

Passivity of Oxide Film and Sulfide Inclusion on Nickel

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The passivity of oxide films formed on nickel in acid and neutral Na_2SO_4 solution, both with and without additions of chloride ions, at 25°C , has been investigated. It is found that the role of Cl^- in pitting of nickel is related to its ability to destroy the oxide films at local weak points, mainly at the grain boundaries, and the overall resistance of oxide films formed in the presence of Cl^- decreases due to the more defective oxide formation by Cl^- . In addition, the sulfide inclusion is observed to be the pit nucleation site, indicating that the localized attack starts in the sulfide inclusion, which is less noble than the surrounding oxide film, and then spreads to the active metal below the sulfide inclusion.

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INTRODUCTION

It is generally acknowledged that metals and alloys form oxide films which are susceptible to general or local breakdown in the presence of aggressive halide ions. Although various theories¹⁻³ have been proposed to explain the effect of halide ions, such as Cl^- , in order to understand the fundamental mechanisms of oxide film breakdown, there is still no agreement as to the exact mechanisms by which these ions damage metals. The basic question has therefore been whether or not the chloride ions are incorporated into the passive films on metals

and alloys. Surface analysis techniques have been revealed⁴ that the chloride ions exist only in the outer layer of oxide films formed on steel below the critical pitting potential, but the inner layer does not contain incorporated Cl^- .

Furthermore, metals and alloys contain sulfur as an impurity which has a low solubility so that most of sulfur is present as sulfide inclusions. It has since long been known⁵⁻⁸ that the sulfur has deleterious effects on materials and that localized corrosion of materials, particularly pitting, can be initiated at sulfide inclusions. With the high sulfur contents and the strong segregations that were common in the steels, this observation could often be made. Since sulfide inclusions exposed in the surface of a

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stainless steel are not coated with passivating oxide films, there easily occurs gaps in the passive film, particularly in acid solutions, exposing the active metal and giving rise to localized attack. In addition, it is known⁹ that the sulfides in a commercial stainless steel containing manganese comprise manganese sulfides with variable amounts of dissolved iron and chromium. The sulfides are electronic conductors and can be polarized to the potential of a passive stainless steel surface.¹⁰ At this potential the sulfides are not thermodynamically stable and tend to dissolve.

In the present paper, the effect of Cl^- on the passivity of oxide films formed on nickel in acid and neutral Na_2SO_4 at 25°C is investigated to understand better on initiating pitting of nickel in terms of anodic polarization behavior and open-circuit potential decay profile. Also, surface analysis techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive analysis of X-ray (EDAX) were used to study the effect of sulfide inclusions as sites of pit nucleation in pure nickel.

EXPERIMENTAL

A polycrystalline pure nickel rod (99.998% purity, 5.0 mm diameter) was obtained from Alfa Products. Specimens with 3 mm length were cut from it and annealed by heating at 850°C in vacuum (3.5×10^{-5} torr) for 46 hours followed by furnace cooling. For localized charging with sulfur, the whole surface of this annealed specimen was tightly enclosed by an envelope of 2 mm thick stainless steel with a hole of 0.1 mm diameter at center of one of two flat sides and

then exposed to SO_2 gas with a flow rate of 70 ml/minute at 1 atm at 500°C for 50 minutes, so that SO_2 gas can pass only through a hole of 0.1 mm diameter to react with nickel specimen. After SO_2 exposure, an envelope of stainless steel was removed and the SO_2 -exposed specimen was cleaned ultrasonically with acetone and deionized water. Nickel wire was then attached to the specimen surface, where SO_2 gas did not react, using silver epoxy for the electrical connection, and the wire was encapsulated in Pyrex tubing and sealed with polyester embedding material. Therefore, only SO_2 -reacted surface side was exposed to the test solution. All specimens were mechanically ground using 600-grit SiC paper, and then further polished with $0.05 \mu\text{m}$ gamma alumina powder on a wet polishing wheel. The crevice between the specimen and the embedding material was coated with a thin film of microshield lacquer to avoid crevice corrosion.

The electrolyte used was either acid or neutral 0.25M Na_2SO_4 , both with and without addition of Cl^- , deaerated for at least three hours by purging argon gas before the experiment; continuous deaeration was maintained during the experiment.

The electrochemical cell consisted of a nickel working electrode, a platinum counter electrode, and a saturated calomel electrode (SCE), to which all potentials are referred. Prior to the potentiodynamic anodic polarization studies, the air-formed oxide was removed by applying active anodic potentials, -200 mV in acid solution and -550 mV in neutral solution, for 3 minutes without surface modification confirmed by measuring the current-time behavior and observing the surface by optical microscopy. The potentiostat was then turned

off until a stable open-circuit potential was reached. Then, potential scanning at 0.1 mV/sec was started from this potential in the anodic direction. In addition, in order to investigate the surface morphology developed on annealed pure nickel at either active or passive potentials in 0.25M Na₂SO₄ (pH: 2) + 300 ppm Cl⁻ at 25°C, each potential was applied potentiostatically for 20 minutes, and the surface was then examined by optical microscopy.

To determine the fracture morphology caused by sulfur penetration on nickel during 500°C treatment of one side surface with SO₂, the tension specimen (0.5x0.5x3.0 cm) one entire side of which had been exposed to SO₂ at 500°C for 50 minutes, was pulled to failure, and the fracture surface was examined by SEM. TEM, XRD, and EDAX were used to examine the formation of second-phase produced by SO₂ charging and sulfide inclusions.

RESULTS AND DISCUSSION

(1) Effect of Chloride Ions on Passivity of Oxide Film

The anodic polarization behaviors of annealed pure nickel in 0.25M Na₂SO₄ (pH: 2) with various concentration of Cl⁻ are shown in Figure 1. The passive current density increases significantly with increasing Cl⁻ concentration. The grain boundary attack that is found after anodic potentiodynamic polarization is shown in Figure 2. In the acid Na₂SO₄ solution, pitting only occurs on the active anodic region of potential, shown in Figure 3, and may be due to preferential chemical dissolution of the oxide film at defect sites; pitting does not occur if the potential is maintained in the passive region.

It is, however, well known that aggressive chloride ions can lead to pitting of nickel when the potential is maintained in what is normally the passive potential region, which is confirmed by addition of 500 ppm Cl⁻ to Na₂SO₄ solution (see Figures 1 and 2). In addition, similar anodic polarization behaviors of annealed pure nickel in neutral Na₂SO₄ solution are shown in Figure 4; with increasing Cl⁻ concentration the passive current density increases somewhat but the corrosion potential is not affected.

In order to determine the influence of Cl⁻ on the stability of oxide films, open-circuit potential decay profiles are obtained for oxide films formed both with and without Cl⁻ in neutral Na₂SO₄ solution. Figure 5 shows the open-circuit potential behavior for oxide films produced on annealed pure nickel at 0.38 V for 30 minutes with different concentration of Cl⁻ and then immersed in a fresh Cl⁻-free neutral Na₂SO₄ at 25°C. The overall shape of the potential decay is not altered on oxide films

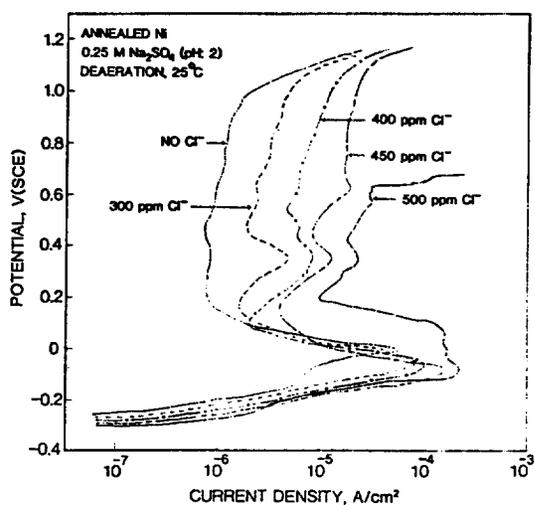


Fig. 1. Effect of chloride ions on the anodic polarization curve of annealed pure nickel in 0.25M Na₂SO₄ (PH:2) at 25°C.

formed in the presence of Cl^- , but resistance of the film decreases with increasing Cl^- concentration. This results indicate that more defective oxide films are formed on annealed pure nickel in the presence of Cl^- ; the overall

decrease in the resistance of oxide films formed with Cl^- is probably due to the initial hinderance of film formation by Cl^- , giving rise to a more defective oxide film. It may be that the Cl^- affects the nature of oxide films.

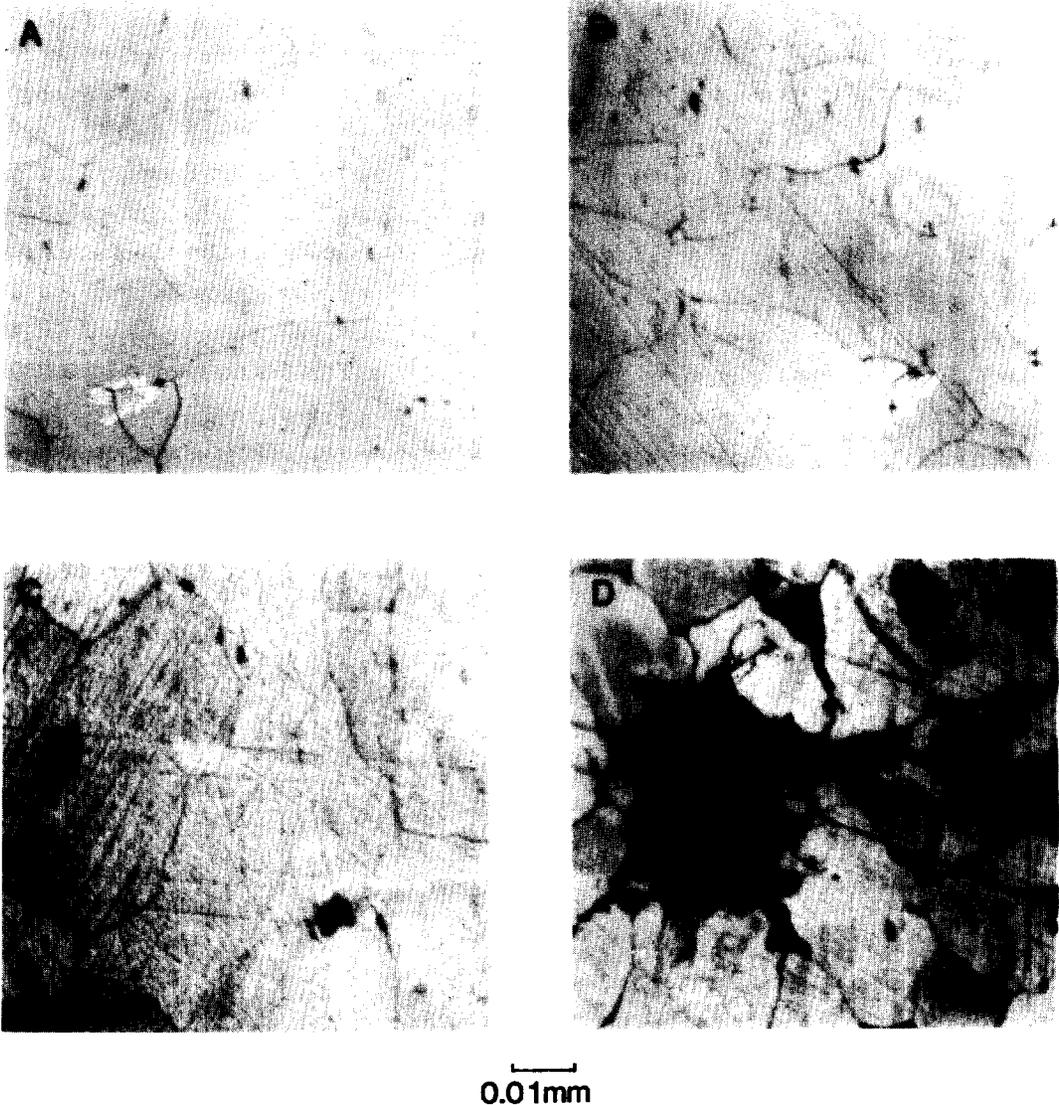


Fig. 2. Optical microscopy picture showing the grain boundary attack after polarization test in 0.25M Na_2SO_4 (PH:2) with A) no Cl^- , B) 300 ppm Cl^- , C) 400 ppm Cl^- , and D) 500 ppm Cl^- .

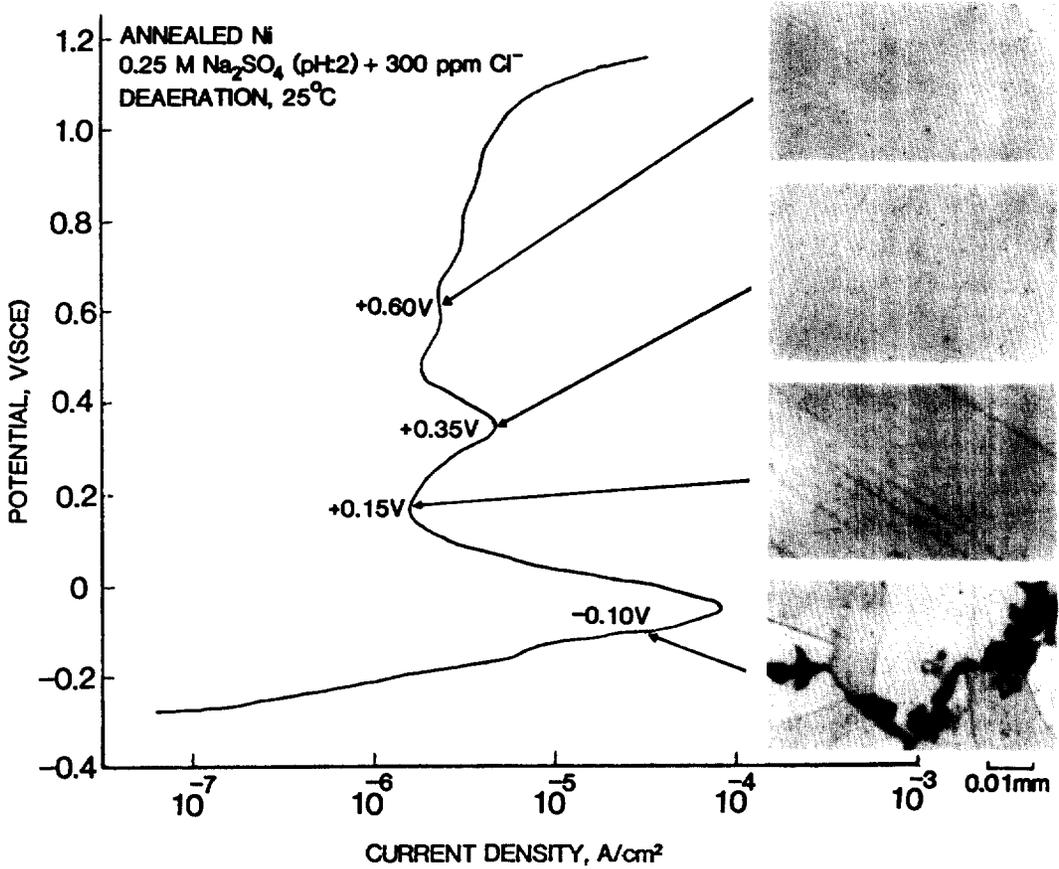


Fig. 3. Anodic polarization curve of annealed pure nickel in 0.25M Na₂SO₄ (PH:2) + 300ppm Cl⁻ at 25°C, along with surface morphology produced by polarization at each potential for 20 minutes.

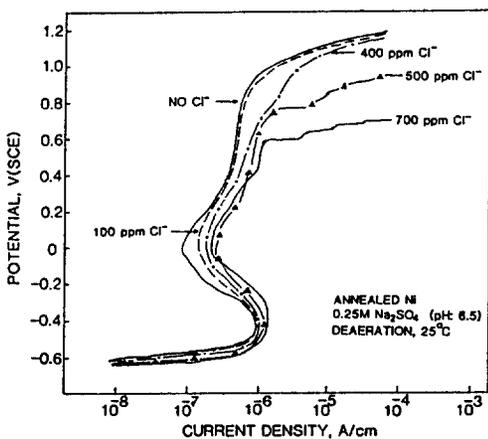


Fig. 4. Anodic polarization behavior of annealed pure nickel in 0.25M Na₂SO₄ (PH:6.5) with various amounts of Cl⁻ at 25°C.

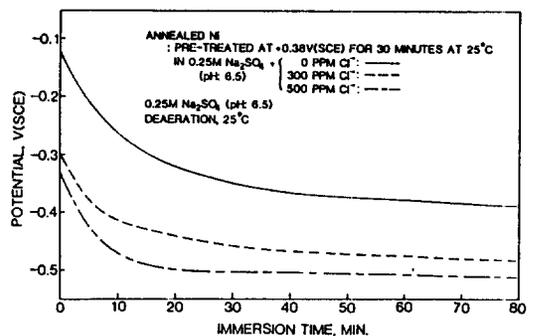


Fig. 5. Open-circuit potential decay profile of annealed pure nickel, previously anodized at 0.38V for 30 minutes in 0.25M Na₂SO₄ (PH:6.5) with different concentration of Cl⁻ as a function of immersion time in 0.25M Na₂SO₄ (PH:6.5) at 25°C.

Previous research¹¹ has shown that pitting can occur even in the absence of Cl^- . It is now believed that the pits form at defect sites, probably local weak points, in the oxide films. The role of Cl^- in pitting may be related to its ability to destroy the passive films at local weak points on the surface. However, the exact processes in which Cl^- operates locally on the passive films are the considerable subject. The increasing probability of pitting with increasing Cl^- concentration can be explained in terms of an increasing extent of retardation of the oxide repassivation reaction; the more Cl^- in the solution, the greater is the possibility that the oxide cannot effectively repassivate in those areas where it has broken down. Once the Cl^- begins to concentrate in the localized regions of high current density associated with $\text{Ni} \rightarrow \text{Ni}^{++} + 2e^-$ at the breakdown areas, the process may become autocatalytic with Cl^- increasing continuously, and thereby interfering even more with repassivation, with time. The corresponding increase in acidity also interferes with repassivation by increasing the rate of film breakdown.^{12,13} Eventually, the Cl^- concentration and the acidity may be high enough in local areas to prevent effective repassivation and the continued anodic current increase is due to growth of pits at the surface. The determining factor for pitting thus appears to be the Cl^- concentration and acidity within the local film breakdown areas.

(2) Sulfide Inclusion

Figure 6 shows the anodic polarization behavior of nickel specimen, small areas of which have been exposed to SO_2 at 500°C for 50 minutes, along with that of annealed pure

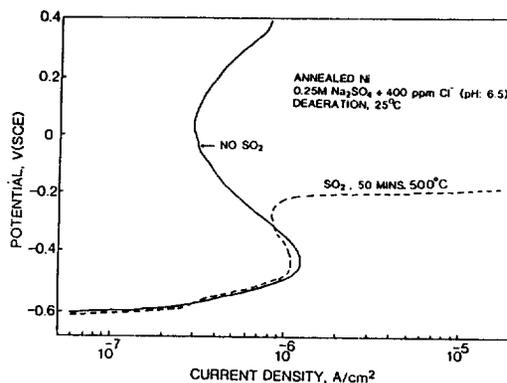


Fig. 6. Effect of SO_2 exposure on the anodic polarization curve of nickel in $0.25\text{M Na}_2\text{SO}_4$ (PH: 6.5) + 400 ppm Cl^- at 25°C .

nickel, in $0.25\text{M Na}_2\text{SO}_4 + 400 \text{ ppm Cl}^-$ (pH: 6.5). The SO_2 -exposed specimen develops pits at very low potential, but the corrosion potential is not affected significantly. TEM examination revealed second-phase particles along the grain boundaries (Figure 7). These particles were identified as nickel sulfide by XRD shown in Figure 8 and were detected down to about $60 \mu\text{m}$ from the original SO_2 -exposed surface. Also, SEM picture (Figure 9) showed the typical intergranular fracture surface caused by sulfur segregation along the grain boundaries.

Figure 10A, 10B, and 10D shows the characteristic X-ray images showing the distribution of Ni, S, and EDAX, respectively, registered on the nickel surface below the hole in the envelope after SO_2 exposure and before corrosion test. The intergranular pitting along with destruction of grains which is found after anodic potentiodynamic polarization of the same specimen in $0.25\text{M Na}_2\text{SO}_4 + 400 \text{ ppm Cl}^-$ (pH: 6.5) is shown in Figure 10C with EDAX result (10E). These results indicate that in nickel, pits preferentially nucleated at sulfide inclusions.



Fig. 7. TEM picture showing the grain boundaries of nickel. A) before SO₂ exposure and B) after SO₂ exposure at 500°C for 50 minutes.

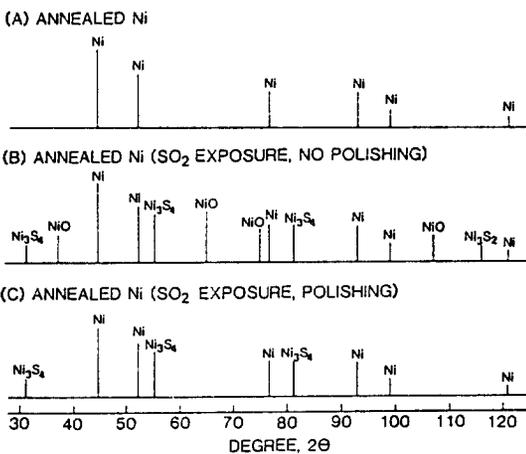


Fig. 8. X-ray diffraction spectra of annealed nickel showing nickel sulfide peaks after SO₂ exposure at 500°C for 50 minutes.

From the shape of the pits and the presence of some sulfides, one could presume that the dissolution began at sulfide inclusions and progressed deeper. The sulfides underwent selective dissolution because of the pH of the electrolyte decreased at the anode. Similar experimental results¹⁴ have been reported on nickel in chloride solution. Wranglen¹⁵ presumed that sulfide inclusions acted as local cathodes because of their significant electrical conductivity and catalytic efficiency, leading to increased activity of the surrounding metal and to pitting. Herbsleb¹⁶ tested the above presumption concerning catalytic efficiency of sulfides in the cathodic process of oxygen depolarization during the corrosion, but the results did not confirm Wanglen's presumption and concluded that sulfide inclusions did not reduce the resistance of mild steel. Hence, although the interpretations of the role of sulfides in pit nucleation are different, it can be concluded that pitting is a special form of

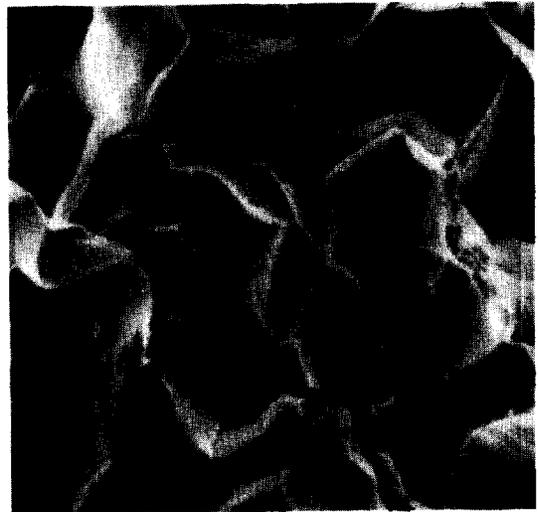


Fig. 9. Typical intergranular fracture of nickel exposed to SO₂ at 500°C for 50 minutes.

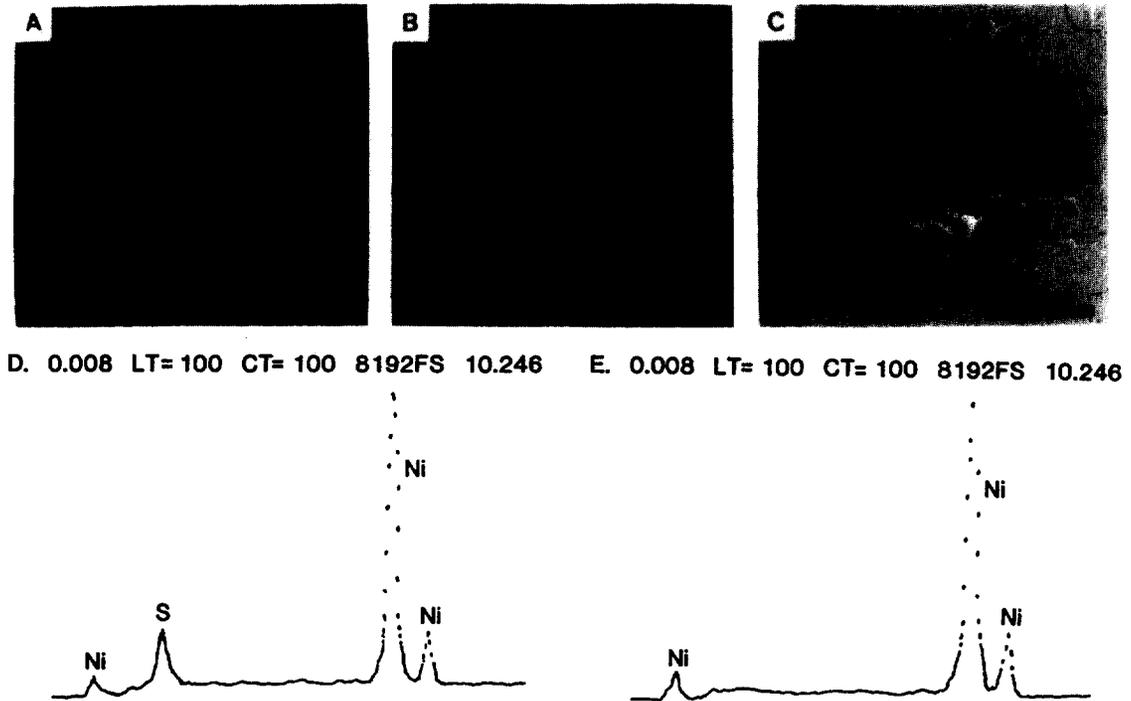


Fig. 10. Electron microprobe images showing A) distribution of Ni before corrosion test, B) distribution of S before corrosion test, C) surface morphology after corrosion test, D) EDAX before corrosion test, and E) EDAX after corrosion test. Corrosion test was done in 0.25M Na_2SO_4 (PH:6.5) + 400 ppm Cl^- at 25°C.

crevice corrosion which initiates and develops in a microcavity at the sulfide/metal boundary or is formed by sulfide dissolution. But a more complex mechanism for pit nucleation can be involved.

CONCLUSIONS

The passivity of oxide films formed on annealed pure nickel in Na_2SO_4 solution, both with and without addition of Cl^- , at 25°C has been studied. Increasing Cl^- concentration increases defect sites on oxide films due to the hinderance of oxide formation by Cl^- and then decreases the passivity of oxide films. In addition, there is an indication that the sulfide inclusion

acts as a pit nucleation site, and then produces the grain boundary pitting which easily propagates to the nickel metal below the sulfide inclusion.

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