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The electrochemical corrosion and passivation behaviour of Monel (400) in concentrated acids and their mixtures

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The electrochemical polarisation behviour of Monel (400) in different compositions of binary and ternary solution mixtures of concentrated phosphoric, sulphuric, formic and acetic acids has been studied by potentiostatic polarisation technique at 25°C. The cathodic polarisation curves are almost linear and similar in all the binary and ternary solution mixtures and cathodic reaction is hydrogen evolution. The anodic polarisation curves reveal active, passive and transpassive behaviour in all the solution mixtures. The magnitude of the critical current density (i_c) and passivity current density (i_p) is higher in binary solution mixtures of phosphoric-formic acid than binary solution mixtures of either phosphoric-acetic acid or phosphoric-sulphuric acid. In the ternary solution mixtures of phosphoric-sulphuric-formic acids and phosphoric-sulphuric-acetic acids, the passivity is improved in comparison to their binary solution mixtures. Addition of sulphuric acid is found to improve the passivity in case of ternary solution mixtures. The effect of temperature on polarisation behvaiour of Monel (400) in a selected composition of solution mixture (60% $H_3PO_4 + 4\%\ H_2SO_4 + 36\%$ HCOOH) has been studied at 25, 37, 45 and 56°C. Higher temperature increased the corrosion and enhanced the surface reflection. The stability of the passive film formed on the surface of the alloy has been examined by current decay method. Examination of the surface of working electrode, after polarisation studies was done using scanning electron microscopy (SEM) and atomic force microscopy (AFM) in contact mode.

1. Introduction

A nickel-copper alloy, (Monel 400) is more corrosion resistant than nickel under reducing condition and more resistant than copper under oxidising conditions [1]. These characteristics together with its higher strength, very adequate ductility and ease of cold working make it generally more attractive than either of the pure metals for a wide variety of applications, nearly all of which exploit its corrosion resistance.

In the chemical and process industries the alloy is used for vessels, pipelines, filter and valves in many different media. Its availability in almost all forms and the readiness with which it can be formed and welded, make it an important candidate for many applications. Copper and nickel, the constituent metals of the alloy have been subjected to corrosion studies in different acidic media [2–6] Monel 400 is an important alloy of copper and nickel. Addition of copper provides improvement in the resistance of nickel to non-oxidising acids [7]. In particular, alloys containing 30 to 40% copper offer useful resistance to non-aerated sulphuric acid. The corrosion behaviour of Monel electrodes in $KF \cdot 2HF$ melts [8], a few acids [9, 10] and in presence of chloride ions has been recently studied [11, 12]. However, the corrosion behaviour of monel (400) in common concentrated acids and their mixtures is scarcely known. This has drawn the attention of the authors because Monel (400) is an important and useful alloy and phosphoric, sulphuric, formic and acetic acids are very common acids; and both the alloy and the acids are used in many useful industrial applications. These acids individually and/or their mixtures are useful in chemical applications in industry and are also useful for electropolishing [13–16] of different metals and alloys.

Therefore, the corrosion behaviour of the alloy (Monel 400) has been investigated in binary and ternary solution mixtures of phosphoric, sulphuric, formic and acetic acids and the investigations have also been extended at higher potentials (transpassive) to examine the suitability of these electrolytes for the purpose of electropolishing.

2. Experimental

The experimental setup, working procedures and preparation of the specimens are the same as described elsewhere [15, 16]. The electrochemical polarisation studies of the alloy (Monel 400) were performed potentiostatically (Weking POS 73) without giving any treatment to the sample, in aerated solution under unstirred

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condition. Prior to the polarisation measurements, the working alloy electrode of 2 cm^2 exposable surface area was immersed in the experimental solution for about 30 minutes to attain a stable value of open circuit potential (OCP). The solution mixtures (phosphoric, sulphuric, formic and acetic acids) were prepared by taking required volume of each acid from their concentrated stock solutions and compositions are reported in volume percent. All the experiments were performed at $25 \pm 1°C$ unless otherwise mentioned. Effect of temperature (25–56°C) was investigated for a selected composition of the solution mixture. A saturated calomel electrode was used as a reference electrode. The chemical composition (wt%) of the alloy is 30 Cu, 1.6 Fe, 1.0 Mn, 0.15 C and balance nickel. The surface examination of the working electrode was done using scanning electron microscopy (Philips XL-20) and atomic force microscopy (METRIS - 2000 Burleigh) in contact mode.

3. Results and discussion

The open-circuit potential of the alloy (Monel 400) lies between −160 to −40 mV and −520 to −80 mV in different binary solution mixtures of phosphoric acid-formic acid and phosphoric acid-sulphuric acid, respectively while it acquires −600 mV, −440 mV and +100 mV in individual concentrated phosphoric acid, formic acid and sulphuric acid, respectively at 25°C. In above binary solution mixtures the OCP tends to become more noble with increasing content of either formic acid or sulphuric acid in phosphoric acid. However, in case of phosphoric acid-acetic acid solution mixtures no definite of variation in OCP is observed and the value ranged between −720 to −240 mV. Also, in the case of ternary solution mixtures of phosphoric acid-sulphuric acid containing either formic acid or acetic acid no regular trend of variation in OCP is observed with respect to the variation in composition of the solution and the OCP ranged between −660 to −160 mV in these solutions.

The electrochemical corrosion behaviour of the alloy (Monel 400) in different binary and ternary solution mixtures of different compositions of phosphoric, sulphuric, formic and acetic acids at 25°C are depicted in Figs 1–7. In general the nature of the cathodic curves in individual acids and their binary and ternary mixture solutions is found similar except some variation in current. The curves are usually linear and reveal that hydrogen evolution is the cathodic reaction in each case.

It is evident from the figures that the alloy shows a well defined active-passive transition and in most of the cases transpassivity is also observed. In general the anodic Tafel slope value ranged between 50 to 110 mV dec^{-1} in different binary and ternary solution mixtures at 25°C in the active region. In a few cases the passive region is not well established and a secondary current peak has been obtained in the passive region. The results reveal that the composition and content of the acids in solution mixtures influence the active-passive and transpassive behaviours of the alloy. The results have been discussed under separate heads for clear presentation which follows-

3.1. Phosphoric and formic acids solution mixtures

It is seen from the polarisation curves in Fig. 1 that the alloy shows active corrosion behaviour in concentrated formic acid. Initially well developed Tafel behaviour has been observed which is followed by distinct limiting current density. The anodic Tafel slope is found between 45 to 85 mV dec^{-1}. Above a potential 600 mV, the current density increases steadily. Such gradual increase in current at higher potentials indicating limiting nature implies that either the reaction is mass transfer

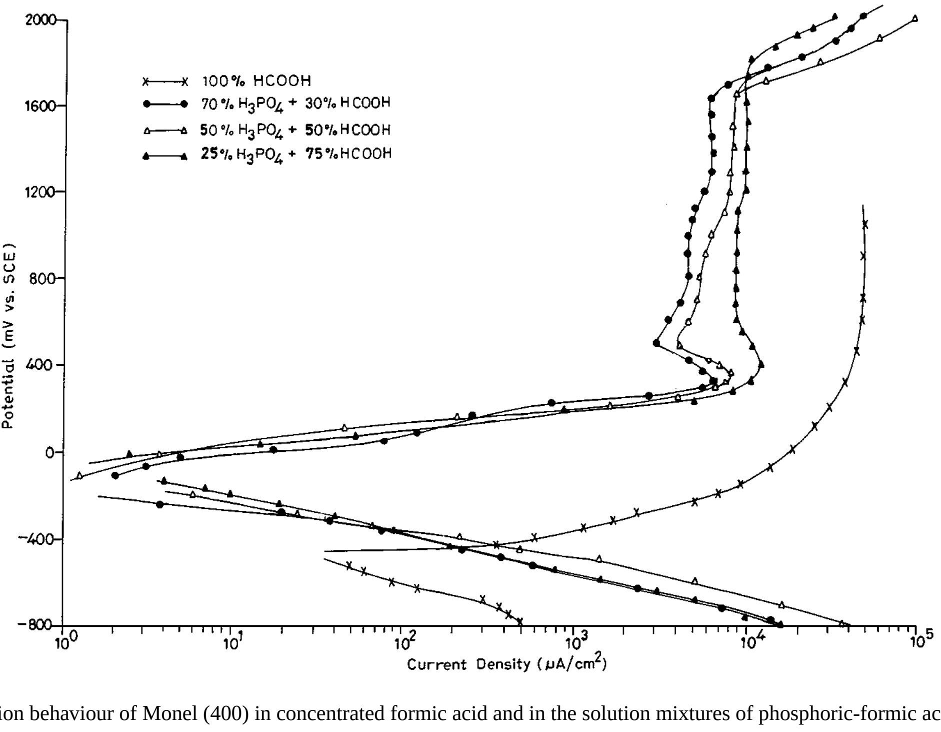


Figure 1 Polarisation behaviour of Monel (400) in concentrated formic acid and in the solution mixtures of phosphoric-formic acid.

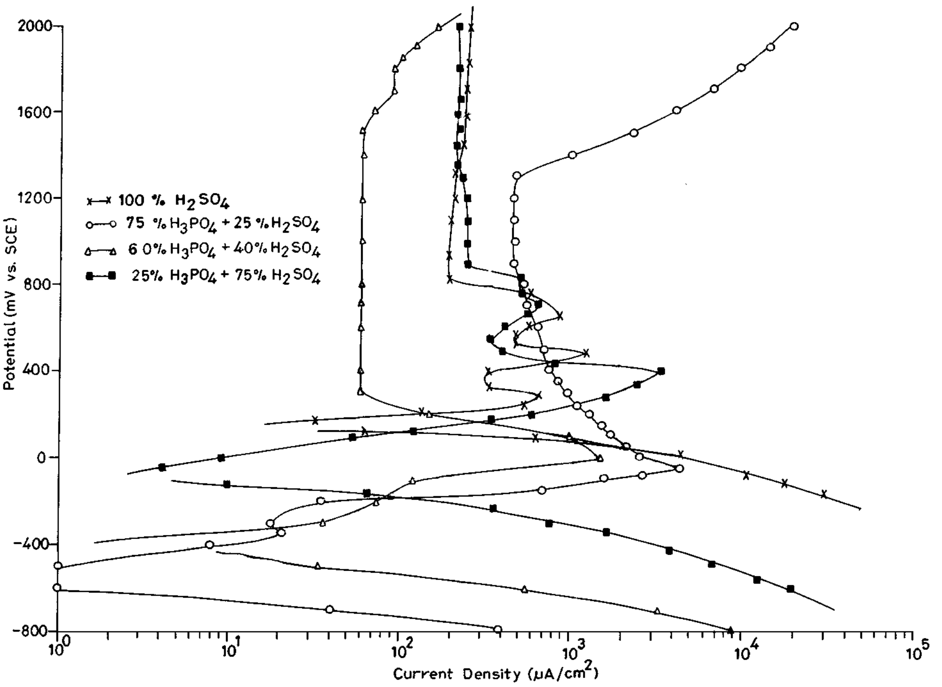


Figure 2 Polarisation behaviour of Monel (400) in concentrated sulphuric acid and in the solution mixtures of phosphoric-sulphuric acids.

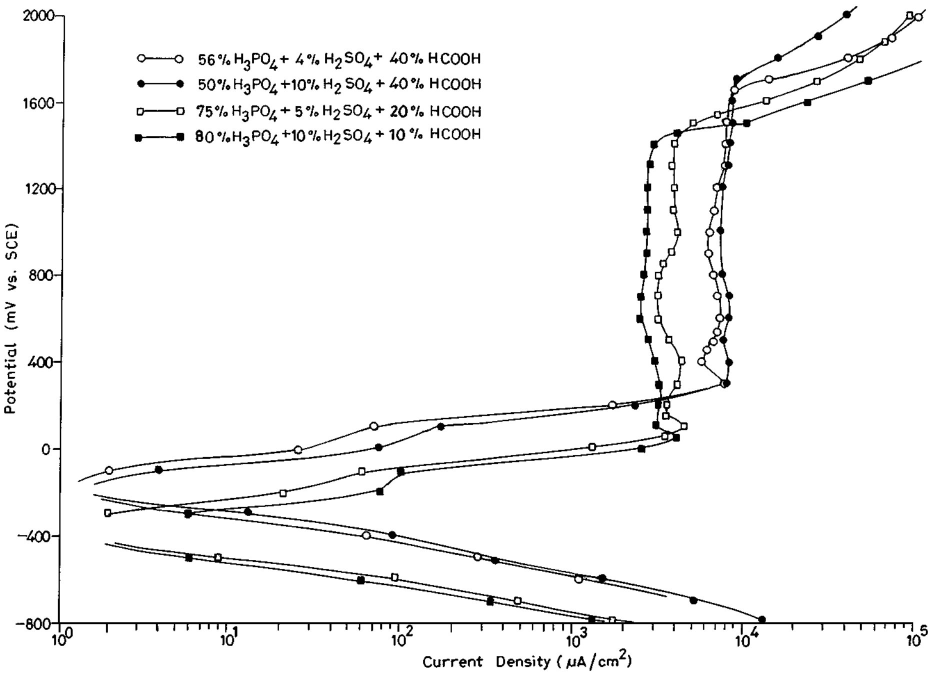


Figure 3 Polarisation behaviour of Monel (400) in ternary solution mixtures of phosphoric-sulphuric and formic acids.

controlled or it is sluggish in this potential region in comparison to initial ones. It is also likely that the corrosion product which formed becomes saturated and may stick to the metal surface.

The corrosion behaviour of the alloy in formic acid seems to partially resemble with reported polarisation behaviour of copper [3] and nickel [5] in aqueous formic acid. The anodic behaviour of the alloy also suggests that the anodic polarisation behaviour of copper is affected when alloyed with nickel. This effect is manifested with an increase in nobility of the corrosion potential, widening of the typical active zone; also passivation zone disappears entirely and no active passive transition was observed. This result is in accordance with Uhlig's hypothesis [17].

On increasing the content of formic acid from 30 to 75% in phosphoric acid, the anodic polarisation curves shift towards higher current-density side. The nature of the anodic polarisation curves at higher concentrations of formic acid (60 and 75%) in mixture is quite similar to each other and the curves almost overlap. On increasing the content of formic acid in phosphoric acid, the viscosity of the binary solution mixture decreases. Due to high dielectric constant of both the acids and resulting decrease in viscosity of the solution mixture, the anodic polarization curve shifts towards higher current

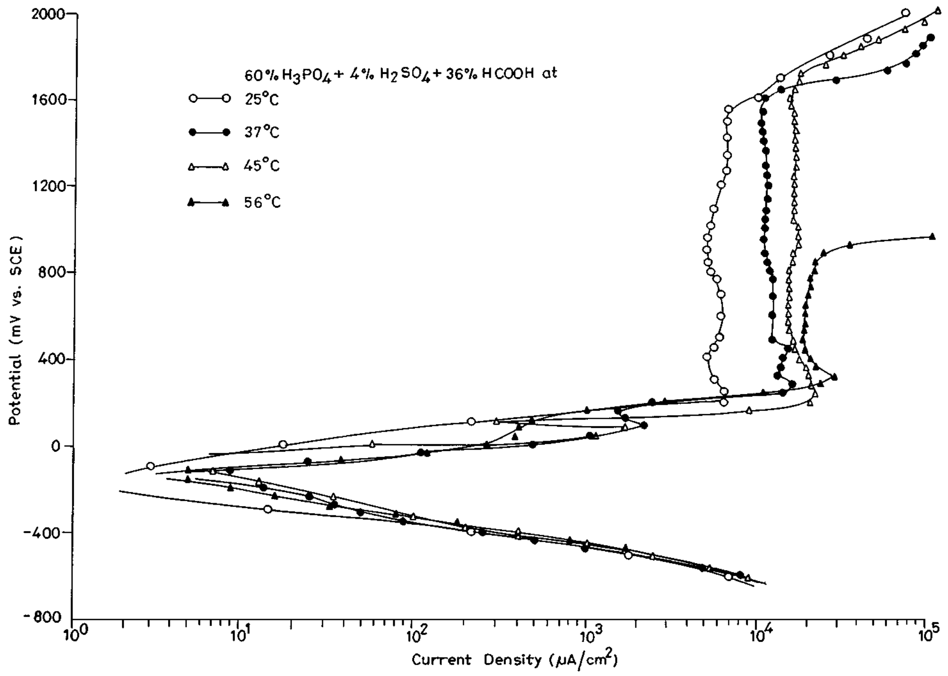


Figure 4 Polarisation behaviour of Monel (400) in 60% $H_3PO_4 + 4\%\ H_2SO_4 + 36\%$ HCOOH at different temperatures.

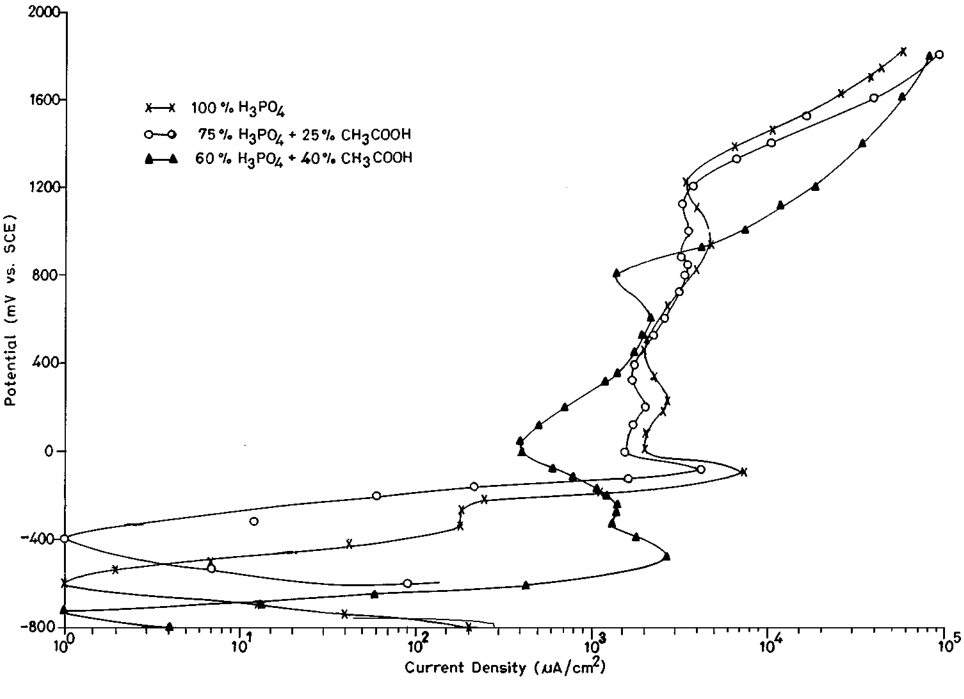


Figure 5 Polarisation behaviour of Monel (400) in concentrated phosphoric acid and in the solution mixtures of phosphoric-acetic acids.

density. The passive region is associated usually with a high value of current density which can be considered either due to the formation of a salt film or the high porosity of the film on the surface. However, it is difficult to ascertain the nature and the composition of the film on the basis of the results of the present investigation. The magnitude of the current in the passive region and the nature of the curve indicate that the protective character of the film decays with increasing content of formic acid in phosphoric acid solution mixtures.

The transpassive region (1.64–1.80 V) is usually associated with the evolution of a gas, particularly oxygen or metal dissolution or breakdown of the passive film leading to localised corrosion. The type of reaction actually operative in particular case is determined by the nature of the metal/electrolyte interface and the potential at which the process ensuses. The evolution of gas on the surface in binary solution mixture was observed in the transpassive region.

In the binary solution mixtures of phosphoric and formic acids, on increasing the content of formic acid, bright grey surface is observed after the polarisation experiment. On microscopic examination of the surface, mild grain boundary attack is observed on the alloy surface.

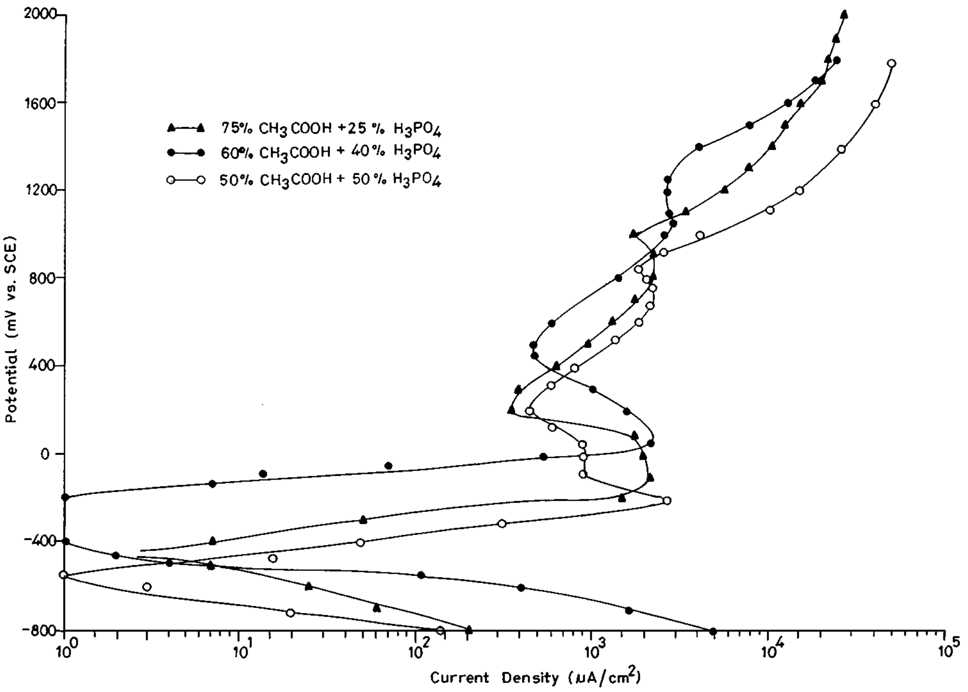


Figure 6 Polarisation behaviour of Monel (400) in the solution mixtures of phosphoric-acetic acids.

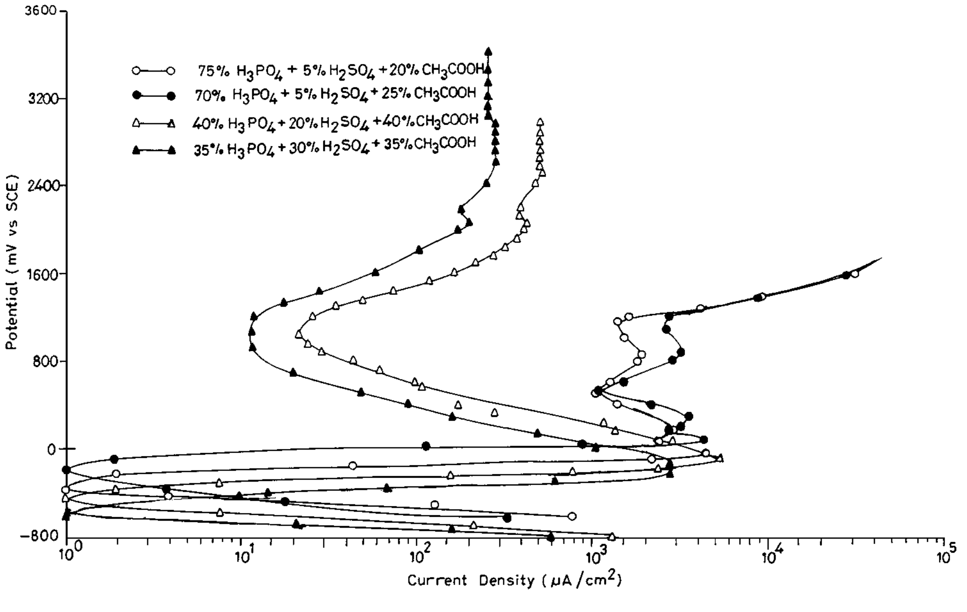


Figure 7 Polarisation behaviour of Monel (400) in the solution mixtures of phosphoric, sulphuric and acetic acids.

3.2. Phosphoric and sulphuric acids solution mixtures

The cathodic polarisation behaviour in these solution mixtures (Fig. 2) resembles closely to those observed in binary solution mixtures of phosphoric and formic acids (Fig. 1) and hence the cathodic reaction is hydrogen evolution.

The anodic polarisation curves in the binary solution mixtures of phosphoric and sulphuric acid are substantially modified in comparison to either concentrated sulphuric or phosphoric acid alone (Fig. 2). A well defined active-passive transition is observed on the addition of sulphuric acid in phosphoric acid. The curves shift towards lower current density side due to an increase in the content of sulphuric acid (25 to 50%) in phosphoric acid. However, a further increase in sulphuric acid content from 60 to 75%, results in shift of the anodic polarisation curves towards higher current density side with respect to 50% $H_3PO_4 + 50\%$ H_2SO_4 and in these solution mixtures the alloy did not exhibit transpassive region upto 2.4 V, rather the passivity continued. In the lower concentration of sulphuric acid (25 to 50%) in phosphoric acid the transpassive region is observed between 1.24–1.80 V. The breakdown potential moved substantially in the noble potential direction with increasing content of sulphuric acid in the mixture.

Invariably the surface of the alloy is found to suffer with localised attack (mainly grain boundary attack). The critical potential for passivity shifts towards noble direction on increasing the content of sulphuric acid from 25 to 75% except in 50% $H_3PO_4 + 50\%$ H_2SO_4 composition of the binary solution mixture. This may be due to some structural arrangement or change/interaction between two concentrated acids. The passivity is improved (low passivity current density) in binary solution mixtures of phosphoric-sulphuric acids in comparison to phosphoric-formic acids (Fig. 1).

The secondary current peak is also observed within the passive region which may correspond to different anodic reactions perhaps due to dissolution and precipitation. At higher concentration of sulphuric acid (60–75%) in the solution mixture, a higher passivity current is observed. It is understood that on increasing the concentration of sulphuric acid (25 to 100%) a hydrated sulphate film is formed on the surface. However, at higher concentration of sulphuric acid (60 and 75%) the hydrated film may be transformed partially to an oxide film at higher potentials. Therefore, the breakdown potential is not observed at higher concentration of sulphuric acid (60 and 75%) upto 2.4 V and the film in these solutions remains stable to a high potential and resists dissolution. The role of water can be visualised and examined in the above cases. Initially on increasing the content of sulphuric acid in phosphoric acid water content decreases and the breakdown of the passive film is observed in the solution mixtures containing 25 to 50% of sulphuric acid. At very high content of sulphuric acid (from 60 to 100%) the water content subsequently decreases and the breakdown of the passive film is not observed. This can be attributed to the lowest activity of H_2O in the solution which participates in the film formation on the surface. Since, the passive film is associated with the formation of hydrated sulphate contaminated with some oxide at highest concentration of sulphuric acid, the nature of the modified surface is insufficient electrode for charge transfer reaction associated with oxygen formation and its subsequent evolution [2].

The results are quite similar to the earlier reported results for monel (400) in varying concentrations of sulphuric acid [18]. The corrosion rate has been found to decline with increasing concentration of sulphuric acid but increased between 85 to 96% and thereafter again substantially decreased with increasing concentration of sulphuric acid. The passive film formed on the alloy on the alloy containing more than 30% nickel in the alloy has passibly similar structure to that on pure nickel [18]. It is likely that nickel leaches out after an initial active dissolution of the alloy and forms β-$NiSO_4 \cdot 6H_2O$ which is likely because of the higher dielectric constant of sulphuric acid (100 at 25°C) than phosphoric acid ($\sim$61 at 25°C). Several workers [19, 20] have also reported that passive current for nickel at higher concentration of sulphuric acid (18.8 M) is due to the presence of hydrated sulphates particularly β-$NiSO_4 \cdot 6H_2O$ on the surface.

After the polarisation experiment, the surface appears to have uniform film but some evidence of pitting is also observed. The pits are varied in nature. It ranged from shallow, etch type, hemispherical and covered pits. Some of these looked like a total solar eclipse in nature.

3.3. Phosphoric-sulphuric and formic acids solution mixtures

The polarization behaviour of the alloy shows (Fig. 3) that on increasing the content of formic acid (from 10 to 40%) in ternary solution mixture the critical current density (i_c) and passivity current density increase largely and critical potential for passivation shifts towards noble direction with respect to addition of formic acid. Further, on increasing the content of phosphoric acid in ternary solution mixture, i_c and i_p decrease significantly from 8000 to 4000 μA/cm^2 and 7000 to 2500 μA/cm^2, respectively. Perhaps it is due to decrease in dielectric constant and increase in viscosity with increasing content of phosphoric (from 60 to 80%) in ternary solution mixtures.

Further, on increasing the content of sulphuric acid (keeping either content of H_3PO_4 (60%) or formic acid (40%) constant) the passivity current increases. However, on increasing the content of phosphoric and sulphuric acids, the passivity current decreases. The potential at which transpassive region starts shifts towards noble direction with increase of formic acid content (10 to 40%) in ternary solution mixtures. The magnitude of passivity current is although high in ternary solution mixtures, yet it is lower in comparison to binary solution mixture of phosphoric-formic acids (Fig. 1).

In ternary solution mixtures of phosphoric, sulphuric and formic acids, mild grain boundary attack with etch type of pits are observed. On increasing the content of formic acid in ternary solution mixture the brightness of the surface improved and smoothing of the surface and spots like a vaccination mark are observed. The pits have a milder depth and hence, forms a mildly reflective surface. The grain boundaries accompany the specular surface. No pitting and grain boundary attack are seen rather an improvement in shining and brighenting have been observed in 60% $H_3PO_4 + 4\%$ $H_2SO_4 + 36\%$ HCOOH solution mixture. Elimination of scratches shows clearly smoothing of the surface in this solution mixture.

3.4. Influence of temperature

The effect of temperature on polarization behaviour of monel (400) in 60% $H_3PO_4 + 4\%$ $H_2SO_4 + 36\%$ HCOOH solution mixture has been studied at 25, 37, 45 and 56°C. It is observed from Fig. 4 that on increasing the temperature of the solution mixture the anodic polarisation curves shift towards higher current density region due to enhanced rate of corrosion of the alloy at higher temperature. The potential at which transpassive region commence decrease from 1600 to 880 mV at 56°C. Such a decrease in the potential might have been due to decrease in the over potential for oxygen evolution reaction [21]. On increasing the temperature of the solution the surface become mild grey to silvery plated like after polarisation experiment. In general, increasing temperature induces high currents, shallow pits and bright surfaces.

Apparent activation energy has been calculated from Arrhenius plot in different potential regions. Its value has been found to be 76.65 kJ/mole and 57.44 kJ/mole in the active and passive region, respectively. The higher value of the activation energy in the active region in comparison to that in passive region suggests that the surface kinetic steps control the rate of reaction. Turner *et al.* [4] have reported 59 kJ/mole activation energy for critical passivating current for nickel in sulphuric acid. This value is high for diffusion in solution and low for solid state diffusion and it seems therefore, that the reaction is limited by the charge transfer through the double layer. The apparent activation energy obtained in the passive region though apparently shows the ease of process in the passive region i.e. passive state dissolution, the reaction that occurs in this region can not be considered as a single and simple process and it is thus a complex one e.g. metal dissolution, passivation and repassivation of the film, film resistance and its characteristics. Therefore, the activation energy obtained in the passive region can not be associated or assigned with only single phenomenon occuring in this region. Hence, it is difficult to extend any adequate explanation with observed values of the activation energy and various factors have to be taken into account.

3.5. Phosphoric and acetic acids solution mixtures

Figs 5 and 6 represent the cathodic and anodic polarization behaviour in each composition of solution mixture. A well defined critical current density (i_c) was found in every case in negative potential region except in 70% $H_3PO_4 + 30\%$ CH_3COOH (+120 mV) and 40% $H_3PO_4 + 60\%$ CH_3COOH (+40 mV) compositions of the solution mixtures. The critical current density largely decreases with increasing the content of acetic acid in phosphoric acid. The passive region is ildefined in the entire composition of binary solution mixtures and a secondary current peak is also observed in the passive region. Wide and prominent passive region is not observed in any case. This reflects that the passivity is either semistable or unprotective in nature. Such behaviour of the alloy in the passive region may be because of chemisorption of the acetic acid anions which inhibits the formation of oxide on the metal surface. The secondary current peak is observed at higher potentials (above 600 mV); may be due to dissolution and precipitation of corrosion product. Coverage of the electrode by the corrosion product temporarily delays the current density increase. Similar to the present result the transpassivation of nickel in acetic acid has been attributed to chemisorption of acetic acid anions [22].

The general shape of the curves recorded for monel 400 remains quite similar to that of nickel metal in acetic acid solution [6] except a secondary current peak in the passive region, which is not observed in the case of nickel. Copper also shows active, passive and transpassive behaviour in aqueous acetic acid solution. There exists a general agreement [23] during anodic dissolution of copper in acetic acid, that the anodic layers on copper present a simple Cu_2O or a duplex Cu_2O/CuO, $Cu(OH)_2$ structure depending on the applied potential. The passive film of Cu(II) compounds has a duplex structure a lower layer grown via a solid state mechanism and upper layer formed by nucleation and growth from the solution [23]. It has been also postulated [24] that copper forms two types of layer consisting of Cu(II) compound which is protective while under certain condition depending on the electrode potential and temperature etc. Cu(I) layer is firstly formed, which is porous in nature followed by the growth of Cu(II) passive film. The presence of Cu(II) compound was found necessary to slow down the copper dissolution. Further, a slight oxidation of copper surface through the pores of the passive film and its chemical dissolution would have led to copper corrosion at higher potential.

On increasing the content of acetic acid in phosphoric acid i_c decreases which may be due to dielectric constant and viscosity decrease with increasing content of acetic acid in binary solution mixture. At higher concentration, acetic acid dimerises. Therefore due to decreases in dielectric constant and dimerisation of acetic acid i_c decreases with an increase of acetic acid content in phosphoric acid.

It is to be pointed out that the anodic polarisation curves of the alloy showed active, passive and transpassive behaviour in different compositions of binary solution mixture of phosphoric-formic acids (Fig. 1) and phosphoric-acetic acids (Figs 5 and 6). However, the current densities in different characteristics region are always higher in binary solution mixtures of phosphoric acid with formic acid. The higher current densities observed in the case of formic acid containing solutions is attributed to more aggressiveness of formic acid than acetic acid. This is partly because of the many fold higher dielectric constant of formic acid (56.1 at 25°C) than acetic acid (6.19 at 25°C). After polarisation experiment, distinct grain boundary attack was observed on the surface in binary solution mixtures of phosphoric and acetic acid. The grain boundary attack decreases with increasing the content of acetic acid in phosphoric acid.

3.6. Phosphoric-sulphuric and acetic acids solution mixtures

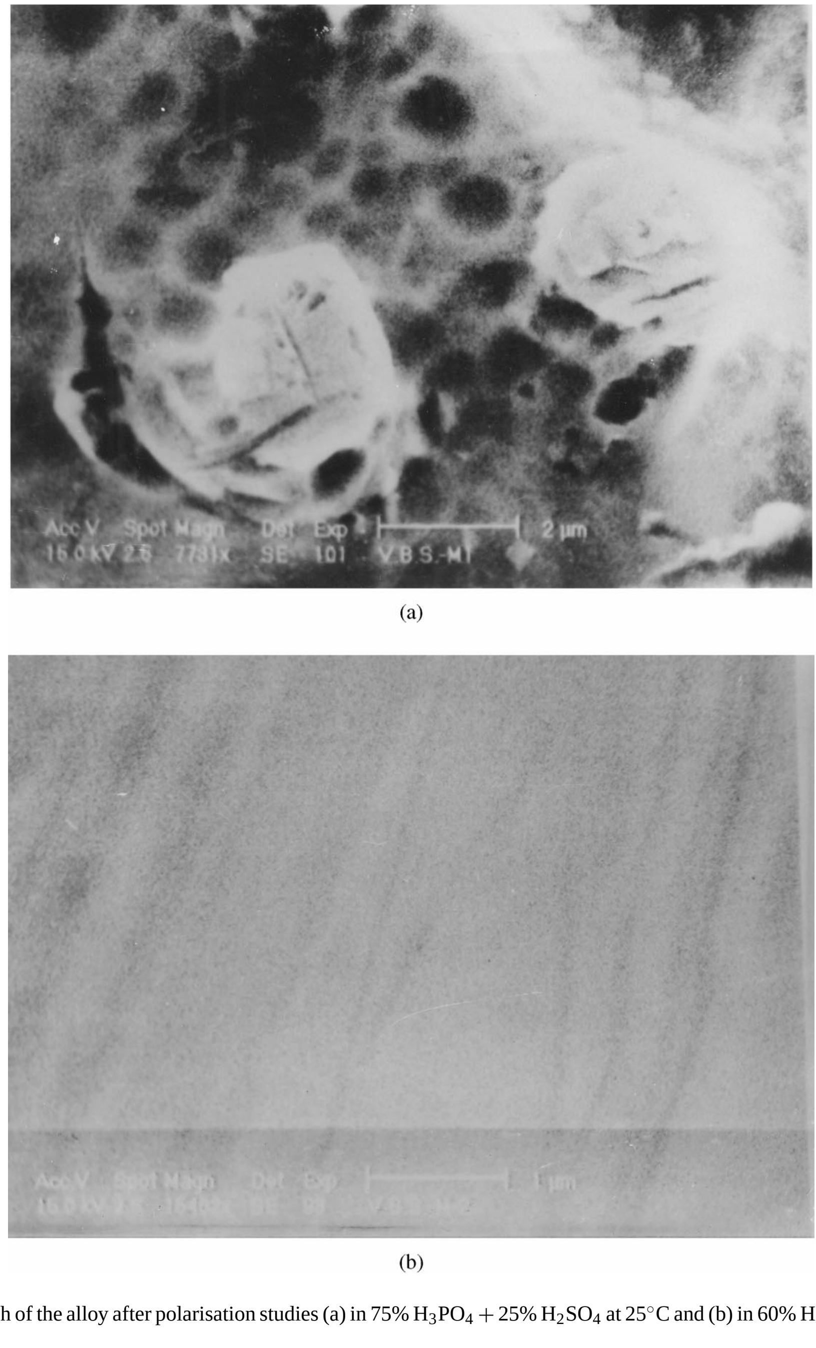
The anodic polarisation curves (Fig. 7) show active, passive and transpassive behaviours for the alloy in different compositions of ternary mixtures. It is observed from the figure that on increasing the content of sulphuric acid (5 to 30%) in ternary solution mixture the anodic polarisation curves shift towards lower current density region. Thus, on increasing the content of sulphuric acid passivating effect (low i_p) of sulphuric acid is enhanced and the passive range also increased. However, the evidence of chemisorption is also very clear as on increasing content of acetic acid from 20 to 25 and 35 to 40% in ternary solution mixture the curves shift towards right side i.e. higher current density and the passivity zone become shorter also. The transpassive region is observed to start at 1.2 V for all the compositions of ternary solution mixtures.

At higher concentration of sulphuric acid (20 and 30%) in ternary solution mixtures a current plateau is observed above 2.0 V. However, the anodic brightening was not observed in these solution mixtures. These experimental results suggest that the mass transfer control, a necessary condition for the electropolishing of the surface is not obtained in the present investigation, though a well defined current plateau is observed [25] in these composition of ternary solution mixtures. On increasing the content of sulphuric acid (5 to 20%) in ternary solution mixtures grain boundary attack diminishes and on further increase of content from 20 to 30% dull grey but an uniform film is observed on the surface, after polarisation experiment.

It is important to observe the results of the electrochemical studies of the alloy (Monel 400) reveal that the secondary current peak and a current plateau in the transpassive region is not obtained in the binary and ternary solution mixtures of phosphoric, sulphuric, formic and acetic acids except in few cases. In practice, the electropolishing of the alloy is also not achieved in any solution mixture. This indicates that the mass transfer control which is essential criterion for electropolishing is perhaps not arrived in the present case and hence the electropolishing is not observed for the alloy.

3.7. Cuurent decay studies

The characteristic of the passive film regarding stabilities was investigated by current decay experiments. The experiments were carried out in selected compositions of solution mixtures (binary solution mixtures of phosphoric acid with formic acid) holding the specimen at 800 mV in the passive region. A regular decrease in the current (from 14000 to 13000 μA/cm^2 and from 12000 to 8000 μA/cm^2) was observed with increasing time upto roughly 4–5 minutes, in the passive region followed by a constancy in the value of the current for a longer period ($\sim$1 hour) in 25% $H_3PO_4 + 75\%$ HCOOH, 75% $H_3PO_4 + 25\%$ H_2SO_4 solution mixtures, respectively. However, in the binary



(a)

(b)

Figure 8 SEM micrograph of the alloy after polarisation studies (a) in 75% $H_3PO_4 + 25\%$ H_2SO_4 at 25°C and (b) in 60% $H_3PO_4 + 4\%$ $H_2SO_4 + 36\%$ HCOOH at 56°C.

solution mixtures of phosphoric-sulphuric acids (40% $H_3PO_4 + 60\% H_2SO_4$ and 25% $H_3PO_4 + 75\% H_2SO_4$), the current decreases during the first few seconds and then started to increase followed by a plateau. Thus, the alloy at higher concentrations of sulphuric acid (60 and 75%) with phosphoric acid in binary solution mixtures shows a tendency to be passivated but pits are also initiated on the surface [26]. An uniform film was observed in the former case and the passive film with small pits are seen on the surface of the alloy in the later case after the polarisation experiment. The variation in current with respect to time is very little and it may be considered to remain almost constant. This indicates that the properties of the film on the surface does not change with change in concentration of the solution composition and its protective nature is maintained.

The polarization studies of the alloy in different solution mixtures show that current densities for the alloy (monel 400) in different characteristic region are always lower than for nickel and higher in comparison to that of copper in sulphuric acid as reported earlier [4]. Thus, the copper-nickel alloy (monel 400) is found to be more corrosion resistant than nickel and less corrosion resistant in comparison with copper. The addition of copper to nickel seems to improve the corrosion resistance of nickel based alloy.

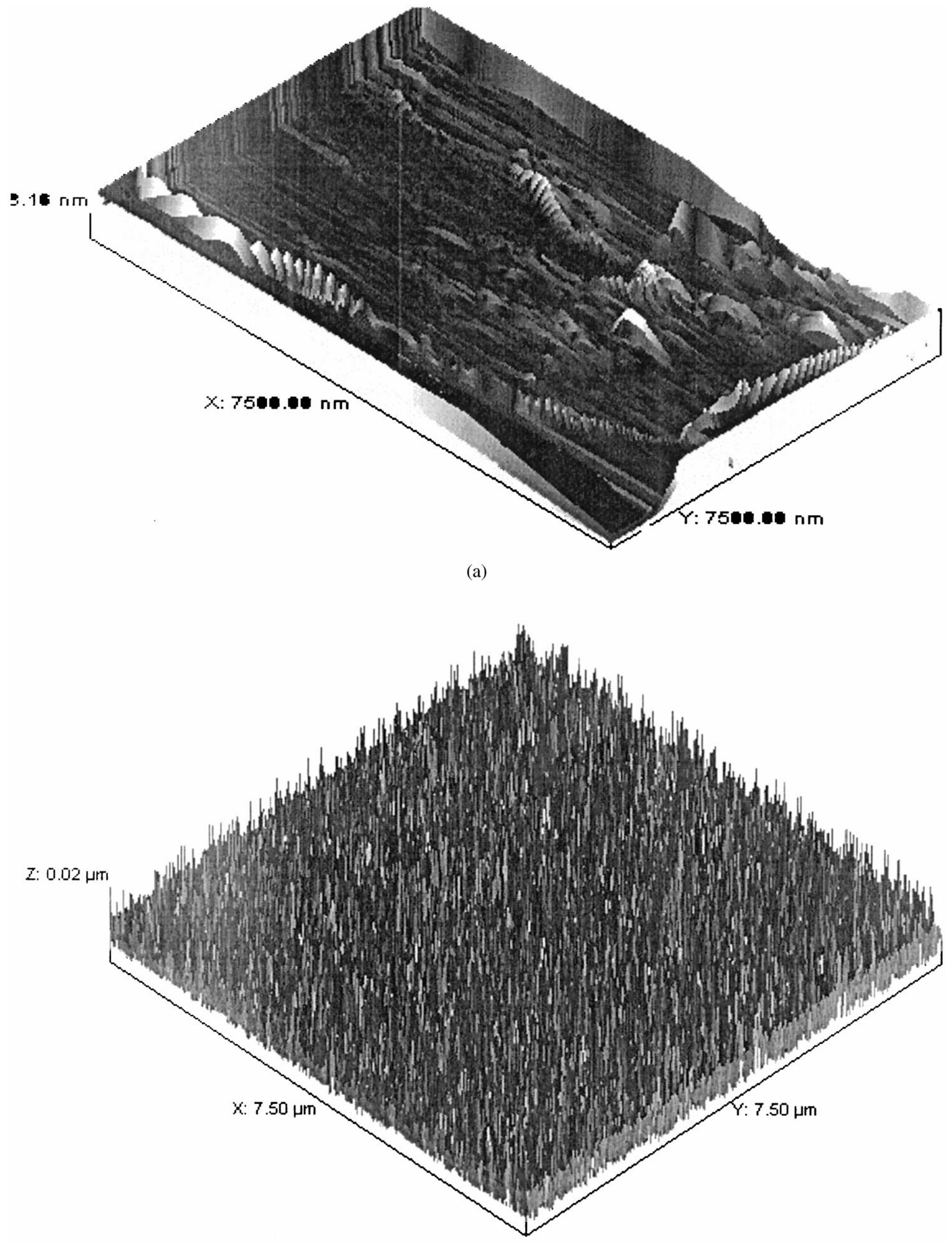


Figure 9 AFM image of surface morphology of the alloy specimen corresponding as in Fig. 8a and b.

3.8. SEM and AFM studies

SEM examination of the alloy surface after polarisation studies in 75% $H_3PO_4 + 25\%$ H_2SO_4 solution mixture reveals interesting features. The surface is covered with film and contains pits. The pits do not have definite shape. The corrosion product is seen to spread on the surface. The pits are covered, shallow and round shape in nature and some of these looks like solar eclipse ring. A magnified and more resolved view of the surface shows that the pits are shallow and some corrosion product is embedded within the pits (Fig. 8a, top). The film appears to be multilayered which may consist of hydrated salt or mixture of the salt and some oxide. The selective dissolution of the alloy is examined from the micrograph and the corrosion product spreads along the peripheri of the circular pits. The shallow pits of milder depth and grain boundary dissolution (in 60% $H_3PO_4 + 4\%$ $H_2SO_4 + 36\%$ HCOOH) at higher temperature gives better reflection to the surface (Fig. 8b, bottom). This is evidenced by near elimination of the scratches and pits from the surface.

The same surface when examined by AFM (in contact mode) clearly reveals the formation of layer consisting of several racks and multilayers one over other in a systematic way in 75% $H_3PO_4 + 25\%$ H_2SO_4 solution mixture. Two types of layer are seen on the surface. The projection along z-axis shows uneven dissolution of the film if at all, has not been uniform in the transpassive region (Fig. 9a, top). However, in the case of 60% $H_3PO_4 + 4\%$ $H_2SO_4 + 36\%$ HCOOH solution mixture, a bright and uniform surface containing a few very shallow pits is observed. The general morphology of the film resembles more to honey comb like structure which is characteristic of electropolishing of a specimen. This suggests that at higher temperature the alloy showed a tendency of smoothing and brightening. It becomes more obvious from the micrograph (Fig. 9b, bottom) where the hills and valleys are identified but the difference in their heights does not vary significantly.

4. Conclusions

The cathodic polarisation curves are almost linear and similar in all binary and ternary solution mixtures and the cathodic reaction is hydrogen evolution. The alloy (monel 400) shows active, passive and transpassive behaviours in all binary and ternary solution mixtures. The current density increases with increasing content of formic acid either in binary or ternary solution mixtures. This is ascribed to the high dielectric constant of the acids and low viscosity of formic acid. However, the critical current density decreases with increasing content of acetic acid in binary and ternary solution mixtures, may be due to low dielectric constant and low viscosity of the acetic acid. In the binary solution mixtures of phosphoric-acetic acids, the secondary current peak is observed in each case at higher potentials perhaps by the dissolution and precipitation mechanism. The passivity of the alloy in solution mixtures of phosphoric and sulphuric acid is considered to be due to the formatin of hydrated salt on the surface. Electropolishing is not observed in any solution mixture, however, at higher temperature better surface reflection is observed. The results based on SEM and AFM are in accordance with electrochemical polarisation studies.

Acknowledgement

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