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Versatility of Superaustenitic Stainless Steels in Marine Applications

G. Latha and S. Rajeswari

Corrosion of construction materials in marine applications is a major problem. The frequent variations in chloride ion concentration and temperature experienced by a system pose a serious threat. This investigation evaluated the performance of superaustenitic stainless steels in marine applications by potentiodynamic anodic polarization studies. The concentrations of metal ions such as iron, chromium, and nickel at different impressed potentials were analyzed by inductively coupled plasma spectrometry, which revealed little tendency for leaching of metal ions.

Keywords
inductively coupled plasma spectrometry, seawater, superaustenitic stainless steels

1. Introduction

IN THERMAL and nuclear power stations, about two-thirds of the total input heat (enthalpy) of the fuel is dissipated from the condenser of the steam turbines. To minimize this heat, various cooling systems can be applied depending on environmental and technical regulations. Among the various systems, the "once-through" cooling system is the conventional solution, well known and in wide practice all over the world. In once-through cooling systems that require a large quantity of water, seawater forms the ultimate sink for the heat (Ref 1-6).

For applications where seawater forms the major sink, certain precautions must be taken to ensure reliability and cost optimization (Ref 7). Any outage such as rectification/modification of the material at a later stage could result in total plant shutdown and stoppage of power generation, causing heavy direct as well as consequential losses in revenue. As such, it is preferable to adopt proven equipment and materials for this critical system to ensure a "fit and forget" solution.

Over the past three decades great progress has been made in the selection of highly resistant materials to address the ever-increasing corrosion problems in marine environments (Ref 8). Although the conventional austenitic stainless steels, such as type 316L, appear to be reasonably corrosion resistant and cost effective, they are prone to local attack such as pitting and crevice corrosion due to the aggressiveness of the environment (mainly chloride ions and temperature).

Improving the corrosion resistance of currently used materials can be achieved by modifying the material with the addition of elements such as nitrogen, chromium, molybdenum, and nickel. This investigation studied the localized corrosion behavior of two superaustenitic stainless steels—alloy 926 and alloy 31—by means of cyclic anodic polarization and inductively coupled plasma spectrometry.

2. Experimental Procedure

2.1 *Electrochemical Cell Assembly*

The electrochemical cell consisted of a 500 mL capacity with a three-electrode system. Natural seawater collected from the coastal area of Madras, India, served as the electrolyte. Saturated calomel electrode (SCE) was used as the reference electrode, platinum foil as the counterelectrode, and the test materials as the working electrode.

2.2 *Electrode Preparation*

The elemental compositions of the materials (alloy 926, alloy 31, and the reference type 316L) are given in Table 1. The materials were cut into 1 by 1 by 0.3 cm samples for electrochemical studies. Each piece was attached with a brass rod using silver paste for electrical contact. Then the samples were mounted in an epoxy resin to expose only one side with 1 cm^2 surface area. The mounted samples were polished successively up to 800-grit emery paper; final polishing was done using diamond paste in order to obtain a scratch-free mirror finish. The electrodes were ultrasonically cleaned with soap solution, degreased using acetone, thoroughly rinsed in distilled water, and dried.

2.3 *Pitting Corrosion Studies*

Potentiodynamic anodic cyclic polarization studies were conducted in order to evaluate the pitting corrosion behavior of the alloys. The potential was applied to the working electrode from the corrosion potential in the noble direction at a scan rate of 1 mV/s until the breakdown potential (E_b) was attained where the alloy entered the transpassive region or pitting. The sweep direction was then reversed after reaching an anodic current density of 3 mA/cm^2 until the potential where the reverse scan current density equals the upscan current density. The potential at which the reverse anodic scan meets the passive re-

Table 1 Chemical composition of the alloys

Alloy	Composition, wt%							
	Ni	Cr	Mo	N	C	S	Mn	Cu
Type 316L	12.7	17.2	2.4	0.02	0.03	0.003	1.95	...
Alloy 926	25.0	21.0	6.5	0.20	0.03	0.002	0.70	0.96
Alloy 31	31.0	27.0	6.5	0.20	0.03	0.002	0.68	0.90

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gion is termed the repassivation potential or pit-protection potential (E_p).

The parameters of interest recorded during these studies were:

- Corrosion potential, E_{corr}
- Pitting potential, E_b
- Repassivation potential, E_p
- Safe region to corrosion attack, ΔE

2.4 *Crevice Corrosion Studies*

To create crevices on the mounted electrodes, a crevice assembly was designed as described by Dayal et al. (Ref 9). The tip of the glass rod was brought into close contact with the electrode surface using a nut and threaded rod arrangement.

2.5 *Accelerated Leaching Studies*

The simulation of longtime contact of the material in the environment is achieved by imposing an anodic potential in the passive region of the material. In the study, the working electrode was immersed in 100 mL of seawater and allowed to stabilize at an impressed potential. The potentials chosen for the investigation were +200 mV, 400 mV, 600 mV, and breakdown potential for alloy 926 and alloy 31. Since the breakdown potential for type 316L occurred at 325 mV, studies were not performed at 400 and 600 mV.

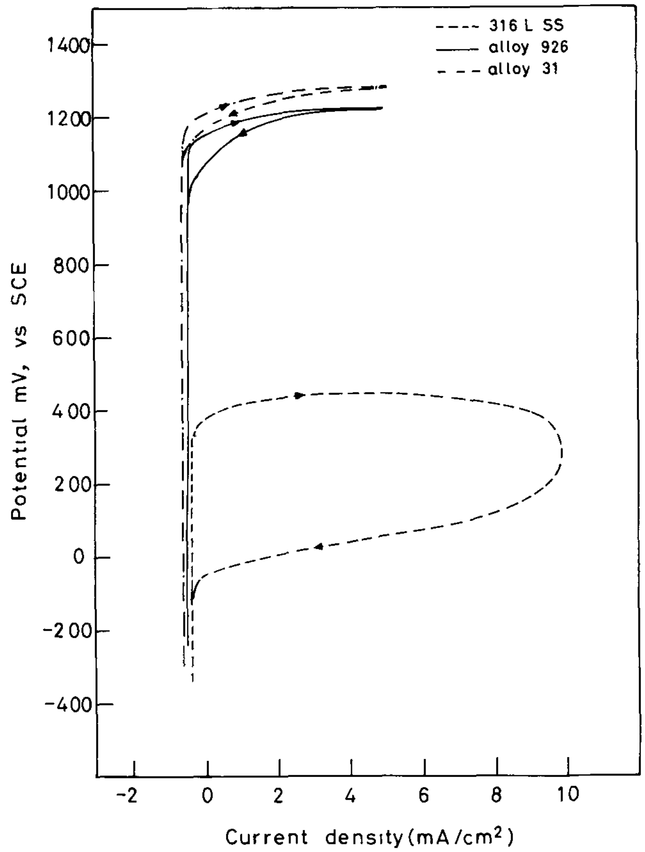

Fig. 1 Pitting corrosion behavior of type 316L, alloy 926, and alloy 31 in seawater

3. Results and Discussion

3.1 *Critical Pitting Potential*

The corrosion potentials (E_{corr}) of type 316L, alloy 926, and alloy 31 were −328, −228, and −206 mV, respectively. Compared to the reference material, the corrosion potential values shifted toward the noble region—due to the presence of higher amounts of nickel, molybdenum, chromium, and nitrogen.

Figure 1 depicts the anodic cyclic polarization curves of the three materials. Note that the critical pitting potential for the reference material was 365 mV, whereas alloy 926 and alloy 31 exhibited critical pitting potentials of 1125 and 1182 mV, respectively. Pitting potential is the criterion for evaluating resistance to pitting attack. The pitting potential of a material is directly influenced by the amount of passivating elements present in the alloy. Higher pitting resistance can be obtained by increasing the pitting potential of the material in the noble region. Thus, alloy 926 and alloy 31, with 0.2% N, 6.5% Mo, and 21 to 27% Cr, exhibited increased E_b values and exhibited better pitting corrosion resistance in the marine environment.

The increased pitting resistance of the superaustenitic stainless steels can be explained based on the following postulates. If a pit grows in the austenitic phase, the conditions prevailing at that pit site have been reported to be similar to those of the active dissolution state. During active dissolution, nickel and chromium generally dissolve, whereas nonactive elements such as nitrogen can enrich at the surface. Such an enrichment of the passive film inhibits the anodic dissolution of the materials by two orders of magnitude, presumably through the formation of iron nitride. This will certainly inhibit the autocatalytic process of pit formation and increase the opportunity for any pit to heal.

Earlier studies have reported that the addition of small amounts of nitrogen can enhance pitting resistance and passivating characteristics (Ref 10-13). Kamachi Mudali et al. (Ref 14, 15) indicated that the addition of nitrogen improved the pitting corrosion resistance for austenitic weld metal. Truman et al. (Ref 16) reported a remarkable increase in pitting corrosion of austenitic stainless steels due to the addition of more than 0.25 wt% N. A synergistic influence of nitrogen and molybdenum on pitting corrosion resistance was reported by Truman et al. (Ref 16) and Sedricks (Ref 17). Newman et al. (Ref 18) have noticed an enrichment of molybdenum and nitrogen in the passive film/metal interface, with the enrichment of nitrogen at a level of at least seven times the original concentration of nitrogen present in the alloy. They have proved this enrichment of nitrogen and molybdenum at the interface to be the predominant factor for preventing further dissolution of substrate consequent to the destruction of the passive film.

3.2 *Repassivation Potential*

The repassivation potentials (E_p) determined from the polarization curves for the three alloys are shown in Fig. 1. The mean value of repassivation potential for alloy 926 and alloy 31 increased in the noble direction due to the presence of nitrogen and molybdenum. New pits cannot be initiated above these potentials, and hence it can be inferred that the increased nitrogen and molybdenum content hinders the development of new pits and slows the kinetics of pit growth.

The significant role of nitrogen in the pit protection potential can be explained as follows. When the passive film breaks at some weak sites, the alloying elements such as iron, chromium, and nickel dissolve, whereas nitrogen enriches at the surface. The hydrolysis of metal ions then increases the acidity of the local solution in the vicinity of the pit site, which accelerates the anodic dissolution at the site. This autocatalytic effect expedites pit formation and development. Enrichment of nitrogen inhibits the anodic dissolution of the metal ions, presumably through the formation of nitride (Ref 18). This inhibits the autocatalytic process of pit formation and increases the opportunity for any pit to repassivate.

Relative corrosion resistance (ΔE) is defined as the difference between the repassivation potential and the corrosion potential of the system. This value can be used to rank the alloy (Ref 19-21). Type 316L, alloy 926, and alloy 31 exhibited corrosion potentials of −328, −228, and −206 mV, respectively. The mean value of ΔE for type 316L was 693 mV, whereas alloy 926 and alloy 31 showed higher ΔE values of 1353 and 1388 mV, respectively. The higher ΔE values reflect the enhanced pitting corrosion resistance, which is due to the presence of higher amounts of alloying elements—primarily nitrogen, chromium, and molybdenum.

3.3 *Effect of Temperature on Pitting Potential*

Temperature dependence of the pitting potential in the seawater for the three alloys is shown in Fig. 2. It is evident that the two superaustenitic stainless steels showed high resistance to pitting attack over a wide range of temperatures, whereas the type 316L showed a lower corrosion resistance at all the temperatures studied. The high corrosion resistance of superaustenitics is due to their chromium content and increased molybdenum and nitrogen levels (Ref 22).

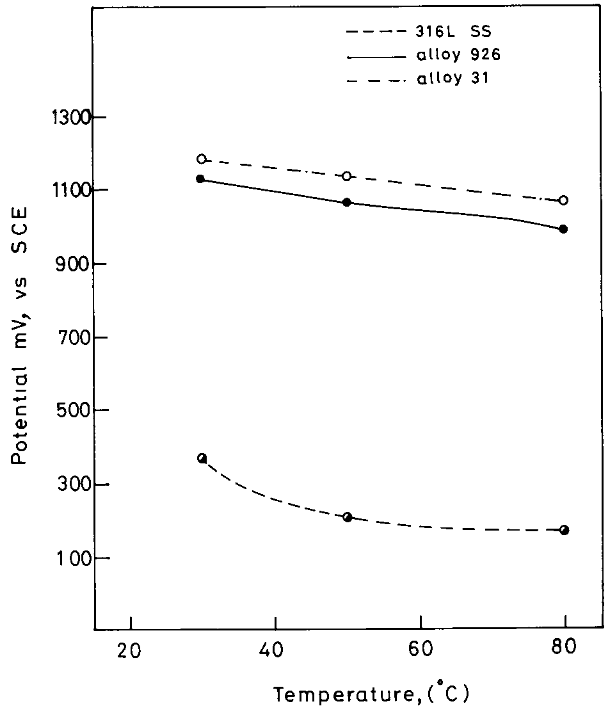

Fig. 2 Temperature dependence of the pitting potential in seawater

3.4 *Crevice Corrosion Potential*

Crevice corrosion of materials in marine applications is attributed to the presence of chloride ions. Oxygen present in the crevice is consumed quite rapidly in either the cathodic reaction or passivation. This depletion in oxygen concentration leads to the formation of a concentration cell. In addition, acidification of the crevice area can take place as a result of anodic reaction and hydrolysis of the metal ions.

Critical crevice potentials were determined from the polarization curves and are shown in Fig. 3. The presence of 0.2% N and 6.5% Mo in alloy 926 and alloy 31 increased the E_{cc} values in a more noble direction. Thus, the present study has shown the beneficial effect of nitrogen and molybdenum in improving the crevice corrosion resistance of the superaustenitics.

Clayton (Ref 23) suggested a chemical mechanism for the formation of ammonium ions and reported that the pH was controlled by the formation of nitride from the anodically segregated nitrogen. Kamachi Mudali et al. (Ref 24) have suggested that the dissolution of nitrogen at the pit site and subsequent formation of ammonium ions and nitrate compounds improve pitting resistance:

$$N + 4H^+ + 3e^- \rightarrow NH_4^+$$

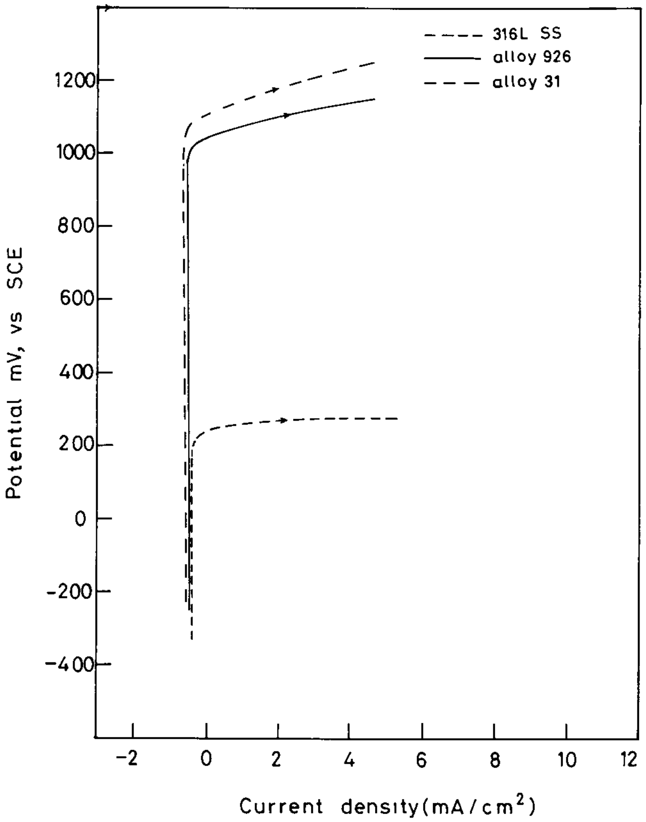

Fig. 3 Crevice corrosion behavior in seawater

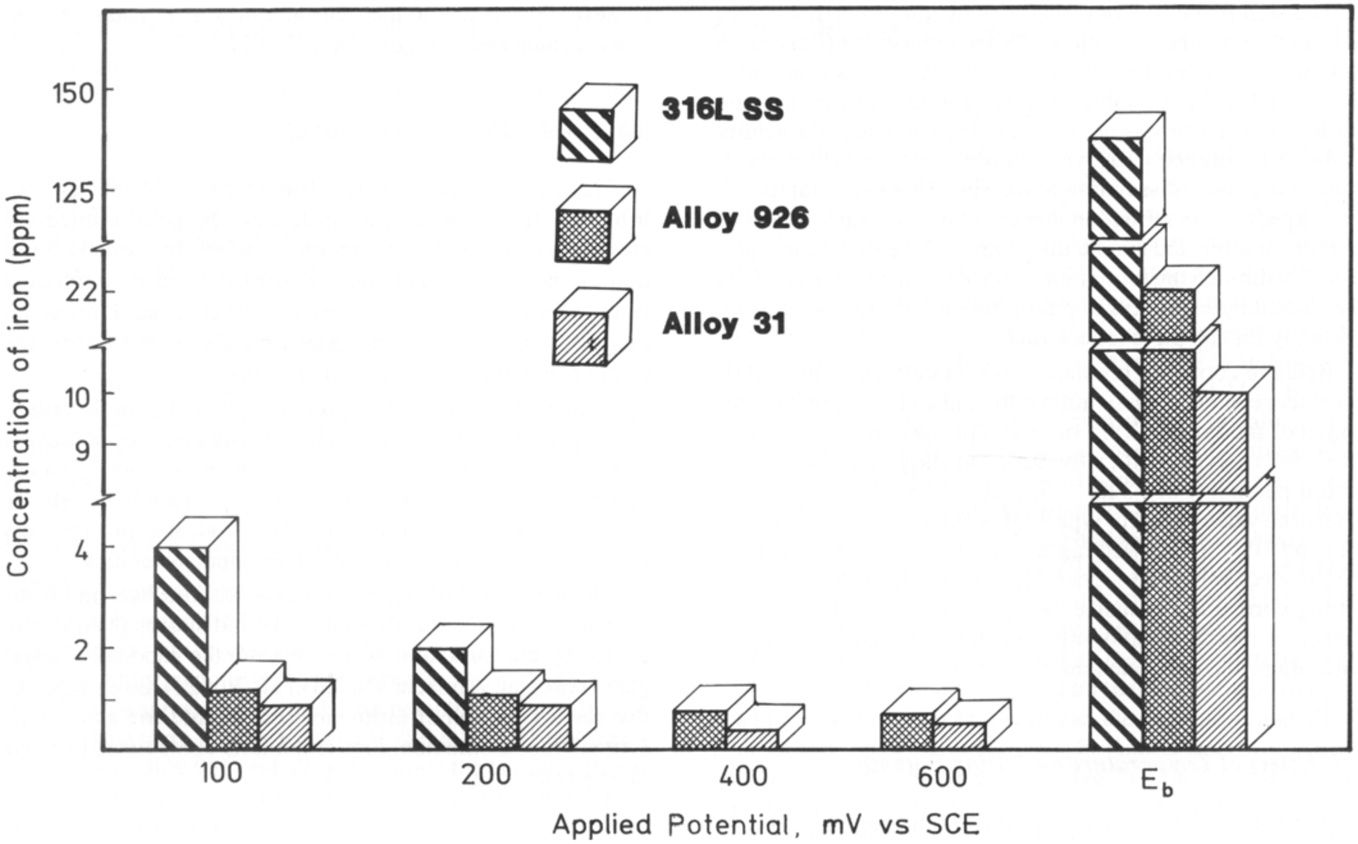

Fig. 4 Concentration of iron present in the solution after accelerated leaching at different imposed electrode potentials

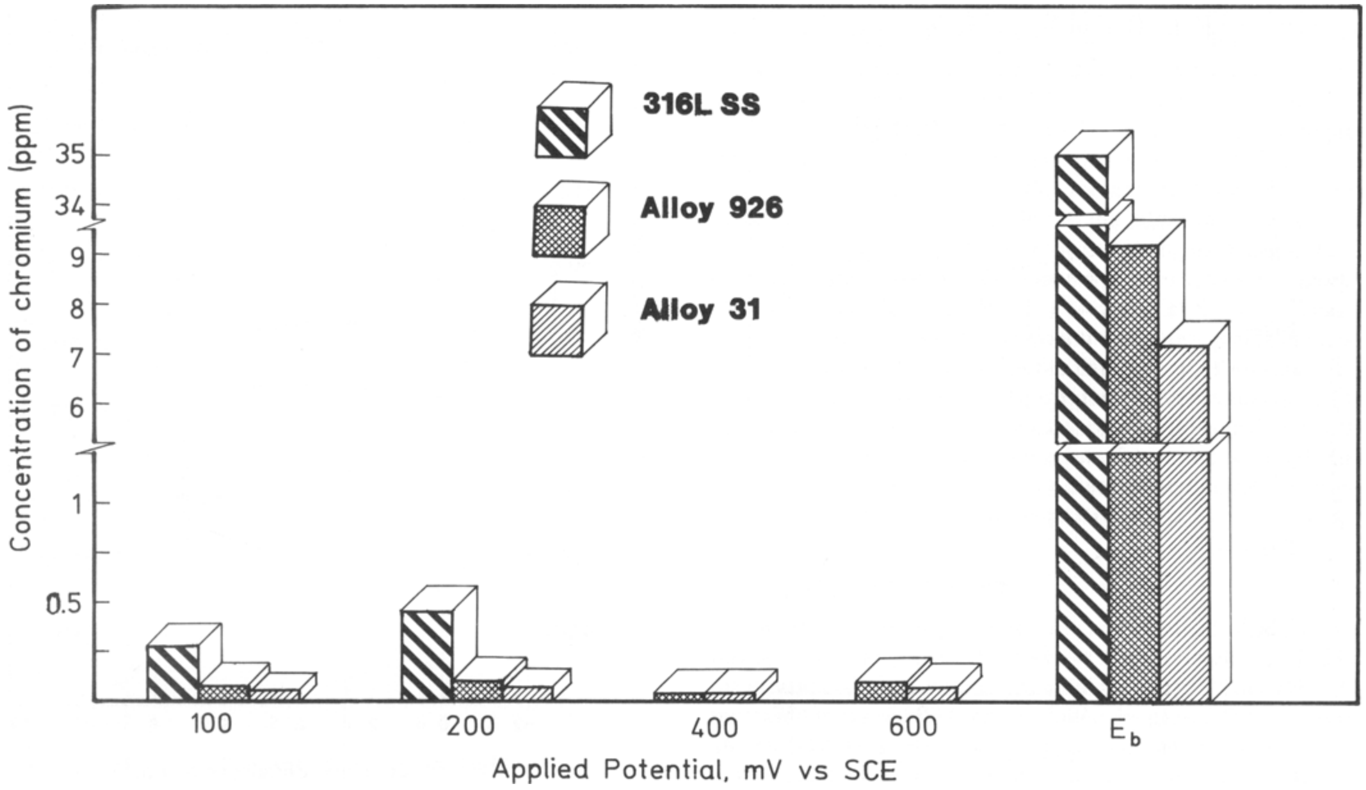

Fig. 5 Concentration of chromium present in the solution after accelerated leaching at different imposed electrode potentials

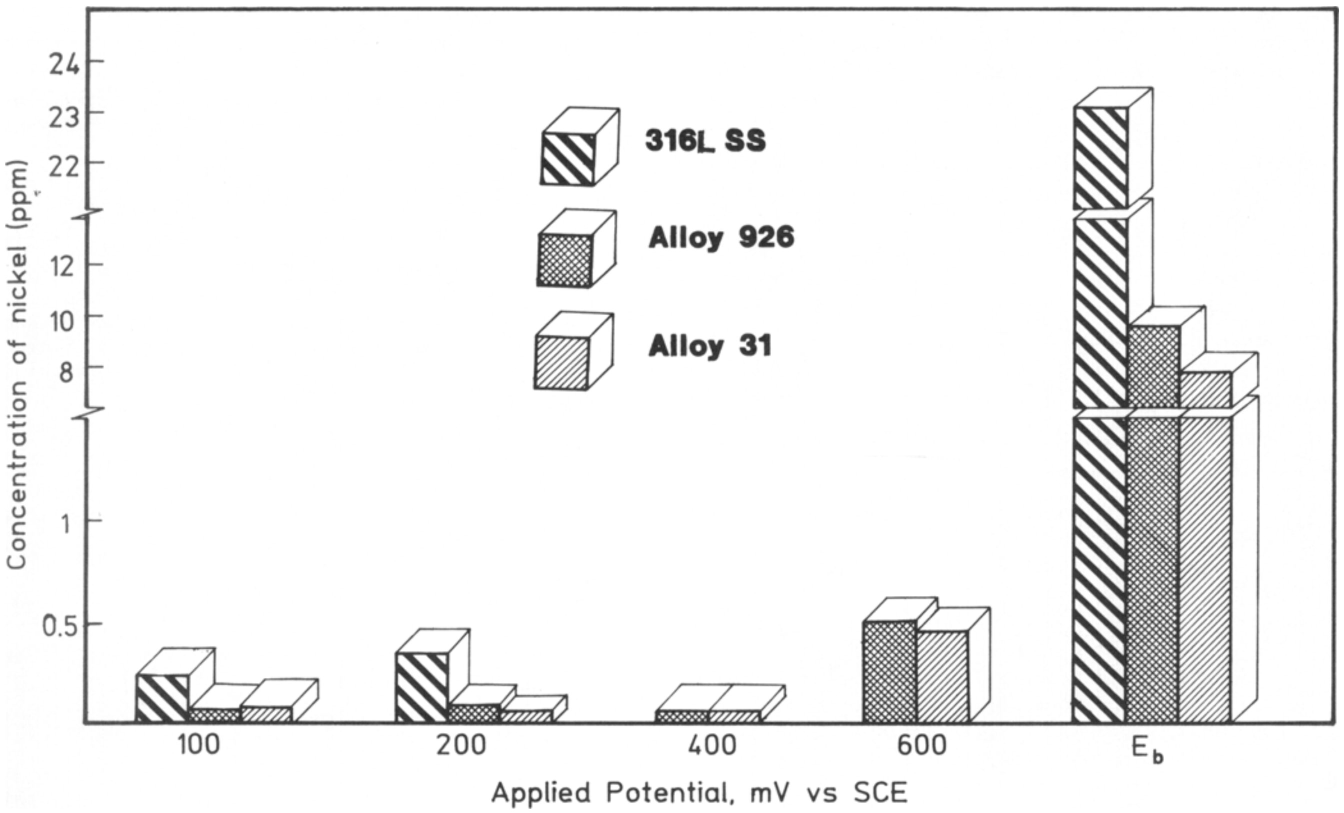

Fig. 6 Concentration of nickel present in the solution after accelerated leaching at different imposed electrode potentials

Thus, the effect of localized decrease in pH at the crevice area can be avoided by using superaustenitic stainless steels in marine environments.

3.5 *Accelerated Leaching Studies*

The results of the accelerated leaching study are presented in Fig. 4 to 6, which show the concentration of the metal ions—iron, chromium, and nickel—leached from the alloys at the impressed potentials. For type 316L, significant amounts of metal ions were released into the solution, even in the passive region. Alloys 926 and 31 exhibited leaching characteristics, but the concentration of metal ions leached out at 200, 400, and 600 mV were negligibly low compared to type 316L. Metal ions leached from the alloys in the following order: type 316L > alloy 926 > alloy 31.

The increased tendency for release of metal ions in type 316L can be explained as follows. Seawater contains an excessive amount of chloride ions, which first adsorb on a discrete site on the passive metal surface. The adsorbed halide ions bond with the metallic ions to form a soluble complex that dissolves in the solution. This process results in continuous thinning of the entire passive film, which is disrupted until the bare metal surface is reached at the end of the induction period. Previous workers (Ref 25, 26) have suggested the formation of a transitional complex by the adsorption of three or four halide ions on the surface of the passive film around a lattice cation. This complex readily abstracts the cation from the passive film lattice as a soluble species, resulting in thinning of the film by formation of a discrete site that exhibits a stronger anodic field. This field rapidly abstracts another cation through the thinned site of the film during the course of its interaction with halide ions, again resulting in a soluble complex formation. The traverse of cations of the passive film is thus facilitated until the bare metal is reached. The release of metal ions into the solution varies from alloy to alloy, depending on the passive film characteristics.

In the present investigation, alloy 926 and alloy 31 exhibited a very low tendency to leach metal ions compared to type 316L at all impressed potentials. This can be attributed mainly to the stable passive film that inhibits metal dissolution by forming a barrier layer between the metal and the environment, thus preventing the bare metal contacting solution (Ref 27). The extreme stability of the passive films formed on alloy 926 and alloy 31 may be due to strengthening of the passive film/metal interface by nitrogen enrichment.

4. Conclusions

The critical pitting and pit protection potentials of superaustenitic stainless steels were more noble than type 316L. This indicated the beneficial effect of molybdenum, nitrogen, and chromium for improving the pitting resistance of austenitic stainless steels.

Superaustenitic stainless steels showed superior resistance to crevice corrosion due to the presence of nitrogen. This is attributed to the formation of ammonium ions and ammonium nitride at the pits present in the crevices, which slows pit growth kinetics by increasing the pH of the solution inside the pits.

The pitting resistance of superaustenitic stainless steels in marine applications is maintained over a wide temperature range.

Accelerated leaching studies indicated that the release of iron, chromium, and nickel from superaustenitic stainless steels was considerably less compared to type 316L.

Thus, the superaustenitic stainless steels can be useful in marine applications where standard stainless steels are inadequate and where economic considerations prohibit the use of more expensive materials.

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