General and crevice corrosion study of the in-wall shielding materials for ITER vacuum vessel

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Abstract. Vacuum vessel In-Wall Shield (IWS) will be inserted between the inner and outer shells of the ITER vacuum vessel. The behaviour of IWS in the vacuum vessel especially concerning the susceptibility to crevice of shielding block assemblies could cause rapid and extensive corrosion attacks. Even galvanic corrosion may be due to different metals in same electrolyte. IWS blocks are not accessible until life of the machine after closing of vacuum vessel. Hence, it is necessary to study the susceptibility of IWS materials to general corrosion and crevice corrosion under operations of ITER vacuum vessel. Corrosion properties of IWS materials were studied by using (i) Immersion technique and (ii) Electro-chemical Polarization techniques. All the sample materials were subjected to a series of examinations before and after immersion test, like Loss/Gain weight measurement, SEM analysis, and Optical stereo microscopy, measurement of surface profile and hardness of materials. After immersion test, SS 304B4 and SS 304B7 showed slight weight gain which indicate oxide layer formation on the surface of coupons. The SS 430 material showed negligible weight loss which indicates mild general corrosion effect. On visual observation with SEM and Metallography, all material showed pitting corrosion attack. All sample materials were subjected to series of measurements like Open Circuit potential, Cyclic polarization, Pitting potential, protection potential, Critical anodic current and SEM examination. All materials show pitting loop in OC2 operating condition. However, its absence in OC1 operating condition clearly indicates the activity of chloride ion to penetrate oxide layer on the sample surface, at higher temperature. The critical pitting temperature of all samples remains between 100° and 200°C.

1. Introduction
One of the key issues of study the corrosion attack on IWS materials during operation phase of ITER vacuum vessel. As IWS block assemblies will be placed between shells of vessel and will be immersed in water which will be used for baking and cooling of vacuum vessel. The IWS block assemblies comprises of number of plates stacked together with spacers in between the plates. Thus there will be numbers of crevices will be form and it may be cause rapid and extensive crevice corrosion. Also there will be high possibility of galvanic corrosion due to various IWS materials in same electrolyte [1]. In addition local accumulation of the aggressive compounds like chloride and other anions might be higher for ITER condition due to the different operational modes [2].
The schematic diagram of IWS assemblies between inner shell and outer shell of vacuum vessel are shown in figure 1.

![Schematic diagram of In-wall shielding block between double shell vacuum vessel](image)

**Figure 1 schematic of In-wall shielding block between double shell vacuum vessel**

The materials of IWS that used for corrosion study:

1. Austenitic steel 316L(N) – IG – ribs, brackets, washers, fixing plates;
2. Borated steel 304B7 (~ 1.75-2.25 % wt. B) – plates for inboard region;
3. Borated steel 304B4 (~ 1 – 1.24 % wt. B) – plates for outboard region;
4. Ferritic steel 430 – plates for outboard region;
5. Austenitic steel XM-19 (bolts designation B8R) – bolts

The corrosion properties of IWS materials were studied by (1) Immersion technique and (2) Electrochemical Polarization techniques

## 2. Corrosion study

### 2.1. Corrosion study by Immersion method

Three custom designed Autoclaves from SS 316L material were used to conduct this study. The eight test coupons of each material were placed in autoclaves and heated to three different operating conditions for a specific time period as per table-1. The Operating cycle were repeated for 5 times in a sequential manner [4].

|   | OC1 | OC2 | OC3 |
|---|-----|-----|-----|
| 1 | Water at a temperature of 100 °C and the pressure of 1.1MPa | Water at temperature of 200 °C and the pressure of 2.4MPa | Draining out water from the autoclave and then Using hot Nitrogen gas at 150 to 200 °C |
| 2 | 5 Days | 5 Days | 5 Days |

- OC1 = Water temperature 100° C, pressure 1.1 MPa
- OC2 = Water temperature of 200° C, pressure 2.4 MPa.
- OC3 = Hot Nitrogen gas 150-200 degree C after draining out the solution from the autoclave

![Schematic of test autoclave](image)

**Figure 2 Schematic of test autoclave**

### 2.1.1. Testing procedure for Immersion test in W1000 HP water chemistry
These tests were carried out with the Chloride concentration level of 1000ppb and Hydrogen Peroxide of 2ppm (referred as W1000HP water) in each of the autoclaves. The test coupons of IWS sample materials were subjected to a series of examinations before and after the Immersion Test as follows:

- Loss or gain of weight of sample
- Micro structural analysis using optical microscope and SEM
- Analysis of elements on area to be covered by crevice former before the test
- Analysis of elements over corrosion affected area.
- Measurement of surface profile and hole diameter of test coupons near the crevice location before and after the test
- Material hardness of each sample for (i) as received and (ii) after preparing and (iii) after completion of test
- Oxygen concentration in water was measured before and after each cycle of OC1 and OC2.

The test specimens clamped by XM-19 crevice former and M10 nuts at the torque of 80 N-m. All the crevice assembly was kept on their respective stand and placed the stand into their respective autoclaves. Water chemistry of W1000HP was checked before starting the experiment, prior to filling the water into the autoclaves. To minimize the oxygen concentration and chloride concentration in water, Argon gas was purged for 48 hours at 150cm³/min before start of testing (temperature rising of autoclave). The water chemistry achieved as described in table 2.

| Required Operational Parameters       | Test Result of initial water        | Test results after Argon purging |
|--------------------------------------|------------------------------------|---------------------------------|
| Conductivity (at 20°C) µS/cm          | At 27.8°C, 199.800 µS/cm           | At 27.8°C, 199.800 µS/cm        |
| Oxygen, µg/kg                        | 6500 µg/kg                         | 1080 µg/kg                      |
| Chloride µg/kg                       | 5800 µg/kg                         | 1000 µg/kg                      |
| Sulphate, µg/kg                      | 200 µg/kg                          | 200 µg/kg                       |
| Copper, µg/kg                        | Not Detectable                     | Not Detectable                  |
| Iron, µg/kg                          | 15000 µg/kg                        | 15000 µg/kg                     |
| Hardness (Ca, Mg etc.) µg/kg         | 20900 µg/kg                        | 20900 µg/kg                     |
| Oil products, organic, µg/kg         | Nil                                | Nil                             |
| pH at RT                             | 6.6                                | 6.6                             |

All the autoclaves were then cycled through following Operating conditions described in table 3.

| Autoclave | Immersion Test Sample | No. of Samples | Operating Conditions |
|-----------|-----------------------|----------------|----------------------|
| 1         | ITS 1: SS 304B4 + CF1 + CF1 | 8              | OC 1 OC 2 OC 3     |
| 2         | ITS 2: SS 304B7 + CF1 + CF1 | 8              | OC 1 OC 2 OC 3     |
| 3         | ITS 3: SS 430 + CF1 + CF1  | 8              | OC 1 OC 2 OC 3     |

2.1.2. Observations
(a) Material hardness of test samples
Material hardness was measured at the surface of the specimen with 2.5 mm diameter tungsten ball at 187.5 kg load. Two samples were taken before the Immersion test to generate the base line data and compared with the hardness after test.
Table 4 Material hardness of samples

| Material | Average Hardness Before Immersion Test (HB 2.5/187.5) | Average Hardness After Immersion Test (HB 2.5/187.5) |
|----------|------------------------------------------------------|------------------------------------------------------|
| SS 304B4 | 176                                                  | 190                                                  |
| SS 304B7 | 195.5                                                | 221                                                  |
| SS 430   | 145                                                  | 167                                                  |

(b) Weight loss/gain measurement
Each sample was weighed before and after the test to find out % weight loss due to corrosion. The marginal weight loss observed in SS 430 coupon material and hence the corrosion rate calculated by following formula.
Rate of corrosion (mm/year) = (87480 x W) / ( A x t x D)
Here W = Weight loss, A = Area under crevice, t = time of exposure and D = Density
The corrosion rate calculation is shown in table 5.

Table 5 Weight measurement of samples

| Specimen No. | Cross Sectional Area of entire Specimen (cm2) | Weight loss (gm) | Corrosion Rate in mm/Yr | Average Corrosion Rate in mm/Yr |
|--------------|------------------------------------------------|------------------|--------------------------|----------------------------------|
| 0            | 37.441                                          | 0.0156           | 0.00261                  |                                  |
| 5            | 37.572                                          | 0.0155           | 0.00259                  |                                  |
| 6            | 37.609                                          | 0.0153           | 0.00255                  |                                  |
| 7            | 37.696                                          | 0.0153           | 0.00254                  |                                  |
| 8            | 37.572                                          | 0.0152           | 0.00254                  |                                  |
| 9            | 37.528                                          | 0.0175           | 0.00293                  | 0.00267                          |
| 10           | 37.572                                          | 0.0177           | 0.00296                  |                                  |
| 11           | 37.528                                          | 0.0159           | 0.00266                  |                                  |

(c) Optical Microscopy
The samples removed from the experiment were followed by diamond polishing and optical observation at both side. The crevice corrosion has found on both sides of samples. Following table 6 shows the images of crevice at 100X and 200X magnification showing presence of crevice corrosion.

Table 6 Microscopic images of samples

|        | SS 304 B4 | SS 304 B7 | SS 430 |
|--------|-----------|-----------|--------|
| 100x   | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| 200x   | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |

(d) Scanning Electron Microscopy (SEM)
The SEM analysis was carried out on samples of each IWS materials before immersion which considered as base line data. After test, two samples of each material were polished by 600 grit polishing paper and followed by SEM analysis. Following table 7 shows images of SEM analysis.
(e) Microstructure Examination
Microstructure examination was carried out at sample surface for all the materials to collect the evidences of the corrosion under optical metallography. The testing was carried out on two samples of each material to collect the baseline data of each material type. Two samples from each material were considered for microstructure after the test from top and bottom position in the autoclave as per the testing procedure.

| Table 7 SEM images of samples |
|--------------------------------|
| Before test | SS 304 B4 | SS 304 B7 | SS 430 |
| After Test | ![Image](image1) | ![Image](image2) | ![Image](image3) |

| Table 8 Microstructure of samples |
|----------------------------------|
| Before test | SS 304 B4 | SS 304 B7 | SS 430 |
| After Test | ![Image](image4) | ![Image](image5) | ![Image](image6) |

(f) Conclusion of Immersion testing:
- On visual observation, along with SEM and metallography of the crevice former area and nut tightening area of the specimen of all material type showed pitting corrosion attack for W1000HP water condition. Therefore, immersion test and observation was repeated for operating condition with W100HP water and found that all material specimens showed pitting attack.
- The materials SS304 B4 and SS 304 B7 showed marginal weight gain after crevice corrosion experiment. The marginal weight gain is due to a thin layer of oxidation on the surface after exposure.
- SS 430 material after crevice corrosion experiments showed weight loss of very negligible quantity indicating that the material in a given environment showed mild effect of general corrosion. The corrosion rate is calculated as 0.00267 mm/year.

2.2. Corrosion study by Electro-Chemical Polarization method
The susceptibility of various materials for galvanic/general corrosion was studied as part of the Electro-Chemical Polarization test method. Test specimen materials considered for the Electro-Chemical Polarization test study included SS 304 B4, SS 304 B7, Ferritic SS 430, XM-19, SS 316LN(IG) and three samples (SS 304 B4, SS304 B7 and SS 430), which were exposed for immersion testing. One custom designed autoclave from SS 316L material was used to conduct this study as shown in figure 3.
These testing were carried out with the water having a chloride concentration level of level of 1000ppb and hydrogen peroxide of 2ppm (referred as W1000HP water) and chloride concentration level of level of 100ppb and hydrogen peroxide of 2ppm (referred as W100HP water) in the autoclave. Following table-9 shows the test matrix of test sample, water chemistry and operating condition.

| Sr. No. | Test | Material | Water chemistry | Operating condition |
|---------|------|----------|-----------------|---------------------|
| 1       | ET3  | SS 304 B4 | W1000H         | OC1                 |
| 2       | ET4  | SS 304 B4 | W1000H         | OC2                 |
| 3       | ET7  | SS 304 B7 | W1000H         | OC1                 |
| 4       | ET8  | SS 304 B7 | W1000H         | OC2                 |

The following observations were made for each test listed as per the above table:
- Cyclic Potential measurement before start of polarization.
- Polarization curve (Tafel slope and corrosion rate will be calculated).
- Reverse curve for Pitting potential and behavior.
- Difference between pitting potential and protection potential.
- Critical anodic current density for passivation and passivation potential.
- Corrosion potential.
- Micro structural analysis using optical microscope and SEM before and after the test.
- Oxygen concentration in water will be measured before and after each test.

2.2.1. Test Procedure
The entire specimen polished with 120 grit emery sheet and ensures that it does not contaminate the test solution. Specimens of all eight materials observed using Optical Microscope at the magnification of 100X, 800X and SEM. The sample were inserted from flange of the autoclave and fixed the test specimen and platinum electrodes in their respective position. Autoclave filled with the test solution W1000HP or W100HP and temperature increased to 100 ± 10 or 200 ± 10 degree C. Test was executed by the control and measured software in computer and measured Open Circuit Potential (OCP) till steady graph is observed.

By Filling-in experimental parameters in software, the temperature and pressure values were measured till the experiment is complete.

2.2.2. Observations
(a) Micro Structure examination of samples
Microstructure examination was carried out on all materials surface to collect base line information. It was carried out on one sample of each material for the baseline data. All samples were considered for microstructure at cross section after the electrochemical test as per the procedure.
(b) Scanning electron Microscopy (SEM)
Scanning Electron Microscopy was carried out at sample surface for all the materials to collect the detailed evidences of the corrosion initiation sites and its nature. SEM was carried out on one sample of each material before test to generate the baseline data. Also, SEM analysis was carried out on samples which showed pitting behaviour in electrochemical tests. SEM examination before test was carried out on surface of the sample prepared with 600 grit polishing paper. Following are the images of Sample surface at 1000X, as there was no evidence of pitting in Electro-Chemical test in OC1 condition whereas OC2 Condition indicated pitting hence SEM was carried out after OC2 cycle and compared with baseline data.

| Table 10 Microstructure images of samples |
|-----------------------------------------|
| **After OC1**                           |
| SS 304 B4                               |
| SS 304 B7                               |
| SS 430                                  |
| SS 316L(N) IG                           |
| XM-19                                   |
| **After OC2**                           |
|                                        |

(c) Electro-Chemical test data
Electro-Chemical tests were conducted on all materials including coupons from immersion test for OC1 and OC2 operation condition with W1000HP water chemistry. The following parameters were measured by software.

- Open Circuit Voltage: to study steady state polarization.
- Tafel Plot: To measure the general corrosion rate of the material in a particular test condition.
- Cyclic Polarization Curve: To characterize the susceptibility of material to pitting for a given test condition.
Table 12 Tafel plots of samples

| OC1     | SS 304 B4 | SS 304 B7 | SS 430 | SS 316L(N) IG | XM-19 |
|---------|-----------|-----------|--------|---------------|-------|
| OC2     | [Image]   | [Image]   | [Image]| [Image]       | [Image]|