Measurement and Modification of First-Wall Surface Composition

In The Oak Ridge Tokamak (ORMAK)*

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ABSTRACT

Impurities coming into the plasma from the walls of present-day toroidal plasma confinement devices modify plasma behavior substantially. Small fractions of high-Z ions in the plasma greatly decrease plasma temperatures and increase plasma energy losses. We are attempting to identify and control the sources of impurities from the "first-wall" in ORMAK.¹ Auger electron spectroscopy, soft x-ray appearance potential spectroscopy, and other surface sensitive techniques have been used to characterize the surface composition of the first wall and to develop methods to remove carbon and oxygen. Oxygen glow discharge cleaning has been shown, in the laboratory, to be an effective way of removing carbon from gold films (simulated ORMAK liner material) and the use of oxygen discharge cleaning in ORMAK has resulted in a decrease in plasma contamination, a 50% increase in plasma current and an accompanying increase in plasma temperature. In spite of these improvements the walls of ORMAK are far from clean. Substantial amounts of carbon, oxygen, iron and other elements remain.

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AB

I. INTRODUCTION

Impurities entering the plasma from the walls of experimental thermonuclear devices such as ORMAK strongly influence plasma behavior and are a major problem for present as well as future machines.²⁻⁵ It is the purpose of our present work to identify and minimize sources of wall (or liner) impurities in the Oak Ridge Tokamak.

In tokamaks contamination causes large power losses from the plasma due to (1) increased bremsstrahlung and line radiation, (2) the power required to ionize and heat the incoming flux of impurities, and (3) loss by means of impurity-induced MHD instabilities. The impurities enter the plasma as the result of the interaction of photons, neutrals, ions or electrons with the wall during the discharge, (or "shot" as it is commonly called). All of these processes occur during each discharge cycle. The desorption of impurities by photons and neutrals is important early in the discharge while ion and electron induced phenomena are likely to be important at the limiter throughout the shot. Present tokamaks have shot duration times as long as hundreds of milliseconds while ion containment times are usually tens of milliseconds or less. Ions are lost from the plasma by charge exchange and impinge on the wall as energetic neutrals. These energetic particles may sputter adsorbed layers of gases, thin surface films, or wall material into the plasma. The particles may also cause chemical or structural changes at the surface of the wall which leads to emission of material into the plasma. Photons may cause decomposition of surface layers resulting in desorption of volatile constituents, or, by virtue of electronic excitation processes, may cause atoms or molecules to be desorbed without decomposition. Desorption may also take place by simple wall heating. Ions and electrons can give rise to the same phenomena as neutrals and photons but they are usually confined by the magnetic fields so that they

impinge upon the limiter, an aperture fabricated of refractory material which defines the diameter of the discharge.

II. RATIONALE FOR IMPURITY INVESTIGATIONS

Through the use of UV spectroscopy⁶ the principal impurities in the ORMAK plasma have been shown to be carbon and oxygen. Each of these may contribute 1 to 2% to the plasma density which causes severe energy losses from the plasma and increases the effective average nuclear charge which, in turn, may dramatically alter the plasma dynamics. These impurities must come from the walls since impurities present in the working gas are estimated to be no more than one part in 10^{-4} . The sputtering of wall material and sputtering and evaporation of limiter material contribute only relatively small amounts of plasma impurities since significant quantities of these materials have not been detected in the plasma by UV spectroscopy. The major source of impurities must therefore be desorption of oxygen and carbon contaminants from the wall. In today's tokamaks the entire contents of the plasma are recycled to and from the wall in the early part of the discharge⁵ and the buildup of impurities during the discharge cycle lends further support to their origin being on the wall.⁴

The present wall of ORMAK is 304 stainless steel, .025 cm thick, overcoated with about 500 Å of platinum and then with 2000 Å of gold by a vacuum deposition process. The intent of this design was to make the wall as inert as possible; gold has low sticking coefficients and forms only very weak physisorption bonds with most gases. The platinum layer was found to be effective as a diffusion barrier to the elements in the stainless steel.⁷

Results of Auger analysis (discussed in section IVa) indicate that even freshly prepared and carefully handled surfaces will be significantly contaminated upon exposure to air prior to assembly into ORMAK. Therefore some type of in situ cleaning will be required if clean gold surfaces are to be maintained inside ORMAK. These studies also make apparent the need for in situ monitoring of the ORMAK liner surface conditions during operation. Correlations of surface condition with machine performance and measurement of the effectiveness of cleaning procedures might then be possible.

It has long been observed that the characteristics of tokamak discharges change after exposure of the liner surfaces to air. Discharge cleaning and baking have been used almost universally to "clean up" the machines. In ORMAK discharge cleaning took the form of running both routine shots and low pressure (10^{-4} torr) hydrogen glow discharges. The machine performance changed over periods of days or even weeks, giving better performance as time increased beyond the first few shots.

The present plasma impurity problem then appears to be resolved primarily into finding ways (1) to remove the carbon and oxygen impurities from the gold surfaces, (2) to monitor the cleanliness of this surface in situ, and (3) to maintain clean surfaces once they have been obtained.

III. EXPERIMENTAL

The experimental work was divided into three parts: (1) analysis of samples of wall material removed from ORMAK, (2) development of cleaning techniques in the controlled conditions of the laboratory, and (3) the development of techniques for the in situ analysis in ORMAK.

a. AES Analysis

The examination of wall material was carried out using AES along with sputter depth-profiling techniques. Samples were introduced into the UHV system through a vacuum lock without baking. Analyses were made at pressures in the 10^{-10} torr range or very low 10^{-9} torr range. The AES analyzers used included both a double pass CMA-PHI model 15-25G,⁸ and a single pass CMA, Varian model 981-2707,⁹ operated with a normal incidence electron beam current of 3 to 15 mA at 3-5 KeV. Ion sputtering was carried out with normal incidence 1 keV argon ions at a flux of about 10^{15} ions per cm^2 per minute. For convenience and consistency in reporting data we assume the AES spectra presented in the Physical Electronics Industries Handbook of Auger Electron Spectroscopy¹⁰ are accurate and directly applicable to our data. We report our data in atomic percentages normalized so that the total atom percent for reported elements equals 100 percent. Blanks in the tables mean the element was not apparent in the raw spectra. No attempt is made to correct for chemical effects, line shape, matrix effects, escape depth, or distribution of elements as a function of depth in the sample. Sputtering rates are assumed equal for all elements and equal to one atom layer per minute under the conditions described.*

b. Cleaning Techniques

Several cleaning techniques were investigated using coupons of wall material prepared by the same techniques and in the same equipment used to produce coatings for ORMAK walls. No solvents or other intermediate cleaning were used. Thermal cleaning was examined first, using radiant heat to raise the sample temperature. AES spectra were obtained with the

*For more details on sputter rates the reader is referred to the extensive work by Wehner et al.^{11,12}

sample at both high temperature and at room temperature. The temperature was determined by a thermocouple welded to the sample. Other samples were exposed to the cleaning effects of glow discharges by transferring the samples, under vacuum, to an attached chamber where oxygen, hydrogen and nitrogen glow discharges could be maintained at pressures of about 0.25 torr in slowly flowing gas. Glow discharge currents of 0.5 mA were maintained at about 350 volts. The glow discharge cell is shown schematically in Fig. 1. The samples were usually held at ground potential and positioned near but not in the discharge so as to minimize direct ion or electron bombardment of the sample. The surface to be analyzed normally faced away from the discharge. A few experiments were conducted with the sample facing the discharge. In this case it served either as an electrode for the discharge or could be biased to attract or repel ions or electrons from the discharge.

c. In Situ Analyses

We have developed a "probe" for in situ analyses using the soft x-ray appearance potential spectroscopic (SXAPS) technique¹³ which is capable of providing qualitative or semiquantitative surface analyses. In principle, the apparatus for this technique is quite simple in that no special electron or ion optics which require critical mechanical alignment are necessary. The probe, which is presently being used in ORMAK, is shown schematically in Fig. 2. The analysis is carried out on one surface of an octagonal sample wheel, the position of which can be adjusted from outside the vacuum wall by means of a mechanical linkage. During operation any face of the sample can alternatively be exposed to the plasma and to the SXAPS analysis. The probe was built and tested in the laboratory before being installed in ORMAK. Figure 3 shows such a laboratory spectrum obtained from a stainless steel face on the sample wheel. Only carbon was identified on the gold faces

prepared to simulate the liner material. (Gold has no easily detectable SXAPS.)

IV. RESULTS AND DISCUSSION

a. AES Analysis of ORMAK Wall Material

Table I shows the range of composition of surfaces of coupons typical of wall material prepared and handled using the normal fabrication techniques. The analyses were made after the samples were exposed to the atmosphere for times from a few hours to several days (inside clean, dust-free containers). While all samples exhibited significant quantities of carbon and oxygen several showed the presence of sulfur and silicon as well. For purposes of comparison several similar samples were sputter cleaned with 1 keV argon ions, removed through a vacuum lock, exposed to air for various times, reloaded into the AES system through the lock and again analyzed. The results of these analyses, shown in Table II, indicate that contamination occurs rapidly in air but only as a thin surface film. Two to five minutes of argon sputtering removes it down to pure gold. Table III shows the results of AES analysis of several samples removed from ORMAK. Some (those above the line) are from an old ORMAK liner and others (those below) are from recently removed liner plugs. Because of the contamination (air exposure) during their removal, the initial analysis is useful mainly to indicate the presence of impurities other than carbon and oxygen. Sputtering gives an indication of the levels of carbon and oxygen which existed in ORMAK before the air exposure as evidenced by the increased concentration with depth on some samples. The first samples in this list were removed from an ORMAK liner which had been operated for many months with exposure to hydrogen ions and energetic hydrogen neutrals during experimental shots and also to hydrogen glow discharge cleaning for 12-16 hours each night. The analyses were performed several months after the liner was removed. Protection against gross contamination, dust, fingerprints, etc. was provided but there was no effective protection against air-borne vapors or gases. As expected carbon and oxygen

were present in varying amounts on all samples. The presence of iron, chromium, and nickel in the ratio 75:20:10 would be expected if stainless steel is sputtered or vaporized into the liner interior. The relatively low chromium and nickel concentrations are puzzling in view of the presence of significant quantities of iron. One possible explanation is that iron is selectively transported in the form of a volatile iron compound such as an iron carbonyl. The presence of copper on the plug samples, although minimal, is no doubt explained by sputtering from the ORMAK neutral particle injection structures. The high carbon content of the film from the plug samples is surprising in view of the fact that this plug was exposed to extensive oxygen glow discharge cleaning each night during its service in ORMAK. The high silicon areas on plug No. 2 seem to be related to a visible spot of contamination, perhaps due to oil or grease from improper handling during plug assembly.

b. Cleaning

Thermal cleaning is perhaps the simplest and most obvious technique for cleaning a gold surface when adsorbed gases are the major contaminants. A sample of ORMAK wall material was heated using radiant heat while periodically monitoring the surface by AES. The sample temperature was increased each hour by 100°C with AES analysis made just before each increase. Table IV shows the results of this experiment. Increasing temperatures produced some improvement by reducing carbon and oxygen surface concentrations but at temperatures of 400°C and higher no further depletion of carbon takes place and components of the stainless steel begin to appear on the surface. It appears that thermal cleaning of the liner surface is not a promising method of completely removing carbon contamination.

The products of a hydrogen glow discharge should be highly chemically reducing so it would be expected that carbon and oxygen would both be converted to volatile compounds and thus be easily pumped from the ORMAK system. We exposed samples of wall material to a hydrogen glow discharge in the cell described in Fig. 1 with the results shown in Table V. There were significant reductions in the carbon levels initially, but exposures of several hours did not produce surfaces significantly cleaner than shown.

Oxygen glow discharge cleaning was conducted in the same manner with the results shown in Table VI. We found that carbon is greatly reduced during the first hour and removed below the limit of detection, about 0.2 atomic percent, within a few hours. The data in the table also show an increase in oxygen on the gold surface as a result of the discharge, but desorption at room temperature resulted in substantial removal of the oxygen in several hours. There was no appreciable change in the time scale or extent of oxygen discharge cleaning when the polarity of the discharge was changed.

Experiments with nitrogen glow discharge cleaning produced no significant cleanup when the sample was exposed in the same manner as for the oxygen and hydrogen discharges.

As a result of the above experiments in the laboratory, oxygen discharge cleaning was incorporated into routine ORMAK operations. A weak toroidal magnetic field is used with alternating currents induced around the torus to produce a discharge at pressures near 1×10^{-4} torr. The oxygen discharge is run for 14 to 16 hours each night, followed by a hydrogen discharge which is continued for one or two additional hours before the routine ORMAK operations are begun. This procedure has produced a fifty percent increase in the circulating current in ORMAK and an accompanying increase in electron and ion temperatures.

SXAPS IN ORMAK

The SXAPS probe was installed in ORMAK and spectra obtained prior to and following shot sequences. Initial studies indicated the presence of carbon and oxygen but, with time, these signals became weaker and iron appeared. Iron was found to be common to all sample surfaces. The severity of electrical noise generated by the ORMAK supporting systems reduces the SXAPS signal-to-noise ratio and has caused considerable ambiguity in interpretation. Within a short time after installation the sample wheel and photocathode were so severely contaminated with impurities (which AES showed later to be principally oxygen and iron with lesser amounts of carbon, chlorine, and nickel) that it was no longer possible to correlate the probe behavior with cleaning or with plasma parameters. The impurity deposits on these surfaces after several months of use in ORMAK are readily visible and are hundreds of angstroms thick.

The probe and its housing are positioned between the ORMAK toroidal field coils which are maintained at liquid nitrogen temperature. We speculate that the probe acted as a cold trap and condensed water, hydrocarbons, and other vapors from the liner region. Bombardment of these condensed layers with soft x-rays and/or electrons could explain the buildup of contaminants on the sample wheel and photocathode. This information, if verified by further testing, is useful in that it shows that the ORMAK liner region contains condensable contaminants which should be removable by suitable liquid nitrogen trapping.

The build-up of carbon, oxygen, and iron on the probe elements also indicates that under the present operating conditions in ORMAK the oxygen discharge cleaning is not effective in removing contaminants from surfaces not directly exposed to the discharge. Even the sample wheel surfaces intermittently exposed to the discharge region were contaminated with carbon. These results and those in the preceding section indicate that the oxygen glow discharge cleaning improves the wall condition but does not produce a clean gold surface.

We propose to heat the probe housing for future operation and perhaps to install special arrangements for inert gas sputter cleaning or high pressure oxygen discharge cleaning the probe components so that we may begin each new series of experiments with a clean gold probe surface.

SUMMARY AND CONCLUSIONS

The work thus far has revealed that carbon, oxygen, and iron are major components of the wall impurity problem in ORMAK. Laboratory experiments have shown that some carbon can be removed from gold surfaces by exposure to high temperature vacuum baking and to the products of oxygen and hydrogen glow discharges. The oxygen glow discharge is the more effective and, furthermore, the oxygen remaining on the gold film after the cleaning is desorbed in a few hours at room temperature. The active oxygen species from the discharge is apparently not an ion since neither positive nor negative voltages on the sample prevented or greatly changed the rate of carbon removal. This is consistent with the explanation offered by Lambert and Comrie for the cleanup of hydrocarbons in a stainless steel system using an oxygen glow discharge.¹⁴

The use of a modified form of oxygen glow discharge cleaning in ORMAK has increased the circulating current and plasma temperatures but oxygen and carbon still remain serious plasma contaminants.

An SXAPS probe has been developed and extensively tested in the laboratory. It has also been used with limited success in ORMAK. While only carbon and oxygen were detected initially, iron was detected on all faces of the sample wheel later. The high levels of electronic noise and unexpectedly high levels of contamination in the probe have thus far frustrated any detailed correlation of wall impurity levels with cleaning techniques and plasma quality.

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Table I. Surface Composition of Typical Liner Material

Condition	Composition (Atomic Percent)					
	C	O	Si	S	Cd	Au
As received #1	29	0.4			2.5	68
As received #2	52	0.4		3.5		44
As received #3	71	2	0.2	4		23
As received #3, 2nd spot	76	2	0.4	3		19

Table II. Contamination of a Gold Film Exposed to Air

Condition	Composition (Atomic Percent)					
	C	O	Si	S	Cd	Au
As received	71	2	.2	4		23
Sputtered 40 min ^a	< 1			< 0.5		99
+1 hr in air	21	2		< 0.5	0.3	77
+16 days in air	39	1		1	7	53

^a1 keV argon ions at $\sim 10^{15}$ ions per cm^2 per minute.

Table III. Surface Analyses of Samples from the ORMAK Wall

Sample Description ^a	Composition (Atomic Percent)							
	C	O	S	Fe	Cr	Ni	Cl	Other
Gold liner "As Received"	50	21	3	16	5	1	2	Ca-0.3, N-0.1
Gold liner "As Received"	46	22	1	24		2	1	Ca-1.4, N-0.7
Gold liner Sputtered 2 min	19	33	2	39		3	1	Ca-1.2
Gold liner Sputtered 5 min	10	26	1.5	56		4	2	
Gold liner Sputtered 10 min	3.8	35	0.4	55		5	0.6	
Gold liner Sputtered 30 min		30		55		8		
Be foil "As Received"	53	18	0.5	12			2.2	K-6, Ca-2, N-1.7
Al foil "As Received"	48	25	5	6			3	K-8, F-6
Al foil Sputtered 2 min	18	33	13	8			5	K-15, F-10
Al foil Sputtered 10 min	29	42	7	3				K-7, F-11
Au plug #1 As Received	75	6		11		5.5		Cu-3
Au plug #1 Sputtered 2 min	17	6		11		5.2		Au-59, Cu-1.6
Au plug #1 Sputtered 9 min	16	5		11		3.7		Au-63, Cu-1
Au plug #1 Sputtered 50 min	29	0.9		4		0.9		Au-64, Cu-1
Au plug #1 Sputtered 120 min	6	0.3		1		0.4		Au-91, Cu-1
Au plug #2 As Received	14	23	25	10		3		Au-47, Si-13, Cu-3
Au plug #2 As Received	36	14		17		4		Au-24, Cu-5, Si-10

^aSamples below the line came from a new liner where oxygen glow discharge cleaning was used.

Table IV. Thermal Cleaning of Gold Films by Baking at Progressively Higher Temperatures in Ultra-High Vacuum ($\sim 3 \times 10^{-9}$)

Conditions	Composition (Atomic Percent)						
	C	O	Au	Cd	Cr	Fe	P
"As Received"	29	0.4	68	2.5			
+100°C 1 hr	45	0.7	51	3.6			
+200°C 1 hr	37	0.5	60	2.3			
+300°C 1 hr	26	0.2	74	0.5			
+400°C 1 hr	24	0.2	76		0.2		
+500°C 1 hr	22	0.1	77		0.2	0.1	0.3
+600°C 1 hr	22	0.1	76		0.9	0.8	

Table V. Auger Analysis of Gold Films Cleaned by Exposure to the
Products of a Hydrogen Glow Discharge^a

Condition	Composition (Atomic Percent)		
	Carbon	Oxygen	Gold
As received	19	4	77
1 hr exposure (positive high voltage)	8	1	91
As received	25	1	74
1 hr exposure (negative high voltage)	5	3	92

^a350 volts, 0.5 mA, pressure ~ 250 millitorr.

Table VI. Auger Analysis of a Gold Film Cleaned by Exposure to the Products of an Oxygen Glow Discharge^a

Condition	<u>Composition (Atomic Percent)</u>	
	Carbon	Oxygen
"As Received"	49	0.7
After 5 hr exposure	ND ^b	6.9
10 min after previous spectra	ND	5.6
2 hr after previous spectra	ND	3.6
3 days after previous spectra	0.03	1.5

^a350 volts, 0.5 mA, pressure ~ 300 torr.

^bNot detectable.

FIGURE CAPTIONS

Figure 1. Glow Discharge Cell. Gas is bled into the cell to maintain a pressure of about 0.25 torr. The cell volume is about one liter and the gas removal rate is about 0.01 liter per second. The cell is constructed of standard 1 1/2" stainless steel UHV vacuum fittings, is bakable, and has a base pressure in the 10^{-8} torr range without baking. Most discharges were operated at about 350 volts with currents of 0.5 mA.

Figure 2. SXAPS Probe for ORMAK. The voltage on the sample wheel is varied so that the minimum electron energy required to generate characteristic soft x rays from the surface can be determined. This is done by detecting the increase in photoelectron current from the photocathode as the electron energy is increased through the threshold. Sophisticated electronics are required but the detector is simple and does not require carefully focused electron beams or energy analyzers.

Figure 3. Soft X-Ray Appearance Potential Spectrum from the Sample Wheel of the ORMAK SXAPS Probe. The second derivative of the photoelectron current emitted from the photocathode is shown as a function of electron energy. The spectrum shows the presence of carbon, oxygen, chromium, and iron on the surface which was not cleaned after air exposure. Clean samples give signal to noise ratios of 50:1 or better for iron under the same operating conditions.

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Glow Discharge Cell

SXAPS Probe for ORMAK