Influence of Heat Treatment on Photodesorption of Copper Plated SSCL Beam Tube

A progress report

presented to

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by

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Accomplishments

- Influence of heat treatment procedure on the microstructure of copper layer in the SSCL beam tube has been investigated by SEM and X-ray diffraction.
- A one-meter long tube with electrodeposited Cu film was heat treated at 700°C for 2 hours with a moving stage furnace and was delivered to SSCL on August 6. This sample tube will be referred to as tube #008v afterward;
- A one-meter long tube with electrodeposited Cu film was heat treated at 700°C for 5 hours in a larger furnace and was delivered to SSCL on August 23. This sample tube will be referred to as tube #007v afterward;
- Photodesorption measurements show that the best result was obtained with tube #007v. The photodesorption outgassing of H_2 and CO_2 were reduced a factor of two and CO a factor of three compared to tubes without the heat treatment.

Introduction

The photon-stimulated desorption of H_2, CH_4, CO and CO_2 gasses in the Superconducting Super Collider Laboratory (SSCL) beam line is detrimental to SSCL normal operation. The photodesorbed gas molecules, particularly hydrogen, will demolish the vacuum and scatter the beam[1,2]. There are several approaches to solve this problem[3], one of them is to reduce the amount of hydrogen in the near surface materials of the beam tube. For the present research, the material in concern is an electrodeposited copper film on Nitronic 40 stainless steel tube.

Single crystal copper has a very low hydrogen solubility[4]. However, in the electrodeposited copper films, there are significant amounts of copper oxides, pores, dislocations and grain boundaries which function as storage sites for hydrogen[5-7]. In order to reduce hydrogen and other gases in electroplated copper films, one needs to (1) reduce porosity and oxide contents, (2) enlarge grain size so as to reduce the total grain boundary, and (3) remove the gases from these storage sites. The gases in the copper film can be removed by heating the material in vacuum or hydrogen. Hydrogen is the best reducing elements, it reacts and reduces oxides at an elevated temperature. Due to its high diffusion rate, it can be readily removed from the copper film when the tube is later evacuated. The grain size increases through recrystallization when the material is annealed at an elevated temperature for sufficient time. The recrystallization process also reduces the porosity.

The objective of this research is to reduce photodesorption outgassing of H_2, CO and CO_2 from the SSCL beam line through improvement of the microstructure and chemistry of

copper film on the stainless steel beam tube. One approach to accomplish this objective is to develop an appropriate heat treatment procedure which would both reduce porosity and oxides, and enlarge the grain size of the electroplated copper film.

Experiment

A. Effect of Heat Treatment on the Microstructure and Chemistry of Small Samples

One meter long 33mm OD sample SSCL beam tubes were supplied by SSCL. The tubes were made of Nitronic 40 stainless steel (SS) with Silvex electrodeposited Copper films (50~70μm) on the inner surface of the tubes. Small heat treatment samples (20×20mm) were cut from the tube. Microscopic analysis of the copper film was done using both optical and scanning electron microscopes. Electron microscopic work was accomplished using an ElectroScan Environmental Scanning Electron Microscope. The results of SEM analysis on the original "as received" samples showed a porous columnar type structure as shown in Figure 1. At higher magnifications, a fine distribution of pores was clearly visible in this sample. Both the columnar structure and porosity were a result of the electrodeposition technique used in growing the copper film.

With the proper annealing procedure, the desired effect would be to recrystallize the fine grained columnar structure and grow a large grained structure, while at the same time consolidate the small pores into larger ones that would lead to some overall reduction of the volume of porosity. The first step in setting the annealing conditions was finding the appropriate temperature. A temperature range was studied from 600°C to 800°C at 50°C intervals. The effect of annealing time on the microstructure was also studied from 1 hour to 5 hours. The heat treatment was done in an atmosphere of 10% H_2 + 90% He gases. Hydrogen was introduced to reduce the copper oxides on the "as received" tube which were formed during electroplating and shipment. The use of a reducing atmosphere during the annealing procedure brought about some change in the chemistry of the copper film. The change is noticed in the color of the copper film from a dull, light copper color to a deep, dark, rich copper color. Although the exact nature of the change is not yet known, it is believed that the surface oxides of the original copper film were reduced back to pure copper. It was observed that the grain size increases with increasing annealing temperature and time. Figure 2 shows the SEM image of a copper film annealed at 700°C for 5 hours. It can be seen that the annealed sample exhibits both of the desired effects. The large grained structure is seen with a concentration of large pores on the grain boundaries. Using a linear intercept method, average porosity and average grain diameter were approximated for the original and the annealed

sample. The average porosity decreased from 22.9 ± 7.2% in the original sample to 10.2 ± 4.1% in the annealed sample. The average grain size increased from 5.6 ± 2.5 microns in the original sample to 20.5 ± 10.8 microns in the annealed sample.

X-ray diffraction profiles of the original sample and the annealed sample also show that the grain size and crystal perfection have been dramatically improved by the annealing treatment. Figures 3 is the x-ray diffraction profiles of (111) peak of original sample and 700° C-5 hours annealed sample. The original sample has a broad peak with FWHM (full width at half maximum) of 0.45°. The broad diffraction profile is due to the small grain size and crystal distortion. The x-ray diffraction profile of the 700°C-5 hours annealed sample is much sharper with FWHM of 0.18° so as to reveal the $K\alpha 1$-$K\alpha 2$ doublet. The conclusion is that the annealed sample has larger grain size and less defects.

B. One-Meter Long Tube Treatments

Based on the results from small samples, we decided to anneal one-meter long SSCL beam tubes at 700°C. The first tube (#008v) was treated with a 150mm-long furnace on a traveling stage. The schematic of the furnace setup is shown in Fig. 4. It is expected that the temperature of the copper film on the inner surface is lower than the outer surface. The temperature of the furnace was controlled at 715°C. The furnace moving speed was so designed that it took 2 hours for the 150mm-long furnace to pass each spots of the tube. To prevent the treated copper film from oxidation during shipping and handling, the tube was passivated by vapor deposition of approximately 200 to 300 angstroms of gold after the annealing. This tube was delivered to SSCL on August 6 for photodesorption measurements.

The second tube (#007v) was treated at 700°C for 5 hours in a larger furnace with quartz outlet to introduce the protection gas into the tube. Since the whole tube is treated in the furnace simultaneously, we was able to choose a longer annealing time. This tube was delivered to SSCL on August 23 for photodesorption measurements.

C. Photodesorption Measurement

Photon stimulated desorption (PSD) experiments were conducted on the National Synchrotron Light Source (NSLS) at BNL and on the VEPP2M storage ring at BINP, Novosibirsk, Russia[8]. In addition to the two tubes treated in VPI (#007v and #008v), other tubes either untreated, or different materials or treated elsewhere were measured in the same setup. They are listed in Table I, runs #1-#8 are for tubes without heat treatment in VPI, run #9 is for tube #008v and run #10 for #007v. Samples were installed in the beamline and pumped to vacuum of 10^{-8} torr, and then exposed to photons and measured. Each beam tube sample is exposed to approximately 10^{23} photons which represents 100 days of SSC operation.

The PSD experiment results are shown in Table II. Photodesorption coefficient is defined as desorbed gas yields in molecule per photon. The total amount of photodesorbed H_2, CO and CO_2 and total photon exposure for each run is also listed in the table. Among the ten measurements, run #2 was on a pure copper tube, run #3 in a 1100 gauss dipole magnetic field, run #4 on a sample of different vendor, run #5 and #6 on a same 350°C vacuum baked sample, and run #7 on a 2 microns gold flushed sample. In order to evaluate the effect of heat treatment, we will analysis the results for run #9 and #10 and compare them with run #1 and #8 which are plated Cu without heat treatment.

Photodesorption coefficients for H_2, CO, CO_2 and CH_4 versus accumulated photons for run #1, #8, #9 and #10 are given in Fig. 5-8. Compared to run #1 and #8, run #9 on the sample annealed at 700°C for 2 hours with a moving stage furnace did not show any reduction in photodesorption. Run #10 on the sample heat treated at 700°C for 5 hours in a larger furnace achieved the best result. Compared to run #8, the photodesorption outgassing of H_2 and CO_2 were reduced a factor of two and CO a factor of three.

Discussion

The results of SEM analysis on the original "as received" sample and the sample heat treated at various temperatures for different times have given us a guideline on the heat treatment of the Cu plated SSCL beam tube. An annealing at 700°C for 5 hours can recrystallize the fine columnar grain and consolidate the small pores. This leads to some overall reduction of grain boundary and porosity. X-ray diffraction results confirmed that the crystal structure in the heat treated sample is much more perfect than that of the original sample. The reducing gas also eliminated oxides in the plated copper film. Since the copper oxides, pores, dislocations and grain boundaries function as storage sites for trapping hydrogen and other gases, the improvement of the microstructure and chemistry of the electroplated copper film can reduce the photon stimulated desorption. Run #10 on a sample heat treated at 700°C for 5 hours in a larger furnace has confirmed this anticipation.

The first tube (run #9) did not have the expected results. This is probably due to the following reasons: (1) The heat treatment time is short compared with the second tube (run #10). The first tube was heat treated on a traveling oven for 2 hours in the contrast of 5 hours for the second tube. Due to the temperature drop at both ends of the furnace, the effective time is much less than 2 hours. (2) At both ends of the tube, no heat treatment effect was expected since the flange removes heat away and the furnace can not make full pass over the two ends. So that the microstructure in the both ends of the tube is not improved. (3) The heat up area is localized in a 150mm range, the gas inside the tube will remove heat from the

hot region more rapidly than in the case of the second tube case. We expect a more dramatic temperature drop inside the tube. The real temperature of the copper film is likely to be lower than the prescribed temperature. (4) Although we have considered the above effects in the first sample treatment, the effects were under-estimated due to lack of quantitative information. Further investigation on the above effects should be conducted if the traveling stage furnace is chosen as a practical way to treat the SSCL tube.

The result from run #10, though encourage, is only an early step in finding an appropriate heat treatment procedure. Further investigation on the heat treatment temperature and time, surface cleaning before the treatment, content of the protection gas, and vacuum degassing after heat treatment will bring about more promising results. It is possible to achieve an order of magnitude or more reduction of photodesorption.

Conclusions

Annealing the SSCL beam tube at 700°C for 5 hours in a reducing gas can reduce porosity, surface oxides and grain boundaries. As a result, the photodesorption outgassing of H_2 and CO_2 were cut down by a factor of two and CO by a factor of three. The unsatisfactory result on the sample treated on a traveling oven is due to insufficient annealing temperature and time. More experiments are needed to further improve the microstructure and chemistry of Cu plated SSCL beam tube.

Personnel Involved

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Undergraduate Students -- David Jones and Jonathan Rowley

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Table I: Sample tubes for photon stimulated desorption (PSD) experiments[5]

Run	Tube#	Materials and Treatment	Source, Year	Set Up
#1	024	Cu Plated Stainless Steel	Silvex, 1988-90	Unbaked
#2	025	Copper C10100	Hitachi	Unbaked
#3	030	Cu Plated Stainless Steel	Silvex, 1988-90	Unbaked, 1100 gauss †
#4	029	Cu Plated Stainless Steel	Fluhman, 1992	Unbaked
#5	032	Cu Plated Stainless Steel	Silvex, 1988-90	350°C Vacuum Baked ⇧
#6	032rot	Re Run #5, Rotated 140°	Silvex, 1988-90	No Backfill
#7	033	Au Flashed Cu Plated SS	Silvex, 1993	Unbaked
#8	034	Cu Plated Stainless Steel	Silvex, 1993	Unbaked
#9	008v	Cu Plated SS, 700°C-2 Hours Scanning Annealing, Au Flashed	Silvex, 1988-90	Unbaked
#10	007v	Cu Plated SS, 700°C-5 Hours Annealing	Silvex, 1988-90	Unbaked

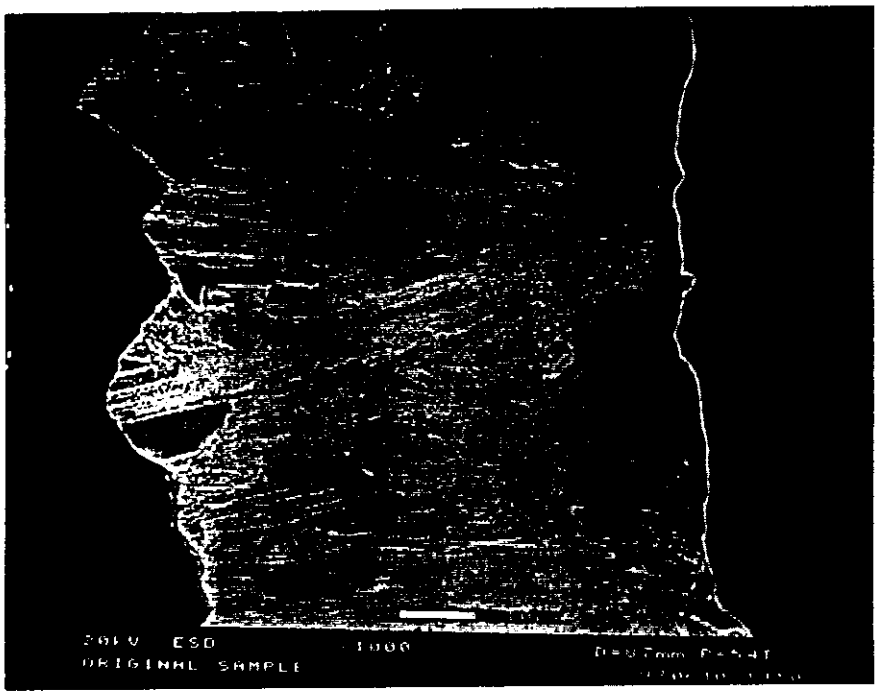
† Measured in a 1100 gauss magnetic field.

⇧ Vacuum baked prior to PSD exposure (SSC can not be vacuum baked).

Table II: Photodesorption coefficients and amount of photodesorbed H_2, CO and CO_2 for different test samples at approximate 10^{23} photons/m (BNL runs)

Run#	Yield, Molecules/Photon			Gas Desorbed (Torr-Liter)			Total Photons
	H_2	CO	CO_2	H_2	CO	CO_2	
#1	1.4×10^{-4}	2.0×10^{-5}	1.1×10^{-5}	1.7	3.5×10^{-1}	2.4×10^{-1}	9×10^{22}
#2	1.0×10^{-4}	2.6×10^{-5}	2.0×10^{-5}	7.9×10^{-1}	2.3×10^{-1}	2.5×10^{-1}	7×10^{22}
#3	1.4×10^{-4}	1.9×10^{-5}	1.7×10^{-5}	9.8×10^{-1}	2.3×10^{-1}	1.7×10^{-1}	2×10^{23}
#4	1.5×10^{-4}	2.8×10^{-5}	1.2×10^{-5}	8.2×10^{-1}	1.8×10^{-1}	1.8×10^{-1}	2×10^{23}
#5	9.0×10^{-5}	1.2×10^{-5}	9.4×10^{-5}	5.2×10^{-1}	8.2×10^{-2}	1.1×10^{-1}	7×10^{22}
#6	7.0×10^{-5}	1.1×10^{-5}	5.0×10^{-6}	4.0×10^{-1}	6.1×10^{-2}	3.1×10^{-2}	1×10^{23}
#7	1.4×10^{-4}	1.2×10^{-5}	9.5×10^{-6}	1.0	1.3×10^{-1}	1.2×10^{-1}	1×10^{23}
#8	1.0×10^{-4}	2.5×10^{-5}	2.1×10^{-5}	1.05	3.0×10^{-1}	3.1×10^{-1}	1×10^{23}
#9	1.6×10^{-4}	3.0×10^{-5}	2.9×10^{-5}	1.68	4.4×10^{-1}	5.5×10^{-1}	1×10^{23}
#10	6.8×10^{-5}	1.4×10^{-5}	1.6×10^{-5}	4.5×10^{-1}	8.8×10^{-2}	1.6×10^{-1}	1×10^{23}

Figure 1
Original Sample



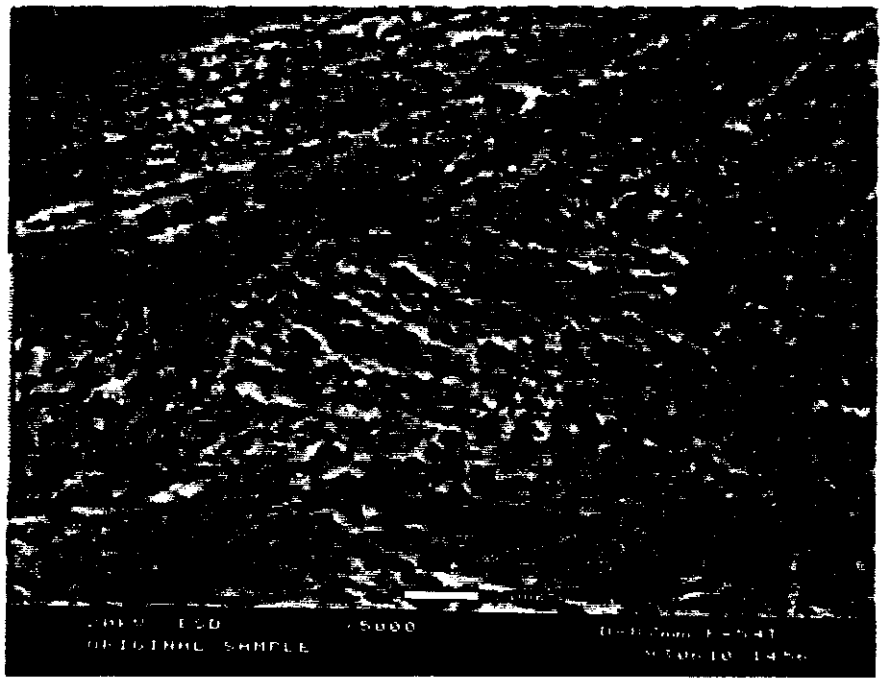


Figure 2
Annealed Sample

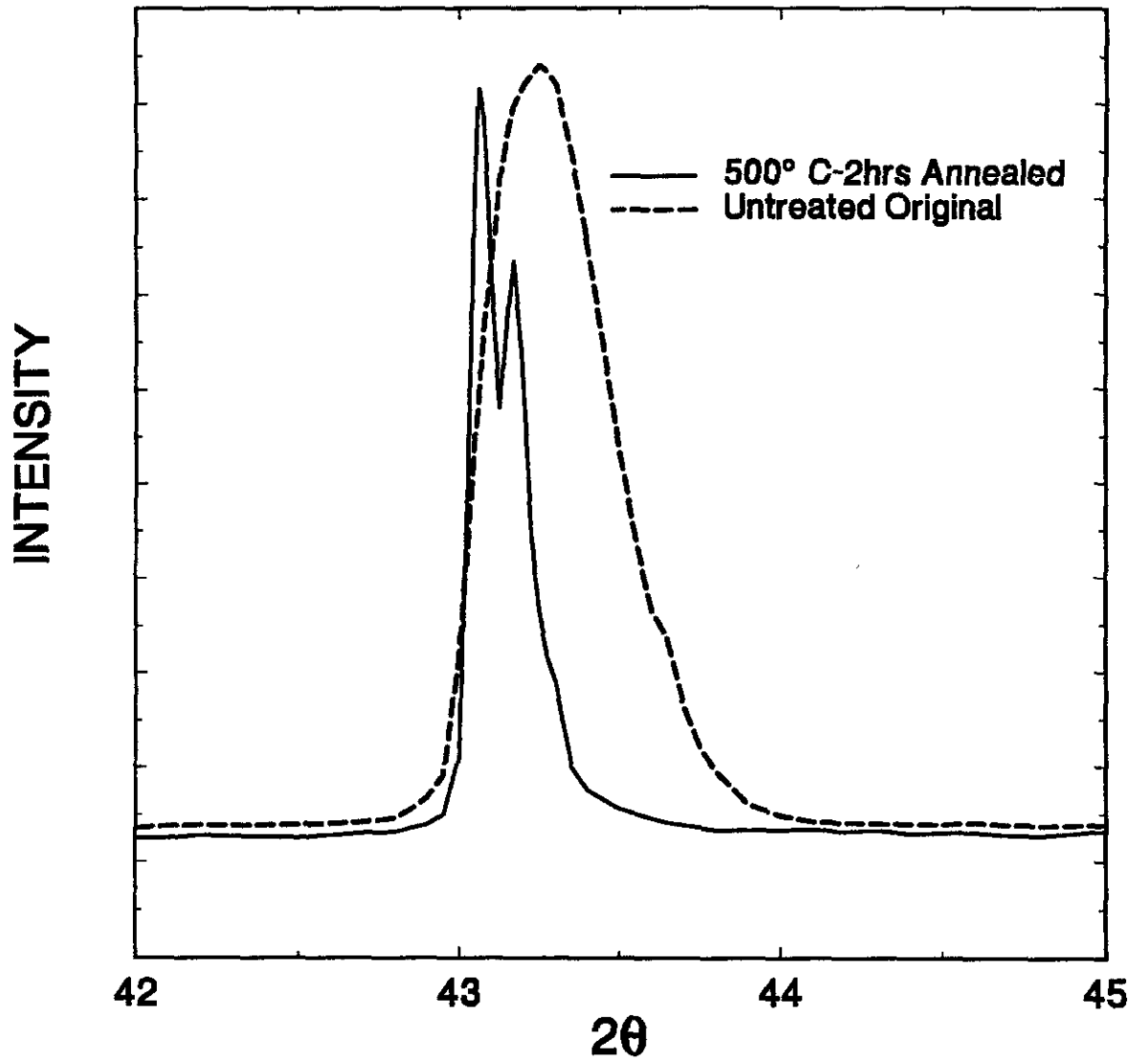


Figure 3. X-ray diffraction profiles of (111) peak of the original sample and the 700°C-5 hours annealed sample. The original sample has a broad peak with FWHM (full width at half maximum) of 0.45°. The annealed sample has a sharper peak with FWHM of 0.18° and shows the Kα1-Kα2 doublet.

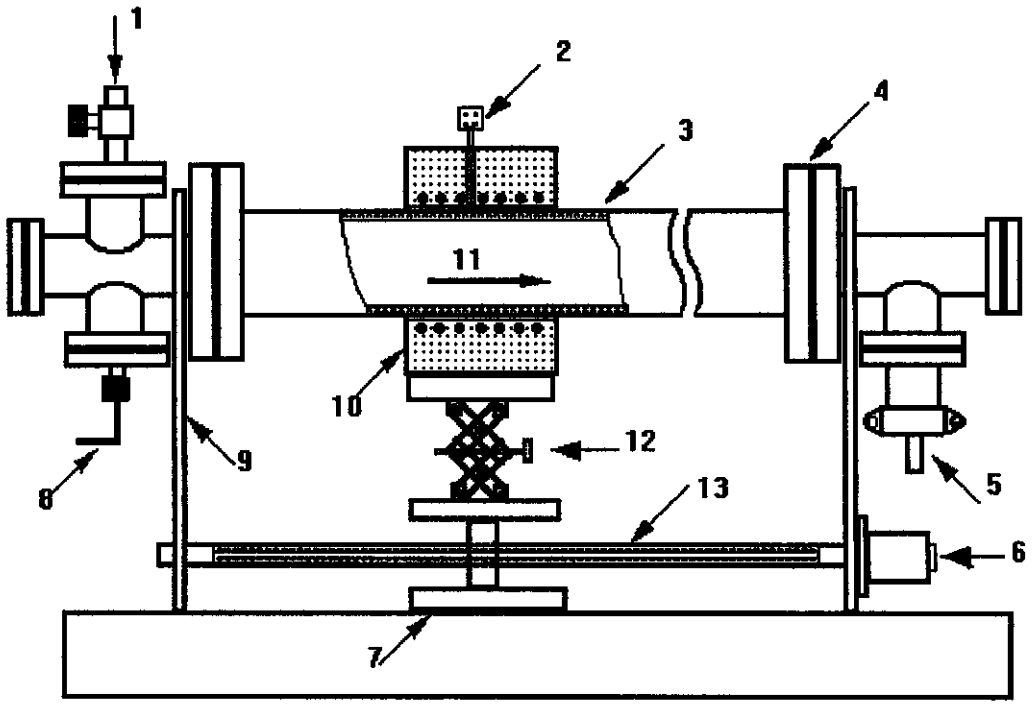


Figure 4. Schematic of the traveling stage furnace used for annealing SSCL tube #008v. 1-Gas Inlet; 2-Thermocouple; 3-SSCL Tube; 4-Flange; 5-Gas/Vacuum Outlet; 6-Stepping Motor; 7-Traveling Rail; 8-Vacuum Sensor; 9-Tube Supporter; 10-Furnace; 11-Reducing Gas Flow; 12-Adjustable Furnace Stage; 13-Driving Screw.

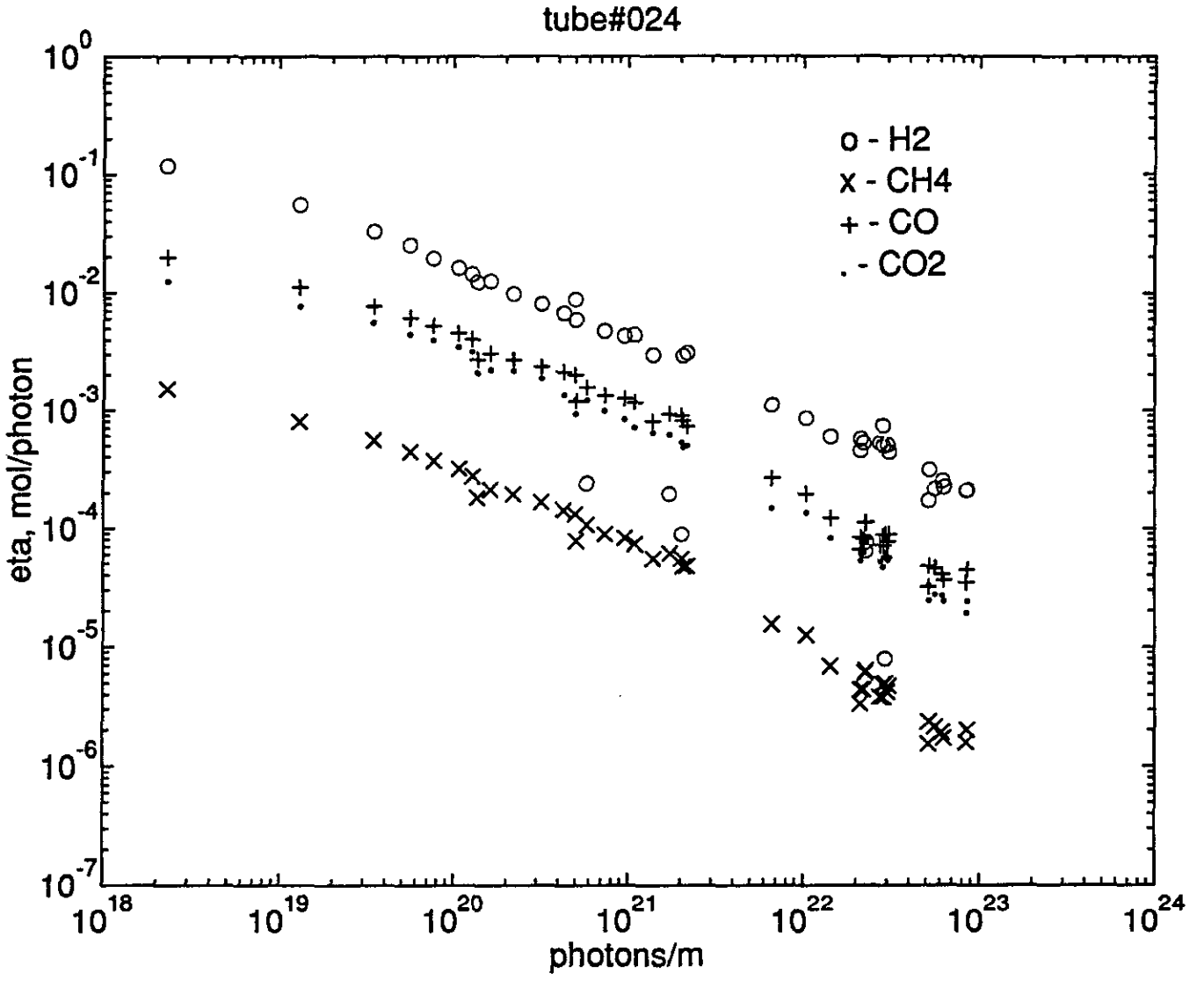


Figure 5. Photon desorption measurement results of tube #024 (1988-90 Silvex Cu plated SS untreated).

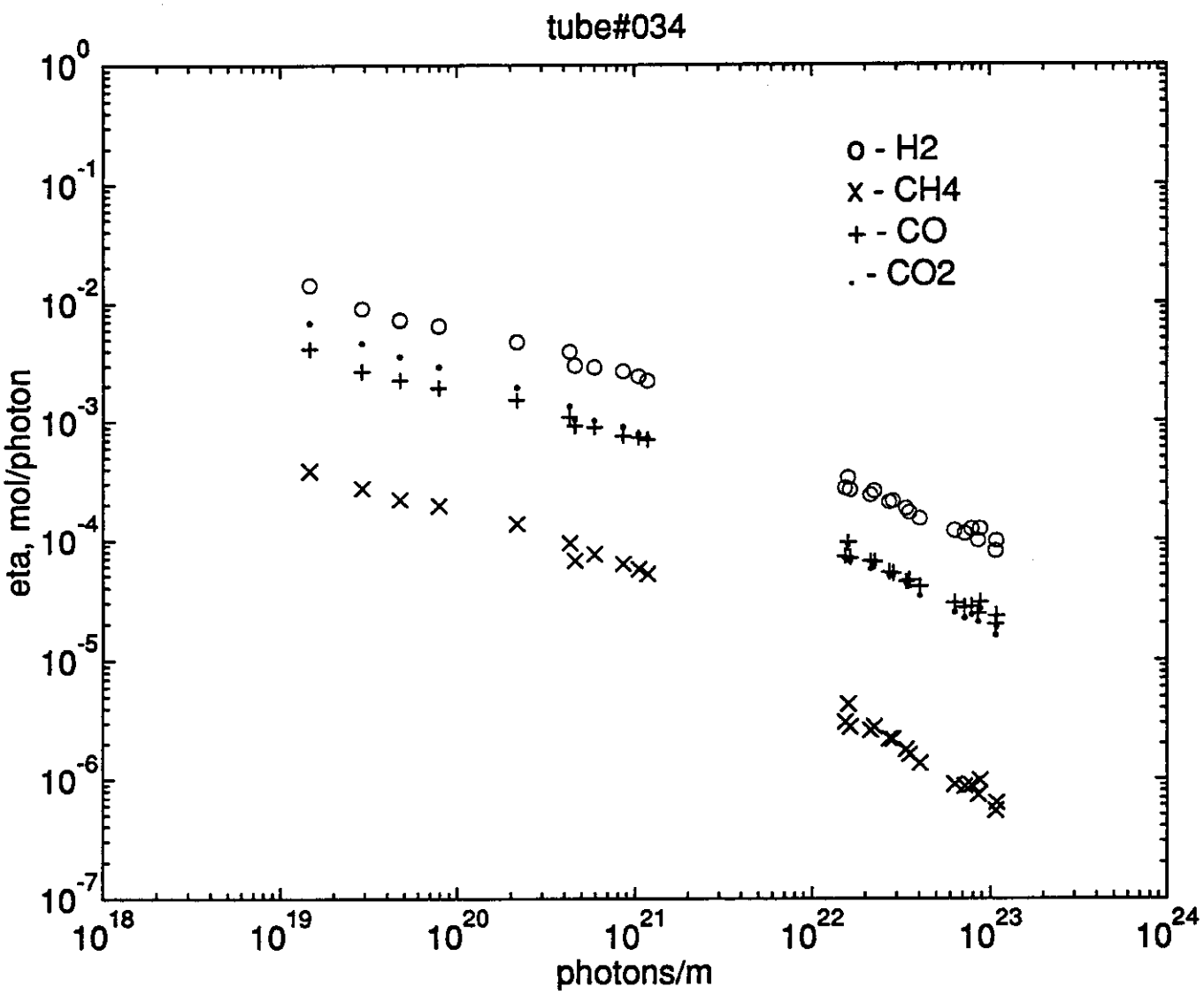


Figure 6. Photon desorption measurement results of tube #034 (1993 Silvex Cu plated SS untreated).

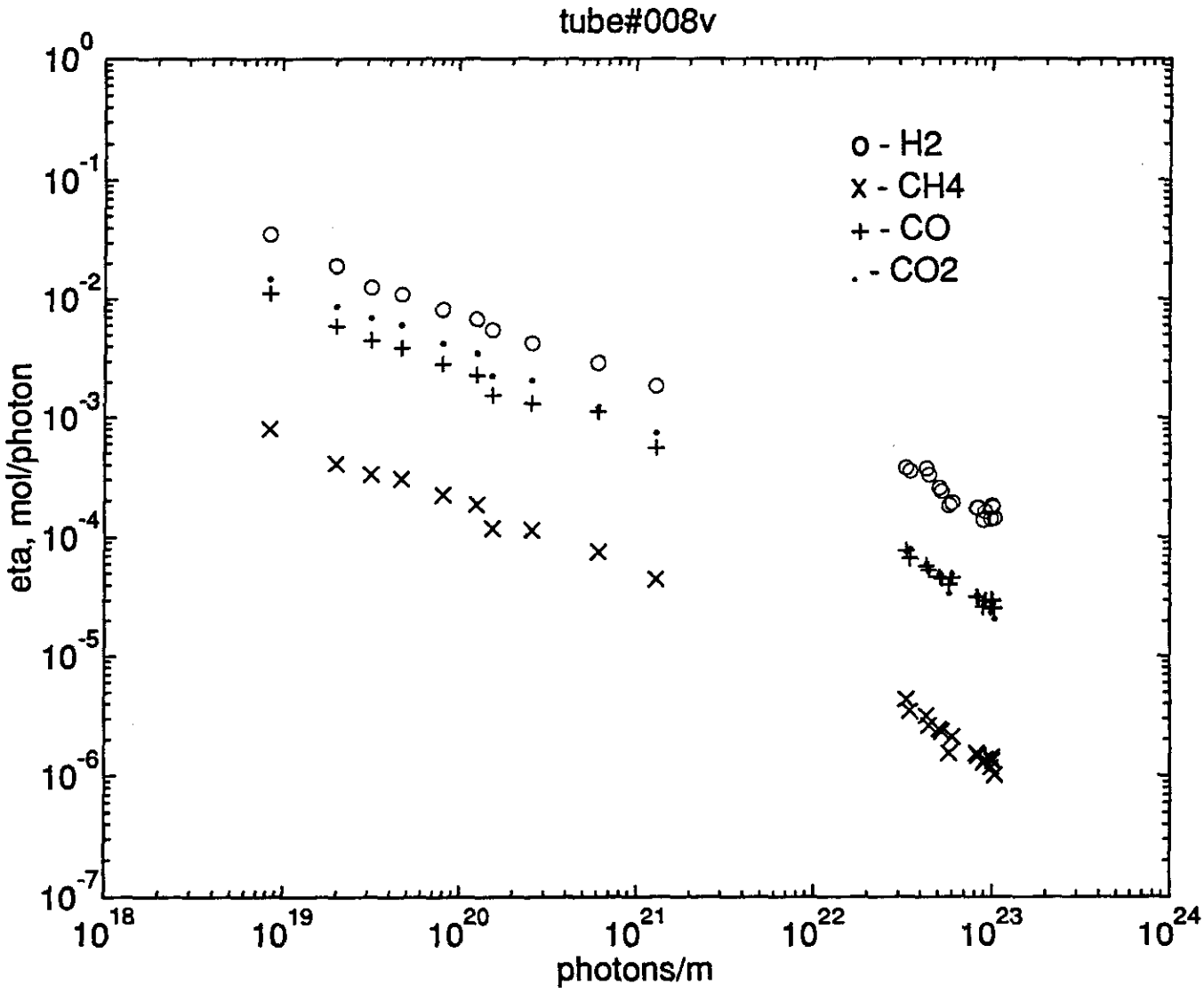


Figure 7. Photon desorption measurement results of tube #008v (1988-90 Silvex Cu plated SS, Annealed at 700°C for 2 hours with a moving stage furnace).

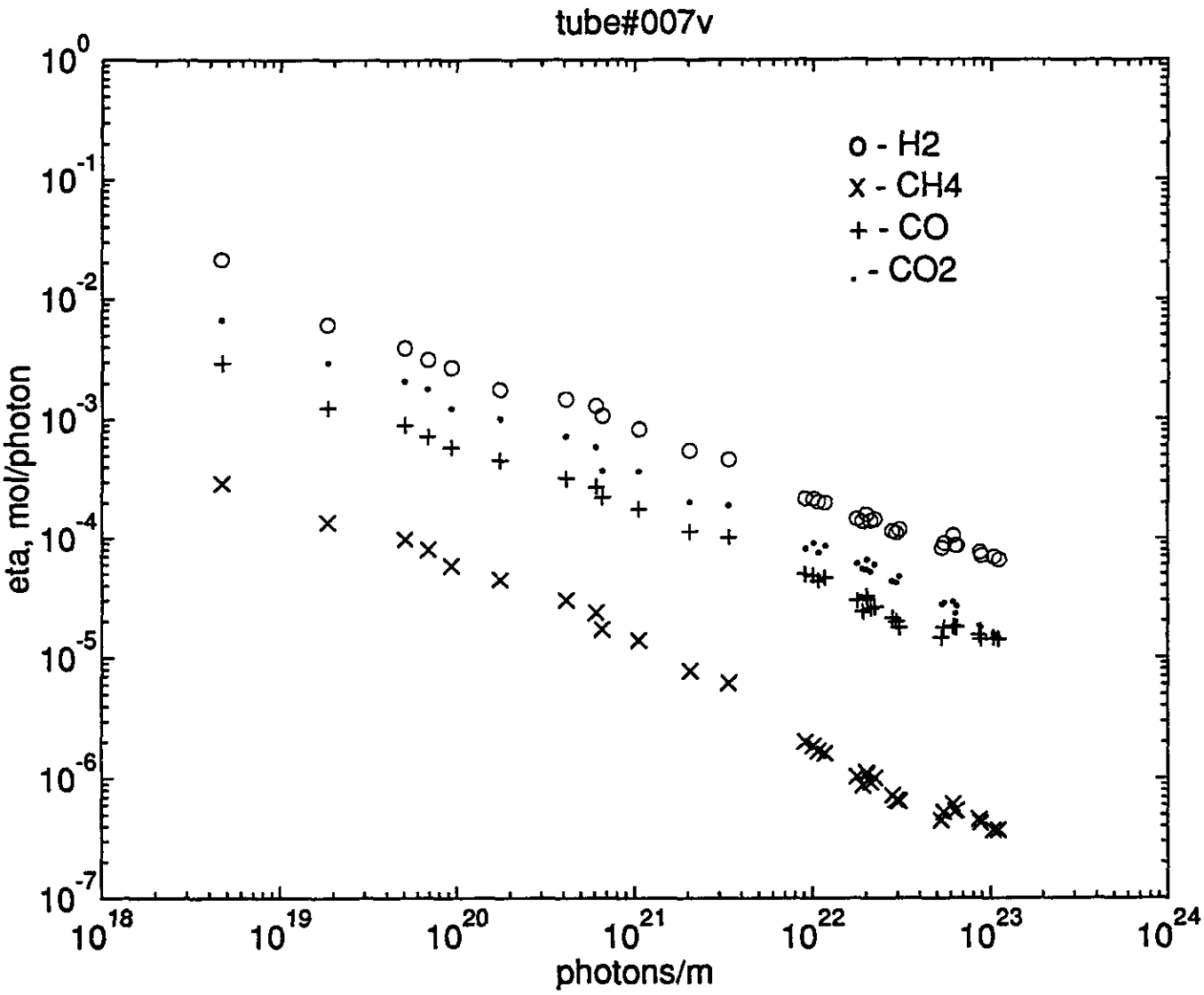


Figure 8. Photon desorption measurement results of tube #007v (1988-90 Silvex Cu plated SS, Annealed at 700°C for 5 hours in a large furnace).