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 H_2SO_4 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 (O_2 content maintained at approximately 0.05%).

Heat	5312	5314	5908	5317	5901	5321	5323
Wt.% Fe	.02	.04	.09	.11	.14	.18	.22

Heat	5911	5325	5566	5567	5568	5569
Wt.% Fe	.29	.41	1.0	4.9	9.9	15.0

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% $FeCl_3$ (500 ppm Fe^{+3}) 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% HNO_3-5% 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/cm^2 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% $MgCl_2$, 1.1% KCl, 0.5% $CaCl_2$ and 0.8% Na_2SO_4.) 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/cm^2. 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

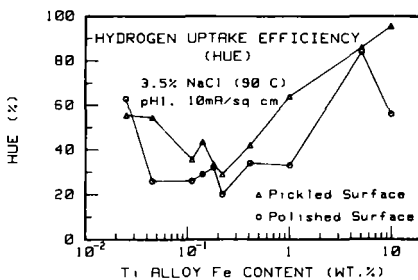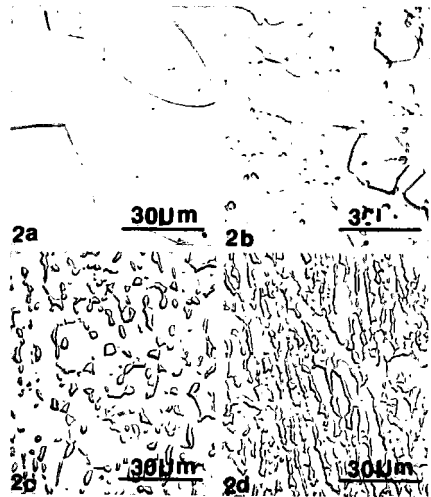Fig. 1 graphically depicts the effect of alloy iron content on

Fig. 1: Hydrogen uptake for Ti-Fe alloys, cathodically charged in acidified brine at 90°C.

Fig. 2: Micrographs of Ti-Fe alloys
a) .05Fe, b) 0.1Fe, c) 1.0Fe,
d) 2.0Fe

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 up-
take 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 evalu-
ation 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 path-
ways 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 (.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 de-
creased 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 recom-
bination.

This hypothesised 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%
FeCl$_3$ 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% HNO$_3$	2% HCl/.145% FeCl$_3$ (500 ppm Fe^{+3})
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 tita-
nium 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 occur-
red (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-
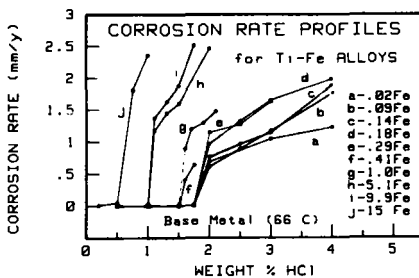product of microstructural differences.

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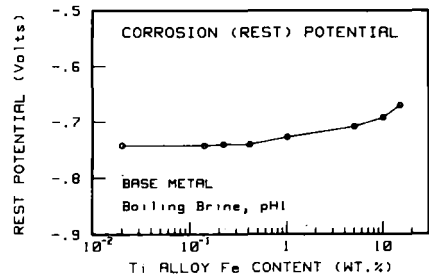the passive to active transition
converges.

Fig. 4: Corrosion potential, E_{corr},
in boiling, concentrated, acidic
brine.

Electrochemical Tests

Slow anodic and cathodic polarization scans in boiling con-
centrated 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 func-
tion 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 in-
creased 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
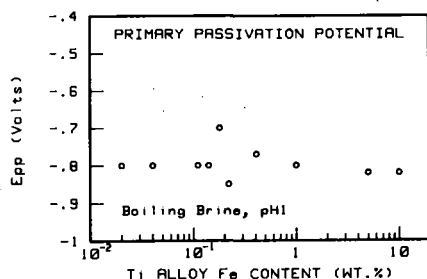is interesting to note that E_{corr}, measured after 16 hours

Fig. 5: Primary passivation poten-
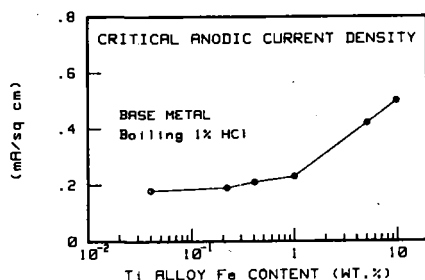tial, E_{pp}, showing no effect of Fe
level.

Fig. 6: Critical anodic current den-
sity, i_c, in boiling HCl. Note the
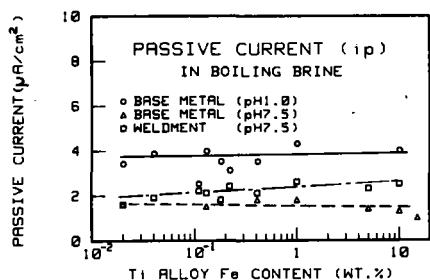increase with iron level.

Fig. 7: Passive current density, i_p,
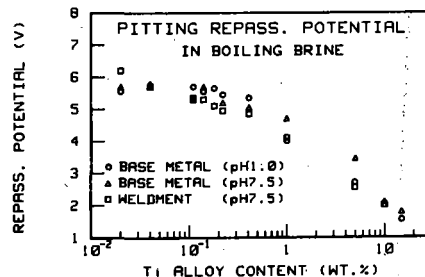in boiling concentrated brine. Little
effect of iron content is seen.

Fig. 8: Repassivation potential, E_p,
in boiling concentrated brine. Note
the small decrease up to .3% Fe.

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 (E_p) as plotted in Fig. 8, clearly show reduction with increased Fe, and are relatively independent of pH and base metal/weldment sample type. The E_p 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 (E_b), 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
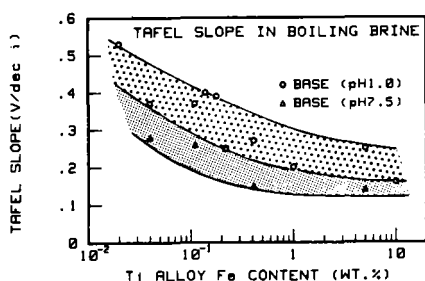

Fig. 9: Cathodic Tafel slope in boiling concentrated brine, showing a decrease with increased Fe and an increase with lower pH.
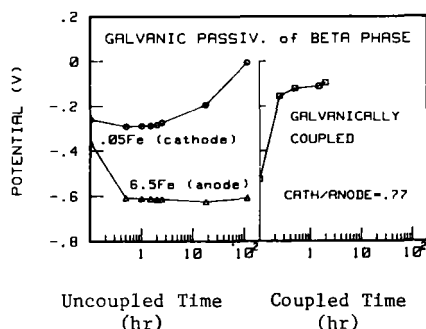
Fig. 10: Galvanic passivation of β in 1% HCl at 66°C, showing that open circuit potentials for α are passive & for β they are active. Passivation occurred quickly after coupling.

obtained on the polarization plots under the conditions
tested. However, the alloy effect trend is considered quali-
tatively 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 β phase in the microstructure (Fig.
2). Higher iron levels proportionately stabilize more β phase
at any given sub β transus anneal temperature until at some
iron level between 1% and 2%, 760°C produces continuous β
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 β phase compo-
sition 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 pro-
file are limited to increasing critical current (i_c) and re-
ducing 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 suffici-
ently to offset the increased i_c and achieve passivation.
These relationships consequently explain the increased cor-
rosion rates and rest potentials (E_{corr}) observed for higher
iron alloys under active corrosion conditions.

Because β phase composition changes little with iron content
in binary alloys below about 5% to 7% at 760°C, the corrosion
current (i_{corr}) is a function of the amount of β phase (anode)
in the alloy. This suggests that the relative amounts of α
and β phases are important in the resultant interphase galvan-
ic couple for establishing passivation in HCl media.

In order to demonstrate anodic protection of β phase by α,
simple galvanic coupling tests were conducted between Ti-.05Fe
(α) and Ti-6.5Fe (β) sheet samples at 66°C, with a anode/cath-
ode area ratio of 1.3 in 1.0% HCl. Fig. 10 illustrates how
open circuit potentials differentiate the more noble α phase
and the β anode. When coupled, the potential very quickly
reaches a passive level, clearly illustrating the galvanic
protection provided to the intrinsically less corrosion
resistant β 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 α/β volume ratio seldom de-
creases 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 meas-
urable reduction in passive to active transition (useful pas-
sive 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 α/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 (<.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.

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