THE EFFECTS OF IRON ON THE CORROSION RESISTANCE OF TITANIUM

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Introduction

Iron occurs in one form or another in most environments where titanium is being used. It occurs in solid solution in the metal or as microscopic particles of metallic iron embedded or smeared into the surface of titanium equipment from contact during fabrication or maintenance with iron tools or other implements. Iron is also found in solution in many process streams, sometimes as an ingredient, more often as a contaminant from corrosion of iron pipes and other iron base alloy components in contact with the solution.

Its effect on the corrosion properties of titanium are therefore of considerable practical importance since the durability of titanium equipment may be affected. Over the years, considerable information from research and experience has been accumulated which have a bearing on this problem. This paper is an attempt to present this information and discuss its implications with respect to the corrosion resistance of titanium.

Iron as a Contaminant in the Metal

Effect on Corrosion Resistance

Other investigators(1) have reported the detrimental effects of iron as a contaminant on both the corrosion resistance of titanium and its resistance to hydrogen embrittlement. Titanium is an active-passive metal and the transition from passive to active behavior usually occurs rather suddenly. Corrosion tests conducted at TIMET in which small additions of iron were made to high purity titanium confirm that in an actively corroding environment the corrosion rate increases as the iron content of the metal increases.

Preferably, however, titanium is not used in an environment where it will actively corrode. The more important question then is, does iron content affect the transition from passive to active behavior; does titanium having a high iron content start to corrode at a lower acid concentration than material having a low iron content?

A series of carefully controlled tests were run in dilute solutions of boiling HCl using specimens of high purity titanium with additions of iron to cover the range from 0.012 to 0.169% Fe. Welded specimens were also included. The data from these tests are plotted in Figures 1 and 2 as scatter bands comparing the corrosion rates at the highest and lowest iron levels.

It is interesting to note that the transition from passive to active behavior occurs at about pH 2 regardless of iron content. It is only at corrosion rates greater than 2 mpy that any effect due to iron content is detectable. This was also true for the welded specimens. These data suggest that iron content has no effect on susceptibility to corrosion.

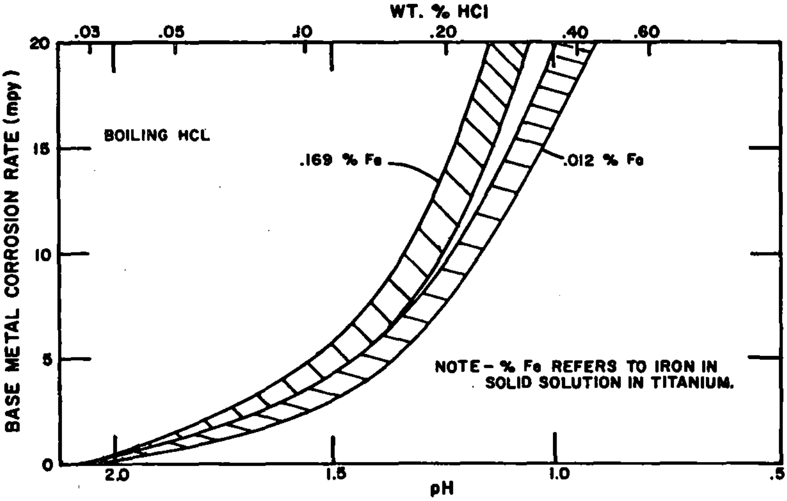

FIG.1, EFFECT OF IRON ON CORROSION OF CP TITANIUM IN BOILING HCl SOLUTIONS.

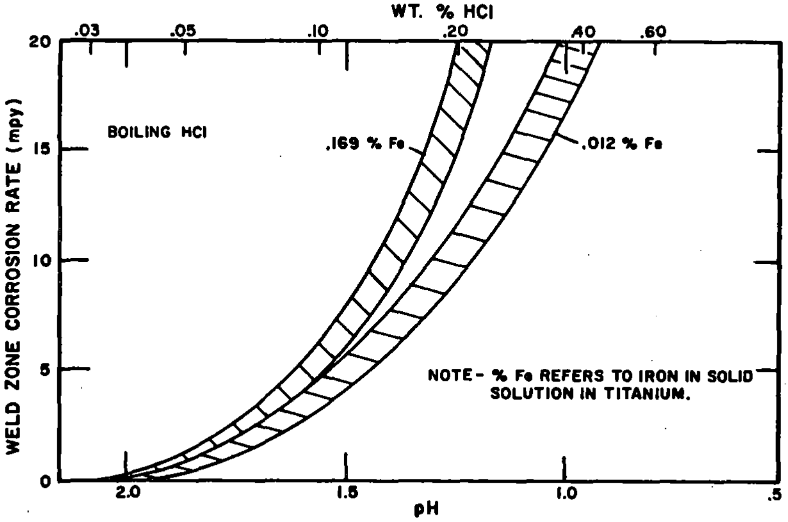

FIG. 2, EFFECT OF IRON ON CORROSION OF CP TITANIUM WELDS IN BOILING HCl SOLUTIONS.

It has been suggested(1) that high residual iron causes preferential weld attack. The data plotted in Figure 3 shows a higher rate of attack on the welds than on the base metal but there is nothing to indicate this is caused by the iron content. The preferential weld attack is also observed at 0.012% Fe as well as at 0.169%. Apparently some factor other than residual iron content is responsible for the increased rate of corrosion observed on the welds.

Effect on Hydrogen Absorption

It has been advocated(1) that titanium for use in chemical process equipment should have a maximum residual iron content of 0.05% because of alleged detrimental effects on corrosion resistance and hydriding susceptibility. The effect of iron in solid solution on corrosion resistance has been discussed in the previous section. It has been shown that reasonable doubt exists that iron in solid solution is harmful at the residual concentrations normally found in C.P. titanium.

On the basis of TIMET's tests, the alleged effects of iron on hydriding can also be questioned. Cotton(1) measured diffusion rates of hydrogen in titanium at various iron levels and showed that a correlation exists between diffusion rate and iron content. This apparently served as the basis for the conclusion that iron in solid solution promotes hydriding. The data in Table 1 of Cotton and Hines(2) paper however fails to show any correlation between hydrogen absorption and iron in solid solution in the absence of surface iron contamination. In fact, their highest hydrogen pickup was observed at iron levels of only 0.04 and .068%.

Cotton and Hines(2) did show that hydrogen diffusion is very temperature dependent and is not significant at temperatures below 80°C (176°F). It is agreed that the diffusion rate of hydrogen in titanium does increase with increasing iron levels when the temperature is above 80°C (176°F). However because of this diffusion temperature threshold hydriding is primarily a high temperature problem. In the twenty years service history of titanium in chemical process equipment, no failures involving hydriding, as far as is known, have occurred where the operating temperature was below the 80°C diffusion threshold except under conditions of extreme stress.

Hydriding is the result of a two-step process consisting of absorption followed by diffusion. The rate of absorption is dependent on the ability of the hydrogen to penetrate the oxide film covering the titanium surface. This will be the controlling step when the absorption rate is less than the diffusion rate and will therefore determine hydriding susceptibility. If absorption does not occur, then obviously hydriding will not occur but if absorption does occur then hydriding will follow provided the temperature is high enough for diffusion to take place.

An experiment was conducted in an effort to examine the effect of iron on the absorption step of hydriding. This was done by cathodically charging freshly pickled specimens having varying iron contents and measuring the amount of hydrogen absorbed. The specimens were charged in 1% NaCl adjusted to pH 1. A current density of exactly 9.6 ma/cm^2 was impressed on the specimen with a potentiostat and maintained for precisely 15 minutes. The solution temperature was held at 90°C (190°F) by a constant temperature bath. A two compartment cell was used connected by a salt bridge. This was to prevent any mixing of the anolyte and catholyte.

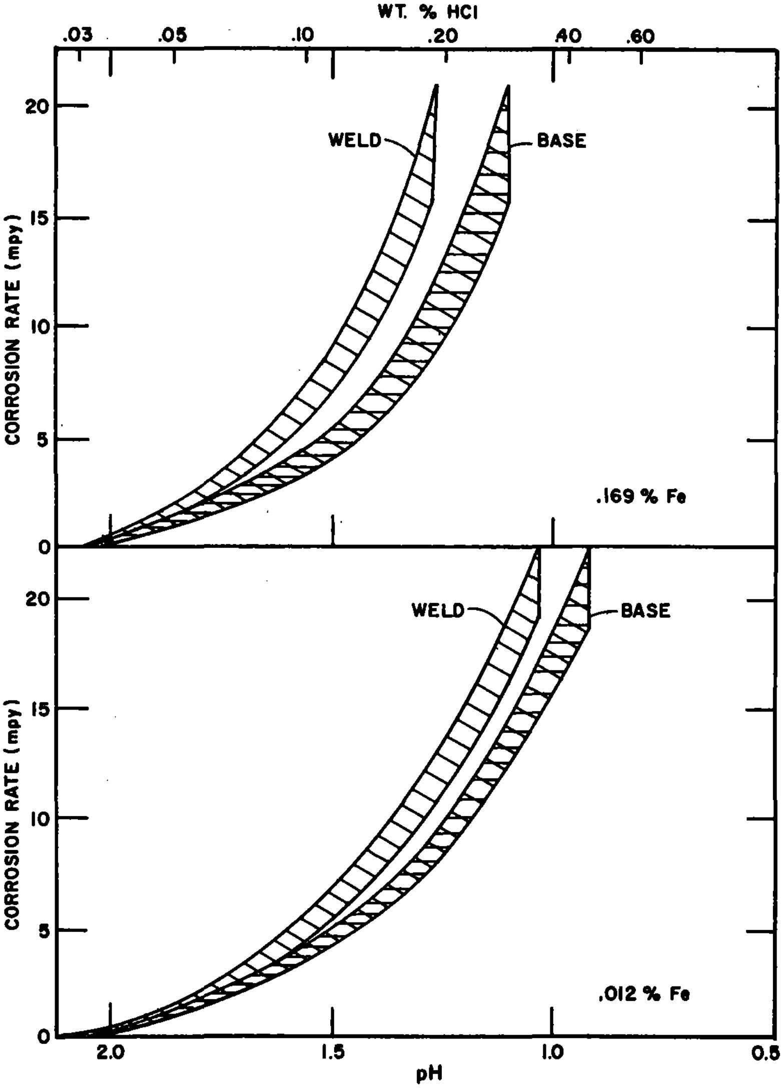

FIG. 3, EFFECT OF pH ON PREFERENTIAL WELD ATTACK AS A FUNCTION OF IRON CONTENT OF THE TITANIUM.

The hydrogen content of the specimens was measured before and after charging by vacuum hot extraction. The hydrogen uptake efficiency (HUE) was then calculated as the percent of the total hydrogen evolved that was absorbed.

The results are plotted in Figure 4. These data indicate that less hydrogen was absorbed as the iron content increased. A ready explanation for this is not apparent.

A rerun of this experiment produced the same results so the effect is reproducible. This suggests that iron dissolved in the metal at the low levels normally present in C.P. titanium does not make it more susceptible to hydriding.

Crevice Corrosion

Crevice corrosion is a localized form of attack in crevices so it is difficult to evaluate the extent of corrosion numerically. For the purposes of this study the corrosion rate was calculated assuming uniform attack. Recognizing that this assumption is false, the rates cannot be used to estimate service life but they do serve to indicate the relative magnitude of the attack on the various specimens.

To evaluate the effect of iron, a series of crevice corrosion tests were run in boiling saturated NaCl solutions adjusted to pH 1 with HCl. The specimens used in this experiment were prepared by adding varying amounts of iron (.012% to 0.20%) to a high purity (EL-60) sponge base. The data from these tests are plotted in Figure 5 as a broad scatter band. In general, as the iron content increased, the severity of crevice corrosion attack decreased. We do not intend to imply on the basis of these tests that high iron levels are beneficial from a crevice corrosion standpoint but on the other hand they raise a reasonable doubt about the allegations that high residual iron levels make titanium more susceptible to crevice corrosion.

Iron as Metallic Particles Embedded or Smeared into the Titanium Surface

There is no doubt that iron particles embedded in the surface of C.P. titanium are very deleterious. By breaching the protective oxide film on the titanium surface they serve as entry points for hydrogen and as initiation sites for pitting. This has been clearly demonstrated to be the cause of service failures on numerous occasions(1,7).

It should be pointed out that smeared or embedded iron particles need only be of concern for high temperature applications. Some power plant surface condensers containing titanium tubes have now been in service nearly twenty years. Considering the many millions of feet of tubing involved, it is certain that some contained embedded iron particles yet no failures have ever been reported. These units operate at temperatures of about 130°F (54°C). Salt evaporators on the other hand, which operate at about 265°F (129°C) have experienced a number of pitting failures that have been clearly related to embedded iron particles.

The reason for this temperature dependence can be explained on the basis of titanium's resistance to hydrochloric acid. As Figure 1 illustrates, unalloyed titanium will begin to corrode at about pH 2 or 0.035 Wt. % in boiling HCl. As the temperature decreases the concentration

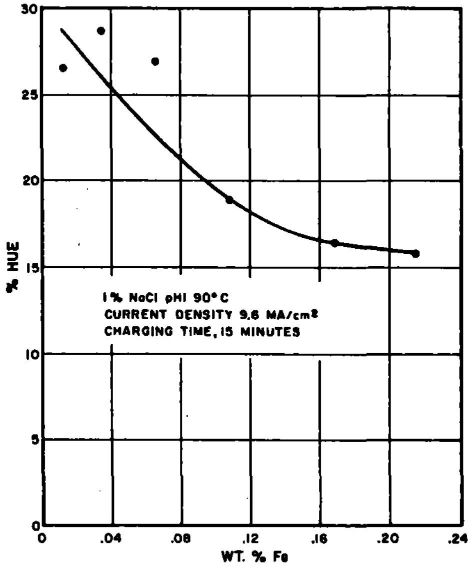

FIG. 4, HYDRGEN UPTAKE EFFICIENCY (HUE)

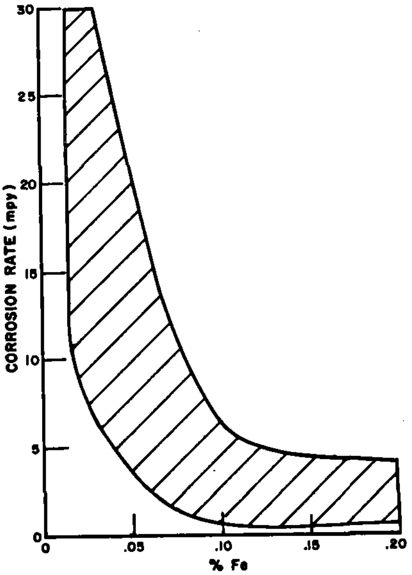

FIG. 5, EFFECT OF IRON ON CREVICE CORROSION OF CP TITANIUM IN BOILING SATURATED NaCl pH1 of acid required to initiate corrosion at ambient temperature increases so that at ambient temperature the metal is resistant to 5 Wt. % HCl.

Various investigators(3,4) have reported that pH levels of about 1 are developed in pits and crevices. This would be sufficient to cause unalloyed titanium to corrode at temperatures a little less than boiling but obviously not at ambient. This would also explain why ASTM Grade 7 (Ti-Pd) and ASTM Grade 12 (Ti-Code 12) do not appear to be susceptible to this surface iron contamination problem or crevice corrosion. These alloys are resistant to greater than 2 Wt. % boiling HCl.

Iron in Solution

Many process streams contain dissolved iron from corroding iron pipe or equipment or as an impurity. This is most frequently in the form of ferric ions and as such is beneficial to titanium. Electrochemical studies(5,6) have shown that ferric ions act as cathodic depolarizers and tend to shift the corrosion potential of the titanium exposed to the solution in the positive direction thus making it more passive.

This explains why titanium is being used successfully in many process streams where the acid concentration is high enough to cause severe corrosion of the titanium but no attack is observed because of the presence of ferric ions in the solution.

Effect of Iron Oxide Deposits on the Surface of Titanium

Titanium in service, frequently accumulates a coating of iron oxide carried over from rusting iron equipment up stream. Although unsightly, this is not detrimental. In fact, corrosion potential measurements indicate that a titanium surface covered with iron oxide has a more passive potential than a clean titanium surface.

Titanium tubes in power plant surface condensers are noted to accumulate a thin iron oxide film on the shell side due to iron carried over in the steam. One of these condenser tubes was removed from service after sixteen years. The outside surface was covered with an iron oxide film but microscopic examination revealed no evidence of corrosion.

Galvanic Effects of Iron-Titanium Couples

The galvanic couple between titanium and iron generates a potential of 0.5 to .6 volts depending on the temperature and the environment. Since titanium is the cathodic member of the couple the effect is to accelerate the corrosion of the iron. If the surface area of the titanium is small in comparison to the iron, the increased corrosion due to the galvanic couple may be insignificant. On the other hand, if the surface area of the iron is small in comparison to the titanium, very rapid attack on the iron may be observed. For example, a cast iron reducer used to connect a feed pipe to the titanium shell of a heat exchanger failed after only a few months operation. There are numerous carbon steel heat exchangers in service in oil refineries however where the original carbon steel tubes have been replaced with titanium. Although the galvanic couple in this case has undoubtedly caused some increase in the corrosion rate of the steel, it has not been great enough to cause a problem.

Laboratory tests(7) have shown that a galvanic couple with iron will not cause hydriding of titanium in clean sea water. This is due to the fact that the potential of the titanium must be reduced to < -.7 volts before hydrogen evolution will occur at the pH 8 of sea water. Laboratory experiments have demonstrated however that titanium will absorb hydrogen when coupled to iron in sea water if H_2S is present. This is attributed to localized reduction of the pH by the dissociation of the H_2S.

Conclusions

In the great majority of cases where titanium is being used in corrosive environments, the effect of iron at the levels normally found in C.P. titanium (≃ .1%) is insignificant and has not led to any problems. However in some cases, high solid solution iron levels have been blamed for premature failures due to pitting or hydrogen embrittlement. Tests conducted at TIMET have indicated that solid solution iron has little, if any, effect on susceptibility to pitting or hydrogen embrittlement.

Iron particles embedded in the surface of C.P. titanium are very deleterious. They serve as initiation sites for pitting and also as entry points for hydrogen.

Ferric ions in the corrosive solution are beneficial and serve as an excellent passivating agent for titanium. Iron oxide deposits on the surface of titanium also have a passivating effect.

Galvanic couples of iron with titanium can lead to accelerated corrosion of the iron and in some environments, hydrogen embrittlement of the titanium. The magnitude of the effect is dependent on surface area ratios and the characteristics of the environment. Titanium is being widely used successfully in applications where galvanic couples with iron exist and in only a few cases have problems been encountered.

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