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SURFACE OXIDES PRODUCED DURING DISCHARGE IN WATER AMBIENT IRON SURFACE: A CONVERSION ELECTRON MÖSSBAUER SPECTROSCOPIC STUDY

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Oxide layers are produced on iron surface, under discharge in water ambient, applying both anodic and cathodic potentials to iron foil. Non-stoichiometric $Fe_{1-x}O$ containing different ratios of Fe^{3+} and Fe^{2+} has been detected by using CEMS. Corrosion of these samples in 0.5 M H_2SO_4 shows that, cathodically discharge treated iron foil has higher corrosion resistance as compared to the anodically treated sample. This is attributed to the microstructural differences in the $Fe_{1-x}O_x$ films formed during the discharge.

Introduction :

Corrosion resistance of materials is known to be a surface property and therefore, various techniques have been employed to modify near surface region. The techniques such as ion implantation/1/, ion beam mixing/2/, laser treatment/3-4/, have been attempted to improve surface properties of materials. The process of discharge in liquids has been used to obtain fine amorphous particles, as well as it has been applied in spark errosion/5/. In the present study, surface modification of iron foils is carried out using discharge in water. The resulting chemical and microstructural changes on the surface are studied by the use of Mössbauer spectroscopy.

Experimental:

Samples of 25 μm thick iron foils were throughly washed in acetone and distilled water. These samples were then immersed in water and subjected to the action of an electrical discharge either cathodically or anodically, maintaining the discharge current at a fixed value. Room temperature electrochemical corrosion studies of both these samples were carried out in 0.5 M H_2SO_4 [pH=3]. The solution was deaerated by purging (oxygen free) argon gas for 8 hours.Three sweep polarisation technique used by Ashworth et al./1/ was adopted to eliminate any possible interference of the air formed oxide film during evaluation of corrosion properties. The voltage sweep rate of 1.33 mV/sec was employed with the use of ramp generator.

Conversion Electron Mössbauer Spectroscopic [CEMS] study of all samples were carried out by using a gas [He + 4% ethanol mixture] flow proportional counter system/3/.

Results and Discussion :

Fig.1 shows the third sweep of the potentiokinetic I-V plots, for virgin Fe foil and discharge treated Fe foil in water ambient. As is evident, critical current density in water treated sample is ∼ 103 times smaller as compared to that obtained in the case of virgin sample. The fig.1(b) displays corrosion curves for "anodically" and "cathodically discharged " treated samples. The cathodically treated sample shows much better corrosion resistant behaviour, in the sense that it has lower critical current density which is the measure of the dissolved material. In order to understand this difference due to anodic and

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cathodic treatment, CEMS spectra of both the samples are recorded. Both the samples show, presence of FeO with no trace of higher oxides (Fig.2). This essentially signifies a relatively high quenching rate process. The spectrum of anodically treated sample can be fitted with following contributions:

1. A Doublet with isomer shift of 0.66 mm/sec and quadrupole splitting of 1.08 mm/sec. ($Fe_{1-x}O$)
2. Another doublet with an isomer shift of 1.17 mm/sec and quadrupole splitting of 1.13 mm/sec. ($Fe_{1-x}O$)
3. A sextet with hyperfine field of 330 kOe which corresponds to α-Fe.

The spectrum of cathodically treated sample have following contributions :

1. A doublet with isomer shift of 0.82 mm/sec and quadrupole splitting of 0.73 nm/sec. ($Fe_{1-x}O$)
2. A doublet with isomer shift of 1.18 mm/sec and quadrupole splitting of 0.66 mm/sec. ($Fe_{1-x}O$)
3. A singlet with isomer shift of 0.31 mm/sec which can be attributed to the presence of Fe^{3+} ions in the tetrahedral sites. ($Fe_{1-x}O$)
4. A sextet with hyperfine field of 330 kOe which corresponds to α-Fe.

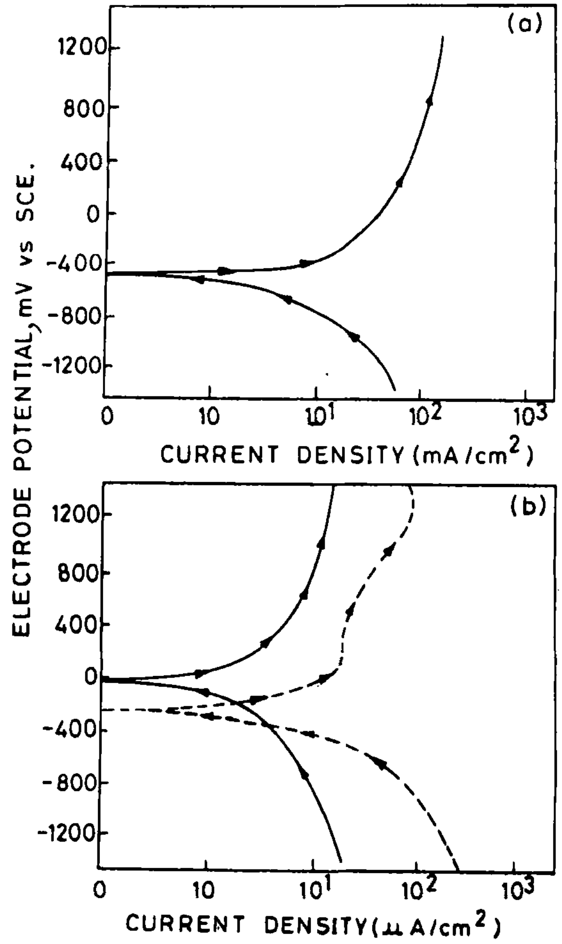

Fig.1 :Final sweep of the potentiokinetic polarisation curve for (a) as it is Fe foil (b) discharge treated Fe foil (-----) cathodically and (———) anodically in water.

The doublet with higher value of I.S. (0.82 mm/sec) in cathodically treated sample as compared to the corresponding doublet (0.66 mm/sec) in anodically treated sample suggests that $Fe_{1-x}O$ has different defect structure in two cases. The broad line width of these doublets and their isomer shift values which are intermediate between typical Fe^{2+} and Fe^{3+} ions show the presence of electronic exchange in Fe-O structure/6/.

The area ratios of FeO to Fe in both the cases show that in anodic case it is higher (0.74) as compared to that in cathodic case (0.31). Since the experimental conditions during the preperation of these two samples were identical except for the polarities of the electrodes, difference in the extent of oxide formation can be interpreted due to electrochemical oxygen evolution at the anodic element. It seems that surface of the anodically treated sample is locally melted due to the discharge with concurrent oxygen evolution which eventually leads to the oxide formation of relatively higher thickness as

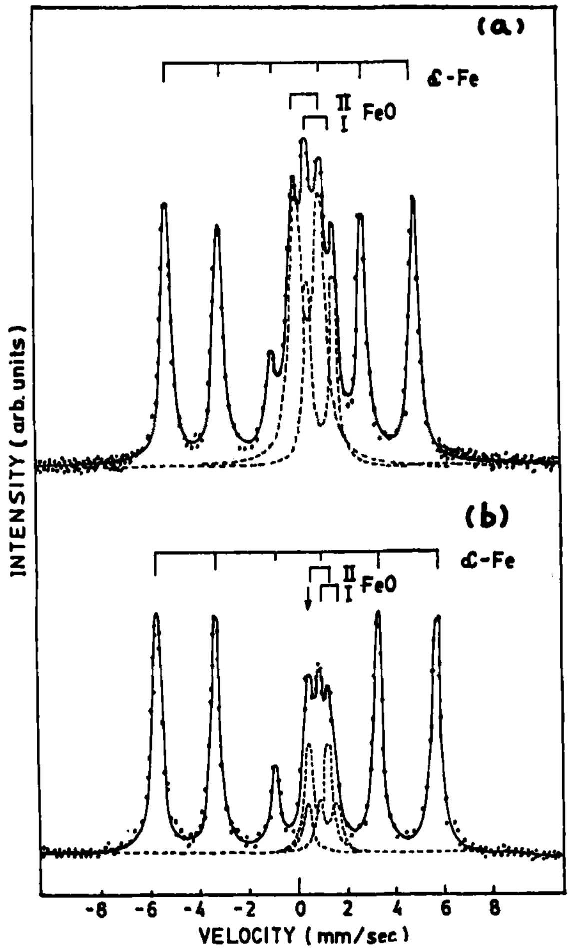

Fig.2 :Room temperature CEMS spectra of discharge treated Fe foil in water (a) anodically (b) cathodically treated

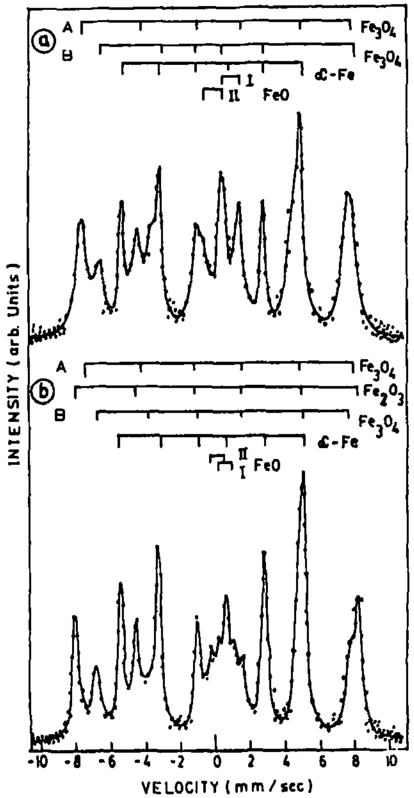

Fig.3 : Room temperature CEMS spectra of discharge treated Fe foil in air (a)anodically (b)cathodically

compared to that in the cathodically treated sample. It is interesting to note that the cathodically treated sample in air ambients exhibits the presence of α-Fe_2O_3 and Fe_3O_4 phase along with FeO phase while the anodically treated sample shows the formation of only Fe_3O_4 phase along with FeO phases [Fig.3]. Therefore it seems that apart from the local heating of the sample during cathodic treatment, the bombardment of positive ions on the surface of iron foil results in the higher oxide composition.

Conclusion :

High corrosion resistant iron surface can be produced using discharge in water ambient.

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