SURFACE COMPOSITION CHANGES OF STAINLESS STEEL BY EXPOSURE TO ATOMIC HYDROGEN

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ABSTRACT

Stainless steel samples are exposed to atomic hydrogen of thermal energy and the induced surface composition changes are measured with AES. With regard to the discharge cleaning of tokamaks special attention is given to the light impurities C, O, S, N. C as well as O can be removed considerably from the surface, however at the expense of an increased segregation of S. The results are discussed and compared to those obtained by discharge cleaning in tokamaks.

1. INTRODUCTION

Due to the high chemical activity of atomic hydrogen, controlled thermonuclear reaction (CTR) devices enclose a highly reducing atmosphere /1/. Our measurements are especially related to the discharge cleaning of present day tokamaks, which has recently been reviewed by Dylla /2/. Dylla concludes that in optimized cleaning discharges the surface cleaning is purely chemical. This has first been stated by Dietz and Waelbroeck /3/ and has been investigated by this group with the aid of gas analysis methods /4,5,6/.

We intended to investigate in a model experiment the removal of low-Z impurities from first wall materials by incident atomic hydrogen of thermal energy. Surface composition measurement have been performed by Auger electron spectroscopy (AES).

There is only one tokamak, to our knowledge, where discharge cleaning of the present day performance and surface analysis on a sample, which adequately represents the first wall status, has been performed simultaneously. This work has been done by Dylla, Staib et al. on PDX; the discharge cleaning was of the glow discharge type /7/, the sample as well as the first wall material was stainless steel and the surface analysis was performed with AES, XPS and SIMS /8,9/. We will compare our measurements with these PDX-results.

2. EXPERIMENTAL PROCEDURE

Our experimental device has been described in a previous publication /10/, which reports on similar experiments in Inconel, see also /11/. Briefly: In a preparation system, atomic hydrogen is produced by thermal dissociation of molecular hydrogen on a hot tungsten ribbon (2000 K) /12/. The samples are exposed to a given atomic hydrogen fluence and then transferred by vacuum locks to an AES analysis system. The procedure is repeated several times so as to measure the surface composition in dependence on increasing hydrogen fluence.

During exposure the samples are heated by the radiation from the hot tungsten ribbon and in a controlled manner by RF. Sample temperatures of 160°C, 250°C and 400°C have been maintained.

We found that a removal of oxygen from stainless steel was only possible or that it was at least strongly increased, when the walls of the preparation system were cooled. We attributed this to an enlarged pumping speed for certain gases by cryocondensation. Therefore we installed a liquid nitrogen cryotrap in the preparation system. During exposure a hydrogen flux of 10^{-4} or $4 \cdot 10^{-4}$ mbar·l/s through the preparation system was maintained and the outflowing gas was mass analysed. Occasionally, the liquid nitrogen trap was heated up after an exposure in order to identify the formerly pumped gases.

3. RESULTS AND DISCUSSION

The samples were made from stainless steel, German standard number 1.4301, which is equivalent to SS 304. They were mechanically polished and degreased with acetone and methanol just before their installation into the vacuum system. The initial surface composition as measured with AES is given in table 1 (B), along with the specified bulk composition (A) and the concentrations measured after the samples have been exposed to atomic hydrogen and subsequently sputter etched by ion bombardment (C).

		Fe	Cr	Ni	C	O	S	Cl	K	Ca	N
A	min	65	18	8							
	max		21	9	0,3		0,05				
B	min	25	1	3	40	16				1	
	max	30	2	5	50	20	1	1	1	3	1
C (± 1%)		65	13	10	10	2					

Table 1

Chemical composition of stainless steel (atom%)

A: Specified bulk composition. The specifications of Si, Mn, P are omitted because these elements were not detected by AES.

B: Typical ranges of initial surface concentration as measured with AES.

C: Concentrations measured after exposure to a hydrogen atom fluence of 10^{20} cm^{-2} and subsequent sputter etching by argon ions (2 keV, 10^{18} cm^{-2}).

The initial contamination is predominantly made up of carbon and oxygen. Compared to our Inconel results /11/ the concentration of carbon is slightly higher and that of oxygen is higher by a factor of 2. (The composition of Inconel may be derived from that of stainless steel by exchanging the concentrations of Fe and Ni). The PDX stainless steel sample exhibited a similar oxygen content (14%) but considerably more carbon (80%), which was attributed to a homogeneous hydrocarbon layer /9/. Data (C) of table 1 will be discussed later.

Before exposing to atomic hydrogen the samples were heated in vacuum to the desired temperature and the same was done in molecular hydrogen at the operating pressure. These procedures did not change the impurity concentrations on the surface significantly. However, the Cr concentration increased with increasing temperature, e.g. at 400°C from 1% to above 20% in half an hour. In this respect stainless steel does not differ from Inconel /11/.

The exposure to thermal atomic hydrogen causes, briefly 1) a fast removal of

carbon, 2) a slow removal of oxygen, 3) segregation of sulphur and possibly nitrogen and phosphorous.

3.1 CARBON

Figure 1 shows the carbon concentration versus the hydrogen fluence for the different sample temperatures. At the lower ones (160°C, 250°C) the carbon concentration decreases fast to a minimum of some atomic %. At 160°C the decay is exponential down to a concentration of 3%, at 250°C this holds down to around 20%. To this exponential part of the curves an apparent cross section might be attributed, which quantifies the removal of a carbon atom by an impinging hydrogen atom. The evaluated cross section are around $1 \cdot 10^{-7}$ cm^2 and fit well to the corresponding data that we found for Inconel /11/.

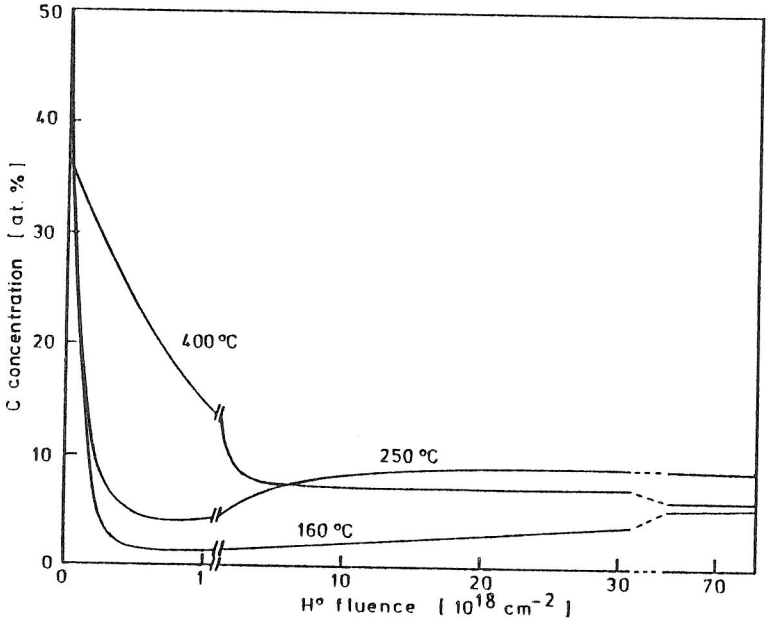

Fig.1. Carbon concentration versus atomic hydrogen fluence at different sample temperatures. Scale enlarged at low fluences.

There is nearly general consensus in the cleaning discharge literature, see e.g. /2,13/, that the removal of surface carbon predominantly proceeds via hydrogenation, especially to methane. We have discussed this with reference to non-discharge literature /11/. Though methane enriches significantly in the outflowing gas during an exposure in our apparatus (also higher hydrocarbons are identified) we cannot identify the reaction products from the sample because they are masked by those from the hot tungsten ribbon. This is a drawback of our simple atomic hydrogen production scheme by thermal dissociation.

At 400°C sample temperature the surface carbon decay is comparatively slow. Furthermore, the carbon AES peak shape is a mixture of the graphitic and carbidic peak shapes, whereas it is purely graphitic along the steeply falling

carbon lines for 160°C and 250°C. The carbon curves differ significantly at higher hydrogen fluences starting from around 10^{18} cm^{-2}. At 160°C sample temperature, there is a slow continuous increase, a flat maximum appears at 250°C and at 400°C there is a slow continuous decrease. In this range of fluences the carbon AES peak shape is purely carbidic.

We ascribe these characteristics to a flux of carbon from the bulk to the surface, which increases with the sample temperature. By sputter etching the samples after finishing the exposure to hydrogen, we find a negative carbon concentration gradient from the bulk to the surface down to a sputter depth corresponding to $1...2.10^{17}$ ions/cm^2 (argon, 2 keV). The final concentrations after sputter etching to 10^{18} ions/cm^2 are given in table 1. The still remarkable concentrations of carbon (10%) and oxygen (2%) have not been found for Inconel, where a similar sputter etching revealed the bulk concentration of the metals within the specification of Inconel.

Finally, we note that the carbon concentrations that we achieved by exposure to atomic hydrogen are consistently lower than that of the PDX sample after discharge cleaning (20%) /9/.

3.2 OXYGEN

The removal of oxygen from the stainless steel surface, as shown in fig. 2, was achieved with the cryotrap held at liquid nitrogen temperature. At hydrogen fluences of the order $10^{16}...10^{17}$ cm^{-2} there is a hump in the oxygen concentration curve, which cannot be resolved in the drawing. The removal rate of oxygen is low compared to that of carbon, however the removal is continuous. The rate increases raising the sample temperature from 160°C to 250°C. At 400°C the oxygen decay is similar to that at 250°C at lower fluences, but it is very slow at higher fluences, the concentration levelling off at 6%.

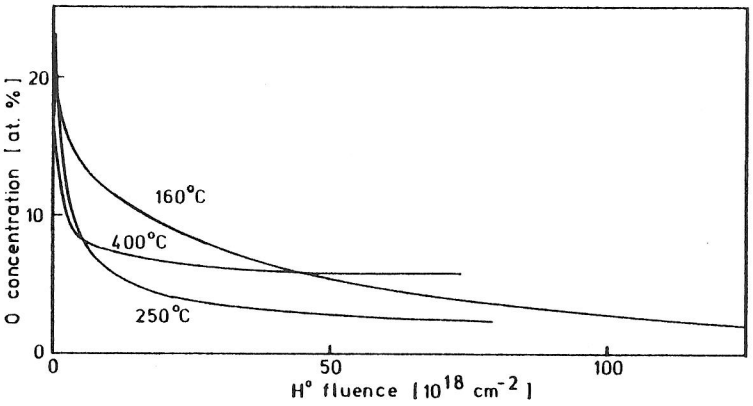

Fig. 2. Oxygen concentration versus atomic hydrogen fluence at different sample temperatures.

Compared to the PDX sample exhibiting 35% oxygen after discharge cleaning, more than an order of magnitude lower oxygen concentrations (~2%) have been achieved in our experiment, however at the expense of an increased sulphur contamination, see below.

The difference between the PDX and our results might have simple reasons, e.g. a different pretreatment of the samples, i.e. a different preoxidation, or different fluences applied. However, there might also be a basic difference in the experimental procedure which influences the chemistry on the surface, e.g. the pumping speed acting on the reaction products or the kinetic energy of the hydrogen ions in PDX. In any case, it is shown that the oxygen can be removed by thermal atomic hydrogen. It is not necessary to provide active hydrogen species of some 100 eV in order to remove oxygen rather completely, as has been stated by Dylla /2/. However, we must be aware of the sulphur contamination.

Concerning the temperature dependence, Waelbroeck et al. /4,5/ report a maximum oxygen removal rate at 400°C wall temperature, analysing the gas flow through the pump during a combined RF glow discharge. This is not reflected in our measurement at 400°C. Either synergistic sputtering (glow discharge voltage around 400 V) is mandatory at 400°C and/or there is a flux of oxygen from the bulk to the surface. The latter could also explain the huge quantities of oxygen of 10...100 monolayers that are reported to be pumped out during discharge cleaning /7,4/.

As stated above the reaction products which carry the impurities of the sample cannot be identified with confidence in our experiment. However, from the experiments it is evident that the oxygen carrying reaction product is pumped by the cryotrap and the only oxygen carrying gas significantly evolved from the cryotrap during warming up after an exposure is water. We do not detect carbon monoxide, which is often reported as a oxygen carrying reaction product during discharge cleaning /4,7,14,15/.

3.3 OTHER IMPURITIES

Some light impurities accumulate on the surface during exposure. This effect is very pronounced for sulphur and occurs also for nitrogen at high temperature (400°C) and for phosphorus at high fluences. During the present experiments on stainless steel the phosphorus concentration did not exceed 1%. Former experiments on Inconel revealed a more than 50% substitution of sulphur by phosphorus at very high atomic hydrogen fluences of the order 10^{21} cm^{-2}, with the sum of the concentrations of both elements remaining nearly constant at 20%.

Similarly, the summarized concentrations of oxygen and sulphur (160°C, 250°C) and those of oxygen, sulphur and nitrogen (400°C) are plotted in fig. 3 versus the hydrogen fluence. Except for a hump in the 250°C curve at lower fluences, the sum of the concentrations is near 20% over about 3 orders of magnitude of hydrogen fluence. Possibly there is a fixed number of adsorption sites on the surface which are occupied either by oxygen or by sulphur and at high temperature (400°C) also by nitrogen. A site competition of oxygen and sulphur as segregants has been observed both on the free surface and at grain boundaries of an iron alloy, and also a site competition between sulphur and phosphorus on various materials including nickel and stainless steel has been reported /16/.

In our experiments sulphur segregates at temperatures, at which a thermal segregation is not expected. We assume that the segregation of sulphur is a chemisorption induced due to a hydrogen coverage on the surface /11,17/.

On the PDX sample /9/, chlorine, sulphur and nitrogen increase from a total of 1% to a total of 5% during discharge cleaning. Adding the oxygen concentration

(35%) the PDX sample arrives at a total impurity content, carbon excluded, of 40% compared to a corresponding concentration of some 20% in our experiment.

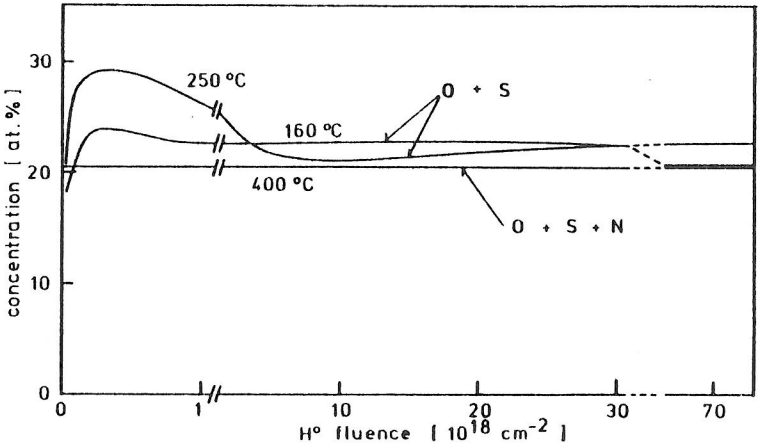

Fig. 3. Added concentrations of O and S (sample temperature 160°C, 250°C) and of O, S and N (sample temperature 250°C) versus atomic hydrogen fluence. Scale enlarged at low fluences.

4. CONCLUSIONS

Analysing our results and comparing them to what is reported on dicharge cleaning we conclude: 1.) The surface of the first wall of a CTR device which is to be cleaned from light impurities has to be considered in context with the bulk, because there may be a flux of impurities from the bulk to the surface due to thermal and chemisorption induced segregation. 2.) One has to be aware of synergistic effects of the chemical activity of atomic hydrogen on the one hand and the kinetic energy of the hydrogen ions in a glow discharge on the other. McCracken and Stott state in a review on tokamak plasma-surface interaction, "that the understanding of discharge cleaning is probably no less difficult than the understanding of normal tokamak discharges" /13/.

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