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THE SURFACE CLEANLINESS OF 316 L + N STAINLESS STEEL

STUDIED BY SIMS AND AES*

by

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Abstract

Some cleaning methods for 316 L + N stainless steel including solvent cleaning, high temperature treatment in vacuo and gas discharge cleaning have been studied by SIMS and AES with a view to providing a clean vacuum chamber surface with low gas desorption under ion bombardment. After solvent cleaning the main surface contaminant was found to be C and its associated compounds. Laboratory investigations on small samples of stainless steel showed that clean surfaces could be obtained by heating in vacuo to 800°C followed by exposure to air and by argon or argon/10% oxygen discharge cleaning. Due to a cross contamination within the vacuum system, the 800°C treated chamber gave positive desorption coefficients under ion bombardment. The pure argon discharge cleaned chambers proved stable giving negative desorption coefficients up to 2200 eV ion energy even after several weeks storage between discharge treatment and installation. No results have yet been obtained on the stability of an argon/10% oxygen discharge cleaned vacuum chamber.

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INTRODUCTION

The vacuum system of the Intersecting Storage Rings (ISR) at CERN, Geneva¹⁾ consists of two intersecting rings, each one kilometre long, of 316 L + N stainless steel tube 16 cm in diameter pumped by sputter-ion pumps and titanium sublimation pumps. After baking this system sector by sector at 300°C for 24 hours the average pressure is $\leq 2 \times 10^{-11}$ torr, the residual gas composition being $\approx 90\%$ H₂ with traces of H₂O, CH₄, CO and CO₂.

When the high energy proton beam is in the ISR, interaction of the protons with the molecules of the residual gas produces ions. These ions are repelled by the positive space charge of the beam (approximately 100 V per ampère of stacked proton beam) and bombard the walls of the vacuum chamber with energies typically of the order of 1 to 2 keV. This ion bombardment desorbs gas still adsorbed on the walls even after the 300°C bakeout. The pressure increases and hence the ion bombardment. This can result in a runaway process giving pressures up to $\approx 10^{-6}$ torr and consequent rapid beam loss.

Analysis of one of these so called pressure bumps revealed the following gas composition: H₂ - 40%, CO - 40%, CH₄ - 10%, H₂O - 10%. However, this composition can show considerable variations especially in the proportion of H₂.

As a measure of the cleanliness of the surface of the vacuum chamber, we introduce the net desorption coefficient η defined as the number of desorbed gas molecules per bombarding ion, minus the sticking probability of the ion itself. Ideally a surface with $\eta < 0$ is required.

In order to identify the surface contaminants which are not removed by our solvent cleaning methods and a 24 hour 300°C bakeout but can be desorbed in large quantities under ion bombardment, samples of 316 L + N stainless steel were studied with Secondary Ion Mass Spectrometry (SIMS) and Auger Electron Spectroscopy (AES).

EXPERIMENTAL

A standard stainless steel UHV system capable of attaining pressures $< 2 \times 10^{-10}$ torr after 250°C bakeout and $\approx 5 \times 10^{-9}$ torr without bakeout was used in the present studies. The system was pumped with a 110 l s^{-1} ion pump in conjunction with a liquid N_2 cooled Ti sublimation pump. For operation in the SIMS mode, where the system was back filled with $\approx 10^{-6}$ torr of argon, a turbomolecular pump replaced the ion pump.

The SIMS system (Balzers AG) consisted of a primary ion gun operated to give 3 keV argon ions at a current density $\approx 10^{-9} \text{ A cm}^{-2}$ on the specimen. The positive and negative secondary ions were detected and mass analysed using a quadrupole mass analyser with an off-axis secondary electron multiplier²⁾.

The Auger electron spectrometer was a standard cylindrical mirror analyser with an axial electron gun (Physical Electronics, Inc.). The electron gun was operated at 3 keV producing a current of 50 μA at the sample. The modulation frequency was 40 kHz and a modulation amplitude of 5 V peak-to-peak was used.

Samples could be heated by electron bombardment on the reverse side to which the SIMS and AES analyses were made. The temperature was measured with a Pt/Pt-Rh thermocouple spot welded to the front surface. Analyses were made as close to the thermocouple as possible.

RESULTS

The composition of 316 L + N stainless steel (in weight %) is typically as follows :

Fe	Cr	Ni	Mo	Mn	Si	N	P	C	S
64.3	17.7	13.6	2.66	0.87	0.66	0.17	0.016	0.016	0.007

Note the low C content. Another element not shown here but present on the surface is O which is an essential component of the passivation (oxide) layer of the steel.

An atomically clean surface is defined here to be one which exhibits neither Auger transitions other than those which can be assigned to the constituents of the sample including O nor shows transitions corresponding to an excess of any constituent.

Figure 1 (top) shows the Auger spectrum from an uncleaned and unbaked sample of stainless steel. The major surface impurity is C (≈ 80 at. %) which obscures the underlying stainless steel surface (Fe, Cr, Ni and O). From the shape of the peak the C appears to be in the form of graphite³⁾ although it is probable that oil and other complicated hydrocarbons are present on the uncleaned surface.

The centre spectrum shows the same sample after passing through the ISR solvent cleaning procedure which involves vapour degreasing in trichlorethylene, ultrasonic cleaning in hot Na_2CO_3 solution followed by rinsing in first tap water, then demineralized water and finally rinsing in alcohol. A separate investigation of this procedure⁴⁾ showed that the Cu originated in the Na_2CO_3 bath and that the tap water baths were responsible for the Ca. However, the C contamination is greatly reduced revealing the underlying Fe, Cr, Ni and O.

The bottom spectrum is the result of heating the specimen alone at $\approx 1 \times 10^{-8}$ torr for 4 hours at 300°C . The situation is little changed. The O is somewhat reduced due to desorption of H_2O but the C, Ca and Cu remain. This therefore is the final state of the ISR vacuum chamber surface on which, according to AES, the major impurity is C (≈ 30 at.%).

Figure 2 shows the corresponding positive and negative SIMS spectra. The high ionization cross-section of Na and K result in exaggerated peak heights for these elements. In addition the secondary ion yield of certain metals is strongly dependent on the chemical state of the metal surface⁵⁾. For example, the yield of Cr^+ from oxidised Cr is 10^3 times that from clean, unoxidised Cr. Thus the interpretation of peak heights in SIMS spectra as a direct quantitative measure of the amount of material present is to be avoided.

In the uncleaned specimen (Figure 2, top) the major surface contaminants seen via SIMS are H and C and their various combinations. S^- and Cl^- are also observed.

The appearance of Cu^+ , Ca^+ and phosphates is evident after the solvent cleaning. The H and C are much reduced but hydrocarbons are still present (Figure 2, centre).

A bake at 300°C (Figure 2, bottom) improves the situation somewhat with a decrease in H^+ , H^- , OH^- from H_2O but still leaving some C compounds, Ca^+ and phosphates. The presence of Si (mass number 28) in the stainless steel makes positive identification of CO in the SIMS spectra difficult - neither it nor CO_2 (mass number 44) were definitely identified.

Inspection of the top Auger spectrum in Figure 3 reveals that heating to 800°C at $\approx 1 \times 10^{-8}$ torr produces a surface practically devoid of C, without O but with a layer of S which has diffused from the interior and segregated at the surface. The low energy Fe and Ni peaks (47 and 61 eV) are evident. Because of their relatively small escape depth ($\approx 5 \text{ \AA}$) the low energy peaks are particularly sensitive to overlying material, and their strength may be used as a measure of the amount of overlying contamination.

Exposing this sample to air results in the centre Auger spectrum of Figure 3. This is atomically clean stainless steel surface. That very little overlying contamination is present is verified by the continued presence of the low energy Fe peak now split by oxidation⁶⁾.

Baking this sample to 300°C in vacuum (Figure 3, bottom) still leaves a relatively clean surface with a slight increase in C and S. Again the low energy Fe peak is still evident.

The SIMS spectra in Figure 4 (top) taken from the same sample after heating to 800°C reveal an absence of hydrocarbons, phosphates, Na^+ , K^+ and H^+ ; a reduction in H^- but, in accordance with the Auger spectra, a large increase in S^- .

Exposure of the sample to air (centre) results in a slight increase in hydrocarbons (probably from the warming up of the liquid N_2 cryopanel in the vacuum system) and an increase in H^+ , H^- and OH^- from adsorption of H_2O . The S^- and the SO_2^- have decreased.

The three hour 300°C bake (Figure 4, bottom) removes the hydrocarbons and reduces the H^+ , H^- and OH^- . Some C^- is still evident and S^- , Cl^- and Br^- have increased.

Heating to temperatures greater than 800°C does little to ameliorate the situation.

An alternative cleaning method employs ions produced in a glow discharge to bombard and scrub the internal walls of the vacuum system before installation in the ISR⁷⁾.

For investigation of the discharge cleaning process a miniature stainless steel discharge cell was placed in the SIMS/AES system. As shown schematically in Figure 5 a stainless steel specimen could be rotated from its position integral with the discharge cell wall to a position suitable for analysis via AES or SIMS without breaking the vacuum. Thus the cleaning effect of the argon ion bombardment could be monitored in situ after various ion doses.

Figure 6 (top) shows the state of the specimen, i.e. the chamber wall, before discharge. Only the Auger spectra will be shown.

The centre spectrum is taken from the discharged specimen after an argon ion dose of 1.6×10^{19} ions cm^{-2} and before exposure to air. Further doses did not change the spectrum. One can now clearly see the base constituents of the steel such as Fe, Cr, Ni, Mo and even N. However, the C is still present but in the form of carbide shown by the characteristic peak shape³⁾.

The low energy Fe and Ni peaks are very strong indicating that very little overlying contamination is present.

The result of exposure to air is shown in the bottom spectrum. There one sees that the C contamination, although still visible, is much reduced and the split low energy Fe peak is evident.

The set up for gas discharge cleaning of ISR sections is similar to that shown schematically in Figure 5. With the chamber at 300°C and a continuous flow of argon gas (99.995% pure) at $\approx 10^{-2}$ torr a glow discharge is initiated. Even after baking a vacuum chamber at 400°C for 27 hours the initiation of the argon glow discharge results in a distinct rise in pressure⁸⁾ ($\Delta P \approx 5 \times 10^{-2}$ torr at a base pressure of $\approx 1 \times 10^{-2}$ torr of argon). Mass analysis of this pressure rise revealed

80% H_2 , 15% CO, 1% CO_2 , 3% H_2O and 1% hydrocarbons. Thus the argon ions are desorbing gases which have low desorption rates at $400^\circ C$, namely large binding energies.

In addition to surface gas the stainless steel itself is sputtered and all insulators and windows in such a discharge become coated with a layer of stainless steel. However, because of the geometry, the sputtered material is not removed from the chamber but is merely transported from side to side with only the volatile components being removed. C itself is non volatile and is therefore not completely removed for this reason.

The effect of introducing 10% oxygen into the argon gas used in the discharge is spectacular⁹⁾. An atomically clean surface is obtained after a dose of only 1×10^{18} ions cm^{-2} compared to 1.6×10^{19} ions cm^{-2} with pure argon which even then did not remove all the C.

The before and after argon/10% oxygen discharge Auger spectra are shown in Figure 7. The effect of the oxygen is obviously to oxidise the C forming CO and CO_2 which is then pumped from the system.

In practice the installation of pure argon glow discharged vacuum chambers in the ISR has resulted in negative desorption yields up to ion energies of 2200 eV (≈ 20 A of proton beam)¹⁰⁾. Also the cleanliness of these argon discharged chambers is preserved even after several weeks storage in air prior to installation in the ISR.

No results have yet been obtained on chambers discharged cleaned using the argon/10% oxygen mixture.

The stability of sections treated at $800^\circ C$ in vacuo prior to installation in the ISR has not been as good as might be expected. A test section exhibited positive desorption yields at low beam currents (≈ 2.5 A)⁹⁾. However, the $800^\circ C$ treated surface in this case was not the chamber itself but a stainless steel liner inserted in a normal solvent cleaned chamber. During the 24 hour $300^\circ C$ bakeout it is possible that the liner became contaminated by the outgassing products of the normal vacuum chamber, hence the positive desorption coefficient.

CONCLUSION

It has been shown by means of SIMS and AES that our normal solvent cleaning is unable to provide a contaminant-free stainless steel surface.

The major impurity is C which, from the Auger spectra, appears to be in the form of graphite although SIMS spectra show the existence of carbon compounds and CO is desorbed during the argon discharge cleaning. Heating small samples of stainless steel in vacuo to 800°C followed by exposure to air resulted in a clean surface as seen via SIMS and AES, but a similarly treated liner installed in the ISR gave positive desorption yields at relatively low ion energies. This was probably due to cross contamination from the normal ISR vacuum chamber in which the liner was installed.

A pure argon discharge resulted in relatively clean stainless steel samples in the laboratory, although the C contamination had not been entirely removed. Chambers treated in this manner could be stored in air for several weeks before installation in the ISR where they remained stable under ion bombardment with energies up to 2200 eV.

In the laboratory, investigation via AES shows that an argon/10% oxygen discharge was more efficient in producing a clean C-free stainless steel surface than a pure argon discharge. Such a treatment has not yet been investigated for stability in the ISR.

The provision of an 800°C vacuum furnace capable of accommodating large vacuum chambers is a costly installation whereas the setting up of a gas discharge facility requires only standard vacuum equipment, a suitable DC power supply and a source of gas. In addition, chambers up to 10 m in length even with complicated side arms may easily be discharge cleaned by placing the positive central electrode in a suitable position.

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FIGURE CAPTIONS

- Figure 1 Auger spectra from a 316 L + N stainless steel specimen, as received (top) after solvent cleaning (centre) and after baking at 300°C for 4 hours (bottom).
- Figure 2 Positive and negative SIMS spectra from a 316 L + N stainless steel specimen, as received (top), after solvent cleaning (centre) and after baking at 300°C for 4 hours (bottom).
- Figure 3 Auger spectra from a 316 L + N stainless steel specimen after heating to 800°C for 40 minutes in vacuo (top), after exposing to air (centre) and after a 3 hour 300°C bake (bottom).
- Figure 4 Positive and negative SIMS spectra from a 316 L + N stainless steel specimen after heating to 800°C for 40 minutes in vacuo (top), after exposing to air (centre) and after a 3 hour 300°C bake (bottom).
- Figure 5 Schematic diagram of the miniature discharge cell installed in the SIMS/AES vacuum system showing the sample which can be rotated from its position integral with the wall of the cell to the Auger spectrometer. The SIMS equipment is not shown.
- Figure 6 Auger spectra from a 316 L + N stainless steel specimen before argon discharge in the cell (top), after an ion dose of 1.6×10^{19} ions cm^{-2} (centre) and after exposure to air (bottom).
- Figure 7 Auger spectra from a 316 L + N stainless steel specimen before argon/10% oxygen discharge (top), after an ion dose of 7.6×10^{16} ions cm^{-2} (centre) and after 1×10^{18} ions cm^{-2} (bottom).

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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Fig. 6

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