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PROVOCATIVE QUESTIONS IN METAL/SOLUTION REACTIONS TO WHICH MÖSSBAUER SPECTROSCOPY SHOULD BE APPLIED

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ABSTRACT

Eight problems in the field of metal/solution chemistry capable of attack by Mössbauer spectroscopy are outlined. These include: studies of corrosion beneath a coating; chemical factors associated with the delamination of a coating during corrosion; the chemical nature of the bond between steel and an organic coating; the effect of cobalt on the corrosion of galvanized steel; corrosion inhibition in aqueous solution; the behavior of inhibitors in organic coatings; the nature of the inhibition of corrosion by tin ions and the ion exchange properties of iron corrosion products.

Huit problèmes concernant la chimie d'interface métal/solution, utilisant la spectroscopie Mössbauer, sont présentés. Ils comprennent des études de corrosion sous un recouvrement dont les propriétés chimiques sont associées à sa séparation en différentes couches durant la corrosion; la nature chimique de la relation entre l'acier et un recouvrement organique; l'effet du cobalt sur la corrosion de l'acier galvanisé; l'inhibition de la corrosion en solution aqueuse; le comportement des inhibiteurs dans les recouvrements organiques; la nature de l'inhibition de la corrosion par l'étain sous forme d'ions et les propriétés de l'échange ionique des produits de la corrosion du fer.

Reviews have previously been prepared on the application of Mössbauer spectroscopy (MS) to the field of corrosion.^{1,2} The purpose of this paper is to outline a number of problems and unanswered questions in metal/solution reactions to which MS can and should be applied. It is hoped that this paper will stimulate specialists in MS to apply their talents to an attack on the problems cited.

Underfilm Corrosion. Organic coatings are often applied to metallic substrates to reduce corrosion. After a period of time, most coatings lose their protective properties in a highly localized manner when exposed to aqueous environments. Deterioration occurs in isolated spots at the coating/substrate interface and gradually spreads with time. Electrical measurements in our laboratory³ show promise for detection of these points of local breakdown at an early stage, but the electrical measurements are largely sensitive to changes in the coating rather than changes in the substrate.

Studies of the substrate require a technique that will scan the steel surface, coated with an

organic material, with a highly collimated beam of gamma rays and monitor spectral lines due to re-emission that do not overlap the spectrum for pure iron. The work of Graham and Cohen⁴ has shown that the common corrosion products of iron yield characteristic Mössbauer spectra. The most promising energy regions to monitor are those which fall outside the metallic iron spectrum in the case of Fe_2O_3 and Fe_3O_4 and those near the center of the iron spectrum in the case of $\gamma\text{-FeOOH}$ and FeCO_3 . Once an active site has been located, an entire spectrum may be obtained. The difficulties of performing such an experiment are severe: (a) availability of a highly collimated beam of sufficient intensity, (b) obtaining a sufficient number of reemitted gamma rays that reach the detector, (c) interferences from materials in the coating and iron compounds in the substrate, and (d) devising a scanning technique that will be vibration-free.

Cathodic Delamination. Organic coatings on a steel substrate often delaminate during corrosion as a consequence of the fact that the anodic reac-

tion is highly localized and the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- = 2\text{OH}^-$, occurs at the periphery of the anodic area because water and oxygen are supplied through the coating. The important unanswered question is whether the delamination occurs because of chemical changes at the coating/metal oxide interface or because the oxide itself changes in chemical composition. Since the oxide is generally of the order of 5 nm in thickness and the organic coating thickness generally is 10 μm or more, innovative experimental methods are required. Using ^{57}Co at the interface for emission spectroscopy is not attractive because the chemistry of cobalt is not identical to that of iron. Use of conversion electron techniques does not appear promising because of the thickness of the coating. The Mössbauer technique is appealing because of its non-destructive nature. The development of a satisfactory experimental procedure to address this question is, therefore, worthy of pursuit.

Character of Steel/Organic Coating Bond. A test for paint adherence to steel involves exposing the painted metal to either a hot aqueous solution or to condensing moisture. In some cases the paint loses adherence to the steel after such exposure and can be readily peeled off. If the painted steel panel is thoroughly dried after exposure to boiling water, good adherence between the paint and the steel is regained. The effect of water on the adherence appears to be reversible. It is suggested that MS be applied to a better understanding of this phenomenon. One possible approach is to coat a steel substrate with a thin layer (5 nm) of cobalt doped with ^{57}Co and determine the emission Mössbauer spectrum of a painted sample while exposed to boiling water and again after the coating is completely dry. Differences in the spectrum may provide clues as to the character of the steel water interaction at the paint/steel interface.

Alloyed Galvanized Steel. It has recently been reported by a manufacturer of galvanized steel that electrogalvanized steel containing small amounts of cobalt exhibits superior corrosion performance. This result is unexpected because the relatively high exchange current density for the cathodic reaction on cobalt as compared to that on zinc suggests that cobalt should increase the corrosion rate. It is proposed that zinc be electroplated on steel from a plating bath containing cobalt doped with ^{57}Co and that the emission spectrum be ob-

tained before and after exposure to various corrosive environments. The purpose of the experiment is to determine (a) the chemical state of cobalt in the zinc before corrosion and (b) the chemical state of cobalt at the surface during the corrosion process. The availability of information on the emission spectra of many cobalt oxides, hydroxides, and hydroxyoxides⁵ may be very useful here.

Corrosion Inhibition in Aqueous Solution. The mechanism of corrosion inhibition is still poorly understood. For example, it is not known if inhibitors for the corrosion of iron function because of an interaction with metallic atoms at the surface or through interaction with a thin oxide film present on the surface. Basic information is required concerning the character of the chemical bond between the substrate and the inhibitor molecule.

It is proposed that emission MS be applied to this question. A thin layer (5-10 nm) of cobalt doped with ^{57}Co should be prepared on a cobalt substrate and the emission pattern should be obtained while the cobalt is exposed to an aqueous environment of pH 2-5. The exact pH to be used will be determined by the rate of dissolution of the cobalt in the medium. If the cobalt dissolves more rapidly than a spectrum can be generated, useful data will not be obtained. Of course, the reaction can be halted by plunging the wet sample in liquid nitrogen and the spectrum be determined at low temperature. The same experiment should then be performed with an aqueous solution which contains known corrosion inhibitors such as benzotriazole, pyridine, a polyamine, etc. Differences in the Mössbauer spectrum in the presence and absence of the inhibitor may yield information about the chemical bond between cobalt atoms at the surface and the inhibitor molecule. Innovative approaches are required as is skill in the interpretation of data.

Behavior of Inhibitors in Organic Coatings. Corrosion resistance is often built into organic coatings (paints) by the addition of a corrosion inhibitor. One of the means which has been hypothesized for the effectiveness of inhibitors is based on the solubility of the inhibitor. It has been suggested that when the coating is wetted by rain, water absorption by the coating is rapid and some of the inhibitor enters into solution and migrates to the metal interface by a diffusion pro-

cess. It is thus available at the metal/coating interface whenever the coating is wet. Such a hypothesis requires that the inhibitor be very slightly soluble because high solubility would cause rapid leaching of the active ingredient from the coating.

It is proposed that an organic coating be formulated with a ferromagnetic or antiferromagnetic material that will serve as a model for a corrosion inhibitor. A cobalt additive should be doped with ^{57}Co and the emission spectrum should be determined immediately after the coating is formulated and then after the coating has been alternately wetted and dried for many cycles. The emission spectrum should be taken as a function of temperature and changes in particle size or particle size distribution should be sought by means of Mössbauer measurements as a function of temperature. Candidate materials that might serve as a model for a corrosion inhibitor include Co_2VO_4 , MnCo_2O_4 , LiCoPO_4 , CaCoSiO_4 , and $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ doped with ^{57}Co . The criteria in the choice of the model for the corrosion inhibitor are its solubility and the rate of solution. The solubility behavior of the known corrosion inhibitor, SrCrO_4 , should be approximated by the model inhibitor.

Corrosion Inhibition by Tin Ions. Tin ions are effective inhibitors⁶ for the corrosion of iron in many different aqueous media. The question remains unanswered as to the mechanism by which the tin ion serves as an inhibitor. Does it adsorb at kink sites and make the active cathodic and anodic regions less active? Does it form an intermetallic compound such as FeSn_2 at the surface? Or is there formed a corrosion resistant iron tin oxide? There is a special interest at the present time as to the effectiveness of tin ions in reducing corrosion of steel by high temperature water.

It is proposed that steel specimens be exposed to aqueous solutions containing dissolved tin ions (containing ^{119}mSn) at temperatures up to 300°C and that the emission spectrum of tin be obtained after the steel sample has been cooled to room temperature or below. The low f factor for elemental tin at room temperature suggests that it would be necessary to generate the emission spectra at liquid nitrogen temperature. Hopefully, spectra characteristic of specific tin species may then be obtained.

Ion Exchange Properties of Corrosion Products.

The costs of cleaning corroded steel surfaces before painting is very high, particularly when the steel is in relatively inaccessible areas such as on bridges and tall structures. Environmental hazards associated with sandblasting are limiting the applicability of this cleaning method. There is great interest in the development of coating materials that can be applied to poorly prepared surfaces and yet give superior corrosion performance. There is thus great interest in understanding better the surface properties of iron corrosion products so that coatings can be designed to adhere well to those corrosion products that have good integrity and are intimately attached to the steel base metal.

Recent work by Fowkes⁷ suggests that adherence between inorganic materials and polymers can be viewed as an acid/base interaction. Increased knowledge of the acid/base character of iron corrosion products is a worthwhile goal. It is suggested that high surface area $\gamma\text{-FeOOH}$ be prepared using ^{57}Fe and that transmission Mössbauer spectra be determined while the oxyhydroxide is suspended in aqueous solution in the absence and presence of ions that will exchange with the protons on $-\text{OH}$ groups at the surface. $\gamma\text{-FeOOH}$ is selected as the iron corrosion product to be used because the spectrum is a simple doublet. Spectra should be taken as a function of pH in the presence of ions such as Na^+ , Ca^{++} , Rb^+ , and Sr^{++} . Changes in linewidths, chemical shift, and quadrupole splitting should be sought as indicative of the ion exchange process.

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