CHAPTER 4

SCANNING ELECTRON MICROSCOPY (SEM)

Corrosion ultimately results in loss of metal through aggressive attack on its surface resulting in significant damages over the metal surface which could easily be observed. This chapter deals with study of morphological changes over the metal surface due to the corrosion process using scanning electron microscopy (SEM). The role of this technique is to provide magnified image and the objective is to observe the features that are beyond the resolution of the human eye (100 (am).

4.1. SEM - An overview [1]

SEM is one of the most versatile and widely used techniques of modern science as it allows the study of both morphology and composition of biological samples and physical materials.

Electron microscope takes advantage of the wave nature of rapidly moving electrons, where visible light has wavelengths from 4,000 to 7,000 Å and electrons accelerated to 10,000 keV have a wavelength of 0.12 Angstroms. Optical microscopes have their resolution limited by the diffraction of light of about 1000 diameters magnification. Electron microscopes, so far, are limited to magnifications of around 10,000,000 diameters, primarily because of spherical and chromatic aberrations.

The SEM generates a beam of electrons in vacuum. That beam is collimated by electromagnetic condenser lenses, focused by an objective lens and scanned across the surface of the sample by electromagnetic deflection coils. The primary imaging method is by collecting secondary electrons that are released by the samples. The
secondary electrons are detected by a scintillation material that produces flash of light from the electrons. The light flashes are then detected and amplified by a photomultiplier tube.

By correlating the sample scan position with the resulting signal, an image can be formed that is strikingly similar to what would be seen through an optical microscope. The illumination and shadowing gives a natural looking surface topography.

There are other imaging modes available in the SEM. Specimen current imaging uses the intensity of the electrical current induced in the specimen by the illuminating electron beam which produces the image. It can often be used to show subsurface defects. Backscatter imaging uses high-energy electrons that emerge nearly 180 degrees from illuminating beam direction. The backscatter electron yield is a function of the average atomic number of each point on the sample and thus can give compositional information.

SEM is often coupled with X-ray analyzers. The interaction between energetic electron beam sample and the sample generate X-rays that are characteristic of the elements present in the sample. Many other imaging modes are also available that provide specialized information.

By scanning through an electron probe across a specimen, high resolution images of the morphology or topography of a specimen, with great depth of the field, at very low or very high magnifications can be obtained. Compositional analysis of a material may also be obtained by monitoring secondary X-rays produced by electron-specimen interaction. Thus, detailed maps of elemental distribution can be produced.
from multi-characterization of fine particulate matter in terms of size, shape and
distribution as well as statistical analysis of these parameters, may be performed.

There are many different types of SEM designed for specific purposes ranging
from routine morphological studies to high-speed compositional analyses or to the
study of environment-sensitive materials.

4. 2. Principles of SEM

When a high-energy primary electron interacts with an atom, it undergoes
either inelastic scattering with atomic electrons or elastic scattering with the atomic
nucleus. In an inelastic collision with an electron, some amount of energy is
transferred to the other electrons. If the energy transfer is very small, the emitted
electron will probably not have enough energy to exit the surface.

If the energy transferred exceeds the work function of a material, the emitted
electron can exit the solid surface. When the energy of the emitted electron is less
than about 50 eV, by convention it is referred to as a secondary electron (SE), or
simply a secondary. Most of the emitted secondaries are produced within the first few
nm of the surface. Secondaries produced much deeper in the material suffer
additional inelastic collisions, which lower their energy and trap them in the interior
of the solid.

Higher energy electrons are primary electrons that have been scattered without
loss of kinetic energy (i.e., elastically) by the nucleus of an atom, although these
collisions may occur after the primary electron has already lost some of its energy to
inelastic scattering. Backscattered electrons (BSEs) are considered to be the electrons
that exit the specimen with an energy greater than 50 eV, including Auger electrons.
However, most BSEs have energies comparable to the energy of the primary beam. The higher the atomic number of a material, the more likely the back scattering will occur. Thus as a beam passes from a low Z- (atomic number) to a high Z-area, the signal due to backscattering, and consequently the image brightness, will increase. There is a built-in contrast caused by elemental differences. The secondary electron contributions can be grouped into three viz., SE (I), SE (II) and SE (III). SE (I)s result from the interaction of the incident beam with the sample at the point of entry. SE (II)s are produced by BSEs on exiting the sample. SE (III)s are produced by BSEs which have exited the surface of the sample and further interact with components on the interior of the SEM usually not related to the sample. SE (II)s and SE (III)s come from regions far outside that defined by the incident probe and can cause serious degradation of the resolution of the image.

It is usual to define the primary beam current $i_o$, the BSE current $i_{BSE}$, the SE current $i_{SC}$, such that the Kirchoff current law holds,

$$i_o = i_{BSE} + i_{SE} + i_{SC} \quad (4.1)$$

These signals can be used to form complementary images. As the beam current is increased, each of these currents will also increase. The backscattered electron yield $\eta$ and the secondary electron yield $\delta$, which refer to the number of backscattered and secondary electrons emitted per incident electron respectively, are defined by the relationships

$$\eta = \frac{i_{BSE}}{i_o} \quad (4.2)$$

$$\delta = \frac{i_{SE}}{i_o} \quad (4.3)$$
In most currently available SEMs, the energy of the primary electron beam can range from a few hundred eV up to 30 keV. The values of δ and η will change over this range, however, yielding micrographs that may vary in appearance and information content as the energy of the primary beam is changed. The value of the BSE yield increases with atomic number Z, but its value for a fixed Z remains constant for all beam energies above 5 keV. The value of δ decreases slowly with increasing beam energy after reaching a peak at some low voltage, usually around 1 keV. For any fixed voltage Z, however, δ shows very little variation over the full range of Z. Both the secondary and backscattered electron yields increase with decreasing glancing angle of incidence because more scattering occurs closer to the surface. This is one of the major reasons why the SEM provides excellent topographical contrast in SE mode; as the surface changes its slope, the number of secondary electrons produced changes as well. With the BSEs this effect is not so prominent, since to fully realize it, the BSE detector would have to be repositioned to measure forward scattering.

4. Use of SEM in the study of corrosion – earlier work

Number of authors have reported the corrosion inhibition potential of various organic compounds for assessing the morphological changes through SEM during inhibition. Migahed [2] investigated the corrosion inhibition of steel pipelines in oil fields by N, N-di-(poly oxyethylene) amino propyl lauryl amide. The strong adsorption ability of the surfactant molecules leads to the formation of a monolayer, which isolates the surface from the environment and thereby reduces corrosion attack.
on the surface. SEM was used to examine the surface morphology of carbon steel samples both in the presence and absence of inhibitor.

Yan Li et al., [3] studied berberine as a natural source of inhibitor for mild steel in 1M H₂SO₄. The surface morphology analysis for mild steel specimens in sulphuric acid in the absence and presence of the inhibitor proved berberine to be an excellent corrosion inhibitor for mild steel.

Peng Zhao et al., [4] investigated the inhibition effect of metal free phthalocyanine (H₂Pc), copper phthalocyanine (CuPc) and copper phthalocyanine tetrasodium (CuPc.S₄Na₄) on mild steel in HCl with the help of SEM images in the presence and absence of the test compounds.

SEM and Auger Electron Spectroscopy (AES) were used to study the surface morphology, the thickness of the adsorbed film over aluminium surface in HCl medium having hexamine – KI and hexamine – CaCl₂ as corrosion inhibitors. It was observed that higher corrosion resistance and improvement in the surface morphology of aluminium was due to the marked layer enrichment on the aluminium surface from the blend additives [5].

Corrosion inhibition of pipeline steel grade API 5Lx52 immersed in 1M H₂SO₄ aqueous solution using heterocyclic organic molecules was studied by Morales et al., [6] using SEM analysis as one of the techniques.

Migahed et al., [7] investigated the effect of gamma ray pre irradiation on the efficiency of two types of polymeric surfactants as corrosion inhibitors for 304 stainless steel in 2M HCl. SEM was used to examine the surface morphology of
stainless steel samples after immersion in HCl solution in absence and presence of inhibitors.

Lopez et al., [8] conducted the morphological and compositional studies on the corrosion layers formed on carbon steel with two different heat treatments in chloride media containing CO₂ by means of SEM.


Thus, it is certain that SEM [11-13] technique could give us a better understanding of the surface of various metals and alloys in the study of corrosion inhibition.

4.4. Experimental

Properly ground and mirror finish polished mild steel specimens of size 1 x 1 cm were used for this study. These coupons were dipped in both 1M HCl and H₂SO₄ media with and without the green inhibitor of optimum concentration (which showed higher inhibition efficiency in weight loss studies) separately for 12 hours. Then they were removed, rinsed quickly with rectified spirit. The analysis was performed in HITACHI-model S-3000 H Scanning Electron Microscope.

4.5. Results and Discussion

The SEM micrographs obtained (with appropriate magnification) are depicted in Fig. 4.1 to 4.17.
Fig. 4. 1. SEM micrograph (2000 X) of polished MS surface

Fig. 4. 2. SEM micrograph (2000 X) of MS in 1M HCl

Fig. 4. 3. SEM micrograph (2000 X) of MS in 1M H₂SO₄
Fig. 4.4. SEM micrograph (2000 X) of MS in 1M HCl with 30% of *D. metel* extract

Fig. 4.5. SEM micrograph (2000 X) of MS in 1M H$_2$SO$_4$ with 30% *D. metel* extract

Fig. 4.6. SEM micrograph (1000 X) of MS in 1M HCl with 20 ppm of *D. stramonium* extract
Fig. 4. 7. SEM micrograph (1000 X) of MS in 1M H₂SO₄ with 20 ppm *D. stramonium* extract

Fig. 4. 8. SEM micrograph (2000 X) of MS in 1M HCl with 50 ppm *S. nigrum* extract

Fig. 4. 9. SEM micrograph (2000 X) of MS in 1M H₂SO₄ with 50 ppm *S. nigrum* extract
Fig. 4. 10. SEM micrograph (2000 X) of MS in 1M HCl with 50 ppm *S. tuberosum* extract

Fig. 4. 11. SEM micrograph (2000 X) of MS in 1M H₂SO₄ with 50 ppm *S. tuberosum* extract

Fig. 4. 12. SEM micrograph (2000 X) of MS in 1M HCl with 20 ppm *P. nigrum* extract
Fig. 4. 13. SEM micrograph (1000 X) of MS in 1M H₂SO₄ with 20 ppm *P. nigrum* extract

Fig. 4. 14. SEM micrograph (1000 X) of MS in 1M HCl medium with 20 ppm of *R. serpentina* extract

Fig. 4. 15. SEM micrograph (2000 X) of MS in 1M H₂SO₄ medium with 20 ppm of *R. serpentina* extract
Fig. 4. 16. SEM micrograph (2000 X) of MS in 1M HCl medium with 25 ppm of *S. nux-vomica* extract

Fig. 4. 17. SEM micrograph (1000 X) of MS in 1M H$_2$SO$_4$ medium with 25 ppm of *S. nux-vomica* extract

The figure 4.1 shows the SEM micrograph of plain mild steel specimen of 2000 X magnification. This figure indicates the finely polished characteristic surface of mild steel and shows some scratches also which may arise during polishing.

Perusal of images as depicted in fig. 4.2 and 4.3 revealed that the specimens immersed were highly damaged in the presence of 1M HCl and H$_2$SO$_4$ respectively due to the direct attack of aggressive acids. The uniform corrosion of mild steel could be observed in both the images which matched well with previous reports [14, 15].
From fig. 4.4 and 4.5 it could be concluded that *D. metel* extract prevents the surface damage through the formation of protective layer. The formation of corrosion products and scratched nicks over the metal surface are visible in that picture. The extract of *D. stramonium* also shows (Fig. 4.6 and 4.7) a very fine protective layer over the metal surface. SEM images of *S. nigrum* and *S. tuberosum* extracts are depicted in Fig. 4.8-4.9 and 4.10-4.11 respectively. The SEM images showed the formation of a protective layer by the extract of *S. nigrum* over the MS surface. The images obtained with *S. tuberosum* showed the scratches as well as the corrosion products over the metal surface.

Fig. 4.12 and 4.13 show the formation of a protective film by the black pepper extract on the metal surface which inhibits the corrosion well in both the acid media. Extract of *R. serpentina* could also form a fine protective layer and a dark black mark in Fig. 4.14 (in HCl medium). The micrographs also showed the scratches formed during metal polishing also covered well by the inhibitor.

The comparision of micrographs (Fig. 4.16 and 4.17) obtained in the case of test coupons immersed in *S. nux-vomica* extract with those of the blank also revealed that a protective coating of the extract was formed over the surface of the metal. This could be due to the adsorption of the phytoconstituents on the surface of the MS.

Thus by scanning electron microscopy studies it is observed that the extent of surface damage was less in acid media in the presence of all these green inhibitors. From all these micrographs the formation of a protective layer could be confirmed which supports that the corrosion inhibition action of the green inhibitors is mainly through adsorption process.
References:


