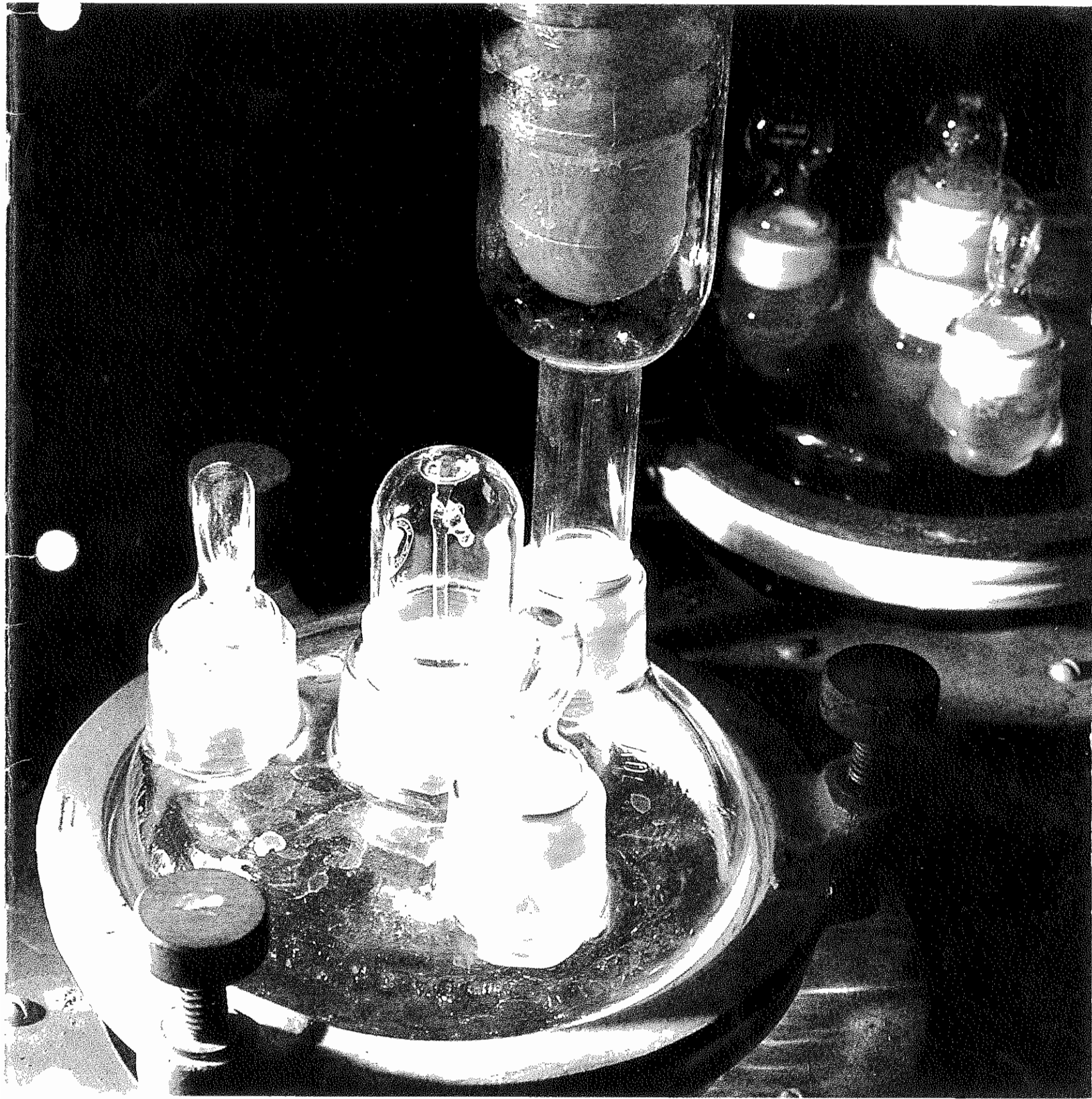


Zircadyne[®] Corrosion Properties



 TELEDYNE WAH CHANG ALBANY



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PROPERTIES DATA: The properties listed in this brochure are average values based on laboratory and field test data from a number of sources. They are indicative only of the results obtained in such tests and should not be considered as guaranteed maximums or minimums. Because the chemical composition of your media may differ from that tested, materials should be tested under actual service conditions to determine their suitability for a particular application.

Introduction

Zirconium is used in a wide variety of industrial and chemical processing applications. This wide use is due to zirconium's excellent resistance to many chemical solutions, even at elevated temperatures and pressures. Zirconium is very resistant to corrosive attack in most organic and mineral acids, strong alkalis, and some molten salts. Because of zirconium's unique corrosion properties, it is an excellent material for use in chemical processes which require alternate contact with strong acids and alkalis. Zirconium alloys are not readily attacked by oxidizing media unless halides are present. These alloys, which exhibit excellent oxidation-resistant properties to 400°C in air, steam, carbon dioxide, nitrogen, and oxygen, have little need for anodic protection systems.

Zirconium's corrosion resistance is due to the natural formation of a dense, stable oxide film on the metal surface. This adherent oxide film is

self-healing and protects the base metal from chemical and mechanical attack such as functional wear and abrasion at temperatures up to 300°C.

Zirconium alloys have a high resistance to localized forms of corrosion, pitting, crevice corrosion, and stress-corrosion cracking. The combination of these factors makes zirconium alloys suitable for use in a wide variety of corrosive environments.

Teledyne Wah Chang Albany (TWCA) is continually generating new corrosion data for a variety of corrosive environments. Please contact us if you have questions on Zircadyne* alloys in specific media not covered in this brochure.

*Zircadyne is a registered trademark for zirconium produced by Teledyne Wah Chang Albany.

Chemical Compositions of Zircadyne Alloys

Grade (ASTM Designation)	Zircadyne 702 (R60702)	Zircadyne 704 (R60704)	Zircadyne 705 (R60705)	Zircadyne 706 (R60706)
Chemical Compositions, Percent				
Zr + Hf, min.	99.2	97.5	95.5	95.5
Hafnium, max.	4.5	4.5	4.5	4.5
Fe + Cr	0.20 max.	0.2-0.4	0.2 max.	0.2 max.
Tin	—	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
Oxygen, max.	0.16	0.18	0.18	0.16

Corrosion Laboratory Facility

Teledyne Wah Chang Albany's Research Center includes a modern, fully equipped corrosion-testing laboratory capable of performing a wide range of corrosion tests and analyses. TWCA's corrosion facility includes equipment for conducting immersion, stress-corrosion cracking, and corrosion-fatigue studies. Fracture mechanics, high pressure, and electrochemical studies are also performed. The corrosion laboratory is complemented by an alloy development group studying higher strength and more corrosion resistant zirconium alloys for specific applications.

The lab's immersion units are capable of running 200 simultaneous immersion tests. These units are used to generate corrosion data on TWCA products and to assist in customer evaluations of these products in their specific media.

The laboratory is also equipped with two slow strain-rate tensile machines (SSRTM) which are used to study stress-corrosion performance of commercial and developmental alloys. This stress-corrosion test, performed at variable temperatures, can be accurately interpreted to predict resistance of alloys to cracking with relatively short testing times. The slow strain-rate tensile test complements conventional test methods

such as U-bend and C-ring testing. In addition, corrosion-fatigue equipment and fracture-mechanics equipment enable TWCA to generate data that are important for establishing design limits.

Electrochemical-testing techniques enable TWCA to study corrosion mechanisms and corrosion-control methods in various media. Electrochemical-testing techniques also offer nearly instantaneous corrosion-rate measurements. Our test units are also valuable in the study of inhibitors and in comparisons of new corrosion-resistant alloys.

Autoclave units enable laboratory personnel to generate test data in corrosive media at elevated temperatures and pressures—up to 500°C and 103 bars in steam and 343°C and 414 bars in chemical corrosives. These units are useful in testing specific corrosive media as requested by many companies in their evaluation of zirconium for possible applications in their plants or processes. It is best to determine corrosion resistance in the actual in-situ condition, because unknown factors may not be considered in a laboratory test. However, if this is not possible, TWCA will develop laboratory techniques that simulate in-situ conditions as closely as is practical.

Technical Center

The Technical Center includes a well-equipped industrial analytical laboratory. In addition to the conventional wet-lab analytical capabilities, TWCA utilizes advanced analytical tools, such as atomic absorption, mass spectroscopy, energy-dispersive x-ray analysis, and scanning electron microscopy. Other capabilities include inductively coupled plasma-mass spectrometry and interstitial gas-testing. A qualified staff of over 20 professionals and 70

support personnel makes this one of the finest metals analysis laboratories in the Northwest.

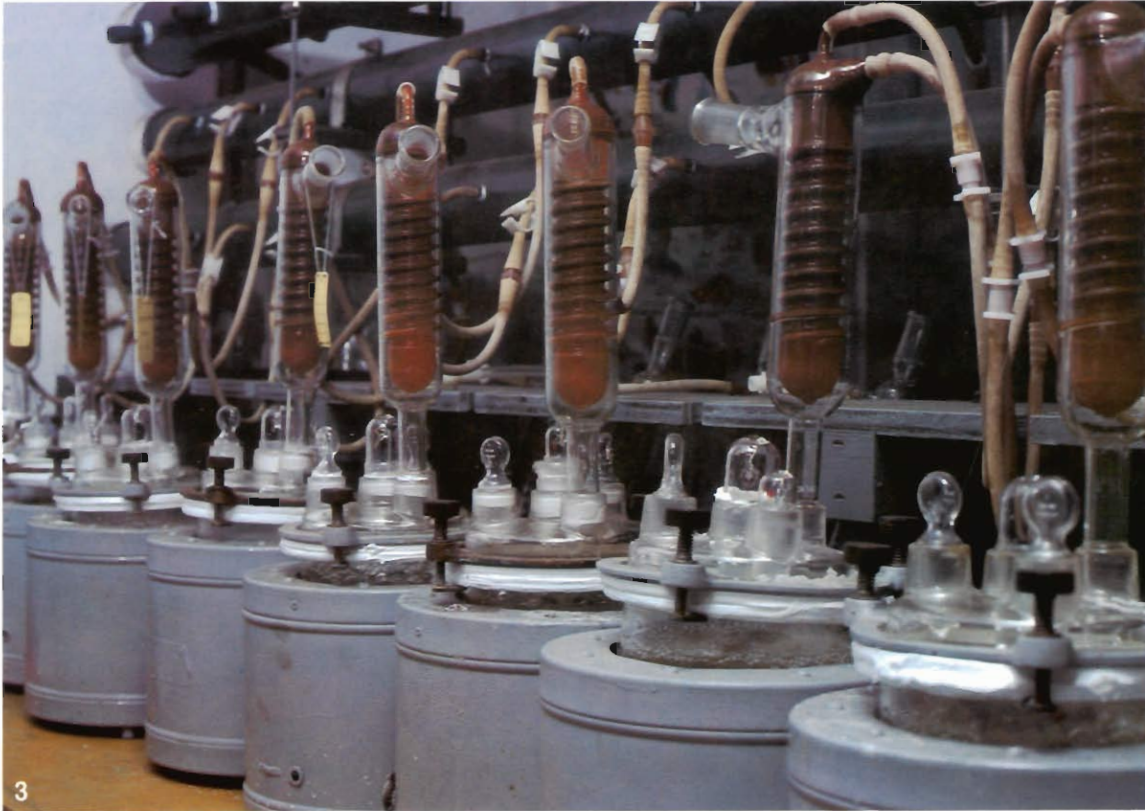
TWCA's fully equipped Physical Testing Laboratory ensures that zirconium products meet stringent physical- and mechanical-property requirements.

In addition, all of these testing services are available on a fee basis to companies in need of outside laboratory services.

Technical Service

TWCA's chemical and metallurgical staff is available for consultation on the metallurgical and corrosion properties of all TWCA products. This staff of engineers will aid fabricators or maintenance departments in the construction of zirconium equipment. For those who

desire to do in-plant corrosion testing, TWCA will provide a complimentary corrosion test kit with Zircadyne 702 and 705 welded coupons and zirconium hanging wire. Tubing specimens are also available on request.



1. This electrochemical testing equipment enables TWCA's corrosion laboratory to study pitting tendencies, active passive transition potentials and the possibilities of anodic or cathodic protection in various media.

2. Autoclaves are used to provide test data on corrosive media at elevated temperatures and pressures.

3. The corrosion laboratory has the capacity to run 200 simultaneous immersion tests.

4. Nearly instantaneous corrosion rate measurements are another benefit of electrochemical tests.

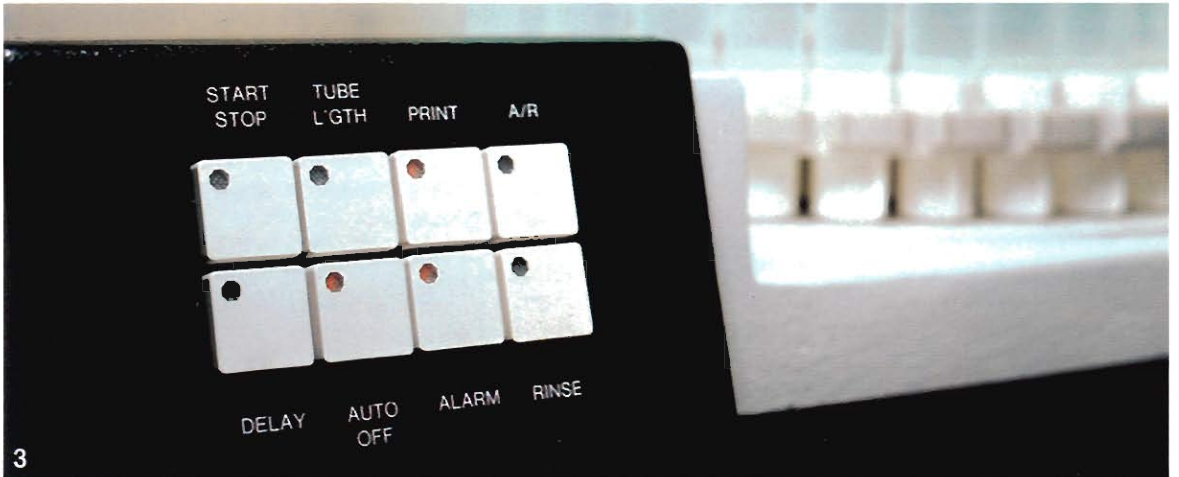
5. This slow strain rate tensile machine is used to study stress corrosion performance of commercial and developmental alloys.



1. This Zeiss Ultraphot enables TWCA metallographers to perform magnifications ranging from 2.5x to 2600x.

2. This Mass Spectrometer is used to measure the abundance of isotopes in an element.

3. TWCA's Direct Current Plasma Spectrometer is capable of trace level analysis for a wide range of materials.



4. This Baldwin Universal Testing Machine is used to determine the physical properties of metals.



5. This AMR 1000 Scanning Electron Microscope has a magnification working range of 10,000 to 100,000x with x-ray fluorescence analysis capabilities.



6. Interstitial gas-testing is another service offered by TWCA's Analytical Laboratory.



7. TWCA's atomic absorption capabilities are the latest in technology with microprocessor controlled instrumentation and graphite furnace capabilities.



Corrosion Resistance of Zircadyne Alloys In Specific Media

Hydrochloric Acid

One of the earliest applications for zirconium was in the handling of hydrochloric acid. Zirconium is still widely used in this area. The corrosion rate of zirconium is less than 5 mpy at all concentrations and temperatures well in excess of the boiling point. Even in 37% HCl, zirconium does not corrode appreciably until temperatures of 130°C are reached (see Figure 1). Zirconium's corrosion-resistant behavior in pure hydrochloric acid is superior to any other engineering metal.

Aeration does not affect zirconium's behavior in hydrochloric acid. However, oxidizing impurities such as cupric or ferric chlorides in relatively small amounts will decrease the corrosion resistance of zirconium in hydrochloric acid. These oxidizing ions should be avoided or electrochemical protection methods should be used to counteract the effect of oxidizing impurities. Please contact our Technical Services Department for more information on this technique.

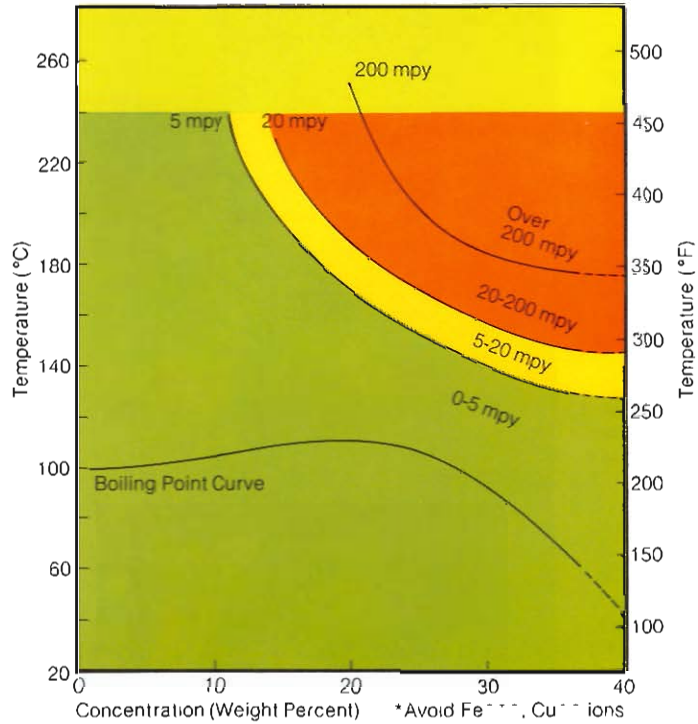


FIGURE 1. Corrosion of Zircadyne 702 in hydrochloric acid solutions.

Solution	Temperature °C	Duration of Test (Days)	Average Corrosion Rate (mpy)		
			702	704	705
32% HCl	30	91	0.03	0.08	0.03
10% HCl + 100 ppm FeCl ₃	30	91	0.9	1.6	0.7
32% HCl + 5 ppm FeCl ₃	30	91	0.1	1.5	0.1
32% HCl + 50 ppm FeCl ₃	30	91	*	*	*
32% HCl + 100 ppm FeCl ₃	30	91	*	*	*

*Severe pitting and stress cracking observed.

Applications Of Zirconium In Hydrochloric Acid

Current applications of zirconium equipment in hydrochloric acid include pumps, valves, piping, condensers, and evaporators. Zirconium heat exchangers, pumps, and agitators have been used for over 20 years in an azo dye coupling reaction. Besides being very corrosion resistant in this environment, zirconium does not plate out undesirable salts which would change the color and stability of the dyes. Heat exchangers

made of zirconium are used by chemical companies in the production of polymers. Other hydrochloric applications where zirconium has been used are phthalic-hydrochloric acid and wet hydrogen chloride-chlorine atmospheres. A very important application for zirconium is in processes that cycle between hydrochloric or sulfuric acid and alkaline solutions.

Sulfuric Acid

The corrosion resistance of zirconium in sulfuric acid is excellent at temperatures well above boiling and at acid concentrations up to 70%. Figure 2 shows the isocorrosion curves of zirconium in H₂SO₄ solutions. Upon exposure to sulfuric acid, a film is formed on the zirconium surface which is resistant to further attack by the acid.

Tests conducted in our corrosion laboratory have shown that welded and non-welded coupons of Zircadyne alloys are about equally corrosion resistant in lower concentrations. These corrosion data, collected for three grades of Zircadyne zirconium (702, 704 and 705), are illustrated in the isocorrosion diagrams shown in Figures 3-5. The diagrams are separated into areas of acid temperature and concentration with the expected corrosion rates shown within each area outlined by a solid line. The dashed lines separate the graph into two regions, where at lower concentrations the weld would be expected to behave similarly to the non-welded metal, and where at higher concentrations the welds would be preferentially attacked.

Comparing Figures 3-5, the Zircadyne 702 and Zircadyne 704 are approximately equivalent in their resistance to sulfuric acid, and both are more resistant to sulfuric acid than Zircadyne 705. It is important to note that the data are representative of a pure acid system, and the presence of oxidizing halide contaminants can accelerate the rate of attack.

At temperatures above 200°C and

at the higher concentrations (shown in the area above the dashed lines) the welds and heat-affected zones (HAZ) were found to be much more susceptible to corrosion attack than the base metal. This corrosion attack in the welds and HAZ in Zircadyne 702 and Zircadyne 704 occurs in the alpha phase grain boundaries except in the area of the prior beta grain boundaries which are not attacked. Heat-treating the weldments at the stress-relieving temperatures of 500°C to 600°C does not significantly improve their corrosion resistance. However, heat treatment of weldments in the temperature range of 630°C to 788°C does improve the corrosion resistance. The optimum heat treatment for improving Zircadyne 702's corrosion resistance was determined by experimentation to be ½ to 1 hour at 730-788°C (1400 ± 50 °F). Lower-temperature heat treatments down to 630°C can be used to balance the improvements in corrosion resistance, strength, and fabricability.

In welded coupons of Zircadyne 705, intragranular attack of both the weld and HAZ was observed in 65% sulfuric acid. Annealing the zirconium-welded coupons between 550°C and 1000°C greatly improves the corrosion resistance of the weld in 65% H₂SO₄. For the lower end of this temperature range, a heating time of two hours is recommended. Half an hour is sufficient at 1000°C. Lower temperatures are normally used (550-600°C) to minimize dimensional changes caused by oxide film growth. For details, call TWCA.

*continued on page 8.

Sulfuric Acid*

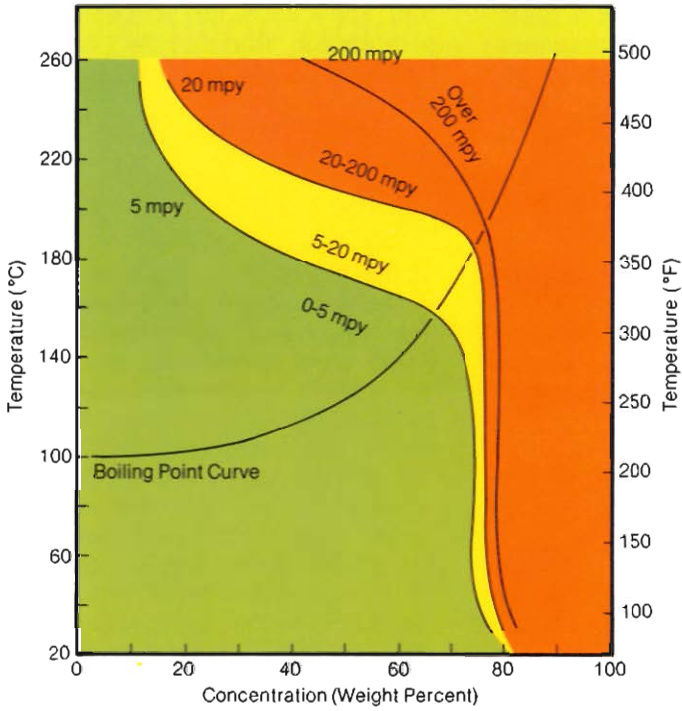


FIGURE 2. Corrosion of Zircadyne 702 in sulfuric acid solutions.

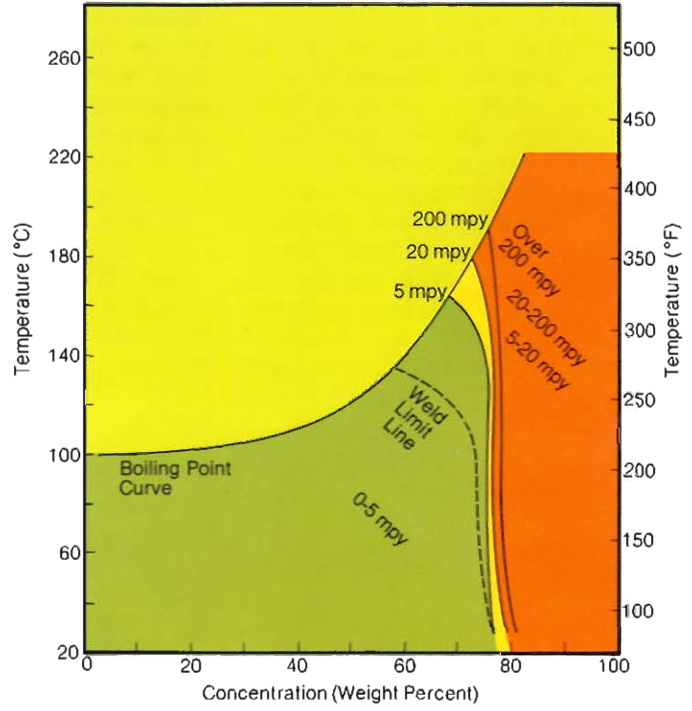


FIGURE 3. Corrosion of Zircadyne 702 in sulfuric acid solutions.

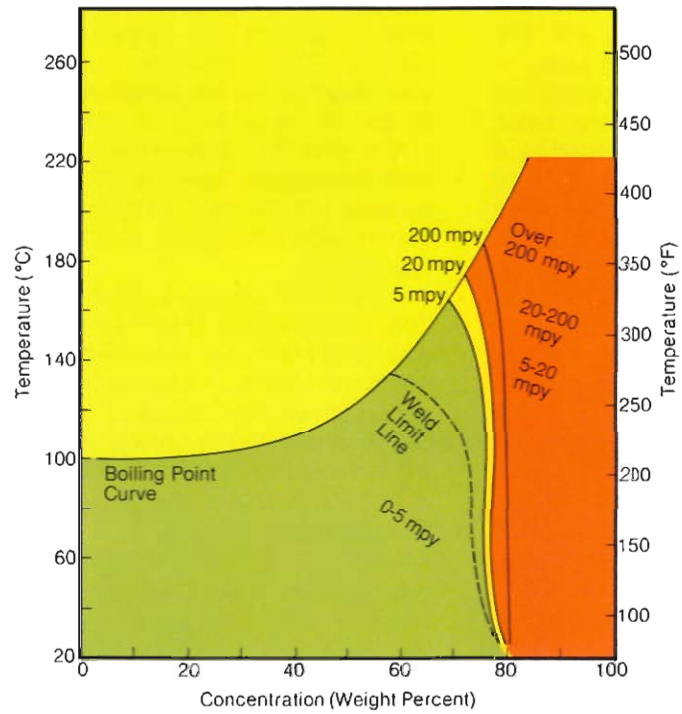


FIGURE 4. Corrosion of Zircadyne 704 in sulfuric acid solutions.

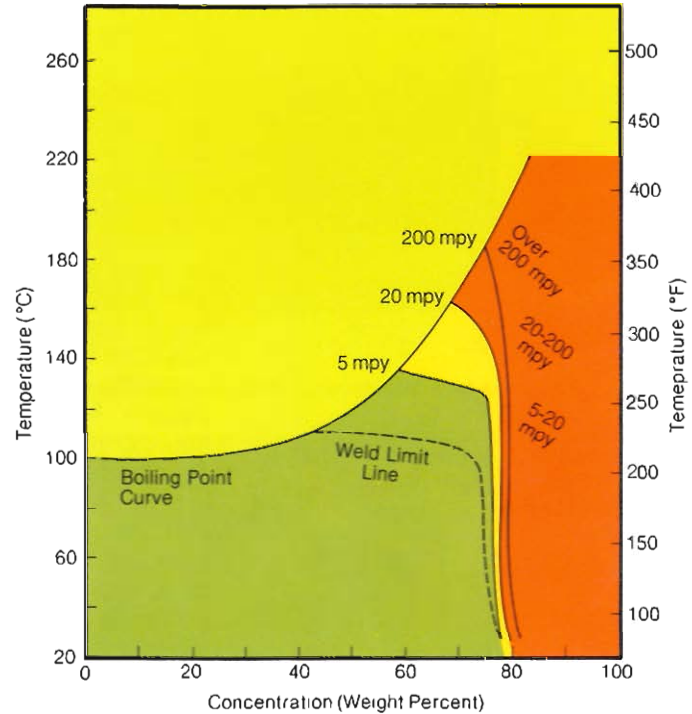


FIGURE 5. Corrosion of Zircadyne 705 in sulfuric acid solutions.

*continued from page 7.

Effect of Impurities

From studies on oxidizing impurities in H_2SO_4 , it was found that ferric, cupric, and nitrate ion impurities in H_2SO_4 affect the corrosion resistance properties of zirconium and its alloys at concentrations above 65% H_2SO_4 . This is shown by the isocorrosion curves in Figures 6 and 7. For example, 200 ppm cupric ions reduce the 0.125 mm/y (5 mpy) isocorrosion curve by less than 5 weight percent acid. In less than 65% H_2SO_4 , 200 ppm impurity levels of these ions for Zircadyne grades 702 and 704, and 60% H_2SO_4 for grade 705, have no effect on their corrosion resistance. In fact below 65%, grade 702 did not experience accelerated attack even

with 1% additions of cupric or ferric ions. Chloride ions were found to have no effect on the corrosion-resistant properties of zirconium in sulfuric acid.

Zirconium can tolerate only very small amounts of fluoride ions in H_2SO_4 even at low-acid concentrations. At concentrations greater than 50% H_2SO_4 , the corrosion rate will be high even with 1 ppm fluoride ions. Figures 8 and 9 show the effect of the fluoride ion in sulfuric acid. Therefore, fluoride ions have to be complexed, using inhibitors such as zirconium sponge and phosphorous pent-oxide, when zirconium equipment is used to handle fluoride ion-contaminated H_2SO_4 solutions.

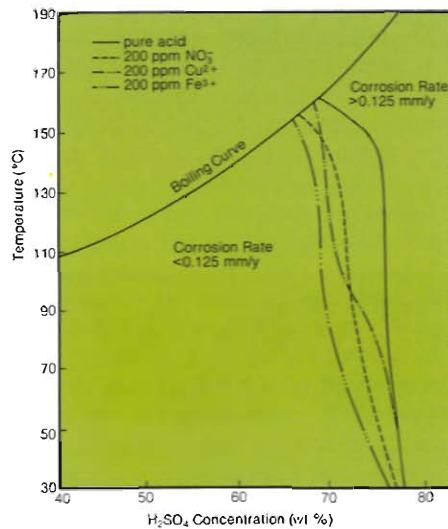


Figure 6

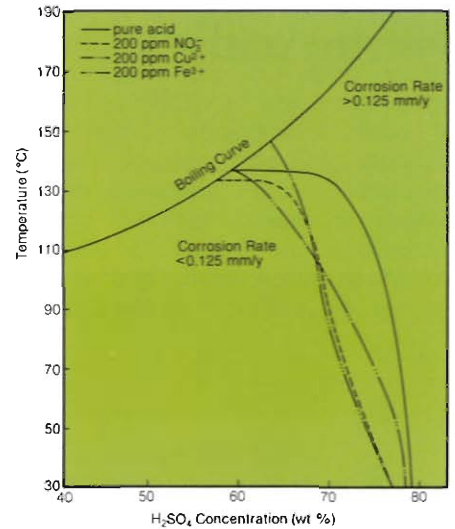


Figure 7

FIGURE 6. Effect of 200 ppm impurity levels in H_2SO_4 on the 0.125 mm/y isocorrosion curve of Zircadyne 702.

FIGURE 7. Effect of 200 ppm impurity levels in H_2SO_4 on the 1.125 mm/y isocorrosion curve of Zircadyne 705.

FIGURE 8. Effect of fluoride ions in boiling H_2SO_4 on the corrosion rate of Zircadyne 702.

FIGURE 9. Effect of fluoride ions in boiling H_2SO_4 on the 0.125 mm/y and 1.25 mm/y corrosion lines for Zircadyne 702.

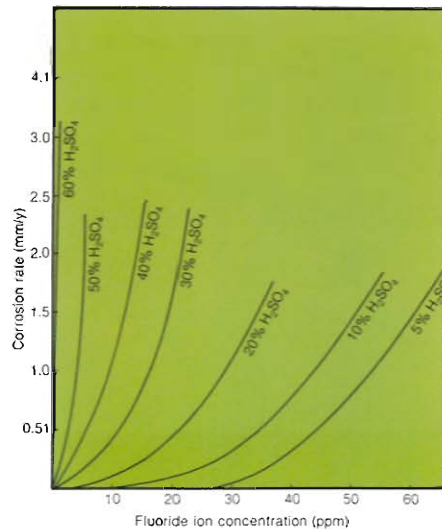


Figure 8

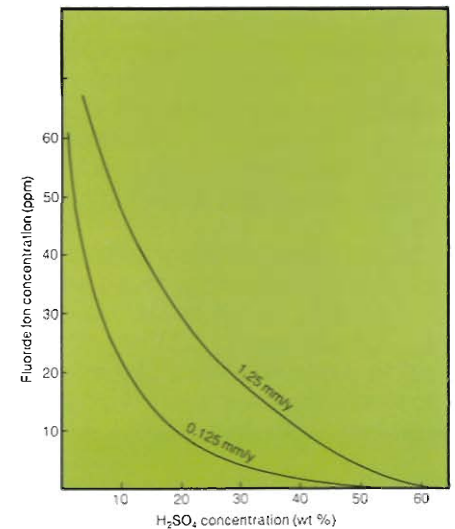


Figure 9

Applications Of Zirconium In Sulfuric Acid

Zirconium is used extensively in 40-70 weight percent sulfuric acid at elevated temperatures. Zirconium has been used to replace impervious graphite heat exchangers and lead heating coils in an environment containing sulfuric acid, zinc and sodium sulfates, hydrogen sulfide, and

carbon disulfide. Zirconium has been used in these applications for over ten years without corrosion problems. Some other examples of sulfuric acid applications include ester manufacturing, steel pickling, alcohol stripping towers and hydrogen peroxide manufacturing.

Phosphoric Acid

Zirconium is corrosion resistant in phosphoric acid at concentrations up to 55% and temperatures exceeding the boiling point. Above 55% H_3PO_4 concentrations, the corrosion rate rises with increasing concentration

and temperature (see Figure 10). The corrosion rate of zirconium is still less than 5 mpy at 60°C and concentrations up to 85%. Fluoride ion impurities in phosphoric acid can cause attack of zirconium.

Nitric Acid

Zirconium exhibits excellent corrosion resistance to nitric acid in all concentrations up to 90% and temperatures up to 200°C. Only one other metal, platinum, is equal to zirconium for this service (see Figure 11). Welded zirconium and its alloys retain this high corrosion resistance. For example, welded Zircadyne 702, 704, and 705 corrode at rates less than .05 mpy in 70% HNO_3 at boiling.

Zircadyne 705 where about 50% of the yield stress may cause stress-corrosion cracking at the same concentration and temperature.

In concentrated nitric acid, stress-corrosion cracking (SCC) may occur above 70% concentration if high tensile stresses are present. For example, the critical stress to cause SCC in Zircadyne alloys 702 and 704 is about 100% of the yield stress at 90% concentration and room temperature. This compares to Zir-

It is inevitable to have the impurities of iron, chromium, and chlorides in many HNO_3 processes resulting, for example, from the corrosion of stainless steels or the contamination of chloride-containing cooling water. Tests have been performed at TWCA to determine the corrosion rates of zirconium in HNO_3 containing ferric chloride, natural seawater, sodium chloride, iron, stainless steel, sodium fluoride, and hydrofluoric acid.

Ferric chloride is a well-known pitting agent of zirconium. However, nitrate ions are effective inhibitors of

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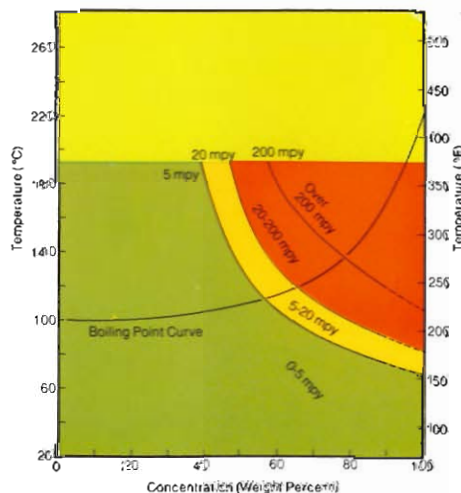


FIGURE 10. Corrosion of zirconium in phosphoric acid solutions.

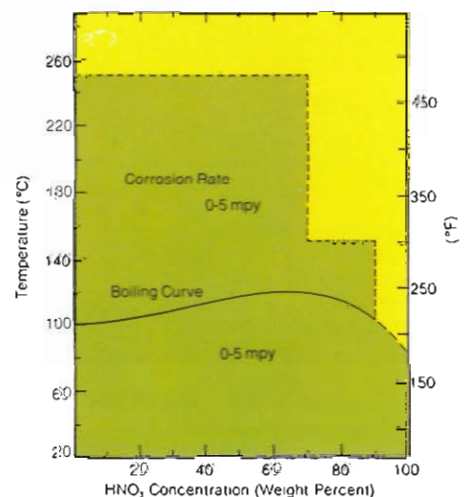


FIGURE 11. Corrosion of zirconium in nitric acid solutions.

Nitric Acid

(Continued from Page 10)

pitting in zirconium. Test results showed that zirconium did not corrode or pit in boiling 30% to 70% HNO_3 with up to 1% FeCl_3 . Similarly, the presence of up to 1% seawater or 1% NaCl did not degrade zirconium's corrosion resistance to aqueous HNO_3 . However, welded specimens could exhibit minor pitting in HNO_3 vapors if a sufficient amount of chloride (e.g., 1% NaCl but not 1% seawater) was present in solutions. This corrosion problem can be attributed to the chlorine gas generated upon the addition of NaCl into HNO_3 . It is suggested that areas that can accumulate chlorine gas be avoided for zirconium equipment when chlorides are present in HNO_3 .

Iron- or stainless-steel (Type 304)-containing HNO_3 solutions were prepared, first, by dissolving iron or stainless steel in 70% HNO_3 at 204 °C using an autoclave. Under these conditions, corrosion rates of iron and stainless steel were estimated to be greater than 25.4 mm/y. Thirty percent to 70% HNO_3 solutions with 1% Fe or 1.45% stainless steel were prepared from the master solution. These solutions contained varying

amounts of Fe^{3+} , Cr^{3+} and Cr^{6+} . Non-welded and welded coupons were tested in 30%, 50% and 70% HNO_3 with 1% Fe or 1.45% stainless steel at boiling temperatures, and in 65% HNO_3 with 1% Fe or 1.45% stainless steel at 204 °C. Test results indicated that the presence of heavy-metal ions had little effect on the corrosion resistance of zirconium.

The presence of fluoride ions in acidic solutions can significantly increase the corrosion rate of zirconium. In mixtures of HNO_3 and HF , the corrosion rate of zirconium is directly proportional to the HF concentration. In one-day tests, the corrosion rates of zirconium in 30%, 50% and 70% containing 10 ppm F^- (as HF) at 80 °C were determined to be 0.20, 0.31 and 0.62 mm/y, respectively. Again, the corrosion of zirconium in HNO_3 - F^- solutions can be controlled by adding an inhibitor to convert fluoride ions into noncorrosive complex ions. Zirconium sponge, zirconium powder, zirconium compounds (such as zirconium nitrate), and phosphorous pentoxide can be used as inhibitors.

Hydrofluoric Acid

Zirconium has no corrosion resistance in hydrofluoric acid and is rapidly attacked even at concentra-

tions as low as .001%.

Acid solutions containing HF are commonly used to etch zirconium.

Caustics

Zirconium is resistant to virtually all alkaline solutions, either fused or in solution, to the boiling temperature. Zirconium is resistant in sodium hydroxide and potassium hydroxide solutions even under anhydrous conditions. It is also resistant to calcium hydroxide and ammonium hydroxide at concentrations to 28% and temperatures to boiling. This corrosion resistance makes zirconium distinctly different from some other highly corrosion-resistant materials, such as tantalum, glass, graphite, and PTFE, which are attacked by strong alkalis. Moreover, steels and stainless alloys, which have good corrosion resistance to alkalis, are subject to cracking in certain concentrations and temperatures.

Zirconium U-bends were tested in

concentrated NaOH at boiling. During the test period, concentration changed from 50% to about 85%, and temperature increased from 149 °C to 300 °C. PTFE washers and tubes used in making U-bends dissolved. However, zirconium U-bends remained ductile and did not show any cracks after 20 days.

Zirconium coupons were tested in a white liquor paper-pulping solution, which contained NaOH and Na_2S , at 120 °C, 177 °C and 227 °C. All coupons had corrosion rates of less than 1 mpy. In the same solution, both graphite and glass corroded rapidly at 100 °C.

A very important application for zirconium is in processes that cycle between HCl or H_2SO_4 and alkaline solutions.

Natural And Polluted Waters

Zirconium has excellent corrosion resistance to seawater, fresh water, polluted water, and brackish water, which makes it a natural choice for

heat exchangers, condensers, and other equipment used in these media.

Zircadyne alloys are replacing Ti-Pd alloys in this type of service.

Molten Salts

Zirconium is resistant to attack in some molten salts. Zirconium is resistant to corrosive attack in molten sodium hydroxide through temperatures

greater than 1000°C. Zirconium is also fairly resistant to potassium hydroxide.

Liquid Metals

Zirconium is resistant to some types of molten metals, but the corrosion rate is affected by trace impurities such as oxygen, hydrogen, or nitrogen in the specific molten metal. Zirconium has a corrosion rate of less

than 1 mpy in liquid lead to 600°C, lithium to 800°C, mercury to 100°C, and sodium to 600°C. Molten metals which are known to severely attack zirconium are molten zinc, bismuth, and magnesium.

Organics And Organic Acids

Zirconium is very resistant to most organics. It is commonly used in the production of acetic acid and acetic anhydride where the corrosion rate is less than 2 mpy in all concentrations and temperatures. Zirconium also shows a high resistance to corrosion in citric, lactic, formic, oxalic, tartaric, tannic, and chlorinated organic acids.

Zirconium's excellent corrosion

resistance in the nitrogen fertilizer environment has led to its use in many applications in plants producing fertilizers and urea. With a zirconium lining in a urea-synthesis process, the reaction can take place at higher temperatures and pressures permitting greater conversion of CO₂ to urea and thereby avoiding the corrosive intermediate products.

Types Of Corrosion

Galvanic Corrosion

Due to the protective oxide film which normally forms on zirconium in air, highly reactive zirconium assumes a noble potential similar to silver and passivated stainless steel. If this passive film is removed, zirconium will become activated and consequently will corrode when in contact with other more noble metals (see Table 1).

Other less noble metals will corrode when in contact with zirconium coated with its oxide film intact. For example, in seawater or acid solutions, carbon steel, aluminum, and zinc will corrode rapidly in electrical contact with zirconium. Therefore, care should be taken to keep them electrically insulated.

**Table 1
Galvanic Series In Seawater**

Cathodic (Most Noble)	Platinum
	Gold
	Graphite
	Titanium
	Silver
	Zirconium
	Type 316, 317 Stainless Steel (passive)
	Type 304 Stainless Steel (passive)
	Type 410 Stainless Steel (passive)
	Nickel (passive)
	Silver Solder
	Cupro Nickels (70-30)
	Bronzes
	Copper
	Brasses
	Nickel (active)
	Naval Brass
	Tin
	Lead
	Type 316, 317 Stainless Steels (active)
	Type 304 Stainless Steel (active)
	Cast Iron
	Steel or Iron
	Aluminum 2024
	Cadmium
	Aluminum (commercially pure)
	Zinc
Anodic (Active)	Magnesium and Magnesium Alloys

Crevice Corrosion

Of all the corrosion-resistant metals, zirconium and tantalum are the most resistant to crevice corrosion. Crevice or contact corrosion is a form of localized corrosion usually associated with small volumes of stagnant solutions caused by lap joints, gasket surfaces, surface

deposits, and crevices under fastener heads. For instance, in chlorine service, many metals are subject to crevice attack; zirconium is resistant to dry chlorine and is, therefore, unaffected.

Zirconium can replace Ti-Pd alloys in chloride-containing media.

Pitting Corrosion

Zirconium is quite resistant to pitting corrosion in chloride, bromide, and iodide solutions. Electrochemical measurements, however, can reveal zirconium's pitting tendency in these halide solutions. The reason zirconium does not pit in most halide environments is that the corrosion potential is lower than the pitting potential. The presence of oxidizing ions (such as Fe^{3+} or Cu^{2+}) in halide solutions will increase the corrosion potential and when the potential

becomes greater than the pitting potential, pits will be initiated. Zirconium will also pit in perchlorate solutions if oxidizing impurities are present. Nitrate and sulfate ions will inhibit pitting of zirconium in certain concentrations. TWCA laboratory personnel will continue to generate new data on the pitting corrosion of zirconium. For more detailed information on zirconium's pitting behavior, contact TWCA's Technical Services Department at (503) 926-4211.

Fretting Corrosion

Fretting corrosion takes place when vibrational contact is made at the interface of tight-fitting, highly loaded surfaces as between the leaves of a spring, or parts of ball and roller bearings. The best way to overcome this type of corrosion (if it

cannot be eliminated mechanically) is to apply a heavy oxide coating on the zirconium which drastically reduces the frictional resistance and prevents the removal of passive protective oxide (see zirconium oxide films).

Stress Corrosion

Zirconium and its alloys are resistant to stress-corrosion cracking (SCC) in many environments (such as NaCl , HCl , MgCl_2 , NaOH , H_2S), which would induce SCC in other alloys. Zirconium service failures due to SCC are few in the chemical applications. The high SCC resistance of zirconium can probably be attributed to its high repassivation rate. Any break in the surface film will be quickly healed provided there is sufficient oxygen content. Even in dehydrated systems, there is generally sufficient oxygen present for repassivation.

Environments known to cause SCC of zirconium alloys include FeCl_3 or

CuCl_2 solutions, $\text{CH}_3\text{OH} + \text{HCl}$, $\text{CH}_3\text{OH} + \text{I}_2$, concentrated HNO_3 and liquid mercury or cesium. Stress corrosion cracking in zirconium alloys can be successfully prevented by:

1. Avoiding high sustained tensile stress.
2. Modifying the environment.
3. Achieving a texture with the hexagonal basal planes perpendicular to the cracking path.
4. Maintaining a high quality surface film, i.e. low in impurities, defects, and mechanical damage.

High Temperature Reaction With Gases

Zirconium will react with oxygen in the air at temperatures above 540°C , producing a white zirconium oxide film that is very refractory, brittle, and porous. At temperatures above 700°C , zirconium will absorb oxygen and become embrittled after prolonged exposure. The oxide film on zirconium provides an effective

barrier to hydrogen up to 760°C . In an all-hydrogen atmosphere, hydrogen absorption will begin at 310°C , and the metal will ultimately become embrittled. Hydrogen can be removed from zirconium by vacuum annealing for prolonged times at temperatures above 750°C .

Corrosion By High Temperature Water And Steam

Zirconium's resistance to air, hot water, and steam makes it a logical choice for power generation applications. The metal can be exposed for prolonged periods in steam without pronounced attack below 425°C.

Zircadyne 704, a zirconium alloy containing 1.5% tin with small additions of iron and chromium, shows an

increased resistance to high temperature water and steam. In comparison, the Zircadyne 705 alloy with 2.5% columbium addition possesses higher R.T. and elevated tensile strengths than Zircadyne 704 and also exhibits good resistance in steam applications.

Zirconium Oxide Films For Corrosion Resistance And Low Friction Surfaces

One of the unique properties of zirconium which makes it attractive for chemical usage is the protective nature of its oxide film. This film gives excellent corrosion resistance in spite of the metal's reactive nature. Should it be mechanically destroyed, this oxide barrier will regenerate itself in many environments. Aluminum and titanium exhibit similar characteristics except that the film on zirconium is considerably more corrosion resistant.

Several methods of oxide formation are possible, depending on the properties desired. Normal methods include:

1. Anodizing.
2. Autoclaving in high-temperature water or steam.
3. Formation in air.

Anodizing forms a film that is very thin, but may be useful in some applications. Since it is formed near room temperature, it does not have the coherence to the underlying metal that the other, thermally produced coatings do.

Autoclave film formation is a practice common to the nuclear reactor industry. In this process, the uniform film of high integrity which is formed is superior to that formed at the lower operating temperatures. In addition to the slower corrosion rate, the rate of hydrogen absorption is drastically reduced. Films can be formed in 14 days in 360°C pressurized (2700 psi) deionized water or in 1-3 days at 400°C (1500 psi) in high-purity steam.

The most common film used in the chemical industry is one formed in air. Often, this film is formed during

the final stress relief of a component at about 550°C for times of ½ to 4 hours at temperature. This film will range in color from a straw yellow through an iridescent blue or purple, to a powdery tan or light grey. Such films need not be taken as a sign of metal contamination. This low-temperature stress relief does not cause significant penetration of oxygen into the metal; it does, however, form an oxide layer which is diffusion-bonded to the base metal.

In addition to the corrosion resistance imparted by the oxide film, Atomic Energy of Canada Limited has found that a properly formed film serves as an excellent bearing surface against a variety of materials in several environments and over a broad temperature range (Canadian Patent No. 770,080 and AECL Publication CRE-996).

This treatment consists of cleaning the surface followed by 4-6 hours at 550°C in air.

The resultant oxide layer, approximately .0002" thick, is equivalent to sapphire in hardness and is diffusion-bonded to the base metal. The oxide layer can be damaged by striking action, but serves as an excellent bearing surface for sliding contacts. Oxidized zirconium pump shafts are an example of a common application.

For more detailed information on this subject, send for a paper entitled, "Improved Wear Resistance of Zirconium by Enhanced Oxide Films", by John Haygarth and Lloyd Fenwick of TWCA.

Zirconium For Heat Transfer Applications

In process heat transfer, the rate of exchange of heat between the source and the receiver is critical. The driving force is the temperature difference across an impedance. This impedance consists of source and receiver film coefficients, the resistance due to a metal barrier and any scale which may have formed on this metal barrier.

The actual design of a shell and tube heat exchanger, following preliminary sizing, entails selections of a suitable material of construction and determination of the minimum allowable tubing wall thickness. The ideal corrosion-resistant material will allow continuous operation without scale formation and accompanying degradation of film coefficients. Increased flow rates are possible due to the dimensional stability present in

the tubing diameter, yielding higher and constant film coefficients. Since zirconium is corrosion resistant, a corrosion allowance is seldom required thus minimizing the actual wall thickness and resistance to heat transfer.

These factors all contribute to a stable, dependable heat transfer surface which allows equipment to operate for extended periods of time in numerous media. Fouling problems are often eliminated with a change to zirconium tubes.

Zirconium tubing is also available with a finned surface for increased heat transfer rates. Finned tube exchangers are typically much smaller than smooth tubed exchangers for the same total heat transfer requirement.

Health And Safety

Zirconium is non-toxic and consequently does not require serious limitations on its use because of health hazards.

Finely divided zirconium is pyrophoric because of its heat-producing reaction with oxidizing elements such as oxygen. Large pieces of sheet, plate, bar, tube and ingot can be heated to high temperatures without excessive oxidation or burning. However, small pieces with a high surface-area-to-mass ratio, such as machine chips and turnings, are easily ignited and burn at extremely high temperatures. It is recommended that large accumulations of chips and other finely divided material be avoided. Also, in storing the chips and turnings, care should be taken to place the material in non-flammable containers and isolated areas.

One effective storage method is to keep the material covered with water

in the containers and in turn, use oil on the water to keep it from evaporating. If a fire accidentally starts in zirconium, do not attempt to put it out with water or ordinary fire extinguishers. Use dry sand, powdered graphite, or commercially available Metal-X* powder. Large quantities of water can be used to control and extinguish fires in other flammables in the vicinity of a zirconium fire.

In some cases when the corrosion-resistance of zirconium is exceeded, a finely divided corrosion product, which may be very pyrophoric, can form on the surface of the metal. This film can be rendered non-pyrophoric by simple oxidation treatments with hot steam.

Please contact us for more detailed information on this subject.

*Metal-X is a registered trademark for powder produced by Ansul Manufacture in Marinette, Wisconsin.

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About the Cover . . .

Immersion test apparatus are used in Teledyne Wah Chang Albany's Corrosion Laboratory to study the corrosion resistance of zirconium in various aqueous environments.