Elllpsometric-Electrochemical Study of the Passive Films Formed on Stainless Steels in 2 N HNO_3

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Ellipsometric - electrochemical studies were carried out on the passive films formed on stainless steels 304, 304L and 316L in 2 N nitric acid medium. Corrosion potentials of all the stainless steels were found to be in the range -120 mV/SCE to -100 mV/SCE and changed to ca. + 120 mV/SCE within 40 minutes of exposure. A film was formed which had a thickness of 12 - 19 A° with a refractive index of ca. 1.66 (1 - 0.06 i) indicating the formation of hydroxides of iron/chromium. The thicknesses of these hydroxide films increase on stepping the potentials upto + 400 mV/SCE in steps of 100 mV. The films formed at + 500 mV/SCE to + 900 mV had a refractive index close to 2.0 (1 - 0.10 i) indicating thereby the formation of CrOOH. The compositions of the film changed once again followed by significant increase in thicknesses at + 1000 mV/SCE. The refractive index values of ca. 2.46 at + 1000 mV/SCE suggest the formation of Cr_2O_3/Fe_3O_4 on all the stainless steels.

Transpassive anodic dissolution was observed in all the cases at +1100 mV andΔvalues increased abruptly. However, the increase in values can not be correlated to optical constants of the surface because of surface roughness due to anodic dissolution.

Stainless steels become readily passive in oxidising acids and show a very low corrosion rate. Electrochemical studies have shown a very low anodic current density and potentiokinetic polarization technique gives a clear picture of the conditions necessary to achieve this passivity. Since, the reasons for passivity have been a subject of debate, it is worthwhile to investigate the surface characteristics of stainless steels in the passive state by ellipsometric method.

There have been some studies(1-8) on the characterization of these passive films but most of them have either been in sulphuric acid medium or in chloride medium and do not give a complete picture of passive - transpassive behaviour as well as of composition of films. The object of the present study is to compare the compositions as well as thicknesses of the films formed on 304, 304L and 316L stainless steels as a function of polarization potentials in 2 N HNO_3 medium.

EXPERIMENTAL

AISI stainless steels 304, 304L and 316L chosen for the study were of commercial grade and were solution annealed before the study. The specimens of the size 15mm x 15mm x 2mm were mounted on araldite and the electrical connections were taken by spot welding a SS 304 wire from the back of specimens. The specimens were first polished with emery paper and then on the rotating wheel with diamond paste. The specimen was left in 2 N HNO_3 for 40mts during which time the corrosion potential varied from the initial value of -120 mV/SCE to ca. + 120 mV/SCE. Gaertner ellipsometer model L119X was used to measure the optical constants of the surfaces under study. Measurements were made using mercury green light (λ = 5461 A°). Angle of incidence was maintained at 70° and the fast axis of compensator was kept at + 45° with reference to the plane of incidence. Ellipsometeric measurements were made to get Δ and Ψ values. The specimens were then anodically polarised at various anodic potentials from + 300 mV/SCE in steps of 100 mV. Specimens were held at every potential for 5 minutes and ellipsometric measurements were taken. Polarization measurements were discontinued at + 1100 mV/SCE after reaching the transpassive region and ellipsometric reading were recorded again.

RESULTS AND DISCUSSION

Fig. 1 represents the variation of Δ and Ψ for various stainless steels at different anodic potentials. It can be seen that Δ values decreased with increase in potentials of specimens from open circuit potential upto + 900 mV/SCE in the case of all the three stainless steels. A sudden decrease in Δ values between + 900 and 1000 mV shows rapid film growth in this range.

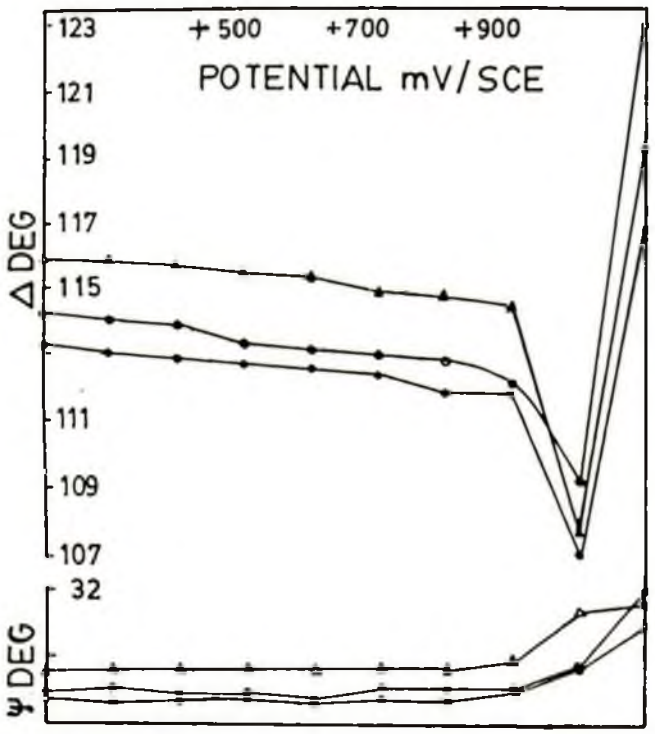


Fig. 1 Variation of and for various stainless steels in 2N HNO_3 at different anodic potentials

There was a gradual but small increase observed in values for all stainless steels at potentials upto + 900 mV showing that the film grown at anodic potentials had low adsorption coefficient. It should be noted here that for films with a very low absorption coefficient, Ψ increases with thickness while for those with high absorption coefficient, Ψ decreases with thickness. Relatively large icrease in Ψ values between + 900 and + 1000 mV indicated that the adsorption coefficients of the films decreased further. The decrease observed in Δ values can be due to two factors viz. a) increase in film thickness b) change in film composition and further analysis showed that both of these factors contribute to the decrease in Δ values during polarization in the present investigation.

One should have a prior knowledge of the complex refractive index of the bare substrate in order to calculate the complex refractive index and thickness of an oxide film by ellipsometeric measurements taken on a film covered surface. It is very difficult to achieve this bare surface by cathodic reduction in a metal or alloy/electrolyte system. The values of the refractive index of the substrate for computation of films' refractive indices in the present work were chosen from the earlier reported work (7,8). The values of S.S. 304 and S.S. 304L was taken as 2.87 (1-1.488i) and that for S.S. 316L as 2.86 (1-1.532i). Using these values , theoretical charts of Δ and Ψ were prepared for the film refractive index range $1.5 \leq n_f \leq 3.2$ and $0.0 \leq k_f \leq 0.5$ and for films thicknesses 0-100 A°. The refractive indices of the films formed on various stainless steels at various potentials were computed by comparing the theoretical curves with the experimental Δ -Ψ plots.

Fig. 2 represents the comparsison of theoretical Δ-Ψ charts with the experimental Δ -Ψ plot for S.S. 304. It appears that initially, the refractive index of the film in this case was 1.7 (1-0.1i) which increased gradually on enhancing the potential. The exact refractive indices and thicknesses were arrived at, by narrowing the range of approximate refractive index values of the film fed to the computer and the results of the computation are shown in table 1.

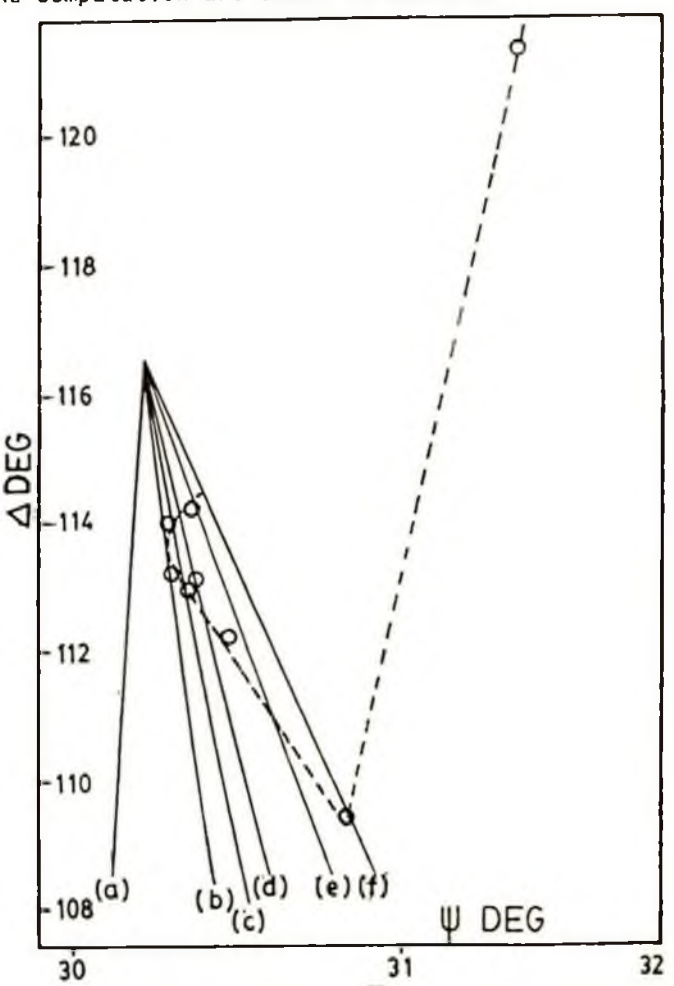


Fig. 2 Experimental Plot for S S 304 in 2N HNO_3 at various anodic potentials versus SCE

Theoretical Plots with $\bar{n}_f$

(a) 1.6 (1-0.1i)
(b) 1.7 (1-0.1i)
(c) 2.0 (1-0.15i)
(d) 1.8 (1-0.1i)
(e) 2.0 (1-0.1i)
(f) 2.50 (1-0.05i)

TABLE 1

OPTICAL CONSTANTS OF THE FILM FORMED ON S.S. 304 IN 2 N HNO_3; ANGLE OF INCIDENCE = 70°

Potential/ SCE (mV)	Deg. Δ	Deg. Ψ	$\bar{n}_f$	Thickness (A°)
O.C.P.	114.24	30.37	1.66(1-0.06i)	18.6
+ 300	113.99	30.30	1.64(1-0.08i)	20.4
+ 400	113.88	30.35	1.65(1-0.07i)	21.3
+ 500	113.32	30.36	2.07(1-0.15i)	15.1
+ 600	113.21	30.31	2.04(1-0.18i)	15.7
+ 700	113.09	30.39	2.07(1-0.14i)	16.3
+ 800	112.90	30.36	2.07(1-0.16i)	17.0
+ 900	112.18	30.48	2.06(1-0.12i)	21.0
+1000	109.29	30.83	2.54(1-0.06i)	28.1
+1100	122.99	31.44	---	--

The refractive index of the film was initially 1.66(1-0.6i) and the thickness of film at open circuit potential was 18.6 A°. This refractive index remained more or less constant upto + 400 mV/SCE and changed to 2.07 (1-0.15i) at + 500 mV. Thickness of the film which was 18.6 A° AT O.C.P. increased upto 21.3 A° at +400 mV but decreased to 15.1 A° at + 500 mV as the refractive index of the film increased. Film refractive index again remained same in the potential range + 500 to +900 mV while thickness of the film in this range increased to 21.0 A°. The most significant observation in the present study was made at +1000 mV when the film grew rapidly upto 28.1 A° and film refractive index changed to 2.54 (1-0.6i). Anodic dissolution was observed at + 1100 mV and as stated earlier, Δ and Ψ values observed at + 1100 mV cannot be related to the surface properties because of surface roughness.

Fig. 3 represents the comparison of theoretical Δ - Ψ chart with experimental Δ - Ψ plot for S.S. 304L. The refractive index of the film at O.C.P. in this case seems close to 1.7 (1-0.1i). By feeding the approximate narrow range of refractive index back to computer, the refractive indices as well as thicknesses of films obtained at various potentials have been shown in table 2.

In this case too, the film refractive index changed from 1.65 (1-0.08i) at O.C.P. to 1.98 (1-0.11i) at + 500 mV/SCE and finally to 2.52 (1-0.10i) at + 1000 mV while the thickness first increased from 18.5 A° at O.C.P. to 28.7 A° at + 400 mV, and then decreased to 19.8 A° at + 500 mV. However, it increased once again from 19.8 A° at + 600 mV upto 37.5 A° at + 1000 mV after which, the anodic dissolution was observed.

Fig. 4 shows the comparison of the theoretical with experimental plot of and for S.S. 316L. The approximate film refractive index in this case appears to be 1.95 (1-0.05i). The results of the

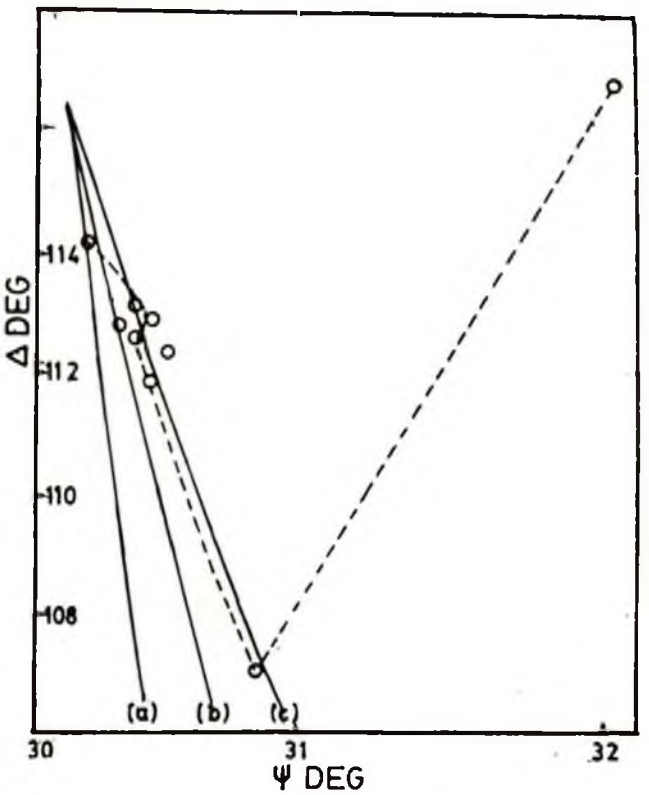


Fig. 3 Experimental Δ - Ψ Plot for SS 304L in 2N HNO_3 at various anodic potentials vs. SCE. Theoretical Δ - Ψ plots with $\bar{n}_f$ (a) 1.7 (1-0.1i), (b) 1.8 (1-0.1i), (c) 2.0 (1-0.1i)

TABLE 2

OPTICAL CONSTANTS OF THE FILM FORMED ON S.S. 304L IN 2 N HNO_3; ANGLE OF INCIDENCE = 70°

Potential/ SCE (mV)	Deg. Δ	Deg. Ψ	$\bar{n}_f$	Thickness (A°)
O.C.P.	114.20	30.30	1.65(1-0.08i)	18.5
+ 300	112.95	30.52	1.66(1-0.05i)	28.9
+ 400	112.90	30.41	1.66(1-0.07i)	28.7
+ 500	112.67	30.46	1.98(1-0.11i)	19.8
+ 600	112.67	30.46	1.98(1-0.11i)	19.8
+ 700	112.42	30.57	2.07(1-0.08i)	20.1
+ 800	111.94	30.51	2.00(1-0.11i)	23.3
+ 900	111.74	30.54	2.00(1-0.11i)	25.2
+1000	107.04	30.87	2.52(1-0.10i)	37.5

exact calculations by the procedure mentioned earlier and shown in table 3 indicate in this case too, refractive index of the film at corrosion potential which was 1.66 (1-0.05i) remained more

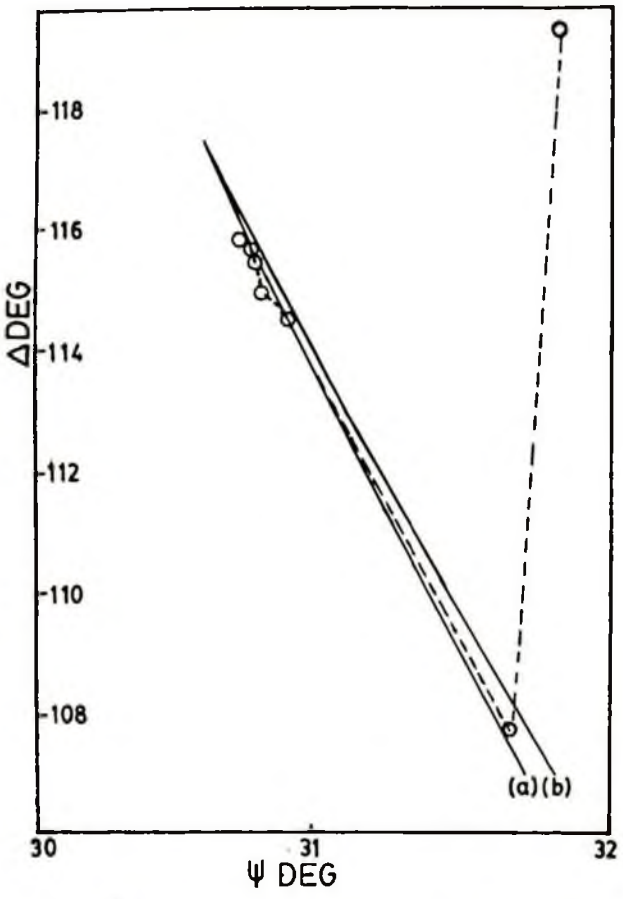


Fig. 4 Experimental Δ -Ψ plot for SS 316L in 2N HNO_3 at various anodic potentials Theoretical Plots with $\bar{n}_f$: (a) 1.95 (1-0.05i) (b) 2.50 (1-0.0i)

or less same upto + 400 mV while thickness grew from 12.9 A° to 14.4 A°.

At + 500 mV, as in the earlier two cases film refractive index increased to 1.83 (1-0.06i) and thickness decreased to 12.4 A°. On increasing the potential further, thickness of the film grew once again upto 37.7 A° while refractive index changed to 2.54 (1-0.01i) at + 1000 mV.

Thus, the films formed on stainless steels can be divided into three broad categories viz. having complex refractive indices of ca. 1.65 (1-0.06i), ca. 2.0 (1-0.1i) and ca. 2.54 (1-0.05i). There has been a confusion about the composition of the films within refractive index 1.65. Genshaw and Sirhi(9) assign a value of 1.62 to $Cr(OH)_3$ while the same authors report a value of (2.0±0.1) for CrOOH.Ord(10) gives a value of 1.7 to FeOOH. Smialowska and Staehle(11) during passivation studies of iron on chromate solution also obtained films having a refractive index between 1.6 and 1.7 at open circuit potential. They assumed these

TABLE 3

OPTICAL CONSTANTS OF THE FILM FORMED ON S.S. 316L IN 2 N HNO_3 ANGLE OF INCIDENCE = 70°

Potential/ SCE (mV)	Deg.	Deg.	$\bar{n}_f$	Thickness (A°)
O.C.P.	115.87	30.77	1.66(1-0.05i)	12.9
+ 300	115.83	30.80	1.66(1-0.04i)	13.4
+ 400	115.71	30.81	1.66(1-0.04i)	14.4
+ 500	115.46	30.82	1.83(1-0.06i)	12.4
+ 600	115.41	30.83	1.87(1-0.06i)	12.0
+ 700	114.94	30.85	1.88(1-0.07i)	14.7
+ 800	114.82	30.86	1.88(1-0.07i)	15.1
+ 900	114.54	30.93	1.86(1-0.05i)	17.4
+1000	107.76	31.67	2.54(1-0.01i)	37.7

films to consist a mixture of iron hydroxide and chromium hydroxide. Smialowska et al.(12) during their studies on the surface films grown on austenitic steel in chloride solution, obtained the films with a refractive index of 1.65(1-0.3i) in 5N H_2SO_4 + 0.5N NaCl solution. The authors assign these films to hydroxides or mixture of hydroxides and oxides. Matsuda et al.(8) also found that the air formed film on S.S. 304 had a refractive index of 1.5-0.6i. From these contradicting reports, it is very difficult to predict the composition of the films with a refractive index of 1 .65 (1-0.06i) because the value is very close to FeOOH (10) as well as to $Cr(OH)_3$ (9). We therefore conclude, that, it is a mixture of both these compounds. The film formed on S.S. 304 and S.S. 304 L with a refractive index of ca. (2.0+0.1) between + 500 mV and + 900 mV/SCE can be concluded to be CrOOH (8,9). However, the film formed on S.S 316 L contains 2% Mo in the base alloy. The films formed at + 1000 mV/SCE and having a refractive index of 2.54 can be said to consist of either Cr_2O_3 or Fe_3O_4 or both (8,9,12,13) because 2.55 is the value reported for Cr_2O_3 (8,9) while the values of 2.5 and 2.58 (12,13) have been reported for Fe_3O_4. If both of these compounds are incorporated in the oxide film, ellipsometric measurements are not sufficient to predict their relative composition in the film.

On the basis of above discussion, it can be concluded that the films formed at open circuit potential on stainless steels consist of hydroxides of iron and chromium while on anodising beyond + 400 mV, the passive film converts into CrOOH and finally to Cr_2O_3/Fe_3O_4 at + 1000 mV after which anodic dissolution takes place. During transition from $Cr(OH)_3$ /FeOOH to CrOOH at Ca. + 500 mV, the films thickness decrease slightly. These observation are not in argreement with the work of Okamoto and Shibata (2) on the stability of passive films on stainless steel in relation to

potential of passivation. Okamoto et al(2). have not observed any decrease in film thickness. The decrease in thickness of films, observed by us can, however, be explained on the basis of model proposed by Okamoto et al. as the hydroxide/ oxyhydroxide films formed upto + 400 mV/SCE consist of significant amount of bound water. At ca. + 500 mV, this bound water gets desorbed while film converts into CrOOH and thins down slightly. The studies of Chance et al(14). on the characterization of passive films formed on a ferritic stainless steel in 0.5m sodium sulphate solution have also indicated that the films in the prepassive region which were composed of iron and oxygen changed to chromium and oxygen films. The authors have laso reported that the surface film thickness reaches a maximum in early prepassive region and then thins out to a minimum in the passive region. On increasing the potential further, this CrOOH film thickens again first slowly upto + 900 mV and then, rapidly at + 1000 mV by getting converted to Cr_2O_3. At this stage, possibly iron also enters into the film in the form of Fe_3O_4.

CONCLUSION

1. The passive films formed on S.S. 304, S.S. 304L and S.S. 316L at open circuit potential consist mainly of FeOOH and $Cr(OH)_3$ with thicknesses in the range of 12 - 19 A°.
2. On increasing the potential upto + 400 mV/SCE, these hydroxide, oxy-hydroxide films increase in thickness.
3. At + 500 mV/SCE, these hydroxide films convert into a passive film of CrOOH which is slightly less in thickness than the hydroxide/oxyhydroxide films formed upto + 400 mV. The slightly lower refractive index of the film observed in case of S.S. 316L between + 500 mV and + 900 mV/SCE could be due to participation of Mo in the film formation.
4. The films formed at + 500 mV/SCE increase in thickness first slowly upto + 900 mV and then rapidly at + 1000 mV/SCE.
5. At + 1000 mV/SCE the CrOOH film converts into Cr_2O_3 and iron possibly enters the film in the form of Fe_3O_4.
6. Transpassive dissolution of the films on stainless steels in 2 N HNO_3 takes place at +1100 mV/SCE.

ACKNOWLEDGEMENT

The authors are grateful to Dr. R. Kirshnan, Head, Metallurgy Division for his keen interst and encouragement during these investigations.

REFERENCES

1. V.V. Andreeva, Corrosion., 20, (1964) 35.
2. G. Okamoto and T. Shibata, Corrosion Sci., 10, (1970) 371.
3. T.N. Rhodin, Corrosion., 12, (1956) 123t, 465t.
4. K.N. Goswami and R.W. Staehle, Electrochim. Acta., 16, (1971) 1895.
5. G.M. Bulman and A.C.C. Tseung, Corrosion Sci., 13, (1973) 531.
6. G. Okamoto, Corrosion Sci., 13, (1973) 471.
7. K. Sugimoto and Y. Sawada, Corrosion Sci., 17, (1977) 425.
8. S. Matsuda K. Sugimoto and Y. Sawada, Trans. Japan Inst. Metals., 18,(1977) 66.
9. M.A. Genshaw and R.S. Sirohi, J. Electrochem. Soc., 118, (1971) 1558.
10. F.C. Ho and J.L. Ord, J. Electrochem. Soc., 119, (1972) 139.
11. Z. Szklarska - Smialowska and R.W. Staehle, J. Electrochem. Soc., 121, (1974) 1146.
12. C.E. Leberknight and B. Lustman, J. Opt. Soc. Amer., 29, (1939) 9.
13. A.B. Winterbottom, J. Iron Steel Inst., 165, (1950) 9.
14. R.L. Chance and S.W. Gaarenstroom, Corrosion (NACE)., 36, (1980) 94.