Fuzzy Prediction of Corrosion Resistance of Duplex Stainless Steel to Biotic Iron Reducing bacteria and Abiotic Synthetic Seawater Environments: A Phenomenological Approach towards a Multidisciplinary Concept

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A composite fuzzy function model was developed to predict the corrosion resistance of duplex stainless steel in two environment; a biotic environment containing single-type corrosion-related bacteria iron reducing bacteria and a control, abiotic synthetic seawater environment. Based on this model, it was predicted that the fuzzy probability of resistance to corrosion for duplex stainless steel in the biotic environment is lower than that of the abiotic environment. To validate the model, stress corrosion testing (slow strain rate test) was conducted on duplex stainless steel samples in these environments. The obtained results validated the predicted results by the model as measured by change of important mechanical features of duplex stainless steel in these environments such as time-to-failure and reduction in area. This is a phenomenological rather than a mechanistic approach to examine the suitability of use of fuzzy logic in such applications.

Keywords: Microbiologically Influenced Corrosion (MIC) – Duplex Stainless Steel - Fuzzy Composite Functions- Iron Reducing Bacteria.

1. INTRODUCTION

Microbiologically influenced corrosion (MIC) is an electrochemical corrosion influenced by micro-organisms that can affect the rapid degradation/corrosion of engineering materials [1]. While MIC has been around for over a century or so, its systematic study in terms of explaining it by the aid of electrochemistry, is relatively new and it is still a phenomenon many aspects of which are unknown. For example, while there are MIC models that can predict the possibility of MIC [2-4] in
systems, none of them apply fuzzy mathematics in terms of trying to explain the likelihood in statistical form.

The main concepts of this multidisciplinary research are the following four elements:

(a) Duplex stainless steels , (b) Fuzzy Logic , (c) Iron reducing bacteria and (d) Stress Corrosion Cracking. Therefore, in order to understand the logic and importance of this research, each of the concepts and elements will be very briefly explained.

(a) **Duplex stainless steel**

In strategic industries, after carbon steel and conventional stainless steels, a new generation of steels is becoming more frequently used. These steels are known as duplex stainless steels (DSS). Contrary to carbon steel, DSSs contain relatively high corrosion resistant alloying elements such as chromium and, again contrary to conventional stainless steels that have single-crystal microstructures, Duplex stainless steels generally have a dual crystal structures ferrite/austenite ratio of 1:1. The duplex structure is less resistant to crevice corrosion[5]. This implies that dual microstructures can be vulnerable to corrosion despite their other superior properties. Also, nitrogen content of ferrite and austenite may render them vulnerable to fail by pitting [6].

(b) **Stress Corrosion Cracking**

The type of corrosion that is caused by tensile stresses in a material in the presence of a specific corrosive medium is called stress corrosion cracking [7]. Duplex stainless steels are more corrosion resistant than the ferritic grades, and stronger than austenitic grades [8]. As mentioned earlier, DSS have two phases, austenite and ferrite. The crack can be initiated in either or both. Although DSS are regarded considerably resistant to SCC, they may be susceptible to SCC in chloride containing environments [9]. MIC-assisted SCC is a very new topic and especially the predictability of such enhanced failures in biotic environments containing IRB by applying fuzzy logic is being reported for the first time.

(c) **Iron Reducing bacteria**

Iron-reducing bacteria (IRB) reduce insoluble ferric compounds into the soluble ferrous ions, therefore the metal beneath the protective ferric oxide film is converted into the vulnerable ferrous film and thus corrosion is continued where the ferrous ions, oxidised by trace amounts of oxygen into ferric ions, are reduced by IRB and this process repeats itself, more details about IRB have been discussed elsewhere [10-15].

(d) **Fuzzy Logic**

Fuzzy logic and calculations have been used in corrosion studies [16-18] but to the best of our knowledge, fuzzy logics has not been applied in researches about MIC-related SCC. A fuzzy restriction may be visualized as an elastic constraint on the values that may be assigned to a variable. The calculus of fuzzy restrictions is concerned, in the main, with:

(i) Translation of propositions of various types into relational assignment equations.

(ii) The study of transformations of fuzzy restrictions which are induced by linguistic modifiers, truth-functional modifiers, compositions, projections and other operations.

In this paper, we want to show the strength of fuzzy logics in being a very useful tool for application in multidisciplinary areas such as MIC and its enhancement by SCC. Therefore in this
context, a phenomenological rather than a mechanistic approach will be adapted. In this regards, we will not focus on the corrosion mechanisms and/or the microbiology involved.

1.1 Basic concepts:

1.1.1. Environment vs. Material

When it comes to MIC, two scenarios can be suggested namely;

a) Suitable Environment
b) Susceptible Material

With regards suitable environment, it can be defined as an environment in which “biofilm” formation is favoured. Biofilms are defined as matrix-enclosed bacterial populations’ adherent to each other and/or to surfaces or interfaces [19] and they are the main cause of inducing corrosion. The details of biofilms and their contributions to MIC have been the topic of many studies [20-22]. When the environment is “biotic”, it means that it contains micro-organisms. When biotic environments contain corrosion-related bacteria, then these environments can be called as “suitable environment”. Examples of such suitable environments are natural environments such as seawater or artificial environments such as laboratory-made broths where necessary nutrients for growing micro-organisms are made up.

Susceptible material is the one which is prone to undergo biofilm formation and thus MIC. For example, many field and laboratory evidences suggest that some materials show better resistance to MIC than others; arranging from the least resistant to more resistant metallic alloys duplex stainless steel [23-27] and titanium alloys [28-30] can be mentioned.

It will be the combination of these two parameters that will increase the likelihood of MIC. In other words, there can exist three probabilities (The underlined phrases are fuzzy concepts):

Probability (1)-likelihood of MIC is relatively high if both suitable environment and susceptible material exit, such as duplex stainless steel in seawater,

Probability (2) -likelihood of MIC is relatively low if either suitable environment or susceptible material exits, such as stainless steel in seawater,

Probability (3) -likelihood of MIC is too low if neither suitable environment nor susceptible material exits, such as titanium alloy an alkaline environment.

In this context, we will concentrate on one susceptible material (i.e., carbon steel) and three bacterial environments suitable for the microbial corrosion of it. In other words, we will compare the fuzzy probability of microbial corrosion of duplex stainless steel in these environments with each other to find out in which one duplex stainless steel is less (or more) likely to undergo corrosion (or more specifically, MIC) than the others.

1.1.2. Algorithm and methodology

For the same susceptible material (carbon steel), three sets are defined as in equation (1) for two suitable environments:
\[ \mathbf{G} = \{ \mathbf{G}_j \}, \quad j = 1, 2, 3, \ldots, N \]

\[ \mathbf{S} = \{ \mathbf{S}_i \}, \quad i = 1, 2, 3, \ldots, M \]  \hspace{1cm} (1)

\[ \mathbf{A} = \{ \mathbf{A}(i) \}, \quad i = 1, 2, 3, \ldots, M \]

The set \( \mathbf{G} \) measures all practically achievable universal properties (mechanical, physical and chemical parameters) of carbon steel. Among these parameters are factors such as alloying elements, mechanical properties, crystal structure, electrochemical properties and the like.

The set \( \mathbf{S} \) measures required ranges of the universal properties of duplex stainless steel favoring its resistance to microbial corrosion. Among these parameters are a wide range of variables. Alloying elements, for example, is very important as it has been reported that if amount of certain alloying elements, such as sulphur, is high enough, it is much more likely for microbial tubercles to develop \cite{31}.

The set \( \mathbf{A} \), on the other hand, measures fuzzy probability of each member of the sets \( \mathbf{G} \) to become a member of the set \( \mathbf{S} \). In other words, \( \mathbf{A} \) would measure the fuzzy possibility of risk of MIC within the given universal parameters. More technically, a membership function \( F_{\mathbf{A}(i)} \) measures the fuzzy likelihood of a member of \( \mathbf{G} \) (such as \( \mathbf{G}_j \)) to become a corresponding member of \( \mathbf{S} \) (such as \( \mathbf{S}_i \)).

Our aim is to find out a general algorithm that would allow define \( \mathbf{A} \). Fuzzy membership functions for each set are defined to arrive at composite function of membership functions. By defining the composite functions fuzzy rules to characterize the environment and its important parameters are defined.

A fuzzy method known as “generalization of compositional rule of inference” is utilized in this study. In this method, a fuzzy rule is transformed into a general form of multi antecedents (inputs) and consequents (outputs). Also Kosko decomposition method for decomposing a fuzzy rule and Mamdani minimum fuzzy implication will be used.

By utilizing Mamdani minimum fuzzy implication, the minimum value of membership functions of the given fuzzy sets is calculated. Then, by maximum-minimum technique, first the minimum values of membership functions are calculated. After that, among the selected minimum values, the maximum value is picked up. If in any case, the membership functions of some elements are equal, one of the functions is chosen.

1.2. Fuzzy Model

1.2.1. Universal properties of Abiotic synthetic seawater environment

Assume that there are various \( U \) universal features that can favour resistance to non-microbial, abiotic, synthetic seawater corrosion of duplex stainless steel and not necessarily be related to each other. We may assume that for each \( \mathbf{G}_j \), there is a feature such as \( \mathbf{K} \) so that \( \mathbf{K} = 1, 2, 3, \ldots, U \).

When \( \mathbf{G}_j \) is considered for a special universal feature such as \( \mathbf{K} \), it may also be assumed that the parameter will be a random variable such as \( x(j, K) \) that obeys a normal distribution function. For any
factor that can avoid corrosion and is expressed as $S_i$, one may assume that $m(i,K)$ and $M(i,K)$ are, respectively, the permissible minimum and maximum thresholds for the universal feature $K$ to be expressed by $S_i$.

This will be translated as equation (2) in terms of fuzzy probability function:

$$F_{A(i,K)}(G_j) = \text{Prob} \left( m(i,K) \leq x(j,K) \leq M(i,K) \right)$$  \hspace{1cm} (2)

where $K = 1, 2, 3, \ldots, U$, $i = 1, 2, 3, \ldots, M$, $j = 1, 2, 3, \ldots, N$

Equation (2), in terms of a membership function $F_{A(i,K)}(G_j)$, defines the fuzzy likelihood of an existing universal feature such as $K$ from the range of universal features $G_j$ to become an element of $S_i$, to resist abiotic corrosion.

1.2.2. Universal properties of IRB-containing Environment

Assume that there are various $V$ universal features that can resist MIC of duplex stainless steel by IRB and not necessarily be related to each other. We may assume that for each $G_j$ there is a feature such as $L$ so that $L=1,2,3,\ldots,V$.

When $G_j$ is considered for a universal feature such as $L$, it may also be assumed that the parameter will be a random variable such as $x(j,L)$ that obeys a normal distribution function. For any factor, expressed as $S_i$, that can avoid biofilm formation and thus resist microbial corrosion, one may assume that $m(i,L)$ and $M(i,L)$ are, respectively, the permissible minimum and maximum thresholds for the universal feature $L$ to be expressed by $S_i$.

Therefore the related membership function, in terms of fuzzy probability function, can be shown as equation (3):

$$F_{A(i,L)}(G_j) = \text{Prob} \left( m(i,L) \leq x(j,L) \leq M(i,L) \right)$$  \hspace{1cm} (3)

where $L = 1, 2, 3, \ldots, V$, $i = 1, 2, 3, \ldots, M$, $j = 1, 2, 3, \ldots, N$

Equation (3), in terms of a membership function $F_{A(i,L)}(G_j)$, defines the fuzzy likelihood of an existing feature such as $L$ from the range of the universal features $G_j$ to become an element of $S_i$, not suitable for biofilm formation.

1.3. Fuzzy Composite Functions

Equations (2) and (3) define how “close” the value of a given universal feature of duplex stainless steel can be to the range of risky values to become not eligible for MIC by IRB and corrosion by the abiotic environment. Now these membership functions need to be defined as a single function in accordance with fuzzy functions. In other words, a composite function $F_{A(i)}$ must be defined as a function of $F_{A(i,K)}(G_j)$ and $F_{A(i,L)}(G_j)$.
A composite function for each GjϵG can be defined for the universal features of IRB-environment and abiotic environment, respectively, as equations (4):

\[
F_{K(i)}(G_j) = \frac{\text{Max} \quad K} { } \left\{ F_{A(i,K)}G_j \right\} 
\]  (4)

\[
F_{L(i)}(G_j) = \frac{\text{Max} \quad L} { } \left\{ F_{A(i,L)}G_j \right\} 
\]  (5)

Equations (4) and (5) explains that among the membership functions for the IRB-environment, the maximum values must be picked up. The fuzzy subset \( A_{L(i)} \) (a member of G) defined by the membership function \( F_{L(i)}(G_j) \) shows that with what (fuzzy) probability a certain range of the universal features of the IRB-environment can have the conditions of not becoming a promoter for duplex stainless steel microbial corrosion, as, again, indicated by \( S_i \). The same logic with \( F_{L(i)}(G_j) \) for the abiotic environment. It must be noted that the values of \( F_{K(i)}(G_j) \) and \( F_{L(i)}(G_j) \) can be assumed to be not arbitrary variables which are independent of each other.

Equation (6) defines the fuzzy membership function, \( F_{A(i)} \), for the fuzzy subset \( A(i) \) (belonging to A) in such a way that it can measure the fuzzy possibility, \( S_i \) (belonging to S) of a combined range of universal features \( G_j \) (belonging to G) for becoming the value necessary for resistance to microbial corrosion.

Assuming \( Gj\epsilon G \):

\[
\begin{cases}
\text{If max} \left\{ F_{K(i)}G_j, F_{L(i)}G_j \right\} = 0. \text{ Then } 0 \\
\frac{F_{A(i)}G =} { } \left\{ F_{K(i)}G_j, F_{L(i)}G_j \right\} \neq 0. \text{ Then } \beta_K F_{K(i)}G_j + \beta_L F_{L(i)}G_j \\
\end{cases} 
\]  (6)

Where \( \beta_K + \beta_L = 1 \) and \( \beta_K, \beta_L \leq 1 \)

Equation (6) addresses the probability for microbial corrosion of duplex stainless steel not to happen in, respectively, abiotic environment and IRB-containing environment in terms of coefficients (weights) \( \beta_K \) and \( \beta_L \). Obviously, all of the \( \beta \) values cannot exist at the same time, in other words, when IRB-environment is being considered (\( \beta_L \)), it is assumed that \( \beta_K = 0 \) and so on.

The fuzzy possibilities will then be expressed as related to the value of the related \( \beta \) values. For example, if \( \beta_K > \beta_L \), this means that the IRB-containing environment is less likely to cause corrosion of duplex stainless steel than the abiotic environment.
We will take mechanical response and behavior of duplex stainless steel in these two environments as one of the universal features of duplex stainless steel that can be affected by these environments. Stress corrosion cracking is based on three factors (tensile stress, vulnerable materials and corrosive environment). In our choice of SSRT, we have the opportunity of linking the universal features of the environment with the effect of tensile stresses on duplex stainless steel as reflected in the maximum loads and the average loads exhibited for this material in each of these three environments.

\[ \beta_m = \frac{Load_{Average}}{Load_{Maximum}} \quad m=L,K \]  

In the next section, the related \( \beta \) values will be calculated based on the obtained slow strain rate tests (SSRT) results for conducting these tests on duplex stainless steel samples in IRB and abiotic environments. The \( \beta \) values can be directly linked with the fuzzy probability of resistance to corrosion by duplex stainless steel in each of these environments as \( \beta \) values are in fact weights that determine specific environment will be more corrosion-MIC resistant. The application of SSRT is to show that mechanical testing can be used to highlight the involved likelihood in the estimation of failure.

2. VALIDATION

2.1.1. Experimentation:

2.1.1.1. Susceptible Materials: The susceptible material duplex stainless steel samples with the following universal features were selected.

2.1.1.2. Chemical Composition:

The chemical composition of the duplex stainless steel used for the experimental purposes in this study is given in Table 1:

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>N</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>0.025</td>
<td>0.21</td>
<td>1.67</td>
<td>0.31</td>
<td>0.002</td>
<td>22.55</td>
<td>3.12</td>
<td>0.159</td>
<td>5.73</td>
</tr>
</tbody>
</table>
2.1.1.3. Mechanical Properties:

The mechanical properties of the duplex stainless steel used in the experiments are summarized in Table 2:

Table 2. Mechanical properties and heat treatment specifications of the as-received carbon steel (according to the manufacturer)

<table>
<thead>
<tr>
<th>Yield strength (MPa)</th>
<th>UTS (MPa)</th>
<th>Elongation %</th>
<th>Hardness HBR</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>605</td>
<td>796</td>
<td>36</td>
<td>234.0</td>
<td>Solution annealed</td>
</tr>
</tbody>
</table>

2.2. Suitable Environments

2.2.1. Media:

A media was used that contained 35 g/l of NaCl added to the ingredients listed in Table 3 and the pH of the medium before autoclaving was adjusted to 8.20 using 0.1 N NaOH solution. After autoclaving the measured pH was ≥ 7.5. These single-type and mixed cultures were subjected to a series of controlled microbiological experiments to verify their isolation, purification and growth and based on the obtained results, the environment suggested in Table 3 was used to support the growth all of them. It was during these experiments that it was found out that—especially for the sustained growth of the IRB—the iron must have been supplied via the susceptible material. The details of these experiments have been explained elsewhere in details [32].

Table 3. Composition of Postgate B Medium

<table>
<thead>
<tr>
<th>Chemical</th>
<th>g L⁻¹ of distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂HPO₄</td>
<td>0.5</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>1.0</td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td>1.3</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>2.0</td>
</tr>
<tr>
<td>Lactic acid (88%)</td>
<td>2.7</td>
</tr>
<tr>
<td>Yeast Extract</td>
<td>5.0</td>
</tr>
</tbody>
</table>

2.2.2. Bacterial cultures:

The IRB culture used in this series of experiments was a subculture of a preserved muddy marine sediments. The procedures to isolate and purify the IRB is summarized in Figure 1.
2.3. Test Procedure

2.3.1. SSRT test specifications:

The SSRT tests were carried out on the samples at room temperature conditions. The tensile specimens for SSRT SCC tests were all subjected to a dynamic slow strain rate of $0.12 \times 10^{-6} \text{ s}^{-1}$. This strain rate was constant through all SSRT tests performed in all the three environments tested. During the tests, viability of the cultures was being tested regularly.
3. RESULTS AND DISCUSSION

3.1. Biofilm Characterisation:

The biofilm was formed unevenly on the DSS surface in the single-type IRB environment (figure not provided). EDXA analyses of the biofilm (Figure 2) confirmed that it contained elements such as sulphur and nickel in addition to iron and chromium.

![Energy Dispersive X-ray Analysis (EDXA) spectrum](image)

**Figure 2.** EDXA of a randomly spot, selected on the biofilm covering the surface of DSS SAF 2205 exposed to the single-type IRB environment.

DSS is known for its vulnerability to hydrogen embrittlement (Griffith and Turnbull 2001). It has been shown [32] that synthetic seawater is capable of hydrogen production. EDXA spectra of the IRB biofilm covering DSS indicated the existence of sulphur in the biofilm (Figure 2). Therefore, the biofilm thus produced was able to highly corrode the steel. This was also confirmed by observing the relatively high density of pitting observed (estimated as 30 pits cm$^{-2}$).

3.2. SSRT Results:

Steels when exposed to a microbial environment can develop a biofilm on their surface. One of the consequences of biofilm formation could be the development of pits that are also known to be initiators of stress corrosion cracking (SCC) of metals and alloys.

Susceptibility of the test material (carbon steel) to SCC in the two environments (IRB and abiotic environments) has been compared employing slow strain rate testing (SSRT). The choice of SSRT was based on the fact that it was the most commonly used techniques for comparing SCC susceptibility of different materials and/or environments.
SCC results were analysed and explained on the basis of the time-to-failure and reduction of area of the specimens. Time-to-failure ($T_f$) and reduction of area (ROA) are two parameters by which loss of ductility due to the role of environment can be indicated. If in a certain environment, the material fails sooner, i.e. shorter $T_f$, in comparison with another environment for the same material, it is a manifestation of the greater role of the first environment in failure. In the same way, lower ROA is also a measure of enhanced role of the environment in loss of ductility.

Figure 3 shows a typical load vs. time for the duplex stainless steel sample in IRB and abiotic environments. Table 4 summarizes the mechanical features of the failures in terms of time-to-failure and reduction of area for duplex stainless steel in these environments.

![Figure 3](image-url)

**Figure 3.** Typical load vs. time curves for duplex stainless steel in two environments (IRB-environment and abiotic environment). (Other similar data are not shown)

Figure 4 compares Time-to-fail ($T_f$) and Reduction of Area (ROA) for duplex stainless steel under SSRT tests carried out in the tested environments:

![Figure 4](image-url)

**Figure 4.** Compassion of some mechanical features of duplex stainless steel samples failed in the tested environments. (White bars) Time-to-fail ($T_f$) in hours and (Black bars) Reduction of Area (ROA), in percentage.
Tf values and corresponding ROAs’ as given in Figure 3 are consistent, i.e., a lower Tf is always accompanied by a low value of ROA. As mentioned earlier, a low Tf and/or ROA is indicative of the loss of ductility, that is to say, possibility of environmentally-assisted embrittlement.

As suggested from Tf and ROA data for specimens tested in the two environments given, duplex stainless steel has shown almost higher susceptibility to SCC in the single-type IRB environments whereas it has shown a relatively lower susceptibility to corrosion in abiotic environment. In fact, on the average, Tf has decreased in IRB environments by about 23% in comparison with abiotic environment.

The maximum and average load values for the three environments are given in Table 4:

Table 4. Load and β values for duplex stainless steel tested by SSRT in two suitable environments

<table>
<thead>
<tr>
<th>Environment</th>
<th>Maximum Load (N)</th>
<th>Average Load (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abiotic</td>
<td>5014.7295</td>
<td>5507.7778</td>
</tr>
<tr>
<td>IRB</td>
<td>4329.334</td>
<td>5149.63</td>
</tr>
</tbody>
</table>

Based on the values given in Table 4, the corresponding β values for and synthetic sweater and IRB- environments, respectively, will be as given in equations (8) to (9). Instead of subscripts K and L the tested environments’ designations have directly been used.

\[ \beta_{\text{Abiotic}} = 0.91 \]  
(8)

\[ \beta_{\text{IRB}} = 0.84 \]  
(9)

Based on equations (8) and (9) and recalling equation (6), it is possible to see that the model is successfully matched with obtained experimental results. In other words, the model predicts that the fuzzy possibility of resistance to corrosion for duplex stainless steel in the biotic IRB environments is lower than that of the abiotic environment. As seen from equations (8) and (9) and comparing them with Figures 3, 4 and Table 4, the theoretical prediction of the model is experimentally justified. In other words, the probability of duplex stainless steel’s resistance to corrosion in the IRB-containing environment is about 84% whereas in the abiotic environment, it is about 91%. Therefore, DSS failure in IRB environment is relatively higher than abiotic environment.

4. CONCLUSIONS

- A fuzzy model based on universal features of two environments, a single-type iron reducing bacteria (IRB) and one abiotic synthetic seawater for duplex stainless steel was developed.
This model predicted that for the same susceptible material (duplex stainless steel) in these two suitable environments tested, the fuzzy probability of resistance to corrosion, of duplex stainless steel in IRB-environment will be less than that of synthetic seawater environment and therefore duplex stainless steel would show a higher susceptibility to microbial corrosion.

The mechanical tests carried out (slow strain rate tests) on these environments validated the expected predictions.

Abbreviations:
- EDXA: Energy Dispersive X-ray Analysis
- DSS: Duplex stainless steel
- IRB: Iron reducing bacteria
- MIC: Microbiologically influenced corrosion
- ROA: reduction of Area
- SCC: Stress corrosion cracking
- SSRT: Slow strain rate testing
- UTS: Ultimate tensile strength

References

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