Corrosion and Hydrogen Embrittlement Behavior of Titanium in Aqueous Sulfidic Solutions

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Aqueous sulfidic solutions which contain H₂S, or mixtures of H₂S and NH₃ are corrosive to carbon steel and other commonly used alloys particularly if the sulfidic solutions also contain chloride and cyanide ions. Titanium has been considered as a candidate construction material for services in petroleum refining and related processes, which involve handling aggressive aqueous sulfidic solutions. The corrosion and electrochemical behavior of titanium in aqueous sulfidic solutions was therefore investigated to provide answers regarding the corrosion and embrittlement behavior of titanium in these solutions. This paper summarizes the results of this study of the corrosion and electrochemical behavior, including galvanic effects, of titanium in aqueous acidic and alkaline sulfidic solutions. Variables investigated include the effect of solution pH, temperature and solution composition on the corrosion and electrochemical behavior of titanium. The effect of chloride and cyanide ions in aqueous sulfidic solutions on the corrosion behavior of titanium was also studied. Surfaces of titanium electrodes exposed to sulfidic solutions were also examined by reflection electron diffraction and the results of these tests are compared with thermodynamic predictions (Pourbaix diagrams).

An important factor which may also limit the utilization of titanium as a heat exchanger material is its ability under certain conditions to absorb hydrogen due to either superficial corrosion or galvanic coupling to more active materials. The absorbed hydrogen may lead to titanium hydride formation and embrittlement of titanium. This paper also discusses the results of an investigation of the effect of solution pH and composition, temperature, and impurity elements such as chlorides, cyanides, phosphates, etc. in solutions on the mechanism and rate of hydrogen absorption and formation of titanium hydride. In addition the effect of hydrogen and mechanical loading rate (strain-rate) on the ductility and embrittlement of titanium is also discussed.

Introduction
Titanium has been finding increasing acceptance as a construction material in the chemical and petroleum industries because of attractive mechanical properties and generally good corrosion resistance. As a result, there has been a growing literature on the corrosion behavior of titanium in acidic solutions of HCl, H₂SO₄ and in nearly neutral chloride solutions1~7, but not in sulfidic solutions. Aqueous sulfidic solutions which contain H₂S or mixtures of H₂S and NH₃ are corrosive to carbon steel and other commonly used alloys, particularly if the sulfidic solutions contain also chloride and cyanide ions.8

The corrosion and electrochemical behavior of titanium in aqueous sulfidic solutions, including galvanic effect and cathodic hydrogen absorption was therefore investigated to provide answers regarding the corrosion and embrittlement behavior of titanium in aggressive sulfidic solutions. This paper discusses the corrosion, electrochemical and hydrogen embrittlement behavior of titanium in aqueous sulfidic solutions. In addition, the effect of hydrogen on the ductility of titanium will also be considered.

The topics which are discussed in this paper, after the above brief introduction include: (a) corrosion and electrochemical behavior of titanium in sulfidic solutions, (b) galvanic behavior of titanium in sulfidic solutions, (c) factors influencing hydrogen absorption and embrittlement of titanium.

Corrosion Behavior of Titanium in Sulfidic Solutions
The aqueous sulfidic solutions used in this study included acidic sulfidic solutions prepared by saturating distilled water at different temperatures with H₂S, and alkaline sulfide solutions (pH 9~10) prepared with ammonium sulfide in the concentration range 2 to 20% (NH₄)₂S with and without
the addition of smaller concentrations of chloride and cyanide ions in the form of their sodium salts. The chemistry of aqueous sulfidic solutions is fairly complex and the stability of different species as described previously depends on both solution pH and the redox potential of the solution. In the potential region corresponding to the natural corrosion potential of titanium in aqueous sulfidic solutions the predominant stable species are H$_2$S in acidic solutions, SH$^-$ in neutral and mildly alkaline solutions and S$^-$ in fairly alkaline solutions, as shown schematically in Fig. 1.

Fig. 2 shows the thermodynamic equilibrium potential—pH diagram for the system Ti–H$_2$O$^+$. This diagram shows that at very active potentials Ti is the stable species and corrosion is not expected to occur. In the active potential region at high cathodic polarizing potentials cathodic hydrogen evolution occurs and titanium hydride (TiH$_2$) becomes a thermodynamically stable phase (not shown in the diagram).

In strong acidic solutions at more noble potentials Ti$^{3+}$ and Ti$^{4+}$ as soluble corrosion products become the thermodynamically stable species. In mildly acidic and neutral to alkaline pH solutions, a series of titanium oxides with increasing titanium valence, i.e., TiO, Ti$_2$O$_3$, and TiO$_2$, become thermodynamically stable with increasing potential. It is noted that although these oxides are thermodynamically stable in their respective potential—pH regions, formation of these oxides in many instances depends on kinetic factors and these oxides may not be formed. For example, the steady-state corrosion potentials of Ti in the sulfidic solutions investigated in this study, were found to be within the region of stability of TiO$_2$. However, examination of the surface of titanium specimens, which were exposed in aqueous sulfidic solutions, with reflection electron diffraction failed to reveal the presence of a titanium oxide film. This suggests that either the film was amorphous or too thin to be detected.

Previous studies by other investigators also indicate that TiO$_2$ forms only under extreme conditions of oxidation, i.e., air at elevated temperature, or anodic treatment at high anodic potentials. Soviet investigators who studied the nature of films of titanium polarized in H$_2$SO$_4$ also reported the absence of a well defined crystalline oxide film in the above potential regions; they were able to detect TiO$_2$ in the form of anatase only on specimens polarized at potentials greater than +0.1 V (NHE).

The corrosion behavior of titanium in sulfidic solutions was investigated by weight loss measurements of titanium coupons exposed in different sulfidic solutions and temperatures for up to 332 hrs. and by corrosion potential and polarization measurements. Typical corrosion data of titanium in acidic and alkaline sulfidic solutions, shown in Table 1, indicated that titanium remains passive and is subject to negligible corrosion. Passivation of titanium in these solutions is also confirmed by the data on the time variation of the natural corrosion potential of pre-activated titanium in aqueous sulfidic solutions shown in Fig. 3. The specimens were activated with HF prior to immersion in test solution.

The data in Fig. 3 show that the corrosion potential of titanium immediately upon immersion in test solutions was about −0.8 V (SCE) and pro-
gressively increased reaching a steady–state value after several minutes. In H₂O sat’d with H₂S, the steady–state corrosion potential of about −0.45 V (SCE) was not achieved until about 35 minutes. In 7% (NH₄)₂S solution as well as in alkaline sulfidic solutions containing NaCl, the corrosion potential was stabilized at about −0.65 V (SCE) after about 5 minutes of immersion. In a solution which contained 7% (NH₄)₂S and 2.27% NaCN a steady–state corrosion potential of about −0.65 V (SCE) was also attained, but only after exposure time of about 40–50 minutes.

The progressive increase in the corrosion potential of active titanium with immersion time is interpreted as due to formation of a passive film. Although the exact nature of the passive film on titanium in these solutions has not been established it is reasonable to assume that it is a thin oxide film (50–100Å). The passive film is also assumed to be free of pores or cracks since at the steady–state corrosion potential any exposure of base metal through defects of this type is unlikely. It should be noted that the steady–state corrosion potential of titanium in these solutions is almost 0.5 V above the equilibrium potential for the reaction Ti+2H₂O=TiO₂+4H⁺+4e and that titanium is extremely reactive metal. The argument against the existence of pores in passive films on iron has been given by Vetter¹² and similar arguments apply to titanium.

The considerable hysteresis observed in the potential time dependence of titanium in solutions containing cyanide ions (Fig. 3) is attributed to adsorption of cyanide ions in competition with water molecules on the titanium surface which tend to interfere with the passivation reaction. Chloride ions apparently exhibit no similar effect.

Typical anodic and cathodic potentiostatic quasi–steady–state polarization behavior of passive titanium in sulfidic solutions is shown in Fig. 4. The polarization curves in Figs. 4 and 5 were obtained after the titanium electrode had attained a steady–state corrosion potential. The polarization curves were determined beginning from −0.1 V (SCE) toward higher potentials at 25 to 50 mv internals by measuring the steady–state current at the end of a 3 minute arrest at each potential.

The cathodic polarization in both acidic and alkaline sulfidic solutions on “passive” titanium (Fig. 4) exhibits a Tafel type behavior with a slope
of about 150 mV/decade of current. In the acidic solution (3.34% NaCl sat'd with H$_2$S) the cathodic reaction corresponds to the overall reaction: $2H_2S + 2e = H_2 + 2HS^-$ and it is limited by hydrogen overvoltage at low polarizing potentials and by H$_2$S diffusion at more negative potentials.\textsuperscript{131} In alkaline sulfidic solutions, the cathodic reaction corresponds to decomposition of H$_2$O. The experimentally determined cathodic Tafel slopes are consistent with a model proposed by Meyer\textsuperscript{14) for passive zirconium, which assumes that the overall kinetics of the cathodic reaction is controlled by both charge transfer through the passive oxide film and through the Helmholtz layer at the oxide-solution interface. Additions of chloride ions in sulfidic solutions were found to have no significant effect on cathodic polarization of passive titanium, Cyanide ions, however, were found to promote the cathodic activation of passive titanium\textsuperscript{13} as shown in Fig. 5.

The anodic polarization behavior of passive titanium in sulfidic solutions is more complex due to redox processes involving various sulfur species.\textsuperscript{15} In acidic solutions, redox interferences are less significant. The anodic polarization curve in this solution (Fig. 4) shows an initial Tafel like behavior which is attributed to activation controlled growth of the passive oxide film, prior to development of the oxide as a diffusion barrier. At potentials higher than $-0.3 \text{ V (SCE)}$ the oxide film apparently becomes of sufficient thicknesses to act as an ionic diffusion barrier and the current becomes essentially constant as the voltage increases giving a plateau on the $i-E$ plot. This is likely due to the fact that the decrease in current due to oxide film thickening is counter-balanced by the increase in current resulting from the voltage rise. The anodic polarization behavior of passive titanium in alkaline solutions shows similar Tafel like behavior near the corrosion potential, but exhibits interference from oxidation reactions involving SH$^-$. These effects are discussed in more detail elsewhere.\textsuperscript{151}

**Galvanic Behavior of Titanium in Sulfidic Solutions**

A knowledge of the polarity of titanium with respect to other commonly used construction materials when it is galvanically connected to them in contact with aqueous sulfidic solutions is necessary in order to be able to predict whether or not titanium is anodic or to predict conditions which may lead to hydrogen uptake and embrittlement (when it is the cathodic member of a galvanic couple).

To study the galvanic behavior of titanium in aqueous sulfidic solutions the following experimental methods were used: (a) open circuit potential measurements of uncoupled titanium and other commonly used materials, (b) corrosion rates of uncoupled titanium and titanium galvanically coupled to several alloys, and (c) measurements of galvanic currents flowing between titanium and several commonly used alloys in contact with aqueous sulfidic solutions.

The open circuit potential measurements of uncoupled titanium and several other commonly used metals and alloys in sulfidic solutions are
The data in Fig. 6 show that titanium is slightly anodic by about 100 to 250 mV to other commonly used metals and alloys in aqueous sulfidic solutions which are free of cyanide ions. On the other hand, in sulfidic solutions which also contain cyanides and chlorides, titanium is cathodic by about 200 to 300 mV as compared with other commonly used materials. The observed reversal is galvanic polarity of titanium in sulfidic solutions containing cyanide and chloride ions is attributed to breakdown of protective sulfides or other “passive” films, present on carbon steel and commonly used alloys, by the cyanide or chloride ions which results in active corrosion and the more active corrosion potential for these alloys.

The galvanic potential measurement were supplemented with corrosion data obtained in sulfidic solutions by exposing uncoupled titanium test coupons as well as test coupons coupled to several commonly used construction materials. In cyanide-free sulfidic solutions, titanium is anodic to several materials such as carbon steel, Type 304 SS, Inconel 600 or Incoloy 800, and these materials were not subject to any corrosion acceleration due to galvanic coupling. Titanium although anodic in these tests did not corrode, or suffer any other adverse effects. This immunity to corrosion of titanium when anodic in a galvanic couple is attributed to self-passivation of titanium in these solutions, which is further enhanced by the anodic growth of the oxide film.

In sulfidic solutions containing cyanides or chlorides, in which titanium is cathodic the data shown in Table 2 indicate that carbon steel, Type 304 SS, Inconel 600 and Incoloy 800 when galvanically coupled to titanium, corrode at a higher rate than when exposed in the same solution uncoupled.

It should be noted that the data shown in Table 2 are weight loss data when the anode to cathode area ratio A/C≈1:1. To determine the effect of different anode to cathode area ratios on corrosion acceleration due to galvanic coupling to titanium, the galvanic currents flowing between carbon steel and titanium for different A/C values were determined in a sulfidic solution containing cyanides. The data shown in Fig. 7 indicate that the galvanic current and, therefore, the corrosion rate acceleration of carbon steel when galvanically coupled to titanium, in cyanide containing sulfidic solutions, is maximum at A/C≈1:1 and decrease by about a factor of 5 as the A/C becomes 4/1 and higher.
Factors Influencing Hydrogen Absorption and Embrittlement of Titanium

Hydrogen is one of the most dangerous impurities in titanium and titanium-base alloys and therefore absorption of hydrogen in titanium is a phenomenon of considerable technological importance.

The TiH system forms an interesting contrast to the well known Fe–H system. In the Fe–H system, the affinity between metal and hydrogen is only slight, they form no chemical compounds and the hydrogen gas dissolves in the metal in comparatively small concentrations. In the Ti–H system on the other hand, the mutual affinity is great, a chemical compound is formed, and hydrogen dissolves in the metal in relatively large quantities. The maximum concentration of hydrogen which can be absorbed by titanium corresponds approximately to the composition of TiH₂.

One of the ways in which hydrogen can be absorbed in titanium is either by atomic hydrogen generated on the metal surface during natural corrosion or during cathodic polarization, i.e., when titanium is galvanically connected to a more active metal. A study of hydrogen absorption under conditions of cathodic polarization is therefore of significance from a practical standpoint, since absorption of hydrogen in titanium may lead to formation of titanium hydride (TiH₂) and embrittlement of titanium.

For the hydrogen absorption studies the electrode and cell design was similar to that described previously. The titanium electrodes were cathodically polarized at 10 ma/cm² at different times and the amount of hydrogen absorbed in the ti-
tanium electrodes was determined using a high vacuum extraction method at 1400°C. Fig. 8 shows the effect of solution pH on the amount of hydrogen absorbed when identical electrodes were polarized at 10 ma/cm² for 24 hrs. in solutions of different pH at 82°C. The data shows quite a pronounced effect of solution pH on the rate of hydrogen absorption, with considerably higher rate in acidic than nearly neutral to alkaline solutions.

It is also of interest that not only the amount of hydrogen is affected by pH, but also the morphology of the titanium hydride phase formed on the metal surface as a result of hydrogen absorption. As shown in Fig. 9, in acidic solutions the titanium hydride forms a continuous layer on the metal surface. On the other hand, in mildly alkaline sulfidic solutions only isolated patches of titanium hydride were detectable on the metal surface with most of the surface area being free of titanium hydride. This is attributed to different kinetic mechanisms which control the rate of hydrogen absorption in acidic and mildly alkaline solutions.

As shown in Fig. 10 in acidic solutions hydrogen absorption appears to follow a parabolic time dependence which apparently implies that the overall kinetics of hydrogen absorption is controlled by solid state diffusion of hydrogen in titanium and growth of the titanium hydride layer. In mildly alkaline sulfidic solutions on the other hand, the overall kinetics of hydrogen absorption shows a linear time dependence, and the overall rate is controlled by the interface hydrogen generating reaction.17) The spotty formation of titanium hydride on titanium in mildly alkaline solutions is probably due to competitive adsorption of hydroxyl ions or water molecules which tend to promote passivation of titanium and thus interfere with hydrogen absorption.

Temperature is another important parameter affecting hydrogen absorption in titanium. Experiments with a variety of sulfidic as well as acidic sulfate solutions, indicate that the rate of hydrogen absorption in titanium is significant at temperatures higher than 72°C, but negligible at lower temperatures. The role of temperature on the rate of hydrogen absorption is illustrated with data in Fig. 11 which show hydrogen absorption of titanium cathodically polarized at 10 ma/cm² in distilled water sat'd with H₂S (1 Atm) at different temperatures17).

Several experiments were also carried out to determine the effect of promoter elements on the rate of hydrogen absorption in titanium cathodically polarized at 10 ma/cm² in an acid sulfide solution of pH≈1. The data18) shown in Fig. 12 demonstrate the pronounced effect of sulfur and phosphorus containing impurities in increasing the rate of hydrogen absorption as indicated with thickness measurements of the titanium hydride layer. The influence of arsenic and antimony containing impurities was not as pronounced.

There is little doubt that the promoter elements exert their influence on increasing hydrogen ab-

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* After prolong exposure, diffusion of hydrogen and formation of titanium hydride thin plates far deep into the metal structure were also detectable.
sorption by adsorbing on the titanium metal surface. However, the mechanism of their action in promoting absorption of hydrogen is not known. It is possible that the promoter increases the Ti–H bond on the metal surface and thus increases the coverage of adsorbed atomic hydrogen which thereby increases the permeation rate. Other explanations such as formation of hydride of the promoter element during cathodic polarization as an essential element of hydrogen entry is also possible18). Similar experiments with sulfidic solutions showed that cyanide ions tend to promote hydrogen uptake, whereas chloride ions have essentially no effect10).

The presence of even comparatively small concentration (a few tens of ppm or more) of hydrogen in titanium and titanium alloys can lead to brittle failure. This effect, referred to as hydrogen embrittlement, can be divided into two quite dissimilar types. Because the most striking difference between these two types of embrittlement is the strain rate at which they appear, the two types of hydrogen embrittlement are generally referred to as impact embrittlement and low-strain-rate embrittlement.

Impact embrittlement becomes more severe with increasing hydrogen content, decreasing temperature, increasing strain–rate (or loading rate) and when notches are introduced into the sample. In contrast to impact embrittlement, low-strain–rate embrittlement becomes more severe as the strain rate decreases. In addition, ductility is lost over a finite intermediate temperature range, so that an alloy susceptible to slow–strain–rate embrittlement will often be ductile if tested at either a higher or lower temperature range.

With commercially pure titanium (almost entirely alpha–titanium) contaminated with hydrogen, impact embrittlement is the most common form of failure, but low–strain–rate embrittlement also is known to occur. The role of hydrogen and tem-
perature on the impact embrittlement of titanium is shown schematically in Fig. 13 which is reproduced from the paper by Lenning et al.\(^{19}\). With α/β–titanium alloys, low-strain-rate embrittlement is most often observed. The effect of small additions of hydrogen and temperature on low–strain–rate embrittlement of α/β–titanium alloys was demonstrated by Williams\(^{20}\) and illustrated in Fig. 14.

Embrittlement of titanium and its alloys is attributed to formation of titanium hydride crystallites in the form of thin plates. Titanium hydride may be formed either by thermal precipitation due to rapidly decreasing solubility of hydrogen in Ti with decreasing temperature, or may precipitate from supersaturated solution when the alloy is stressed. If the excess of hydrogen before testing is present in the form of titanium hydride, impact embrittlement is observed. When, on the other hand, the excess of hydrogen before testing is present in supersaturated solution, low–strain–rate embrittlement is observed.

**Concluding Remarks**

- Titanium in both acidic and alkaline sulfidic solutions exhibits stable passivity and negligible corrosion.
- Titanium when galvanically coupled to carbon steel and commonly used alloys in sulfidic solutions may be cathodic or anodic depending on the aggressiveness of the corrosive solution.
- Cathodic polarization in sulfidic solutions promotes hydrogen uptake and embrittlement of titanium. The rate of hydrogen uptake is strongly influenced by solution pH, the presence of promoter impurities, and is significant only at temperature of 72°C and higher.
- Even comparatively small hydrogen contents (a few tens of ppm or more) are sufficient to cause embrittlement of titanium. With commercially pure titanium contaminated with hydrogen, impact embrittlement is the most common form of failure. With α/β–titanium alloys low–strain–rate embrittlement is most often observed.

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