Characteristics of Oxide Films Formed on Welded Surface of Carbon Steel for Boiler Tube

Hiroshi Takaku and Li-Bin Niu (Shinshu University, Nagano City, Japan),
Masaki Yoshida (Naigai Chemical Products Co., LTD., Tokyo, Japan)

Presented at IAPWS 2012 Annual Meeting at NIST, Boulder, CO., USA

Background and Objective

The oxide films formed on the equipments of the water-steam circuit are very important to mitigate and/or suppress the corrosion in power plants. The corrosion is controlled by the characteristics/nature of oxide films which are influenced by the corrosive impurities such as chloride, sulfate and so on. On the other hand, the properties of the materials used for equipments in power plants also influence the formation of oxide films and their corrosion resistance. From these stand points, particularly the welded parts (weldments) of the equipments such as boiler tubes are not uniform in their properties; the weldments consist of the base metal, weld metal and weld heat-affected zone in the adjacent area.

However, the detailed knowledge of characteristics of oxide films formed on weldments of the boiler tube have not been obtained sufficiently.

In this work, the characteristics of oxide films formed on the weldment of a carbon steel for boiler tube are investigated and evaluated by some analytical equipments such as XPS after the electrochemical corrosion tests.

Testing Methods

Table 1. Chemical Composition of Base Metal (BM) and Weld Metal (WM) of STB 410 Carbon Steel for Boiler Tube Used

(mass %)

	C	Si	Mn	P	S	Cu	Fe
BM	0.17	0.21	0.66	0.01	0.007	–	bal.
WM	0.1	0.76	0.66	0.01	0.007	0.24	bal.

– : Not added and not analyzed

Table 2. Water Quality (test water temperature; 308 K)

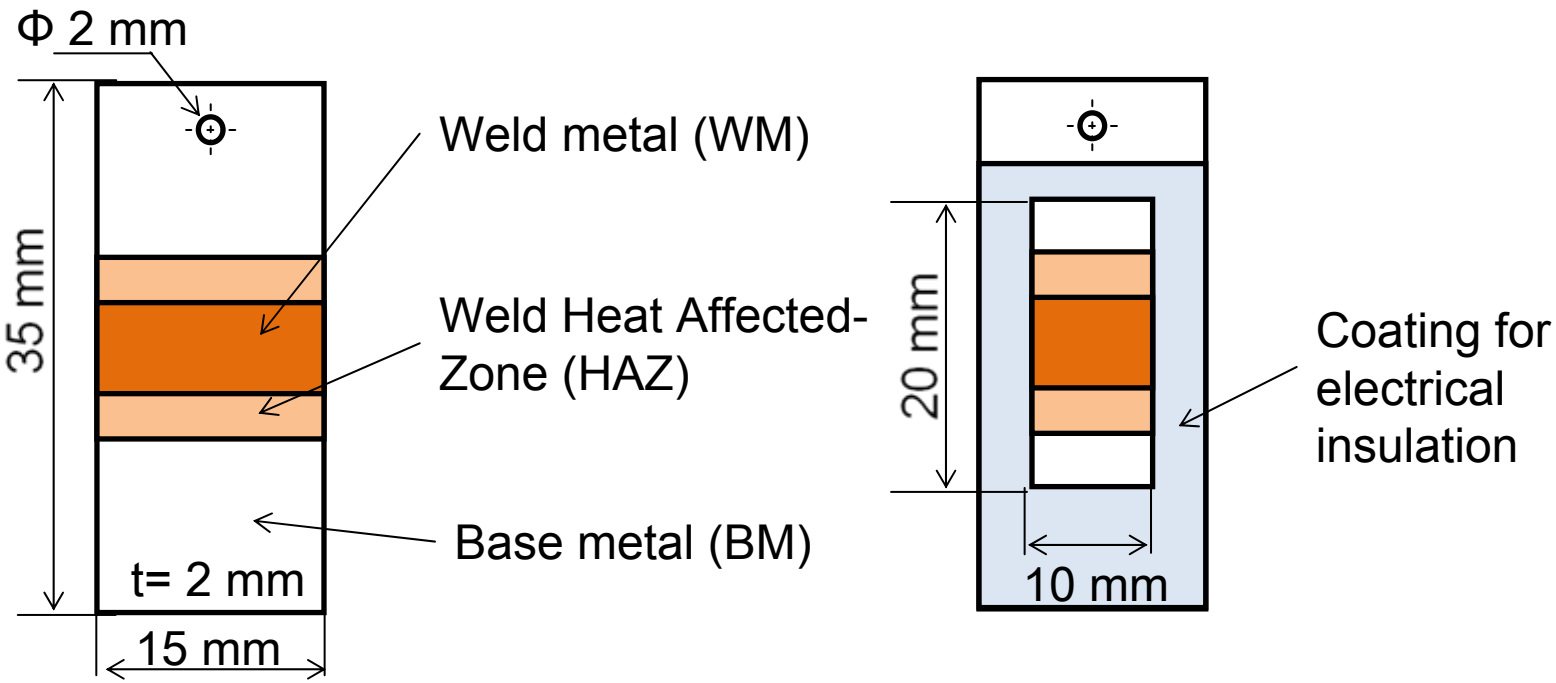
Base water (Simulated all volatile treatment AVT)	Cl^-	Electric conductivity
DO < 7 μg/L*, pH : 9.5±0.1**	100 mg/L	3.46 μS/cm

*DO: Controlled by N_2H_4 10 mg/L addition and also continuous N_2 bubbling

**pH: Conditioned with NH_3

Figure 1. Configuration and Size of Specimens Used

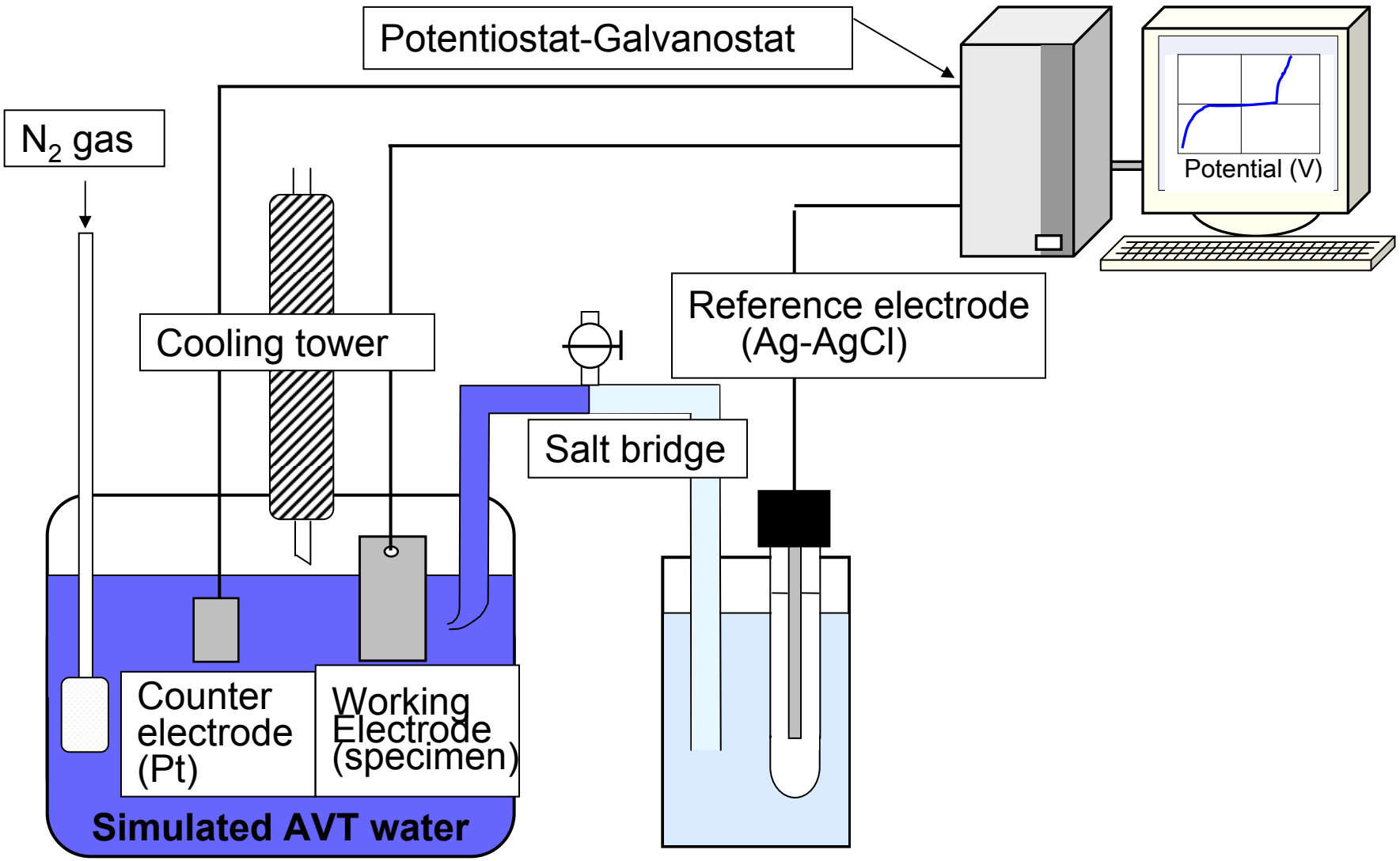
Test specimens were cut from actual boiler tubes after welding



(a) Specimens for tests of corrosion potential and polarization at constant potential

(b) Specimens for test of dynamic anodic polarization

Figure 2. Schematics of Equipments for Electrochemical Corrosion Tests



Methods for Electrochemical Corrosion Tests

At first, the cathode pre-treatment at - 1.0 V (vs. Ag-AgCl) for 10 minutes was conducted for all specimens before the following electrochemical corrosion tests.

(a) Corrosion potential measurement: Test duration time is 20 hours.
(Corrosion potential measured was approximately - 0.74 V)

(b) Anodic polarization measurement;
Range of potential swept; from $E_{corr.}$ To +1.0 V
Sweeping velocity of potential; 20 mV/min.

(c) Potentiostatic polarization measurement at constant potentials of - 0.6 V, - 0.3 V and 0 V; These potentials are more noble than corrosion potential of - 0.74 V.

Observation and Analyses of Specimen Surfaces after Electrochemical Corrosion Tests

- Equipments for observation of specimen surface:
  Digital Camera and SEM (scanning electron microscope)

- Analyses for oxide film (to identify the characteristics of the oxide film):

  (1) XRD (X-ray Diffraction);
  scanning range; 20 ° ~ 70 °
  scanning velocity; 3 ° / min.

  (2) XPS (X-ray Photoelectron Spectroscopy);
  path energy; 156.094 eV
  background base; Shirley method
  parameter; C. Wagner et al. (1979)

Figure 3. Anodic Polarization Curve (showing the oxide forms)

(Corrosion potential measured; - 0.74 V)

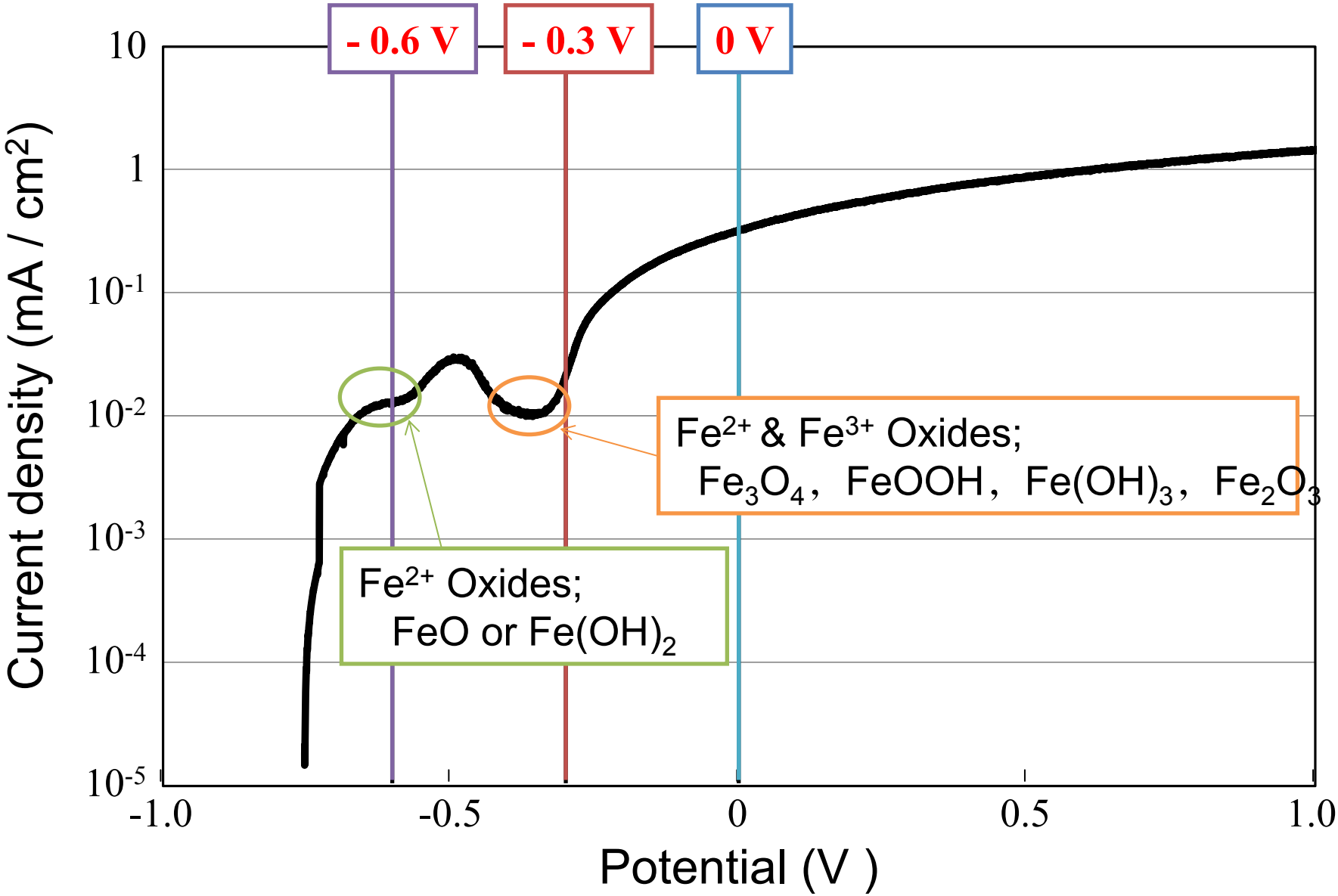


Figure 4. Change in Current and Time during Potentiostatic Polarization Measurement at Constant Potentials

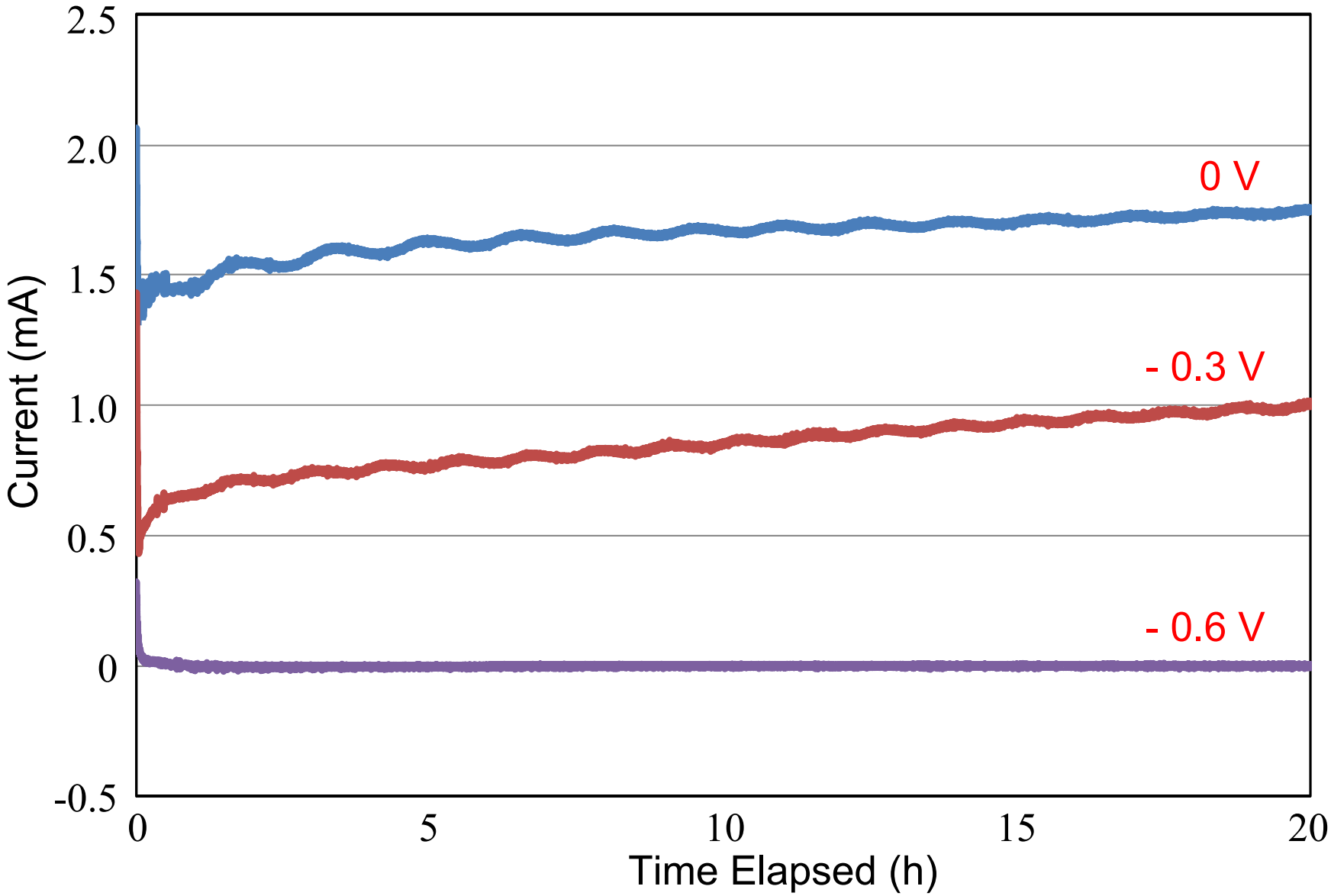


Figure 5. Surface Aspect after Potentiostatic Polarization Measurement at Constant Potential of 0 V

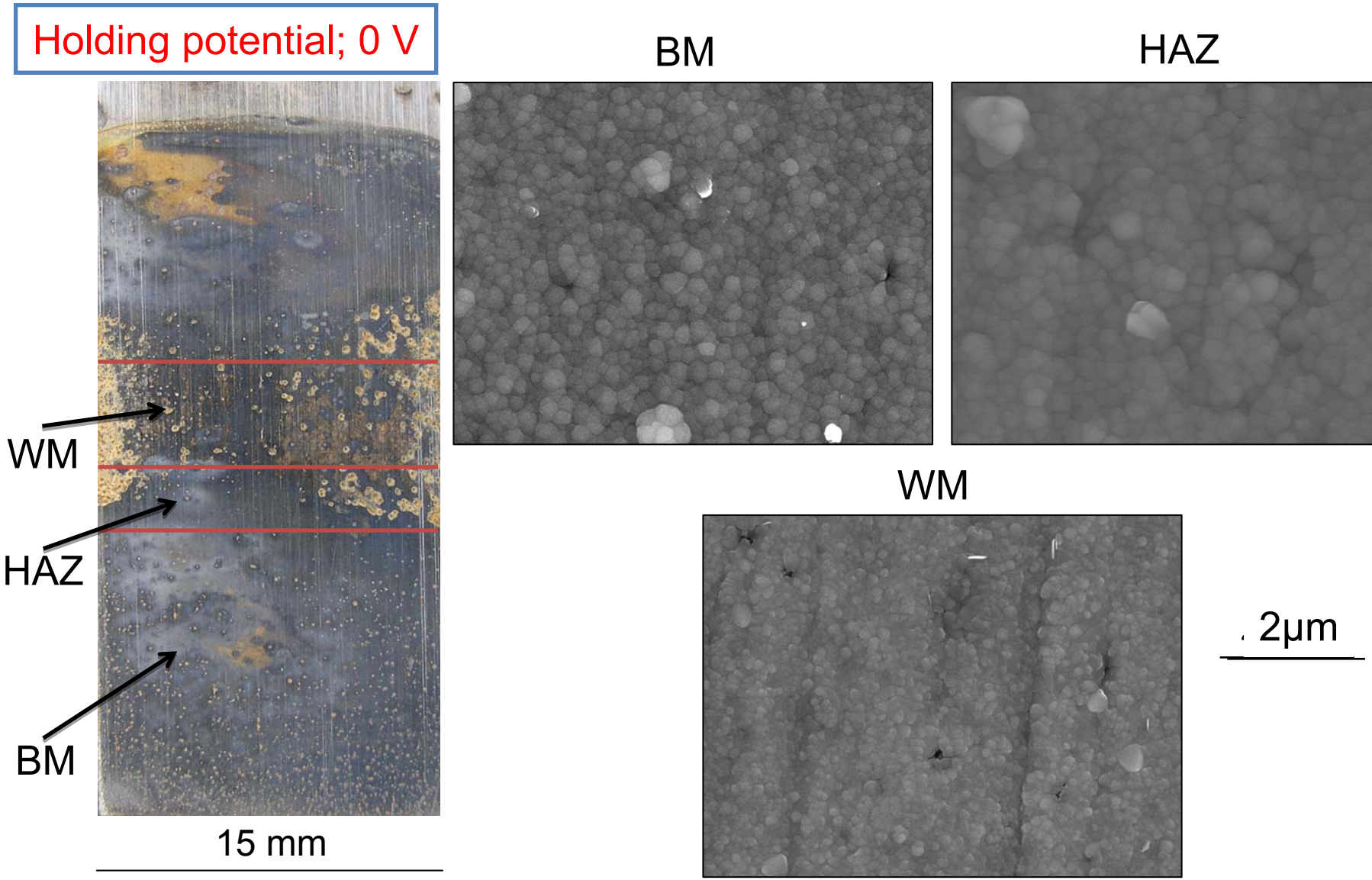


Figure 6. XPS Results at Each Location

Holding potential; 0 V

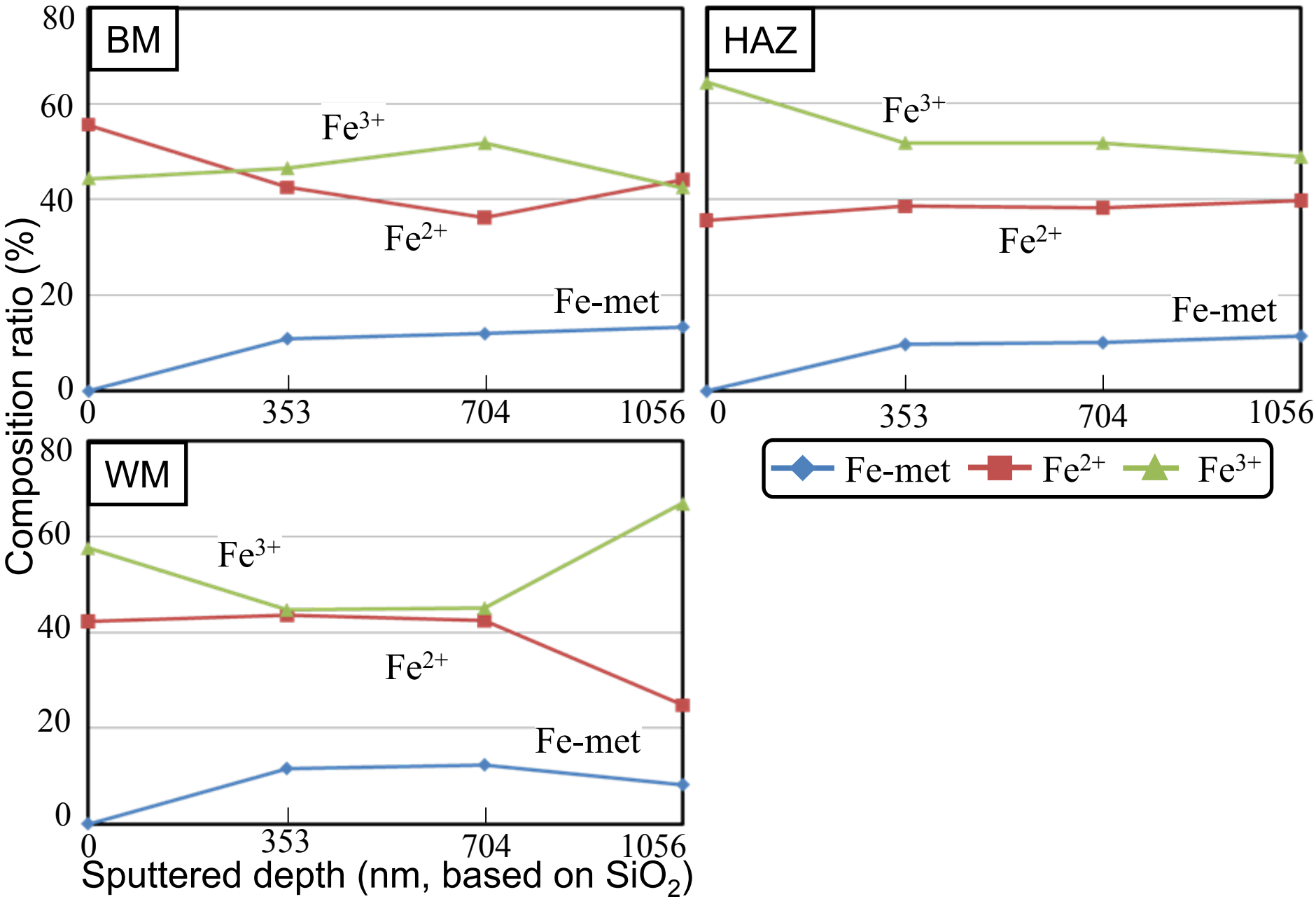


Figure 7. XRD Results

Holding potential; 0 V

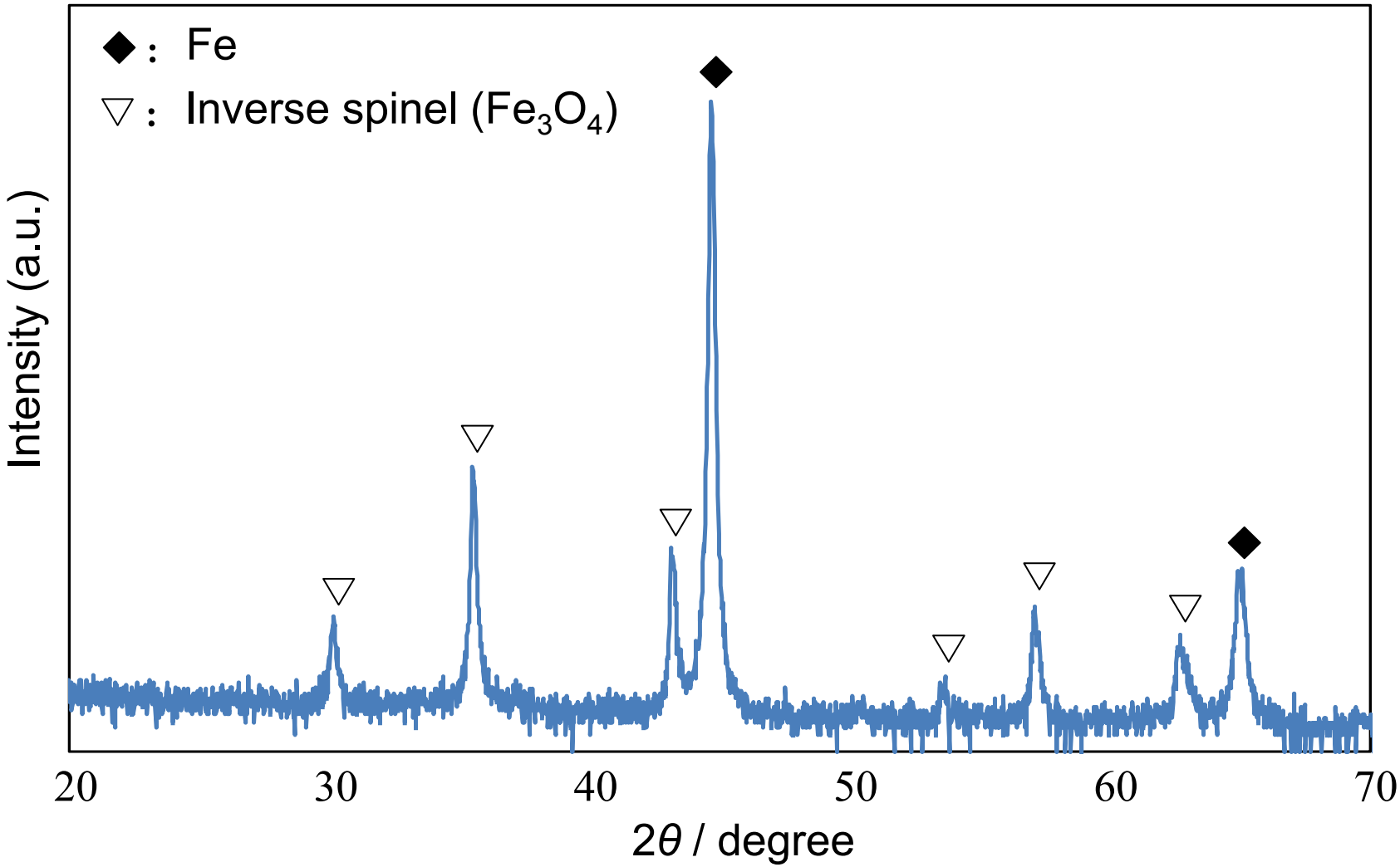
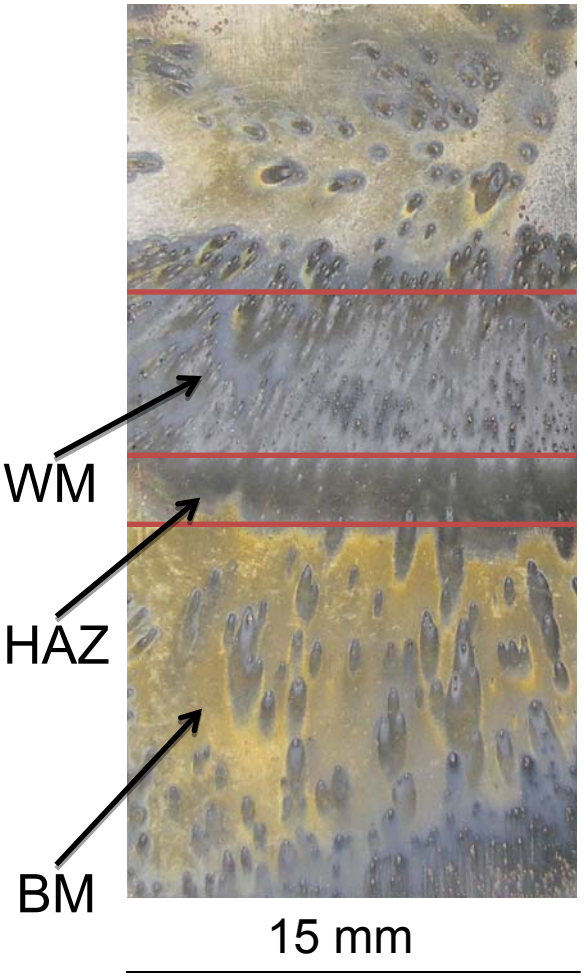
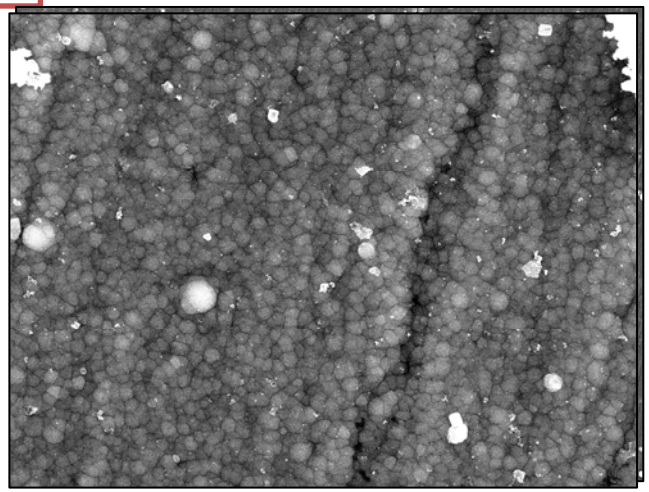


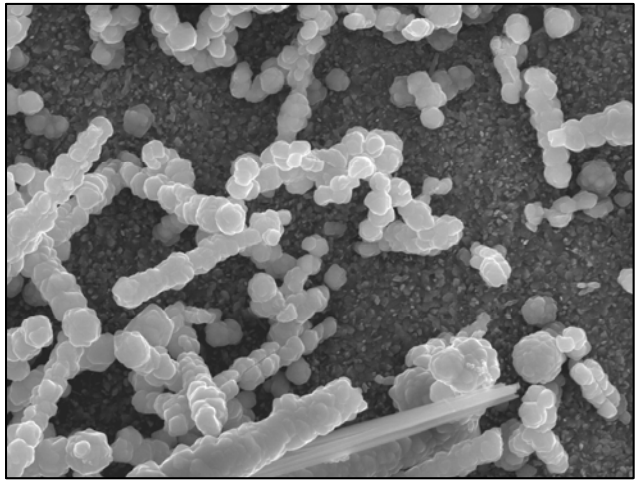
Figure 8. Surface Aspect after Potentiostatic Polarization Measurement at Constant Potential of – 0.3 V

Holding potential; - 0.3 V



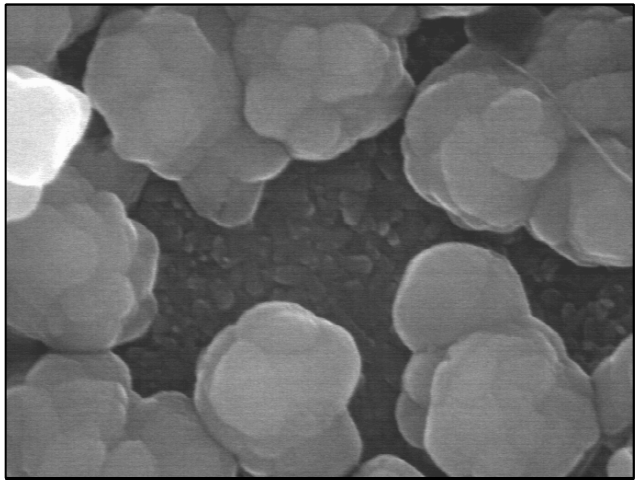


BM



HAZ

WM



1μm

Figure 9. XPS Results at Each Location

Holding potential; - 0.3 V

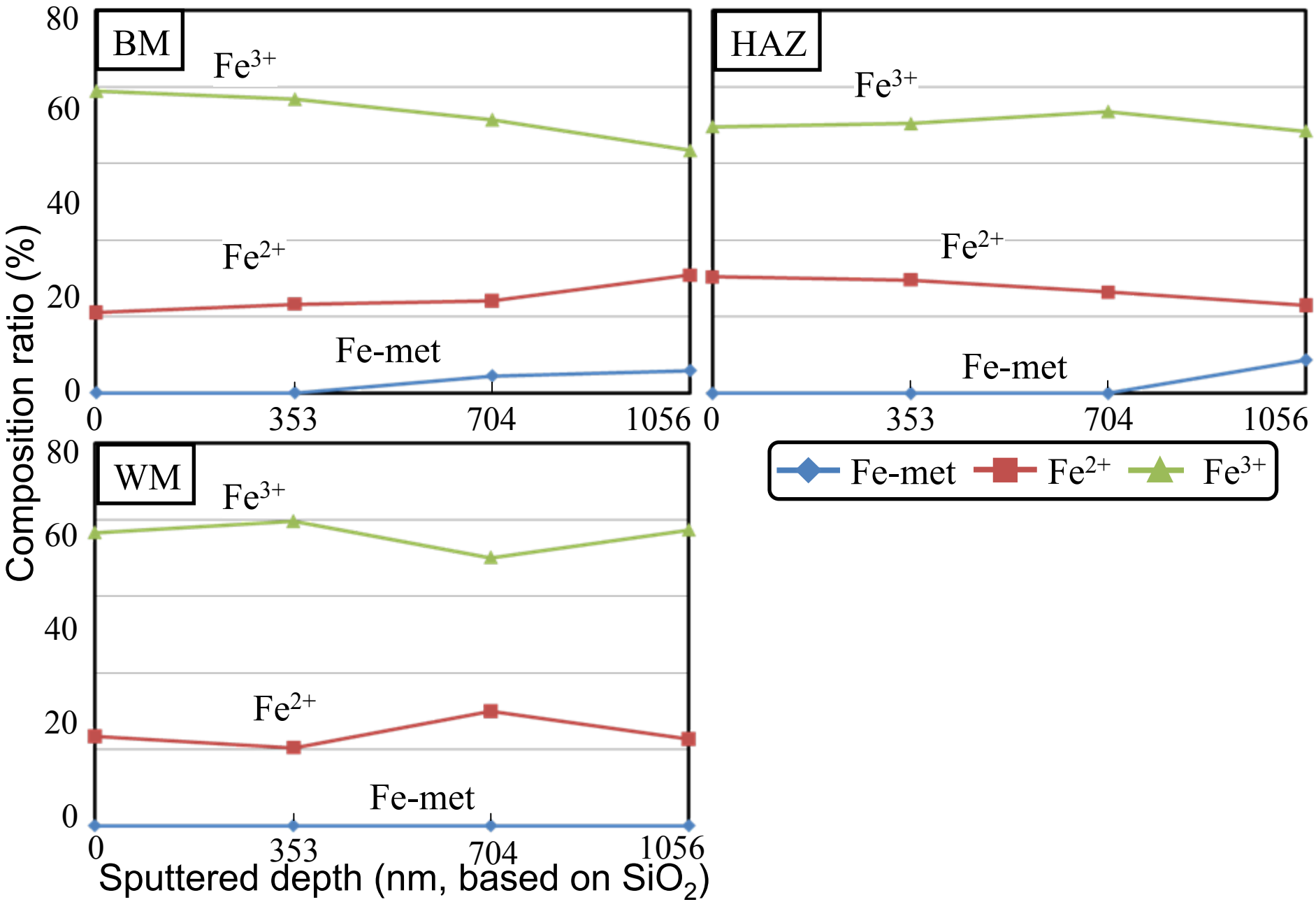
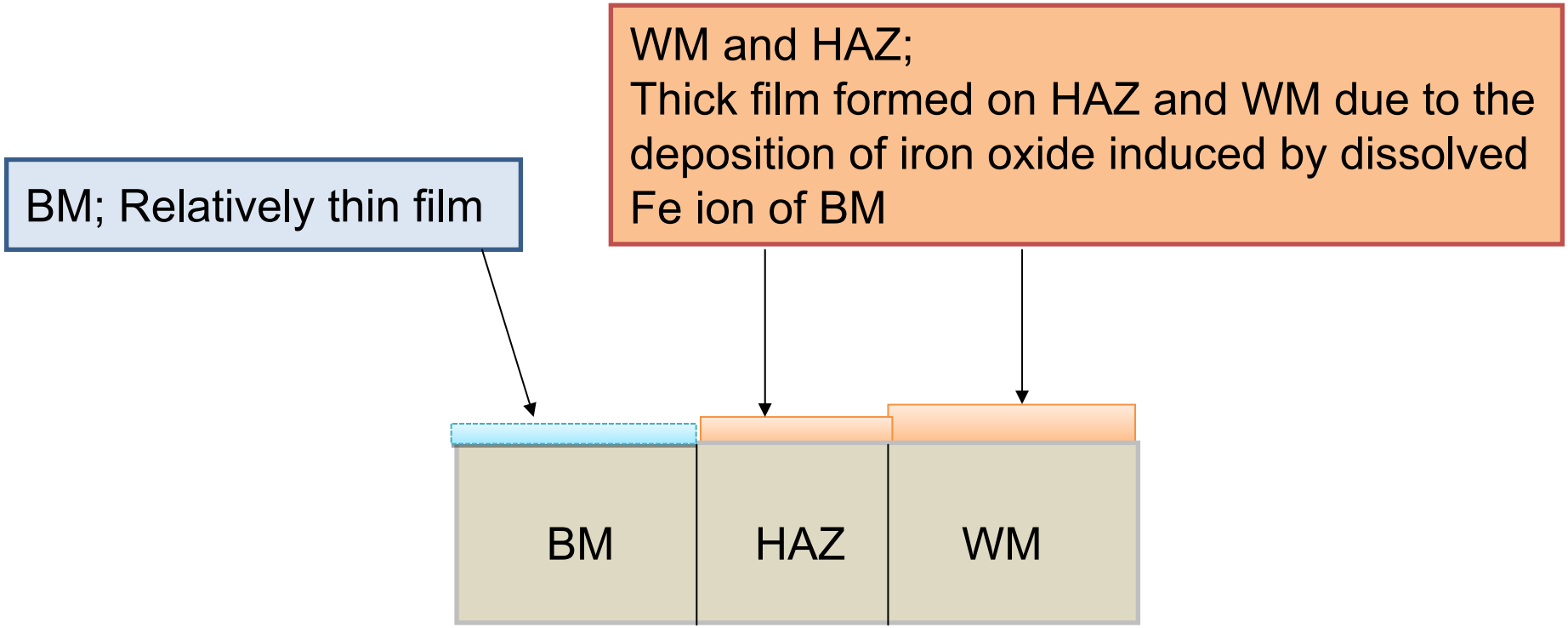


Figure 10. Film Thickness at Each Location

Film Thickness Formed at Holding Potential of - 0.3V;
BM < HAZ < WM



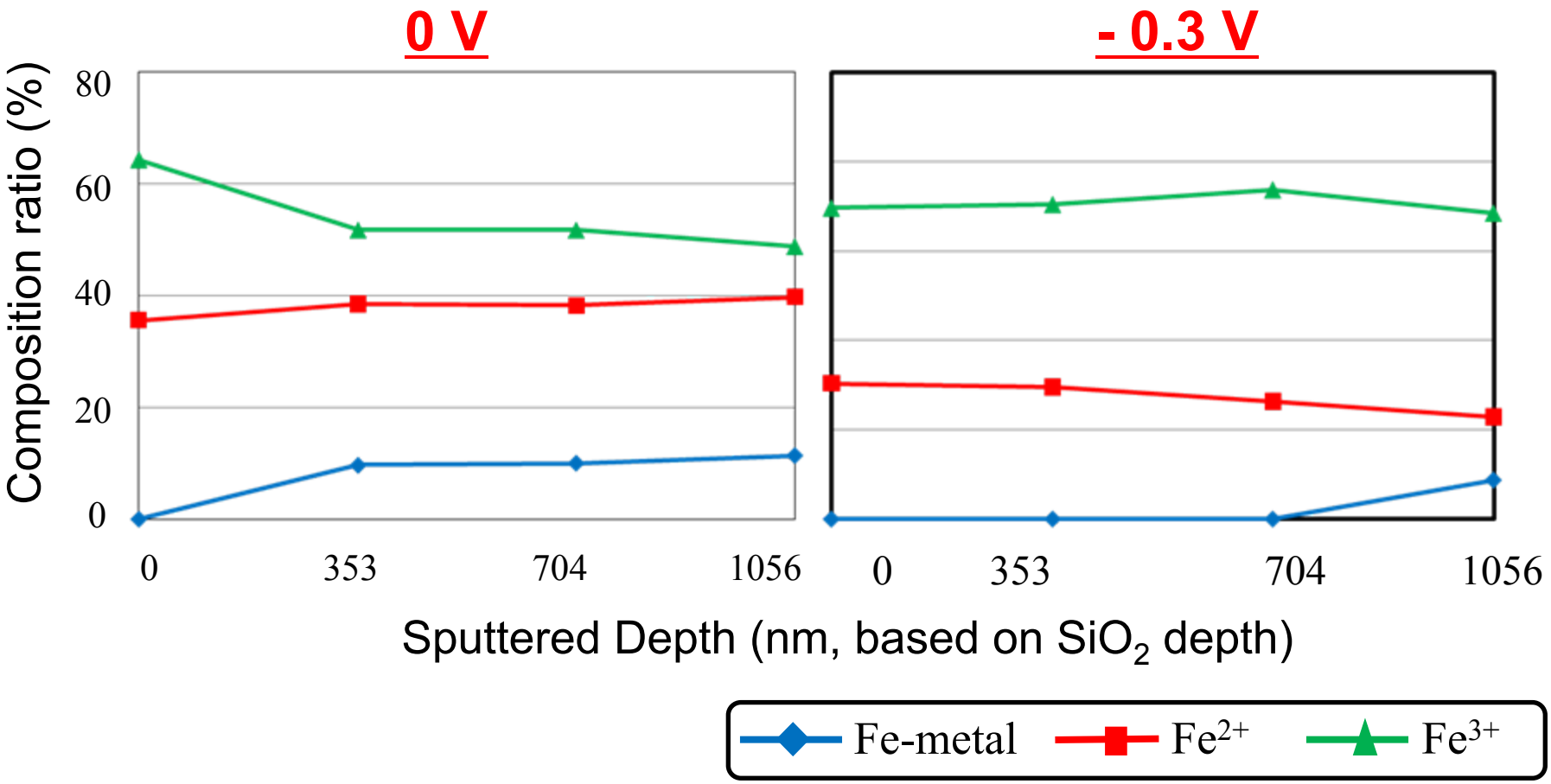


Figure 11. Depth Profile of Films Formed on HAZ Specimens (Potentiostatic polarization at constant potentials of 0 V and – 0.3 V)

Figure 12. Surface Aspect after Potentiostatic Polarization Measurement at Constant Potential of – 0.6 V

Holding potential; - 0.6 V

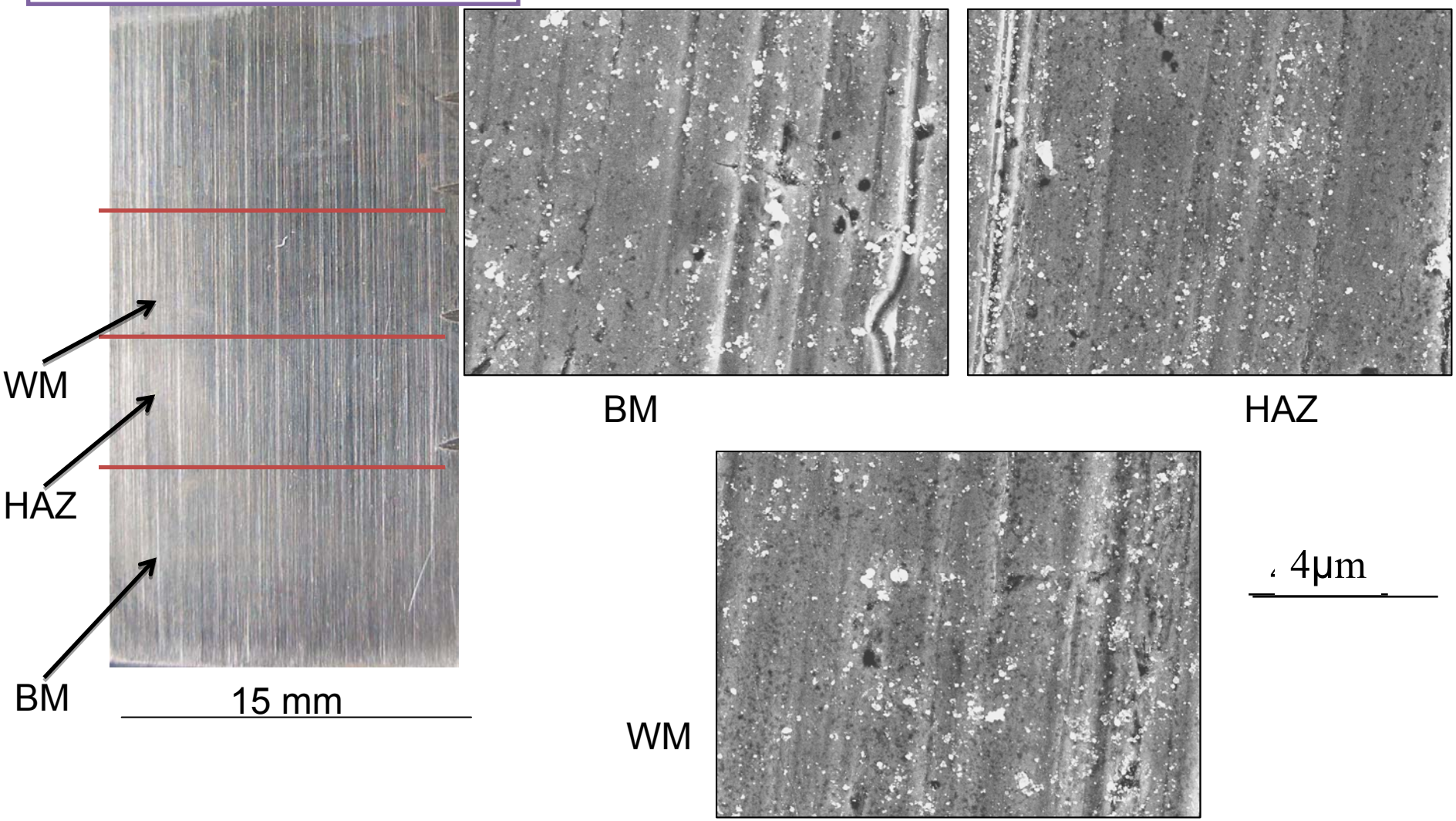


Figure 13. XPS Results at Each Location

Holding potential - 0.6 V

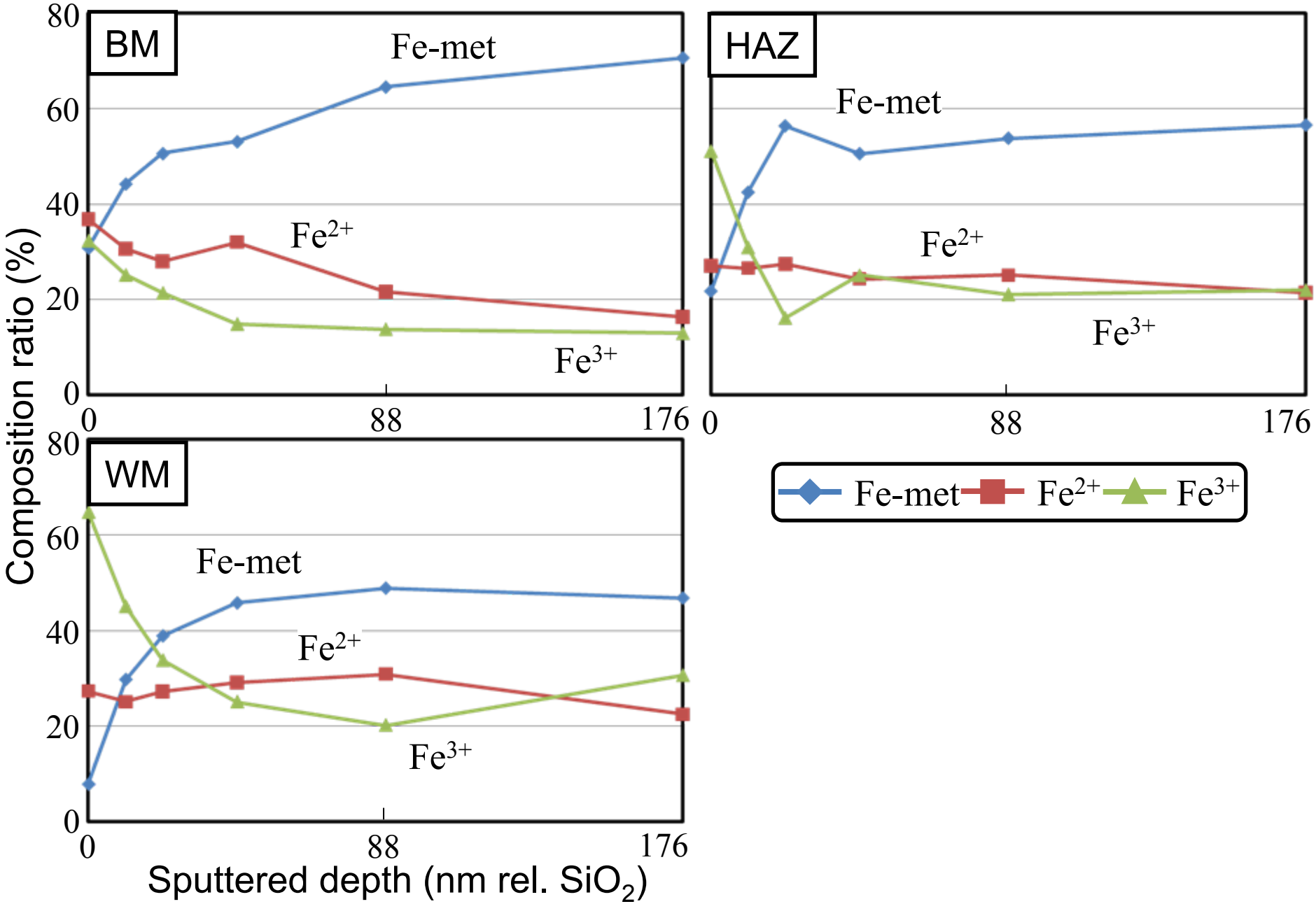
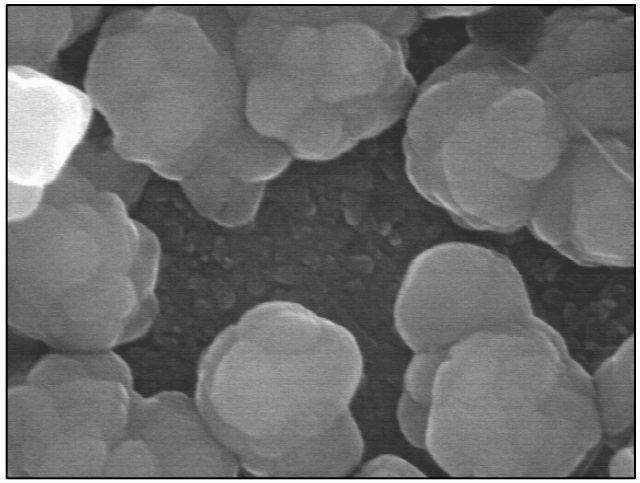


Figure 14. Characteristics of Inner Films Formed on WM and HAZ (Holding Potential of – 0.3 V)

Surface of WM



1.0μm

Effect of Cu on film formation

- Tight Cu and CuO formed at the inner side of scale
- Fine oxide particles formed
- Acceleration of Magnetite formation

Predominant dissolution of base metal (relatively high dissolution rate)

Tight film formed under Cu existence

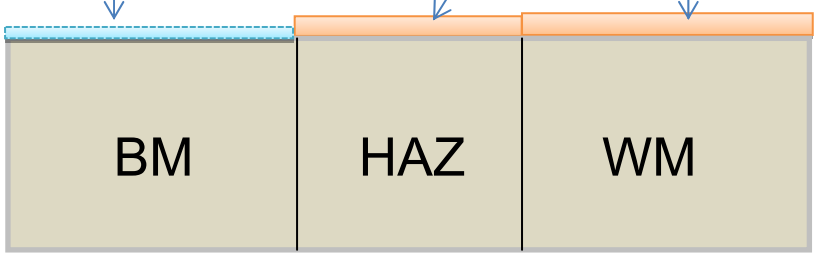
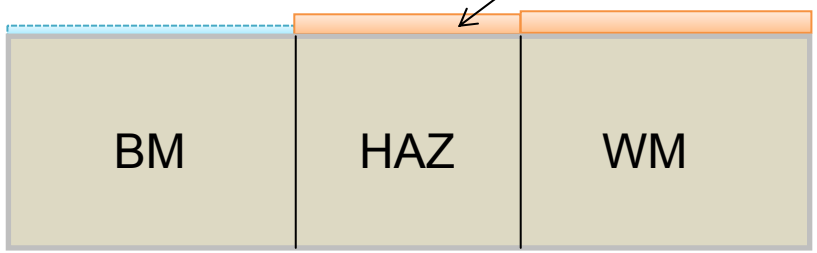


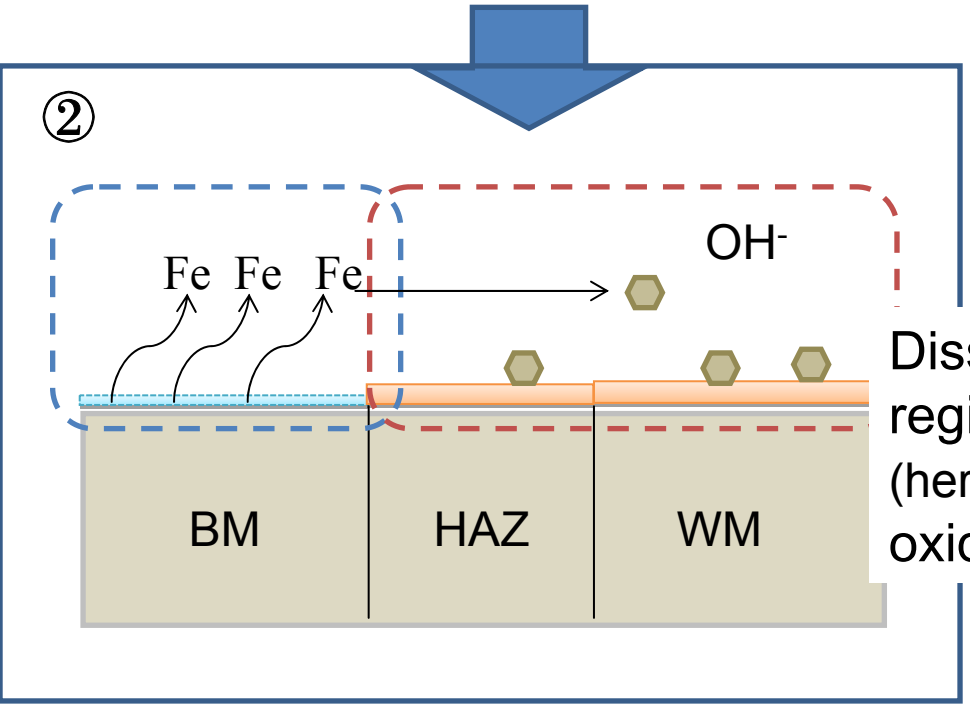
Figure 15. Schematics of Film Formation of WM & HAZ at - 0.3 V

Passive film; suppress metal dissolution → Acceleration of anodic dissolution of BM

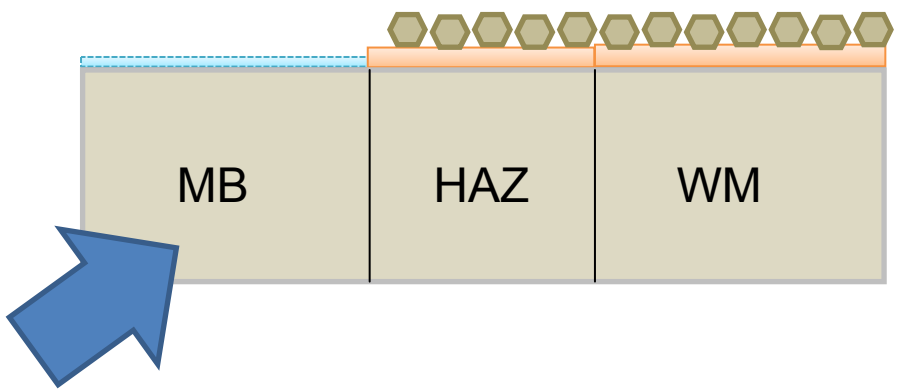
① Tight Film formed under Cu existence



②



③ Corrosion products/deposition formed on WM & HAZ surfaces



Dissolved Fe ions diffuse to HAZ and WM regions to keep the ionic/electrical balance (here, existence of sufficient OH-), thereby Fe oxide will be formed and deposited there

Figure 16. pH and Potential Diagram of Cu-H_2O System

(Cu is passive region at 0 V potential and at pH 9.5)

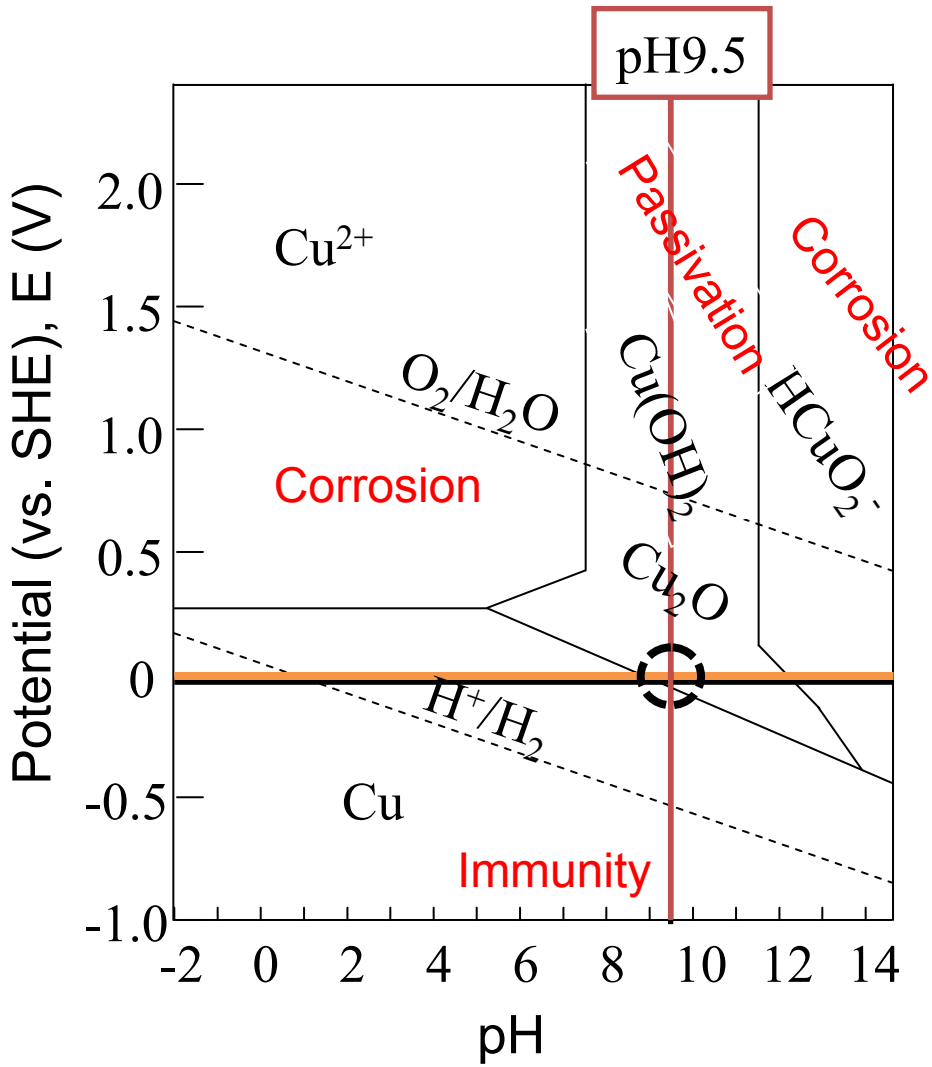
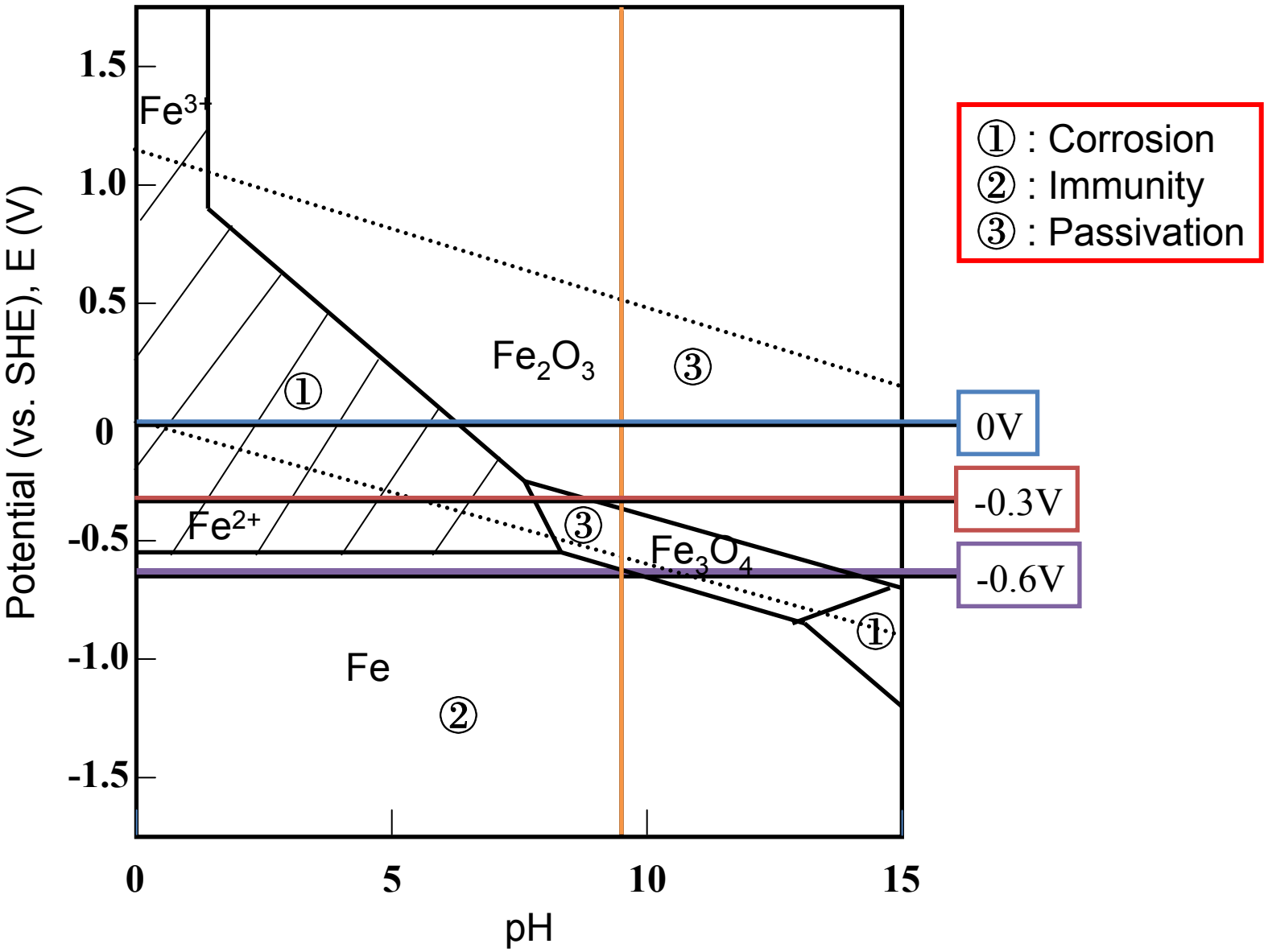


Figure 17. pH and Potential Diagram of Fe-H_2O System



Conclusion

(1) The films formed at the constant holding potential of 0 V were Fe_3O_4 in all parts (namely, base metal; BM, weld metal; WM and weld heat affected-Zone; HAZ). The films formed on these parts were relatively thin.

(2) At the holding potential of - 0.3V, the film thickness was different in each part of weldments. The reason of this phenomenon may be due to the followings; The WM and HAZ contain Cu which will form the tight film, but the BM with no Cu will be subjected to the anodic dissolution more easily than the WM and HAZ. Thereafter, the iron dissolved from BM will form the oxide which will deposit on the WM and HAZ as the iron oxide.

(3) At the holding potential of - 0.6 V, all parts show the metallic colors, and the films formed were extremely thin, furthermore no increasing of films thickness was observed in all parts.

Summary: the characteristics of oxide films formed on weldments of STB 410 carbon steel for boiler tubes are influenced by electrochemical potential and so on. However, under the passivation condition, results obtained in this work show that the severe corrosion problem such as the formation and growth of deep corrosion pits will not occur in the weldments (BM, WM and HAZ).