

ISOLATING CORROSION OF STEEL PLATES COUPLED WITH TITANIUM

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ABSTRACT: Over twenty six percent of the bridges in the United States are structurally deficient or functionally obsolete. Corrosion of steel used in structures like bridges and buildings is a problem that has gained increased interest and focused concern. Steel is often the metal that is preferred for use in such applications due to a synergism of ease of availability, acceptable mechanical properties and cost effectiveness. Through the years, titanium has grown in strength, stature and significance to be recognized as an emerging high performance metal that is both stronger and lighter than steel. A distinctive property of titanium and its alloys is its non-corrosive nature. However, a major drawback in the selection and use of pure titanium or its alloy counterpart is the prohibitively high cost. Therefore, it may be possible to combine steel and pure titanium and/or its alloy in structures by restricting steel for bulk of the structure and selectively using titanium and its alloys for the critical but low volume elements, such as, gusset plates and bearings. A hybrid use of titanium in conjunction with steel for structural members will result in better performance while concurrently proving to be both cost-effective and economically affordable. The synergistic use of structural steel and titanium in close proximity with each other could result in accelerated corrosion of steel in the immediate vicinity of titanium. The corrosion performance of titanium plates coupled with steel members is presented. A few viable strategies for minimizing galvanic coupling effects between steel and titanium are discussed. Corrosion experiments were conducted to measure the severity of corrosion when titanium and steel form a galvanic couple, and copper and steel was a comparative system. The study revealed that adequate precautions are needed to minimize localized corrosion when titanium gusset plates are coupled with structural steel members.

Keywords: Structural members, steel, joining, gusset plate, titanium, environment, exposure, corrosion

1. INTRODUCTION

The annual highway bridge inventory (e.g., ASCE Report Card [1]) has time and again revealed that more than 20 percent of bridges in the United States are structurally deficient or functionally obsolete due to deterioration related to aging. The poor health of the infrastructure can be devastating both in terms of human toll and economic impact. Failures can be minimized or obviated through a judicious combination of appropriate choice of materials and adoption of novel and innovative structural design. A gradual loss of cross-sectional properties due to corrosion of structural steel members or connections is a well known phenomenon that has for long been documented (Figure 1). However, steel continues to be the most preferred, widely chosen and used material for cost-sensitive structures primarily because of its ease of availability, affordability, acceptable mechanical properties, familiarity, and technology readiness.

In highway bridges, the key elements that exert a noticeable influence on effective functioning of the structure are the joints between different members. Joints are often made from an assemblage of plates. Examples of connection elements or "gusset plates" that serve to connect the ends of truss members involved using structural fasteners are shown in Figure 2. Fasteners used in newer structures are mostly bolts; and rivets were mostly used in the older structures. Failure of the joints in a bridge truss due to a gradual loss of strength as a direct consequence of environmental

degradation or corrosion can be devastating. This necessitates the need to improve the performance of gusset plates through an observable reduction of corrosion-related deterioration coupled with a concurrent increase in structural strength. Furthermore, failure of the joints, or connections, is often rapid and brittle, and the consequences can be catastrophic when compared to failure of the structural member.



Figure 1. Corrosion Affected Elements of a Steel Bridge

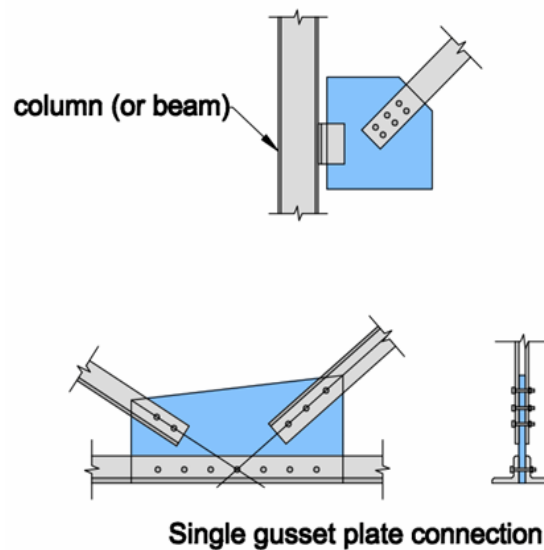


Figure 2. Schematic Showing Configuration of Two Typical Gusset Plates

In the last three decades, i.e., since the early 1980s, titanium has progressively gained increased importance based on both need and significance. This culminated in the titanium metal and its alloy counterparts being recognized as modern high performance metals that are both stronger and lighter than many of the most widely chosen and preferentially used steels in the industry. The applications span a spectrum of both load-bearing and even non load-bearing applications. Another attractive property of pure titanium metal and its alloy counterparts is its non-corrosive nature. A recent study on built-up welded beams made from both pure titanium metal and a titanium alloy demonstrated the potential for viable use of welded structures for both the defense-related and civilian applications [2-5].

On account of its light weight, excellent corrosion resistance, high strength, attractive fracture behavior coupled with high melting point, titanium is often chosen and used in a spectrum of industries dealing with both performance-critical and non-performance critical components and has gradually grown to become one of the most important non-ferrous metals for load-bearing applications. At temperatures below 300°C, alloys of titanium present good formability coupled with high mechanical strength. One such alloy is Ti-6Al-4V. This alloy is often chosen and used primarily because of its excellent tensile strength and fatigue strength, adequate ductility, acceptable fracture toughness and overall good resistance to corrosion. Despite its superior structural performance and corrosion resistance, it is not cost effective to use pure titanium metal and its alloys for large structures, such as bridges. However, it may be possible to use structural steel for the main members of a large structure in combination with pure titanium metal or its alloy counterpart for the critical but low volume locations, such as: (i) connections, (ii) bearings, and (iii) similar elements.

The likelihood of failure of a gusset plate and the concomitant collapse of a bridge may be minimized if the gusset plates are made from non-corrosive and high strength pure titanium metal or its alloy counter part. The use of titanium for the entire bridge structure is not practical at this time. However, it is feasible to provide titanium gusset plates in a bridge structure primarily because of the small tonnage of the gusset plates relative to the entire structure. This implies that the main members are made from the routinely used structural steel, but the connections are made from either pure titanium or its alloy counterpart. The structural performance of gusset plates made from pure titanium metal and its alloy counter part has been the subject of a recent study, which demonstrated titanium gusset plates to be both structurally sound and an economically viable alternative to the use of steel gusset plates [6-8].

The proposed solution will necessitate the need for a synergistic use of structural steel and titanium in close proximity to each other. Use of these two metals could lead to potential galvanic effect that serves to exacerbate conditions that are conducive for the corrosion of steel. Such a problem can be overcome by isolating the parts from each other either through the prudent use of coatings or a physical barrier, i.e., a transition piece. This kind of mixing coupled with the use of a transition piece will invariably necessitate the need to use fasteners (structural bolts). The use of bolted non-corrosive high strength titanium gusset plates in highway bridges can be a potentially viable solution to minimize gusset plate failures that can occur either due to corrosion related deterioration, or inadequate strength.

The primary objective of this study was to investigate viable and prudent alternatives for isolating pure titanium metal and its alloy counterpart along with the steel parts so as to minimize or even prevent the occurrence of accelerated galvanic corrosion of steel. The specific objective of this study was to evaluate and concurrently establish a viable method to isolate titanium gusset plates from the surrounding steel elements in a connection in order to prevent the triggering of accelerated galvanic corrosion, while concurrently assessing the effects of coupling two dissimilar metals, i.e., steel and titanium. Despite high cost, the corrosion resistance of pure titanium and its alloys is an important consideration in its selection as an economical and viable structural material with acceptable mechanical properties. Titanium provides excellent corrosion resistance in a range of environments under varying degree of aggressiveness due to the stable, protective and adherent titanium di-oxide film that forms instantly when a fresh surface of the metal is exposed to a moisture-containing environment, be it aqueous or gaseous [9, 10]. Titanium is preferred due to its immunity to "MIC" (Microbiologically Influenced Corrosion). At temperatures below 180°F (82°C), the occurrence of both crevice corrosion and pitting corrosion are mostly non-existent [10]. Furthermore, the pure metal and its alloy counterparts are immune to stress corrosion cracking (SCC) for bridge exposure conditions, and the strength loss due to corrosion fatigue resistance is

minimal. The adherent titanium dioxide film that forms on the surface acts as an excellent barrier to the ingress of hydrogen gas. However, when titanium is coupled with other metals, there occur conditions that are “locally” conducive for the initiation of galvanic corrosion. Due to the nobility of titanium in the galvanic series, the logic of coupling titanium with other dissimilar metals will only tend to accelerate corrosion of the other metal in the couple.

Dissimilar metal joints of titanium and steel with parts in intimate contact and susceptible to galvanic corrosion were investigated in this study. For the case of a steel structure in close proximity to titanium, steel would be anodic and more active (corrosion prone) when compared to titanium. Electrical isolation of the two metals is a means to eliminate galvanic corrosion and to ensure that no accelerated corrosion of steel is due to the titanium. A careful review of the published literature was conducted and is used to identify the corrosion data for steel and titanium joints while concurrently providing useful information related to viable techniques for isolation. In general, isolation of two dissimilar metals may be accomplished by using: (i) several coats of a zinc-rich primer, (ii) bituminous paint, and in some instances (iii) a high performance isolation tape. The structural performance of a primer, paint or tape is up until now untested and is susceptible to both wear and tear.

The effects of aggressive environmental conditions on (a) titanium, and (b) dissimilar metal combinations with pure titanium or its alloy counterpart as one of the metals in a joint can generally be categorized into two types [9-23]:

- (a) Galvanic Corrosion
- (b) Hydrogen-Induced Damage

These two topics are briefly reviewed in this paper. A brief discussion is included on aspects pertinent to the crevice corrosion experienced by dissimilar metals. An experimental evaluation of mixed-mode use of titanium in synergy with steel is presented and briefly discussed. Copper/steel galvanic action was included as a comparative system, since copper has a well known and strong galvanic action on steel. The results of galvanic corrosion tests are included along with the precautions that need to be taken in order to either prevent or minimize problems due to corrosion related to coupling of pure titanium and/or its alloys with structural grade steel.

2. GALVANIC CORROSION

In the case of a steel structure using titanium gusset plates, steel would be expected to be anodic (more active and corrosion prone) when compared to titanium. Therefore, isolation of the two metals may be necessary in order to ensure adequate long-term performance of the structure that contains titanium gusset plates while remaining sections of the structure are made from structural steel. A brief review of the existing literature is presented in this section to identify existing corrosion data specific to steel and titanium joints and the potential use of possible isolation techniques [12-22, 24].

Galvanic corrosion happens due to the different electric potentials exhibited by dissimilar metals. When these metals are placed in contact with each other, in the presence of an electrolyte, a galvanic couple is formed due to a tendency of the electrons to flow from the more negative metal (anode) to the more positive (cathode) of the two metals. This is an important aspect to be taken into consideration when attempting to join titanium to another metal because titanium is essentially cathodic relative to a large majority of the other metals it is likely to come in contact with. If proper steps to account for and minimize galvanic corrosion are not taken, both the integrity and useful life of the structure are likely to be compromised.

If the area of titanium (cathode) is noticeably large relative to that of the other metal, severe galvanic corrosion will occur. If the need for dissimilar joints is inevitable, it is best to: (i) use two metals that are close to each other in the galvanic series, (ii) insulate the joint, and (iii) provide cathodic protection. Use of large areas of the less noble metal coupled with heavy sections to allow for reduced corrosion has also been recommended [24]. However, such approaches tend to defeat the very purpose of using titanium gusset plates.

An important consideration with specific reference to the severity of galvanic corrosion is physical separation between the two metals in the galvanic table. A typical galvanic series is summarized in Table 1 for metals in sea water from US Army Missile Command Report RS-TR-67-11, "Practical Galvanic Series" [24]. The table related to the galvanic data provides useful guidance with respect to selecting metals to be joined, such that metals having a minimal tendency to interact galvanically can be coupled with minimal galvanic effects. Alternatively, the table also provides useful information on both the need and degree of protection required to minimize the anticipated galvanic interactions. The closer a metal is to another in the galvanic series, the more compatible will be the two metals with concomitant minimum galvanic interaction. Conversely, the farther one metal is from the other then greater will be the tendency for the occurrence of galvanic corrosion. The influence of joining dissimilar metals with one of the metals being titanium is provided in a TIMET report on corrosion resistance of metals [9]. In this report, it is shown that an increase in corrosion in mils per year (or mm per year) due to coupling with the listed metals can be different by an order of magnitude. In fact, coupling of titanium with low carbon steel was found to be the worst case for facilitating ease of environmental degradation or corrosion.

Table 1. Galvanic Table from MIL-STD-889 [Reference 24]

Active (Anodic)	Active (Anodic)	Active (Anodic)	Active (Anodic)
1. Magnesium	24. Al 2014-0	47. Uranium 8% Mo.	70. Silicone Bronze 655
2. Mg alloy AZ-31B	25. Al 2024-T4	48. Brass, Naval, 464	71. Stainless steel 304 (passive)
3. Mg alloy HK-31A	26. Al 5052-H16	49. Yellow Brass	72. Stainless steel 301 (passive)
4. Zinc (hot-dip, die cast, or plated)	27. Tin (plated)	50. Muntz Metal 280	73. Stainless steel 321 (passive)
5. Beryllium (hot pressed)	28. Stainless steel 430 (active)	51. Brass (plated)	74. Stainless steel 201 (passive)
6. Al 7072 clad on 7075	29. Lead	52. Nickel-silver (18% Ni)	75. Stainless steel 286 (passive)
7. Al 2014-T3	30. Steel 1010	53. Stainless steel 316L (active)	76. Stainless steel 316L (passive)
8. Al 1160-H14	31. Iron (cast)	54. Bronze 220	77. AM355 (active)
9. Al 7079-T6	32. Stainless steel 410 (active)	55. Copper 110	78. Stainless steel 202 (passive)
10. Cadmium (plated)	33. Copper (plated, cast, or wrought)	56. Red Brass	79. Carpenter 20 (passive)
11. Uranium	34. Nickel (plated)	57. Stainless steel 347 (active)	80. AM355 (passive)
12. Al 218 (die cast)	35. Chromium (Plated)	58. Molybdenum, Commercial pure	81. A286 (passive)
13. Al 5052-0	36. Tantalum	59. Copper-nickel 715	82. Titanium 5A1, 2.5 Sn
14. Al 5052-H12	37. AM350 (active)	60. Admiralty brass	83. Titanium 13V, 11Cr, 3Al (annealed)
15. Al 5456-0, H353	38. Stainless steel 310 (active)	61. Stainless steel 202 (active)	84. Titanium 6Al, 4V (solution treated and aged)
16. Al 5052-H32	39. Stainless steel 301 (active)	62. Bronze, Phosphor 534 (B-1)	85. Titanium 6Al, 4V (anneal)
17. Al 1100-0	40. Stainless steel 304 (active)	63. Monel 400	86. Titanium 8Mn
18. Al 3003-H25	41. Stainless steel 430 (active)	64. Stainless steel 201 (active)	87. Titanium 13V, 11Cr 3Al (solution heat treated and aged)
19. Al 6061-T6	42. Stainless steel 410 (active)	65. Carpenter 20 (active)	88. Titanium 75A
20. Al A360 (die cast)	43. Stainless steel 17-7PH (active)	66. Stainless steel 321 (active)	89. AM350 (passive)
21. Al 7075-T6	44. Tungsten	67. Stainless steel 316 (active)	90. Silver
22. Al 6061-0	45. Niobium (columbium) 1% Zr	68. Stainless steel 309 (active)	91. Gold
23. Indium	46. Brass, Yellow, 268	69. Stainless steel 17-7PH (passive)	92. Graphite
		70. Silicone Bronze 655	
End - Noble (Less Active, Cathodic)			

The Galvanic Table (Table 1) lists metals in the order of their relative activity when exposed to seawater environment. The list begins with the more active (anodic) metal and proceeds down to the least active (cathodic) metal of the galvanic series [24]. The galvanic series in the table applies to an electrolyte solution that is representative of seawater. The series will however be different for other types of solutions.

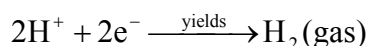
Another important consideration for the galvanic effect is kinetic factors. Table 1 shows the tendency of possible galvanic effects thermodynamically. The galvanic effect also depends on reaction kinetics of both the anode and the cathode. For example, the potential difference between stainless steel and aluminum is larger than that of carbon steel and aluminum. However, a stronger galvanic effect is found to exist between carbon steel and aluminum couple. [25].

The environment to which the metals will be exposed is also an important consideration. Stainless steel and aluminum are far apart in the galvanic series, and the potential difference is on the order of 650 mV. However, for applications in ambient temperature (298 K) and laboratory air (Relative Humidity of 55 pct), the occurrence of galvanic corrosion is unusual [26]. For galvanic corrosion to occur, it is essential for the following three conditions to exist:

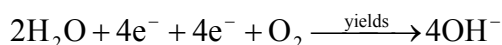
- (i) Metals of dissimilar electric potentials must be present.
- (ii) There must be an electrically conductive path between the two metals.
- (iii) Both metals must be in contact with a continuous electrolyte.

When the two metals are in direct contact with each other, there is a tendency for the electrons to flow from the anodic metal to the cathodic metal. A progressive loss of electrons from the anodic metal causes the release of positive ions into the electrolytic solution, thereby corroding the anode. The additional electrons that are gained by the cathodic metal are consumed by an electrochemical reduction reaction. Two of the most common reactions that are favored to consume electrons at the cathode are the following:

- (i) In acidic solutions, the reduction of hydrogen:



- (ii) In neutral or alkaline solutions, the reduction of oxygen:



The rate at which galvanic corrosion occurs is often influenced by several concurrent and mutually competing factors to include the following [27]:

- (a) Location of the two metals in the galvanic series and the electrolytic medium to which they are being exposed to.
- (b) The relative surface areas of the two metals in use.
- (c) Both the nature and kinetics of reactions occurring on the surfaces of the two chosen metals.
- (d) The nature and conductivity of the electrolyte.

Galvanic corrosion is not easily favored to occur if any one of these conditions does not exist. By eliminating any one or combination of these conditions, the electric circuit is broken and the electrochemical reactions responsible for galvanic corrosion cannot easily proceed. The most effective steps taken to prevent galvanic corrosion are often those taken during the design of the structure [27].

3. PREVENTION OF GALVANIC CORROSION ON A STEEL/TITANIUM COUPLE: A FEW OPTIONS

It is preferred to avoid the selection of multiple metals during the design process. Selecting metals that have minimal difference in galvanic potential plays a key role in minimizing corrosion related problems. In situations where this is not possible, it is important to minimize the ratio of exposed surface area of the cathode to the anode. Copper/steel galvanic action is a classic case to demonstrate this. Steel bolts (more active) in a copper plate are subject to intense galvanic action, i.e., large cathode (copper) and small anode (steel). Whereas, copper bolts in a steel plate, while not desirable, have a lesser detrimental galvanic effect on steel because the anode has a larger surface area than the cathode.

Electrically insulating the anode from the cathode is another effective method to break the galvanic circuit and concurrently prevent the occurrence of galvanic corrosion. This is often achieved through the selective use of both non-conductive spacers and sleeves for situations where corrosion of the bolts is of concern. In many practical situations, use of this method of prevention may not be feasible since a large mechanical stress has to be either transferred or sustained across the two metals, and this will tend to damage the weaker material of the insulator.

Prevention of galvanic corrosion can also be achieved by exercising care to isolate the metal junction from the environment containing the electrolyte. Frequently this is made possible by applying a moisture resistant paint or moisture displacing grease on the surfaces both at and immediately surrounding the junction, thus keeping it free of contact with the electrolyte [28]. The effectiveness of this method is dependent on both the maintenance and upkeep of the coatings. Minor imperfections in the paint system can lead to a progressive intensification of corrosion that occurs “locally”, such as an imperfection, resulting in initiation and rapid progression of degradation of the protective coating.

One other attractive method that has been used to reduce galvanic corrosion on a certain metal is to take advantage of the nature of galvanic corrosion and to introduce a third metal that is more anodic into the galvanic circuit. When this is done, the third metal will selectively corrode, sparing the other two cathodic metals from environmental attack and concomitant degradation. For example, in marine environments for immersed structures, zinc anodes are used to offset the detrimental galvanic action on steel by copper alloys. The zinc, being more anodic than the other metals used in the structure behaves in a sacrificial manner, thereby preventing the occurrence of corrosion of the other two metals. If the zinc anodes are continuously replaced, then the other metals used in the structure will be spared from environmental attack and resultant degradation through corrosion.

The key determinant in the conjoint use of steel and titanium (be it pure or alloy counterpart) is the presence of moisture. The initiation and occurrence of galvanic corrosion can be minimized if moisture can be prevented from entering the metal joints. One effective and commonly used method to prevent the penetration of moisture into a gusset plate joint is to seal the joint using a suitable polymer or any other commercially available sealant subsequent to installation of the bolts. Also, for the purpose of minimizing corrosion, it is essential to avoid having a small area of the anode relative to the area of the cathode. A few other methods of protection exist and are available in the published literature. For example, Erb [24] provided a number of viable recommendations to minimize both the initiation and progress of galvanic corrosion. A few of his essential recommendations are:

1. Sacrificial—Apply a sacrificial coating having a potential similar to or near that of the anodic member to the cathodic member.

2. Sealing –Make the surfaces essentially impervious to water by sealing.
3. Resistance - Increase the resistance of the electrical circuit by either painting or coating of all the surfaces.
4. To use a large area for the anode, this will reduce the galvanic current density on the anode resulting in lowering the level of attack.
5. To design an overall small ratio of cathode-to-anode.

In seawater environment, all exposed edges must be sealed, and an interposing material that is compatible with both the anode and the cathode must be used as the non-compatible material. If allowable, an external joint can be coated on its exterior surface using an effective paint system. It is advisable to utilize as many corrosion protection techniques as possible, since the intrinsic effects of each protection technique would provide substantially better protection when compared to the use of any one technique.

Special consideration must be given to both the material and protection of bolts in a dissimilar material couple, as they are easily susceptible to corrosion and often of critical importance to the overall integrity of the connection. If the bolts are made of mild steel, they are exposed to the possibility of intense corrosion and resultant degradation essentially due to the relatively high surface area ratio of titanium to steel present in a bolted connection. Ideally, the bolts in such a situation would be made of the cathodic metal, which in this case is titanium. Another, more feasible recommendation would be to use stainless steel or galvanized bolts for this application. The galvanic behavior of stainless steel is quite similar to that of titanium so as to minimize both the initiation and occurrence of galvanic corrosion under normal operating temperatures. Galvanized steel provides a sacrificial coating of zinc on steel bolts, which will tend to preserve the underlying metal for a fixed time period until the zinc gradually corrodes away.

Substantial additional protection can also be provided using a coating of paint having low moisture/oxygen permeability. This would tend to effectively isolate the joint of the two metals from the electrolyte (even ambient air qualifies as an electrolyte once the humidity reaches a certain level), and thereby minimize the effects of galvanic corrosion. Periodic inspection coupled with maintenance of the paint would be both essential and necessary to prevent spot degradation, as this leads to intensified corrosion of the steel that is exposed at these locations. The type of paint to be used and its composition will vary based on: (i) nature of the environment to which the metal will be exposed, and (ii) performance expected from the coating. Often these requirements are unique to a specific project and the application of a coating is often dictated on a case-by-case basis.

4. HYDROGEN CRACKING IN TITANIUM-BASED ALLOYS

In most situations, titanium can be safely chosen and used without any problems in hydrogen-containing environments and under conditions where galvanic couples or cathodic protection systems favor exposure of the metal surface to gaseous hydrogen. However, there have been a few failures linked to hydrogen embrittlement caused by the formation and presence of hydrides. In most cases, the oxide film which covers the surface of titanium provides an effective barrier to the penetration of hydrogen. However, titanium has the tendency to easily absorb hydrogen from hydrogen-containing environments under some circumstances [9].

At temperatures below 170°F (77°C), the formation of hydrides tends to occur slowly and has minimal to no practical significance except in conjunction with a high tensile stress. In the presence of trace amounts (about 2%) of moisture in the hydrogen gas, passivation of the titanium metal is favored to occur such that absorption of hydrogen is prevented even at high pressures and

temperatures. A serious problem occurs when cathodically impressed or galvanically-induced currents generate atomic (nascent) hydrogen directly on the surface of the titanium metal (be it pure metal or alloy counterpart) [9].

Careful laboratory investigations and experiments have demonstrated the following three conditions to exist simultaneously for the purpose of hydriding the unalloyed titanium [9]:

1. pH of the solution is less than 3, the metal surface is damaged by abrasion, or the impressed potentials are more negative than -0.7V.
2. The temperature is above 170°F (77°C) or else only surface hydride films will tend to form, which do not adversely affect the properties of the base metal. The occurrence of failure due to hydriding is rarely encountered below this temperature.
3. There must be a mechanism for generating hydrogen. This may be through the following mechanisms: (i) galvanic couple, (ii) cathodic protection by impressed current, (iii) corrosion of titanium, and (iv) dynamic abrasion of the surface with sufficient intensity to depress the metal potential below that required for the spontaneous evolution of hydrogen.

Most of the hydriding related failures experienced by the titanium metal that have occurred while in service can be explained on this basis [29-31]. Hydriding can be either avoided or retarded by altering at least one of the three conditions listed above.

Titanium and its alloys are considered to be reasonably resistant to chemical attack. However, when exposed to a hydrogen-containing environment, both hydrogen cracking and hydrogen-induced secondary phase formation may occur. For example, Tal-Gutelmacher and Eliezer in their independent study [18] found that the fully-lamellar microstructure almost always had a tendency for higher hydrogen absorption when compared to the alloys having a duplex (i.e., $\alpha+\beta$) microstructure. The hydrogen-induced damage experienced by both pure titanium metal and its alloy counterparts was characterized by a noticeable loss of ductility coupled with a concurrent reduction in the stress-intensity threshold for crack propagation. The presence of significant amounts of the β -phase coupled with the formation and presence of the brittle titanium hydride phases resulted in severe degradation of both the mechanical and fracture behavior of the chosen alloys. These researchers also observed that upon exposure to an electrochemical hydrogen environment, strain was induced in both the as-fabricated and/or as-received specimens and the aged counterpart [23]. Their study provided the following useful information [23]:

1. Due to its affinity for hydrogen, the occurrence of hydrogen-induced cracking in titanium was observed upon exposure to a hydrogen-containing environment.
2. The key mechanism that governed hydrogen-induced cracking was the formation and presence of brittle titanium hydride phases.
3. For the case of the widely preferred, chosen and used Ti-6Al-4V alloy, the severity of hydrogen-induced cracking depended on the amount of β -phase present in the microstructure.

5. CREVICE CORROSION OF SIMILAR AND DISSIMILAR COUPLING OF TITANIUM AND ITS ALLOYS

In this section, the key and relevant findings from a few studies conducted by others on crevice corrosion are briefly summarized.

5.1 Corrosion of Metal Crevices in the Engineered Barrier System of a Potential Nuclear Waste Repository

Crevice corrosion is favored to occur when the corrosion potential (E_{corr}) exceeds the repassivation potential for crevice corrosion (E_{rcrev}). The purpose of research done by He and co-workers [14] was to evaluate the specific role of both similar and dissimilar metal-to-metal crevices on the corrosion behavior of: (i) Type 316L stainless steel, (ii) Titanium Grade 7, (iii) mill-annealed Alloy 22, and (iv) welded plus solution annealed Alloy 22, under simulated environmental conditions.

In the test assembly, the crevice specimen was sandwiched between two serrated washers, a bolt, and a nut. The crevice specimen was machined from a certain metal, while the serrated washers, bolt, and nut were machined from a dissimilar metal. The initiation of crevice corrosion and propagation occurred by galvanically coupling the crevice specimen to either an alloy (referred to in this study as Alloy 22) or titanium (Grade 7) plate. After adequate time for the propagation of corrosion, these researchers determined the following:

- (i) Initiation of crevice corrosion did not occur under the coupling, and
- (ii) Initiation of crevice corrosion did not occur even after the addition of a corrosion inducer.

In a companion experiment, the crevice specimen was machined from a welded plus solution annealed alloy (Alloy 22) and titanium (Grade 7) was used as the coupling plate. No crevice corrosion was evident in either of the two specimens.

5.2 Monitoring of Crevice Corrosion in Titanium and its Alloys Using Microelectrodes

Both titanium and its alloys are highly resistant to corrosion primarily because of the tendency to form surface oxide films. For this specific reason, both pure titanium metal and its alloy counterparts are frequently chosen for use in industrial and emerging biomedical applications. However, like most metals, titanium eventually becomes susceptible to crevice corrosion when exposed to environments spanning a range of aggressiveness. Other key factors that exert an influence on crevice corrosion are: (i) temperature, (ii) solution chemistry, and (iii) pH of the solution. Therefore, mechanistic aspects of crevice corrosion in both high chloride-containing and temperature-related conditions were studied by the careful measurement of crevice pH, crevice potential, crevice current, and chloride-ion concentration within a crevice of the titanium metal [16].

Upon successful completion of several monitoring experiments, the tests clearly revealed that the initiation or onset of crevice corrosion in titanium occurred at around 100°C. This initiation was ascribed to a ‘local’ increase in chloride ion content coupled with a concurrent decrease in pH within the crevice as a function of time. Continuation of the crevice corrosion was facilitated by the formation and presence of acidic ions in the crevice of the titanium metal. For the case of pure titanium, the acidity of the crevice environment was found to be high. However, presence of trace amounts of molybdenum in the titanium enables the acidity in the “local” environment to drop due to the creation and presence of a passive film immediately around the crevice. Therefore, the crevice corrosion resistance of a titanium alloy that contained molybdenum was found to be noticeably superior to the crevice corrosion resistance of pure titanium metal.

5.3 Corrosion Behavior of Titanium-Clad Carbon Steel in Weak Alkaline Solutions

Since titanium is well noted for its high corrosion resistance, it can be safely used as a material for a container, which has to hold a high-level radioactive nuclear waste for prolonged period of time.

Pure titanium metal is noted for its ability to offer a high resistance to corrosion since its surface oxide layer is chemically stable. Once the surface of the titanium metal is damaged, an oxide layer tends to form both at and immediately around the damaged area thereby protecting the base metal from the oxygen-containing environment. Researchers have measured the polarization curves for titanium, carbon steel, and titanium-clad carbon steel, which were placed in three different solutions: (a) bentonite-contact solution, (b) sodium sulfate solution, and (c) borate solution [11]. These three solutions were chosen for the purpose of testing primarily because each is representative of environmental concern for exacerbating the initiation and continued occurrence of corrosion.

The researchers used titanium (Grade 2), carbon steel, and titanium-clad carbon steel fabricated using the technique of explosive welding. Optical microscope images of the surface were taken of each of the chosen test specimens. It was observed that the specimens immersed in the solutions containing sulphate ions (SO_4) were partially covered with rust (a corrosion product), while test specimens that were immersed in the borate solution revealed no visible change. The amount of corrosion product that formed on the test specimen when exposed to the solution at 353 K was noticeably more than the amount of corrosion product that formed on the specimen surface when exposed to the same solution at ambient temperature (298 K). Upon careful removal of the corrosion products from the surfaces of the exposed specimens, it was observed that the depth of corrosion was not uniform. Also, it was observed that the corrosion loss on steel side of the titanium-clad specimen was noticeably larger than the loss due to corrosion experienced by the steel specimen. These researchers also observed that the steel side of the titanium-clad steel specimen when exposed to the SO_4 solution did undergo corrosion, but the same side did not significantly corrode when placed in a solution containing borate solution under open circuit conditions. Also, in the SO_4 -containing solution, the titanium side of a titanium-clad specimen is cathodically polarized. Therefore, a 'local' bimetallic corrosion condition is conducive for accelerating corrosion on the steel side.

5.4 Corrosion and Micro structural Aspects of Dissimilar Joints of Titanium and Type 304L Stainless Steel

Several processes for the joining of dissimilar metals, such as 304L stainless steel and Titanium Grade 2, in an attempt to produce joints having adequate strength, ductility, and corrosion resistance have also been examined [20]. In this specific study, the researchers did make an attempt to investigate whether titanium could be used to construct the electrolytic dissolver unit, while 304L stainless steel could be safely used for components of the nuclear fuel-reprocessing plant. Since 304L stainless steel yields unacceptably high corrosion rates in the chosen environment, these researchers opted to choose titanium as the material for the purpose of construction primarily because it has shown acceptably low corrosion rates under these conditions. A high corrosion resistance in a severely corrosive environment coupled with adequate mechanical strength and ductility were the minimum requirements [20].

Considering both the size and geometry of the mechanical setup it was found that solid-state welding processes, such as: (a) friction welding, and (b) explosive welding, could be safely considered for the joining of 304L stainless steel with titanium [20]. Once the dissimilar metals were joined, a three-phase corrosion test was conducted in an environment of boiling nitric acid for test specimens created using the two welding processes. These experiments essentially involved exposing the chosen metals to the liquid, condensate, and vapor phases of nitric acid for time periods of 48 hours. Upon completion of the exposure to the environment, the corrosion rates in each of the three phases were measured. It was observed that the corrosion rates in the condensate phase were noticeably higher than in the liquid and vapor phases for both the friction welded joint

and the explosive bonded joint. The corrosion rate for the friction welded joint was found to be acceptable. However, the corrosion attack was noticeably significant at the joint interface. For the explosive bonded joint, the corrosion rate was found to be acceptable because all of the corrosion attack took place on the stainless steel portion of the joint. Based on an extensive investigation, and additionally considering corrosion resistance to be the most critical requirement, the explosive bonded joint between titanium and 304L stainless steel was validated for connecting these two dissimilar metals.

5.5 Joining of Titanium/Stainless Steel by Explosive Welding and Effect on Interface

Titanium clad steel is currently gaining acceptance and is being chosen for use in components that are exposed to environments having a range of aggressiveness. Since information pertaining to explosively welded Ti-6Al-4V to stainless steel and their corrosive behavior is lacking, the goal of the study was to examine the metallurgical properties and corrosion patterns occurring at the interfaces when joining titanium to steel.

Once the Ti-6Al-4V and stainless steel were explosively welded, the resultant titanium clad samples measuring 15mm x 15mm were held in a 3.5% NaCl solution for time duration of (i) 672 hours, (ii) 1344 hours, and (iii) 2016 hours. For each test, the weight loss or gain experienced by the test samples was determined to a precision of 1/10,000. It was observed that the mass of the test sample increased with time of exposure to the environment for both the original and titanium clad plates. Also, mass of the titanium clad plate rose quickly up to 1344 hours of exposure to the environment, while mass of the welded plates rose at a slower rate from 1344 hour to 2016 hour of exposure to the environment.

The rate of mass increase gradually slowed primarily because the surfaces of both metals were initially clean at the beginning of the corrosion tests. Consequently, the oxide layer that formed on the surfaces grew rapidly during the preliminary stages of exposure to the environment and resultant degradation due to corrosion. Therefore, the corrosion rate of titanium clad stainless steel specimens was comparatively large during the initial stage of the test, but gradually decreased with an increase in exposure time to the environment.

6. EXPERIMENTAL EVALUATION OF GALVANIC CORROSION

An experimental research effort was conducted in this study for the purpose of evaluating the existence of galvanic effects between steel and titanium. Steel and copper galvanic action was included as a reference system. Tests were performed on three different test specimen combinations. The corrosion rates experienced by the test specimens were determined from these tests so as to establish the following: (a) a test procedure, and (b) a benchmark performance measure, for continuing studies in the subsequent phase of this project.

6.1 Materials

Copper was chosen to be the reference metal in the galvanic corrosion experiments primarily because of strong, detrimental galvanic effects on steel. The copper chosen was high-strength copper (Alloy 182), which is also known as RMA Class 2 chromium-copper. High-strength copper is stronger, harder, and more resistant to wear than pure copper. This copper alloy is often chosen for use in industrial applications including mold making, cable shields, and welding electrodes and is commercially available. The Ti-6Al-4V alloy was chosen for use in the experiments. This alloy was provided by Allegheny Technologies Inc., (ATI Wah Chang, based in

Albany, OR) in the form of plates in the size 0.25 in (thickness) x 12 inch (width) x 36 in (length). The chemical composition of the alloy is given in Table 2. The third metal used in the experiments was steel, whose chemical composition is given in Table 3. Other physical and mechanical properties related to the test plates are given in Tables 4 and 5.

Table 2. Nominal Expected Chemical Composition of Ti-6Al-4V (in weight percent)

Material	Ti	Al	N	V	C	Fe	H	O
Ti-6Al-4V	90.0	6.0	0.05	4.0	0.1	0.4	0.02	0.20

Table 3. Chemical Composition (in weight %) of Experimental Steel

Iron	Fe	Balance
Carbon	C	0.50
Manganese	Mn	0.69
Phosphorus	P	0.016
Sulfur	S	0.008
Silicon	Si	0.44
Chromium	Cr	3.15
Nickel	Ni	0.10
Molybdenum	Mo	1.45
Columbium	Cb	0.005
Aluminum	Al	0.008
Copper	Cu	0.13
Vanadium	V	0.03
Titanium	Ti	0.001

Table 4. Summary of Relevant Mechanical Properties of the Chosen Materials

Material	Orientation	Elastic Modulus		Yield Strength		UTS		Elongation GL=0.5" (%)	Reduction in Area (%)	Tensile Ductility ln(A ₀ /A ₂) (%)
		ksi	GPa	ksi	MPa	Ksi	MPa			
Ti-6Al-4V	Longitudinal	138	126	137	948	154	1060	7.8	23.8	27.0
	Transverse	20	137	151	1047	171	1181	11.5	21.7	25.0
Commercially Pure (Grade 2)	Longitudinal	16	115	63	431	81	551	14.7	43.4	57.0
	Transverse	15	108	55	381	67	465	18.9	47.0	63.0

Table 5. Summary of Relevant Physical Properties of the Chosen Materials

Material	Density gm/cc	Coefficient of Thermal Expansion per degree C	Poisson's Ratio	Shear Modulus	Flexural Toughness
Ti-6Al-4V Titanium Alloy	4.42	$8.8 \text{ to } 9.2 \times 10^{-6}$	0.29 to 0.39	41 GPa	40 to 60%
Commercially Pure Titanium	4.5	$8.6 \text{ to } 9.2 \times 10^{-6}$	0.29 to 0.39	41 GPa	70% or more

6.2 The Test Specimen and Experimental Procedures

Three different test specimen combinations were used during the galvanic corrosion experiments:

- (a) Titanium alloy and Steel
- (b) Titanium alloy and Copper
- (c) Copper and Steel

Copper was used as a reference to facilitate comparison with titanium. For each combination of the chosen test specimens, the cathode surface area measured 23.25 in^2 , while the anode surface area measured 1.375 in^2 , resulting in a cathode to anode surface area ratio of 17:1. The electrolyte used was 5 M NaCl solution at ambient temperature (298 K). The test setup is shown in Figure 3.

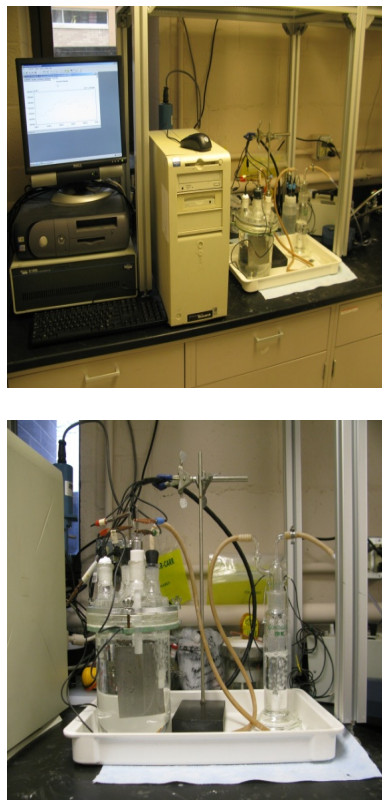


Figure 3. The Experimental Setup for Conducting Galvanic Corrosion Tests

Each galvanic corrosion test was run for 24 hours and the potential (V) and current (A) recorded at periodic intervals. Two experiments were performed for each of the three combinations of test materials chosen. Faraday's Law was used to calculate the corrosion rate (mils per year) for each galvanic corrosion experiment. According to this law, the corrosion rate (mpy) is determined using the expression:

$$\text{Corrosion Rate (mpy)} = \frac{0.13 I_{\text{corr}} (E.W.)}{d}$$

In this expression, I_{corr} is the corrosion current density, ($E.W.$) is the equivalent weight in grams/equivalent, d is the density, and the corrosion rate constant is taken to be 0.13 derived based on milli-inches (amp-cm-year). The resulting corrosion rate works out to be in mils per year (0.001 inch per year) when this expression is used.

Prior to the initiation of the galvanic corrosion tests, the test specimens were mechanically ground on progressively finer grades of silicon carbide (SiC) impregnated emery paper using copious amounts of water both as coolant and lubricant. For the titanium and copper specimens, 240-grit, 400-grit, and 600-grit SiC impregnated emery paper was used for mechanical grinding and polishing. The same combination along with 1200-grit emery paper was used for the steel specimen. Each specimen was initially wet ground on all six faces until a mirror-like surface finish was obtained. The polished specimens were then cleaned using methanol with subsequent immersion in an ultrasonic cleaner. The polished and cleaned surfaces were then rinsed in de-ionized water prior to the initiation of exposure to the chosen environment.

The galvanic corrosion tests were conducted in a 2 liter glass test cell. The reference electrode was a saturated calomel electrode (SCE). In order to saturate the 5M NaCl solution with air, an air bubble machine was used in the experiment. A glass tube was connected to the gas wash bottle. Subsequently, the gas wash bottle was connected to the air bubble machine.

Prior to initiation of the galvanic test, the open circuit potentials (OCP) were measured on both electrodes. During the galvanic corrosion tests, the combined potential and galvanic current were both recorded using a potentiostat meter [Gamry PC4/750].

6.3 Results and Discussion

The test results are summarized in Table 6. Variation of the potential with time for the galvanic combination of titanium and steel for time duration of 24 hours is shown in Figure 4. The corresponding variation of galvanic current density with time is shown in Figure 5. The corrosion process for steel can be expressed as:

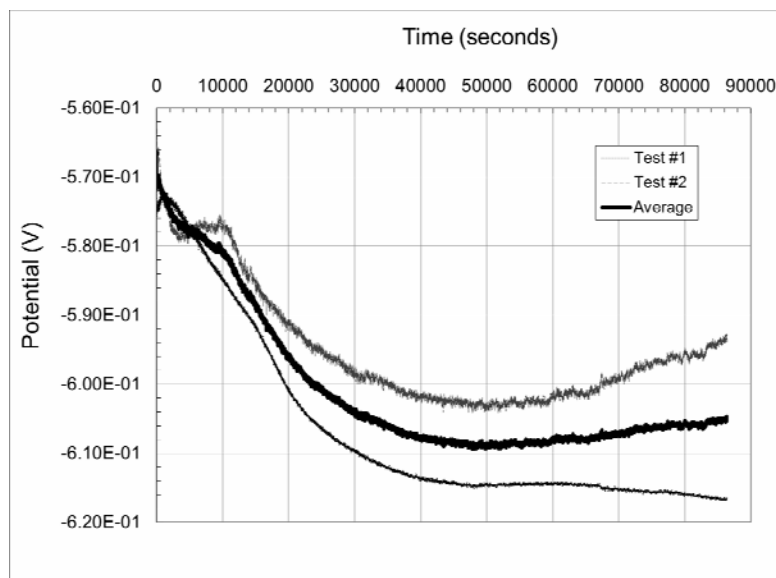
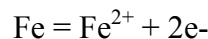


Figure 4. Potential Changes with Time for the Titanium-steel Galvanic Couple

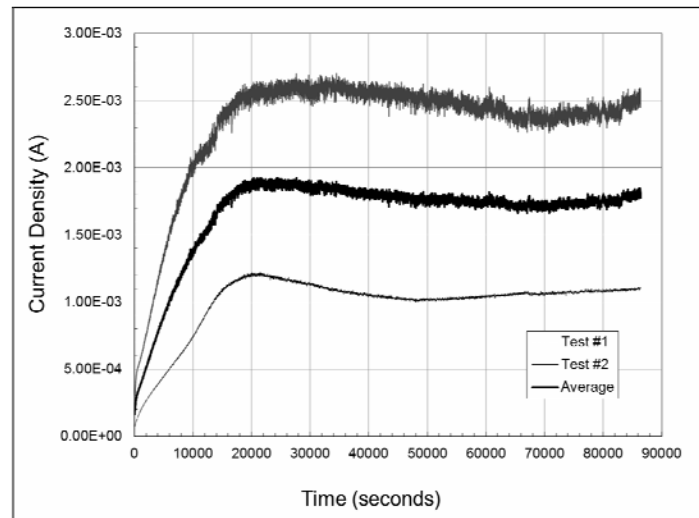


Figure 5. Readings of Current Density as a Function of Time for the Titanium-steel Galvanic Corrosion Tests

Table 6. Corrosion Rate in mils (Thousandths of an Inch) per Year

Titanium and Steel		Titanium and Copper		Copper and Steel	
Test #1	Test #2	Test #1	Test #2	Test #1	Test #2
78.8	177.6	2.3	1.4	163.4	177.6
Average:	128	Average:	2	Average:	171

Assuming the initiation and progression of corrosion to occur uniformly, the corrosion rate (mils per year) can be estimated using Faraday's law.

Since occurrence of galvanic corrosion between the titanium gusset plates and connecting members made of steel could be an issue, the galvanic corrosion tests were performed in order to effectively determine if future testing was needed. Copper was used as the reference metal. After performing two sets of galvanic corrosion tests for each of the three metal combinations chosen, the following are the key findings:

1. Even though titanium is more noble (greater positive potential) than copper in the galvanic series, the galvanic current of the titanium/steel couple is noticeably smaller than the copper/steel couple. This indicates that titanium is more readily polarized and has smaller cathodic reaction kinetics, with a concomitant reduction in the galvanic effect when compared to that of the copper/steel couple.
2. On account of titanium being more noble than copper, the galvanic effect between Ti/Cu was found to be negligible as shown in Table 6.
3. In addition to the potential difference in the galvanic series, the nature and kinetics of the reactions occurring on the surfaces of the two metals is a critical factor in controlling the galvanic effect of the two different metals.

Additional testing is planned for the near future with the prime objective of both developing and consolidating the key strategies to study galvanic corrosion of titanium and steel. The preliminary tests reported in this paper have formed the basis for continued tests. Similar tests are also being conducted using both coatings and other isolating films in order to develop a cost-effective solution for the joining of titanium and steel.

7. CONCLUSIONS

The use of titanium alloys on a steel structure is feasible provided steps are taken to limit the exposure of steel to galvanic corrosion. A careful selection of the bolt materials when using titanium gusset plates will be essential to ensure integrity of the structure when exposed to a corrosive environment. Additional corrosion protection can be gained by the isolation of titanium/steel joints from the environment through the application and maintenance of an impermeable paint or physical barriers. Every research endeavor involving the use of a titanium/steel couple will present unique environmental conditions, and the specific decision regarding protection against galvanic corrosion should be made on a case-by-case basis depending on both nature of the environment and service requirements of the structure. In this paper is presented and discussed the key findings from an experimental study that evaluated the galvanic corrosion of titanium and steel couple.

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