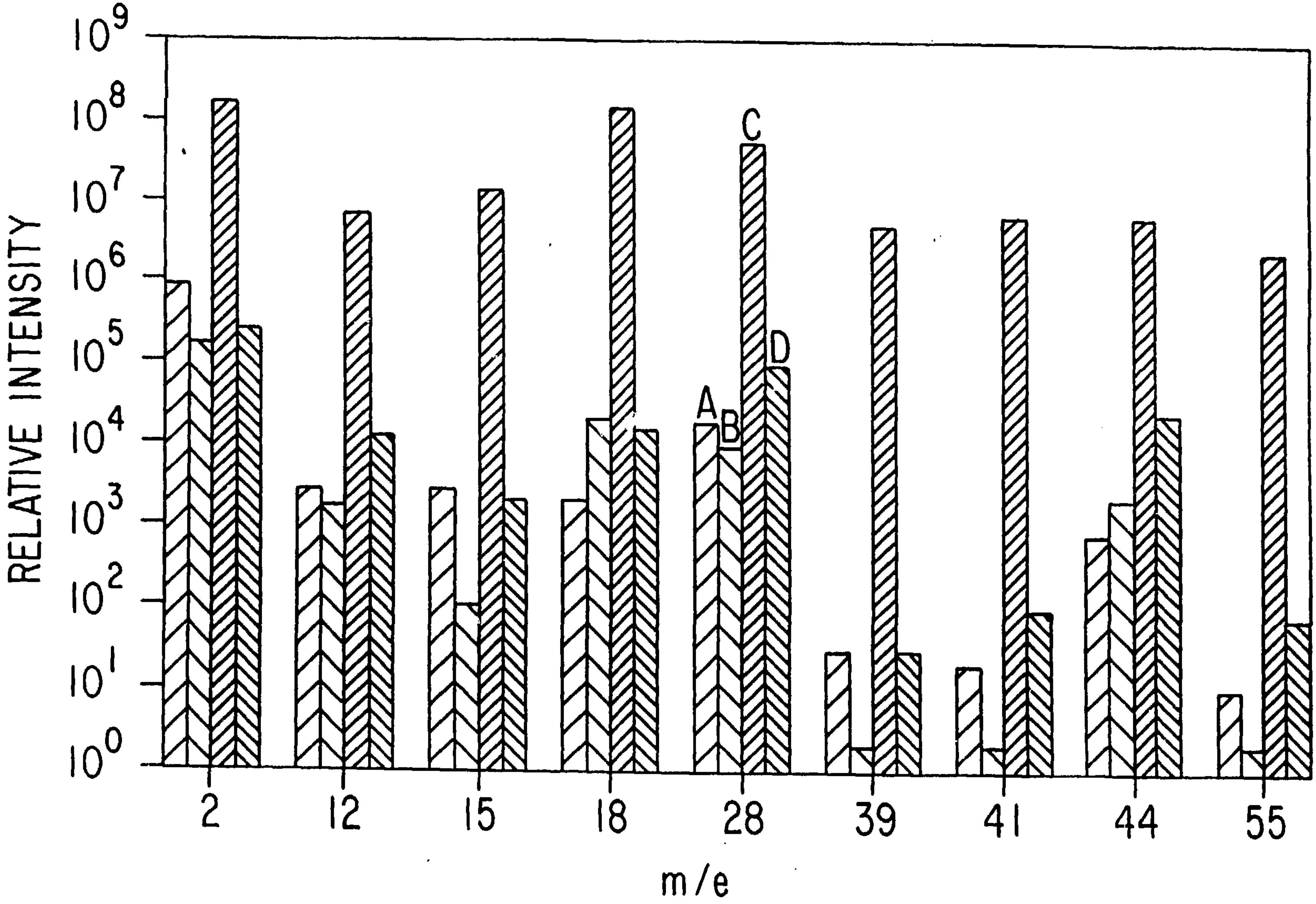
RELATIVE INTENSITY
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
A
B
C
D
2
12
15
18
28
39
41
44
55
m/e

FIGURE 2

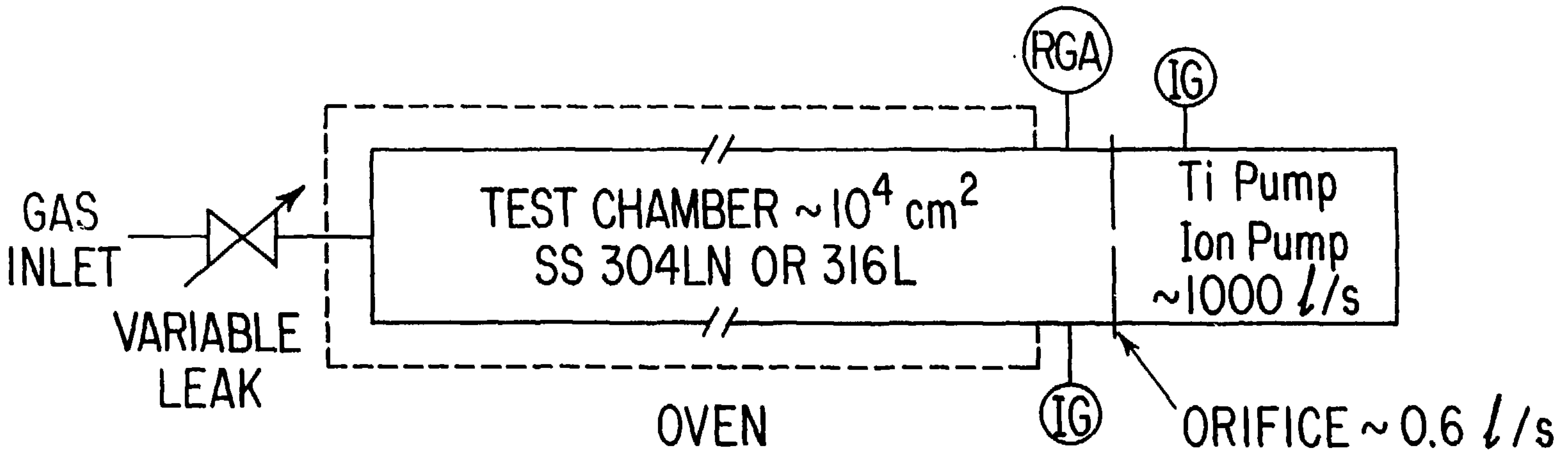
RGA
IG
GAS INLET
TEST CHAMBER ~10^4 cm^2
SS 304LN OR 316L
Ti Pump
Ion Pump
~1000 ℓ/s
VARIABLE LEAK
OVEN
IG
ORIFICE ~ 0.6 ℓ/s

FIGURE 3

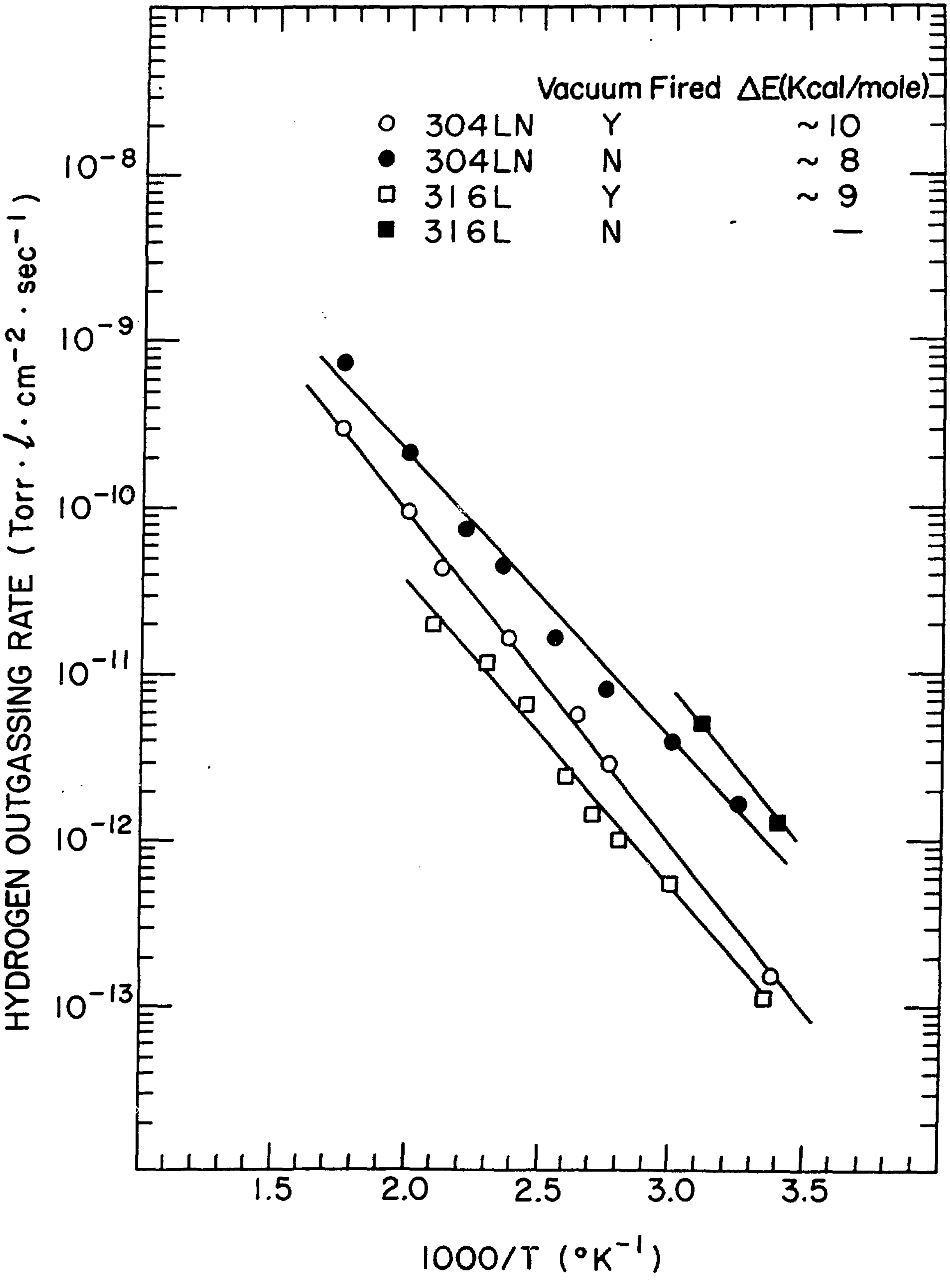
HYDROGEN OUTGASSING RATE (Torr · ℓ · cm⁻² · sec⁻¹)
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
1.5
2.0
2.5
3.0
3.5
1000/T (°K⁻¹)
Vacuum Fired ΔE(Kcal/mole)
○ 304LN Y ~10
● 304LN N ~ 8
□ 316L Y ~ 9
■ 316L N —

FIGURE 4

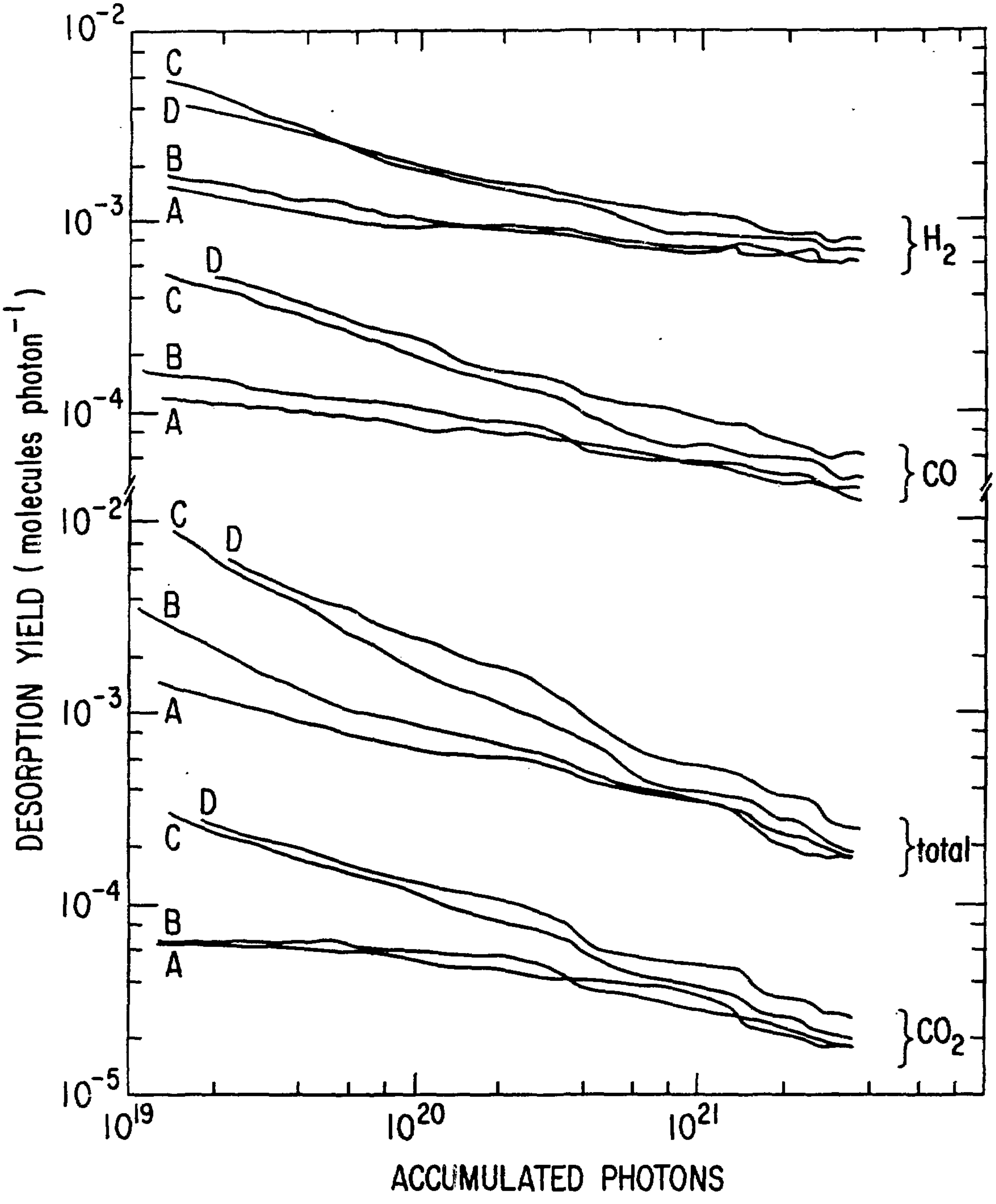
DESORPTION YIELD (molecules photon^{-1})
ACCUMULATED PHOTONS
10^{-2}
10^{-3}
10^{-4}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{19}
10^{20}
10^{21}
C
D
B
A
H_2
D
C
B
A
CO
C
D
B
A
total
D
C
B
A
CO_2

FIGURE 5