GA–A26751

COLLATERAL EFFECTS OF THERMO-OXIDATION ON DIII-D IN-VESSEL COMPONENTS AND FIRST RESULTS FROM THE IN SITU OXIDATION IN DIII-D

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JULY 2010

GENERAL ATOMICS

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This is a preprint of a paper to be presented at the Nineteenth International Conference on Plasma Surface Interactions, May 24-28, 2010, in San Diego, California, and to be published in the *Proceedings.*

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Work supported in part by
the U.S. Department of Energy under
DE-AC52-07NA27344, DE-FC02-04ER54698
and DE-AC05-00OR22725

GENERAL ATOMICS PROJECT 30200
JULY 2010

GENERAL ATOMICS

ABSTRACT

Thermo-oxidation has the advantage of being able to remove tritium from carbon-based codeposits on all internal surfaces without mechanical intervention into the torus. (i) *Ex situ* experiments: In preparation for a thermo-oxidation experiment in DIII-D, the collateral effects of thermo-oxidation were studied for a variety of in-vessel components in *ex situ* laboratory experiments. Specimens were oxidized in 10 Torr (~1.333 kPa) dry air at a specimen temperature of 350°C (623 K) for 2 h. After oxidation, components were examined for visual change. For some of the components, surface analysis was also performed before and after oxidation. (ii) DIII-D oxidation: Initial assessment of the impact of *in situ* oxidation in DIII-D was based on operational tests and visual inspection of materials specimens inserted into the vessel on stalks. Tokamak systems tested (wave heating components, cryopump systems) worked as expected during the subsequent plasma recovery.

I. INTRODUCTION

Tritium retention in carbon-based codeposits may be one of the important contributors to the in-vessel tritium inventory in future tokamaks containing carbon-based plasma-facing materials. Thermo-oxidation is highly effective at removing codeposits, and can release tritium from shaded areas and tile gaps without mechanical intervention into the torus. In the event that some carbon plasma-facing components are required in ITER during DT operations, thermo-oxidation, or a combination of plasma-oxidation and thermo-oxidation may be a viable technique to keep the tritium inventory within the license limit of 700 g in the torus [1].

The effectiveness of thermo-oxidation to remove deuterium from D-containing codeposits formed in several tokamaks (e.g., TFTR, DIII-D and JET) has been demonstrated in laboratory test stand experiments, e.g., Refs. [2–9]. These lab experiments have demonstrated that the lower limit of temperature and oxygen partial pressure for achieving effective D removal from tokamak codeposits are in the range $300°-350°C$ and 10–100 Torr, respectively. Some oxidation experiments have also been performed in actual tokamaks TEXTOR [1] and HT-7 [11], but these were done at low oxygen pressures (5–200 mTorr) [10,11] and a significant fraction of the injected oxygen was absorbed on the walls [10]. Nevertheless, the reaction products (CO, CO_2 and D_2O) observed in lab experiments [12,13] were also seen in TEXTOR [10].

In order to demonstrate the safety and effectiveness of thermo-oxidation in a "more realistic" tokamak environment, an *in situ* experiment has now been carried out in DIII-D. This was the first controlled oxidation experiment in any tokamak within the effective temperature range, and at pressures >1 Torr. The DIII-D *in situ* oxidation experiment was performed at $350°C$ with a 9.5 Torr He-O_2 mix (80% He, 20% O_2) for 2 hours. The primary goal of the experiment was to determine the impact of thermo-oxidation on plasma recovery and to document any collateral effects on in-vessel components. As will be discussed later in this paper, the initial assessment was primarily done by operational tests and visual inspection. In addition, post-oxidation analysis of some tiles removed from DIII-D is being performed using nuclear reaction analysis (NRA) at Sandia National Laboratories, Albuquerque and laser thermal desorption spectroscopy (TDS) at the University of Toronto Institute for Aerospace Studies (UTIAS) to determine the amount of deuterium removed from tile surfaces; these results are to come and will be presented elsewhere.

Earlier collateral-effects studies of selected DIII-D in-vessel components were performed by Fitzpatrick, et al. [14] in pure oxygen at $350°C$ and 2 and 15 Torr O_2

pressure. At 15 Torr, copper wires developed an exfoliating oxide. At 2 Torr O_2 pressure, copper components developed a thin oxide layer but did not flake. Non-copper components, including structural, mechanical and diagnostic components, were not affected by oxidation at 2 Torr O_2 pressure. The current study, performed in a different oxidation apparatus set up by LLNL at General Atomics (GA), expands the range of components, and uses dry air (10 Torr), enabling us to confirm that oxidation in air should be the same as in pure O_2 as long as the O_2 partial pressure is the same. Furthermore, oxidation in air should also be similar to the in situ oxidation experiment in DIII-D with a He-O_2 mix; in both cases oxygen is the only reactive gas.

II. EXPERIMENT

A. Specimens

Components for testing were selected by DIII-D researchers on the basis of their potential vulnerability to thermo-oxidation. Particular attention was paid to copper components, as earlier work [14] showed that copper readily oxidizes and develops a thin ($<1\ \mu$m) layer of CuO, which may flake off with friction. Components tested included electron cyclotron heating (ECH) components (waveguide and mirror), ion cyclotron heating (ICH) components (copper joints and Faraday shield), a molybdenum Langmuir probe, a cryopump flame-spray surface, and Macor™ and alumina materials. The complete list is presented in Table I. The components were spare or surplus parts; none had been previously exposed to plasmas in DIII-D.

Table I. Summary of oxidation results. All tests performed at 350°C, 10 Torr dry air for 2 hours.

	Component	**Material**	**Methodology**	**Observations**
Plasma heating components	ECH waveguide	Ag-coating SS	Visual inspection	No visible change
	ECH mirror	OFHC copper	Visual inspection	Mild darkening of surface
	ICH joints	Cu	Visual inspection	Heavy oxidation and flaking
	ICH Faraday shield	Cu-electroplated Inconel	EDS, SEM, visual inspection	Black CuO layer formed; no flaking even with friction
Diagnostics	Langmuir probe	Molybdenum	Visual inspection	Slight colour change
	Ionization gauge filament	Tungsten	Visual inspection	No visible change
Cryopump materials	Cryopump shield coating	Metco 55 on Inconel™	Visual inspection	Slight darkening; no flaking
Other materials		Macor™	Visual inspection	No visible change
		Alumina	Visual inspection	No visible change
		Aluminium	Visual inspection	Slight whitening
		Boron nitride	Visual inspection	No visible change
		SFL6 glass	Visual inspection	No visible change

B. Pre- and post-oxidation characterization of specimens

Particular copper surfaces were analyzed both before and after oxidation with energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM). EDS performed at 20 kV provides the atomic composition of the surface within 2–3 μm. SEM images were obtained with 1000× magnification. Other specimens were examined for visual changes.

C. Oxidation facilities and procedure

The *ex situ* oxidation experiments reported here were performed at GA in a 0.457 m stainless steel (SS) vacuum chamber, pumped with a turbomolecular pump. The specimens were enclosed in a double-walled SS box placed within the vacuum chamber and were heated by a radiant heater bulb; this arrangement helped to reduce heat losses from radiation. The temperature was measured using a K-type thermocouple, with the junction sandwiched between the specimen and its support. After reaching 350°C, the chamber was isolated from the pumps, and dry air was admitted to a pressure of 10 Torr (2 Torr O_2 partial pressure). The pressure was measured using a Barotron™ capacitance manometer. The pressure and temperature were maintained for 2 hours and then the system was pumped down and permitted to cool.

The procedure differs from the earlier oxidation study performed at UTIAS [14] in three ways: (i) here we used 10 Torr dry air, instead of 2 Torr pure O_2; (ii) there is no flow of air in the present experiment, while continuous flow of O_2 was used in [14]; (iii) here only the specimen was heated by a radiant heater from within the chamber, compared with the whole chamber being heated in [14] using external heaters.

III. RESULTS

Most components were unaffected by oxidation in air, as was also the case with pure oxygen [14] (Sec. III.A). The exceptions were Cu components, which developed CuO layers of varying thickness (up to 1 μm) (Sec. III.B and Table II). SEM photos of a Cu gasket, before and after oxidation, are shown in Fig. 1. The oxidation of Cu was determined to be manageable: for many surfaces, the presence of CuO was of no concern since the oxide layer did not flake. For the ECH mirrors, pulsing of radio-frequency power was expected to clean the surfaces, but these mirrors were scheduled for replacement in DIII-D regardless. The ICH antenna was scheduled for removal and plating with nickel; the formation of the oxide layer merely adds a “cleaning” step to that process (Sec. III.B).

Table II. Summary of EDS results on copper components. All tests performed at 350°C, 10 Torr dry air for 2 hours.

Component	Material	State	% Cu	% O	% C
Gasket	OFHC Cu	Pre-oxidation	67.52	5.60	26.88
		Post-oxidation	27.37	45.14	24.10
Faraday shield	Cu-electroplated Inconel™	Pre-oxidation	72.21	4.02	23.77
		Post-oxidation	40.40	47.59	12.01

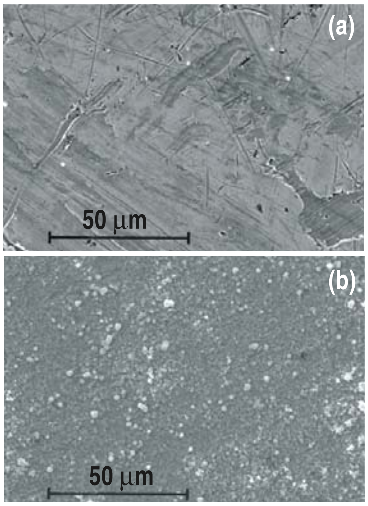

Fig. 1. *Ex situ* experiment in the LLNL chamber at GA: SEM pre-oxidation (a) and post-oxidation (b) photos of Cu gasket.

A. Components unaffected or slightly affected by oxidation

Electron Cyclotron Heating. An OFHC copper mirror with a 'smooth' surface darkened slightly by oxidation. Unlike "unpolished" copper components, the oxide layer was very thin as evidenced by only a minimal colour change, and did not flake.

A silver-coated, SS waveguide was also tested. There was no visual change to the silver surface, and only a slight yellowing of the SS cross-section was seen where the waveguide was cut. These results are consistent with those reported in [14].

Langmuir Probe Wires. A molybdenum Langmuir probe wire changed colour only slightly by oxidation. Unlike the Glidcop™ and OFHC copper Langmuir probe wires tested in [14], whose oxide layers could be removed with friction, the oxide remained firmly fixed to the molybdenum wire.

Cryopump Shield Coating. Under oxidation, the surface of a Metco 55 copper *flamespray* coating on Inconel™ turned dark grey, but the oxide layer did not flake, even with friction (Fig. 2). When examined under an optical microscope, the surface appeared as an aggregate of small, smooth spheres, ~0.1 mm in diameter. This result is consistent with those for polished copper surfaces (e.g., the ECH mirror), which were found to oxidize less than unpolished copper surfaces.

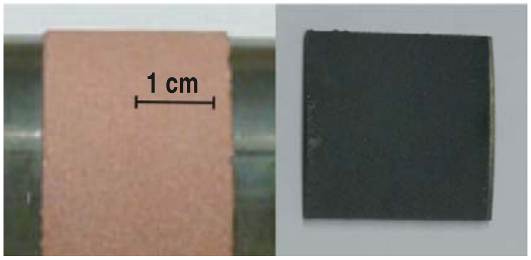

Fig. 2. METCO55 cryopump shield flamespray specimen subjected to *ex situ* oxidation in the LLNL chamber at GA: pre-oxidation (left), post-oxidation (right). Copper portion has turned dark grey. Post-oxidation specimen was cut from larger specimen on left.

Other Materials. Macor™, alumina, boron nitride, and SFL6 glass material coupons were tested; no visual changes were observed after oxidation. A tungsten ionization gauge filament showed no visible change. An aluminium block was tested, and whitened slightly.

B. Components affected by oxidation

Two components from the ICH system were affected by oxidation. A specimen of the ICH Faraday shield (Cu-electroplated Inconel) developed a thick, black layer of CuO after oxidation, which was strongly adhered to the copper surface beneath. ICH bellows and joints, also copper, developed a thick, flaking coating of oxide. The severity of oxidation in the actual DIII-D component is expected to be much less than that observed in these 350°C tests, since the ICH antenna only reached 285°C during previous 350°C vacuum-bakes of the vessel. Nevertheless, a plan was developed to clean the oxide coating from these components. Since they are scheduled to be plated with nickel, the removal of the oxide will be easily achieved by wiping with 10% HCl solution. These results, obtained using 10 Torr dry air, are consistent with those obtained at UTIAS [14] using 2 Torr pure O_2 at the same temperature.

C. Influence of carbon on oxidation of copper

The University of Toronto collateral effects experiments were performed in a chamber which has previously been extensively used for studies of oxidative removal of carbon codeposits from tokamak tile specimens. Consequently, C impurities had already been deposited on the chamber walls. The first set of collateral experiments performed in this chamber showed evidence of enhanced oxidation on a Cu gasket [14] [Fig. 3(a)]. The Cu oxidation experiments were then repeated in a brand new SS chamber with no prior C exposure and the results showed only minimal evidence of oxidation, with minimal colour change. To test the hypothesis that carbon promotes the oxidation of copper, the C-contaminated chamber was cleaned by etching the SS walls with 30% HCl solution. In the experiment that followed, the copper gasket oxidized only minimally [Fig. 3(b)]. Subsequent oxidations of carbon tiles resulted in copper again oxidizing heavily, changing colour to red-grey [Figs. 3(c) and 3(d))].

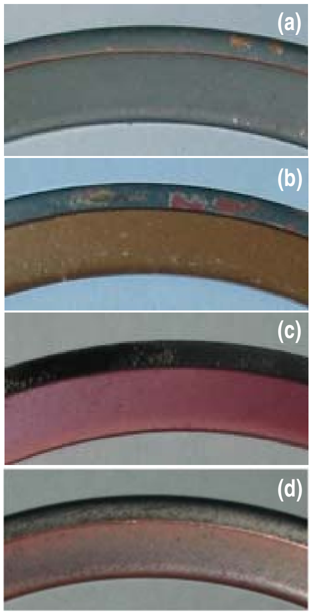

Fig. 3. *Ex situ* experiment at U. Toronto demonstrates that exposure to carbon influences severity of copper oxidation. (a) Copper gasket oxidized in chamber previously baked with carbon many times. (b) Gasket oxidized in cleaned system (walls etched with 30% HCl). (c) Gasket oxidized in system with carbon-deposited specimen. (d) Gasket oxidized in system with co-deposited CFC tile.

D. Preliminary assessment of the effect of *in situ* oxidation in DIII-D

Preliminary results suggest that the impact of in situ oxidation on DIII-D components was less severe than expected from the *ex situ* lab results. Material witness specimens were inserted into the vessel on stalks and were removed after the oxidation for analysis and visual inspection. Thermocouples attached to the various material specimens showed they reached 360°C, exceeding the 350°C target wall temperature. Residual gas analysis (RGA) showed that $>80\%$ of the oxygen was consumed throughout the first 1.75 hours of the experiment; the vessel was then evacuated and filled with a subsequent 9.5 Torr charge of 80% He/20% O_2 for the remaining 15 minutes. The trends in the RGA signals indicate that most of the oxygen consumed was transformed to CO_2, CO and D_2O, in agreement with laboratory oxidation results [12,13]. A strong H_2O signal was also observed by the RGA after the oxidation, perhaps due to the additional heating to vessel surfaces from convective flow.

Copper material specimens mounted in DIII-D showed modest oxidation less severe than in *ex situ* experiments. Visual inspection of a copper mirror specimen did not indicate darkening, as had been observed in *ex situ* experiments, although the mirror appeared qualitatively to be less reflective (Fig. 4). A mini copper gasket darkened slightly (Fig. 5), but did not turn gray as expected from *ex situ* experiments. A METCO55 (99% Cu flamespray) coupon, similar to the coating used on the cryopump shield, also darkened less severely than expected. The reduced severity of the oxidation may be due to the consumption of oxygen during the experiment, which reduced the partial pressure of oxygen available as compared to the *ex situ* tests.

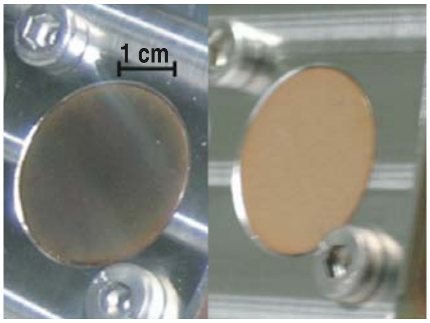

Fig. 4. Copper mirror specimens inserted in DIII-D during *in situ* oxidation: pre-oxidation (left), post-oxidation (right). The mirror is similar in colour, but qualitatively appears to be less reflective after oxidation.

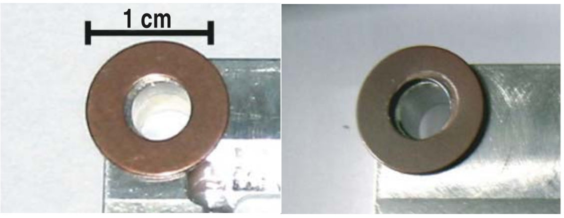

Fig. 5. Copper gasket inserted in DIII-D during *in situ* oxidation: pre-oxidation (left), post-oxidation (right). The copper has darkened slightly by oxidation.

Visual inspection of SS witness specimens, a Grafoil™ specimen, molybdenum mirrors, and thermocouples showed no obvious changes. Six additional graphite tiles were also mounted on stalks and underwent oxidation in DIII-D. The tiles had been previously exposed to DIII-D plasmas in previous campaigns and were pre-characterized for ^{13}C and D content, using the methods described in [15]. Post-oxidation surface analysis is planned for the tiles and SS witness specimens.

The best indicator of collateral impact is the performance of tokamak systems. Preliminary results show that recovering good plasma performance requires conditioning efforts similar to those following a cold vent to atmosphere. The ECH and ICH systems performed normally after the oxidation, although spectroscopy showed the presence of copper and oxygen in the plasma when these systems were first engaged. These impurity levels declined in the subsequent plasma shots. The cyropump pumping speed was unaffected. A detailed assessment of the plasma recovery will be published elsewhere.

IV. SUMMARY

Ex situ oxidation tests: Thermo-oxidation of a variety of potentially vulnerable components and materials used in DIII-D resulted in little or no change for most specimens. The notable exception is copper, which developed a thin coating of oxide. The CuO layer varied between component specimens; the cryopump shield coating was barely affected, while others (e.g., ICH joints) developed a flaking layer of CuO, ~1 μm thick. The results, for 350°C and 10 Torr dry air, are consistent with earlier UTIAS results for the same temperature, but 2 Torr pure O_2 [14]. The results support our previous recommendation [14] for the need to carefully choose copper components for future tokamaks which may need thermo-oxidation for tritium removal. The formation of copper oxide, possible flaking of the oxide layer, or its hydrogenic reduction to copper dust must not impede the design goals.

In situ oxidation in DIII-D: Preliminary results of the DIII-D *in situ* oxidation experiments show the oxidation of copper surfaces was less severe than expected from *ex situ* experiments. This may be due to the consumption of oxygen by chemical reactions with codeposits during the experiment. Residual gas analysis confirms that most of the oxygen was converted to CO_2, CO and D_2O, in agreement with previous lab results [12,13]. Copper surfaces darkened slightly, but not to the severity observed in *ex situ* experiments and they did not flake. Visual inspection shows no change to SS witness coupons, thermocouples, or the Grafoil specimen.

The best indicator of collateral impact is that the functionality of the components was unchanged; the ECH, ICH and cryopump systems worked as expected during the subsequent plasma recovery.

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ACKNOWLEDGMENTS

This work was supported by Collaborative Research Opportunities Grant from the National Sciences and Engineering Research Council of Canada and the US Department of Energy under DE-AC52-07NA27344, DE-FC02-04ER54698, and DE-AC05-00OR22725. We thank Dr. D. Wall of GA for EDS analysis and SEM images, and Mr. C. Perez for his work on the experimental facility at U. Toronto.