Zirconium and Zirconium Alloys for Use in Sulfuric acid Applications

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Abstract

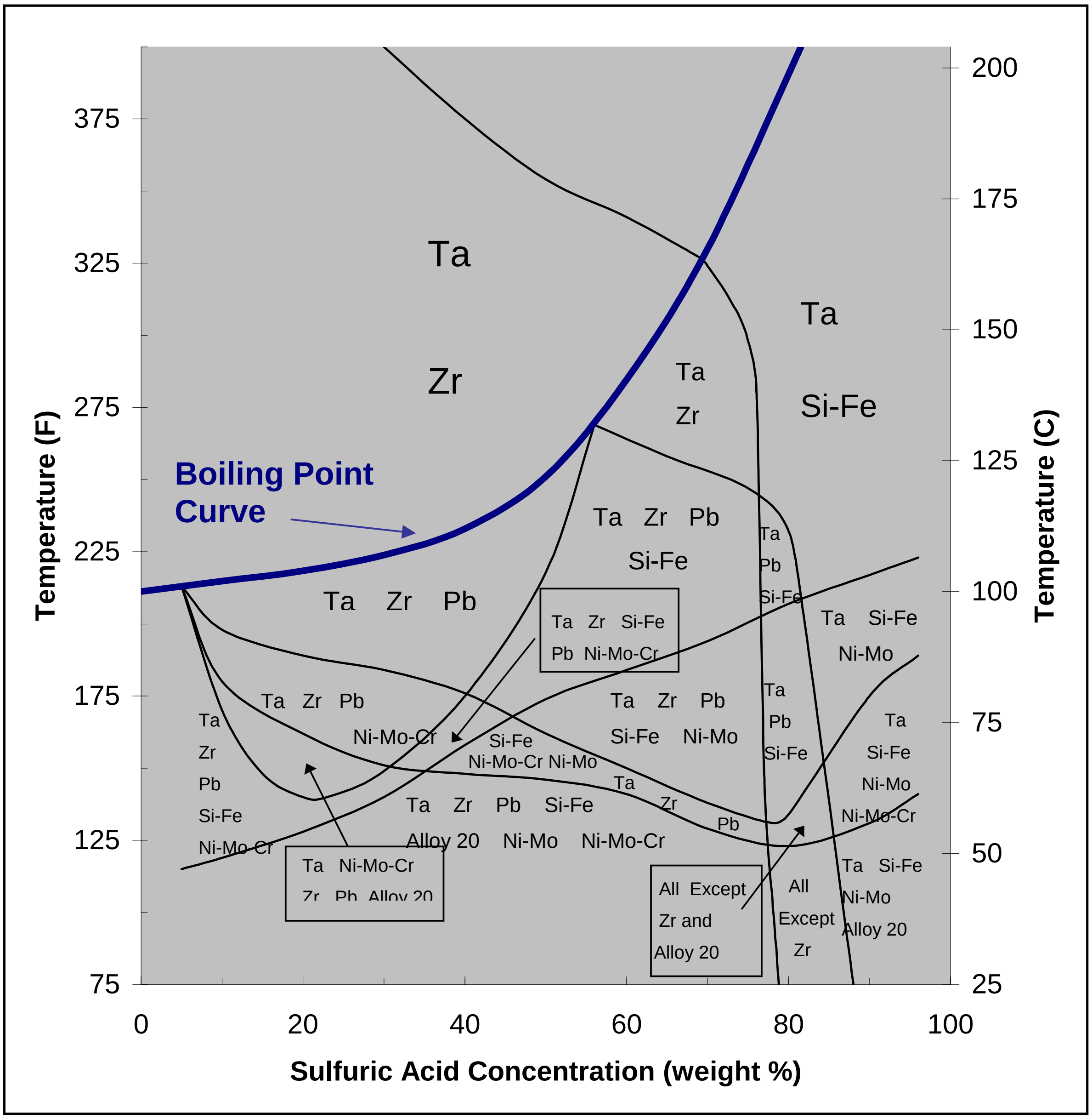
Sulfuric acid is produced in the largest quantity and is one of the most important inorganic chemicals in the world. Sulfuric acid is used commonly during the manufacture of chemicals as many chemical processes use sulfuric acid as catalysts, dehydrating agents, absorbents, and as oxidizing or reducing agents. Although zirconium has been used in a wide variety of chemical processing industry applications for over 40 years, one of the earliest chemical processing applications for zirconium was in the sulfuric acid environment. Zirconium is one of the few materials that is resistant to sulfuric acid at the full concentration range through 70% and above boiling temperatures. During the past 2 decades the use of Zircadyne® zirconium in sulfuric acid has continued to increase throughout the world and in many new applications.[1] Zirconium has been used in processes such as the production of methyl methcrylate, alcohol, certain organic synthesis reactions, sulfuric acid recovery systems as well as sulfuric acid pickle tank heaters. Zirconium has been chosen for sulfuric acid environments due to its high corrosion resistance and low environmental impact. Use of zirconium as grid coils for sulfuric acid pickle baths allowed a more efficient and environmentally safe method of acid heating.

This paper will describe the corrosion resistance of zirconium in a three general sulfuric acid application areas and will show why zirconium was a material of choice for use in these applications. This paper will also describe the factors (alloy composition, impurities, heat treatment, stress, acid concentration, temperature) that could affect the corrosion resistance of zirconium. A method for heat treatment of zirconium for improved corrosion resistance in elevated concentrations and temperatures will also be discussed. This paper will also describe a new low tin zirconium alloy that was developed for improved corrosion resistance in the higher sulfuric acid concentrations and higher temperatures.

Introduction

One can often look to the production and/or use of sulfuric acid as an indication of the industrial activity of a nation. Few chemicals are manufactured without sulfuric acid being involved. It is a strong di-basic acid and can be a reducing acid, an oxidizing acid, and/or a dehydrating agent. In the chemical industry, sulfuric acid has many diverse applications. The largest quantities are used in the manufacture of phosphate and nitrogen based fertilizers. The petrochemical sector utilizes sulfuric acid in alkylation and paraffin refining. The inorganic branch of the chemical industry uses sulfuric acid in the production of nitric acid, hydrochloric acid, chromic acid, hydrofluoric acid and sulfate salts, such as aluminum sulfate and sodium sulfate. The organic chemical segments employ sulfuric acid in the manufacture of explosives, soaps, detergents, dyes, iso-cyanates, plastics, pharmaceuticals, etc.

Corrosion of metals by sulfuric acid is very complex, as there are oxidizing and reducing conditions depending on concentration. The graph in Figure 1 gives approximate conditions where different metals can be used successfully. As the Figure shows, there are several alternatives if the temperature is low, from ambient to the boiling point. Once the process temperature requires operation at boiling point or above, very few construction materials are available. At the higher concentrations, above approximately 65%, the environment is oxidizing, while at low concentrations the conditions are reducing. This requires different metals to be used depending on the conditions.



Materials shown in this Figure will exhibit a corrosion rate of less than 20 mpy (0.5mm/yr) except for Zr and Ta, which have a corrosion rate of less than 5 mpy (0.125mm/yr).

Figure 1: Suitability of Materials in Sulfuric Acid

Zirconium is very resistant to strong acids like sulfuric acid because the protective oxide coating is chemically inert and thermodynamic stable. Figure 2 shows the iso-corrosion curve for zirconium in sulfuric acid. As the curve shows, zirconium resists corrosion attack at concentrations up to 70% and above the boiling point. In concentrations greater than 70% the strong oxidizing power of sulfuric acid can cause breakdown of the protective oxide film on zirconium.[3] At concentrations below 20%, zirconium resists attack to temperatures well above boiling to over 200°C. A prime advantage of zirconium over other metals is at temperatures above 175°F (80°C), where the sulfuric acid concentrations range from 10% to 65%. Weld areas exhibit higher corrosion rates as shown by the Weld Limit Line and will require heat treatment if conditions exceed this line.

The Zr705 grade, in many instances, has slightly less corrosion resistance than that of Zr702. Figure 3 shows the difference in corrosion resistance of Zr702 and Zr705 alloys.[2]

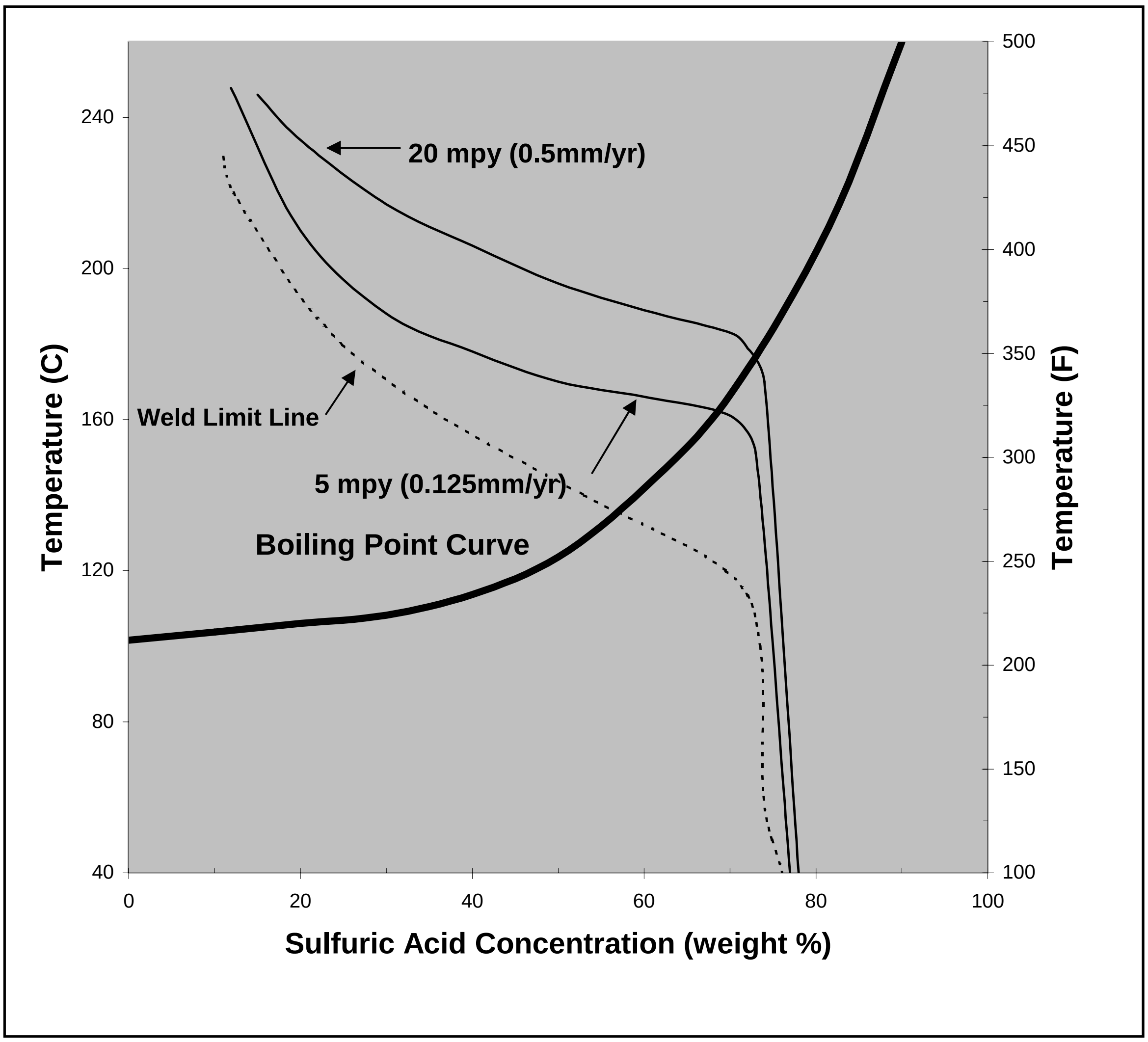


Figure 2: Iso-Corrosion Diagram for Zr 702 in Sulfuric acid

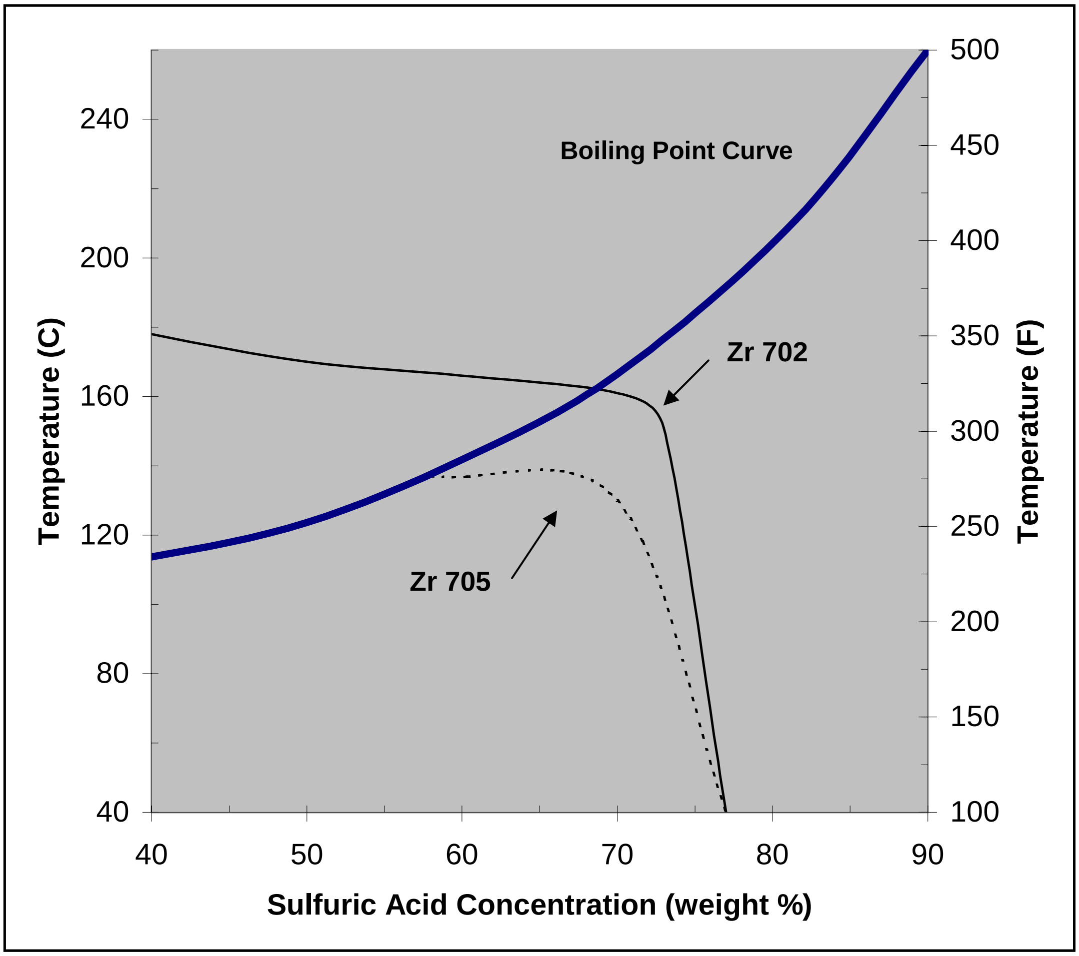


Figure 3: Comparison of Zr 702 and Zr 705 Iso-corrosion Curves, 5mpy (0.125mm/yr)

Zirconium Alloy Grades

Zirconium alloys for chemical processing are available in four ASTM grades, Zr702, Zr704, Zr705 and Zr706 but only two of these alloys (Zr702 and Zr705) are commonly produced and currently approved for use in the ASME Boiler and Pressure vessels. Table 1 and Table 2 show the mechanical and chemical properties of the commercial zirconium alloys. Zr702 has the lowest strength and generally the best corrosion resistance of the chemical processing grades. The Zr705 alloy, with 2-3% niobium has higher strength and better formability than that of the Zr702 grade. Both Zr702 and Zr705 have been utilized in sulfuric acid applications.

Zirconium grade	702	704	705	706
ASTM Desg.	R60702	R60704	R60705	R60705
Tensile St., Min. ksi (MPa)	55(379)	60(413)	80(552)	74(510)
Yield Str., Min. ksi (MPa)	30(207)	35(241)	55(379)	50(345)
% Elongation, (0.2% offset)	16	14	16	20
Min. Bend Test Radius	5T	5T	3T	2.5T

Table 1. Mechanical Properties of Zirconium Alloys

Zirconium Grade	702*	704	705*	706
ASTM Design.	R60702	R60704	R60705	R60706
Zr+Hf, min.	99.2	97.5	95.5	95.9
Hafnium, max.	4.5	4.5	4.5	4.5
Fe+Cr, max.	0.2	0.2-0.4	0.2	0.2
Sn	--	1.0-2.0	---	--
Hydrogen, max.	0.005	0.005	0.005	0.005
Nitrogen, max.	0.025	0.025	0.025	0.025
Carbon, max.	0.05	0.05	0.05	0.05
Niobium	--	--	2.0-3.0	2.0-3.0

*Approved for use in ASME Boiler and Pressure Vessel applications

Table 2. Chemical compositions of Zirconium Alloys

Application Areas for Zirconium in Sulfuric Acid

Zirconium is used in three general types of application areas for sulfuric acid. These regions include the lower concentration/high temperature; the mid-concentration and below boiling temperature; and the higher concentration range. The following reviews the application ranges which zirconium is currently used.

I. Low Concentration / High Temperature

Pulp Digestion Applications: <5% concentrations at above boiling temperatures

At the lower concentrations and lower temperatures, many materials would have acceptable corrosion resistance in sulfuric acid. At temperatures above boiling, few materials will provide adequate corrosion resistance with the exception of zirconium or tantalum. Zirconium was considered for use in the lower concentration of acid at temperatures well above the boiling point because of this excellent corrosion resistance. In 1984, Tennessee Valley Authority selected Zircadyne® Zirconium 705 for an application at the Muscle Shoals, Alabama facility for use in the production of ethanol from wood pulp.[4] The hardwood pulp was dissolved using sulfuric acid at the lower concentrations, high pressures, and high temperatures to convert this sugar to ethanol. Hydrolysis equipment for the first and second stage equipment had to withstand maximum temperatures of 220°C, pressures of up to 400psi and sulfuric acid concentrations of 5% where few materials would be resistant. This process was also found to be very abrasive. ZR 705 grade was chosen over Zr702 grade because of its higher strength and comparable corrosion resistance in this severe environment. Zr705 is, however, susceptible to delayed hydride cracking (DHC) so the pressure vessel required stress relief anneal to prevent this metallurgical phenomenon from occurring. The stress relief at 550°C for 4-6 hrs at temperature reduced the susceptibility of the zirconium to the DHC and formed a thicker abrasion resistant oxide film on the surface.

II. Lower to Medium Concentrations / Up to Boiling Temperatures

Steel Pickling Applications: 10- 40% concentration

Pickling is a process that is used to remove surface oxides from various metals by immersion in an acidic solution. Sulfuric and Hydrochloric acids are the most common environments for use in iron and steel pickling. Sulfuric acid is used extensively in the pickling of steel, since steel is readily attacked by sulfuric acid. In the pickling of iron and steel, the acids used can be very corrosive to metals used in pickling acid containment and heating equipment. While tanks that hold the pickling solutions can be lined by fluoropolymers, plastics or rubber, the equipment that will heat the acid must be very corrosion resistant and be able to transfer heat. Usually immersion coils, such as serpentine, grid or u-shaped coils are used to heat the pickling baths. Zirconium use in sulfuric acid pickling is an excellent choice due to its good resistance in sulfuric acid even with oxidizing impurities. The sulfuric acid concentration used in this application ranges from 5% to 40% and the acid is generally heated to temperatures between 60 and 100°C.

One of the first companies to use zirconium in sulfuric acid pickling applications was Goodyear's Metal Products Division in Akron, Ohio. Goodyear had difficulty in finding a corrosion resistant material to heat the sulfuric acid pickling solutions.[5] In 1972, the company tried a number of materials including thermoplastic resin tubes and black iron pipes encased in lead. The thermoplastic resin tubes had poor results since due to the abrasion and subsequent leaking of the tubes. The black iron resulted in cracks through the lead and subsequently severe attack on the iron pipe. In 1972 Goodyear tried Zircadyne® zirconium grid coils in this applications with good results. This was the first time zirconium had been applied in this application.

Shortly after installation of the zirconium grid coils in the pickling application, a corrosion problem occurred causing failure of a unit. After a failure analysis was performed, it was found that large quantities of chloride existed in pickling bath. Although no chloride was known to be added to the sulfuric acid bath it was found later that the pickle operator added sodium chloride (rock salt) to rejuvenate the sulfuric acid pickling acid. It was found that although this extended the life of the bath, it added significant chloride ions to the bath and caused the Zr heating coils to experience localized (pitting) attack. Testing performed at Wah Chang in sulfuric acid solutions with iron and chloride showed that although the sulfate ion is an effective inhibitor for zirconium, this inhibiting effect is overcome if high levels of chloride ions are in the bath in the presence of iron. This problem has also occurred when low level, chloride-containing pickling inhibitors were added to the pickling bath. Upon replenishing the sulfuric acid solution, the chloride ions remained and eventually concentrated. When the concentration of chloride continued to increase, it caused a localized attack on the zirconium. In order to eliminate the corrosion on the zirconium, It was found by laboratory testing that the molar ratio of the SO_2 to Cl_2 should be a minimum of 54, i.e. (sulfate to chloride ratio). Figure 4 shows the affect of chloride as the acid concentration increases..

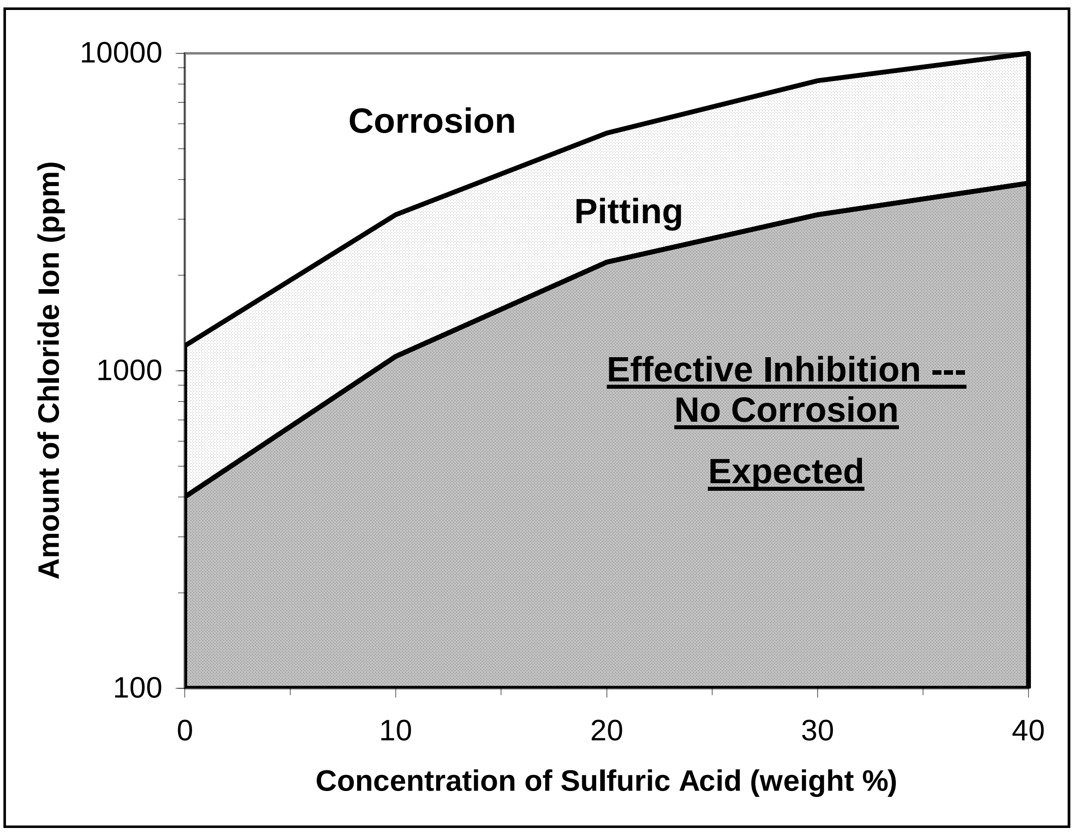


Figure 4. Effect of Chloride Ions on Corrosion of Zirconium

In sulfuric acid pickling, it was also found that the use of fluoridated water could also present a corrosion problem if the fluoride was allowed to concentrate in the bath. Generally fluorine is added to some drinking water systems in very low levels. After a period of time the fluorine may build up to a level that would cause an increased corrosion rate on zirconium. Even a small amount of fluoride will cause some materials, like zirconium, to experience higher corrosion rates. Figure 5. shows the effect of fluoride ion in sulfuric acid.

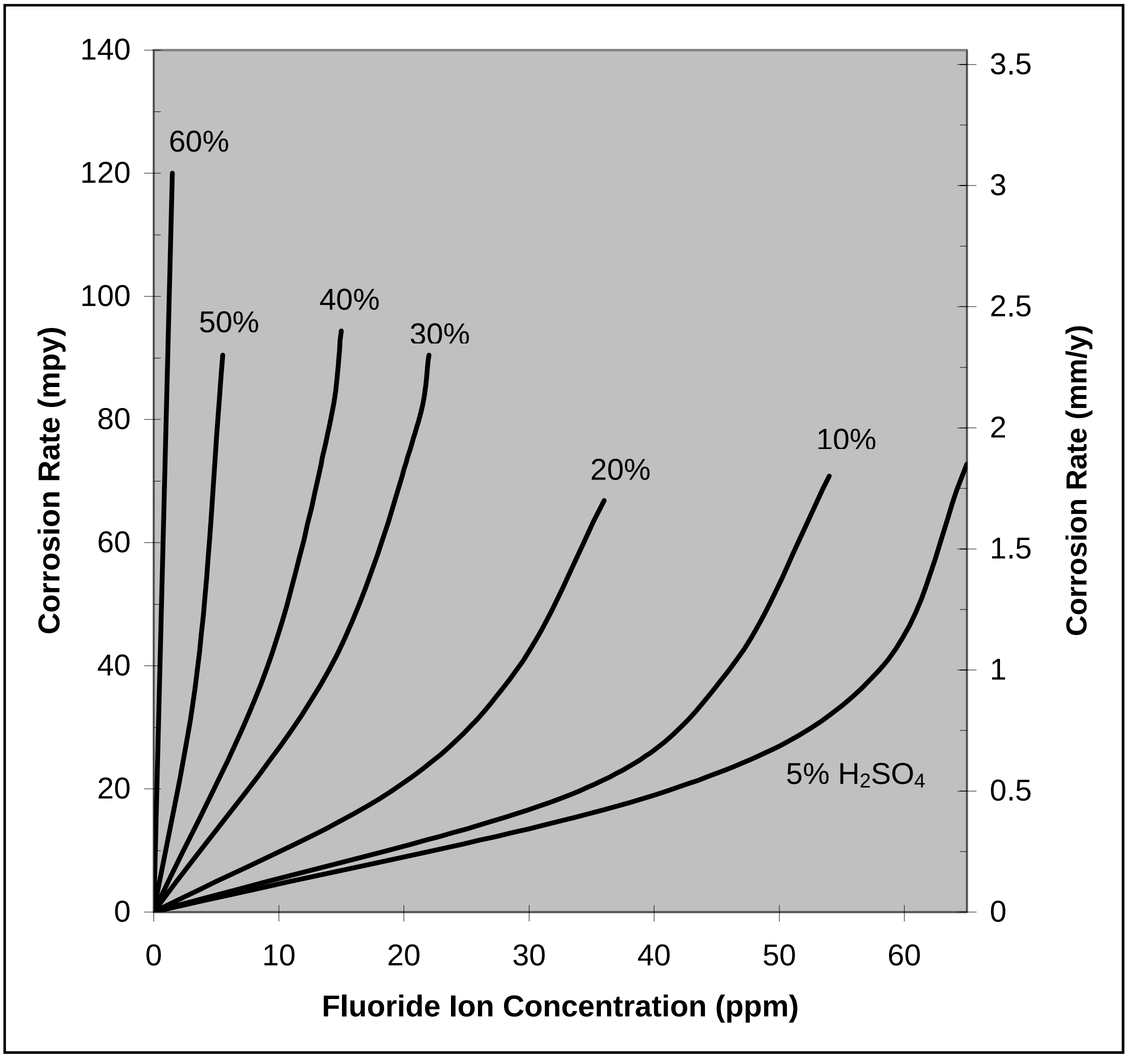


Figure 5: Effect of Fluoride Ions on the Corrosion of Zr 702 in Boiling Sulfuric Acid

III. Mid to Higher Concentrations
50%-70% Concentrations: Methyl methcrylate, Secondary butyl alcohol.

Zirconium has been used for the past 25 years in the production of acrylic monomers such as methyl methracylate and methacrylic acid.[6] This corrosive media includes a mixture of organics, sulfuric acid and water. In the methyl methracrylate application, the sulfuric acid concentration ranges from 25-35% and temperatures exceeding 150°C. In this monomer service, it was found that the "effective" acid concentration was actually in the 45-55% range due to the other constituents. Zirconium is also being used in secondary butyl alcohol application where the sulfuric acid concentration is in the 50%-70% range at temperatures from 90°C to that of 160°C.[7]

The Zirconium Grade 702 was shown to be the best material of construction in these types of applications.[9] When the acid concentration exceeds the 55% range, zirconium welds will experience preferential attack. A primary reason for the lower corrosion resistance in the weld area and heat affect zone is the distribution of the second phase or intermetallic particles in the grain boundaries. When the weld cools the intermetallic compounds concentrate in the grain boundaries forming a continuous path for corrosion to take place. Heat treatment can be performed which disperses (agglomerates) the second phase thereby eliminating the continuous network. Heat treatment will eliminate preferential attack and result in corrosion resistance of the weld area and heat affected zone to be similar to that of the parent metal. Heat treatment is typically performed at 775 ± 15°C for one hour per inch (25.4 mm) of thickness. Figure 6 & 7 show the weld structure before and after the heat treatment.

In the sulfuric acid concentration range of 64 to 69%, zirconium has been shown to exhibit stress corrosion cracking tendencies.[8] This has been confirmed in laboratory studies as well as actual in-service applications. This susceptibility increases significantly when small amounts of oxidizing ions, such as Fe^{+3} and NO_3^- are present. These ions change the chemical make-up of the acid. Chloride ions do not seem to cause SCC in zirconium exposed to 65% acid.

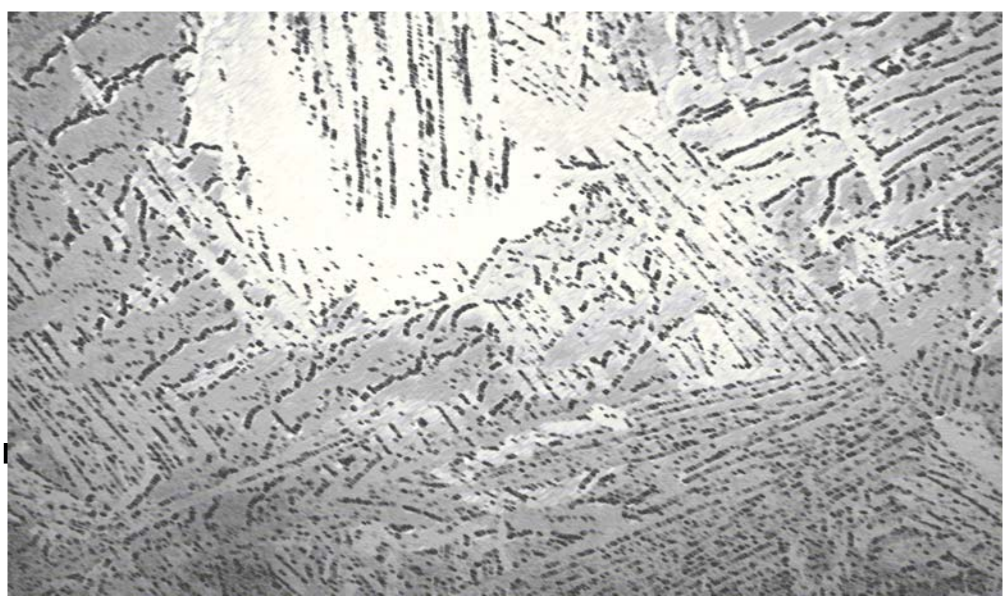


Figure 6. Zirconium weld structure before Heat Treatment, 750X

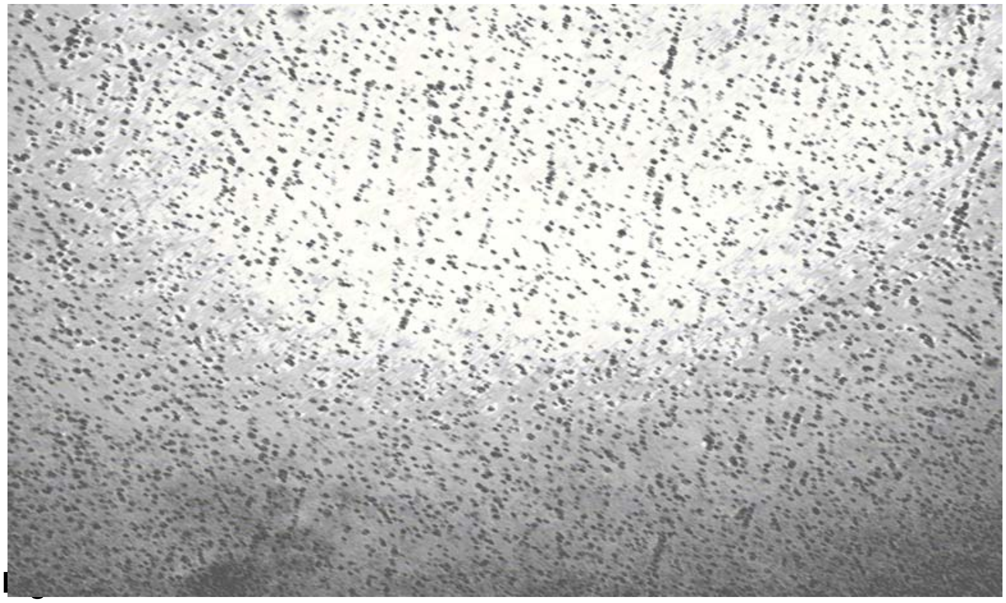


Figure 7. Zirconium weld structure after heat treatment, 750X

Other impurities have also been shown to affect the corrosion resistance at the higher concentrations of acid. Figure 8 shows the effect of ferric, cupric and nitrate ions on the corrosion resistance of zirconium.

Finally it has been shown that in the higher concentrations of sulfuric acid, the amount of tin present in zirconium may also be a significant factor in the corrosion resistance.[10] While tin content in zirconium is not usually is factor for corrosion resistance in most environments, tests have shown that zirconium with lower levels of tin will result in a lower corrosion rate at the higher sulfuric acid concentrations exceeding 55-60%. Typically tin content in Zircadyne® zirconium Grade 702 will exceed 2000ppm. Testing has shown that if tin is controlled to around 1500ppm or less, the corrosion resistance will be improved in both the welded and non-welded areas. A low tin Zircadyne® zirconium grade has been developed for these higher concentration applications

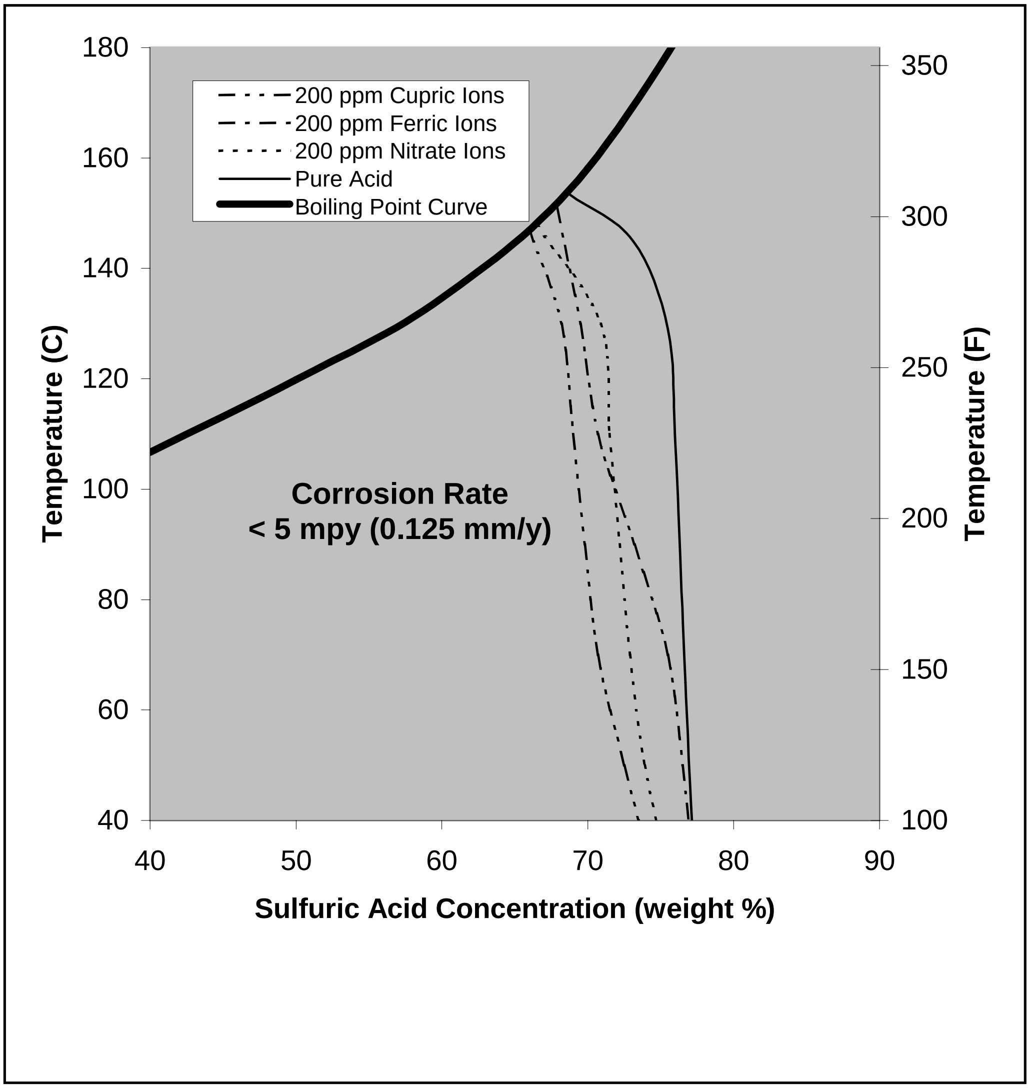


Figure 8. Effect of Impurities in Sulfuric Acid on the 5mpy (0.125mm/yr) iso-corrosion curve of Zircadyne® 702.

Conclusions

1. Zirconium has excellent corrosion resistance in all concentrations of sulfuric acid up to 70% and well above boiling
2. Zirconium should not be used in sulfuric acid in the presence of fluoride ions.
3. Chloride ions should be controlled in the sulfuric acid, especially at the lower concentrations.
4. Zirconium welds should be heat treated if the concentration of acid is above the weld limit line.
5. Low -Tin Zirconium should be considered if the acid concentration exceeds 55%.

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