A Study on the Influence of PTAW Process Parameters on Pitting Corrosion Resistance of Nickel Based Overlays

K. Siva*, N. Murugan

* Professor, Hindusthan College of Engineering and Technology, Coimbatore, India
b Professor, Coimbatore Institute of Technology, Coimbatore, India

Abstract

Pitting is a form of extremely localized attack that results in holes in the metal. It is one of the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. In this study, effects of plasma transferred arc welding parameters on the pitting corrosion resistance of Colmonoy 5 overlays deposited on austenitic stainless steel plates is investigated. Overlays were deposited as per designed experiments using response surface methodology. Potentiodynamic polarization technique was used for conducting the corrosion tests. A mathematical model for the pitting potential measured during the corrosion tests was developed using the multiple regression technique and it was used to correlate the effect of process parameters on the pitting potential of the overlays.

© 2013 The Authors. Published by Elsevier Ltd. Selection and peer-review under responsibility of the organizing and review committee of IConDM 2013

Keywords: Plasma transferred arc welding, overlay, Colmonoy, pitting corrosion, dilution, pitting potential, potenio-dynamic polarization, regression analysis;

1. Introduction

Among the available hardfacing alloys, nickel based ones have gained popularity in recent years owing to their excellent performance under conditions of abrasion, corrosion and elevated temperature with relatively low cost[1,2]. Colmonoy 5, a cobalt free nickel based alloy is widely employed as hardfacing material in applications like Petroleum, Chemical and other marine environments, Aircraft automotives, Paper and Pulp industries, Railways and Mining industries, Nuclear engineering, etc. among which chemical and marine environments are more vulnerable locations for pitting corrosion attacks. Colmonoy alloys are machinable and have superior fusion characteristics. In many of the cases, such alloys are required over the surface as overlay to provide superior properties than the bulk material and a suitable low cost bulk material leads to economical solutions in many situations. Normally, as the weld metals could have compositional and micro-structural inhomogeneity, they are more susceptible to corrosion where systematic and scientific based corrosion studies become inevitable [3, 4].

The hard-facing material can be deposited through various welding processes. But PTA process is preferred on many occasions due to its better process control, ease of use, high deposition rate and lower heat input. It achieves smooth and
thin deposits of overlays through the controlled feeding of powder. In the present study, Colmonoy 5 was deposited on austenitic stainless steel 316 L plates through PTA hardfacing. The resulting overlays are of excellent wear resistant, corrosion resistant and high temperature properties with fabulous metallurgical bonding and low dilution [5].

![Weld bead geometry](image)

Dilution as shown in Fig.1 is an intermixing of hard surfacing alloy with base metal which degrades all the desirable properties of the overlay and spoils the ultimate purpose for which it is applied. In this study, an attempt was made to understand the effect of dilution on pitting potential which is a measure of pitting corrosion resistance of the hardfacing layer. Moreover, development of mathematical models could be helpful to study the main and interaction effects of the significant process parameters affecting the pitting corrosion resistance of the weld bead. The literature available indicates that not many works have been carried out to develop mathematical models for studying the pitting corrosion behaviour of Colmonoy alloys influenced by the PTAW process parameters. Therefore, an investigation was carried out to develop a model correlating the process parameters to pitting potential.

The significant PTA process parameters chosen to carry out the PTA deposition of Colmonoy were welding current (A), Oscillation width (O), Travel speed (S), Preheat temperature (T) and Powder feed rate (F). The gas flow rate and Torch stand off distance were kept constant. The experiments were conducted based on the central composite rotatable design matrix. Regression analysis was used to develop the model and the analysis of variance method was used to test their adequacy.

### 2. Electrochemical Corrosion Testing

#### 2.1 Specimen preparation

Overlay specimens obtained from the experiments conducted for bead geometry analysis (described elsewhere [6]) were used for preparing the specimens for conducting pitting corrosion studies. A typical overlay specimen is shown in Fig.2.

![Typical cross section of hardfaced plate for Trial No.12](image)

Specimens of size 34 mm × 29 mm × 15 mm were cut using wire cut EDM process from the overlay specimens for corrosion tests. The chemical compositions of the materials and the working levels of PTA process parameters used in the present study are presented in Tables 1 and 2 respectively.
Table 1 Chemical composition of substrate and hardfacing alloy used

| Materials used | Elements, weight % |
|----------------|-------------------|
|                | C     | B     | Si    | Mn | S    | P    | Cr   | Ni   | Mo   | Cu   | Co   | Fe    |
| SS 316L (Base plate) | 0.02  | -     | 0.33  | 1.62| 0.02 | 0.03 | 16.66| 10.56| 2.17 | 0.63 | 0.13  | 66.13 |
| Colmonoy 5 (Powder) | 0.56  | 2.52  | 4.2   | -  | - | - | 11.0 | bal | - | - | 0.04 | 0.4 |

Table 2 Control Parameters and its Levels

| Parameter          | Units | Notation | Factor levels |
|--------------------|-------|----------|---------------|
| Welding current    | A     | A        | -2 | -1 | 0  | +1 | +2 |
| Oscillation width  | Mm    | O        | 12 | 14 | 16 | 18 | 20 |
| Travel speed       | mm min⁻¹ | S  | 89 | 96 | 103 | 110 | 117 |
| Preheat temperature| °C    | T        | 250 | 300 | 350 | 400 | 450 |
| Powder feed rate   | gm min⁻¹ | F  | 38 | 40 | 42 | 44 | 46 |

As per ASTM standard G 61-86, overlay specimens were ground with 220 grit SiC wheel to produce flat surface [7]. The surface of the test specimen was then wet polished with 600 grit SiC paper. Then the specimens were rinsed thoroughly with de-ionized water and acetone and then dried in a stream of air before conducting the experiment. The representative specimens used for the pitting corrosion tests are shown in Fig.3.

![Representative specimens for corrosion experiments](image)

2.2 Experimentation

Electrochemical pitting corrosion studies on the hardfaced specimens were carried out using Potentiodynamic anodic polarization technique as per the ASTM code G 61-86. The schematic diagram of the corrosion testing set up used for the present study is shown in Fig.4. The setup consists of ACM Gill 5500 Potentio-stat and Galvano-stat instrument with a flat cell in three electrode configuration.
The working electrode for the corrosion test was overlay specimen. A Saturated Calomel Electrode (SCE) and platinum gauze were used as reference and counter electrodes respectively. All the three electrodes were connected to corrosion testing instrument through leads provided in the flat cell. Overlay specimen was placed on the flat cell of 250 ml capacity in such a way that the hardfacing portion was exposed to the test solution. 1 square centimetre area of the overlay specimen was exposed to corrosion tests by masking the remaining area by epoxy resin. Test solution of 3.5% sodium chloride was prepared and its temperature was maintained at 30 ± 2°C. The corrosion test parameters are presented in Table 3.

| S.No. | Description                  | Parameter Values                                                                 |
|-------|------------------------------|----------------------------------------------------------------------------------|
| 1     | Surface Finish              | Wet polish with 600-grit SiC paper                                               |
| 2     | Test Solution               | 3.5% NaCl (Non de-aerated)                                                       |
| 3     | Temperature                 | 30 ± 2°C                                                                         |
| 4     | Cell settling time          | 55 minutes                                                                        |
| 5     | Initial Potential           | -400 mV                                                                          |
| 6     | Final Potential             | 1400 mV                                                                          |
| 7     | Scan Rate                   | 300 mV/min both in forward and reverse direction                                 |
| 8     | Area of specimen exposed    | 1cm²                                                                              |
| 9     | Equipment used              | ACM Gill 5500 Potentiostat                                                       |
| 10    | Parameters Studied          | Corrosion potential ($E_c$) and Pitting potential ($E_p$)                         |

2.3 Determination of Pitting potential

The pitting corrosion is almost a common denominator of all types of localized corrosion attack and the pitting potential has been considered to be a measure of the susceptibility of the hardfacings to the localized corrosion. Higher the pitting potential better will be the resistance of the material to pitting corrosion [8-9]. The pitting corrosion test was commenced by measuring the open circuit potential after the hardfaced samples had been immersed for 55 minutes in a non de-aerated chloride solution kept in the flat cell to allow for rest potential to settle. A potential scan was applied beginning at -400 mV and scanned in more noble direction to 1400 mV at a rate of 300 mV/min. These values were selected after conducting trial runs and as well as referring from the literature available for the equivalent metals and alloys. Kwok et al [10] reported that the potential could be increased from 200 mV below the corrosion potential in the anodic direction at a scan rate of 300 mV/min during electrochemical measurements for laser surface modified austenitic stainless steel using NiCrSiB alloy, which was an equivalent to Colmonoy.

The current density was measured continuously using the data acquisition software provided with the instrument. With the help of the software a graph was plotted with current density in logarithmic scale as abscissa and potential as ordinate.
The pitting potential $E_{\text{pit}}$ was measured from the anodic polarization curves at the point where there was a very big rise in the current density and the corrosion potential $E_c$ was measured at the point where there was a change from the cathodic reaction to anodic reaction. The reverse scan was continued until the hysteretic loop closed at the same scan rate of 300 mV/min towards more active direction. Two test runs were carried out for each specimen and the average values of pitting potential were obtained. The average values of pitting potential are presented in Table 4.

| S.No. | PTA Process Parameters | Percentage Dilution %D | Corrosion parameters | $E_c$, mV | $E_p$, mV |
|-------|------------------------|-------------------------|----------------------|---------|--------|
| 1     | -1 -1 -1 -1 1          | 24.513                  | -350                 | 248     |
| 2     | -1 -1 -1 -1 -1         | 28.119                  | -347                 | 135     |
| 3     | -1 1 -1 -1 -1          | 26.416                  | -312                 | 284     |
| 4     | 1 -1 -1 -1 1           | 28.760                  | -348                 | 240     |
| 5     | -1 -1 1 -1 -1          | 20.194                  | -348                 | 333     |
| 6     | 1 -1 1 -1 1            | 10.803                  | -325                 | 398     |
| 7     | -1 1 1 -1 1            | 16.791                  | -395                 | 225     |
| 8     | 1 1 1 -1 -1           | 33.353                  | -412                 | 102     |
| 9     | -1 -1 -1 -1 -1        | 15.845                  | -335                 | 368     |
| 10    | 1 -1 -1 1 1           | 24.844                  | -390                 | 150     |
| 11    | -1 1 -1 1 -1          | 14.480                  | -410                 | 225     |
| 12    | 1 1 -1 1 1           | 19.420                  | -300                 | 202     |
| 13    | -1 -1 1 1 1          | 12.246                  | -340                 | 378     |
| 14    | 1 -1 1 1 -1          | 26.240                  | -332                 | 280     |
| 15    | -1 1 1 1 -1          | 17.020                  | -310                 | 316     |
| 16    | 1 1 1 1 1           | 20.893                  | -334                 | 280     |
| 17    | -2 0 0 0 0          | 7.278                   | -375                 | 425     |
| 18    | 2 0 0 0 0          | 28.475                  | -344                 | 155     |
| 19    | 0 -2 0 0 0          | 17.334                  | -345                 | 342     |
| 20    | 0 2 0 0 0          | 22.391                  | -349                 | 310     |
| 21    | 0 0 -2 0 0          | 13.132                  | -367                 | 370     |
| 22    | 0 0 2 0 0          | 16.977                  | -312                 | 302     |
| 23    | 0 0 0 -2 0          | 22.244                  | -300                 | 295     |
| 24    | 0 0 0 2 0          | 27.180                  | -350                 | 158     |
| 25    | 0 0 0 0 -2         | 15.320                  | -372                 | 328     |
| 26    | 0 0 0 0 2          | 13.477                  | -347                 | 374     |
| 27    | 0 0 0 0 0          | 18.617                  | -362                 | 342     |
| 28    | 0 0 0 0 0          | 17.490                  | -320                 | 305     |
| 29    | 0 0 0 0 0          | 20.140                  | -349                 | 330     |
| 30    | 0 0 0 0 0          | 17.890                  | -300                 | 295     |
| 31    | 0 0 0 0 0          | 18.620                  | -364                 | 320     |
| 32    | 0 0 0 0 0          | 21.200                  | -335                 | 270     |

A - Current, O - Oscillation width, S - Travel speed, T - Preheat temperature and F- Powder feed rate

After polarization tests, the specimens were examined microscopically. It was found that the overlay specimens having higher dilution had larger pits. The darkened spots present in the photomicrograph shown in Fig.5 confirm the presence of pits on the surface of overlay specimen after the pitting corrosion test. The growth of pits was due to the reduction in pitting potential and shifting of protection potential in the more active direction. The pitting potential Vs current density variation could be understood from the typical polarization curve of the hardfaced specimen shown in Fig.6.
In the present study, it is observed that $E_p$ values vary from 102 to 425 mV. The lower values of $E_p$ of the specimens were probably due to the higher content of secondary phases resulting from dilution. Secondary phases become the active anodic sites for pit initiation in the presence of chloride ion. Chen and Szklarska-Smialowska [11] reported that for the boride strengthened Nickel based alloys, when potentiostatic tests were conducted at 45°C and 25°C, the pitting potentials were measured as 300 mV and 400 mV respectively. It was interesting to note from their works that a higher content of chromium provided greater resistance to pitting whereas, the boride precipitates were appeared to promote pit initiation and growth. In this study, the hardfaced layers were found to contain precipitates of both chromium and boride. In the polarization test results of nickel based alloy, Alloy 690 in NaCl solutions without thio-sulphate concentrations reported by Tsai and Wu [12], pitting potential varied approximately from 350 to 450 mV. Kwok et al [10] observed that $E_p$ varied from 50 to 300 mV for laser surface modified stainless steel using NiCrSiB alloy in 3.5% NaCl solution. All the above observed $E_p$ values meant for compositionally equivalent alloys, reported in literatures are in well agreement with the results obtained in the present study.
3. Development of a Mathematical Model for Estimation of Pitting potential \((E_p)\)

The response function can be expressed [13] as
\[
E_p = f(A, O, S, T, F)
\]  
(1)

The second order polynomial (regression equation) used to represent the response surface for \(k\) factors [14] is given by,
\[
Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i<j}^{k} b_{ij} x_i x_j
\]
(2)

The selected polynomial for five factors can be expressed as
\[
Y = b_0 + b_1A + b_2O + b_3S + b_4T + b_5F + b_{11}A^2 + b_{22}O^2 + b_{33}S^2 + b_{44}T^2 + b_{55}F^2 + b_{12}AO + b_{13}AS + b_{14}AT + b_{15}AF + b_{23}OS + b_{24}OT + b_{25}OF + b_{34}ST + b_{35}SF + b_{45}TF
\]
(3)

Where \(b_0\) is free term of the regression equation, the coefficients \(b_1, b_2, b_3, b_4, \text{ and } b_5\) are linear terms, the coefficients \(b_{11}, b_{22}, b_{33}, b_{44}, \text{ and } b_{55}\) are quadratic terms, and the coefficients \(b_{12}, b_{13}, b_{14}, b_{15}, b_{23}, b_{24}, b_{25}, b_{34}, b_{35} \text{ and } b_{45}\) are interaction terms. The values of the coefficients of the regression equation were determined using Systat software (version 11). The equation thus obtained is given by,
\[
E_p = 320.034 - 54.707 A - 25.874 O + 19.374 S - 7.541 T + 24.293 F - 2.810 AO + 24.310 AS - 21.435 AT + 35.246 AF - 23.438 OS - 1.937 OT + 23.440 OF + 18.687 ST + 0.560 SF - 1.435 TF - 14.784 A^2 - 5.784 O^2 - 3.284 S^2 - 30.659 T^2 + 0.466 F^2
\]
(4)

Also, the insignificant coefficients were eliminated using Student t-test without much affecting the accuracy of the model. Thus, the final mathematical model developed for pitting potential [15] with the parameters in coded form is given below:
\[
Pitting \ potential, \ E_p = 320.50 - 47.083 A - 20.0 O + 13.5 S - 1.667 T - 32.250 OS - 13.354 A^2 - 4.354 O^2 - 1.854 S^2 - 29.229 T^2
\]
(5)

The adequacy of the model so developed was then tested by using analysis of variance technique (ANOVA) and it was found that the model was adequate [16].

3.1 Validation of model

Three conformity experiments were conducted to verify the developed model Eq.(5). Three overlays were deposited using different values of PTA process parameters other than the values available in the design matrix and the pitting potentials were measured for those overlays and presented in Table 5. It is clear from the table that the measured \(E_p\) values are quite close to the predicted values.

\[
\begin{array}{cccccc}
\text{Conformity test run} & \text{PTA Parameters} & \text{Predicted} & \text{Observed} & \text{Error}^a \\
 & A \ (A) & O \ (mm) & S \ (mm/min) & T \ ^\circ C & F \ g/min & E_p \ (mV) & E_p \ (mV) & \% \\
1 & 1 & 1 & 1 & 1 & 1 & 249.813 & 240.813 & 3.39 \\
2 & 2 & 0 & 1 & 0 & -1 & 148.564 & 145 & -2.45 \\
3 & 0 & -1 & 1 & 2 & 1 & 259.792 & 266 & 2.33 \\
\hline
\text{Mean} & & & & & & & 1.09 \\
\end{array}
\]

\(a\) Error \(\% = [(\text{Observed } E_p - \text{Predicted } E_p) / \text{Predicted } E_p] \times 100\)

4. Effects of PTA Process Parameters on Pitting Corrosion Resistance

4.1 Direct effect of process parameters on Pitting potential \((E_p)\)

Graphs are drawn with the help of the developed models to provide satisfactory explanation about the direct and interaction effects of various welding parameters on pitting corrosion resistance of the overlay and are presented in Figs.7
and 8 for quick analysis. The possible causes for the effect of PTAW process parameters on the pitting corrosion parameter were analyzed and are presented below:

It is evident from Fig. 7 that pitting potential gradually decreases with increase in welding current. When the welding current increases, dilution increases as a result of which pitting potential decreases. This is mainly due to the increased heat input with the increase in welding current. As the welding current is increased from 130 A (-2) to 170 A (2), correspondingly heat input through the process increases from 13.176 kJ/cm to 18.419 kJ/cm. This increase in heat input resulted in a decrease of pitting potential from 361 mV to 172 mV as illustrated in Fig. 7. So, for an amount of increase in heat input of 5.243 kJ/cm from the process, pitting potential totally decreases by 189 mV. Hence, decrease in pitting potential indicates that there is decrease in pitting corrosion resistance of the hardfacing.

Pitting potential decreases with increase in oscillation width. When the oscillation width increases, dilution gets increased. This could be due to the main cause of decrease in reinforcement. As a result of increase in dilution, pitting potential is decreased. So, the pitting corrosion resistance decreases with increase in oscillation width.

![Fig. 7 Direct effect of PTA process parameters on pitting potential (Ep)](image)

It is clear from Fig. 7 that pitting potential increases with increase in travel speed. When the travel speed increases the deposition of powder over the substrate will decrease, which also result in decrease in heat input. As the travel speed is increased from 89 mm/min (-2) to 117 mm/min (2), respective heat input decreased from 18.202 kJ/cm to 13.846 kJ/cm resulting in an increase of corresponding pitting potential from 286 mV to 340 mV as depicted in Fig. 7. Here, for a total decrease of 4.356 kJ/cm heat input, pitting potential increased by 54 mV. Now, with decrease in heat input, dilution decreases, which results in an increase in pitting potential. So, the pitting corrosion resistance increases with increase in travel speed. It is evident from Fig. 7 that initially pitting potential increases when preheat temperature increases and decreases finally with further increase in preheat temperature. This could be attributed to the following: At lower preheat temperature; the heat received from the plasma arc will not spread in the stainless steel substrate due to its lower thermal conductivity resulting in cushioning of arc. So the dilution will be decreasing initially, which in turn will cause increase in pitting potential. As the preheat temperature is further increased, dilution will be increased finally, resulting in decrease of pitting potential. It is clear from Fig. 7 that there is no significant change in pitting potential with increase in powder feed rate which could possibly be due to the less melting of substrate.

4.2 Interaction effect of oscillation width and travel speed on Pitting potential

It is observed from Fig. 8 that when oscillation width is at a lower value, E_p increases with increase in travel speed. It is because low value of oscillation width results in less heat of plasma reaching the base metal and more reinforcement for the bead. These effects could provide low dilution leading to high value of pitting potential of the specimen. When oscillation width increases to higher values the reverse trend is observed. These above observations were further visualized using response surface and contour plots shown in Figs. 9 and 10 respectively. The changes in E_p for subsequent changes in travel speed and oscillation width were clearly depicted in these figures.
Fig. 8 Interaction effect of Travel speed (S) and Oscillation width (O) on pitting potential (E_p)

Fig. 9 Response surface showing interaction effect of Travel speed (S) and Oscillation width (O) on pitting potential (E_p)

Fig. 10 Contour plot showing interaction effect of Travel speed (S) and Oscillation width (O) on Pitting potential (E_p)
5. Summary

The following conclusions could be drawn from the above investigations on the effects of PTA process parameters on pitting potential:

- Mathematical model was developed to predict pitting potential of Colmonoy hardfacing deposited on austenitic stainless steel plates using regression analysis.
- Pitting potential decreases with increase in welding current and oscillation width which indicates decrease in pitting corrosion resistance.
- Pitting potential increases with increase in travel speed indicating increase in pitting corrosion resistance of the overlay and powder feed rate has no significant influence on pitting potential.
- Higher the preheat temperature lower the pitting potential.

References

[1] Qian Ming, Lim LC and Chen ZD, Laser cladding of nickel-based hardfacing alloys, Surf. Coat. Tech., 1998, 106:174-182.
[2] Lim LC, Qian Ming and Chen ZD, Microstructures of laser-clad nickel-based hardfacing alloys, Surf. Coat. Tech., 1998, 106: 183-192.
[3] Zumelzu E, Sepulveda J and Ibarra M, Influence of microstructure on the mechanical behavior of welded 316 LSS joint, J. Mat. Proc. Tech., 1999, 94: 36-40.
[4] Gorhe DD, Raja KS, Namjoshi and Radmilovic SA, Electrochemical methods to detect susceptibility of Ni-Cr-Mo-W alloy22 to inter-granular corrosion, Met. & Mat. Trans., 2005, 36:1153-1167.
[5] Cary HB, Modern Welding Technology, Stephen Helba et al. (eds.), Prentice Hall Inc., New Jersey, 2002, p.721–726.
[6] Siva K, Murugan N and Raghupathy VP, Modeling, analysis and optimization of weld bead parameters of nickel based overlay deposited by plasma transferred arc welding, Ar.Comp. Mat. Sc. & Surf. Engg, 2009, 3:174-182.
[7] ASTM G 61-86, Standard test method for conducting cyclic potentio-dynamic polarization measurements for localized corrosion susceptibility of Iron-, Nickel-, or Cobalt-based alloys, in annual book of ASTM standards, p 224 - 228.
[8] Kamachi Mudali U, Dayal RK, Gnanamoorthy JB, Kanetkar SM and Ogale SB, ‘Localized Corrosion Studies on Laser Surface Melted Type 316 Austenitic Stainless Steel’, Met.Trans. J., JIM, 1991, 33(9): 845-853.
[9] Kamatchi Mudali U, Dayal RK, Gnanamoorthy JB and Rodriguez P, Relationship between pitting and inter-granular corrosion of nitrogen bearing austenitic stainless steels, ISIJ International, 1996,36 (7): 788-806.
[10] Kwok CT, Cheng FT and Man HC, Laser surface modification of UNS S31603 stainless steel using NiCrSiB alloy for enhancing cavitation erosion resistance, Surf. Coat. Tech., 1998, 107: 31-40.
[11] Chen TY and Szklarska-Smialowska Z, The pitting corrosion characteristics of boride-strengthened nickel and iron based microcrystalline alloys, Corrosion Sc., 1988, 28(1): 97-107.
[12] Tsai WT and Wu TF, Pitting corrosion of Alloy 690 in thiosulfate-containing chloride solutions, J. Nucl. Mat., 2000, 277: 169-174.
[13] Montgomery DC, Design and analysis of experiments, John Wiley & Sons Inc., New York, 2001.
[14] Khuri AI and Cornell JA, Response surfaces, Designs and analyses, Marcel Dekker Inc., New York, 1996.
[15] Murugan N and Kannan T, Effects of flux cored arc welding parameters on pitting corrosion resistance of duplex stainless steel clad metals, Corr. Engg. Sc. & Tech., 2007, 42: 29 – 35.
[16] Giridharan PK and Murugan N, Effect of pulsed GTAW process parameters on pitting corrosion resistance of Type 304 SS welds, Corrosion, 2007, 63(5): 433-441.