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SURFACE INVESTIGATIONS OF ALUMINUM IN 2M HYDROCHLORIC ACID SOLUTION IN THE PRESENCE OF POTASSIUM IODATE INHIBITOR

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Abstract

The results of investigations by using optical, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) to study the surface morphology, the composition of adsorbed film formed on the surface of aluminum samples in 2M hydrochloric acid solution containing ppm optimum KIO_3 dose. The data reveal that the additive improves the surface morphology of aluminum, due to the marked layer enrichment of Al- surface by inhibitor components. Detailed studies were carried out to investigate the effect of oxygen in the inhibition process. The nature and strength of the passive film and the mechanism of its formation are explained based on detailed studies conducted under experimental conditions.

Keywords: Aluminum, KIO_3, SEM, EDS, optical microscopy, corrosion inhibitor

Introduction

Aluminum is considered as one of the most important metals due to its economic and technical importance as well as the wide range of industrial applications like reflectors, decorative products, buildings, airspace, aircraft and architectural [1]. It owns as excellent corrosion resistance and its usage as one of the primary metals of commerce due to the barrier oxide film that is bonded to its surface and that, if damaged it re- forms immediately in most environments.

The study of the corrosion of aluminum and its alloys is a subject of a pronounced importance because of its widespread applications in many industries. Aluminum is reactive metal (E^o = -1.66 Vs NHE), its resistance to corrosion in solutions of pH between 4- 9 in presence of chloride ions is weak [2]. This corrosion resistance is attributed to the presence of this; adherent and protective surface oxide film. Above and below this pH range, solubility of the oxide film increases, and aluminum exhibits uniform attack [3]. In addition to corrosion resistance, other properties are colorless and nontoxic corrosion products, appearance, electrical and thermal conductivity, reflectivity and lightness or good strength or weight ratio [3].

Aluminum when introduced in acids after air exposure exhibits a period of induction, which is due to the slow dissolution of the film. Pure aluminum has many longer induction periods than impure metal for the sites of impurities constitute defects in the film [4]. The formed film on aluminum metal is amphoteric in nature and dissolves in strong acids and alkalis, resulting in varying rates of corrosion of the metal [5].

Hydrochloric acid solutions are used for pickling of Al and Al-alloys and for chemical or electrochemical etching of Al foil and lithographic plates used as substitutes for zinc [6]. Since, the metal dissolution in such solutions is rather large, it is necessary to inhibit it by the addition of inhibitors which effectively eliminate the undesirable destructive effect of acids on the base metal and improve etching qualities and provide good pickled metal surface [7].

Inhibitors are chemicals that directly or indirectly coat a film on a metal surface to protect it from its environment [8]. Most inhibitors are adsorbed by the metal surface from a solution or dispersed, but some are applied directly as a coating [9]. Generally, the dissolution of metal can be suppressed by the action of adsorptive inhibitors which may prevent the adsorption of the aggressive ions, and by the formation of a more resistant film on the metallic surface [7].

The previous work [10] studied potassium iodate as an effective corrosion inhibitor for aluminum in 2M HCl solution. In this context, the present work has additional aim to clarify the nature of the protective film by surface analytical techniques (SEM and EDS) in addition to optical microscopy. The adsorption mechanism of KIO_3 on the aluminum surface in 2M HCl has been discussed.

Experimental

Specimens measuring (10mm × 10mm × 2mm) cut from pure 99.99% aluminum sample were used. These were polished with emery papers (200- 1000 grades), degreased in acetone, and washed by distilled water before introduction into the solutions. Experiments were conducted in 2M HCl (pH≈ - 0.28) alone, and with 100 ppm KIO_3 inhibitor optimum dose. Examination of Al- surface in 2M HCl and after exposure to inhibited acidic solution (1h immersion) was carried out using optical polarizing microscope (Nikon, Japan) attached with control box and camera AFX IIA. The compositions of all surface elements were identified by energy dispersive X- ray spectroscopy (EDS) with Cu K_α radiation at 35 KV. The electrode surface of aluminum was examined by SEM (Scanning Electron Microscope-JSM- T20- JEOL. Japan) before and after immersion in the test solution in the absence and presence of KIO_3 inhibitor at room temperature for 1h.

Results and discussion

Optical and SEM investigations

The results of morphology investigation of aluminum surface examined by SEM before and after treatment in 2M HCl in the absence and presence of 100 ppm KIO_3 are shown in Figs. 1- 3. Investigation of the scanning electron micrographs of mechanically polished Al electrode without any treatment (clean sample, Fig. 1) shows that Al sample treated with 2M HCl (Fig. 2) has corrosion areas on its polished surface, which do not exist on the clear sample. The presence of such regions can be attributed to the dissolution of Al due to the surface attack by the aggressive chloride ions.

Immersion of the Al sample in 2M HCl solution containing 100 ppm KIO_3 (Fig. 3), shows that there is an improvement in the surface morphology, possibly by diminishing the corrosion areas due to covering of the active sites. This process leads in turn to the coverage of the surface by protective film. This explains why the corrosion rate of Al in 2M HCl in the presence of 100 ppm KIO_3 is lower than that measured in inhibitor- free solution [10]. The same observations are obtained in optical microscopy of the samples (Figs. 4- 6).

EDS measurements

The EDS spectra for pure Al sample Fig.7 show clear peaks for the main constituents (Al & O) on the other hand, the EDS spectra of Al sample immersed in 2M HCl for 1 hour, Fig. 8 show elemental 8.32%O and 91.68% Al composition. The elemental composition of Al surface immersed in 2M HCl in the presence of 100 ppm KIO_3 inhibitor show an increase in oxygen percent and decrease in aluminum percent (11.05%O & 88.95%Al) which indicates the oxidative inhibition of KIO_3 inhibitor to aluminum surface, Fig. 9.

Mechanism of the inhibition of corrosion

It appears from the experimental data that phenomenon of adsorption plays a fundamental role in inhibition process. This assumption is supported by the following explanation:

The value of pH zch, which is defined as the pH at a point of zero charge, is equal to 9.1 for aluminum [11]. So aluminum surface is positively charged at pH ≈ -0.28, corresponding to 2M HCl. Therefore, Cl^- and IO_3^- ions can be adsorbed on aluminum surface via their negative centers. In order to be able to predict the adsorption mechanism of these ions to positively charged aluminum surface, corrosion mechanism of aluminum in hydrochloric acid must be known [12]. According to this mechanism anodic dissolution of Al proceeds according to the following steps:

$$Al + Cl^- \rightarrow AlCl^-_{ads} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$AlCl^-_{ads} + Cl^- \rightarrow AlCl_2^+ + 3e^- \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The cathodic hydrogen evolution follows the steps:

$$H^+ + e^- \rightarrow H_{ads}\,(fast) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$H^+ + H_{ads} \rightarrow H_2 \quad . \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$IO_3^-{}_{ads}$ ions adsorbed on Al surface can interact with $AlCl_{ads}^-$ which are formed in step (1) according to:

$$2AlCl^-_{ads} + IO_3^-{}_{ads} \rightarrow \underset{\text{Rich oxygen}}{Al_2O_3} + I^- + 2Cl^- \ldots. \quad (5)$$

Thus the oxidation reaction of $AlCl^-_{ads}$ to $AlCl_2^+$ as shown by step (2) can be prevented. This phenomenon is attributed to surface interactions with inhibitor molecules, resulting in greater surface coverage [13]. This enhances the inhibition efficiency considerably.

Conclusion

Surface analysis show that IO_3^- formation on aluminum surface produce strong film which is compact, hard and protective. The inhibitor acts through adsorption phenomena and formation of barrier film. KIO_3 can be used as an effective corrosion inhibitor for aluminum in 2M HCl solution.

Fig.(1): SEM micrograph of clean Al sample X_{100} .

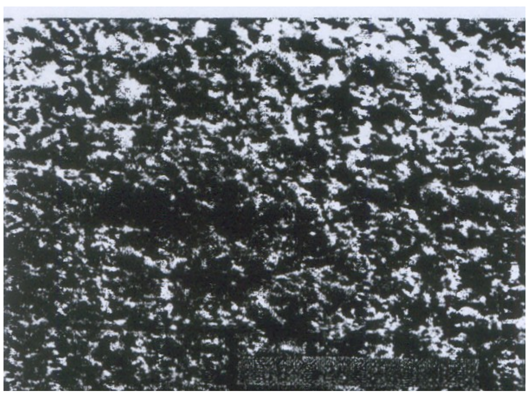

Fig.(2): SEM micrograph of Al sample immersed in 2M HCl for 1h, X_{100} .

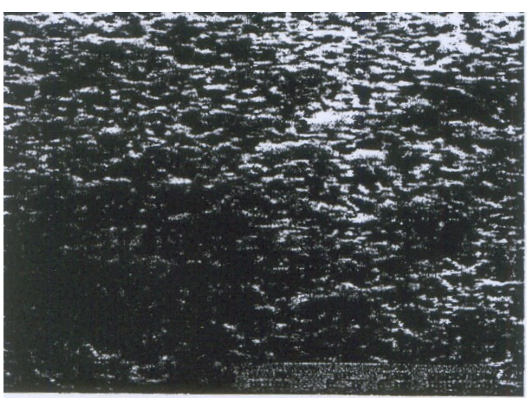

Fig.(3): SEM micrograph of Al sample immersed in 2M HCl containing 100 ppm KIO_3 inhibitor for 1h, X_{100} .

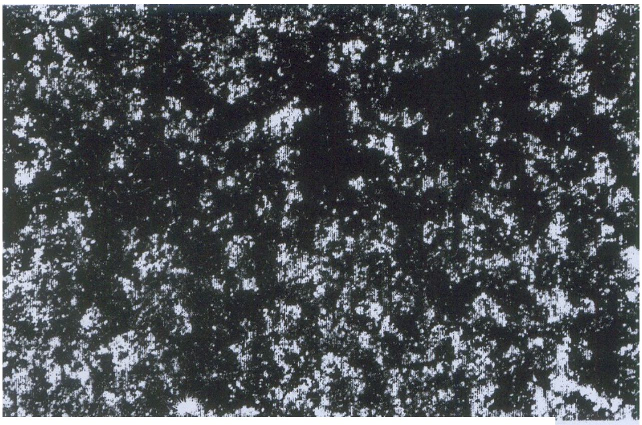

Fig. (4): Optical micrograph of pure Al sample, X_{10}.

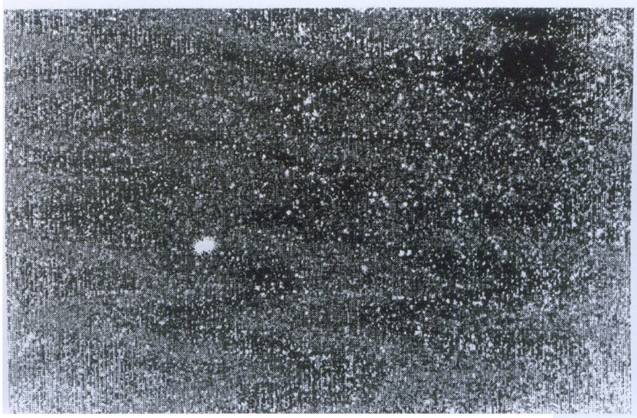

Fig.(5): Optical micrograph of Al sample immersed in 2M HCl, X_{10}.

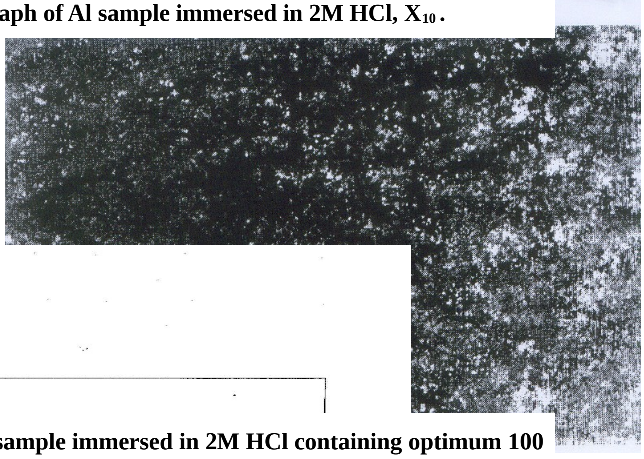

Fig. (6): Optical micrograph of Al sample immersed in 2M HCl containing optimum 100 ppm KIO_3, X_{10}.

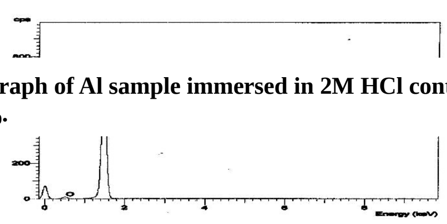

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Fig. (8): EDS spectrum of Al sample in 2M HCl.

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