Effect of 1,2,3benzotriazole on the corrosion of aged 18Ni250 grade Maraging steel in Phosphoric acid solution

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Abstract: The 18 Ni 250 grade maraging steel is a potential high strength steel for advanced technologies such as aerospace, nuclear, and sporting goods. Phosphoric acid and Nitric acid solutions are used in pickling of delicate and precision items where re-rusting after pickling has to be avoided. The present work addresses the study of corrosion behaviour and inhibition using 1,2,3 benzotriazole of aged 18 Ni 250 grade maraging steel in phosphoric acid medium at higher concentration by Potentiodynamic Polarization Technique. The corrosion rates were determined in 1M, 1.5M and 2M by Tafel extrapolation technique in the temperature range 30°C-50°C with different concentrations of inhibitor. The results indicate that the corrosion rate increases with increase in acid concentration and temperature. Inhibition efficiency of 1,2,3 benzotriazole was found to increase with the increase in 1,2,3 benzotriazole concentration and decrease with the increase in temperature. The activation energy E_a and other thermodynamic parameters (∆G˚, ∆H˚ and ∆S˚) have been evaluated and discussed. The standard free energy of adsorption ∆G_ads values indicates that the adsorption is of mixed type. Scanning electron microscopy (SEM) study confirmed the formation of an adsorbed protective film on the metal surface.

Keywords: Maraging Steel, Acid solutions, Organic inhibitor, Polarisation, adsorption.

1. Introduction

Corrosion of structural elements is a major issue for any industry because of the chemical environment of the chemical processing. The significant technical challenges and the high cost directly related to corrosion provide strong incentives for engineers and other technical personnel to develop a firm grasp on the fundamental bases of corrosion. Understanding the fundamentals of corrosion is necessary not only for identifying corrosion mechanisms (a significant achievement by itself), but also for preventing corrosion by appropriate corrosion protection means and for predicting the corrosion behaviour of metallic materials in service conditions. Understanding the mechanisms of corrosion is the key to the development of a knowledge-based design of corrosion resistant alloys and to the prediction of the long-term behaviour of metallic materials in corrosive environments.
Recently, the needs of high reliable substances of high strength and high ductility are gradually increased with the development of aerospace, military, aircraft and tooling applications. Maraging steels are special class of ultra-high strength steels that differ from conventional steels in that they are hardened by a metallurgical reaction that does not involve carbon [1]. The name maraging derives from “martensite-aging” referring to the heat treatment carried out to induce the precipitation of intermetallic [2] in the Fe-Ni martensitic matrix, responsible for the excellent mechanical properties. The alloy is a low carbon steel that contains about 18 wt% Ni, substantial amounts of Co and Mo, together with small additions of Ti. However, depending on the requirements of the application, the composition of the material can be modified. The high strength of maraging steel is achieved by aging the specimen at 400-500°C, where the precipitation of intermetallic takes place. The characteristics of this grey and white steel are high ductility, formability, high corrosion resistance, high temperature strength, ease of fabrication, weldability and maintenance of an invariable size even after heat treatment[3].

Corrosion of Maraging steel is a fundamental academic and industrial concern that has received a considerable amount of attention. These steels have emerged as alternative materials to conventionally quenched and tempered steels for advanced technologies such as aerospace, nuclear and gas turbine applications. Carbon free maraging steels are widely used for the production of high stressed gas vessels from sheet metals for the aircraft shipbuilding industries, shell structural elements of rocket nozzle-space equipment which works in corrosive media and other critical structural elements. They frequently come into contact with acids during cleaning, pickling, descaling, acidizing, etc. Materials used in acidic environment should have good corrosion resistance. According to the available literature, 18 Ni maraging steel, when exposed to atmosphere, undergoes more or less uniform corrosion and gets completely covered with rust [4]. The strategy is to isolate the metal from corrosive agents. The addition of inhibitors to the corrosion medium serves the purpose. Thiosemicarbazones and their derivatives have continued to be subjects of extensive investigation in chemistry and biology owing to their broad spectrum of anti-tumor [5], antimalarial [6], and many other applications including corrosion inhibition of metals [7]. These compounds can be adsorbed on metal surface through lone pairs of electrons present on nitrogen or sulphur atoms but also through pi electrons present in these molecules [8]. Only a few reports on the corrosion inhibition of maraging steel in acid solution using organic inhibitors are available in the literature [9]. The effect of carbonate ions in slightly alkaline medium on the corrosion of maraging steel was studied by Bellanger [10].

Phosphoric acid solutions are used in pickling of delicate and costly components and precision items where re-rusting after pickling has to be avoided. Phosphoric acid has the unique property of dissolving rust quickly while etching iron very slowly. The other advantage of phosphoric acid is that it leaves fine iron phosphate coating on the surface of the alloy, preventing further corrosion. However, the iron phosphate coating is not very thick and durable. Some additional protection like use of corrosion inhibitor is necessary. However no literature seems to be available on the corrosion behavior of maraging steel in the acid medium except previous study by T. Poornina et al[11]. Although the maraging steel alloys, in general, are corrosion resistant compared to conventional steels, their previous study has revealed substantial corrosion of aged maraging steel in phosphoric acid medium at low concentrations. It has been reported the use of effective inhibitor in phosphoric acid medium for aged 18 Ni 250 grade maraging steel. The present work addresses the assessment of corrosion behavior and inhibition of aged 18 Ni 250 grade maraging steel in phosphoric acid medium at higher concentration using 1,2,3 benzotriazole.
2. Experimental Procedure

2.1 Material preparation

The material employed was 18% Ni M250 grade maraging steel under weld aged condition. The maraging steel plates were welded by gas tungsten arc welding-direct-current straight polarity (GTAW-DCSP) using filler material of compositions 0.015% C, 17% Ni, 2.55% Mo, 12% Co, 0.015% Ti, 0.4% Al, 0.1% Mn, 0.1% Si, with the remainder being Fe. The specimen was taken from the plates which are welded as described above and aged at 480±5°C for 3 hours followed by air cooling. The composition of the base metal is given in Table 1.

Cylindrical test coupons were cut from the plate and sealed with epoxy resin in such a way that, the area exposed to the medium is 0.503 cm². These coupons were polished as per standard metallographic practice, belt grinding followed by polishing on emery papers, finally on polishing wheel using legated alumina to obtain mirror finish, degreased with acetone, washed with double distilled water and dried before immersing in the corrosion medium.

1,2,3benzotriazole was used as inhibitor at different concentrations viz. 50, 100, 150 and 200 ppm.

Table 1. Composition of the base metal (% by weight)

| Element | Composition | Element | Composition |
|---------|-------------|---------|-------------|
| C       | 0.015%      | Ti      | 0.015%      |
| Ni      | 17-19%      | Al      | 0.005-0.15% |
| Mo      | 4.6-5.2%    | Mn      | 0.1%        |
| Co      | 7-8.5%      | P       | 0.01%       |
| Si      | 0.1%        | S       | 0.01%       |
| O       | 30ppm       | N       | 30ppm       |
| H       | 2ppm        | Fe      | Balance     |

2.2 Medium

Standard solution of phosphoric acid having concentration 1M, 1.5M and 2M were prepared by diluting analytical grade phosphoric acid by using double distilled water. The experiments were carried out using phosphoric acid solution at temperatures 30, 40 and 50°C (±0.5°C), in a calibrated thermostat.

2.3 Method

2.3.1 Electrochemical Measurement Technique

Electrochemical measurements were carried out using electrochemical work station, CHI604A Electrochemical Analyzer instrument Version 5 software. The arrangement used was a conventional three-electrode compartment glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference. The working electrode was made of weld aged maraging steel. All the values of potential are referred to the SCE. The polarization studies were carried out immediately after the immersion of the sample.

2.3.2 Potentiodynamic Polarization Measurements

Finely polished and dried maraging steel specimens were exposed to the corrosion medium of different concentrations at different temperatures and allowed to establish a steady state open circuit
potential (OCP). The potentiodynamic current–potential curves were recorded by polarizing the specimen to -200 mV cathodically and +200 mV anodically with respect to OCP at a scan rate of 1 mV s\(^{-1}\). The electrode potential is plotted against the logarithm of applied current. The Tafel region is extrapolated to obtain corrosion potential and corrosion current density.

2.3.3 Characterization Using SEM

In order to differentiate between the surface morphology after its immersion in acid in the absence and in the presence of 1,2,3benzotriazole, SEM investigation was carried out using JEOL JSM-6380 LA Analytical SEM.

3. Results and Discussion

3.1 Potentiodynamic Polarization Measurements.

The effect of phosphoric acid concentration, solution temperature and different concentration of 1,2,3benzotriazole on the corrosion rate of aged samples of maraging steel was studied using Tafel polarisation technique. Figure 1(a) represents potentiodynamic polarisation curves as a function of concentration of phosphoric acid at 30\(^0\)C. The corrosion current densities (\(i_{\text{corr}}\)) obtained by the Tafel extrapolation technique increases with increase in concentration of phosphoric acid in the solution for all temperatures.

![Fig.1](a) Tafel polarization curves for the corrosion of weld aged maraging steel at 30\(^0\)C at different concentration of phosphoric acid(b) Tafel polarization curves for the corrosion of weld aged maraging steel in 1M Phosphoric acid at different temperature.

The Figure 1(b) shows the potentiodynamic polarization curves for the corrosion of aged maraging steel in phosphoric acid at different temperatures like 30, 40 and 50\(^\circ\)C with three different concentrations. Corrosion rate of the weld increases with the increase in temperature and concentration of the acid. It would be possibly because of the increased kinetics of the reaction and availability of the reaction species for corrosion.

Potentiodynamic polarization curves for the corrosion of weld aged maraging steel in different concentrations of phosphoric acid in the presence of different concentrations of 1,2,3 benzotriazole are shown in Fig.2. It can be observed that both the cathodic and anodic reactions are suppressed with the
addition of 1,2,3benzotriazole, which suggested that the inhibitor exerted an efficient inhibitory effect both on anodic dissolution of metal and on cathodic hydrogen liberation reaction. The electrochemical parameter corrosion current density ($I_{corr}$) obtained from the polarization measurements are listed in Table 2.

The corrosion rate ($\nu_{cor}$) is calculated using equation,

$$\text{Corrosion rate}(\nu_{cor}) = \frac{3272(E.W)I_{corr}}{D}$$  \hspace{1cm} (1)

Where 3272 is a constant that defines the unit of corrosion rate, $I_{corr}$= corrosion current density in A/cm$^2$, D=density of the corroding material, 8.23 g/cm$^3$, E.W=29.2, equivalent weight of corroding material (atomic weight/oxidation number). The surface coverage ($\theta$) is calculated as,

$$\theta = \frac{(i_{corr}-i_{corr}(inh))}{i_{corr}}$$  \hspace{1cm} (2)

Where, $i_{corr}$ is the corrosion current density in the absence of inhibitor and $i_{corr}(inh)$ is the corrosion current density in the presence of inhibitor.

![Fig. 2 Tafel polarization curves for the corrosion of weld aged maraging steel in 1.5M Phosphoric acid containing different concentrations of inhibitor at 30°C.](image)

The percentage inhibition efficiency ($\% \eta$) = $\theta \times 100$.  \hspace{1cm} (3)

The results indicate that the weld is highly susceptible to corrosion in 2M concentration while its corrosion rate is comparatively lower in 1M concentration even at 50°C in both the cases. Corrosion rate is high at 50°C and is lower at 30°C for every concentration. Corrosion rate of the weld increases with the increase in temperature. It would be possibly because of the increased kinetics of the reaction. Also, corrosion rate shows an increase with the increase in acid concentration. This is because as more acidic ions are present more number of metal ion dissolution will take place leading to an increase in the corrosion rate.

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The corrosion resistance value decreases with increase of both solution concentration and temperature, polarization curves are shifted to high current density region indicating increase in corrosion rate. The nature of polarization curves predicts active corrosion behavior at each temperature and concentration of acids (Fig.1(a) and Fig 1(b)). It is observed from these results that the corrosion potential is shifted to proper values as the concentration of acid is increased. This is in accordance with Muralidharan et al[12] and T. Poornima et al (2010) who proposed dependence of $i_{corr}$ on solution parameters. With increase of solution temperature slopes $\beta_a$ and $\beta_c$ are almost unchanged indicating no change in the mechanism of corrosion with temperature. The hydrogen evolution increases with increase in temperature that leads to increase in cathodic reaction rate [13]. The corrosion rate reaches a maximum value of 101.58 mm y$^{-1}$ for 2M phosphoric acid at 50°C.

1,2,3benzotriazole is fairly effective in bringing down the corrosion rate as its presence brings down the corrosion rate considerably. Among the three concentrations studied, the lowest corrosion rate was obtained at 200ppm of 1,2,3 benzotriazole in phosphoric acid and 650ppm in 1:1 mixture of 2M phosphoric acid and nitric acid solution in all concentrations. Since, 1,2,3benzotriazole is adsorption type inhibitor; it spreads over the surface of the metal like an umbrella and protects the material from corrosion. However, if sufficient quantity is not added then the surface of metal is left uncovered which results in severe corrosion attack. Inhibition efficiency increases with the increase in the inhibitor concentration in all media. The inhibition efficiency of 1,2,3benzotriazole in different acid concentrations is shown in Table 2 for phosphoric acid.

This indicates that the inhibitive action of 1,2,3benzotriazole may be considered due to the adsorption and formation of barrier film on the electrode surface. The barrier film formed on the metal surface reduces the probability of both the anodic and cathodic reactions, which results in decrease in corrosion rate[14]. The inhibition efficiency increases with the increase in inhibitor concentration, reaching a maximum value at higher concentration of inhibitor. It can also be seen from the plots that there is no appreciable shift in the corrosion potential value ($E_{corr}$) on the addition of 1,2,3benzotriazole to the corrosion medium and also on increasing the concentration of 1,2,3 benzotriazole. If the displacement in corrosion potential is more than ±85 mV with respect to corrosion potential of the blank, then the inhibitor can be considered as a cathodic or anodic type [15]. However, the maximum displacement in the present study is ±35 mV, which indicates that 1,2,3benzotriazole is a mixed type inhibitor. As the concentration of the inhibitor increases, it is noticed that the corrosion potential shifts slightly toward more positive potential. This indicates that the inhibitor promotes passivation of weld aged maraging steel through adsorption and decreases hydrogen evolution. The increase in the inhibition efficiency with the increase in inhibitor concentration is attributed to the increased surface coverage by the inhibitor molecules as the concentration is increased.

3.2 Effect of Temperature

The results of Potentiodynamic polarization given in Table 2 indicates that the inhibition efficiency decreases with increase in temperature. However, $i_{corr}$ and hence the corrosion rate of the specimen increases with the increase in temperature for both blank and inhibited solutions. The decrease in inhibition efficiency with the increase in temperature may be attributed to the higher dissolution rates of weld aged maraging steel at elevated temperature and also a possible desorption of adsorbed inhibitor due to the increased solution agitation resulting from higher rates of hydrogen gas evolution[16]. The higher rate of hydrogen gas evolution may also reduce the ability of the inhibitor to
be adsorbed on the metal surface. The decrease in inhibition efficiency with the increase in temperature is also suggestive of physisorption of the inhibitor molecules on the metal surface [17].

The apparent activation energy ($E_a$) for the corrosion process in the presence and absence of the inhibitor was calculated using Arrhenius law Eq. (4) [18],

$$
\ln(\upsilon_{corr}) = B - \frac{E_a}{RT}
$$

(4)

Where $B$ is a constant which depends on the metal type, $R$ is the universal gas constant and $T$ is the absolute temperature.

The plot of $\ln(\upsilon_{corr})$ versus reciprocal of absolute temperature ($1/T$) gives a straight line with slope $\frac{-E_a}{R}$, from which, the activation energy values for the corrosion process were calculated. The Arrhenius plots for the corrosion of weld aged maraging steel in the presence of different concentrations are shown in Fig. 3(a).

Table 2. Results of potentiodynamic polarization studies on weld aged maraging steel in phosphoric acid medium containing different concentrations of 1, 2, 3 benzotriazole.

| Acid concentration | Temperature (°C) | Inhibitor concentration | $I_{corr}\times10^{-4}$ (A cm$^{-2}$) | Corrosion rate $\upsilon_{corr}$(mm y$^{-1}$) | Efficiency $\eta$(%) |
|-------------------|-----------------|-------------------------|-------------------------------------|---------------------------------|-----------------|
| 1M                | 30              | Blank                   | 13.44                               | 15.68                           |                 |
|                   |                 | 50ppm                   | 7.25                                | 8.46                            | 46.04           |
|                   |                 | 100ppm                  | 5.04                                | 5.88                            | 62.50           |
|                   |                 | 150ppm                  | 4.85                                | 5.66                            | 63.90           |
|                   |                 | 200ppm                  | 3.60                                | 4.19                            | 73.27           |
|                   | 40              | Blank                   | 24.81                               | 28.95                           |                 |
|                   |                 | 50ppm                   | 18.82                               | 21.96                           | 22.07           |
|                   |                 | 100ppm                  | 15.01                               | 17.51                           | 39.51           |
|                   |                 | 150ppm                  | 12.74                               | 14.86                           | 48.67           |
|                   |                 | 200ppm                  | 10.26                               | 11.97                           | 58.65           |
|                   | 50              | Blank                   | 55.51                               | 64.76                           |                 |
|                   |                 | 50ppm                   | 30.54                               | 35.63                           | 44.98           |
|                   |                 | 100ppm                  | 27.18                               | 31.71                           | 51.03           |
|                   |                 | 150ppm                  | 24.51                               | 28.60                           | 55.83           |
|                   |                 | 200ppm                  | 18.54                               | 21.63                           | 66.59           |
| 1.5M              | 30              | Blank                   | 14.36                               | 16.75                           |                 |
|                   |                 | 50ppm                   | 7.94                                | 9.26                            | 44.71           |
|                   |                 | 100ppm                  | 6.87                                | 8.02                            | 52.11           |
|                   |                 | 150ppm                  | 6.38                                | 7.45                            | 55.52           |
|                   |                 | 200ppm                  | 5.89                                | 6.88                            | 58.92           |
|                   | 40              | Blank                   | 31.76                               | 37.06                           |                 |
|                   |                 | 50ppm                   | 20.11                               | 23.47                           | 36.67           |
|                   |                 | 100ppm                  | 18.17                               | 21.20                           | 42.79           |
|                   |                 | 150ppm                  | 16.01                               | 18.68                           | 49.59           |
|                   |                 | 200ppm                  | 15.18                               | 17.71                           | 52.21           |
| 2M                | 30              | Blank                   | 66.99                               | 78.17                           |                 |
|                   |                 | 50ppm                   | 40.33                               | 47.06                           | 40.00           |
|                   |                 | 100ppm                  | 37.41                               | 43.65                           | 44.16           |
|                   |                 | 150ppm                  | 30.18                               | 35.21                           | 54.95           |
|                   |                 | 200ppm                  | 28.98                               | 33.82                           | 56.73           |


Table 3. Activation parameters for corrosion of weld aged maraging steel in \( \text{H}_3\text{PO}_4 \) medium containing different concentration of inhibitor

| Acid concentration | Inhibitor concentration | \( E_a \) [KJ/mol] | \( \Delta H^\circ \) [KJ/mol] | \( -\Delta S^\circ \) [J/mol K] |
|--------------------|-------------------------|--------------------|-----------------|-----------------|
| 1M                 | Blank                   | 53.15              | 54.92           | 208.36          |
|                    | 50ppm                   | 71.59              | 59.83           | 212.10          |
|                    | 100ppm                  | 75.66              | 61.78           | 213.35          |
|                    | 150ppm                  | 77.85              | 63.15           | 215.01          |
|                    | 200ppm                  | 79.71              | 69.01           | 215.43          |
| 1.5M               | Blank                   | 54.32              | 59.78           | 206.70          |
|                    | 50ppm                   | 70.02              | 63.43           | 210.02          |
Table 4. Standard free energy of activation (ΔG°) values

| Solution concentration | Temperature (°C) | Blank | 50ppm | 100ppm | 150ppm | 200ppm |
|------------------------|-----------------|-------|-------|--------|--------|--------|
| 1M                     | 30              | 118.05| 124.09| 126.42 | 130.43 | 136.43 |
|                        | 40              | 120.13| 126.21| 128.55 | 132.58 | 138.59 |
|                        | 50              | 122.21| 128.34| 130.68 | 134.60 | 136.68 |
| 1.5M                   | 30              | 122.39| 127.06| 130.10 | 134.60 | 136.80 |
|                        | 40              | 124.46| 129.16| 132.14 | 136.72 | 138.80 |
|                        | 50              | 126.53| 131.26| 134.25 | 138.83 | 140.92 |
| 2M                     | 30              | 109.73| 115.30| 116.95 | 120.41 | 130.46 |
|                        | 40              | 111.77| 117.42| 119.09 | 122.56 | 132.62 |
|                        | 50              | 113.81| 119.53| 121.22 | 124.70 | 134.77 |

The enthalpy of activation (ΔH°) and entropy of activation (ΔS°) for the corrosion of alloy were calculated from Fig. 3(b) by using the transition state theory Eq. (5)[18],

$$u_{corr} = \frac{RT}{Nh} \exp \left( \frac{\Delta S^o}{R} \right) \exp \left( -\frac{\Delta H^o}{RT} \right)$$

(5)

where ‘h’ is Plank’s constant, and ‘N’ is Avagadro’s number.

The chemically stable surface active inhibitors increase the energy of activation and decrease the surface area available for corrosion. The data in the Table 3 shows that the values of E_a for the corrosion of weld aged maraging steel in phosphoric acid in the presence of 1,2,3benzotriazole are higher than those in the inhibited medium. The adsorption of the inhibitor on the electrode surface leads to the formation of a physical barrier between the metal surface and the corrosion medium, blocking the charge transfer, and thereby reducing the metal reactivity in the electrochemical reactions of corrosion.

The increase in the E_a values, with increasing inhibitor concentration indicates the increase in energy barrier for the corrosion reaction, with the increasing concentrations of the inhibitor [19]. The increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the metal surface with increase in temperature and a corresponding increase in corrosion rate occurs due to the fact that greater area of metal is exposed to the acid environment.
The enthalpy of activation (∆H°) values indicates that this is an endothermic reaction in which ∆H° ≫ 0. The calculated values of ∆H° obtained in this study is less than 80KJmol⁻¹, indicating both physical and chemical adsorption behavior of 1,2,3benzotriazole on the metal surface.

The entropy of activation in the presence of inhibitor is large and negative. This implies that the activated complex in the rate determining step represents an association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to activated complex [20]. The entropy of activation value is higher in the inhibited solutions than that in the uninhibited solution, and the value increases with the increase in the inhibitor concentration. This might be the results of the adsorption of organic inhibitor molecules from the solution which could be regarded as a quasi-substitution process between the organic compound in the aqueous phase and water molecules at the electrode surface [21]. The adsorption of organic inhibitor is accompanied by desorption of water molecules from the surface. Thus the increasing in entropy of activation may be attributed to the increase in solvent entropy [22]. The positive H values represents the endothermic nature of dissolution of maraging steel is difficult [23].

The standard free energy of activation (∆G°)can be calculated using free energy equation and tabulated in the Table 4.

### 3.3 Adsorption Isotherms

The corrosion inhibition actions of inhibitors are assigned to form a protective film between the metal surface and the corrosive medium through their adsorption on the metal/solution interface, which separates the metal surface from the corrosive medium. The adsorption process of the inhibitor is usually regarded as a substitution process between the organic inhibitor in the aqueous solution (Inh(sol)) and water molecules adsorbed at the metal surface (H₂O(ads)) as following Eq.(6)[24],

\[ \text{Inh}(\text{sol}) + n \text{H}_2\text{O}(\text{ads}) = \text{Inh}(\text{ads}) + n \text{H}_2\text{O}(\text{sol}) \]  

(6)

Where ‘n’ represents the number of water molecules replaced by one molecule of the adsorbed inhibitor. The adsorption bond strength is dependent on the composition of the metal, corrosion medium, inhibitor structure, concentration and orientation as well as temperature. The basic information on the interaction between the inhibitor and the alloy surface can be provided by the adsorption isotherm. In order to obtain the adsorption isotherm, the linear relation between surface coverage (θ) value and concentration of inhibitor C_{inh} must be found. Verification plots were plotted for each isotherm and it was found that Langmuir adsorption isotherm gives straight line in both the medium as shown in Fig.4 [25].
Fig 4. Langmuir adsorption isotherms for H$_3$PO$_4$ medium

Table 5. Standard free energy of adsorption (ΔG$_{ads}$) for H$_3$PO$_4$ medium

| Solution concentration | Temperature (°C) | 50ppm | 100ppm | 150ppm | 200ppm |
|------------------------|------------------|-------|--------|--------|--------|
| 1M                     | 30               | 27.40 | 27.77  | 27.69  | 27.99  |
|                        | 40               | 29.30 | 29.25  | 28.38  | 28.75  |
|                        | 50               | 31.13 | 29.92  | 29.35  | 29.96  |
| 1.5M                   | 30               | 29.17 | 28.17  | 27.41  | 27.12  |
|                        | 40               | 29.26 | 28.13  | 27.78  | 27.30  |
|                        | 50               | 30.57 | 29.17  | 29.25  | 28.67  |
| 2M                     | 30               | 29.00 | 27.66  | 27.73  | 28.09  |
|                        | 40               | 29.85 | 28.26  | 27.30  | 27.00  |
|                        | 50               | 31.65 | 31.37  | 30.90  | 30.32  |

The values of thermodynamic parameters for the adsorption of inhibitors can provide valuable information about the mechanism of corrosion inhibition. The negative values of ΔG$_{ads}$ (Table 5) indicate the spontaneity of the adsorption process and the stability of the adsorbed layer on the metal surface. In general, the standard free energy values of -20 kJ mol$^{-1}$ or less negative are associated with
an electrostatic interaction between charged molecules and charged metal surface, resulting in physisorption, and those of -40 kJ mol\(^{-1}\) or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, resulting in chemisorption [26, 27].

The calculated values of \(\Delta G^\circ_{\text{ads}}\) obtained in this study range between -27.40 kJ mol\(^{-1}\) to -31.65 kJ mol\(^{-1}\) for Phosphoric acid medium, indicating both physical and chemical adsorption behavior of 1,2,3 benzotriazole on the metal surface. This is also supported by the Enthalpy values (Table 3). These values indicate that the adsorption process may involve complex interactions involving both physical and chemical adsorption of the inhibitor. The fact that both \(\Delta G^\circ_{\text{ads}}\) and inhibition efficiency decrease with the increase in temperature, indicates that the adsorption of 1,2,3 benzotriazole on the weld aged maraging steel surface in both the medium are not favored at high temperature and hence can be considered to be predominantly physisorption. The \(\Delta G^\circ_{\text{ads}}\) value is large and negative; indicating that decrease in disordering takes place on going from the reactant to the alloy adsorbed species. This can be attributed to the fact that adsorption is always accompanied by decrease in entropy.

### 3.4 Characterization Using SEM

In order to differentiate between the surface morphology after its immersion in acid in the absence and in the presence of 1,2,3 benzotriazole, SEM investigation was carried out. Fig. 5(a) represents SEM image of the corroded weld aged maraging steel sample in 1M phosphoric acid in the absence of 1,2,3 benzotriazole. The corroded surface shows detachment of particles from the surface. The corrosion of the alloy may be predominantly attributed to the inter-granular corrosion assisted by the galvanic effect between the precipitates and the matrix along the grain boundaries.

**Fig. 5.** SEM images of the weld aged maraging steel after immersion in 1M \(\text{H}_3\text{PO}_4\) (a) in the absence and (b) in the presence of 1,2,3 benzotriazol

Figure 5(b) represents SEM image of weld aged maraging steel after the corrosion in a medium of phosphoric containing 200ppm of 1,2,3 benzotriazole. The image clearly shows a smooth surface due to the adsorbed layer of inhibitor molecules on the alloy surface, thus protecting the metal from corrosion.
4. Conclusions

1. Corrosion rate of sample increases with increase in temperature because of the increased kinetics of reaction.
2. Corrosion rate shows an increase with the increase in acid concentration. This is because as more acidic ions are present and number of metal ion dissolution will take place leading to an increase in the corrosion rate.
3. 1,2,3benzotriazole is found to be fairly effective as corrosion inhibitor as about 73.27% inhibition was observed in H$_3$PO$_4$ at the highest concentration of the inhibitor.
4. The inhibition efficiency of 1,2,3benzotriazole decreases with the increase in concentration of 1,2,3 benzotriazole and decreases with the increase in temperature.
5. The standard free energy of adsorption values confirm that inhibitor molecules get adsorbed on to the surface of the weld by mixed type adsorption.
6. The adsorption of the inhibitor on the metal surface follows Langmuir Adsorption Isotherm.
7. The SEM observation proves that the inhibition of corrosion is due to formation of an adsorbed passive film on the metal surface.

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