Influence of organic gels on the corrosion of 70/30 cupro-nickel alloy in seawater

by David Edwin Dobb

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University

Abstract:
A comprehensive evaluation of the effects of bacto-agar coatings on the corrosion behavior of 70/30 cupro-nickel alloy in seawater is presented. The study provides a data base for isolating physical effects of bacterial caused biofouling layers from their specific chemical effects. Bacto-Agar (Difco, Detroit Mi.) is shown to be a good candidate material to represent a nonviable biofouling layer because of their chemical and physical similarities. Agar layers ranging in thickness from 0 to 60 microns can be reproducibly applied to tubular section samples of the alloy. Once applied, the agar acts primarily as a diffusion barrier to corrosion reactants and products. It will significantly affect the tarnish rate and corrosion product growth morphology if applied prior to corrosion. Its effects are minimal if applied to a sample that has been precorroded in excess of one day. The major corrosion parameters considered include specimen geometry, exposure time, flow, seawater chemistry, temperature, and sample pretreatment. Data is presented that systematically evaluates each of these parameters when agar is present and when it is absent. Diffusion of OH^- ions generated by the cathodic reduction of O2 at the solution-metal interface appears to be the rate controlling factor during initial exposure. Times in excess of one hour show rate dependence from diffusion through the tarnish layer. Appropriate mechanisms are proposed and discussed. In addition, numerous analytical techniques are developed for study of the micro-thin layers at the sample surface. The combination of mass balance and scanning auger analysis is shown to be crucial toward understanding the corrosion process. Procedures for characterization of the microstructure of agar are also presented.

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TABLE OF CONTENTS

Table of Contents - Continued

Table of Contents - Continued

LIST OF TABLES

List of Tables - Continued

LIST OF FIGURES

List of Figures - Continued

List of Figures - Continued

List of Figures - Continued

List of Figures - Continued

ABSTRACT

A comprehensive evaluation of the effects of bacto-agar coatings on the corrosion behavior of 70/30 cupro-nickel alloy in seawater is presented. The study provides a data base for isolating physical effects of bacterial caused biofouling layers from their specific chemical effects. Bacto-Agar (Difco, Detroit Mi.) is shown to be a good candidate material to represent a nonviable biofouling layer because of their chemical and physical similarities. Agar layers ranging in thickness from 0 to 60 microns can be reproducibly applied to tubular section samples of the alloy. Once applied, the agar acts primarily as a diffusion barrier to corrosion reactants and products. It will significantly affect the tarnish rate and corrosion product growth morphology if applied prior to corrosion. Its effects are minimal if applied to a sample that has been precorroded in excess of one day. The major corrosion parameters considered include specimen geometry, exposure time, flow, seawater chemistry, temperature, and sample pretreatment. Data is presented that systematically evaluates each of these parameters when agar is present and when it is absent. Diffusion of OH^- ions generated by the cathodic reduction of O_2 at the solution-metal interface appears to be the rate controlling factor during initial exposure. Times in excess of one hour show rate dependence from diffusion through the tarnish layer. Appropriate mechanisms are proposed and discussed. In addition, numerous analytical techniques are developed for study of the micro-thin layers at the sample surface. The combination of mass balance and scanning auger analysis is shown to be crucial toward understanding the corrosion process. Procedures for characterization of the microstructure of agar are also presented.

INTRODUCTION

Uses of Cupro-nickel Alloys

Copper and its alloys have been used extensively during the past 60 years for many fresh water and marine applications. Ship hulls and propellers, piping, and condensor tubes are frequently made of copper alloys because of special properties not seen in other metals. Good mechanical workability, excellent electrical and thermal conductivity, and good fouling and corrosion resistance are the main reasons for the widespread acceptance of copper alloys. Fouling and corrosion resistance are the most interesting properties to study from an academic as well as practical standpoint. Fouling resistance is assisted by the release of cupric ions as corrosion products during corrosion. Cu^{+2} has been shown to be toxic to marine organisms that attach to the metal surface.[1] Even if a resistant species gains a "foothold", it will eventually be swept away because of a buildup of nonadhering, nonprotective corrosion products such as paratacamite ($Cu_2(OH)_3Cl$) or cupric hydroxide ($Cu(OH)_2$) between the organism and the metal surface.[2]

Actual metal loss due to corrosion is low, on the order of 0.001 ipy (inches per year) in quiet seawater for 70/30 and 90/10 cupro-nickels. Both alloys have been exposed in service to seawater for periods of 14 to 16 years and still exhibited a similar low corrosion rate.[3] Figure 1, A-D, summarizes the applications of many copper alloys and their corrosion rates in seawater.

Figure 1A shows corrosion rate data in mils per year for one year immersion tests of copper alloys used as condensor tubing and other heat transfer applications. Each alloy was tested for loss of tensile strength, weight loss, degree of impingement (erosion), and pitting susceptibility in clean, flowing seawater. The close grouping of points for a given alloy indicates a very dependable material while badly scattered data indicate the alloy would be a poor choice for seawater applications. The data indicate that the 70/30 cupro-nickel alloy containing higher Fe levels (0.42%) is superior to all other alloys tested.

Figure 1B shows the same type of corrosion data for copper and certain bronzes high in copper. The usefulness of the materials depend on the conditions of service. For example, if the metal is to be used under low velocity flow conditions, the rate of impingement data can be ignored. The data show Duronz IV (95%Cu,5%Al,0.25%As) to be most suitable in general seawater applications, especially if impingement effects are unimportant. Duronz V (98%Cu,2%Si) shows the poorest performance of all of the alloys tested,