THE POSSIBLE RELATIONSHIP BETWEEN LEWIS ACID SITES ON TITANIUM OXIDE SURFACES AND THE PENETRATION OF THE OXIDE FILM BY CHLORIDE ION

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Introduction

The effect of halide ions, particularly Cl^- ion, in activating a passive metal surface is a well known phenomena in the corrosion and stress corrosion cracking (SCC) of metals in aqueous systems and appears to be involved even in the SCC of titanium and titanium alloys in methanol. Although no generalization about the cause of passivation applicable to all metals can be made it is likely that the passivation of very active metals such as titanium and titanium alloys is caused by the rapid formation under most conditions of a coherent relatively thin film of oxides-hydroxides. For such films it is usually stated that chloride ion can penetrate the film although the exact mechanism of penetration is never explained in detail.

In recent years, the development of experimental techniques for obtaining the infra-red spectra of an adsorbed species on an oxide surface has given considerable information about the nature of the groups located at the surface. Recently (1,2) it has been shown that the infra-red spectra of adsorbed ammonia and pyridine on rutile (TiO_2) surfaces indicates that two types of Lewis acid sites are present on the surface. A Lewis acid site is one which can bond to a molecule possessing an unshared pair of electrons. On rutile these sites remain unchanged by adsorption and desorption of water, which is a Lewis base. On mixed oxides other work indicates that the surface also contains Brönsted acid sites in addition to Lewis acid sites and hydration of the surface in some cases changes some Lewis acid sites into Brönsted acid sites. A Brönsted acid site is one which can furnish a proton (H^+) to the adsorbed molecule and its reaction with an adsorbed molecule, like ammonia, will be the formation of NH_4^+ whose infra red spectra differs from that of NH_3 sharing its lone pair of electrons with a Lewis acid site. Another way of distinguishing between the two types of acid sites is to use an amine such as pyridine whose basic strength is so low that it cannot form a stable addition product with a proton but because of its lone electron pair can still react with a Lewis acid site. The value of K_b for NH_3 in water is of the order of 10^{-5} and the corresponding value for pyridine is 10^{-9}.

In the SCC of titanium and titanium alloys by methanol solutions we have present in the corroding medium, water, chloride ion and methanol all of which are Lewis bases. It seems desirable to consider the hypothesis that the interaction of chloride ion with the film on titanium and titanium alloys is an adsorption of this ion on a Lewis acid site. One guess is that Cl^- is a stronger Lewis base than the other basic constituents of the solution, methanol, hydroxyl ion, and water. The adsorption which can be considered as a chemisorption must lead to some modification of the physical properties of the site such as its density or its coherence to adjacent sites in the film. Such behavior would explain disruption of the film and the apparent penetration of the film by chloride ions. On the other hand a Brönsted acid site, could react with cations, forming salts which in turn might aid in the disruption of the film, and supplement the action of the chloride ion.

Our experimental work has been done with the alloy, Ti-6Al-4V whose surface film would be expected to contain the oxides-hydroxides of these three metals and hence possess both Brönsted and Lewis acid sites. The reason for the choice of this alloy is that more data on the SCC of this alloy in the methanol-water system are available than for any other Ti alloy that we have studied. Lewis bases are substances containing atoms with unshared electrons. The choice of bases has been confined to organic molecules containing either oxygen or nitrogen atoms. Of the possible oxygen containing organic compounds, anhydrides have been excluded because of possible reactions with either methanol or water. Esters other than methyl esters are undesirable because of ester exchange with the methanol solvent. Esters also react with water but with methyl esters the extent of hydrolysis would be limited by the high concentration of methanol (24.7 molar) present in the corroding media. Esters would be inert under the experimental conditions employed. Simple aliphatic ketones, such as acetone, cannot be used because experimentally it has been found that condensation of the ketone takes place with liberation of water. Water in higher concentrations than those used in the corroding media is an effective inhibitor of SCC. Organic acids would react with methanol producing additional water and also changing the pH of the corrosion medium. Accordingly the organic oxygen compounds selected for trial have been alcohols, ethers, a methyl ester and a cyclic ketone. All of the organic nitrogen compounds are amines whose basic dissociation constants in water are quite low, 10^{-9} or smaller. In solutions of lower dielectric constant, such as the ones used in the basic dissociation constants would have still lower values. It is probable that these amines in the low concentrations utilized do not cause any appreciable change in the pH of the corroding solution.

Experimental Procedure

The Ti-6Al-4V foil was part of the same lot investigated previously and the chemical composition and tensile properties have been reported (3,4) along with the experimental procedures. This annealed commercial product was used as received, with no additional heat treatment or machining in the form of strips 4 inches long, 0.25-inch wide and 0.0035-inch in thickness. All experiments were made at room temperature using a dead weight load equivalent to 75% of the yield strength. Two different test solutions or corroding media were utilized; their characteristics are listed in Table I.

Experimental Results

The experimental results are expressed in terms of a susceptibility index (S.I.) which is defined by the equation,

$$S.I. = \frac{1 - X}{1 + X}$$

where $X = \frac{t}{t_o}$ or the time to failure of the specimen in the presence of an added Lewis base divided by the time to failure of the specimen when no added Lewis base is present. A positive value for S.I. indicates increased susceptibility to SCC and a negative value increased resistance to SCC. The experimental results for the sodium chloride test solution are given in Table II and those for the ferric chloride test solution are listed in Table III. The notation, <-0.99, used in Table II, indicates that the specimen had not failed after a period of time of 500 hours or more at which time the experiments were discontinued. Any experimental value of S.I. between -0.10 and +0.10 is listed in these tables as 0.

Discussion

In previous work from this laboratory (4) it was shown that for Ti-6Al-4V foil variation of the NaCl concentration from $1\cdot10^{-6}N$ to $1\cdot10^{-1}N$ gave a relationship between the concentration of chloride ion, $[Cl^-]$ and the concentration of water, $[H_2O]_0$ at which

Table I. Composition of Corroding Media

Methanol	Water	Electrolyte	Avg. Time to Failure, hr.
24.7 molar	0.1 molar	10^{-2}N, NaCl	t_o = 2.5
24.7 molar	0.2 molar	10^{-2}N, $FeCl_3$	t_o = 0.68

Table II. Sodium Chloride Test Solution

Added Base	Molar Concentration	S.I.
t-Butyl Alcohol	0.030	-0.15
Cyclohexanol	0.030	0
Methyl Acetate	0.030	<-0.99
Methyl Acetate	0.006	0
Cyclohexanone	0.030	0
Aniline	0.030	<-0.99
Aniline	0.006	-0.21
Pyridine	0.030	<-0.99
Pyridine	0.006	0
Quinoline	0.020	<-0.99
Quinoline	0.004	-0.13
2,6 Lutidine	0.020	<-0.99
2,6 Lutidine	0.004	0
Diethyl ether	0.025	<-0.99
Diethyl ether	0.005	<-0.99
Diphenyl ether	0.015	<-0.99
Diphenyl ether	0.003	<-0.99
Bis(2 methoxyethyl) ether	0.014	<-0.99
Bis (2 methoxyethyl) ether	0.003	<-0.99
1,2 Bis(2 methoxyethoxy) ethane	0.013	<-0.99
1,2 Bis(2 methoxyethoxy) ethane	0.003	0

Table III. Ferric Chloride Test Solution

Added Base	Molar Concentration	S.I.
t-Butyl Alcohol	0.006	-0.70
Cyclohexanol	0.006	-0.91
Methyl Acetate	0.030	-0.14
Cyclohexanone	0.006	-0.18
Aniline	0.006	0
Pyridine	0.030	-0.97
Quinoline	0.007	-0.82
2,6 Lutidine	0.020	-0.98
Diethyl ether	0.025	-0.18
Bis(2 methoxyethyl) ether	0.003	-0.73
1,2 Bis(2 methoxyethoxy) ethane	0.003	-0.53

a minimum in the graph of time to failure against water concentration was observed which can be formulated as,

$$[H_2O]_0^{4.46} = 0.95[Cl^-]$$

This expression might indicate that for the work in the sodium chloride corroding medium a reaction of the type,

$$Cl^- + S\cdot\ x\ H_2O \rightarrow S\cdot Cl\cdot y\ H_2O + (x - y)H_2O$$

is involved where S represents a site on the surface of the oxydehydroxide film. The implication of this equation is that both Cl^- and H_2O must be adsorbed simultaneously for penetration of the film since at a fixed chloride ion concentration either a larger or a smaller concentration of water decreases the suceptibility of the foil to SCC. Both Cl^- and H_2O are Lewis bases. It seems reasonable to assume that the inhibition shown by the organic compounds listed in Tables II and III and its dependence upon the concentration of the organic compound is essentially a displacement of Cl^- or H_2O or both from the Lewis acid site on the surface by a Lewis base stronger than either Cl^- or H_2O. Since methanol is always present in large excess, 24.7 molar, the experimental data do not indicate whether methanol is involved in the presumed surface adsorption or is concerned with some reaction subsequent to penetration of the surface film. It is unfortunate that data are not available for methanol solutions which would show that the efficiency of a given Lewis base, as measured by the minimum concentration needed for inhibition, parallels the basic strength of the compound. From concepts shown to have validity by measurements of the strength of Bronsted bases one feels that amines should be a better Lewis base than ethers but what data are available for non-aqueous solutions shows that such concepts are not strictly valid for Lewis bases but that the order of basic strengths for Lewis-type bases changes with change in solvent. Apparently solvent interaction with Lewis-type bases is of considerable importance particularly if hydrogen bonding is possible with bonds such as N ··· HO or O ··· HO. With amines, for example one would have to consider reactions such as,

$$RNH_2 + HOH \rightarrow RNH_2 \cdots HOH \quad \text{and}$$
$$RNH_2 + CH_3OH \rightarrow RNH_2 \cdots HOCH_3$$

The experimental results indicate that the site S interacts more strongly with the added organic bases than with H_2O or CH_3OH as the concentration of the added organic base showing inhibition of SCC is smaller than the concentration of H_2O and much smaller than the concentration of CH_3OH.

Comparison of the results shown in Table II for the NaCl corroding solution with those given in Table III for the $FeCl_3$ solution show that the compounds acting as inhibitors of SCC in one system are also inhibitors in the other system. However, the efficiency of a given organic Lewis base does change in going from one system to the other. t-Butyl alcohol is a better inhibitor in the $FeCl_3$ system than in the NaCl system. The behavior of various ethers is just the reverse. Apparently the difference is caused by the substitution of Fe^{+3} for Na^{+1}; the chloride ion concentration being kept constant. If the surface oxide contains Brönsted acid sites in addition to Lewis acid sites and if both types of sites can be locii for the highly specific SCC to take place, then the enhanced susceptibility to SCC caused by Fe^{+3} can react with Brönsted acid sites to form some form of iron titanate whose formation disrupts the protective film. Na^{+1} apparently does not give this reaction as is true for most other cations that have been tried(4).Iron titanates compounds are suggested rather than aluminates or vanadates as Fe^{+3} also catalyzes the SCC of pure titanium.

Summary

The inhibiting action on SCC shown by organic compounds whose structure is such that they can behave as Lewis-type bases can be explained by assuming that such molecules can displace Cl^- and H_2O from Lewis acid sites present in the protective film on titanium alloys such as Ti-6Al-4V.

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