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The mechanism of sulfide-induced accelerated corrosion of 90-10 copper-nickel (iron) alloy is investigated. Samples of the alloy are exposed to flowing (2.4 meters per second) seawater, with and without 0.01 milligrams per liter sulfide, for various periods of time. The resulting surfaces are examined by means of Auger electron spectroscopy coupled with inert-ion-bombardment. A detailed depth profile is thereby obtained of concentrations

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in the surface region of a total of nine elements. The results are consistent with the hypothesis that iron hydroxide segregates at the surface to form a protective gelatinous layer against the normal chloride-induced corrosion process. Trace sulfide interferes with formation of a good protective layer and leaves the iron hydroxide vulnerable to ultimate partial or complete debonding. When the alloy is first exposed to "pure" seawater for a prolonged period of time, however, subsequent exposure to sulfide is no longer deleterious. This is apparently due to a layer of copper-nickel salt that slowly forms over the iron hydroxide.

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ABSTRACT

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ADMINISTRATIVE INFORMATION

This investigation is part of an in-house research program of the David W. Taylor Naval Ship Research and Development Center. It was conducted under Program Element 61152N, Task Area ZR0220801, and Work Unit 2823-507.

INTRODUCTION

Corrosion of copper-nickel (iron) (Cu-Ni(Fe)) alloy used in piping on naval craft usually occurs at a rate sufficiently low so that a vessel can remain at sea for years without developing corrosion associated problems. During ship construction, however, the material at times has exhibited accelerated corrosion on internal surfaces which is specifically associated with water found in and around the harbor. The problem appears to result from the presence of sulfide pollutants near the shore line. Conventional analytical methods have thus far failed to detect the presence of sulfur (S) in corrosion films formed in the presence of sulfide. In this investigation an attempt is made to obtain information bearing on the mechanism of sulfide-accelerated corrosion by using Auger electron spectroscopy (AES) combined with ion-bombardment profiling in the analysis of corrosion films.

It is reasonable to assume that an understanding of the problem of sulfide-accelerated corrosion depends on an understanding of the normal corrosion mechanism of Cu-Ni(Fe) alloy. This, in turn, is based on the corrosion mechanism of copper, the major component of the alloy. Morr and Beccaria[1*] have found the minerals malachite, $Cu(OH)_2 \cdot CuCO_3$, and atacamite, $Cu(OH)_2 \cdot Cu(OH)Cl$, in the corrosion products of copper in seawater. Bacarella and Griess[2] found the primary reaction product of the anodic dissolution of Cu in seawater to be $CuCl_2^-$. The anodic process was under diffusion control and its rate was proportional to the square of the chloride ion (Cl^-) concentration. The rate determining diffusion step consisted of diffusion of the $CuCl_2^-$ complex ion corrosion product away from the surface. Efird,[3] using electrochemical hysteresis methods, studied CuNi(Fe) alloy in aerated natural seawater. He proposes the following mechanism for the anode process: In the passivation region, copper is first oxidized to cuprous, $2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e$. In the general corrosion region, the primary corrosion reaction is oxidation of copper to cuprous, with formation of the chloride complex, $Cu + 2Cl^- \rightarrow CuCl_2^- + e$, followed by the hydrolysis $2CuCl_2^- + H_2O \rightarrow Cu_2O + 2H^+ + 4Cl^-$. Ijsseling and Krougman,[4] investigating 90-10 Cu-Ni(Fe) and using scanning electron microscopy with X-ray microanalysis, found a layered structure in the corrosion products, with intermingling between the layers. They describe the top layer as grayish-green, varying strongly in thickness, and consisting "mainly of biological material plus some atacamite." The "dark brown layer under the top layer is enriched in iron and manganese and depleted in copper and nickel." Beneath that is a green layer of atacamite, and under that a layer of cuprous oxide, interchanged with atacamite. All this was obtained in very slowly moving seawater. In general, the authors find that "well-protecting films, resulting in low corrosion currents, are amorphous, rich in iron and nickel, and depleted in copper." Faster flow velocities of seawater tend to favor formation of thinner, more protective films.

There have been a number of studies of Cu-Ni(Fe) corrosion in seawater which have been reported after the present work was underway. MacDonald, Syrett, ard Wing[5] studied the corrosion of 90-10 and 70-30 Cu-Ni(Fe) alloy exposed for

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*A complete listing of references is given on page 21.

approximately ten days to seawater flowing at 5.3 ft/sec (1.62 m/s), by using a.c. impedance, linear polarization, and potential step measurements to determine the polarization resistance (a measure of corrosion resistance). They reported the effect of oxygen concentration and of the presence of sulfide in seawater, as well as differences between the 90-10 and 70-30 alloys. They found that at low oxygen concentration the corrosion process was cathodically controlled, while at high oxygen concentration it was anodically controlled. At low oxygen concentration the 70-30 alloy is more corrosion resistant, while at high oxygen concentration the resistance of 70-30 alloy decreases suddenly to that of the 90-10 alloy. For each alloy, the corrosion resistance generally increases with increasing oxygen concentration. They found two relaxation processes, one of which was consistent with a mechanism of ion or electron transport through a surface film of uneven thickness. Their AES studies showed cupric and nickel oxide, with possibly cupric hydroxy chloride, as the components of the corrosion layer.

Upon introducing sulfide, the authors found a breakdown in passivity. This effect persisted with changing concentration of sulfide, down to 0.85 mg/l, the lowest concentration used. The corrosion film consisted of cuprous sulfide, mainly in the orthorhombic form. Cubic cuprous sulfide, and copper-rich cuprous sulfide, were present in minor amounts. The authors interpret their results as indicating that there is a substantial change in the mechanism of corrosion when sulfide is present in the seawater. They suggest that whereas the reduction of oxygen is normally the only viable cathodic process, in the presence of sulfide the evolution of hydrogen becomes possible. In their view this then becomes the new cathodic process and is responsible for the accelerated corrosion. It should be noted at this point that the sulfide concentration used in the present study, 0.01 mg/l, is nearly two orders of magnitude less than the lowest used by MacDonald, Syrett, and Wing.

Wilson[6] used AES to study the corrosion films which had been formed on 90-10 Cu-Ni(Fe) alloy while it was immersed in slowly flowing heated fresh seawater. The purpose of his investigation was "to determine whether the seawater corrosion product composition was related to the iron distribution." Iron distribution refers to the amount of "precipitated," or "second phase" iron, as compared to iron in solid solution, at constant iron composition. It had already been found by Ross[7] that the corrosion rate was not affected by the iron distribution at ambient temperature. With heated seawater, however, the corrosion rate was directly proportional to the amount of precipitated iron. Wilson found that nickel enrichment in the corrosion layer was inversely proportional to the amount of precipitated iron. The corrosion rate is, therefore, inversely proportional to the amount of iron in solid solution. It was inferred that iron in solid solution (but not precipitated iron) promotes the enrichment of nickel in the corrosion layer, which in turn reduces the corrosion rate. H. P. Hack and J. P. Gudas have exposed 90-10 and 70-30 Cu-Ni(Fe) alloy to natural seawater for the purpose of determining "the ability of a normal corrosion product film to prevent sulfide-induced corrosion." After "preexposure to natural seawater for 0, 30, or 120 days," they found that the "120-day preexposures were sufficient to form a protective corrosion product film that prevented sulfide-induced attack," while the "30-day preexposures were inadequate."

METHOD

The Cu-Ni(Fe) alloy consisted essentially of 88 percent Cu, 9.5 percent Ni, and 1.5 percent Fe. Less than 0.5 percent of each of manganese, zinc, lead, phosphorus, and sulfur were also present. Samples of the alloy, measuring 1/2 in. x 3/4 in. x 1/16 in. (1.27 cm x 1.91 cm x 0.159 cm), were clamped in a jig and immersed in seawater flowing parallel to the 1/2 x 3/4 faces at a velocity of 8 ft/sec (2.4 m/s). All immersions were carried out at the LaQue Center for Corrosion Technology, Wrightsville Beach, North Carolina. Samples were exposed to natural seawater without additions, designated as "fresh seawater" (FSW), and to seawater containing added sulfide (SSW) in concentrations of 0.01 mg/l. Some samples also were exposed to seawater containing added Fe^{++} ion. During all experiments, samples were removed after 30, 60, and 90 days. Samples for each set of conditions were exposed in quadruplicate. Following removal they were wrapped in lint-free tissue, packaged in plastic petri dishes, and mailed to DTNSRDC. Samples representing each seawater exposure condition were then placed, as received, in the ultrahigh vacuum carousel multiple sample holder for AES analysis. The AES was performed in an ultrahigh vacuum system containing a cylindrical mirror analyzer with a 3 kV integral electron gun and an ion-bombardment gun for depth profiling.

RESULTS

The samples which were removed from FSW after 30 days possessed a corrosion layer with a dark color superimposed on the original copper color of the alloy. Those exposed to FSW for 60 days had both dark and gray-blue patches. Those exposed to FSW for 90 days were covered almost completely with a gray-blue layer, which seemed to cover the dark layer. The corrosion film on all these three sets was intact and appeared to adhere well. The samples exposed to SSW for 30 days appeared somewhat lighter in color than the 30-day FSW set. On those exposed to SSW for 60 days the corrosion layer was starting to peel off in isolated spots, exposing a bright surface with the appearance of the original alloy. On the 90-day SSW exposed surface there was considerable peeling of the corrosion layer to expose the copper colored surface underneath.

Auger electron spectroscopy with ion-bombardment profiling (Figure 1) of the 30-day exposed FSW surface yielded a number of noteworthy features. The outer layer, after 3 min ion bombardment, contained carbon, oxygen, chlorine, sulfur, copper, nickel, iron, calcium, and potassium. Additional carbon, from the overlayer of organic molecules deposited on air-exposed surfaces, was probably removed during the first 3 min. Potassium, sulfur, and the remaining carbon decreased steadily from their initial values during the course of ion bombardment. Calcium and chlorine, with minor fluctuations, also followed this behavior. Copper remained reasonably steady during the first 45 min then started to increase rapidly. Nickel increased slowly at first then started to increase rapidly at about 40 min. Iron increased rapidly for 45 min, then decreased fairly rapidly. Oxygen decreased slowly for 45 min, then decreased fairly rapidly, at the same rate as iron. The behavior of iron was striking, in two respects. First, as mentioned, it was the only constituent (of the corrosion film) to go through a substantial maximum well into the corrosion film. Second, and even more striking, is the fact that although iron is only 1 1/2 percent of the bulk alloy composition, it is present in larger amounts than either copper or nickel in the corrosion film.

The AES analysis (Figure 2) of the 30-day exposed sulfide-containing seawater (SSW) yielded many similarities, but also some interesting differences, to the FSW surface. The entire curve was expanded along the time axis as compared to the FSW sample. This may be due either to a change in the physical nature of the film, or merely to a variation in the ion-bombardment conditions. For example, if the

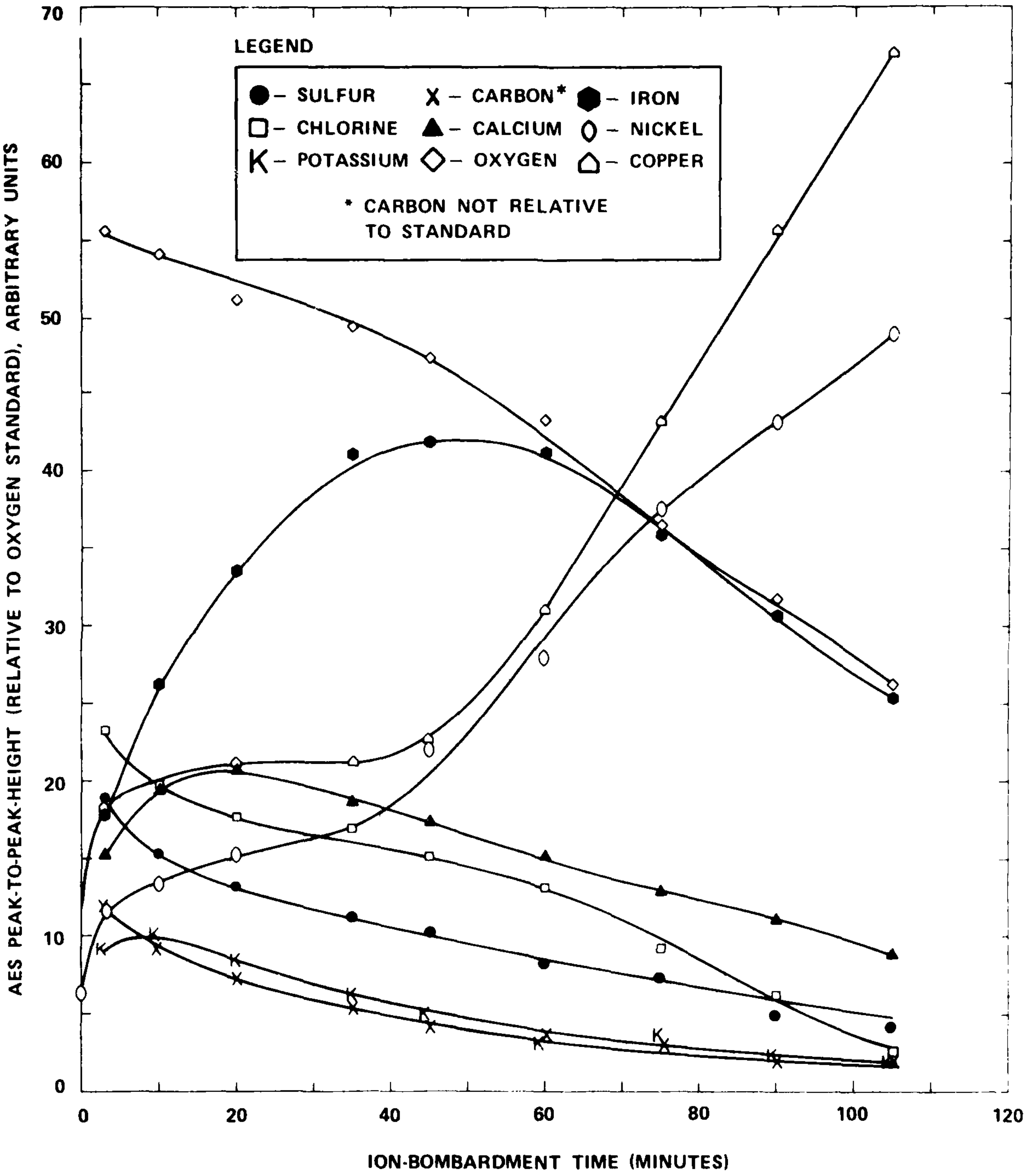

Figure 1 - Depth Profile of Elements in Surface Region as Determined by Auger Electron Spectroscopic Analysis During Ion-Bombardment: Copper-Nickel (Iron) Alloy Exposed to Fresh Seawater for 30 Days

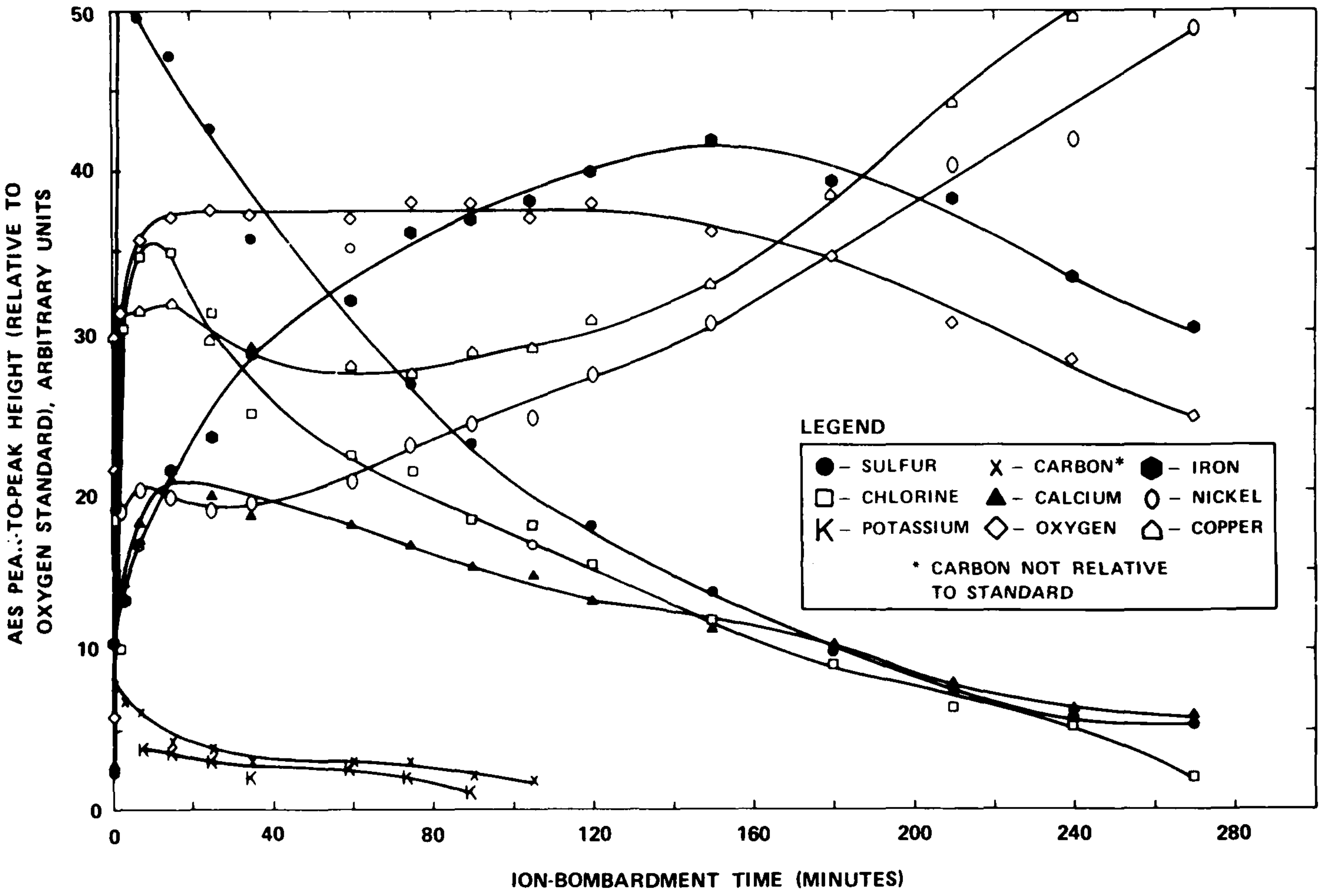

Figure 2 - Depth Profile of Elements in Surface Region as Determined by Auger Electron Spectroscopic Analysis During Ion-Bombardment: Copper-Nickel (Iron) Alloy Exposed to Sulfide-Containing Seawater for 30 Days

incident electron beam for Auger analysis is focused near the top, rather than the bottom, of the ion-bombardment crater, the entire profiling procedure would appear to have slowed down. Except for the time factor, the iron curve is very similar to the previous one. The oxygen curve is also similar, especially on the right side of the iron maximum. Potassium, calcium, and carbon are roughly similar. Sulfur and chlorine, however, show interesting differences. In FSW, sulfur is present in moderate amounts at the start of profiling, and decreases routinely thereafter. In the SSW, sulfur goes through a very large and sharp maximum during the first few minutes of ion-bombardment, thereafter decreasing routinely from that value. Chlorine behaves similarly to sulfur during the first few minutes of profiling, except that the maximum is not as high or as sharp.

The AES analysis of the 60-day FSW sample was rather difficult to perform. The grayish-blue patches were insulating films and yielded only charging and discharging signals. The dark patches were also somewhat insulating, but yielded Auger spectra during the course of ion-bombardment. On these dark patches (Figure 3) iron was present in an amount roughly equal to copper or nickel at the beginning, gradually decreasing as Cu and Ni increased and as the ion-bombardment exposed the substrate. There was very little sulfur in the film. Chlorine, however, was present in significant amounts and went through a maximum during the profiling.

The AES on the 60-day SSW samples was performed both on areas covered with corrosion film (Figure 4) and on bare areas (Figure 5). On the corrosion film, potassium and carbon were present in small amounts, while copper and nickel increased routinely with ion-bombardment. Iron increased with ion-bombardment and appeared to be going through a broad maximum. Sulfur went through a broad maximum, qualitatively paralleling that of iron. Chlorine increased rather sharply then levelled off and declined slowly, while calcium went through a maximum. The maxima or levelling off points of iron, sulfur, chlorine, and sometimes calcium, all occurred in approximately the same region of the time axis. Oxygen went through a relatively early maximum. Chlorine went through a sharper and higher maximum than sulfur and peaked somewhat later.

The AES analysis on the bare spots of a 60-day SSW sample yielded some features strikingly different than on corrosion films of the same sample. Iron peaked rapidly after commencement of ion-bombardment and was present in very large

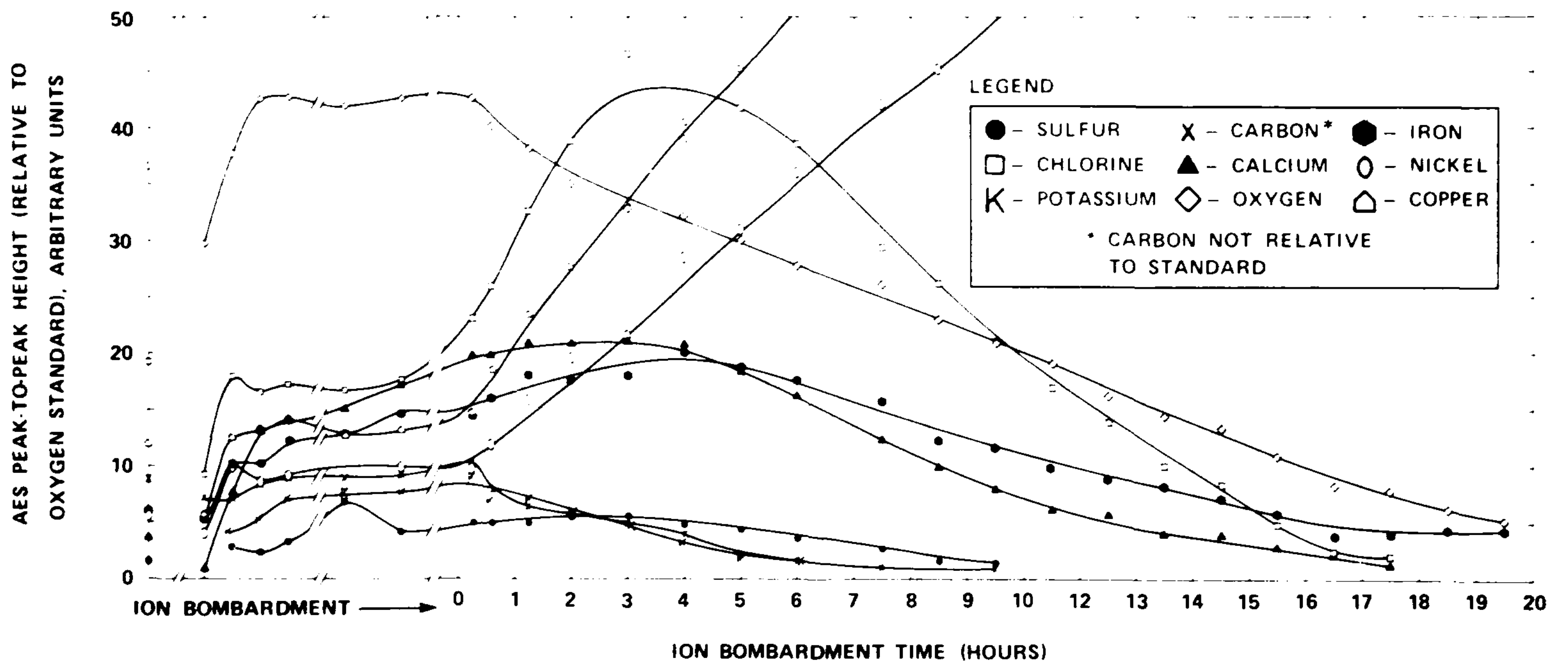

Figure 3 - Depth Profile of Elements in Surface Region as Determined by Auger Electron Spectroscopic Analysis During Ion-Bombardment: Copper-Nickel (Iron) Alloy Exposed to Fresh Seawater for 60 Days

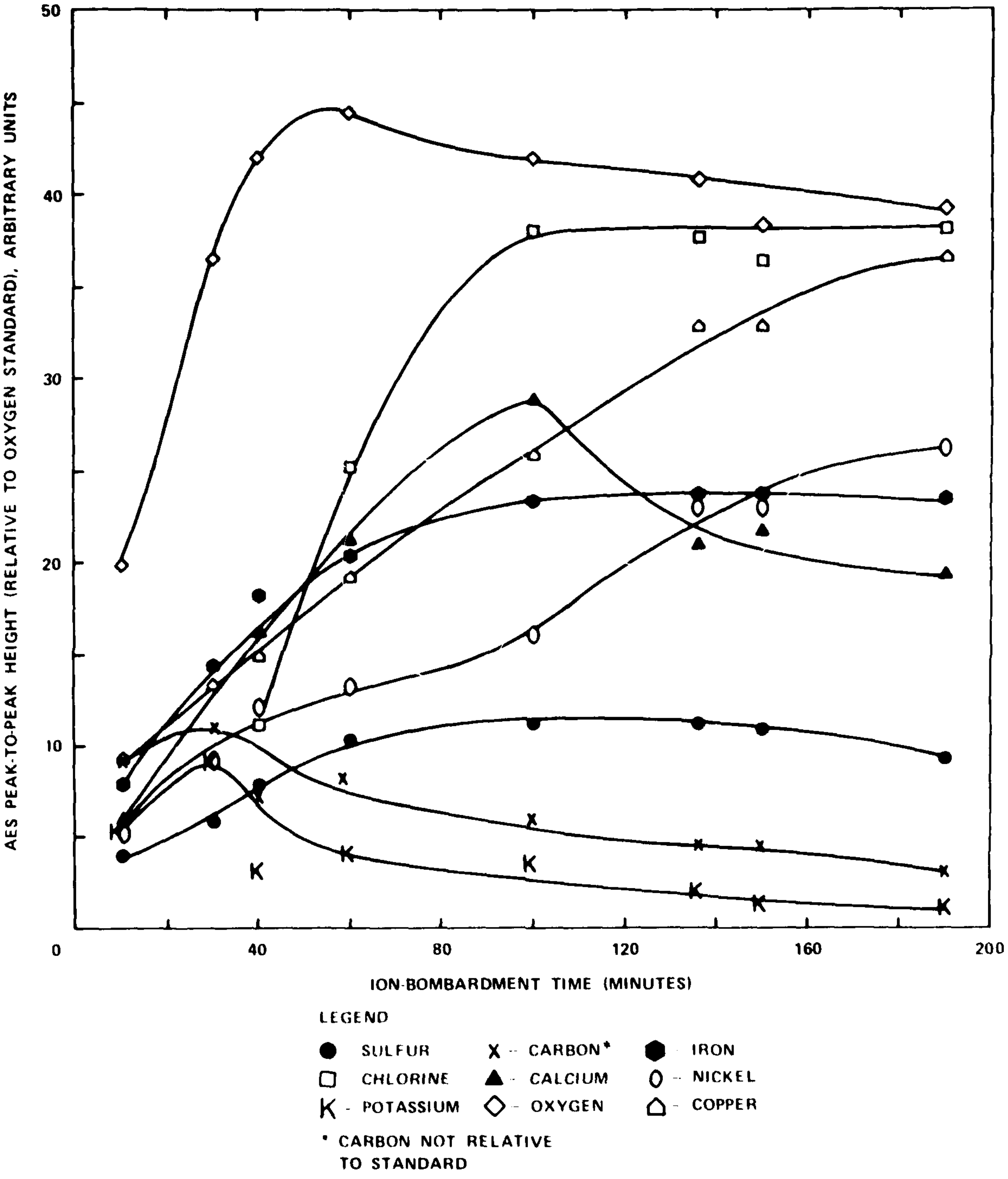

Figure 4 - Depth Profile of Elements in Corrosion-Film on Surface as Determined by Auger Electron Spectroscopic Analysis During Ion Bombardment: Copper-Nickel (Iron) Alloy Exposed to Sulfide-Containing Seawater for 60 Days

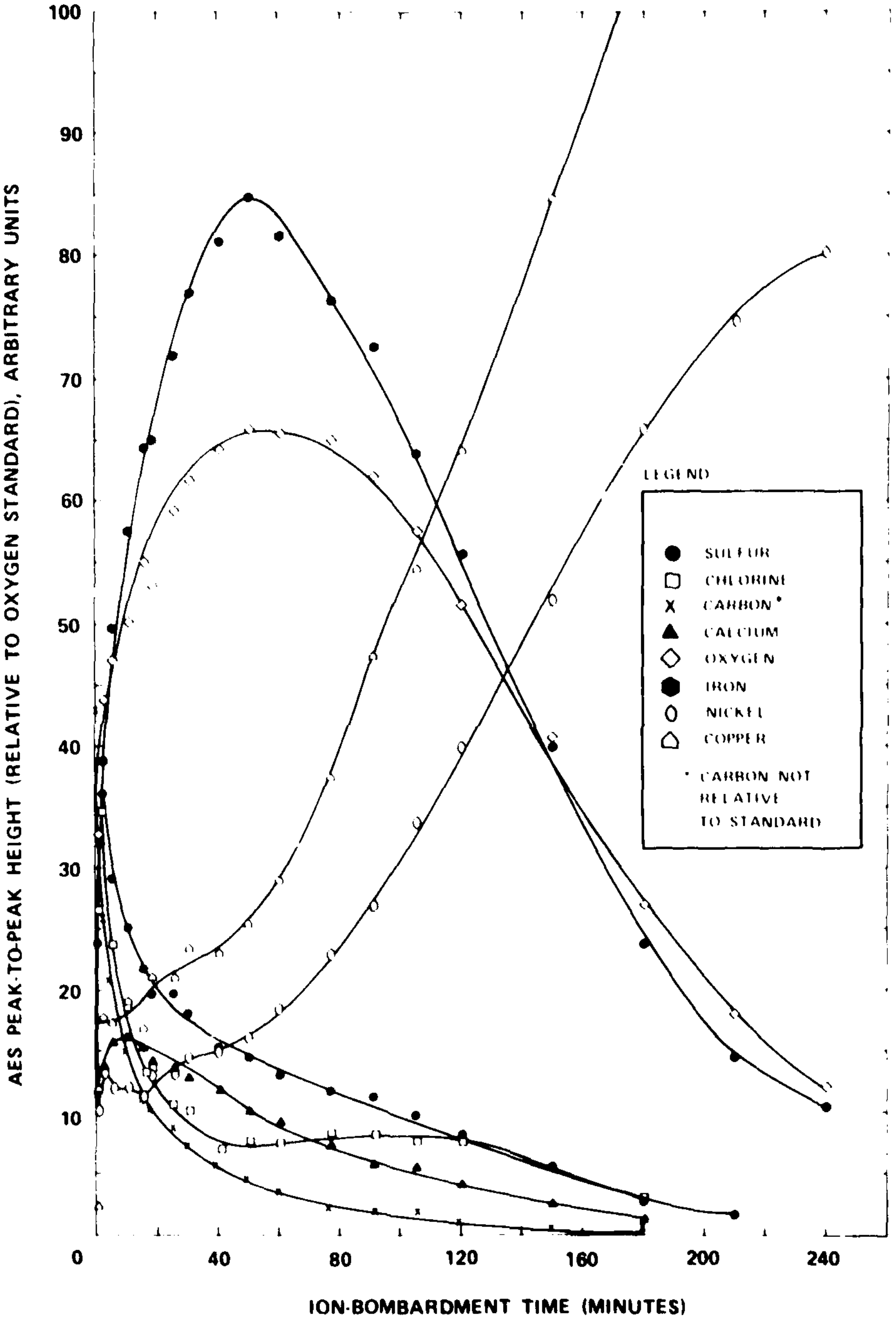

Figure 5 - Depth Profile of Elements in Bare Area of Surface as Determined by Auger Electron Spectroscopic Analysis During Ion-Bombardment: Copper-Nickel (Iron) Alloy Exposed to Sulfide-Containing Seawater for 60 Days

amounts (up to three times as great as copper) for prolonged periods during ion-bombardment. From the beginning sulfur was present in large amounts and went through a high and relatively broad (compared to 30-day SSW) maximum. Chlorine was present in substantially smaller amounts than sulfur. Oxygen concentration was high along with the iron.

The AES analysis on 90-day exposed FSW samples at first yielded spectra with most peaks either undetectable or too small for useful measurement, due to the insulating characteristics of the thick corrosion film. Increase of the incident beam current from 10 μA to 55 μA, however, resulted in useful spectra with measurable peaks. The copper and nickel content (Figure 6) of these curves was greater than the iron content. The nickel curve was sometimes greater than copper, and in general, was higher relative to copper than to bulk composition. There was also evidence of silicon and magnesium, possibly in substantial amounts. AES analysis on 90-day exposed SSW samples once again yielded sharp differences between corrosion film (Figure 7) and bare spots (Figure 8). Now, however, the bare spot composition was low in iron and sulfur, high in copper and nickel, and enormously high in chlorine. The chlorine peaks were many fold greater than any others, and had to be measured at reduced sensitivity. The corrosion film, on the other hand, was relatively high in iron, oxygen, and sulfur, and greatly reduced in chlorine.

Samples which were exposed for 30, 60, or 90 days to seawater containing added Fe^{++} ions (0.2 mg/ml), contained a loosely adhering rust-colored powdery layer. AES analysis confirmed that the rust-colored layer was iron oxide.

DISCUSSION

Exposure of Cu-Ni(Fe) specimens to the flowing FSW yielded specimens with dark coatings after 30 days, dark and blue-gray patches after 60 days, and a nearly complete blue-gray coating after 90 days. The blue-gray coating was apparently growing over the dark coating. The AES analysis indicates that the dark coating was a conducting layer, highly enriched in iron oxide. The blue-gray coating is an insulator which is richer in copper and nickel than in iron, and is especially rich in nickel. It may also contain siliceous minerals deposited by the seawater. A previous investigation[4] has described corrosion layers on Cu-Ni(Fe) in which the upper layer consisted of atacamite (a copper-hydroxy chloride), the next layer was

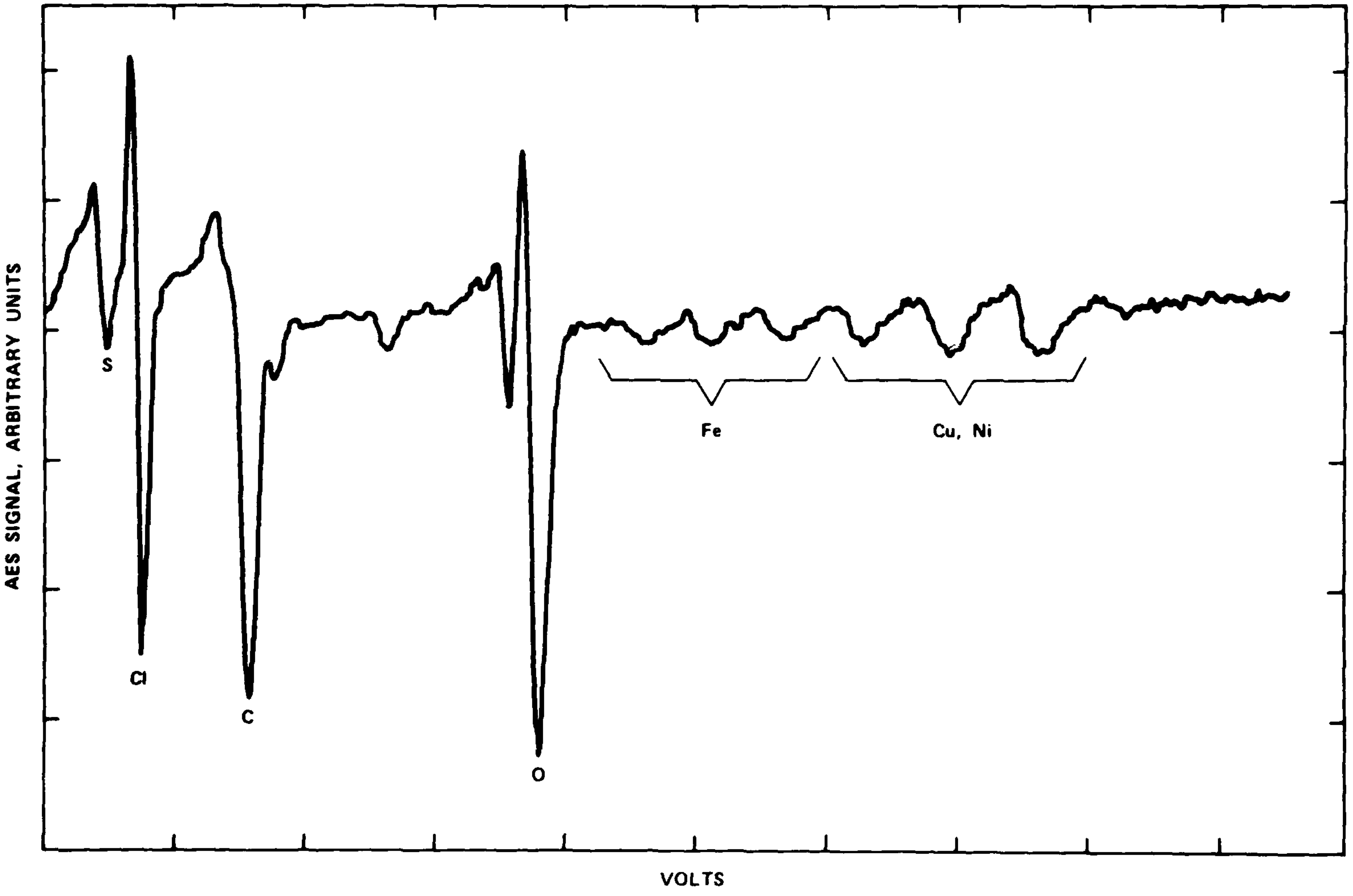

Figure 6 - Auger Electron Spectroscopic Analysis of Surface: Copper-Nickel (Iron) Alloy Exposed to Fresh Seawater for 90 Days

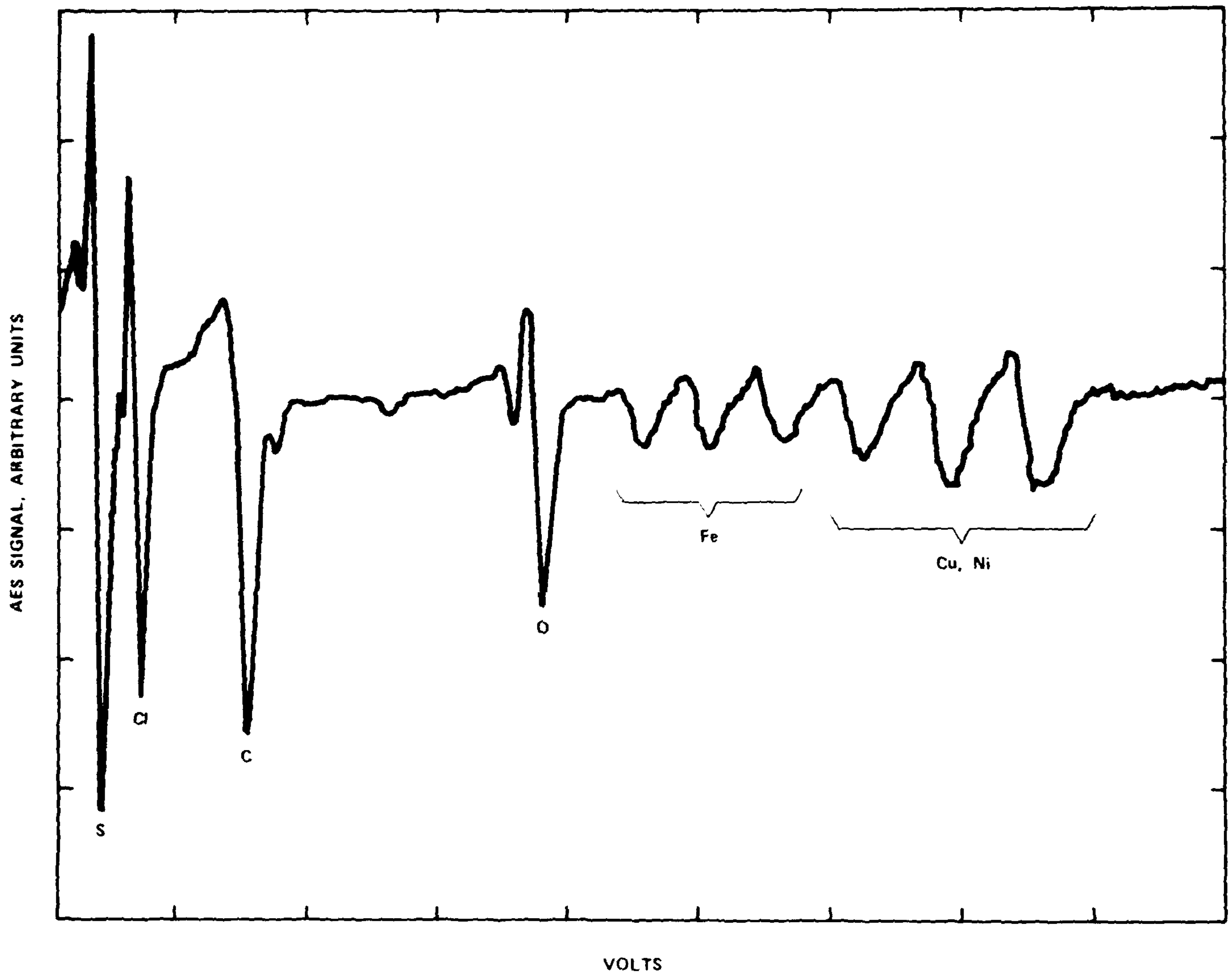

Figure 7 - Auger Electron Spectroscopic Analysis of Corrosion Film on Surface: Copper-Nickel (Iron) Alloy Exposed to Sulfide-Containing Seawater for 90 Days

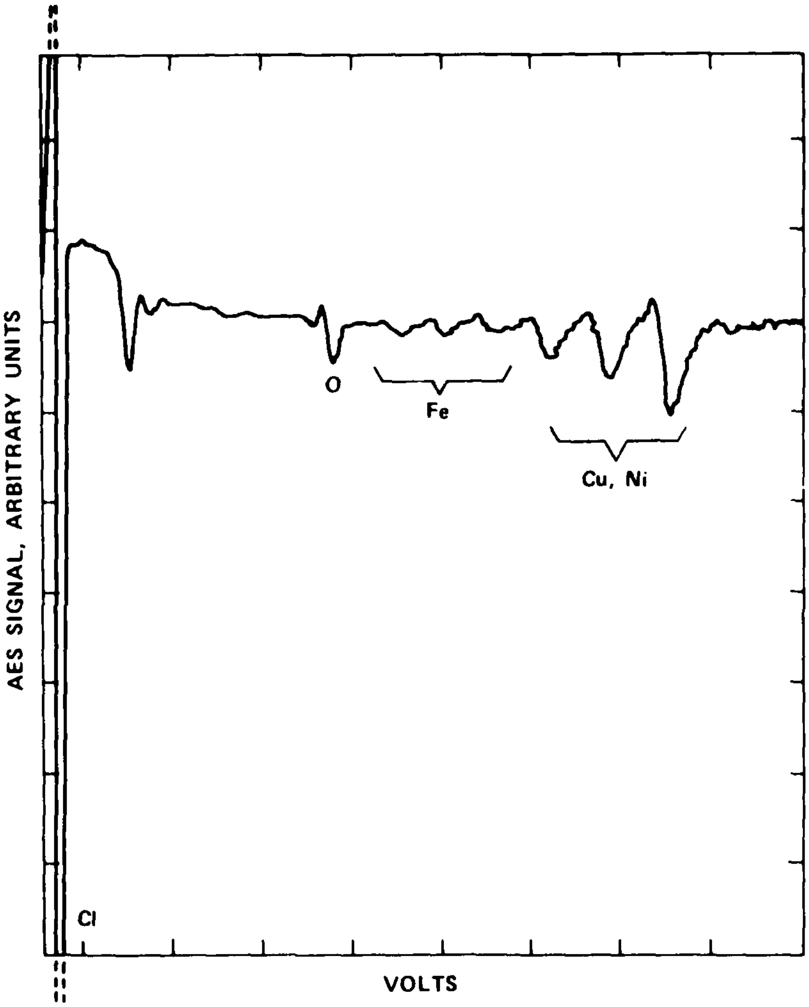

Figure 8 - Auger Electron Spectroscopic Analysis of Bare Area on Surface: Copper-Nickel (Iron) Alloy Exposed to Sulfide-Containing Seawater for 90 Days

enriched in iron, and below that was more atacamite. The detailed nature of the corrosion layer varied with the velocity of flow of the seawater. Our observation in this work confirms the existence of an iron-rich layer, and indicates that it forms rather rapidly, i.e., within the first few weeks, on the alloy surface. The almost perfect parallel decrease of oxygen and iron during ion-bombardment profiling indicates that this iron is present in the form of an oxide. Our results also indicate that copper and nickel slowly grow over this iron layer, probably forming a salt, which is nonconducting when dry. The bluer portions may be atacamite, while the grayer part of this outer layer is apparently a nickel-rich salt. The presence of iron in the alloy is known to provide corrosion protection. We consequently propose the following mechanism for formation of the corrosion layer.

$$Cu \rightarrow Cu^+ + e \tag{1}$$

$$Cu^+ + 2Cl^- \rightarrow CuCl_2^- \tag{2}$$

Summing (1) and (2) gives the anode reaction for copper

$$Cu + 2Cl^- \rightarrow CuCl_2^- + e \tag{3}$$

If the cathodic reaction is due to dissolved molecular oxygen, then

$$1/2O_2 + H_2O + 2e \rightarrow 2OH^- \tag{4a}$$

If, on the other hand, the cathodic reaction involves reduction of the hydrogen ion, then

$$H^+ + e \rightarrow 1/2H_2 \qquad (4b)$$

instead of (4a).

$$Fe \rightarrow Fe^{++} + 2e \qquad (5)$$

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2 \qquad (6)$$

Summing (5) and (6) gives the anode reaction for iron,

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e$$

Once again, the proposed cathodic reaction is (4a) or possibly (4b).

The basic corrosion process of the alloy consists of equation (3), wherein copper is oxidized to the cuprous state, which, in the absence of Cl^-, would form an insoluble hydroxide on the surface, impeding propagation of the reaction. In the presence of Cl^-, however, the Cu^+ forms the soluble complex $CuCl_2^-$, which is then rapidly carried away allowing the corrosion reaction (removal of copper) to propagate. Iron in the alloy competes with the copper for the oxidizing agent in the cathodic reaction (i.e., O_2 or possibly H^+), thereby acting as a sacrificial anode. Because the reduction potential of iron is considerably lower (oxidation potential considerably higher) than copper, it will oxidize more rapidly and segregate at the surface. Alternatively, the O_2 (or H^+) may oxidize Cu to form Cu^+, equations (1) and (4), to be followed immediately by reduction of Cu^+ back to Cu by the iron, equation (5) and equation (1) reversed. The Fe^{++} then combines with OH^- to form the $Fe(OH)_2$, equation (6). In either case the result is the same, with the iron acting as a sacrificial anode to form iron hydroxide, or some other hydroxide. The iron hydroxides constitute a gelatinous precipitate which acts as a barrier to ready access of solutes in the seawater, such as O_2 or Cl^-, to the alloy surface, and also to diffusion of reaction products away from the surface. It is then necessary for the reaction to propagate by means of diffusion across the relatively impermeable iron hydroxide layer, a much slower process. Formation of the $Fe(OH)_2$ layer should, in principle, take place at a maximum rate at the very beginning, then slowing down, perhaps logarithmically, or even slower, with respect to time. The slowing down should take place both because of the depletion of iron in the region of the substrate alloy near the interface, and because of the increased time necessary for the iron to diffuse across the $Fe(OH)_2$ layer as that layer thickens. As the $Fe(OH)_2$ layer builds up rapidly during the first few weeks of exposure, nickel and copper, with oxidation potentials lower than iron, will oxidize slowly to the ionic form, and start diffusing through the iron hydroxide layer. The nickel presumably leaves the surface as a simple ion and the copper as the complex $CuCl_2^-$. As they approach the outer surface of the iron hydroxide some of these ions oxidize further and hydrolyze to form the insoluble coating over the iron hydroxide layer. For example,

$$2CuCl_2^- + 1/2O_2 + OH^- + H_2O \rightarrow Cu_2(OH)_3Cl + 3Cl^- \qquad (7)$$

yields atacamite. This coating is the blue-gray layer which forms within a period of two to four months.

For the case of exposure of the Cu-Ni(Fe) alloy to seawater containing sulfide at 0.01 mg/l concentration, the basic change seems to involve interference with adhesion to the surface of the protective iron hydroxide layer. Sulfide ions will convert $Fe(OH)_2$ to FeS, thereby changing a tight protective amorphous coating to a porous partially crystalline one. This porosity allows the seawater access to the alloy substrate, where the main corrosion reaction, $Cu + 2Cl^- \rightarrow CuCl_2^- + e$, will gradually debond the corrosion layer from the surface. Also, the corrosion layer itself may tend to disintegrate, possibly aided by oxidation of FeS to $FeSO_4$. Under these conditions the layers of nickel and copper hydroxide, or hydroxychloride, do not form over the iron-rich layer. The AES curves for each surface show far greater quantities of $S^=$ in corrosion layers formed in sulfide-containing seawater than in samples exposed an equal amount of time to fresh seawater. The AES curve for 30-day SSW picks up a high $S^{=}$ maximum at the outer surface of the iron-rich corrosion layer, followed by a consistent decrease with distance towards the substrate. Apparently the buildup of iron hydroxide is countered by a removal mechanism, which involves first the adsorption or incorporation of $S^{=}$, followed by its removal along with the removal of iron. When bare surfaces are exposed by debonding of the corrosion layer after formation of the iron hydroxide layer is substantially complete, and the substrate depleted of iron near the interface, they show $CuCl_2^-$, with Cl facing outward. If the formation of iron hydroxide is not complete, the bare substrate may be iron rich. When a nickel- or copper-hydroxide insoluble salt forms over the iron-rich layer, it apparently prevents subsequent attack by sulfide.

CONCLUSIONS

1. Corrosion of Cu-Ni(Fe) alloy in fresh open seawater (presumably caused by oxidation of copper followed by formation of the soluble $CuCl_2^-$ complex ion), is very strongly inhibited by formation of a protective layer of amorphous iron hydroxide at the surface. The formation of the iron hydroxide layer is caused by the favorable free-energy decrease which occurs upon oxidation of iron at the surface.

2. The presence of trace quantities of sulfide ions in seawater interferes with formation of the protective amorphous iron-hydroxide layer, leaving the surface partially exposed to Cl^- induced corrosion.

3. Three months or more exposure of the alloy to fresh (sulfide-free) seawater allows time for formation of a layer of insoluble, strongly-adhering, nickel-copper salt over the iron hydroxide layer. This layer may be responsible for preventing subsequent attack on the iron hydroxide by sulfide ions.

RECOMMENDATIONS

1. The use of a stimulated iron anode in seawater near Cu-Ni(Fe) piping has been proposed by DTNSRDC and found to be effective for protection against sulfide-induced accelerated corrosion in laboratory tests. The method has been successful in some field trials, unsuccessful in others. Evaluation of this method should be continued until a firm conclusion is reached as to its reliability.

2. An alternative method of protection should be developed by investigating methods of accelerating formation of the outer layer which is formed over the iron hydroxide.

3. Efficacy of the protective layers thus formed should be determined for continuous exposure to various sulfide concentrations over long periods of time.

ACKNOWLEDGMENT

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