

in β Cu-Zn-Al alloys than in β' Cu-Zn-Al alloys. The reason for this is far from fully understood, but different diffusion rates in β and β' Cu-Zn-Al alloys could be partly responsible for it.

Conclusion

In order to test the corrosion behavior of recently developed β and β' Cu-Zn-Al alloys, accelerated standard tests as the Swedish Standard tests C316-1970 are found suitable if a modified test temperature of 20°C instead of 75° and 80°C, respectively, is used. Good agreement between these standard tests and field tests is obtained if comparisons are made on the basis of dealloying depth, rather than on the basis of weight loss. In comparison with conventional α and $\alpha + \beta$ Cu-Zn alloys and with α Cu-Zn-Al alloys which are successfully used as material for heat exchanger tubes in marine environments, β and β' Cu-Zn-Al alloys show a larger, more localized, dezincification susceptibility. This localized dezincification, which extends preferentially along grain boundaries into the bulk of the material, explains the unsuitability of tests based on weight loss measurements.

With increasing aluminum content, a decreasing dezincification was determined which could be due to a pile up of aluminum along the frontier between virgin material and dezincified area. Besides the effect of the aluminum content, the results clearly indicate a dependency on the atomic structure. At comparable zinc and aluminum content, the β structure is less sensitive to dezincification than the β' structure. Experimental evidence supports a dezincification mechanism based on an anodic dissolution of the brass fol-

lowed by a redeposition of copper in a porous form from the solution.

Manuscript submitted March 5, 1982; revised manuscript received ca. July 18, 1983.

REFERENCES

1. L. Delaey, E. Aernoudt, and J. Roos, *Metall.* **31**, 1325 (1977).
2. M. Jaenen, Engineering Thesis, Katholieke Universiteit Leuven, Heverlee, Belgium (1977).
3. H. Leidheiser, in "The Corrosion of Copper, Tin and their Alloys," Chap. 6, John Wiley & Sons, New York (1971).
4. H. Logan, in "The Stress Corrosion of Metals," Chap. I, John Wiley & Sons, New York (1966).
5. H. Uhlig, in "Corrosion Handbook," John Wiley & Sons, New York (1963).
6. V. Lucey, *Br. Corros. J.*, **1**, 10 (1965); **1**, 53 (1965).
7. R. Heidersbach and E. Verink, *Corrosion*, **28**, (11), 397 (1972).
8. R. Muller, in "Proceedings of the 8th International Congress Metallic Corrosion," p. 1470, Mainz (1981).
9. F. Mazza and S. Torchio, in "Proceedings of the 8th International Congress Metallic Corrosion," p. 199, Mainz (1981).
10. L. Shreir, in "Corrosion," Vol. 1, Chap. 4.2, G. Newnes Ltd., London (1965).
11. G. Gusmano, R. Cigna, L. Giuliani, and R. Loreti, *Br. Corros. J.*, **15**, 222 (1980).
12. E. Mattsson and M. Linder, Proceedings of Eurocor 1977, p. 445, London (1977).
13. B. Dillon, *Met. Forum*, **1**, 71 (1978).
14. M. Pourbaix, in "Atlas of Electrochemical Equilibria in Aqueous Solutions," NACE, Houston (1974).

Molecular Generality of Surface-Enhanced Raman Spectroscopy: Application to the Study of Surface Resonance Raman-Enhanced Complexes of Iron (II) with 1,10-Phenanthroline on Silver and Iron

R. P. Van Duyne and M. Janik-Czachor¹

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

ABSTRACT

RR and SERS spectra of adsorbed complexes of 1,10 phenanthroline with Fe(II) (*viz.*, Fe(phen)₃²⁺) on silver from highly dilute solution (*viz.*, 5 × 10⁻⁶M) are presented. The first attempt to combine SERS and RRS in order to investigate the surface spectra of Fe(phen)₃²⁺ on an iron substrate is also reported. The results are encouraging with regard to possible application of SERS and RRS to studies of wet metallic corrosion, *in situ*.

Surface-enhanced Raman spectroscopy (SERS) has become a useful *in situ* technique for the molecular characterization of the metal-solution interface (1-8). Surface Raman spectra have been observed for more than 50 different molecules and ions adsorbed on silver. The monolayer detection sensitivity of SERS is made possible through a 10⁶-fold enhancement of the effective Raman scattering cross section for the adsorbed species relative to that for the same molecule in bulk (1, 4). Surface-enhanced Raman spectra have also been observed on Cu and Au substrates with enhancement factors in the 10⁵ range. It is generally accepted that an enhancement factor of at least 10³ is required to observe Raman scattering from molecular monolayers (1, 9, 10). These findings are in agreement with the predictions of the Image Field Enhancement Model (IFE) of SERS (1, 9). This model

predicts that the enhancement factor (ϵ) is critically dependent on the optical properties of the substrate. The nature of the metal enters into the electromagnetic theory through its dielectric constant. Studies of carefully chosen alloys whose dielectric constant can be changed in a controlled way (*viz.*, Ag_{1-x}Pd_x) can be used to test this concept (11).

The IFE model predicts also that such metals as Li and Hg should be strong SERS enhancers (12). The recent results for adsorbates on Li (13) seem to confirm this prediction although the results on Hg have now been retracted (14). Unfortunately, many important metals are expected to yield enhancements below the critical value (9).

The unconfirmed reports of SERS for Ni, Pt (15) and Cd (16) are not pertinent, since no efforts have been made to check whether the Raman bands that have been observed actually exhibit all the characteristic features of surface-enhanced signals. However, it is possible that low enhancement metals can be probed

¹On leave from the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

Key words: complex, iron, phenanthroline, raman spectroscopy.

through a combination of resonance Raman spectroscopy (RRS) and surface-enhanced effects which would bring the total enhancement factor above 10^8 (1, 4, 17). Previous studies of adsorbates on silver have shown that a total enhancement of 10^{10} can be observed by superimposing these effects (1, 4, 18).

In this paper, we will consider the RR and SERR spectra of adsorbed complexes of 1,10-phenanthroline with Fe(II), (*viz.*, $\text{Fe}(\text{phen})_3^{2+}$). This complex is characterized by a small dissociation constant ($K = 5 \times 10^{-22}$) (19) and an intense electronic absorption spectrum in the visible region ($\epsilon_{510\text{nm}} = 1150 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$) (20). The solution RRS of $\text{Fe}(\text{phen})_3^{2+}$ has already been reported (21). In addition, we have studied the adsorption of $\text{Fe}(\text{phen})_3^{2+}$ on an Ag electrode, from a $5 \times 10^{-6} \text{ M}$ $[\text{Fe}(\text{phen})_3] (\text{ClO}_4)_2$ solution, in a manner similar to that reported earlier (18). We also attempted to combine SERS and RRS to investigate the surface spectra of $\text{Fe}(\text{phen})_3^{2+}$ on an iron substrate, where the SERS enhancement for Fe is probably $< 10^8$ (9).

Iron was chosen as a substrate material because of its technological importance. In particular, one is interested in the ability of RRS or SERS to probe, *in situ*, the surface chemical processes associated with corrosion and passivation.

Experimental

All Raman spectra were obtained using the 514.5 nm line of a Coherent Radiation Laboratories Model CR-3 argon ion laser. Descriptions of the Raman detection system and spectroelectrochemical cell have appeared previously (1, 4).

The following systems were investigated:

$\text{Ag}/[\text{Fe}(\text{phen})_3(\text{ClO}_4)_2]$

$\text{C} = 5 \times 10^{-6} \text{ M/Borate buffer/H}_2\text{O}$
pH = 8.4

$\text{Fe/phen; C} = 5 \times 10^{-3} \text{ M/Borate buffer/H}_2\text{O}$
pH = 8.4

The first one served as a reference system for the second.

All solutions were prepared with deionized water (Milli-Q, Millipore Corporation) and were thoroughly deoxygenated with prepurified nitrogen prior to the immersion of an electrode. 1,10-phenanthroline (Aldrich Chemical Company, Incorporated) was recrystallized twice from a mixture of CH_3OH and H_2O (1:10). $[\text{Fe}(\text{phen})_3] (\text{ClO}_4)_2$ (G. Frederick Smith Chemical Company) was recrystallized three times from CH_3OH . Polycrystalline silver electrodes were electrochemically roughened by a single double potential step ($E_1 = -0.6 \text{ V vs. SCE}$ and $E_2 = +0.2 \text{ V vs. SCE}$) anodization pulse passing 20 mC/cm^2 . Polycrystalline iron electrodes were mechanically roughened with grade 800 emery paper.

Results and Discussion

$\text{Ag}/\text{Fe}(\text{phen})_3^{2+}$.—Figure 1(a) shows the surface Raman spectrum of $\text{Fe}(\text{phen})_3^{2+}$ adsorbed on an anodized Ag electrode from a $5 \times 10^{-6} \text{ M}$ solution. At this concentration, the bulk RR scattering is expected to be negligible. To confirm that the spectrum in Fig. 1(a) is a true surface enhanced RR spectrum, both the potential dependence and depolarization ratios were investigated. The standard model of the electrochemical double layer predicts that cationic complexes such as $\text{Fe}(\text{phen})_3^{2+}$ would be most strongly adsorbed at potentials negative to the point of zero charge (pzc), which for silver is approximately -0.7 V vs. SCE (1). The coverage should decrease at potentials positive to the pzc. This behavior was observed for the $\text{Ag}/\text{Fe}(\text{phen})_3^{2+}$. The intense SERS signals found at -0.8 V (Fig. 1(a)) practically disappear below the

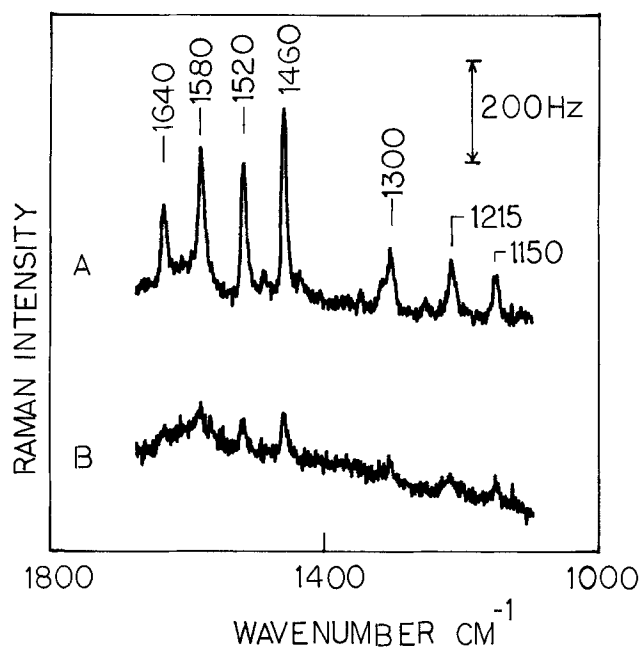


Fig. 1. Effect of potential on the SERS spectrum of $[\text{Fe}(\text{phen})_3]^{2+}$ on silver (a) -0.8 V (b) 0 V . Laser power 60 mW , slits 2 cm^{-1} , solution concentration of $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ $5 \times 10^{-6} \text{ M}$. Laser wavelength 514.5 nm .

noise level at 0.0 V vs. SCE (Fig. 1(b)) where the surface coverage is reduced. Depolarization ratios for the most intense peaks, given in Table I, were found to be above 0.7. In comparison, the corresponding bulk $\text{Fe}(\text{phen})_3^{2+}$ depolarization ratios are much lower (Table I).

In Fig. 2, Raman spectra of $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$ in solution, on a silver electrode, and in the solid state are compared. The relative intensities of the bands in the surface spectrum are similar to those of the solid state but differ from those of the bulk solution.

Fe/phenanthroline.—The Image Field Enhancement Model (IFE) of SERS predicts that an enhancement factor of only *ca.* 10^2 can be expected on transition metal substrates (1, 9). This value is below the minimum enhancement required to observe a surface-enhanced Raman spectrum while using a conventional cw laser/double monochromator system. However, by superimposing an enhancement due to RRS on the SERS enhancement, one might expect to increase the overall enhancement factor enough so that signal from the adsorbed species can be detected (see (17, 18)). We anticipated that in a 1,10 phenanthroline containing solution, the $\text{Fe}(\text{phen})_3^{2+}$ complexes can be formed only within the potential region where Fe^{+2} is the dissolution product (*viz.* active metal dissolution at low anodic potentials). It was of interest to find out if the dissolution of Fe in the presence of 1,10 phenanthroline takes place through the forma-

Table I. Resonance Raman spectra of $[\text{Fe}(\text{phen})_3]^{2+}$ depolarization ratios for the most prominent modes

$\Delta\nu/\text{cm}^{-1}$	a ρ_{solution}	b $\rho_{\text{surf, Ag}}$	c $\rho_{\text{surf, Fe}}$
1150	0.42	0.8	0.6
1215	0.35	0.75	0.55
1300	0.34	0.75	0.54
1460	0.30	0.80	0.46
1520	0.38	0.80	0.5
1580	0.40	0.70	0.5
1640	0.26	0.80	0.55

^a See R. J. H. Clark *et al.*, Ref. (21).

^b Measured at -0.8 V vs. SCE .

^c Measured at -0.5 V vs. SCE .

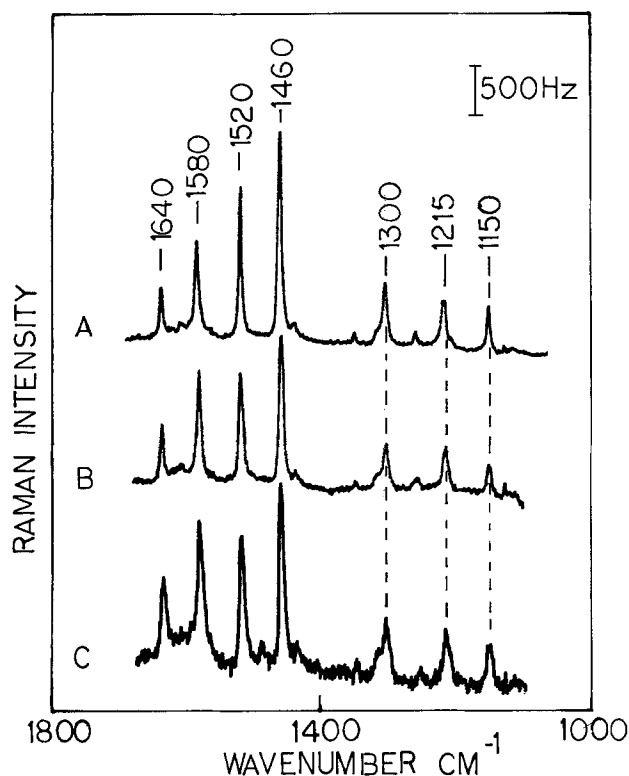


Fig. 2. Comparison of the Raman spectra of $\text{Fe}(\text{phen})_3^{2+}$ in various environments: (a) $5 \times 10^{-3}\text{M}$ aqueous solution, (b) solid $\text{Fe}(\text{phen})_3(\text{ClO}_4)_2$, (c) adsorbed on Ag electrode, as in Fig. 1a ($4\times$ expanded). Laser power 60 mW, slits 2 cm^{-1} , laser wavelength 514.5 nm.

tion of surface complexes of $\text{Fe}(\text{phen})_3^{2+}$, and whether we can observe surface spectra of these complexes.

In Fig. 3a, a Raman spectrum is shown for $[\text{Fe}(\text{phen})_3^{2+}]$ formed during the anodic dissolution of Fe electrode at -0.5V in a borate buffer solution containing 0.005M 1,10 phenanthroline. Since there is a continuous flux of Fe^{+2} into the solution and, therefore, continuous formation of $[\text{Fe}(\text{phen})_3^{2+}]$, one might expect the overall Raman spectrum to arise from scattering off both adsorbed and bulk species. The depolarization ratios for the various peaks in Fig. 3a lie between those for the corresponding bands of the complex in solution and on a silver electrode. This behavior might be expected for spectra having contributions from both bulk and adsorbed species.² In order to verify this hypothesis, the effect of potential on the peak intensities was investigated. Figure 3b shows an example of the spectrum at $+1\text{V}$. At this high anodic potential in the passive region, iron is dissolved as Fe^{+3} so that $\text{Fe}(\text{phen})_3^{2+}$ complexes are not formed. Consequently, all the RR lines characteristic for this complex disappear.

1,10 phenanthroline is an inhibitor of iron dissolution (22). Fischer and Yamaoka (22) have speculated, on the basis of their kinetic and capacitive measurements, that the metal dissolution of iron goes via surface ligand complexes with phenanthroline. This changes the potential distribution within the double layer and results in an inhibitive effect. In the present paper, we were able to show, at least for Fe/borate buffer system, that the $[\text{Fe}(\text{phen})_3^{2+}]$ complexes are indeed present at the iron surface during its anodic dissolution. This finding suggests that the combination of SERS and RRS can be successfully applied in investigations of some corrosion inhibitors for transition metals.

² However, a more precise distinction between the part of the signal due to surface and due to bulk species has not yet been done.

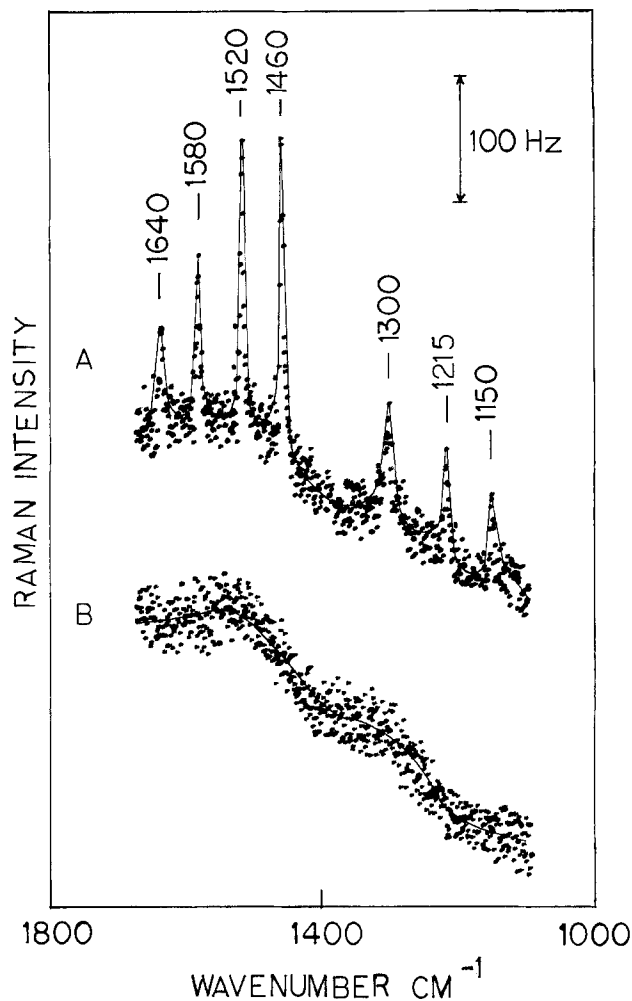


Fig. 3. Effect of potential on the SERS spectrum of $[\text{Fe}(\text{phen})_3^{2+}]$ on Fe electrode, in $5 \times 10^{-3}\text{M}$ 1,10-phenanthroline solution. (a) -0.5V (b) $+1\text{V}$. Laser power 200 mW, slits 2 cm^{-1} , laser wavelength 514.5 nm.

Ogura and Hackerman (23) have studied the anodic behavior of iron in borate buffer containing 1,10 phenanthroline. They have concluded that the light blue complex $[\text{Fe}(\text{phen})]_3^{+3}$ is formed within the passive region instead of the red $[\text{Fe}(\text{phen})]_3^{+2}$, which is formed within the active dissolution region. This is a natural consequence of Fe^{+3} production within the passive region, and Fe^{+2} production within the anodic active dissolution region. The effect of potential on the $[\text{Fe}(\text{phen})]_3^{+2}$ spectrum, presented in Fig. 3a, is most probably a result of this behavior, which obviously is not changed by the presence of the inhibitor. Unfortunately it was not possible to obtain the surface spectrum of $[\text{Fe}(\text{phen})]_3^{+3}$, due to lack of sensitivity. We have found that the molar extinction coefficient of $[\text{Fe}(\text{phen})]_3^{+3}$ is only $\sim 10^2$, in contrast to the value of $\sim 10^4$ for the $[\text{Fe}(\text{phen})]_3^{+2}$, i.e., that the absorbance of the green light by $[\text{Fe}(\text{phen})]_3^{+3}$ is several times lower than that of the Fe(II) complex (20).

In conclusion, the data presented are encouraging with regard to possible application of SERS + RRS to studies of metallic corrosion and dissolution. In the present investigation, the $\text{Fe}(\text{phen})_3^{+2}$ complexes were produced during the anodic dissolution of an iron electrode at low anodic potentials. We were able to detect, *in situ*, the surface signals from these complexes. This is indicative of the formation of these complexes as intermediates in an adsorbed state during the dissolution reaction. This type of structural information is not available from conventional electrochemical experiments. Thus, the combination of

SERS and RRS technique may prove to be a sensitive probe of the mechanism of wet corrosion.

Furthermore, surface enhanced RR spectra on Ag electrode were obtained for highly dilute solutions of the $\text{Fe}(\text{phen})_3^{2+}$ complexes, confirming that SERS has potential for detecting RR scattering from extremely small amounts of the adsorbed species from solution.

Acknowledgments

We gratefully acknowledge the financial support of the Office of Naval Research (Contract N00014-79-C-0369), and the National Science Foundation (Grant CHE-7824866).

Manuscript submitted Sept. 7, 1982; revised manuscript received July 18, 1983.

Northwestern University assisted in meeting the publication costs of this article.

REFERENCES

1. R. P. Van Duyne, in "Chemical and Biochemical Applications of Lasers," Vol. 4, C. B. Moore, Editor, pp. 101-185, Academic Press, New York (1979).
2. M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *J. Chem. Soc., Chem. Commun.*, **80**, (1973).
3. M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.*, **26**, 163 (1974).
4. D. L. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem.*, **84**, 163 (1974).
5. R. P. Van Duyne, *J. Physique*, **38**, C5-239 (1977).
6. M. G. Albrecht and J. A. Creighton, *J. Am. Chem. Soc.*, **99**, 5115 (1977).
7. V. V. Marinuyk and R. M. Lazorenko-Manevich, *Elektrokhimiya*, **14**, 452 (1978). V. V. Marinuyk, R. M. Lazorenko-Manevich, and Ya. M. Kolytyrkin, *ibid.*, **14**, 1019 (1978).
8. B. Pettinger and U. Wenning, *Chem. Phys. Lett.*, **56**, 253 (1978).
9. G. C. Schatz and R. P. Van Duyne, *Surf. Sci.*, **101**, 425 (1980).
10. S. G. Schultz, M. Janik-Czachor, and R. P. Van Duyne, *ibid.*, **104**, 413 (1981).
11. T. E. Furtak and J. Kester, *Phys. Rev. Lett.*, **45**, 1652 (1980).
12. G. C. Schatz, in "Surface Enhanced Raman Scattering," p. 39, Plenum Press, New York (1982).
13. M. Moskovitz and D. P. Dilella, *ibid.*, p. 263.
14. R. Naaman, S. J. Buelow, O. Chesnovsky, and D. R. Herschbach, *J. Phys. Chem.*, **84**, 2692 (1980); L. A. Sanchez, L. R. Burke, and J. R. Lombardi, *Chem. Phys. Lett.*, **79**, 219 (1981); R. L. Burke, J. R. Lombardi, and L. A. Sanchez, *Adv. in Chemistry*, **201**, 69 (1982).
15. H. Yamada and Y. Yamamoto, *Chem. Phys. Lett.*, **77**, 520 (1981).
16. B. H. Loo, *J. Chem. Phys.*, **76**, 5955 (1981).
17. G. Hagen, B. Simic-Glavaski, and E. Yeager, *J. Electroanal. Chem.*, **88**, 269 (1978).
18. T. M. Cotton, S. G. Schultz, and R. P. Van Duyne, *J. Am. Chem. Soc.*, **102**, 7960 (1980).
19. T. S. Lee, J. M. Koltzoff, and D. L. Leussing, *ibid.*, **70**, 2348 and 3596 (1948).
20. A. E. Harvey, J. A. Smart, and E. G. Amis, *Anal. Chem.*, **27**, 26 (1955).
21. R. J. H. Clark, P. C. Turtle, D. P. Strommen, B. Striesand, J. Kincaid, and K. Nakamoto, *Inorg. Chem.*, **16**, 84 (1977).
22. H. Fischer and E. Yamaoka, *Electrochim. Acta*, **10**, 679 (1965).
23. H. Ogura and N. Hackerman, *This Journal*, **121**, 1013 (1974).

Analysis of Passive Films on Austeno-Ferritic Stainless Steel by Microscopic Ellipsometry

Katsuhisa Sugimoto* and Shiro Matsuda

Department of Metallurgy, Faculty of Engineering, Tohoku University, Sendai 980, Japan

ABSTRACT

An ellipsometer which provides the determination of optical properties of a thin film on the microscopic area of a specimen has been developed. Using this ellipsometer the thickness and optical constants of passive films on individual grains in the microstructure of a 22Cr-10Ni austeno-ferritic stainless steel have been measured *in situ* in pH 6.0, $1 \text{ kmol} \cdot \text{m}^{-3} \text{Na}_2\text{SO}_4$ under potentiostatic control. It has been found that the films on α grains are thicker than those on γ -grains in both the passivity and the transpassivity regions. The variation in film thickness from grain to grain has also been measured. Significant differences in film thickness exist at α/γ phase boundaries. The film thickness varies even among grains of the same phase. Passive films on γ -grains are found to be thinner but more corrosion resistant than those on α grains.

Austeno-ferritic, or duplex, stainless steels have been celebrated for their good resistance to dangerous localized corrosion, such as pitting corrosion, crevice corrosion, intergranular corrosion, and stress-corrosion cracking (1-3). Owing to these superior characteristics, the demand for the steels as the material for equipment used in chloride media, for example, seawater heat exchanger tubes, continues to expand (4).

It is important, however, to note that the corrosion resistance of the steels depends on the volume ratio of ferrite (α) to austenite (γ) in the steel. The change in the structure of the steel caused by inadequate heat-treatment or welding, which accompanies the change in the ratio, deteriorates the corrosion resistance of the steels (2, 5). This means the corrosion resistance of the steels is controlled by that of each

phase in the steels. It is important, therefore, to know the properties of the passive film on each phase, which determine the corrosion resistance, for getting a better understanding about the corrosion characteristics of the steels.

Ellipsometry has been known as an effective method for *in situ* analysis of passive films and used extensively in the determination of the thickness and optical properties of the films on Fe-Cr (6), Fe-Cr-Ni (7-11), and Fe-Cr-Ni-Mo (12-15) alloys. There is no report, however, about the application of ellipsometry on the analysis of films on austeno-ferritic stainless steels. This is because an ordinary ellipsometer needs a fairly large measurement area, more than a few square millimeters, and simply gives total information about a film on the area containing many α and γ grains.

The purpose of present investigation is to determine the thickness and optical constants of passive

* Electrochemical Society Active Member.

Key words: microscopic ellipsometry, passive film, austeno-ferritic stainless steel.