EFFECT OF SOLID SOLUTION IRON ON THE CORROSION BEHAVIOR OF TITANIUM

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Introduction

Many concepts and intuitive ideas have evolved concerning the effects of alloy iron content on the corrosion behavior of commercially pure titanium. Most concepts identify detrimental effects associated with additions of iron to titanium, however little experimental verification can be found. Cotton's work on hydriding susceptibility, relative to surface and alloyed iron, provided the initial focal point for these ideas (1,2). It was previously demonstrated that titanium with higher iron contents, exhibit increased corrosion rates under actively corroding conditions, such as in hot, pure reducing acids (3). However, these accelerated, active corrosion test conditions do not reflect conditions under which titanium is normally applied or successfully utilized. Thus, one must address iron content effects on titanium's corrosion performance over a range of passive conditions, and assess changes in the "passive to active transition" (3).

Previous studies in boiling HCl (3), and in hot H₂SO₄ media (4), suggest that iron content up to 0.2% had no measurable influence on C.P. titanium's useful passive range. This paper will more thoroughly pursue characterization of iron content effects in several generic, practical environments for C.P. titanium, with proposal of an electrochemical galvanic model consistent with the observed corrosion behavior.

Experimental

Corrosion studies were performed on a series of nonconsumably arc-melted, 250 gram titanium button heats, formulated to produce the following Ti-Fe binary alloys (O₂ content maintained at approximately 0.05%).

<table>
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<tr>
<th>Heat</th>
<th>Wt.% Fe</th>
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These buttons were hot and cold processed to 1.5mm sheet, with a final 760°C/10Min/AC anneal. Optical microstructures were examined to determine correlations between corrosion behavior and structure.

Weight loss corrosion tests were conducted in boiling 40% nitric acid, glacial (99.8%) acetic acid, and 2% HCl/.145% FeCl₃ (500 ppm Fe³⁺) solutions by standard procedures described elsewhere (5). Nitric acid test solutions were refreshed every 24 hours to avoid inhibiting Ti⁺⁴ ion effects on
corrosion. General corrosion rate profiles were developed in pure, naturally-aerated HCl solutions at 66°C, for both base metal and weldment samples of each heat. Samples were tested after being pickled in a 35% HNO₃–5% HF solution. Weldments were prepared by standard autogeneous TIG welding procedures.

Hydrogen uptake efficiency tests were conducted as previously described (5). Cathodic current densities of 10 mA/cm² were employed in a 3.5% NaCl (pH 1) solution at 90°C. Both as-pickled and metallographically polished sheet samples were charged for 15 minutes.

Anodic and cathodic polarization curves were generated in boiling concentrated brine at pH 1 and 7.5. (Brine composition: 21% NaCl, 1.5% MgCl₂, 1.1% KCl, 0.5% CaCl₂ and 0.8% Na₂SO₄.) A Princeton Applied Research Model #173/376 potentiostat was used to provide a constant scan rate of 0.5 mv/sec. Potentials were measured relative to a saturated Ag/AgCl reference electrode. Critical polarization parameters were derived from these slow scan rate polarization studies after 1 and 16 hour pre-scan exposures, to insure attainment of steady-state rest potentials. Repassivation pitting potentials, Ep, were determined with the more reliable and reproducible galvanostatic method discussed elsewhere (6), employing a fixed impressed current density of 200 mA/cm². Potential-time data, associated with uncoupled and coupled galvanic experiments in naturally aerated 1.0% and 1.5% HCl, at 66°C, were measured with a high impedance voltmeter, relative to the Ag/AgCl reference electrode.

Results and Discussion

Hydrogen Uptake Effects

Fig. 1 graphically depicts the effect of alloy iron content on
the cathodic hydrogen uptake efficiency (HUE) in acidic brine at 90°C. For both pickled and polished sample finishes, a definite minima in HUE is noted, in which cathodic hydrogen uptake increases significantly at the extremes of the iron content range tested. For polished surfaces, reduced uptake appears to occur between 0.05% and 1.0% Fe content levels, whereas a narrower range of 0.1% to 0.4% Fe is implied for the pickled surface condition.

The short, high current density cathodic charging technique utilized to generate this data was intended to favor evaluation of surface hydrogen absorption with limited subsequent hydrogen diffusion into the metal. This is generally valid for the α phase, but significant diffusion may occur at 90°C in the β phase as a result of its higher hydrogen diffusion coefficient. The volume fraction of iron-stabilized β phase in the microstructure increases with iron content greater than 0.05% Fe, and can provide continuous β phase diffusion pathways at iron levels above approximately 1%. This explains increased HUE values at higher iron content.

Explanations for higher HUE in the very low iron alloys are not well developed but may be related to low intrinsic matrix hardness and the larger grain size associated with these low oxygen, single phase α alloys (Fe ≤ 0.05%). These conditions promote the formation of larger hydrides within the matrix at lower supersaturation levels. Fig. 2 illustrates typical variations in microstructure observed in the Ti-Fe alloys investigated.

The alloys of intermediate iron content (0.05% < Fe < 1%) have noncontinuous regions of Fe stabilized β phase (Fig. 2) which may serve to promote recombination of atomic hydrogen at the metal surface, thereby reducing hydrogen uptake. The decreased cathodic Tafel slope discussed later in this paper, suggests that iron may indeed produce structures with lower energy surface features for hydrogen reduction and/or recombination.

This hypothesized mechanism for the observed beneficial effect of noncontinuous iron rich β phase in the microstructure is in competition with the enhanced diffusion in the β phase and its operation would, therefore, depend both on alloy content and microstructure. This explains the minimum seen in Fig. 1. From Fig. 2, it is evident that somewhere between 1% Fe and 2% Fe, for a 760°C anneal, beta becomes a continuous phase and aids in uptake of hydrogen.

Weight Loss Corrosion

Boiling glacial acetic acid, 40% nitric acid, and 2% HCl/.145% FeCl₃ media represents aggressive neutral (relative to redox potentials) acid, oxidizing acid, and oxidizing acid chloride environments, respectively, for screening iron content effects. Weight loss corrosion data of various Ti-Fe binary alloys after 120 hours exposure in these media are presented in Table 1. Clearly, no significant effect of iron content is noted.
Alloy | Glacial Acetic Acid | 30% HNO₃ | 2% HCl/.145% FeCl₃
---|---|---|---
Ti- .02Fe | 0.002 (mm/y) | 0.53 (mm/y) | 0.002 (mm/y)
Ti .11Fe | 0.000 | 0.48 | 0.000
Ti .22Fe | 0.000 | 0.51 | 0.000
Ti .41Fe | 0.005 | 0.46 | 0.000
Ti-1.0 Fe | 0.010 | 0.56 | 0.000
Ti-5.1 Fe | 0.005 | 0.31 | 0.000
Ti-9.9 Fe | 0.005 | 0.46 | 0.000

Table 1: General corrosion rates of Ti-Fe alloys in various boiling acid media.

relative to corrosion rate, as either uniform or localized attack. Thus, iron content imparts no measurable effect on titanium's corrosion performance under conditions where titanium is normally passive (i.e. when the oxide film is stable).

In hot reducing acid media, where the oxide film breaks down and active corrosion can ensue, iron content can affect titanium's general corrosion resistance. Fig. 3 presents "passive to active transition" profiles for Ti-Fe alloy base metal in pure naturally-aerated HCl at 66°C. For base metal, iron contents greater than 0.29% appear to measurably reduce the passive to active transition, or useful passive range. For alloys below 0.29% Fe, no significant change in useful passive range is observed, correlating with previous studies in boiling HCl (3). As expected, increasing iron content did accelerate uniform corrosion only when active corrosion occurred (i.e. when rates > .08mm/yr). Weldments exhibit similar passive to active transition values at iron levels ≤ 0.18% and, in general, demonstrate diminished useful passive ranges compared to base metal in HCl media. This is an apparent by-product of microstructural differences.

Fig. 3: Corrosion rate profiles for Ti-Fe sheet in HCl at 66°C. Note that with iron contents below 0.3%, the passive to active transition converges.

Fig. 4: Corrosion potential, Ecorr, in boiling, concentrated, acidic brine.
**Electrochemical Tests**

Slow anodic and cathodic polarization scans in boiling concentrated brine (pH 1 and 7.5) proved to be valuable in identifying the role of alloyed iron on titanium’s corrosion behavior. Corrosion or rest potential ($E_{corr}$), primary anodic passivation potential ($E_{pp}$), critical current density ($i_c$), and passive current density ($i_p$), were determined as a function of iron content and are plotted in Figs. 4, 5, 6 and 7 respectively. Under active conditions (pH 1 brine), $E_{corr}$ clearly shifts in the noble (positive) direction with increased iron. Primary passivation potentials are relatively insensitive to iron level, whereas $i_c$ increases with higher iron content. Passive current density ($i_p$) is essentially unaffected by iron content in the base metal or weldments at either pH, again suggesting that iron does not significantly affect oxide film stability or protective properties under passive conditions. This agrees with the oxidizing and neutral acid weight loss test data discussed previously. It is interesting to note that $E_{corr}$, measured after 16 hours

![Graphs showing data](image_url)
exposure in neutral concentrated boiling brine, indicated no effect of iron content, with values scattered between -0.50 and -0.62 volts. This further suggests that passive oxide film growth is relatively independent of alloy Fe content.

Repassivation potentials (Ep) as plotted in Fig. 8, clearly show reduction with increased Fe, and are relatively independent of pH and base metal/weldment sample type. The Ep exhibits significant decline between 0.4% and 15% Fe, with very minor reductions, on the order of several tenths of a volt, when Fe increases from 0.02% to 0.2%. From a practical point of view, this data, considered with reported or anticipated corrosion potentials, suggests that titanium alloys with iron as high as 10-15% will not suffer spontaneous pitting in saturated brine at temperatures up to the boiling point. Anodic breakdown pitting potentials (Eb), in contrast, were quite variable and nonreproducible, and were, thus not reported. This parameter is very sensitive to test method, specimen surface condition and other artifacts, and is therefore not considered to be an intrinsic alloy property; whereas the repassivation or protection potential is.

Tafel slopes, derived from cathodic curves, are plotted in Fig. 9 relative to iron content. Tafel slope values decreased continuously with increasing iron content in both acidic and neutral concentrated brine media, suggesting that solid solution iron lowers activation (energy) polarization of the hydrogen reduction process. For neutral brines this relates to the water reduction step at the cathode. With iron levels less than 0.2%, acidic brine produced Tafel values much greater than those generated from neutral brine. These "apparent" Tafel values at low iron content levels, are significantly greater than the 0.05-0.25 (volts/decade current) values typically reported for most alloys in acid solutions and may be questionable, considering the limited Tafel region.

Fig. 9: Cathodic Tafel slope in boiling concentrated brine, showing a decrease with increased Fe and an increase with lower pH.

Fig. 10: Galvanic passivation of B in 1% HCl at 66°C, showing that open circuit potentials for B are passive & for B they are active. Passivation occurred quickly after coupling.
obtained on the polarization plots under the conditions tested. However, the alloy effect trend is considered qualitatively correct.

The Role of Iron on Corrosion Mechanisms

In C.P. titanium iron levels as low as 0.1% Fe can stabilize a significant quantity of $\beta$ phase in the microstructure (Fig. 2). Higher iron levels proportionately stabilize more $\beta$ phase at any given sub $\beta$ transus anneal temperature until at some iron level between 1% and 2%, 760°C produces continuous $\beta$ phase (Fig. 2c and 2d). STEM analysis of annealed 0.1% and 0.2% Fe containing C.P. titanium mill sheet conducted at Sandia National Laboratories (7), indicated retained $\beta$ phase composition to be approximately 6.5 wt.% Fe.

By invoking mixed potential models to ascertain the shape of theoretical anodic and cathodic polarization curves (8) for the Ti-Fe alloys in hot HCl media, it is possible to infer the following: 1) Fe effects on the anodic polarization profile are limited to increasing critical current ($\text{i}_c$) and reducing repassivation potential, $E_p$. As discussed earlier, the levels of $E_p$ obtained render consideration of this factor relatively unimportant and 2) Fe provides increased cathodic depolarization (reduced cathodic Tafel slope) but not sufficiently to offset the increased $\text{i}_c$ and achieve passivation. These relationships consequently explain the increased corrosion rates and rest potentials ($E_{corr}$) observed for higher iron alloys under active corrosion conditions.

Because $\beta$ phase composition changes little with iron content in binary alloys below about 5% to 7% at 760°C, the corrosion current ($\text{i}_{corr}$) is a function of the amount of $\beta$ phase (anode) in the alloy. This suggests that the relative amounts of $\alpha$ and $\beta$ phases are important in the resultant interphase galvanic couple for establishing passivation in HCl media.

In order to demonstrate anodic protection of $\beta$ phase by $\alpha$, simple galvanic coupling tests were conducted between Ti-0.05Fe ($\alpha$) and Ti-6.5Fe ($\beta$) sheet samples at 66°C, with a anode/cathode area ratio of 1.3 in 1.0% HCl. Fig. 10 illustrates how open circuit potentials differentiate the more noble $\alpha$ phase and the $\beta$ anode. When coupled, the potential very quickly reaches a passive level, clearly illustrating the galvanic protection provided to the intrinsically less corrosion resistant $\beta$ phase. A more aggressive environment (1.5% HCl) was used to establish a similar relationship with a cathode/anode area ratio of 2.0, producing similar results. In this case, passivation occurred within an hour after coupling. In commercially pure titanium, the $\alpha/\beta$ volume ratio seldom decreases below 10 so virtually instantaneous passivation would be expected. These simple experiments provide insight as to why C.P. titanium alloys with iron levels less than 0.3% in base metal (Fig. 3) and 0.2% in weldments can exhibit no measurable reduction in passive to active transition (useful passive range) in reducing acid media.
Conclusions

1) Solid solution iron has no measurable effect on corrosion resistance of titanium in hot neutral, oxidizing, or oxidizing chloride acid environments, implying no effect on titanium oxide film formation or stability under passive conditions.

2) Increasing iron content will reduce the "passive to active transition", or useful passive region, for titanium in hot HCl media only when iron levels exceed 0.3 wt.% in base metal, and 0.2 wt.% in weldments. Anodic protection of β phase is provided by a/β phase galvanic interactions below these iron levels.

3) An electrochemical model for the role of solid solution iron on titanium corrosion behavior under active corrosion conditions, is proposed which is consistent with all corrosion data.

4) Surface hydrogen uptake produced from short-term cathodic charging in acidic brine, is enhanced at very low (<0.1%) and very high (>1%) iron levels in titanium.

5) Repassivation potentials generally decrease as iron content increases in titanium. For iron levels less than 0.3%, this reduction is considered to be insignificant, on the order of several tenths of a volt. Spontaneous pitting in boiling concentrated brine will not occur with alloys having Fe levels as high as 15%.

6) The foregoing conclusions suggest that iron levels up to 0.2 wt.% do not impart any significant deleterious effect on the practical corrosion performance of commercially pure titanium.

References