There are two possible approaches to applying ion implantation to the modification of the corrosion behavior of metals and alloys. The first approach is to use ion implantation to produce metastable or amorphous corrosion-resistant surface alloys that are inaccessible by conventional metallurgical techniques, and to apply them to specific applications where corrosion is a severe problem. Secondly, and of a more fundamental nature, ion implantation can be used to introduce controlled amounts of various elements into the surface of a metal as part of a research effort to identify the mechanisms responsible for certain forms of general and localized corrosion. The technique of alloying to produce more corrosion resistant materials is widely used and the choice of a particular alloying element is usually based on the fact that it will enhance the formation of a passive film or will reduce the rate of the various cathodic processes that occur on the metal's surface. It is also possible to
reduce the overall corrosion rate by introducing an element that
displays rapid cathodic kinetics, but it is essential that the
original material passivate in the corrosive environment that is
being considered.

Aqueous corrosion proceeds through an electrochemical mech-
anism and there are various types of electrochemical techniques
used to evaluate the corrosion resistance of alloys. Linear
polarization and Tafel region extrapolation have been used to
evaluate binary Fe-Pb and Fe-Ti surface alloys formed by ion
implantation. The instantaneous corrosion rate of the Fe-Pb
alloys in 0.1 N H₂SO₄ was approximately 3 to 4 times lower than
that of pure iron. The reason for this is a decrease in the
hydrogen exchange current density caused by the presence of the
lead, which is a poison for the hydrogen evolution reaction.
The corrosion rate of the Fe-Ti alloys was approximately two
times higher than that of iron. Auger analysis of the Fe-Ti
alloy before exposure to the acid solution indicated that TiC
was in the region about 4.5 to 34 nm from the surface. SEM
analysis following the electrochemical tests revealed the presence
of square flat-bottomed pits, a morphology which is usually
associated with inclusion etch pits. Thus, it is proposed that
the square pits may have been formed as TiC precipitates were
etched from the sample surface.

The implantation of zirconium into iron reduces the
corrosion rate by an order of magnitude by enhancing the rate
of passivation in a 1 N H₂SO₄ solution. The corrosion rate is
still considerably higher, however, than that observed for an
amorphous Fe\textsubscript{90}Zr\textsubscript{10} coating even though the near-surface concentration of Zr in the implanted sample was estimated to be 20 to 30 atomic percent.

The implantation of Ti into 52100 steel results in the formation of an amorphous Ti-Fe-C surface, which provides modest improvements in corrosion resistance in 1 N H\textsubscript{2}SO\textsubscript{4} and 0.1 N NaCl. The anodic current density in both solutions is about 10\% that of unimplanted 52100 steel, up to an anodic overpotential of about 800 mV. Pitting, which is initiated at low overpotentials, leads to undermining of the implanted layer and its eventual peeling off at higher potentials. Detailed optical and surface analytical studies show that the pitting initiates at surface flaws, which are most likely surface carbides or oxide inclusions. Galvanic action between free Ti beneath the pitted amorphous film and Fe in the bulk steel thus leads to undermining of the amorphous layer.

The effect of the implantation of various ions on the pitting corrosion resistance of 52100 steel in a 0.01M NaCl solution has been investigated. Molybdenum implantation provided very little improvements; however, a combination of both chromium and molybdenum significantly increased the breakdown potential for initiation of pitting corrosion. Finally, tantalum implantation proved to be the most effective in protecting the surface of the 52100 from pitting corrosion.

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TABLE 1. - Corrosion rates, expressed in mils/year, in 0.1 N H₂SO₄ for several different metals and ion-implanted alloys using two different test methods, Tafel extrapolation and three-point linear polarization

<table>
<thead>
<tr>
<th>Test method</th>
<th>Fe</th>
<th>Fe-Pb</th>
<th>Pb</th>
<th>Fe-Ti</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel extrapolation</td>
<td>50±2</td>
<td>12±2</td>
<td>0.42±0.19</td>
<td>96±22</td>
<td>0.69±0.04</td>
</tr>
<tr>
<td>Linear polarization</td>
<td>32±9</td>
<td>16±10</td>
<td>(1)</td>
<td>55±47</td>
<td>0.98±0.52</td>
</tr>
</tbody>
</table>

1Could not measure corrosion rate due to cathodic Tafel slope being indeterminate.
FIGURE 1. Idealized potentiodynamic polarization scan (current vs. voltage characteristic) for a ferrous alloy in 1N H$_2$SO$_4$ at room temperature. The dashed line indicates an improvement in the passivity of the surface and therefore improved corrosion resistance.
Figure Caption

FIGURE 2. Two electrochemical methods used for determining corrosion rates were Tafel region extrapolation and three-point linear polarization. The former determines the corrosion rate graphically whereas the latter requires calculations based on experimental data. When the logarithm of the absolute value of the measured current density is plotted against the sample potential, the resulting curve generally has two linear portions (Tafel regions), one on the anodic and one on the cathodic side of the SSOC (steady-state open-circuit) potential. Extrapolation of the Tafel regions gives a point of intersection, the coordinates of which are the corrosion potential $E_c$ and the corrosion current density $I_c$, or corrosion rate.

The basis for linear polarization, or polarization resistance, lies in the assumption that potential varies linearly with current density for a range of 10 mV from $E_c$, as illustrated in this figure. The slope of this line can be related to the Tafel region slopes (found from log $I$ vs. $E$ curves) to give $I_c$. Some metal/environment systems display linear $E$ vs. $I$ curves, but most are nonlinear as shown by the solid line. The three-point linear polarization method was devised to provide a means for determining the slope of the $E$ vs. $I$ curve in the nonlinear case.
Current density as a function of sample potential for Fe, Pb, and Fe implanted with 30 keV Pb⁺ such that the final retained dose was 1.6 x 10¹⁶ atoms/cm². The potential is shown as volts from the steady-state open-circuit potential. The dashed lines represent the extrapolation from the Tafel region of each curve.
FIGURE 4. Current density as a function of sample potential for Fe, Ti, and Fe implanted with 50 keV Ti to a total retained dose of $7 \times 10^{16}$ atoms/cm$^2$, with the potential shown as volts from the SSOC potential.
FIGURE 5. Polarization curves in demineralized 1M H2SO4 obtained at a rate of 60 V/hour for Fe, Fe-18Cr, Zr, an Fe33Zr67 amorphous coating, and Fe implanted with 140 keV Zr+ to a dose of 2 x 1017 ions/cm².
FIGURE 6. Anodic potentiodynamic polarization curves (10 mV/min) for pure Ti, 52100 steel, and Ti-implanted 52100 steel (2.5 x 10^{13} ions/cm², 190 keV) in deaerated 3.5% NaCl.
FIGURE 7. Anodic potentiodynamic polarization curves for unimplanted 52100 steel and Ti-implanted 52100 steel (4.0 x 10^{14} ions/cm^2 at 190 keV) in 0.1 M NaCl solution.
Idealized potentiodynamic polarization scans (current vs. voltage characteristic) for a ferrous alloy in a buffered pH 6 solution at room temperature. The upper set of curves demonstrate the effect of adding Cl⁻ ions to the solution. $E_b$ defines the pitting potential where a sharp increase in current results when pits form on the surface. The lower set of curves demonstrate the desired result of ion implantation, i.e., force the pitting potential toward higher values.
Figure 9. Potentiodynamic anodic polarization data produced in buffer solution of pH 6 containing 0.01M NaCl for 52100 steel, and for 52100 steel implanted with molybdenum (3.5 x 10^{16} ions/cm^2), chromium (2 x 10^{17} ions/cm^2 at 150 keV), chromium plus molybdenum (2 x 10^{17} Cr/cm^2 at 150 keV, 3.5 x 10^{16} Mo/cm^2 at 100 keV), and tantalum (1 x 10^{17} ions/cm^2 at 150 keV). The curves indicate that tantalum was most effective in protecting the surface from pitting corrosion.