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PREPARATION OF METAL-OXIDE-HYDROXIDE PRO-
TECTIVE LAYERS UNDER CONTROLLED pO_2 - pH_2O -T
CONDITIONS

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Preparation of Metal-Oxide-Hydroxide Protective Layers

Under Controlled pO_2 - pH_2O -T Conditions

Frank Dachtile, E.W. White and Rustum Roy

FINAL REPORT

Office of Naval Research, Metallurgy Program

Contract No. N00014-67-A-0385-C02, ONR 032-502

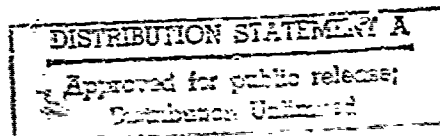
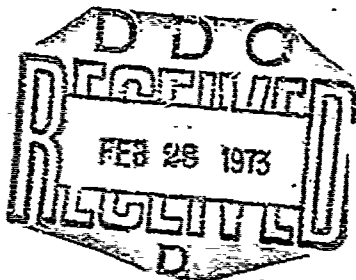
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As work progressed it was covered in eight technical reports, twelve publications and three theses (2 Ph.D., 1 M.S.).		Department of the Navy, Office of Naval Research, Metallurgy Program, Washington, D.C.
13. ABSTRACT		
Surface oxidation of metals was done in hydrothermal systems to 40,000 psi, with modifications to include the use of hydrogen peroxide solutions and high pressure oxygen. Oxidation of iron or steel under some of these conditions produced very dense, adherent films which, however, afforded no corrosion protection. The study of aluminum led to the synthesis of two new crystalline $Al(OH)_3$ phases and contributed to the understanding of the p-t relations in the system alumina-water. Under specific conditions films of the composition $Al(OH)_3$ or $AlO(OH)$ could be formed on the aluminum, crystallizing as bayerite or boehmite, respectively. The bayerite films were found to provide more resistance to attack in acidic media than those of boehmite. Scanning electron micrographs showed clearly that boehmite crystallized unevenly on aluminum in apparent response to epitactical influences. Interface reactions of oxides with steel under a variety of conditions were studied. Promising results were obtained with NiO-steel, heating in argon or vacuum at 600-750°C. The resultant surface consisted primarily of γ-nickel iron and provided a high degree of corrosion protection in warm, humid atmospheres. Soft x-ray spectroscopy techniques were developed for use in characterizing coatings as thin as 200Å thick on iron, titanium, aluminum, chromium and other metals. The oxygen x-ray spectrum was especially useful in distinguishing among the oxides on titanium and in assigning oxygen to oxides or interstitial positions. The oxygen Kα could also yield the ferrous/ferric ratio on steel.		

KEY WORDS	GROUP 1		GROUP 2		GROUP 3	GROUP 4
	ADJ	AT	ADJ	AT		
Hydrothermal oxidation of metals						
Oxygen x-ray emission						
Aluminum Surface Oxidation						
Nickel oxide - Steel interface reactions						
Characterization of surface layers						
X-ray emission band shifts						
Transition metal oxide surfaces						
Oxide film thickness						
Ellipsometry & Microprobe						
Corrosion layers						
Short range order						

Introduction

This research program received ONR support for the period March 1, 1967 to March 31, 1972. Work was concerned primarily with the preparation of oxidation films on metals under various pO_2 , pH_2O , and temperature conditions and the characterization of these films. The thrust of the research was to seek out conditions which would lead to the formation of corrosion resistant oxide or hydroxide films. The earliest work was with metal single crystals in order to establish the influence of orientation on the film forming processes. It was found, however, that the use of metals in polycrystalline form could yield about the same information more conveniently.

The long list of metals considered for study was narrowed down to aluminum and iron, along with titanium, nickel and chromium. Even with this restricted list, the matrix of experiments became extensive when trying to fit process parameters to what is known of the equilibria of these metals with oxygen, water or hydrogen peroxide solutions and then extending the studies to include pressures as high as 40,000 psi in the aqueous systems.

The principal methods for characterization of the corrosion "films" were to be scanning electron microscopy, soft x-ray spectroscopy, and x-ray diffraction. The SEM had just become available at the outset of the program and it was not clear to what extent it would be useful. Soft x-ray spectroscopy also was not a generally employed technique in corrosion research, so considerable effort was to be expended in adopting and extending the capability of this technique. By carefully combining information for SEM and soft x-ray spectroscopy, it was possible to characterize even thin, noncrystalline reaction products.

Results

The major findings of the program were covered in eight technical reports, several publications, two Ph.D. and one M.S. theses and oral presentations at technical society meetings. For convenience, the reports, publications, and theses are compiled in lists I, II, and III along with their abstracts, where necessary.

Overall results may be summarized as follows:

1. Because the chief interest was to determine the composition and structure of the thinnest films capable of protecting the metal surfaces, the procedures used for preparations were not designed to achieve equilibria. However, it was found in general that reaction products on metal surfaces would be formed in a manner congruent with equilibrium diagrams in so far as phase areas were concerned, although the corresponding phases were not necessarily identical. Thus, in the oxidation of aluminum in high pressure-high temperature water to 40,000 psi a reaction diagram is obtained where, with increasing temperature, the product phase sequence is bayerite-boehmite-corundum, whereas for equilibria, the sequence would be gibbsite, diaspor, corundum.
2. Weight loss and potentiometric studies revealed that thin films hydrothermally formed on aluminum in the bayerite product field provided considerably more resistance to corrosion in acid medium than films formed in the boehmite product field. The films were also more resistant than freshly prepared and etched but otherwise unreacted aluminum surfaces.
3. It was found that crystalline orientation definitely controlled the morphology of surface films on aluminum. Epitactical relations could be deduced from oriented growth of boehmite on aluminum stock which had preferred orientation resulting from the rolling operations, although this method is not as specific as methods using oriented single crystal surfaces.
4. Oxidation of steel or iron surfaces in high pressure oxygen or hydrogen peroxide solutions under a range of pressure-temperature conditions resulted in dense adherent films, but the films did not serve as protective barriers in corrosive atmospheres.
5. One line of research led to an investigation of interface reactions between steel and metallic oxides. Hydrothermal approaches were found to be unsatisfactory. Very promising results were obtained in the surface reaction between steel and nickel oxide at temperatures

between 600 and 750°C in vacuum or argon. The resulting surfaces proved to consist primarily of gamma-nickel-iron and were found to be highly effective in protecting the steel from corrosion in warm, humid atmospheres. Further work in this area seems warranted.

6. The scanning electron microscopy studies proved useful in characterizing the morphologies of crystalline reaction products on the surfaces of treated metals. However, it was somewhat disappointing to discover that little morphological information could be obtained from the thin protective layers on aluminum.

7. The soft x-ray spectroscopy studies concentrated on the lighter elements (second and third period). The first phase of the work was to assemble some 80 pure oxide and hydroxide standards for calibration. The second phase consisted of the actual characterization. It was found to be possible to characterize discontinuous thin (less than 200Å) coatings on most metals, even when the corrosion product was x-ray amorphous. The oxygen x-ray spectrum was more useful than anticipated. For example, it was found that the various oxides of titanium could be distinguished, and interstitial oxygen in titanium metal could also be distinguished from discrete oxide layer formation. Similarly, the oxygen K α peak could be used to establish the proportions of ferrous to ferric iron on steel surfaces. Also, it became quite easy to distinguish among aluminum oxides, oxyhydroxides, and hydroxides on aluminum. Again, this applies to discontinuous thin layers, even when x-ray amorphous.

List I. Technical Reports

No. 1 1 August 1968

Title: Structural Characterization of Thin Aluminum Oxide-Hydroxide Layers by the Aluminum and Oxygen X-Ray Emission Bands

Abstract: A new technique is outlined for the characterization of thin films of crystalline and amorphous aluminum oxide, aluminum oxyhydroxides and aluminum hydroxides. Shifts in Al K α and OK α X-ray emission lines of known examples of these compounds are presented and are used to identify unknown Al-O-OH compounds.

No. 2 8 August 1968

Title: Comprehensive Survey of Oxygen X-Ray Emission Band Shifts

Abstract: Shifts in the oxygen K-emission band from some fifty simple oxide compounds have been studied as part of a program to evaluate soft x-ray spectroscopy as a tool for characterizing thin layers on metals. The main peak tends to shift to shorter wavelength as the valence of the coordinating cation increases. For oxides of transition metal element one can determine the cation valence from the O-K α position. For the oxide of the nontransition metals the oxygen peaks tend to be relatively narrow and exhibit little or no resolved fine structure. For oxides containing highly charged cations the OK β' band becomes a well resolved feature on the long wavelength side of the main peak.

No. 3 2 December 1969

Title: Thin Film Characterization by Electron Microprobe and Ellipsometry: SiO₂ Films on Silicon

Abstract: A combined electron microprobe and ellipsometric study of thin SiO₂ films on silicon provides a technique for compositional and morphological characterization of thin films.

No. 4 1 January 1970

Title: Oxygen X-Ray Emission Band Shifts Applied to the Characterization of Transition Metal Oxide Surface Layers

Abstract: By measuring the OK peak intensities, shape and size, one can determine what oxides have formed on Ti, Mn and Fe. In case of Ti, interstitial oxygen can be identified.

No. 5 3 November 1970

Title: Characterization of Corrosion Layers on Aluminum by Shifts in the Aluminum and Oxygen X-Ray Emission Bands.

Abstract: An x-ray emission technique is outlined for the characterization of thin layers of aluminum oxides, aluminum oxyhydroxides, and aluminum hydroxides on aluminum. Shifts in the Al K β and O K α x-ray emission lines of standard compounds are presented and are then used to characterize thin corrosion layers on aluminum.

No. 6 15 June 1971

Title: An Interpretation of the Chemical Effect on the Aluminum and Oxygen X-Ray K-Emission Bands from Hydrated Aluminas

Abstract: Shifts in the Al K β and O K α x-ray emission bands from α and γ -alumina and four hydrated aluminas are interpreted in terms of the relative degree of ionicity of the bonding and the relative strength of the hydrogen bonding in these compounds.

No. 7 6 August 1971

Title: Hydrothermal Oxidation of Aluminum

Abstract: Aluminum surfaces were oxidized under hydrothermal conditions over a pressure range of up to 40,000 psi and temperatures to 500°C. The oxidized surfaces were examined by x-ray diffraction, soft x-ray emission spectroscopy, and scanning electron microscopy (SEM). Crystalline product phases formed on the surfaces over the p-t range were bayerite, boehmite, and corundum, each in a fairly well defined region. Along the 10,000 psi isobar bayerite formed up to 150°C, boehmite from 150 to 425°C and corundum above 425°C, and along the 30,000 psi isobar the temperatures are higher by 25° in each case. SEM revealed the formation of dense mat surfaces, amorphous to x-rays, in early stages of treatment in the bayerite and boehmite reaction regions, with those formed in the bayerite region being denser and of finer texture. Measurement of the Oxygen K α peak position in the soft x-ray emission from the adherent films indicated that in the very earliest stages of hydrothermal oxidation of aluminum the film composition is approximately $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and then with increasing time of reaction approaches the composition of the characteristic phase for the conditions. Preliminary tests have shown that films formed under the bayerite conditions are more resistant to corrosive attack than "boehmite" type films.

No. 8 12 December 1972

Title: Interface Reaction of Nickel Oxide on Steel

Abstract: In vacuum or an argon atmosphere, nickel oxide reacts with steel at 600 to 750°C to form a surface layer of γ -NiFe which affords corrosion protection to the steel in warm, humid conditions.

List II. Theses

George Savanick, PhD 1970

The Chemical State of Oxygen Aluminum and Sulfur in Solids Studied by Soft X-Ray Spectroscopy

Abstract: It was shown that members of a set of six Al-O-OH compounds including $\gamma\text{-Al}_2\text{O}_3$, corundum, boehmite, diaspore, gibbsite, and bayerite can be distinguished from each other with reference to the aluminum band were found to be strongly correlated to the refractive indices of the compound indicating a relation between the chemical effect and the degree of ionicity of the compound. The oxygen band shift was found to be a function of the amount of hydrogen present and the type of hydrogen-oxygen bonds formed. It was demonstrated that the chemical effect in soft x-ray emission spectra can be used to characterize thin surface layers regardless of their degree of crystallinity or uniformity of thickness.

It was found to be feasible to use the chemical shifts in these compounds to identify corrosion products on aluminum provided the unknown is a single phase of one of these compounds. This method can be extended to study the changes in chemistry with depth in stratified oxide layers by plotting peak appearance versus accelerating potential.

The chemical shift technique was extended to the study of oxide films on transition metals. It was shown that these films can be studied without interference from the metal substrate because a unique identification of the oxide can be made with reference only to the oxygen band. This permits the characterization of very thin films on these metals.

The chemical effect in soft x-ray emission bands gives indication of becoming increasingly important in the characterization of materials. The chemical state and near neighbor environment of light elements can be determined from low elemental concentrations. The electron probe extends the capability of this technique to permit the determination of the spatial distribution of the chemical effect over the sample surface and the variation of this effect with depth in surface layers. This technique should find application in a wide range of practical problems in the materials industries.

Paul Donald Gigl, PhD 1972

Pressure-Temperature Studies of the Alumina-Water and the Aluminum-Water System

Abstract (partial): The system alumina-water was studied in the range of 20 to 500°C and at pressures to 60 kb in opposed anvil apparatus. Two new phases were found and designated β' -Al(OH)₃ and δ -Al(OH)₃. The β' -Al(OH)₃ phase was obtained only from gibbsite, in 60% conversions, at pressures over 15 kb and temperatures up to 200°C. On the basis of x-ray diffraction, infrared and thermal analysis it is considered to be a polytype of bayerite. The conditions of formation of this new phase may be a close approximation of the bayerite stability field, although this supposition could not be observed experimentally. Cell parameters are $a_0 = 5.067$, $b_0 = 8.671$, $c_0 = 9.41\text{\AA}$ and $\beta = 90.49^\circ$.

In the presence of water δ -Al(OH)₃ was crystallized from β' -Al(OH)₃, diaspore, boehmite, bayerite, corundum and gibbsite with complete conversions after 75 to 230 hours under a well defined range of p-t conditions. The phase occurred above 18 kb at temperatures above that for the formation of β' -Al(OH)₃. The higher p-t boundary was the locus for the reaction δ -Al(OH)₃ to diaspore (AlOOH) + H₂O, passing through 18 kb, 200°C and 60 kb, 410°C. The phase was isolated as euhedral crystals (0.2 mm). Thermal and infrared analyses, and optical properties show that it is much like the other aluminum trihydroxides. The unit cell is orthorhombic with $a_0 = 5.141$, $b_0 = 5.063$, $c_0 = 7.259\text{\AA}$, and $Z = 2$.

Isobaric and isothermal equilibrium sections are postulated for the system Al₂O₃-H₂O, setting aside boehmite as a metastable phase.

For the balance of the abstract covering the work with aluminum and water see that listed in Table I for Technical Report 7, Hydrothermal Oxidation of Aluminum.

Sheryl Birkhead, M.S. 1972

A Study of Oxy-Hydroxide Layers Formed on Aluminum

Abstract: Aluminum surfaces were oxidized hydrothermally at temperature and pressure conditions necessary to produce characteristic oxyhydroxide (boehmite) or hydroxide (bayerite) surface films. The corrosion of the aluminum substrates in corrosive media was found to be dependent on the morphology and composition of the surface films, with the best protection afforded by thin films of bayerite formed on lightly etched aluminum. Boehmite crystallized more selectively on aluminum surfaces, tending to leave areas subject to attack. Both the morphology of the surface films and x-ray diffraction from them showed a close relationship between crystalline orientation of substrate and films.

List III. Papers Published

The following papers were published during the period of this contract, resulting either from work sponsored solely by this program or in association with related programs in progress during that period:

- Baun, W.L., E.W. White. Clinocllore: A Versatile New Analyzing Crystal for the X-Ray Region λ -27Å. Anal. Chem. 41, 831-832 (1969).
- Baun, W.L., E.W. White. A Vacuum Spectrometer for Studying the Chemical Effect on Soft X-Ray Spectra. In: Advances in X-Ray Analysis 13, 237-247 (1969) Editors: Henke, Newkirk, Mallet; Plenum Press, New York.
- Knausenberger, W.H., K. Vedam, E.W. White, W. Zeigler. Thin Film Characterization by Electron Microprobe and Ellipsometry: SiO₂ Films on Silicon. Appl. Phys. Letters 14, 43-45 (1969).
- White, E.W., G.V. Gibbs. Structural and Chemical Effects on the Al K β X-Ray Emission Band Among Aluminum-Containing Silicates and Aluminum Oxides. Amer. Mineral. 54, 931-936 (1969).
- Gigl, P.D., G.A. Savanick, E.W. White. Characterization of Corrosion Layers on Aluminum by Shifts in the Aluminum and Oxygen X-Ray Emission Bands. J. Electrochem. Soc. 117, 15-17 (1970).
- Johnson, G.G., Jr., E.W. White. X-Ray Emission Wavelengths and KeV Tables for Nondiffractive Analysis. ASTM Data Series DS-46 (1970), American Society for Testing and Materials, 38 pp, Philadelphia, Pa.
- Johnson, G.G., Jr., E.W. White. Two New Reference Tables for X-Ray Emission Analysis. Materials Research and Standards 10, 25-27 (1970).
- Krause, H.B., G.A. Savanick, E.W. White. Oxygen X-Ray Emission Band Shifts Applied to the Characterization of Transition Metal Oxide Surface Layers. J. Electrochem. Soc. 117, 557-558 (1970).
- White, E.W., G.G. Johnson, Jr. X-Ray Emission and Absorption Wavelengths and Two-Theta Tables. 2nd Edition, ASTM Data Series DS-37A (1970), American Society for Testing and Materials, 293 pp, Philadelphia, Pa.
- White, E.W., G.G. Johnson, Jr. X-Ray Emission and Absorption Edge Wavelengths and Interchange Settings for LiF Geared Curved Crystal Spectrometer. Special Publication No. 1-70, 1-68 (1970), Earth and Mineral Sciences Experiment Station, The Pennsylvania State University.

White, E.W. Electron Probe. Analytical Methods for Materials Investigation. Ed. G.A. Kirkendale, Gordon and Breach Sci. Publishers, New York, N.Y. pp 264 (1971).

As a result of soft x-ray contributions made during this program, one of us (E.W. White) was invited to write a chapter for a book on the subject. This chapter, "Application of Soft X-Ray Spectroscopy to Chemical Bonding Studies with the Electron Microprobe," will appear soon in the book, Microprobe Analysis, being published by John Wiley and Sons. This book is edited by C.A. Anderson.

Personnel

The principals are happy to acknowledge the participation in the research by the graduate students and research associate listed below. They were associated with the program at various times in the contract period and made substantial contributions within the scope of their experience and training. Their advanced academic degrees and professional activities are indicative of their continuing involvement with academic or industrial research.

Sheryl Birkhead	Graduate student. Received MS June, 1972. Employed by Flow Laboratories, Rockville, Md.
P.D. Gigl	Graduate student. Received Ph.D. March, 1972. Employed by General Electric Co. (Research and Development), Worthington, Ohio.
R. Hurley	Graduate student. Supported for a brief period by this program. Worked on soft x-ray studies of phosphorous. This work constituted a portion of his M.S. thesis, and a manuscript is now being submitted for publication.
H.B. Krause	Postdoctoral Research Associate. Present position, Associate Professor of Physics, Northern Illinois University, DeKalb, Ill.
G.A. Savanick	Graduate student. Received Ph.D. Sept., 1970. Employed by U.S. Bureau of Mines, Minneapolis, Minn.
S. Stanic	Graduate student. Candidate for Ph.D. in Physics Department, The Pennsylvania State University.

Related Work

As is evident from the titles of publications and theses listed, the work on this program influenced that in other areas. Complete characterization of ultimate protective surfaces remains elusive, but an important advance was made with the combination of electron microprobe and ellipsometric techniques by Drs. E. White and K. Veum. Dr. White continues to expand his pioneering soft x-ray spectroscopy studies.

The hydrothermal oxidation study of aluminum by P.D. Gigl provided many observations which were helpful in an understanding of the alumina-water system. The results are being prepared for publication and should be of interest in the area of ceramics, petrology, and crystallography.

Our experiments with nickel oxide and steel surfaces yielded results that may be applicable in the area of corrosion protection. In addition, they come at a time of a surge of interest in interface reactions of oxide-metal systems. We are in consultation with Dr. G. Simkovich and Dr. Earle Ryba of our Metallurgy Department concerning our findings, and serious thought is being given toward formulating a program that will extend them in a fundamental quantitative manner.

From a characterization standpoint, perhaps the most significant aspect of the work was the result of studies of the oxygen emission band. For the first time, oxide, hydroxide and oxyhydroxide layers were characterized spectroscopically by the information from the oxygen anion rather than from the metal cations present in combination with the oxygen.