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# AN INVESTIGATION ON THE AQUEOUS CORROSION BEHAVIOUR OF PLASMA TRANSFERRED ARC HARDFACED ALLOYS

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## ABSTRACT

In this paper an attempt has been made to investigate the corrosion resistance properties of three widely used hardfacing alloys in various aqueous environments. The corrosion tests were carried out on Plasma Transferred Arc Hardfaced deposits having minimum dilution. It was found that the stainless steel hardfaced deposit had high corrosion resistance compared to Nickel and Cobalt based deposits. The high corrosion resistance of the stainless steel hardfacing was solely due to the presence of high chromium content in the solid solution of the deposit.

**Key Words:** *Plasma Transferred Arc Hardfacing, Dilution, Pitting Corrosion, Stainless Steel, Cobalt and Nickel*

## 1. Introduction

Corrosion is one of three most frequently encountered failure modes for mechanical components. Fabricating novel corrosion resistant coatings with the help of some advanced surface engineering methods is one of the most economic, effective and flexible methods to enhance the corrosion performance for many mechanical components working under corrosive media [1]. Corrosion, fouling and slagging of super heaters are serious problems in boilers utilizing fuels with high alkali and chlorine content. Combustion of biomass, waste, black liquor and high chlorine coals are reported to cause severe materials wastage in super heaters. The corrosion resistance of bulk materials relied on properties of the oxide and sulfide scales formed at test conditions, whereas in case of coatings the coating structure and the coating composition determined the shielding capability [2].

Materials with satisfactory corrosion resistance in chlorine containing environments are highly alloyed. Low alloy ferritic tube coated with a thin layer of corrosion resistant material is an interesting option because of difficulties associated with mechanical properties, workability and high material price of highly alloyed materials [3]. Coatings can be produced on boiler tubes by several methods. Coated tubes are produced by means of co-extrusion; weld overlaying, diffusion treatment, thermal spraying and laser cladding. Weld overlay Ni-Cr-Mo coatings have suffered corrosion damage in boilers combusting chlorine containing fuels, because of iron migration to coating from low alloy base material due to high heat load during welding [4].

Hardfacing is primarily done to enhance the surface properties of the base metal (substrate) and hardfaced materials generally exhibit better wear, corrosion and oxidation resistance than the base metal. At a higher percentage of dilution, the surface properties of the hardfaced materials are not enhanced to the expected level because of the presence of a higher amount of base metal. On the other hand, at a lower percentage of dilution, the surface properties are much superior to those of the basemetal because of the low percentage of base metal in the deposited weld metal. Hence, the welding process, which produces a low percentage of dilution, is generally preferred for hardfacing applications [5]. Conventional weld hardfacing is done by oxyfuel welding, gas tungsten arc welding (GTAW), gas metal arc welding (GMAW), shielded metal arc welding (SMAW) and flux cored arc welding (FCAW). Plasma transferred arc (PTA) hardfacing and laser beam hardfacing are relative newcomers to this arena. At present, majority of the fabrication industries use submerged arc surfacing using wire electrodes. With conventional submerged arc surfacing, percentage dilution levels are higher. To attain low dilution, the surfacing technique used should enable spreading the arc energy uniformly over the area to be surfaced [6]. By keeping these points in mind, an investigation has been carried out to understand the corrosion behaviour of PTA hardfaced surfaces and also

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to analyse the effect of environment on corrosion behaviour of hardfaced surfaces.

## 2. Experimental Work

The polarization studies of the samples were carried out in non-deaerated 3.5% NaCl solution of pH 4, 7 and 11. Analar grade chemicals and double distilled water were used for the preparation of the electrolyte. The specimens were derived from PTA hard faced deposits were prepared as per the metallographic standard. The chemical and physical properties of the base material and hard faced deposits are shown in Tables 1 and 2 respectively. The optimized PTA process parameters for the hard facing of each the powders to attain minimum dilution are shown in Table 3. Specimens of 20 x 40 mm (width and length), as shown in Fig. 1 were prepared to ensure the exposure of 10 mm diameter circular area in the hard faced region to the electrolyte. The schematic circuit diagram of the potentio dynamic polarization set up is shown in Fig. 2.

**Table 1: Chemical Composition (wt %) of Substrate and Hard Faced Deposits**

| Material | C | Si | Cr | Ni | Mn | Cu | Mo | W | B | Fe | Co |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Substrate (carbon steel AISI 1040)** | 0.410 | 0.05 | 0.04 | – | 0.70 | – | – | – | – | Bal | – |
| **Iron-based alloy (stainless steel-316L)** | 0.0025 | 0.50 | 16.74 | 10.67 | 1.47 | 0.47 | 2.0 | – | – | Bal | – |
| **Cobalt-based alloy (Stellite-6)** | 1.85 | 1.00 | 29.0 | 2.50 | 1.0 | – | – | 9.0 | – | 2.50 | Bal |
| **Nickel-based alloy (colmonoy-5)** | 0.43 | 4.02 | 10.25 | Bal | – | – | – | – | 2.15 | 2.84 | – |

**Table 2: Mechanical Properties of Substrate and Hard Faced Deposits**

| Material | Yield strength (MPa) | Ultimate tensile strength (MPa) | Elongation (%) | Vickers's hardness (0.1 kg) | Charpy impact energy at RT (J) |
|---|---|---|---|---|---|
| **Substrate (carbon steel AISI 1040)** | 374 | 590 | 28 | 205 | 20 |
| **Iron-based alloy (stainless steel-316L)** | 290 | 580 | 40 | 372 | 26 |
| **Cobalt-based alloy (stellite-6)** | 541 | 896 | 20 | 440 | 40 |
| **(Nickel-based alloy (colmonoy-5)** | 310 | 655 | 32 | 480 | 34 |

**Table 3: Optimized Process Parameters of PTA Hard Faced Deposits**

| Types of Hard facing | Transferred Arc Current (Amperes) | Travel Speed (mm/ min) | Powder feed rate (grams/ min) | Torch oscillation frequency (Hz) | Stand off Distance (mm) | Dilution (%) |
|---|---|---|---|---|---|---|
| **Iron-based alloy (stainless steel-316L)** | 160 | 180 | 30 | 40 | 11 | 1.65 |
| **Cobalt-based alloy (stellite-6)** | 160 | 165 | 30 | 44 | 11 | 1.85 |
| **(Nickel-based alloy (colmonoy-5)** | 160 | 165 | 30 | 40 | 11 | 2.25 |

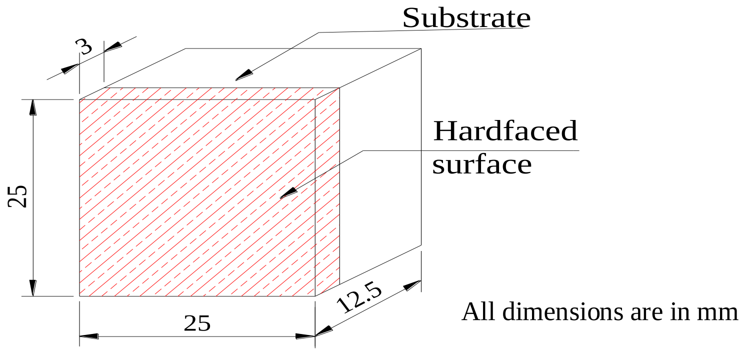


**Fig. 1 Dimensions of Corrosion Test Specimen**

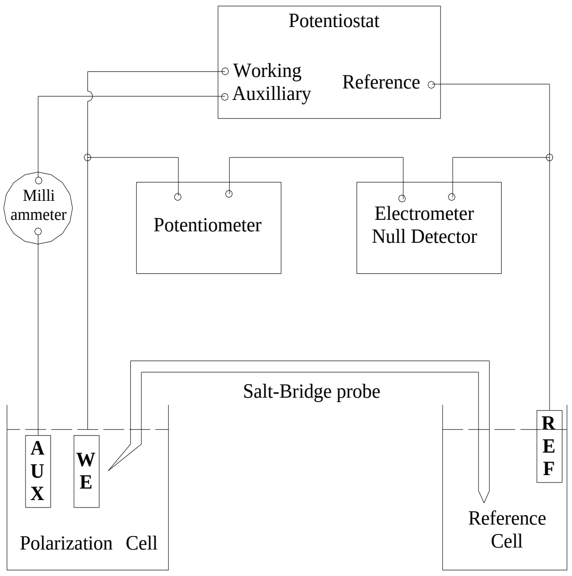


**Fig. 2 Schematic Representation of The Polarization Set-up**

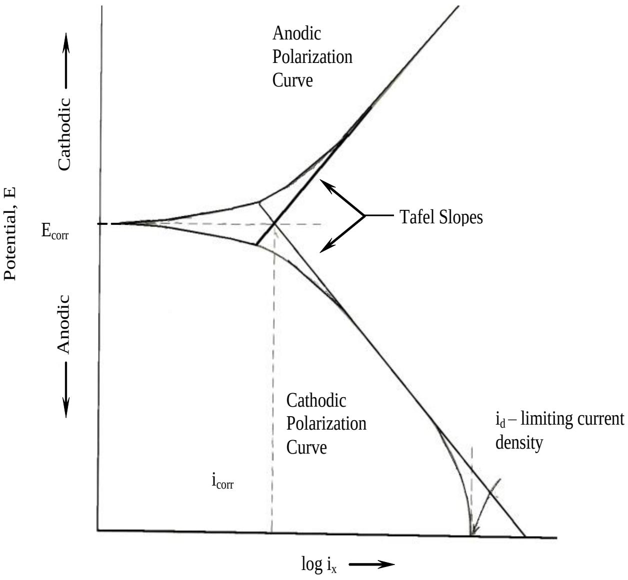


**Fig. 3 A Typical Tafel Plot**

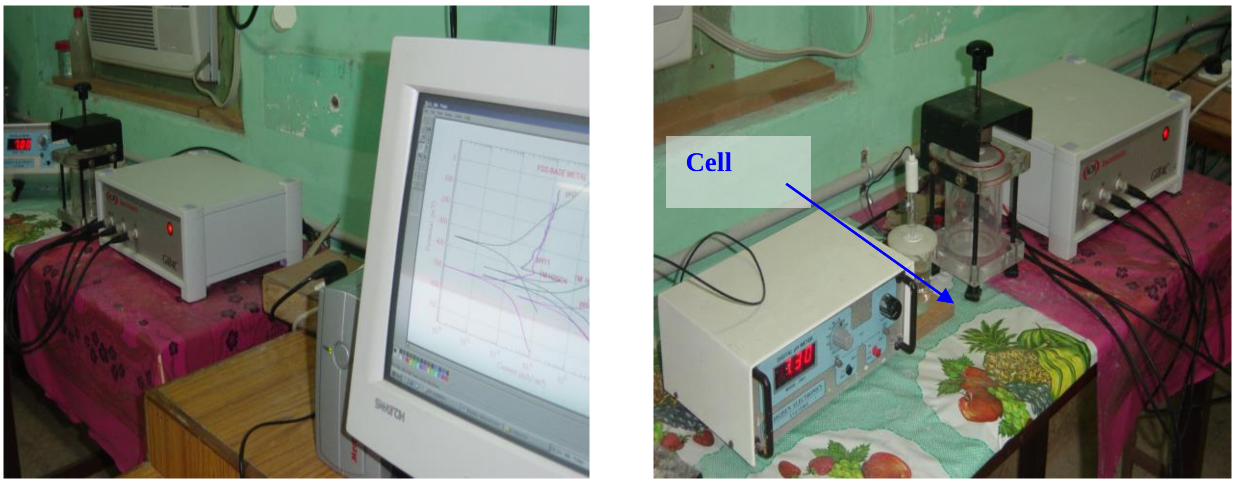
A potentiostat (Gill AC) was used for this study in conjunction with an ASTM standard cell and personal computer. As soon as the specimens attained a steady OCP condition, potentio dynamic polarization was started from 250 mV below that of the OCP and scanned in the anodic direction at a rate of 0.2 mV/s. The potential was monitored with respect to the current during polarization experiments. The corrosion rate was calculated by polarizing the specimen anodically and cathodically and by extrapolating the Tafel regions of anodic and cathodic curves to the corrosion potential. The intersection of these two lines at the corrosion potential yields the corrosion current density, $i_{corr}$. The corrosion potential and corrosion current density were obtained for each Tafel plot directly from the personal computer attached to the polarization set-up. A typical Tafel plot is shown in Fig. 3. Fig. 4 displays the corrosion test set up and the test specimens. Pitting potential ($E_{pit}$) was taken as the criterion for comparison of pitting corrosion resistance. $E_{pit}$ values for various types of hardfaced surfaces were experimentally determined (Fig. 5) and the values are presented in Table 4. Surface exhibiting less negative (i.e., more positive) values of pitting potential were considered to be more corrosion resistant [7].

## 3. Results and Discussions

From the pitting potential values presented in Table 4 and from the bar graphs displayed in Figs. 6 and 7, the following observations can be obtained:

i. Pitting corrosion resistance of substrate (base metal) and hardfaced surfaces are found to be influenced by pH value of the NaCl solution and environment;
ii. Iron based alloy (stainless steel) surface is offering better pitting corrosion resistance compared to all other surfaces and it is almost half to the pitting potential of base metal irrespective of pH value of the NaCl solution and environment.
iii. High pitting corrosion is observed in pH11 solution (basic) and very low pitting corrosion is recorded in pH7 solution (neutral) and moderate pitting corrosion is noticed in pH4 solution (acidic) irrespective of hardfaced surfaces;
iv. The highest pitting corrosion is recorded in 1MHCl solution and slightly lower pitting corrosion is recorded in $1MH_2SO_4$ solution and the lowest pitting corrosion is recorded in 3.5% NaCl solution at pH=7 irrespective of hardfaced surfaces.

Pitting corrosion is an example of non-uniform corrosion resulting from non-homogeneity in metal due to composition, inclusions, coring and distorted zones. These inhomogeneity set up differences of potential at



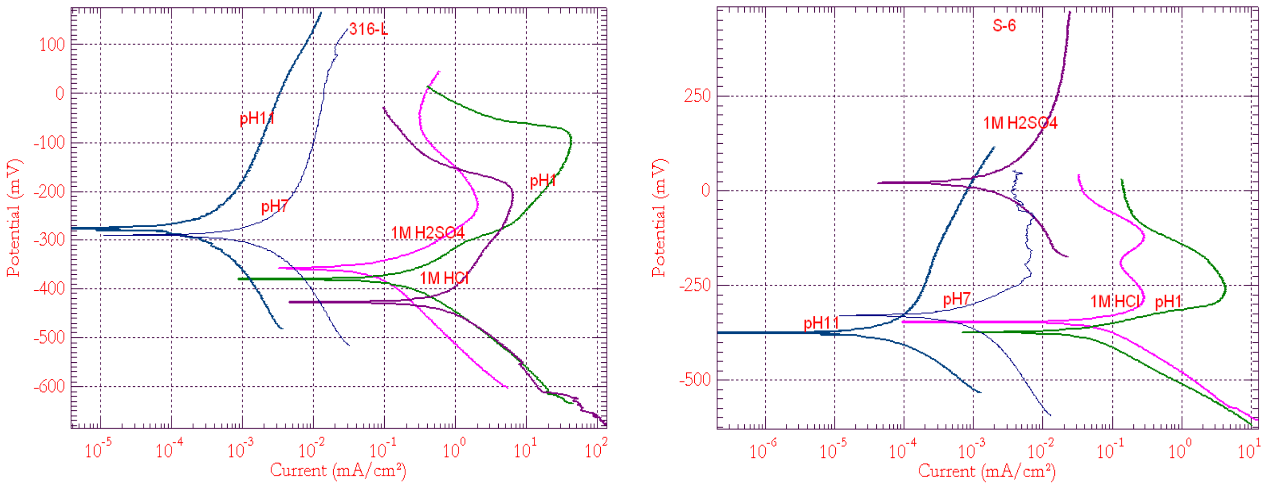
**(a) Potentiostat**

**(b) Potentiostat (close up view)**

**(c) Corrosion Test Cell**

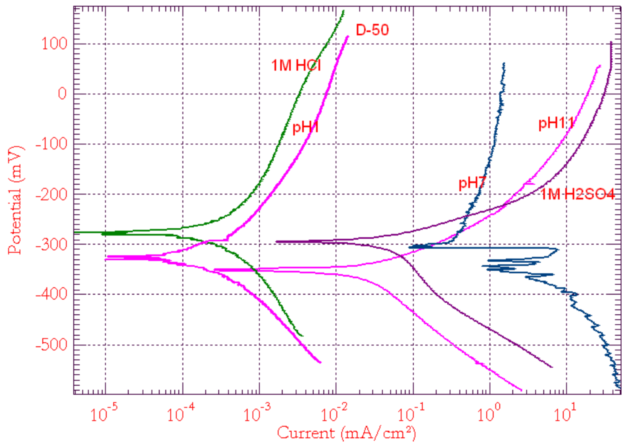
**(d) Hard Faced Test Specimens**

**Fig. 4 Corrosion Test Set Up and the Test Specimens**



**a.** **Stainless Steel Deposit**

**b.** **Cobalt Based (Stellite-6)**

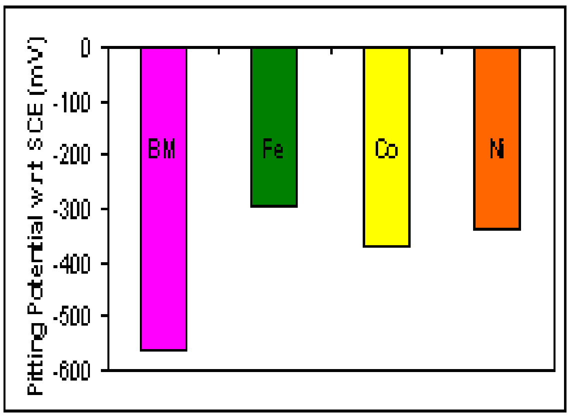


**c.** **Nickel based (Colmonoy-5)**

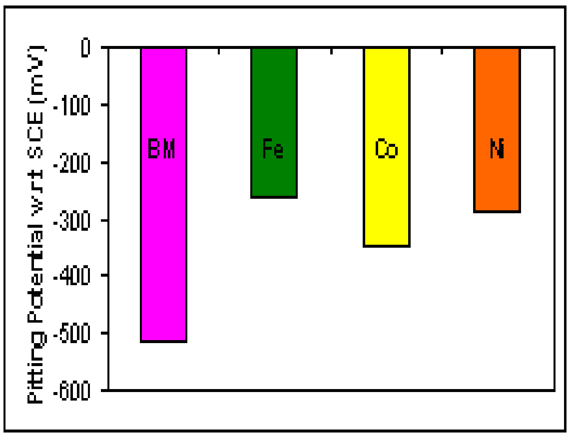
**Fig. 5 Anodic Polarization Behaviour of Hard Faced Surfaces**

**Table.4: Pitting Potential Values with respect to SCE (mV)**

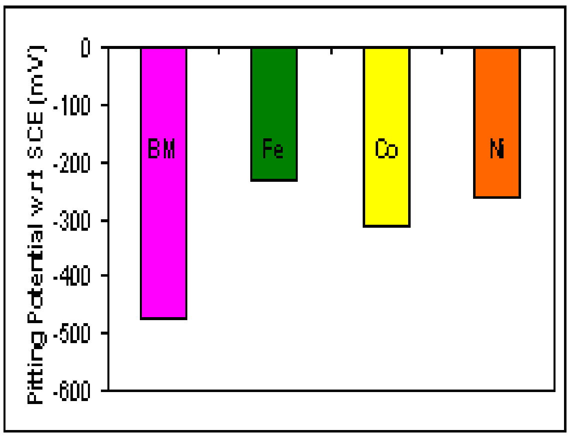
| Surface | 3.5% NaCl solution | | | 1M HCl | $1MH_2SO_4$ |
|---|---|---|---|---|---|
| | pH4 | pH7 | pH11 | | |
| **Base Metal (Carbon Steel)** | -515 | -474 | -560 | -610 | -572 |
| **Iron based (Stainless Steel)** | -265 | -232 | -294 | -363 | -347 |
| **Cobalt based (Stellite-6)** | -344 | -312 | -366 | -392 | -365 |
| **Nickel based (Colmonoy-5)** | -286 | -264 | -336 | -424 | -394 |



(a) pH = 11 (basic)

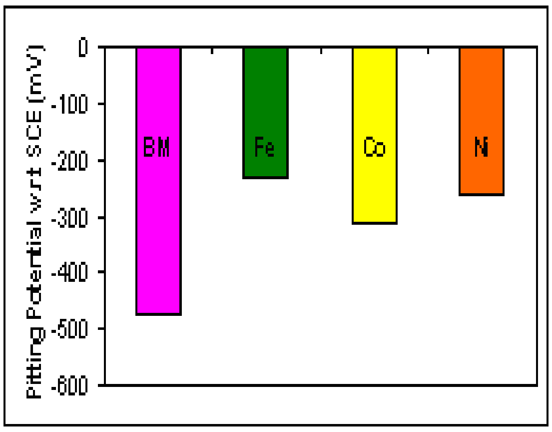


(b) pH = 4 (acidic)

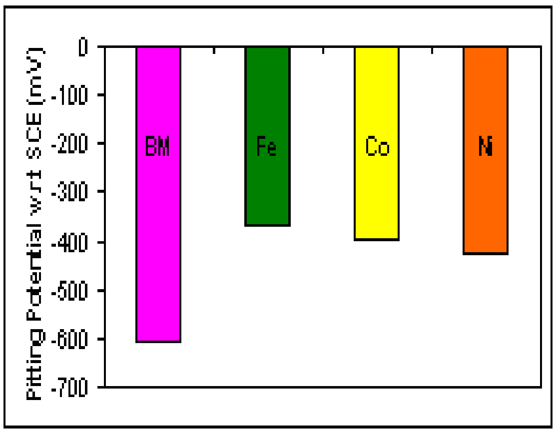


(c) pH = 7 (neutral)

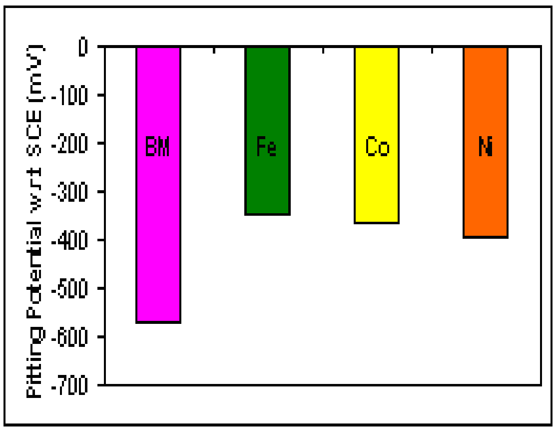
**Fig. 6 Effect of pH Value on Pitting Corrosion Potential**



(a) 3.5% NaCl at pH=7 (neutral)



(b) 1M HCl



(c) 1M $H_2SO_4$

**Fig. 7 Effect of Environment on Pitting Corrosion Potential**

localized spots to cause deep isolated holes. The large pit formed on the surfaces was penetrated in a small area then grew rapidly into a large surface [8]. Chromium is well known and widely utilized as one of the most effective alloying elements for enhancing the electrode potentials and corrosion resistance for iron, cobalt and nickel base alloys. From the Table 1, it is clear that the iron base alloy (stainless steel) contains 16.74%

Chromium, Cobalt base alloy contains 29% Chromium and Nickel base alloy contains 10.25% Chromium. It is well known that to get better corrosion resistance, chromium must be above 10% in an alloy and moreover chromium should be in solid solution, not in the form of carbides or nitrides. Even though, cobalt base alloy contains 29% chromium, it also contain appreciable amount of carbon (nearly 1.85%) and 9% tungsten. This excess carbon will react with tungsten and chromium and they will form tungsten carbide and chromium carbide. The formation of these two carbides are advantageous to resist wear but disadvantageous to resist corrosion. Because of these reactions, the amount of chromium in solid solution will be lower and hence the formation of chromium oxide film (a thin passive film) on the alloy surface is not so uniform.

Chromium oxide film is the main tool to resist corrosion in chromium containing alloys and if the film is not so dense then corrosion resistance of the alloy will be affected. Moreover, the distribution of precipitation reaction products such as chromium carbide and tungsten carbide all over the surface also creates potential difference in the matrix surface. However, in the case of iron base alloy (stainless steel), the carbon content is very less (0.0025%) as compared to cobalt base and nickel base alloys (0.43%). Hence, the chromium carbide formation problem is very less and even it forms it will be in the grain boundary region and that will lead to intergranular corrosion but not pitting corrosion. These may be the reason for better pitting corrosion resistance behaviour of iron base alloy compared to cobalt and nickel base alloys. The formation of Cr-alloyed Ni2Si/NiSi nickel silicides intermetallics may be the reason for improved the pitting corrosion resistance of nickel base alloy compared to cobalt base alloy [9].

Similar observations have been made by other investigators also and they are discussed below. Tam et al., reported that the corrosion resistance of the surface modified specimens was significantly improved as indicated by a shift of the pitting potential in the noble direction [10]. The maximum improvement was achieved in Ni-Cr-Si-B with a shift of the pitting potential by approximately 61 mV and a reduction in the corrosion current density by approximately one order of magnitude. The corrosion resistance of the modified layer was mainly determined by the fineness of the microstructure and the homogeneity of the composition. Niu et al., observed that a large number of small pits due to the preferential pitting corrosion of the dendrites where Cr and Mo contents are lower were found in the surface alloy. The density of pits on the commercial bulk alloy is much lower, although they are larger than those found in the laser cladded alloy [11].

## 4. Conclusions

In this paper, the pitting corrosion behaviour of substrate (base metal) and hardfaced surfaces have been evaluated and following important conclusions have been made:

(i) Iron based alloy (stainless steel) surface is offering better pitting corrosion resistance compared to all other surfaces irrespective of pH value of the NaCl solution and environment and it is mainly because of higher amount of chromium content presents in solid solution;

(ii) High pitting corrosion is observed in pH11 solution (basic) and very low pitting corrosion is recorded in pH7 solution (neutral) and moderate pitting corrosion is noticed in pH4 solution (acidic) irrespective of hardfaced surfaces;

(iii) The highest pitting corrosion is recorded in 1M HCl solution and slightly lower pitting corrosion is recorded in 1M $H_2SO_4$ solution and the lowest pitting corrosion is recorded in 3.5% NaCl solution at pH=7 irrespective of hardfaced surfaces.

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