**CHARACTERIZATION OF THE CORROSION RESISTANCE OF
DUPLEX STAINLESS STEELS
USING
LOCAL CURRENT DENSITY MAPPING TECHNIQUES**

to

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ABSTRACT

An *in situ* investigation of the dissolution behavior of duplex stainless steel has been carried out in acidic solutions containing 2.0 M HCl with 2.0 M H₂SO₄ to determine differences in dissolution rates of the austenitic and ferritic phases. The current density distribution over the dissolving steel surface was measured using a vibrating electrode. The study demonstrated that this technique could quantify the differences in dissolution rates of the austenitic and ferritic phases under the conditions tested. The dissolution rates for the two phases peak at different potentials resulting in multiple current maxima. In addition, transients in dissolution behavior of the two phases at different potentials were observed using optical microscopy. Electron microscopy of the dissolved surface showed very high levels of aluminum and silicon enrichment on the austenitic phase.

INTRODUCTION

Duplex stainless steels owe their corrosion resistance to the presence of the high chromium, molybdenum and nitrogen content of these iron base alloys. The cost of duplex alloys is less than more conventional austenitic stainless steels because of the lower nickel content. Duplex stainless steels have improved corrosion resistance and reduced susceptibility to stress corrosion cracking and intergranular corrosion.

Local variation in dissolution rates of the two phases has been observed [1-5] and found to be potential dependent. In a detailed study by Symnietis [3-5] measurements were made on a duplex alloy with 50% of each phase, and on single phase alloys having compositions close to the austenitic or ferritic phases in the duplex alloy. Variation in weight loss at controlled potentials for the duplex, ferritic and austenitic alloy is shown in Figure 1 [3-5]. The ferritic alloy showed about the same maximum dissolution rate as the austenitic alloy but at a potential about 100 mV lower. The duplex alloy showed a broader peak with a distinctly higher maximum dissolution rate at the potential where the ferritic alloy dissolved. There was an indication of a second peak in the weight loss curve for this alloy close to the potential where the austenite showed a maximum. Dissolution of the duplex alloy was not a simple additive sum of the correct proportions of the separate single phase

FIGURE 1. Active curves for SAF 2205 and corresponding ferritic and austenitic alloys, obtained by the potentiostatic weight loss method. Solution: 2 M $\text{H}_2\text{SO}_4 + 0.1 \text{ M HCl}$. (from Ref. 3)

FIGURE 2. Results of weight loss rates at fixed potentials for a ferritic (Alloy 2) and an austenitic alloy (Alloy 4) having the same composition as those in a duplex alloy in a 2 M $\text{H}_2\text{SO}_4 + 2 \text{ M HCl}$ solution (from Ref. 5).

alloys. The rate for the duplex alloy was much higher than calculated rate from the single phases. Differences in dissolution characteristics is again shown in Figure 2 [5]. The test in Figure 2 used a much higher chloride concentration of 2 M HCl compared to 0.1 M HCl used in Figure 1 and the rate of weight losses was significantly higher. In this solution the austenitic alloy showed a higher weight loss and possibly dominated the weight changes of the duplex alloy. The variations of weight loss with potential for the austenitic alloy also showed a second peak, suggesting that a polarization curve would reflect this behavior by having two current peaks. Also with the higher chloride concentrations, the maximum weight losses occurred at higher potentials.

Polarization measurements yield double peaks particularly when the potential is swept in the negative direction. This was taken to indicate differences in the behavior of the phases in the duplex alloy. The presence of the two peaks were influenced by sweep rate and by the presence of hydrogen evolution [5]. These factors make it difficult to correlate changes in current with the behavior of a particular phase in the alloy. In contrast, weight loss measurements integrate the corrosion behavior over a period of time and do not reflect marked variations in rate with time that have been observed during polarization at fixed potentials [4].

It was considered that scanning methods, that map currents over metal surfaces [6-14], may offer a technique for monitoring the changes that take place at different phases in a duplex alloy. The major advantage of these methods is the ability to measure corrosion surface during exposure. The *in situ* ability can also be used to locate the anodic sites and identify the areas where corrosion initiates and propagates. The magnitudes of the currents at these sites are a direct and sensitive measure of the rate of corrosion. Changes in rate and progress of corrosion as a function of environmental conditions can therefore be rapidly ascertained, overcoming the need for extended periods of exposure to obtain measurable changes in weight for each test condition. The scanning techniques should offer a rapid method for measuring the behavior of ferritic and austenitic phases at different potentials where the rates of passivation for the two phases may differ. Other corrosion related applications are envisaged. For example the effects of differential heating adjacent to welds, or heat treatments that precipitate additional phases at grain boundaries may be studied.

The objective of this project was to demonstrate that the use of the vibrating probe for current density mapping could separate the dissolution behavior of the two major phases in duplex stainless steels, and then study the sensitivity to alloy composition and heat treatments. Only the first aspect of this study was conducted and is presented in this report.

The steels studied were supplied by IRSID.

BACKGROUND

The scanning techniques map variations in current densities over corroding metal surfaces by depending on potential gradients developed in solution due to the flow of currents. Two scanning methods have been used [6,7]. One, a dc method [6], scans a fine-tipped reference electrode over the surface at a fixed distance above it. Variation in the

potential above the surface are a result of IR-drops in the solution and reflect the variations in the current density. The IR-drop is equal in magnitude to the potential differences that exist between anodes and cathodes when electrically shorted on the same metal surface.

A second technique, the vibrating probe electrode, measures the electric field in the solution. This is accomplished with a vibrating electrode [8,9]. The vibrations convert the IR-drop to an alternating voltage with a peak-to-peak amplitude equal to the potential difference over the distance of the vibrations due to the current flowing. The vibrating electrode can also be vibrated in different directions and measures the current density in the direction of the vibrations e.g. normal and parallel to the corroding surface. The direction of current flow can be obtained by summing the vectors constructed from the vibration directions and measured current magnitudes.

The scanning techniques have been used to study a wide range of corrosion problems. Very early work in the 1930's helped establish that corrosion was indeed electrochemical. Recent measurements have been made on stress corrosion cracking [8], pitting corrosion [9], intergranular corrosion [6], weldments [6], biocorrosion [10], and corrosion inhibitors [11].

SIMULATIONS OF RESULTS

In order to analyze the results it is best to compare them with simulated calculations. The necessity for this approach arises because the current density measurements are made at a fixed distance above the surface and not at the metal surface. The currents from the surface spread on entering the solution and as a result the observed boundaries between different areas are not sharply defined and, in general, the current densities are lowered. These effects are presented below using a model to simulate expected variations. The basis of the simulation model is given first.

Simulation model

The current density is directly related to the measured field. The field in a particular direction is also representative of the current density in that direction. By Ohm's law the field divided by the solution resistivity is equal to the current density.

Potential fields in solution are determined by the anodic and cathodic electrochemical processes taking place at the metal surface, their distribution and the current paths in solution. At open circuit, the fields in the solution are a result of the potential gradients between anodes and cathodes and can be solved using the Laplace equations if all the parameters are known. When the surface is under potentiostatic control, the fields are determined by the distribution of currents across the surface and how the currents flow from the surface to an auxiliary electrode. The flow of current from a single site on the surface spreads rapidly in solution and results in a very rapid decrease in current density with distance above the surface. If there is a distribution of currents over the surface, the spreading produces more uniform current densities as the distance from the surface increases. A simplified method has been used where the electrode surface currents are replaced by point current sources or sinks [7]. The observed field in solution is obtained by

summing the fields due to all the point current sources.

In this present study the duplex alloy could be more easily simulated by line current sources rather than point sources. If i is the current per unit length of line on an insulating plane, and the line can be considered to be semi-infinite then from electrostatics or other similar approaches, the variations of the potential V at a given distance r from the line can be determined from the equation

$$\frac{dV}{dr} = \frac{i \rho}{\pi} \frac{1}{r}$$

where ρ is the solution resistivity. In Cartesian coordinates, with x the horizontal distance and z the vertical distance then

$$r = \sqrt{x^2 + z^2}$$

The field normal to the surface F_z can be obtained from these equations and is given by

$$F_z = \frac{dV}{dz} = \frac{i \rho}{\pi} \frac{z}{\sqrt{x^2 + z^2}}$$

When using the vibrating probe, dz is the size of the vibration normal to the surface i.e. in a vertical direction. The potential difference dV is also in this direction. A similar equation for the field in the x -direction parallel to the surface can also be derived. Summing the normal and horizontal fields gives the current density vector in a plane normal to the surface. This vector is plotted as an arrow to display results. For the following simulations and in for other results only the normal current density is plotted.

In order to simulate the results an alloy surface is considered to be made up of strips of austenite and ferrite of equal width as drawn in Figure 3. Each strip is divided again into narrower strips and each narrow strip is replaced by a line having a constant current per unit length. The currents from the lines are chosen so that they sum to give the required current density or current density variations. In other words, the currents from each phase are simulated by a series of elemental lines.

Calculations of simulated normal current density variations

Variations in the observed current densities measured with the vibrating probe vary with the resistivity of the electrolyte, the height of the vibrating probe above the surface, the areas of the different phases, and the current densities flowing from each phase. Examples of the simulation are based on the duplex alloy/acid electrolyte being studied and are shown

FIGURE 3. Schematic showing current line sources. Currents from each phase area are replaced by a series of lines carrying currents to giving the same current density flowing from each phase.

FIGURE 4. Calculated normal current density variation based on current line simulations of metal surfaces. The height of the probe is given in millimeters. The resistivity of the solution was 1 ohm.cm and current densities were 25 and 30 mA/cm². In (a) phase 1 had the lower current density. In (b) phase 2 had the the higher current density.

in Figure 4 for alternating phases. The resistivity of the solution was taken as 1 ohm.cm, close to the value for the acidic solution used in the measurements. In the simulations the widths of the alternating phase strips differed and were taken as 100, 370, 210, 290, and 200 μm , again close to those in the measurements. In Figure 4 a and b the current density for the two phases were 25 and 30 mA/cm² and interchanged to indicate how the resolution of the directly measured currents may vary.

Figure 4 shows the variations of the calculated normal current density at probe heights from 20 to 150 μm in the solution above the surface. At probe heights above the width of the phases it becomes difficult to directly separate the contributions from each phase. It is also more difficult to resolve the shape of the lower current density sources when positioned at the edge of a sample. In order to obtain definitive resolution it is necessary to deconvolute the observed currents in order to determine the surface current densities from each phase.

EXPERIMENTAL ASPECTS

Vibrating Probe Equipment

The vibrating probe electrode is shown schematically in Figure 5. The probe was constructed using two piezoelectric bimorph reeds at right angles to each other which were vibrated at different frequencies. The sensing electrode was attached to a rod extending from the reeds. The shapes, lengths and angles of the probe were designed to achieve vibrations at each frequency parallel to or normal to the metal surface being studied. The sensing electrode was insulated except for its tip which was coated with platinum black to reduce its impedance by increasing its area. Two lock-in amplifiers were used to separate the current density components parallel and normal to the surface which could be accomplished because of the different frequencies of each vibration. The output from each lock-in amplifier was collected by a computer. The computer was also used to scan the position of the vibrating probe supported on a 3-axis stage. A schematic of the scanning equipment is shown in Figure 6.

The compositions of the duplex steels tested are shown in Table 1. Early measurements attempting to resolve variations in current density on the finer grain alloys were unsuccessful. Measurements on the coarse grain samples did show definitive current density variations during active dissolution.

Specimens of the steel were mounted in epoxy. Generally the steel surface was polished to 0.2 μm finish and etched in Murakami's reagent. Other surface preparations were electropolishing in a mixture of 60 volumes 85% H₃PO₄, 20 volumes 98% H₂SO₄, and 20 volumes H₂O or only abraded to a 600 mesh finish. Attempts were made to coat part of the surface to reduce the exposed area using Microstop Stop-off lacquer. In most cases the coating was undermined except when the surface was simply abraded before coating.

Teflon or Mylar tape was wrapped around the epoxy mounting to construct

FIGURE 5. Schematic drawing of the T-linkage vibrating probe electrode vibrating in two dimensions. The two piezoelectric reeds producing the vertical and horizontal vibrations are connected at right angles and vibrate at different frequencies producing a lissajous motion at the tip of the sensing electrode.

FIGURE 6. Schematic drawing of the scanning vibrating probe system used for the corrosion studies.

a cell which contained about 2 cm³ of test solution. A Pt wire counter electrode and a Ag wire reference electrode were also immersed in the solution. The potential of the silver wire was measured against a saturated calomel electrode, generally giving a value close to -100 mV below the calomel electrode. The potentials are referenced to the calomel electrode.

Table 1 Composition of Duplex Alloys

ALLOY	C	Mn	Si	S
T4465	0.025	1.465	0.42	0.001
13011	0.023	1.52	0.36	0.006
	P	Ni	Cr	Mo
T4465	0.022	5.9	22.40	3.11
13011	0.027	6.18	21.41	2.75
	Cu	Co	Al	N
T4465	0.15	0.043	0.013	0.18
13011	-	-	-	0.11

RESULTS AND DISCUSSION

Polarization Measurements

An extensive range of initial measurements were carried out to determine if double peaks in the active to passive transition could be obtained with 2.0 M H₂SO₄ solutions. It is generally believed that the two peaks arise because of the difference in the polarization characteristics of the ferritic and austenitic phases with the maximum for the austenitic phase occurring at the higher potentials. It was found that with the air exposed solutions, the active peak was small and not well defined. Increasing the chloride concentration increased the current density at the current peak [1-3] and also produced the double peaks at high chloride concentrations.

A series of measurements were carried out to obtain an indication as to the effects of changes in procedure on the presence and disappearance of two peaks. The initial objective was to obtain reproducible currents by a particular sequencing of potentials prior to each measurement of the current distribution. Unfortunately, this did not prove possible within the scope of this limited investigation. The polarization behavior of the alloy is complex and it was not possible to establish the dependencies and interdependencies of most

of the variables important in determining the corrosion characteristics of the different phases in the alloy. However, a number of the important variables were identified during the investigation including, the solution composition, the potential scan rate and direction, and the detailed specimen history, as this had dramatic effects. The history included what upper and lower potential limits were reached, and any holding period at these limits or during a potential scan.

Measurements in 0.1 M HCl with 2.0 M H₂SO₄ solution did not show defined double peaks. A series of measurements were carried out with 1.0 M HCl and 2.0 M HCl (with 2.0 M H₂SO₄) solutions. Only when the concentration of chloride was increased to the higher value could the two peaks be clearly seen on decreasing the potential. This was in agreement with the observations of Symnietis who found that the double peaks only became apparent when the chloride concentration was increased.

Polarization measurements on decreasing the potential at 1 mV/s indicated that more than two peaks were present. The results in Figure 7 show three scans on the same sample of alloy numbered 13011. The major difference between the results was the hold time at the most positive potential. The hold times were 5, 60 and 1.5 minutes for curves a, b, and c, respectively. When the potential was held for short periods multiple peaks were observed as in Figure 7a and c. When held for a longer time of 60 minutes only one peak appeared as in Figure 7b. In Figure 7a there are two distinct peaks and a discernible third peak when the potential was decreased. In subsequent runs only one peak developed as shown in Figure 7b. Then two distinct peaks in Figure 7c, at potentials above where the lowest potential peak in Figure 7a was observed. These results strongly suggest that the appearance of the peaks were not distinctly related to one of the two major phases present in the alloy.

Current Density Mapping

The initial series of measurements were carried out on a sample of alloy 2205 annealed for 24 h. There were initial difficulties in current density mapping near the open circuit potential in 0.1 M HCl with 2.0 M H₂SO₄. This arose because of hydrogen, a corrosion product, nucleating bubbles on the vibrating probe. When higher chloride concentration of 2.0 M was used this was no longer a difficulty because the increased open circuit potential reduced the rate of hydrogen formation.

Figure 8 shows variations of current density over a coarse grain duplex alloy designated T4465 obtained using the vibrating probe electrode. The potential was -167 mV. The specimen was 0.15 by 0.2 cm² in size. The current density measured was in a plane perpendicular to the metal surface. This plane was also perpendicular to origins of the arrows along the line of the measurement. The arrows are current density vectors. Their length represents the magnitude of the current density and the angle represents the current flow direction in the perpendicular plane. Anodic currents have upward pointing arrows and cathodic currents point downwards. The origin of the arrows are positioned at the point on the surface above which the measurements were made.

FIGURE 7. Polarization results showing a) three b) one and c) two current peaks in a solution of 2.0 M HCl with 2.0 M H₂SO₄.

The current density vectors varied with position. The maximum magnitudes indicated that the currents from the lighter phase in the micrograph were larger than the currents from the darker phase. The lighter phase was ferrite, and the darker phase austenite. The slope of the vectors increased at the edge of the sample. At the edge of the sample the current spreads out into the adjacent liquid, while at the center of the sample, spreading is prevented by the surrounding current so the predominant direction of current flow is directly upwards.

The component vector of the current density flowing perpendicular to the metal surface (i.e. the component of the vectors pointing upwards in the plane of the page of the photograph) represents the normal current density, which for simplicity, and without loss of information, will be the only current density component used in the analysis below.

A series of current mapping scans were made as a function of potential using the vibrating probe in a 2.0 M HCl plus 2.0 M H₂SO₄ solution. These particular results were chosen because associated applied current (from the controlling potentiostat) during the polarization measurements did show a double peak. The double peak has been attributed to differences in the polarization characteristics of the two major phases. The probe height for the measurements was 100 μ m above the surface. The potential was ramped at a rate of -0.5 mV/s from 100 to -500 mV/SCE. The polarization curve for this scan is shown in Figure 9.

The vibrating probe was used to traverse repeatedly the same line in Figure 8 while the potential was decreasing. One line scan took about 20 seconds and the potential changed by 10 mV. The normal current density component as a function of position and potential is shown as a 3-dimensional plot in Figure 10. It incorporates the variations of the current for each position along the line over a narrow potential range of 10 mV and also the variation of the current as a function of potential for each point along the line. Three maxima at the highest currents in this figure are clearly seen. Two maxima occur close to a single potential but at separated positions above the sample. The singular third peak at a more negative potential was in a position between the other two peaks. The first two peaks were associated with the austenitic phase. These strips of grains were separated by the light ferritic phase as seen in Figure 8. At the lower potential the single current peak occurred over the ferritic phase. This data will be presented in more detail.

The current variations with potential at specific sites above the duplex alloy are given in Figure 11. These measurements, taken from Figure 10, give polarization curves for specific local sites and may be compared with Figure 9 which gives the average polarization current density for the whole area. Not all sites show a double current peak with potential. At positions closer to the right side of the sample the probe was predominantly over austenite and gave one wide, or two indistinct combined peaks, shown in Figure 11h. Positions over ferrite in the middle of the line show distinct double current peaks. At present it is not possible to definitively state that the measured normal currents represents only the polarization behavior of the phase below it. If this were the case then each phase may show

FIGURE 8. Variations of current density over a coarse grain duplex alloy showing the variation of current density in a plane perpendicular to the metallographic surface at -167 mV/SCE. The arrows are current density vectors. The length represents the magnitude of the current density and the angle the current flow direction in the plane. Anodic currents point upwards. The background micrograph was recorded after the polarization experiment.

FIGURE 9. Polarization curve measured at 0.5 mV/s on decreasing the potential from 100 to -500 mV/SCE in 2.0 M HCl with 2.0 M H₂SO₄.

FIGURE 10. Variation in normal current density as a function of potential and x-position. The line scanned was the same as that shown in Figure 8 and the measurements were made at the same time the polarization results in Figure 9 were recorded.

FIGURE 11. Variations in normal current density with potential for the results in Figure 10 at specified distances.

double peaks and the presence of double peaks is not indicative of the presence of two phases in the alloy. However, measurements at a particular position may have incorporated current contributions from adjacent areas or phases, to a sufficient degree, to produce two peaks. In order to obtain a more definitive measurements a larger area and not just a line, must be scanned. The current density at the alloy surface can then be obtained by deconvoluting the normal current density measurements made at a fixed distance above the surface. This procedure has been carried out previously [12]. It was not done in this investigation because it would have been a lengthy procedure to obtain many sets of measurements over a range of potentials and having to wait for currents to reach constant values at each potential.

Variations in normal current density with distance along the line are shown in detail in Figure 12. In Figure 12a at the highest applied potentials, there were distinct maxima over the edge of the specimen. The currents were probably associated with crevices between the metal and its mounting, that developed during earlier potential scans. These maxima were absent at the most negative potentials, below the active range, as seen in Figure 12g and h. This indicates that there was susceptibility to crevice corrosion but the rates were very low. As the potential decreased, the dissolution rates of the phases differed, beginning with austenite dissolving more rapidly, as indicated by Figure 12c. At lower potentials, the variations along the line became more pronounced until the highest current densities were reached in Figure 12d. There was, however, no sharp maximum in the currents above the ferrite. In Figure 12e the maximum current for a given curve was over ferrite. As the currents continued to decrease below the active peak, the dissolution rates were essentially uniform across the sample as shown by Figure 12f.

It is interesting to compare the results of Figure 12d with those of the simulations in Figure 4 as the observed and calculated results show the same shapes. The dimensions for the simulation were based on the micrograph in Figure 8. Line scans for the simulations were at right angles to the strips of the two phases rather than at $\sim 45^\circ$ as was the case in the experimental measurements. The normal current density (as opposed to the horizontal current density component) is not dependent on the angle, but only on its position over the respective phases. Hence the shape of the curves and the magnitudes remain the same as the simulations and only the distance dimension would be expanded. The agreement between the results and simulations shows that the observed variations can be accounted for by differences in dissolution rates of two phases.

The results clearly demonstrate that the vibrating probe current mapping can measure the variations in current density over different phases even if the variations in current density are not large. At the lower potential current maximum, the scanning results suggest approximately equal rates at about 30 mA/cm^2 . When the maximum in applied current was observed at the higher potential, the differences in the dissolution rates of the phases were from 27 to 32.5 mA/cm^2 (Figure 12 d). The ratio of these currents produces a difference in dissolution rate of 1.2 , with the austenite showing the highest rate. Appearances of the dissolved surface suggests a much higher difference. This is due to the

FIGURE 12. The variations in normal current density with distance along the scanned line for the potential indicated. The results were taken from Figure 10. Potential variations during the scan were 10 mV.

fact that topographical differences in height between the two phases increases with the amount of dissolution and can suggest a much higher difference in rate.

Visual Observations of the Surface during Polarization Measurements.

A TV camera and video system was used during all the current density mapping measurements. This allowed for correlating the position of the probe with different phases or heterogeneities. An interesting observation was made during this investigation. Unfortunately, detailed recordings with higher resolution could not be made. The photographs were taken using a Video Graphic Thermal Printer to record the TV screen.

On decreasing the potential distinct observable differences occurred over particular phases when the active current peak was traversed. The results are shown in Figure 13. Figure 13a shows the appearance of the sample was in the passive state as the potential was decreasing. The light phase was the ferrite. As the current peak was approached, the austenitic phase darkened further as seen in Figure 13b, c and d. After the more positive potential current-peak was traversed contrast between the phases was poor, Figure 13e, because the ferrite began darkening. As the current peak at the lower potential was traversed the ferritic phase darkened significantly, Figure 13f. After the current dropped the ferrite regained its lighter appearance. This sequential darkening of the phases was observable even when there was no distinct double current peaks and also when the potential was scanned in a positive direction, with the ferrite darkening at the lower potential.

It is probable that at high currents the concentrated dissolution products absorb sufficient light to indicate where the dissolution is taking place. Even though this interpretation seems likely, darkening may instead, be related to changes in the surface films as they dissolve, thicken or change in composition. Further investigations including solution flow and detailed optical observations should be carried out in the future to clearly define this phenomenon.

Electron Microprobe Analysis

After vibrating probe measurements were completed an attempt was made to determine the composition of the phases using scanning electron microscopy and energy dispersive x-ray analysis. The composition of the ferritic phase was easily determined. However, the austenitic phase was covered by a product high in aluminum and silicon which prevented determination of the underlying metal. Measurements of the phase compositions were therefore made with a metallographically prepared surface and these compositions were used to correlate the ferritic phase.

The build up of the surface product on the austenitic phase can be expected to influence the dissolution behavior of the alloy. It may also contribute to the difficulties in obtaining reproducible polarization curves on repeated potential cycling.

FIGURE 13. Appearance of the alloy surface during polarization showing darkening of the different phases as the two current peaks were traversed on decreasing the potential. The austenitic phase darkened in b, c, and d. The ferritic phase darkened in e and f.

CONCLUSIONS

- 1) The vibrating probe current mapping technique has been utilized to detect and measure the difference in dissolution rate of the austenitic and ferritic phases in coarse grain duplex stainless steel during polarization in highly acidic solutions. The maximum difference in the dissolution rate of the phases in this environment was about 20%
- 2) Simulations of current density variations over the surface have been shown to closely duplicate the observations.
- 3) Optical observations of the surface have shown that the dissolving phase can be identified during the dissolution process.
- 4) An extensive build up of silicon and aluminum dissolution product was observed on the austenitic phase after polarization in the acidic test solution.

FUTURE INVESTIGATIONS

- 1) The polarization characteristics of the alloy phases and the factors that affect the process needs to be determined in more detail. Many factors lead to marked differences in the polarization behavior. The dissolution characteristics should be correlated with the composition of the remanent oxides that remain after active dissolution.
- 2) The variation in dissolution rates of different phases should be determined at constant potentials using vibrating electrode techniques.
- 3) The affects of heat treatment and alloy composition on differences in phase dissolution rates should be investigated using vibrating probe electrodes.

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FIGURE CAPTIONS

- Fig.1 Active curves for SAF 2205 and corresponding ferritic and austenitic alloys, obtained by the potentiostatic weight loss method. Solution: 2 M H_2SO_4 + 0.1 M HCl. (from Ref. 3)
- Fig.2 Results of weight loss rates at fixed potentials for a ferritic (Alloy 2) and an austenitic alloy (Alloy 4) having the same composition as those in a duplex alloy in a 2 M H_2SO_4 + 2 M HCl solution.
- Fig.3 Schematic showing current line sources. Currents from each phase area are replaced by a series of lines carrying currents to give the same current density flowing from each phase.
- Fig.4 Calculated normal current density variation based on current line simulations of metal surfaces. The height of the probe is given in millimeters. The resistivity of the solution was 1 ohm.cm and current densities were 25 and 30 mA/cm². In (a) phase 1 had the lower current density. In (b) phase 2 had the higher current density.
- Fig.5 Schematic drawing of the T-linkage vibrating probe electrode vibrating in two dimensions. The two piezoelectric reeds producing the vertical and horizontal vibrations are connected at right angles and vibrate at different frequencies producing a lissajous motion at the tip of the sensing electrode.
- Fig.6 Schematic drawing of the scanning vibrating probe system used for the corrosion studies.
- Fig. 7 Polarization results showing a) three b) one and c) two current peaks in a solution of 2.0 M HCl with 2.0 M H_2SO_4 .
- Fig. 8 Variations of current density over a coarse grain duplex alloy showing the variation of current density in a plane perpendicular to the metallographic surface at -167 mV/SCE. The arrows are current density vectors. The length represents the magnitude of the current density and the angle the current flow direction in the plane. Anodic currents point upwards. The background micrograph was recorded after the polarization experiment.
- Fig.9 Polarization curve measured at 0.5 mV/s on decreasing the potential from 100 to -500 mV/SCE in 2.0 M HCl with 2.0 M H_2SO_4 .
- Fig.10 Variation in normal current density as a function of potential and x-position. The line scanned was the same as that shown in Figure 8 and the measurements were made at the same time the polarization results in Figure 9 were recorded.

Fig.11 Variations in normal current density with potential for the results in **Figure 10** at specified distances.

Fig.12 The variations in normal current density with distance along the scanned line for the potential indicated. The results were taken from **Figure 10**. Potential variations during the scan were 10 mV.

Fig.13 Appearance of the alloy surface during polarization showing darkening of the different phases as the two current peaks were traversed on decreasing the potential. The austenitic phase darkened in b, c, and d. The ferritic phase darkened in e and f.

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