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Erosion-Corrosion Behavior and Cathodic Protection of Alloys in Seawater-Sand Slurries

J. Yang and J.H. Swisher

An experimental study was conducted on the erosion-corrosion behavior of three alloys in seawater-sand slurries. The idea explored was to select a steel, a copper alloy, and a titanium alloy, which should have good resistance to abrasive wear because of high hardness (within their alloy classes). Then cathodic protection would be used to protect them from corrosion. The alloys studied were 4340 steel, silicon bronze, and titanium alloy Ti-6V-4Al. Limiting conditions for cathodic protection were derived from electrochemical polarization measurements. From erosion-corrosion tests, it was found that erosive wear by sand dominated the metal loss rates of both silicon bronze and Ti-6V-4Al. For the 4340 steel, which was the hardest material, cathodic protection provided good erosion-corrosion resistance. Supplementary measurements showed that ductility loss due to cathodically charged hydrogen in the 4340 steel was negligible under the experimental conditions.

Keywords
corrosion, erosion, cathodic protection

1. Introduction

FOR structures exposed to seawater, it is common to use Cu-Ni alloys and unalloyed titanium for machinery and piping, and frequently painted, low-carbon steels for ship hulls and other less critical applications.[1,2] None of these materials are very hard. Consequently, if moving seawater contains suspended sand, the combined effects of corrosion and erosion can lead to severe metal loss. Of the common alloys used in seawater, only Cu-Ni alloys have been studied extensively in seawater-sand slurries. Syrett[3] reviewed the literature on this subject for research conducted prior to 1976. He believed that the metal loss rate was controlled by mechanical removal of the protective oxide film on the metal surface. Degradation was reported to increase with particle size and amount of entrained sand and with seawater velocity. The addition of Fe to Cu-Ni alloys improved their performance. Polan et al.[4] performed erosion-corrosion tests on a Cu-Ni alloy and found that performance correlated with hardness.

When faced with the problem of selecting an alloy for combined corrosion and erosion resistance, it is often found that good corrosion resistance is accompanied by poor erosion resistance and vice versa. The main reason is that an important hardening mechanism in alloys is the presence of a dispersed second phase, and this second phase facilitates the formation of microscopic corrosion cells in the alloy.

To obtain good combined erosion and corrosion resistance, one strategy is to use an alloy that contains a high percentage of expensive alloying elements like Cr and Ni. These elements impart both solid solution hardening and improved corrosion resistance. Even alloys in this category, like stainless steels, may be unsatisfactory because of vulnerability to pitting attack in seawater.

Another strategy is to select an alloy that is inherently hard and provide electrochemical protection against corrosion. Electrochemical protection can be more economical than the use of high-performance alloys, as evidenced by the wide application of cathodic protection in ship hulls, natural gas pipelines, and oil drilling equipment.[5] Most of the prior research on this general subject has been directed toward containment of coal-water slurries.

Hoey and Bednar[6] studied erosion-corrosion rates of carbon steels, stainless steels, and Ni-hard cast iron in coal-water slurries. With no electrochemical protection, they found that corrosion resistance was more important than hardness in alloy performance. They found, however, that cathodic protection greatly reduced the metal loss rate of C1020 steel at an applied potential of −1.0 V versus a saturated calomel electrode (SCE). Partly as an outgrowth of their results, Swisher[7] conducted a study of the effectiveness of cathodic protection on Hadfield steel and a specialty cast iron. Both alloys are very hard, but have fair to poor general corrosion resistance. More than a tenfold reduction in metal loss rates was found between protected and unprotected specimens in a 500-h test.

Another study of erosion-corrosion rates of steels was conducted by Madsen.[8] He also found in slurry tests that cathodic protection was effective in reducing metal loss rates. He reported that the degradation rate was higher in corrosive slurries than the sum of the pure corrosion and pure erosion rates, i.e., there was a synergistic effect.

Finally, Muira et al.[9] and Sasaki[10] obtained patents on the protection of steel structures in seawater containing entrained sand. The patents are not very specific on experimental parameters, and it was believed that electrodeposited films on the steel surfaces were instrumental in providing protection.

In the present study, the concept of electrochemically protecting hard alloys against the combined effects of erosion and corrosion in seawater-sand slurries was pursued further. A steel, copper alloy, and titanium alloy were studied. The specific alloys selected for the investigation were C4340 steel, silicon bronze, and Ti-6Al-4V. All have high hardnesses within their alloy classes and are not normally used when corrosion resistance is a principal materials selection criterion.

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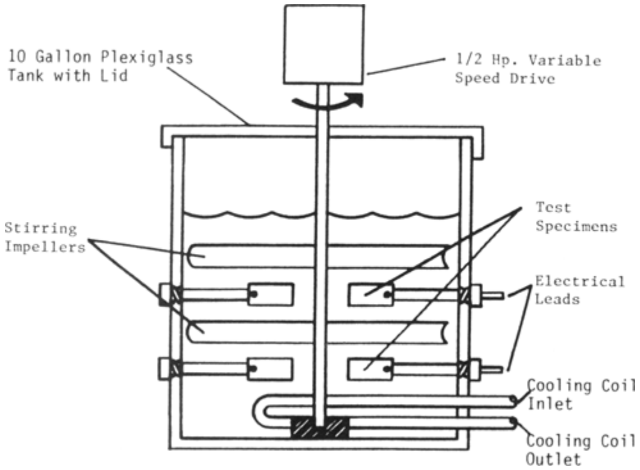

Fig. 1 Erosion-corrosion test apparatus.

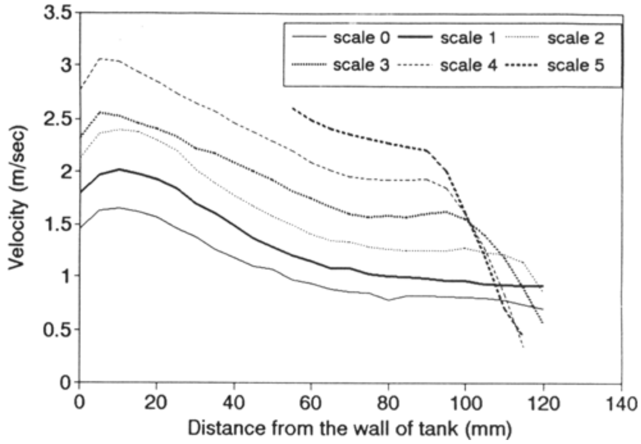

Fig. 2 Velocity profile of water in the apparatus.

Table 1 Chemical compositions of C4340, silicon bronze, and Ti-6Al-4V alloys

	Alloy composition, wt%		
Element	C4340	silicon bronze	Ti-6Al-4V
Al	...	...	6.0
C	0.40	...	0.02
Cr	0.80	...	...
Cu	...	95.85	...
Fe	bal	0.08	0.02
Mn	0.70	0.93	...
Mo	0.25	...	...
Ni	1.83	0.01	...
Si	0.25	3.02	...
Ti	...	...	bal
V	...	...	3.90

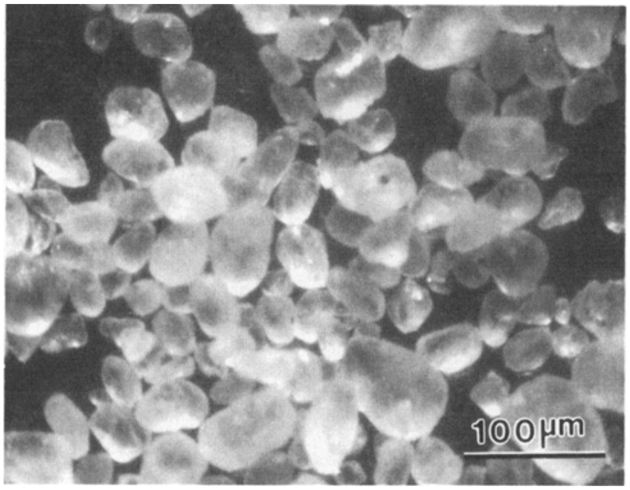

Fig. 3 Photomicrograph of silica sand particles.

2. Experimental

The chemical compositions of the experimental alloys are listed in Table 1. As-received stock of the silicon bronze and Ti-6Al-4V alloys were cut into rectangular specimens, 36 × 19 × 3 mm. The hardnesses of the silicon bronze and Ti-6Al-4V alloys were 94 and 317 HV, respectively. The C4340 steel stock was heat treated to produce a tempered martensite structure and a hardness of 554 HV. The heat treatment consisted of austenitizing for 1 h at 830 °C, water quenching, and tempering for 2 h at 220 °C. Specimens were made to the same dimensions as the other alloys, except that the thickness was 5 instead of 3 mm. The surfaces of the specimens were prepared by polishing with emery paper through No. 600 grit size, washing, and drying.

Electrochemical polarization measurements were made using a Princeton Applied Research, a product of Egne Princeton Applied Research Electrochemical Instruments Division, Princeton, NJ, (Model 243C) apparatus. A 3.5% NaCl aqueous solution was used with a scan rate of 10 mV/min. The open circuit potential between the specimen and a saturated calomel electrode (SCE) was measured over a period of 55 min. The measurements were made in air.

For the erosion-corrosion tests, the apparatus shown in Fig. 1 was constructed. It consisted of a covered plexiglass tank, with an impeller driven by a variable-speed motor to circulate the fluid. Teflon or nylon rods were used to connect the specimens to the walls of the tank. The impingement angle between the flat surfaces of the specimens and the fluid flow direction was 90°. When cathodic protection was studied, graphite anodes with similar dimensions were placed parallel to the specimens in the downstream direction at a distance of 35 mm. A DC power supply was used to impose the protecting voltage. A cooling coil in the bottom of the tank was connected to a refrigerating water bath to maintain a test temperature of 25 °C.

The synthetic seawater was prepared in accordance with ASTM D1141, which involved adding salts and other chemicals to distilled water. The final step was adjustment of the pH to 8.2 with a $0.1M$ NaOH solution.

Fluid velocity profiles in the apparatus were characterized with a pitot tube. Water without sand was used, and the velocity was measured as a function of motor speed (Scale No. rpm) and distance from the wall of the tank. Figure 2 is a graph of the data. Based on these data, the test specimens were positioned within 45 mm of the tank wall at a motor speed setting of 4. At

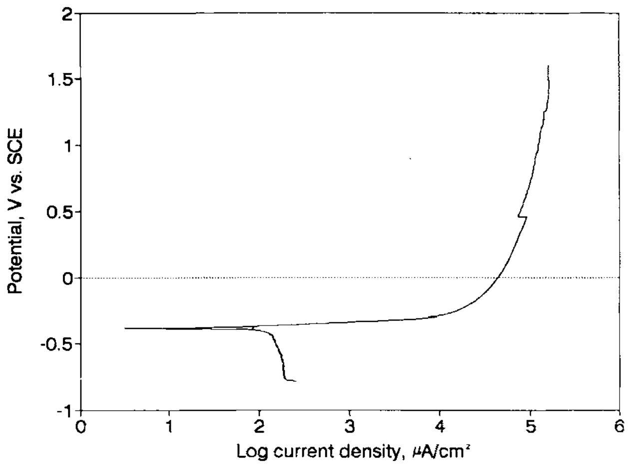

Fig. 4 Potentiodynamic polarization diagram of C4340 in 3.5% NaCl solution.

this setting, the water velocity was approximately 2.4 m/s. The US Navy uses 2.4 m/s as a baseline flow rate in many of its designs. It was not possible to use the pitot tube with sand in the water; consequently, the effect of the sand on fluid velocity was ignored.

A slurry consisting of 4 kg silica sand in 25 L synthetic seawater (9 vol% sand) was used for the erosion-corrosion tests. Ninety percent of the sand was in the particle size range from 105 to 425 μm. As shown in Fig. 3, the sand particles were round or oval in shape, without sharp edges.

After the erosion-corrosion tests, one of each pair of duplicate specimens was chemically cleaned to remove the corrosion products and then weighed to determine the metal loss. The chemicals used, Clark's solution for the steel and HCl for silicon bronze, were in accordance with ASTM G1. Concentrated HNO_3 was used for the titanium alloy. The other duplicate specimens were used to characterize the corrosion product layer and wear scars. The characterization methods included scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD).

A supplementary set of experiments was conducted to determine the extent to which the ductility of C4340 steel specimens was affected by cathodic charging with H_2. Miniature tensile test specimens, 49 mm long and 3.2 mm thick, were made from the steel stock. Then, the specimens were cathodically charged with H_2 under various cell voltages in the erosion-corrosion test apparatus for 3-day periods. Immediately after removal from the apparatus, the specimens were coated with a thin layer of copper by electroless plating to prevent egress of H_2. Tensile testing at a strain rate of 1.26×10^{-4} s^{-1} was carried out in a Material Test System (MTS 810). After testing to failure, the percent reduction in area (RA) was measured, and the fracture surfaces were examined under a scanning electron microscope.

3. Results and Discussion

A summary of the most important results and their interpretation will be given in this section. More detailed information is given in Ref 11.

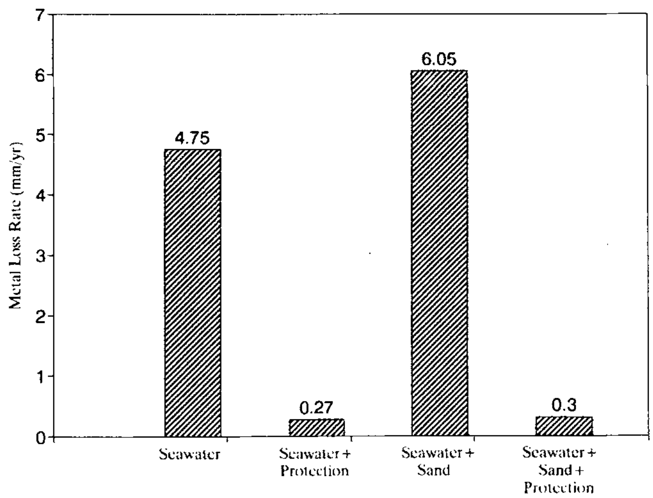

Fig. 5 Metal loss rates of C4340 steel specimens tested under different conditions.

Table 2 Polarization data for C4340, silicon bronze, and Ti-6Al-4V in 3.5% NaCl solution

Material	E_{corr}, V (SCE)	i_{corr}, μA/cm²
C4340	−0.39	107
silicon bronze	−0.21	85
Ti-6Al-4V	−0.18	1.1
Graphite	−0.08	...

Table 3 Tensile ductility of C4340 specimens

Specimen condition	Reduction in area, %
No hydrogen exposure	33.9
Cathodically protected in erosion-corrosion tests	35.5 to 37.0
Severe cathodic charging with hydrogen	2.54

Electrochemical polarization measurements frequently are used to estimate corrosion rates and the impressed voltages needed to provide protection against corrosion. Potentiodynamic polarization diagrams were obtained for the three experimental alloys and the graphite anode material. The measurements were made in a stirred 3.5% NaCl solution. One of the diagrams, for C4340 steel, is given in Fig. 4, and summary data for all the materials are given in Table 2. Electrochemists have differing opinions on whether it is best to use the so-called Tafel slope method or the polarization resistance method to determine E_{corr} and i_{corr}. Computer software is commonly available for both methods. Because the polarization resistance method is gaining in popularity, it was used in the construction of Table 2. Both methods provide somewhat higher values for i_{corr} than one obtains from visual inspection of the diagrams.

As shown in Table 2, the i_{corr} value, which correlates with the corrosion rate, is much lower for Ti-6Al-4V than for C4340 and silicon bronze. This result is consistent with the known high resistance of titanium and its alloys to corrosion in seawater. An unexpected result in the polarization diagram for Ti-

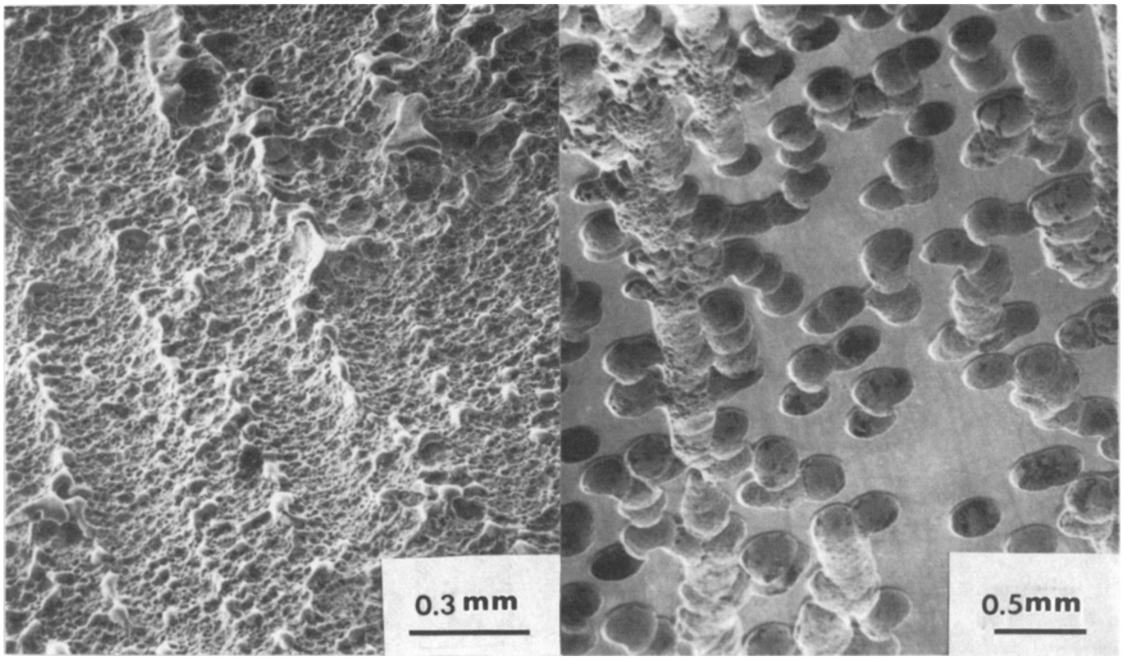

Fig. 6 Scanning electron micrographs of C4340 specimen after testing in seawater-sand slurry for 3 days. (a) Erosion scars near edge. (b) Corrosion pits near center.

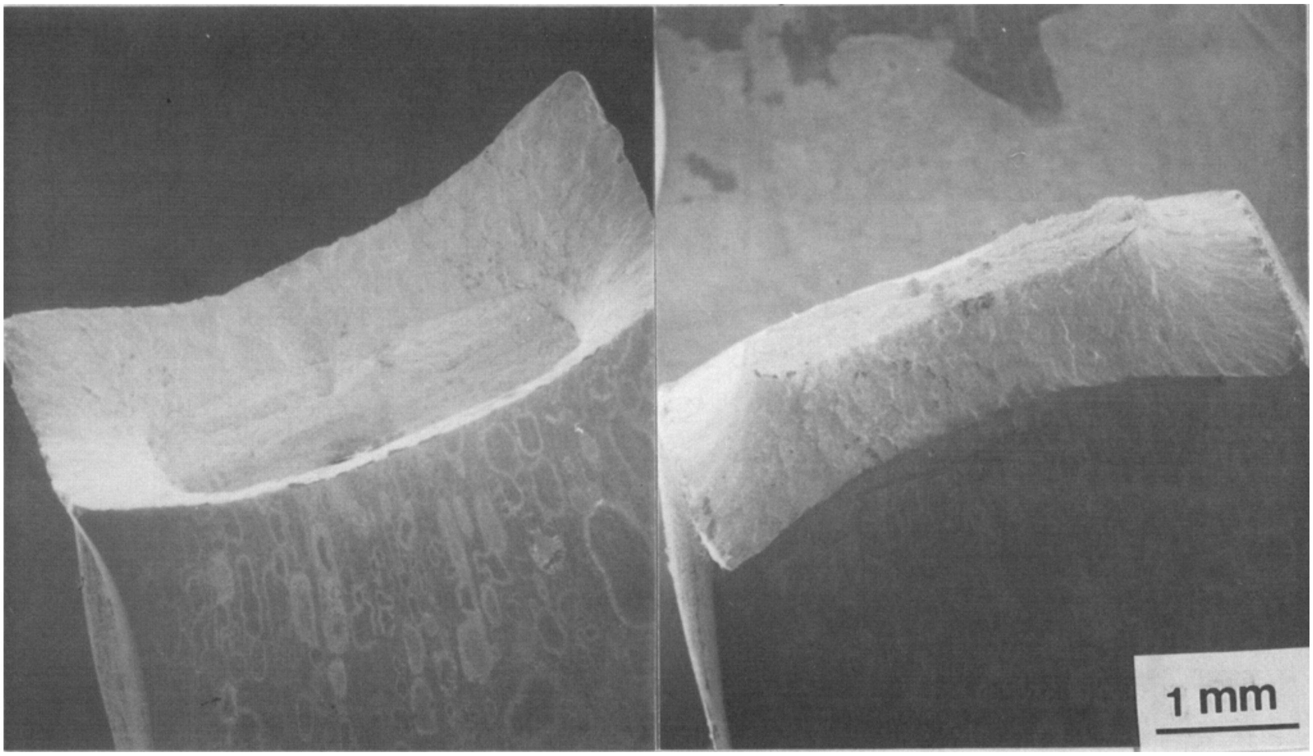

Fig. 7 Fracture surfaces of C4340 specimen after erosion-corrosion test with cathodic protection, followed by tensile testing.

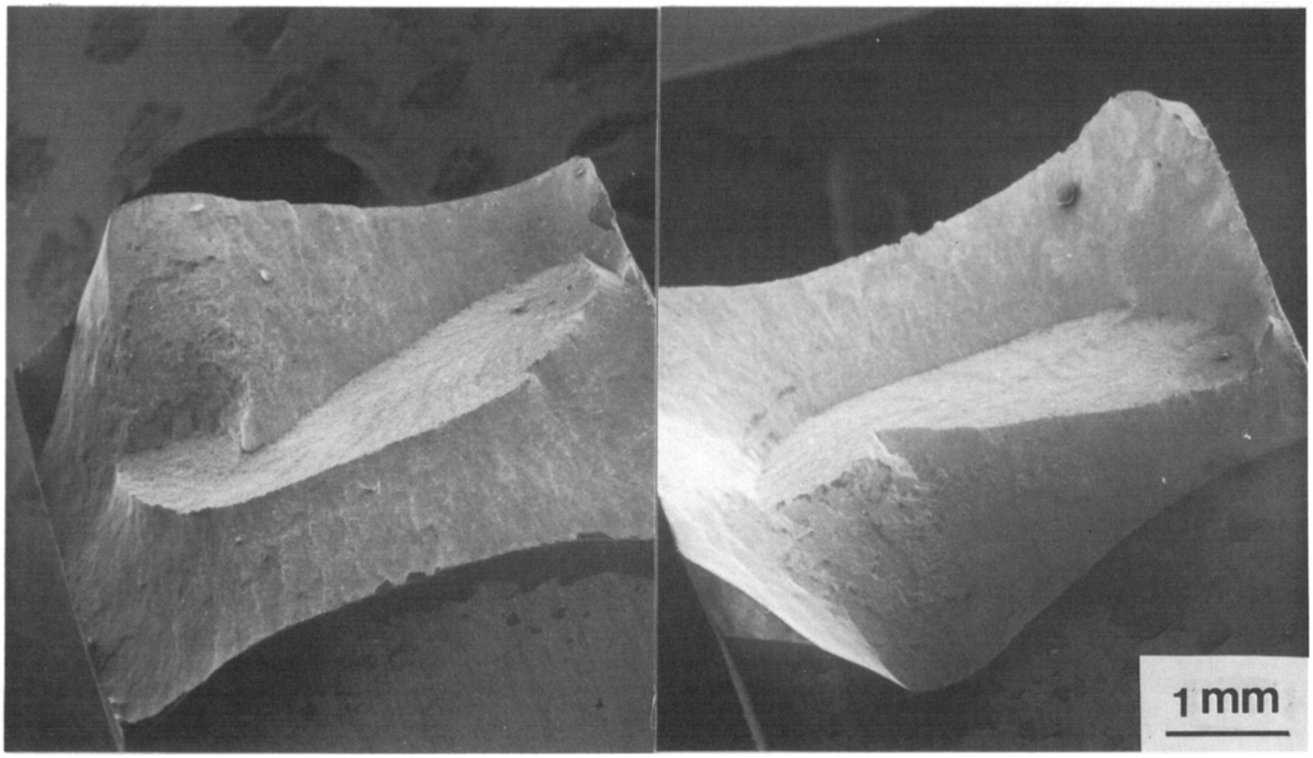

Fig. 8 Fracture surfaces of C4340 specimen after severe cathodic charging with hydrogen, followed by tensile testing.

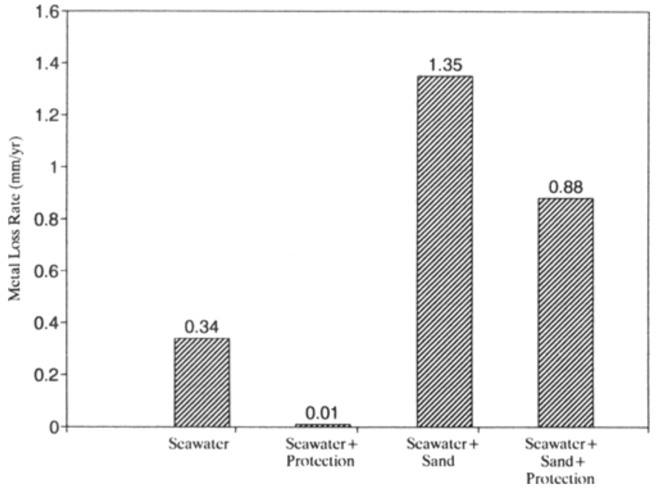

Fig. 9 Metal loss rates of silicon bronze specimens tested under different conditions.

6Al-4V was that the corrosion current did not decrease in the anodic region, indicating that anodic protection in seawater would not be effective. Anodic protection is often effective in oxidizing environments for stainless steels and titanium alloys because of their tendency to form protective oxide films.

Calculations based on the data given in Table 2 were carried out to assist in selecting conditions for cathodic protection experiments for the three alloys. The conclusions drawn from these calculations are as follows. Cathodic protection of C4340 steel should reduce the general corrosion rate to 0.1 mm/year with a cell voltage of 1.46 V between the steel and a graphite anode. Silicon bronze can be protected in the same manner with a cell voltage of 0.72 V. Without cathodic protection, the general corrosion rate of Ti-6Al-4V in seawater is 0.012 mm/year. Achieving a corrosion rate of 0.001 mm/year should be possible with a cell voltage of 0.77 V. These data should be used with caution because protective oxide films, which may form in seawater, could be removed continuously by sand particles.

In the erosion-corrosion tests, it was found that the C4340 steel benefited more than the others from cathodic protection. The metal loss rates for various test conditions are shown in Fig. 5. The duration of the tests was 3 days, and the cell voltage was 1.7 V. This voltage coincided with the onset of visible H_2 bubble evolution on the specimen surfaces. The results show that the metal loss rates were quite high in seawater and the seawater-sand slurry without protection. These results were expected because C4340 steel does not have very good general corrosion resistance. Cathodic protection reduced the metal loss rates by a factor of approximately ten. Because of the high hardness of the steel, the presence of sand in suspension did not have a significant effect.

The scanning electron micrographs in Fig. 6 show the surface of a specimen after testing in the seawater-sand slurry without protection. The combined effects of erosion and corrosion resulted in the development of wear scars and pits on the surface. This appearance contrasted sharply with the appearance of a cathodically protected specimen tested in the same slurry. Here, it was found that the sand merely polished the surface.

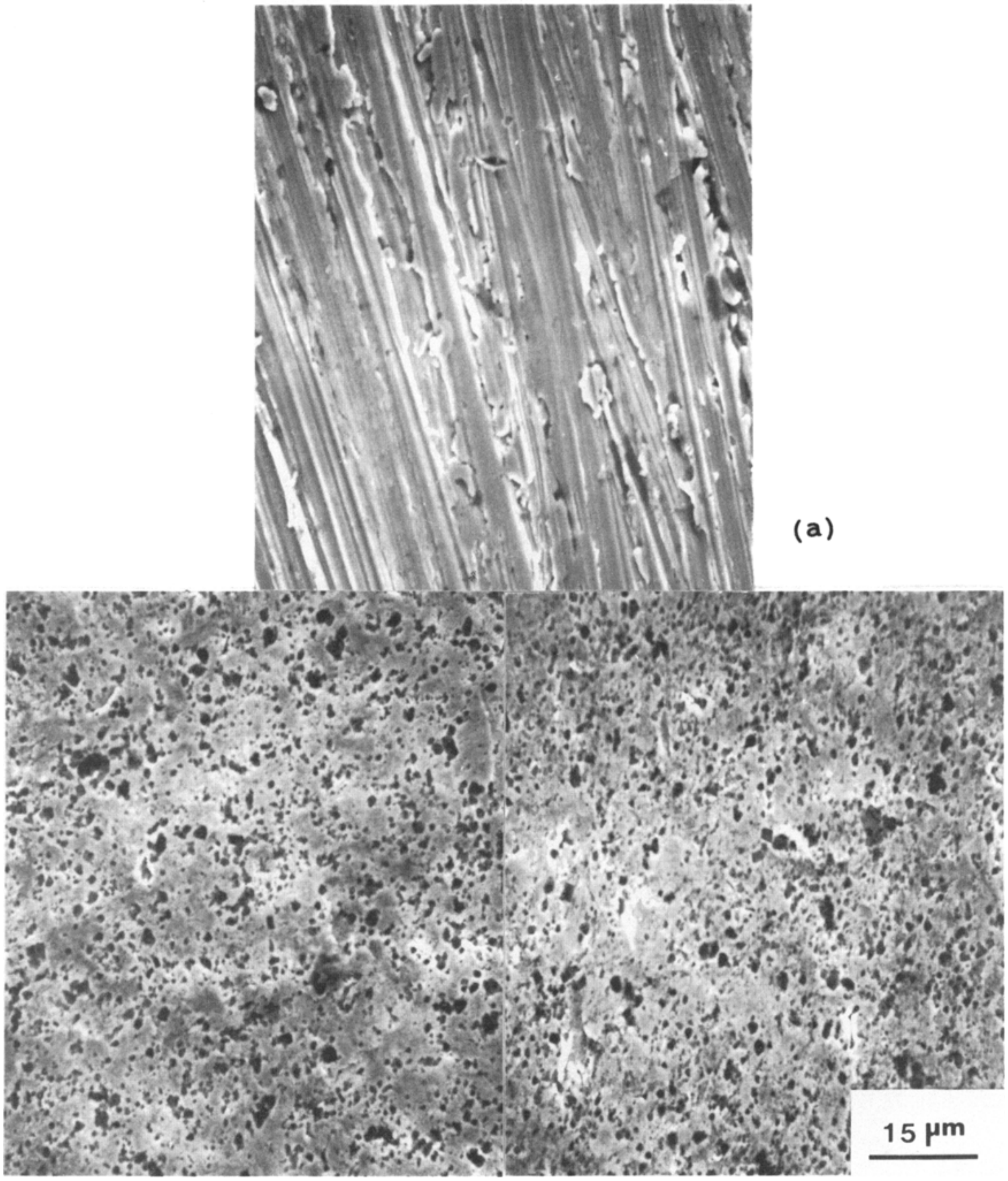

Fig. 10 Surface appearance of silicon bronze tested under different conditions. (a) Before test. (b) After testing in seawater-sand slurry. (c) After testing in seawater-sand slurry with cathodic protection.

Ferritic steels like C4340 are susceptible to embrittlement by H_2 under some exposure conditions. More specifically, cathodic protection of steels must be carried out under carefully controlled conditions or electrochemical charging of the steel with H_2 can reduce its ductility. Therefore, separate experiments were carried out to determine if the conditions used in the erosion-corrosion experiments degraded the mechanical properties of the steel. These experiments consisted of an evaluation of the tensile properties of specimens under three conditions: (a) starting material, (b) material after an erosion-corrosion test with cathodic protection, and (c) material after an erosion-corrosion experiment with a cell voltage approximately twice that in (b). In both (b) and (c), electroless plating of copper was used to minimize the loss of H_2 by outward diffusion during the tensile tests.

The ductilities of the specimens, expressed as percent reduction in area (RA), are listed in Table 3. For the starting material and the material after erosion-corrosion tests, RA values

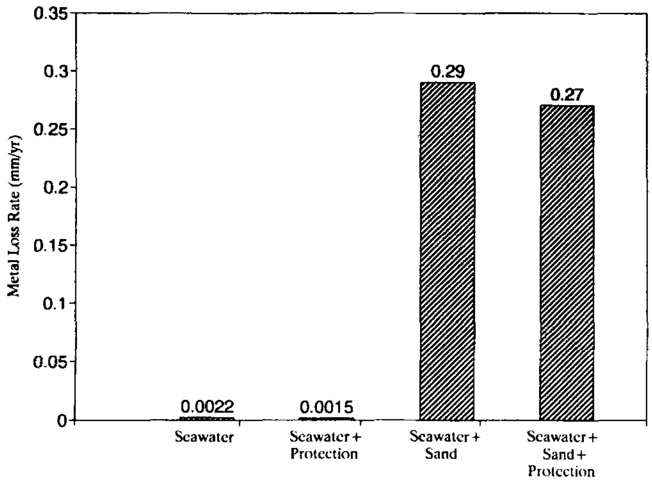

Fig. 11 Metal loss rates of Ti-6Al-4V specimens tested under different conditions.

ranged from 34 to 37%. Severe cathodic charging reduced RA to 2.5%.

Examination of the fracture surfaces after tensile testing was also used to evaluate ductility loss. The mating surfaces of fractured specimens are shown in Fig. 7 and 8. The specimen in Fig. 7 was subjected to an erosion-corrosion test with cathodic protection, then tensile tested to failure. The fracture was of the so-called cup-and-cone type, and at higher magnification, ductile dimples were clearly visible. These characteristics are consistent with an RA of approximately 35%. The specimen in Fig. 8 was subjected to the higher voltage during cathodic protection to deliberately cause hydrogen embrittlement. The fracture was of the quasicleavage type, which is consistent with the RA obtained of 2.5%. Thus, the erosion-corrosion experiments on the C4340 steel were carried out under conditions that reduced the erosion-corrosion rate drastically, without causing a measurable ductility loss due to hydrogen charging.

The results of the erosion-corrosion tests on silicon bronze are plotted in Fig. 9. The test time was 3 days, and the cell voltage was 2.0 V in the seawater test and 1.7 V in the seawater-sand test. With no sand present, the corrosion rate was reduced from a moderate to a very low value with cathodic protection. When sand was added to the seawater, the metal loss rate was quite high, and cathodic protection did not provide a dramatic improvement. The material was not hard enough to withstand the abrasive action of the sand particles. It is likely that an improvement would occur had the material been cold worked prior to testing.

A set of scanning electron micrographs of silicon bronze specimens before and after testing is shown in Fig. 10. In Fig. 10(a), the surface features are characteristic of the use of No. 600 emery paper in specimen preparation. In Fig. 10(b), pitting of the surface can be seen after the seawater-sand test without cathodic protection. The size of the pits was approximately one half of the grain size. In Fig. 10(c), the appearance was the same as in (b), which is consistent with the small change in metal loss rates for the two tests.

The results of the erosion-corrosion tests on Ti-6Al-4V are shown in Fig. 11. Because of the low corrosion rate, the test time was 7 days, rather than the 3-day test time used for the other alloys. The cell voltage was 1.8 V. It can be seen that Ti-6Al-4V, like unalloyed titanium, corrodes very slowly in seawater. With no sand present, cathodic protection reduced the metal loss rate only slightly. When sand was added to the seawater, the metal loss rate increased by more than a factor of 100. Again, cathodic protection did not result in a large improvement. These metal loss rates of approximately 0.3 mm/year are higher than one would like for a high-cost alloy. As was true for the silicon bronze alloy, the abrasive action of sand dominated the rate of degradation.

Neither X-ray diffraction measurements nor scanning electron microscopy was helpful in characterizing or distinguishing between dark films that formed on the specimen surfaces. The formation of either hydride or oxide films was possible. In related research on stress corrosion cracking, Zhang and Vereecken[12] reported that, when protective oxide films on Ti-6Al-4V specimens were damaged, healing of the defects and repassivation of the surface occurred within 10^{-4} s.

Thus, it can be stated that, although the corrosion resistance of Ti-6Al-4V was good and degradation in a seawater-sand slurry was moderate, cathodic protection did not offer benefits that would justify its cost. Perhaps cathodic protection would make the alloy more resistant to stress-corrosion cracking in seawater, which is known to be a problem in stressed Ti-6Al-4V parts.

4. Summary

The objective of showing that hard alloys can be cathodically protected to provide low degradation rates in seawater-sand slurries was demonstrated for C4340 steel. Under the electrochemical conditions used for cathodic protection, no measurable ductility loss due to hydrogen embrittlement was found. Silicon bronze and Ti-6Al-4V alloys were not as hard, and their degradation rates were dominated by sand erosion. Cathodic protection did not offer dramatic benefits for these alloys. Work hardening of the silicon bronze may have improved its performance.

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