Z

ZINC AND ZINC ALLOYS

Zinc as a pure metal finds relatively few applications because of its poor mechanical properties. It is relatively weak. The single largest use of zinc is in the application of zinc coatings (galvanizing) to permit the most efficient use of steel and to conserve energy.

Corrosion of Zinc

Depending upon the nature of the environment, zinc has the ability to form a protective layer made up of basic carbonates, oxides, or hydrated sulfates. Once the protective layers have formed, corrosion proceeds at a greatly reduced rate. Consideration of the corrosion of zinc is primarily related to show general dissolution from the surface. Even air is only slightly corrosive to zinc. Below 390°F (200°C) the film grows very slowly and is very adherent. Zinc-coated steel behaves similarly to pure zinc.

The pH of the environment governs the film. Within the pH range of 6 to 12.5 the corrosion rate is low. Corrosive attack is most severe at pH values below 6 and above 12.5.

Uniform corrosion rates of zinc are not appreciably affected by the purity of zinc. However, the addition of some alloying elements can increase the corrosion resistance of zinc.

White Rust (Wet Storage Stain)

White rust is a form of general corrosion that is not protective. It is more properly called wet storage stain because it occurs in storage where water is present but only a limited supply of oxygen and carbon dioxide is available. Wet stain formation will be accelerated by the presence of chlorides and sulfates.

White rust is a white, crumbly, and porous coating. The surface underneath the white product is often dark gray.

This coating is found on newly galvanized bright surfaces, particularly in crevices between closely packed sheets whose surfaces have come into contact with condensate or rainwater and the moisture can not dry up quickly. If the zinc surfaces have already formed a protective film prior to storage, chances are that no attack will take place.

Short-term protection against wet storage stain can be provided by chromating or phosphating. Painting after galvanizing will also provide protection.

Materials stored outdoors should be arranged so that all surfaces are well ventilated and that water can easily run off of the surfaces. If possible, new zinc surfaces should not be allowed to come into contact with rain or condensate water during transit or storage. This is the best way of preventing wet storage stain. Fig. Z.1 illustrates the stacking of galvanized parts out of doors.
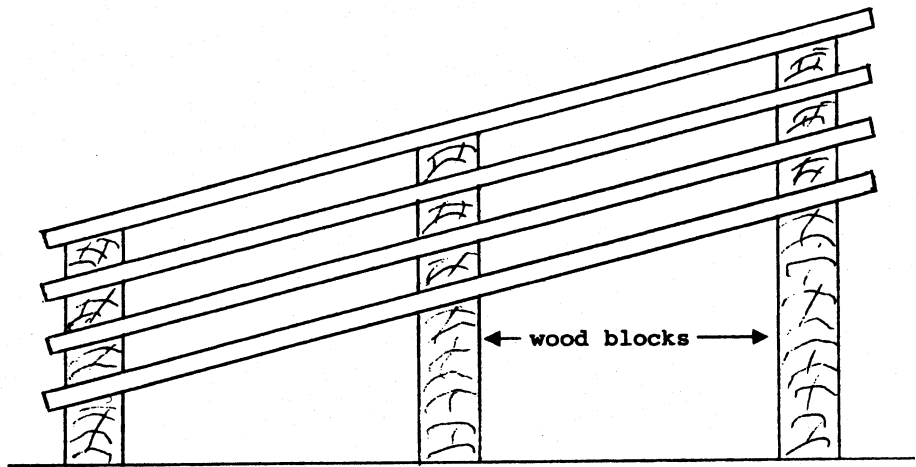
649

Figure Z.1 Stacking of galvanized parts out of doors.

Bimetallic Corrosion

The ratio of the areas of metals in contact, the duration of wetness, and the conductibility of the electrolyte will determine the severity of corrosive attack. Seawater, which is a highly conductive solution, will produce a more severe bimetallic corrosion than most fresh waters, which generally have a lower conductivity. A film of moisture condensed from the air or rainwater can dissolve contaminants and produce conditions conducive to bimetallic corrosion. See Ref. 5.

Bimetallic corrosion is less severe under atmospheric exposure than under immersed conditions. In the former, attack will occur only when the surface is wet, which depends on several factors such as the effectiveness of drainage, the presence or retention of moisture in crevices, and the speed of evaporation.

Under normal circumstances galvanized steel surfaces may safely be in contact with types 304 and 316F stainless steel, most aluminum alloys, chrome steel (>12% Cr) and tin, provided the area ratio of zinc to metal is 1:1 or lower, and oxide layers are present on both aluminum alloys and the two stainless steels.

Prevention of bimetallic corrosion can be accomplished by preventing the flow of the corrosion currents between the dissimilar metals in contact. This can be done by either insulating the dissimilar metals from each other (breaking the metallic path) or by preventing the formation of a continuous bridge of conductive solution between the two metals (breaking the electrolytic path).

If electrical bonding is not required, the first method may be achieved by providing insulation under immersed conditions. For example, a zinc-coated steel bolt and nut may be fitted with an insulating bushing and washers where it passes through a steel surface that cannot be coated.

The second method may be accomplished by the application of paint or plastic coatings to the immersed parts of the metal. If it is not practical to coat both metals, it is preferable to coat the more noble metal, not the zinc.
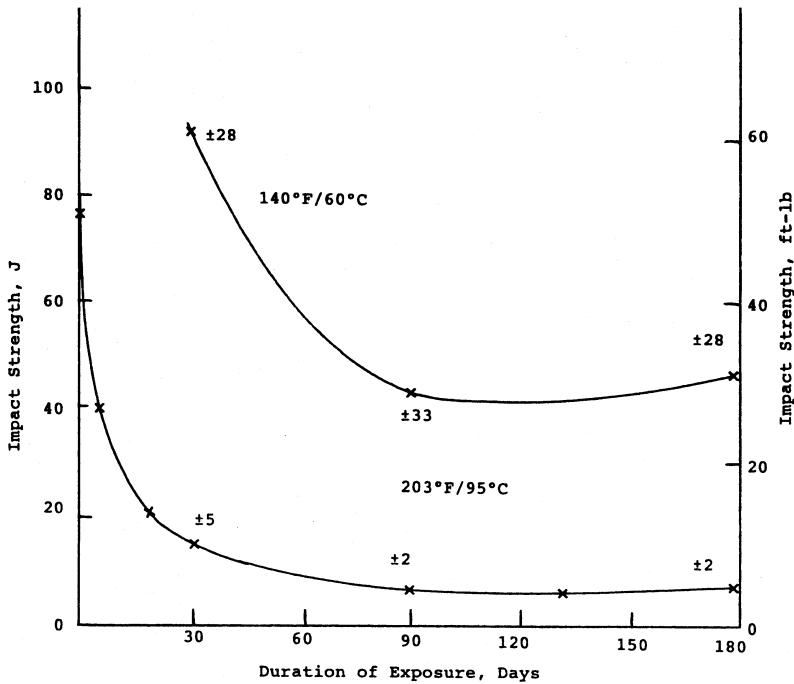
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Figure Z.2 Effect of intergranular corrosion of zinc–aluminum alloys on impact strength.

Intergranular Corrosion

If pure zinc–aluminum alloys are exposed to temperatures in excess of 160°F/70°C under wet or damp conditions, intergranular corrosion may take place. The use of these alloys should be restricted to temperatures below 160°F/70°C and impurities controlled to specific limits of 0.006% each for lead and cadmium and to 0.003% for tin.

Impact strength can decrease as a result of intergranular corrosion as well as by aging. At 140°F/60°C, in high humidity, the loss is minimal. At 203°F/95°C, intergranular attack is ten times greater and loss of impact strength increases. Refer to Fig. Z.2.

Corrosion Fatigue

Galvanized coatings can stop corrosive fatigue by preventing contact of the corrosive substance with the base metal. Zinc, which is anodic to the base metal, provides electrochemical protection after the mechanical protection has ceased.

Stress Corrosion

Zinc or zinc-coated steels are not usually subjected to stress corrosion. Zinc can also prevent stress corrosion cracking in other metals.

Zinc Coatings

Zinc coatings protect the substrate by means of cathodic control. Cathodic overpotential of the surface is increased by the coating, which makes the corrosion potential

more negative than that of the substrate. The coating layer acts as a sacrificial anode for iron and steel substrates when the substrates are exposed to the atmosphere. The coating layer provides cathodic protection for the substrate by galvanic action. Zinc is therefore considered a sacrificial metal.

The electrical conductivity of the electrolyte, the temperature, and the surface condition determine the galvanic action of the coating. An increase in the cathodic overpotential is responsible for the corrosion resistance of the coating layer. Fig. Z.3 illustrates the principle of cathodic control protection by a sacrificial metal coating.

The corrosion of zinc-coated iron i_{corr} is lower than that of uncoated iron since the cathodic overpotential of the surface is increased by the zinc coating and the exchange current density of dissolved oxygen i_{oc} on zinc is lower than that on iron.

If a small part of iron is exposed to the atmosphere, the electrode potential of the exposed iron is equal to the corrosion potential of the zinc coating since the exposed iron is polarized cathodically by the surrounding zinc, so that little corrosion occurs on the exposed iron. Zinc ions dissolved predominantly from the zinc coating form the surrounding barrier of corrosion products at the defect, thereby protecting the exposed iron.
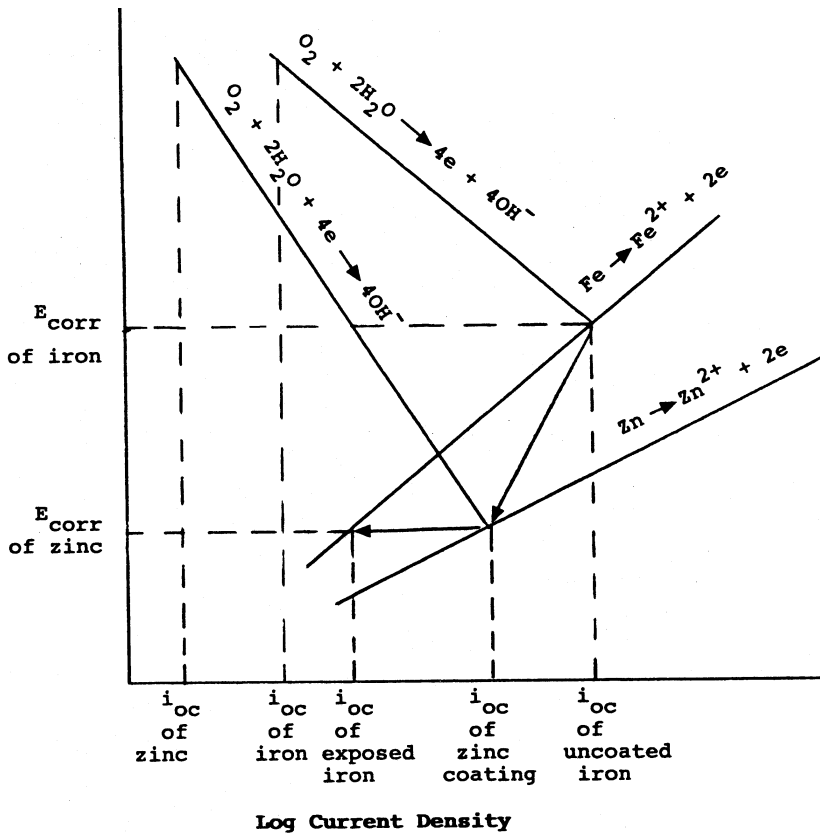

Figure Z.3 Cathodic control protection.

Sacrificial metal coatings protect iron and steel via two or three mechanisms:

1. Original barrier action of coating layer
2. Secondary barrier action of corrosion product layer
3. Galvanic action of coating layer

The surface oxide film and the electrochemical properties based on the metallography of the coating material provide the original barrier action. The original barriers of zinc and zinc alloy coatings result from electrochemical properties based on the structure of the coating layer.

Nonuniformity of the surface condition generally induces the formation of a corrosion cell. Such nonuniformity results from defects in the surface oxide film, localized distribution of elements, and differences in crystal face or phase. These nonuniformities cause a potential difference between portions of the surface, promoting the formation of a corrosion cell.

Many corrosion cells are formed on the surface, accelerating the corrosion rate, as a sacrificial metal and its alloy-coated materials are exposed in the natural atmosphere. During this time corrosion products are gradually formed and converted to a stable layer after a few months of exposure. Once the stable layer has been formed, the corrosion rate becomes constant. This secondary barrier of corrosion protection regenerates continuously over a long period of time. In most cases the service life of a sacrificial metal coating depends on the secondary barrier action of the corrosion product layer.

Zinc metal coatings are characterized by their galvanic action. Exposure of the base metal as a result of mechanical damage polarizes the base metal cathodically to the potential of the coating layer, as shown in Fig. Z.3, so that little corrosion takes place on the exposed base metal. A galvanic couple is formed between the exposed part of the base metal and the surrounding coating metal. Since zinc is more negative in electrochemical potential than iron or steel, the zinc acts as an anode and the exposed base metal behaves as a cathode. Consequently, the dissolution of the zinc layer around the defect is accelerated and the exposed part of base metal is protected against corrosion.

Figure Z.4 is a schematic illustration of the galvanic action of a zinc coating.
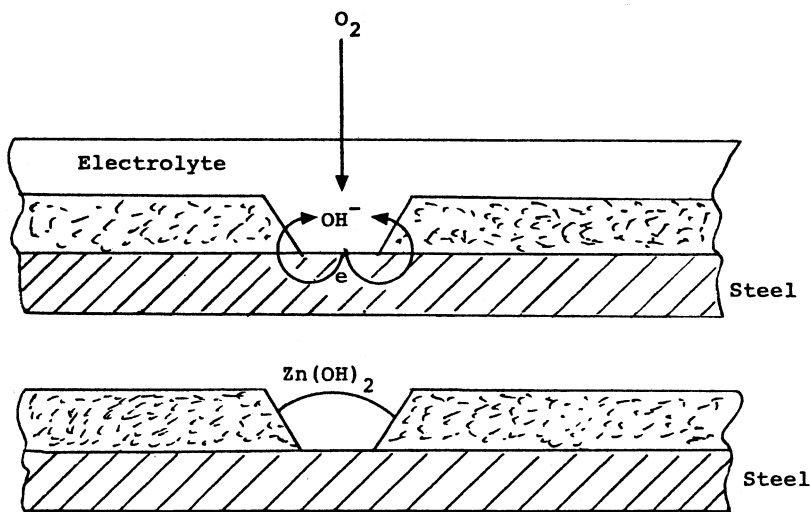

Figure Z.4　Schematic illustration of the galvanic action of a zinc metallic coating.

Corrosion of Zinc Coatings

In general, zinc coatings corrode in a similar manner as solid zinc. However, there are some differences. For example, the iron–zinc alloy present in most galvanized coatings has a higher corrosion resistance than solid zinc in neutral and acid solutions. At points where the zinc coating is defective, the bare steel is cathodically protected under most conditions.

The corrosion rate of zinc coatings in air is an approximate straight-line relationship between weight loss and time. Since the protective film on zinc increases with time in rural and marine atmospheres of certain types, under these conditions the life of the zinc may increase more than proportionately to thickness. However, this does not always happen.

Zinc coatings are used primarily to protect ferrous parts against atmospheric corrosion. These coatings have good resistance to abrasion by solid pollutants in the atmosphere. General points to consider are

1. Corrosion increases with time of wetness.
2. The corrosion rate increases with an increase in the amount of sulfur compounds in the atmosphere. Chlorides and nitrogen oxides usually have a lesser effect but are often very significant in combination with sulfates.

Zinc coatings resist atmospheric corrosion by forming protective films consisting of basic salts, notably carbonate. The most widely accepted formula is $3Zn(OH)_2 \cdot 2ZnCO_3$. Environmental conditions that prevent the formation of such films, or conditions that lead to the formation of soluble films, may cause rapid attack on the zinc.

Duration and frequency of moisture contact is one such factor. Another factor is the rate of drying, because a thin film of moisture with high oxygen concentration promotes reaction. For normal exposure conditions the films dry quite rapidly. It is only in sheltered areas that drying times are slow, so that the attack on zinc is accelerated significantly.

The effect of atmospheric humidity on the corrosion of a zinc coating is related to the conditions that may cause condensation of moisture on the metal surface and to the frequency and duration of the moisture contacts. If the air temperature drops below the dew point, moisture will be deposited. The thickness of the piece, its surface roughness, and its cleanliness also influence the amount of dew deposited. Lowering the temperature of a metal surface below the air temperature in a humid atmosphere will cause moisture to condense on the metal. If the water evaporates quickly, corrosion is usually not severe and a protective film is formed on the surface. If water from rain or snow remains in contact with zinc when access to air is restricted and the humidity is high, the resulting corrosion can appear to be severe (wet storage stain) since the formation of a protective basic zinc carbonate is prevented.

In areas having atmospheric pollutants, particularly sulfur oxides and other acid-forming pollutants, time of wetness becomes of secondary importance. These pollutants can also make rain more acid. In less corrosive areas, time of wetness assumes a greater proportional significance.

In the atmospheric corrosion of zinc, the most important atmospheric contaminant to be considered is sulfur dioxide. At relative humidities of about 70% or above, it usually controls the corrosion rate.

Sulfur oxides and other corrosive species react with the zinc coating in two ways: dry deposition and wet deposition Sulfur dioxide can deposit on a dry surface of galvanized steel panels until a monolayer of SO_2 is formed. In either case the sulfur dioxide that deposits on the surface of the zinc forms a sulfurous or other strong acid, which reacts with the film of zinc oxide, hydroxide, or basic carbonate to form zinc sulfate. The conversion of sulfur dioxide to sulfur-based acids may be catalyzed by nitrogen compounds in the air (NO_x compounds). This factor may affect corrosion rates in practice. The acids partially destroy the film of corrosion products, which will then reform from the underlying metal, thereby causing continuous corrosion by an amount equivalent to the film dissolver, and hence the amount of SO_2 absorbed.

Chloride compounds have less effect than sulfur compounds in determining the corrosion rate of zinc. Chloride is most harmful when combined with acidity due to sulfur gases. This condition is prevalent on the coast in highly industrial areas.

Atmospheric chlorides will lead to the corrosion of zinc, but to a lesser degree than the corrosion of steel, except in brackish water and flowing seawater. Any salt deposit should be removed by washing. The salt content of the atmosphere will usually decrease rapidly inland farther from the coast. Corrosion also decreases with distance from the coast, but the change is more gradual and erratic because chloride is not the primary pollutant affecting zinc corrosion. Chloride is most harmful when combined with acidity resulting from sulfur gases.

Other pollutants also have an effect on the corrosion of galvanized surfaces. Deposits of soot or dust can be detrimental because they have the potential to increase the risk of condensation onto the surface and hold more water in position. This is prevalent on upward-facing surfaces. Soot (carbon) absorbs large quantities of sulfur, which is released by rainwater.

In rural areas overmanuring of agricultural land tends to increase the ammonia content of the air. The presence of normal atmospheric quantities of ammonia does not accelerate zinc corrosion, and petroleum plants where ammonium salts are present show no appreciable attack on galvanized steel. However, ammonia will react with atmospheric sulfur oxides, producing ammonium sulfate, which accelerates paint film corrosion as well as zinc corrosion. When ammonia reacts with NO_x^- compounds in the atmosphere, ammonium nitrite and nitrate are produced. Both compounds increase the rate of zinc corrosion, but less so than SO_2 or SO_3.

Because of the Mears effect (wire corrodes faster per unit of area than more massive materials), galvanized wire corrodes some 10–80% faster than galvanized sheet. However, the life of rope made from galvanized steel wires is greater than the life of the individual wire. This is explained by the fact that the parts of the wire that lie on the outside are corroded more rapidly, and when the zinc film is penetrated in these regions, the uncorroded zinc inside the rope provides cathodic protection for the outer regions.

Galvanized steel also finds application in the handling of various media. Table Z.1 gives the compatibility of galvanized steel with selected corrodents.

Table Z.1   Compatibility of Galvanized Steel with Selected Corrodents

Acetic acid	U	Acrylic latex	U
Acetone	G	Aluminum chloride 26%	U
Acetonitrile	G	Aluminum hydroxide	U
Acrylonitrile	G	Aluminum nitrate	U

Table Z.1   Compatibility of Galvanized Steel with Selected Corrodents (Continued)

Ammonia, dry vapor	U	Ethyl acetate	G
Ammonium acetate solution	U	Ethyl acrylate	G
Ammonium bisulfate	U	Ethyl amine 69%	G
Ammonium bromide	U	N-Ethyl butylamine	G
Ammonium carbonate	U	2-Ethyl butyric acid	G
Ammonium chloride 10%	U	Ethyl ether	G
Ammonium dichloride	U	Ethyl hexanol	G
Ammonium hydroxide		Fluorine, dry, pure	G
Vapor	U	Formaldehyde	G
Reagent	U	Fruit juices	S
Ammonium molybdate	G	Hexanol	G
Ammonium nitrate	U	Hexylamine	C
Argon	G	Hexylene glycol	C
Barium hydroxide		Hydrochloric acid	U
Barium nitrate solution	S	Hydrogen peroxide	S
Barium sulfate solution	S	Iodine, gas	U
Beeswax	U	Isohexanol	G
Borax	S	Isooctanol	G
Bromine, moist	U	Isopropyl ether	G
2-Butanol	G	Lead sulfate	U
Butyl acetate	G	Lead sulfite	S
Butyl chloride	G	Magnesium carbonate	S
Butyl ether	G	Magnesium chloride 42.5%	U
Butylphenol	G	Magnesium fluoride	G
Cadmium chloride solution	U	Magnesium hydroxide sat.	S
Cadmium nitrate solution	U	Magnesium sulfate	
Cadmium sulfate solution	U	2% solution	S
Calcium hydroxide		10% solution	U
sat. solution	U	Methyl amyl alcohol	G
20% solution	S	Methyl ethyl ketone	G
Calcium sulfate, sat. solution	U	Methyl propyl ketone	G
Cellosolve acetate	G	Methyl isobutyl ketone	G
Chloric acid 20%	U	Nickel ammonium sulfate	U
Chlorine, dry	G	Nickel chloride	U
Chlorine water	U	Nickel sulfate	S
Chromium chloride	U	Nitric acid	U
Chromium sulfate solution	U	Nitrogen, dry, pure	G
Copper chloride solution	U	Nonylphenol	G
Decyl acrylate	G	Oxygen	
Diamylamine	G	dry, pure	G
Dibutylamine	G	moist	U
Dibutyl cellosolve	G	Paraldehyde	G
Dibutyl phthalate	G	Perchloric acid solution	S
Dichloroethyl ether	G	Permanganate solution	S
Diethylene glycol	G	Peroxide	
Dipropylene glycol	G	pure, dry	S
Ethanol	G	moist	U

Z

Table Z.1 Compatibility of Galvanized Steel with Selected Corrodents (Continued)

Phosphoric acid 0.3–3%	G	moist, wet	U
Polyvinyl acetate latex	U	Silver nitrate solution	U
Potassium carbonate		Sodium acetate	S
10% solution	U	Sodium aluminum sulfate	U
50% solution	U	Sodium bicarbonate solution	U
Potassium chloride solution	U	Sodium bisulfate	U
Potassium bichromate		Sodium carbonate solution	U
14.7%	G	Sodium chloride solution	U
20%	S	Sodium hydroxide solution	U
Potassium disulfate	S	Sodium nitrate solution	U
Potassium fluoride 5–20%	G	Sodium sulfate solution	U
Potassium hydroxide	U	Sodium sulfide	U
Potassium nitrate		Sodium sulfite	U
5–10% solution	S	Styrene, monomeric	G
Potassium peroxide	U	Styrene oxide	G
Potassium persulfate 10%	U	Tetraethylene glycol	G
Propyl acetate	G	1, 1, 2-Trichloroethane	G
Propylene glycol	G	1, 2, 3-Trichloropropane	G
Propionaldehyde	G	Vinyl acetate	G
Propionic acid	U	Vinyl ethyl ether	G
Silver bromide	U	Vinyl butyl ether	G
Silver chloride		Water	
pure, dry	S	potable, hard	G

G = Suitable application; S = Borderline application; U = Not suitable.

Zinc Alloys

Small alloy additions are made to zinc to improve grain size, give work hardening, and improve properties such as creep resistance and corrosion resistance. There are a number of proprietary compositions available containing additions of copper, manganese, magnesium, aluminum, chromium, and titanium

Zinc–5% Aluminum Hot Dip Coatings

This zinc alloy coating is known as Galfan. Galfan coatings have a corrosion resistance up to three times that of galvanized steel. The main difference between these two coatings lies in the degree of cathodic protection they afford. This increase in corrosion protection is evident both in a relatively mild urban industrial atmosphere and in a marine atmosphere, as can be seen in Table Z.2. The latter is particularly significant because unlike the case for galvanizing, the corrosion rate appears to slow after about 4 years, and conventional galvanized steel would show rust in 5 years. See Fig. Z.5. The slower rate of corrosion also means that the zinc–5% aluminum coatings provide full cathodic protection to cut edges over a longer period. Refer to Table Z.3.

Table Z.2   Five-Year Outdoor Exposure Results of Galfan Coating

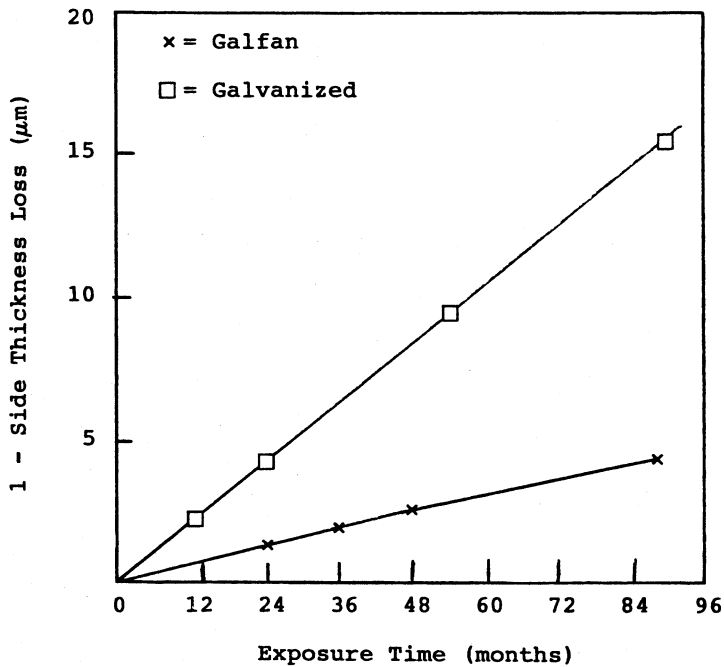| Atmosphere	Thickness loss (μm)		Ratio of improvement
	Galvanized	Galfan	
Industrial	15.0	5.2	2.9
Severe marine	>20.0	9.5	>2.1
Marine	12.5	7.5	1.7
Rural	10.5	3.0	3.5

Source: Ref. 1.

Figure Z.5   Seven-year exposure of Galfan and galvanized steel in a severe marine atmosphere.

Table Z.3   Comparison of Cathodic Protection for Galvanized and Galfan Coatings

Environment	Amount of bare edges exposed after 3 years (coating recession from edge) (mm)	
	Galvanized	Galfan
Severe marine	1.6	0.1
Marine	0.5	0.06
Industrial	0.5	0.05
Rural	0.1	0.0

Source: Ref. 1.

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Because Galfan can be formed with much smaller cracks than can be obtained in conventional galvanized coatings, it provides excellent protection at panel bulges. This reduced cracking means that less zinc is exposed to the environment, which increases the relative performance factor compared with galvanized steel.

Zinc–55% Aluminum Hot Dip Coatings

These coatings are known as Galvalume and consist of zinc–55% aluminum–1.5% silicon. This alloy is sold under such trade names as Zaluite, Aluzene, Alugalva, Algafort, Aluzink, and Zincalume. Galvalume exhibits superior corrosion resistance over galvanized coatings in rural, industrial, marine, and severe marine environments. However, this alloy has limited cathodic protection and less resistance to some alkaline conditions and is subject to weathering discoloration and wet storage staining. The latter two disadvantages can be overcome by chromate passivation, which also improves atmospheric corrosion resistance.

Initially, a relatively high corrosion loss is observed for Galvalume sheet as the zinc-rich portion of the coating corrodes and provides sacrificial protection at cut edges. This takes place in all environments. After approximately 3 years, the corrosion–time curves take on a more gradual slope, reflecting a change from active, zinc-like behavior to passive aluminum-like behavior as the interdentric regions fill with corrosion products. It has been predicted that Galvalume sheets should outlast galvanized sheets of equivalent thickness by at least two to four times over a wide range of environments.

Galvalume sheets provide excellent cut-edge protection in very aggressive conditions, where the surface does not remain too passive. However, it does not offer as good protection on the thicker sheets in mild rural conditions, where zinc–5% aluminum coatings provide good general corrosion resistance. When sheared edges are exposed or localized damage to the coating occurs during fabrication or service, the galvanic protection is retained for a longer period.

Zinc–15% Aluminum Thermal Spray

Zinc–15% aluminum coatings are available as thermally sprayed coatings. These coatings have a two-phase structure consisting of a zinc-rich and an aluminum-rich phase. The oxidation products formed are encapsulated in the porous layer formed by the latter and do not build up a continuous surface layer as with pure zinc coatings. As a result, no thickness or weight loss is observed even after several years of exposure in atmospheric field testing.

It is normally recommended that thermally sprayed coatings be sealed to avoid initial rust stains, to improve appearance, and to facilitate maintenance painting. Sealing is designed to fill pores and give only a thin overall coating, too thin to be directly measurable. Epoxy or acrylic system resins, having a low viscosity, are used as a sealer.

Zinc-Iron Alloy Coatings

Compared with pure zinc, the zinc–iron alloy coatings provide increased corrosion resistance in acid atmospheres but slightly reduced corrosion resistance in alkaline atmospheres.

Electroplated zinc–iron alloy layers containing more than 20% iron provide a corrosion resistance 30% higher than zinc in industrial atmospheres. In other atmospheres the zinc–iron galvanized coatings are as good as coatings with an outer zinc layer. Sheradized coatings are superior to electroplated coatings and equal to galvanized coatings of the same thickness. However, the structure of the layer and its composition affect the corrosion resistance.

If the zinc layer of a galvanized coating has weathered, or if the zinc–iron alloy layer forms the top layer after galvanizing, brown areas may form. Brown staining can occur on sheradized or hot dip galvanized coatings in atmospheric corrosion through the oxidation of iron from the zinc–iron alloy layers or from the substrate. Such staining is usually a dull brown rather than the bright red-brown of uncontrolled rust. Usually there is a substantial intact galvanized layer underneath, leaving the life of the coating unchanged. Unless the aesthetic appearance is undesirable, no action need be taken.

See Refs. 1–3.

ZINCATING

This is an immersion coating of aluminum base materials with zinc to facilitate electroplating of other metals on the aluminum article. Zincating is a chemical replacement where aluminum ions replace zinc ions in an aqueous solution of zinc salts, thus depositing a thin adherent film of metallic zinc on the aluminum surface. Adhesion of the zinc depends on metallurgical bonding.

ZINC EMBRITTLEMENT

This is a form of liquid metal embrittlement of austenitic stainless steels. It most commonly occurs in fire exposure or welding of these steels while in contact with galvanized steel parts.

ZIRCALOYS

These are zirconium alloys Zr2.5Nb and Zr-1Nb, which are hafnium free and are classified as nuclear grade. See "Zirconium and Zirconium Alloys."

ZIRCONIUM AND ZIRCONIUM ALLOYS

Zirconium and its alloys can be classified into two major categories: nuclear and nonnuclear. The major difference between these two categories is in the hafnium content. Nuclear grades of zirconium are essentially free of hafnium (<100 ppm). Nonnuclear grades of zirconium may contain as much as 4.5% hafnium, which has an enormous effect on zirconium's nuclear properties but little effect on its mechanical and chemical properties. The commercially available grades of zirconium alloys are shown in Table Z.4.

The majority of the nuclear-grade material is produced as tubing, which is used for nuclear fuel rod claddings, guide tubes, pressure tubes, and ferrule spacer grids. Sheets and plates are used for spacer grids, water channels, and channel boxes for nuclear fuel bundles.

Nonnuclear zirconium applications make use of ingots, forgings, pipes, tubes, plates, sheet, foils, bars, wires, and castings to construct highly corrosion-resistant equipment. Included are heat exchangers, condensers, reactors, columns, piping systems, agitators, evaporators, tanks, pumps, valves, and packing.

In spite of the reactive nature of zirconium metal, the zirconium oxide (ZnO_2) film that forms on the surface is among the most insoluble compounds in a broad range of chemicals. Excellent corrosion protection is provided in most media. When mechanically destroyed, the oxide film will regenerate itself in many environments. When placing zirconium in a corrosive medium, there is no need to thicken this film.

Several methods are available to produce the oxide film. They include anodizing, autoclaving in hot water or steam, formation in air, and formation in molten salts.

Table Z.4   Commercially Available Grades of Zirconium Alloys

Alloy designation (UNS no.)	Composition (%)									
	Zr + Hf, min.	Hf, max.	Sn	Nb	Fe	Cr	NI	Fe + Cr	Fe + Cr + Ni	0, max.
Nuclear grades										
Zircaloy-2 (R60802)	—	0.010	1.20–1.70	—	0.07–0.20	0.05–0.15	0.03–0.08	—	0.18–0.38	—
Zircaloy-4 (R60804)	—	0.010	1.20–1.70	—	0.18–0.24	0.07–0.13	—	0.28–0.37	—	—
Zr-2.5Nb (R60901)	—	0.010	—	2.40–2.80	—	—	—	—	—	—
Chemical grades										
Zr 702 (R60702)	99.2	4.5	—	—	—	—	—	0.2 max.	—	0.16
Zr 704 (R60704)	97.5	4.5	1.0–2.0	—	—	—	—	0.2–0.4	—	0.18
Zr 705 (R60705)	95.5	4.5	—	2.0–3.0	—	—	—	0.2 max.	—	0.18
Zr 706 (R60706)	95.5	4.5	—	2.0–3.0	—	—	—	0.2 max.	—	0.16

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Anodizing

A very thin film(<0.5μm) is formed by anodizing. As the thickness of the film grows, the color changes. Although the film formed is attractive, it does not have the adhesion of thermally produced films and has very limited ability to protect the metal from mechanical damage.

Autoclave Film Formation

The nuclear industry uses this method. These films, in addition to providing a slower corrosion rate, reduce the rate of hydrogen absorption.

Film Formation in Air or Oxygen

This is the most common method used in the chemical process industry. The film is formed during the final stress relief of a component in air at 1022°F (550°C) for 0.5 to 4 h. It ranges in color from straw yellow to an iridescent blue or purple to a powdery tan or light gray. These colors are not indications of metal contamination. This treatment does not cause significant penetration of oxygen into the metal, but it does form an oxide layer that is diffusion bonded to the base metal.

Film Formation in Molten Salts

In this process, developed and patented by TWC, zirconium subjects are treated in a fused sodium cyanide containing 1–3% sodium carbonate or in a eutetic mixture of sodium and potassium chlorides with 5% sodium carbonate. Treatment is carried out at temperatures ranging from 1112 to 1472°F (600–800°C) for several hours. A thick protective, strongly cohesive oxide film ranging from 20 to 30μm is formed. This film has improved resistance to abrasion and galling over thick films produced by other methods.

Electrochemical Protection

Zirconium performs well in most reducing environments as a result of its ability to take oxygen from water to form stable passive films. Most passive metals and alloys require the presence of an oxidizing agent such as oxygen in order to form a protective oxide film. Zirconium's corrosion problems can be controlled by converting the corrosive condition to a more reducing condition.

By impressing a potential that is arbitrarily 50–100 mV below its corrosion potential, zirconium becomes corrosion resistant in oxidizing chloride solutions. Tables Z.5 and Z.6 demonstrate the benefits of electrochemical protection in controlling pitting and stress corrosion cracking. Pitting penetration in oxidizing chloride solutions is considerably higher than general corrosion rates, which may be low for unprotected zirconium. Electrochemical protection eliminates this local attack.

Table Z.5   Corrosion Rate of Zirconium in 500 ppm Fe^{3+} Solution after 32 Days

			Penetration rate (mpy)	
Environment	Acidity	Temperature (°C)	Unprotected	Protected
10% HCl	3 N	60	7.1	<0.1
		120	51	<0.1
Spent acid (15% Cl)	5 N	65	36	<0.1
		80	36	<0.1
20% HCl	6 N	60	3.6	<0.1
		107	59	<0.1

Source: Ref. 4.

Table Z.6   Time to Failure of Welded Zirconium U Bends in 500 ppm Fe^{3+} Solution after 32 Days

			Time to failure (days)	
Environment	Acidity	Temperature (°C)	Unprotected	Protected
10% HCl	3 N	60	<0.1	NF
		120	<0.1	NF
Spent acid (15% Cl)	5 N	65	<0.3	NF
20% HCl	6 N	60	NF	NF
		107	<0.1	NF
28% HCl	9 N	60	2	NF
		94	<0.1	NF
32% HCl	10 N	53	1	32
		77	<0.1	20
37% HCl	12 N	30	0.3	NF
		53	1	NF

NF = no failure.
Source: Ref. 4.

As can be seen from Table Z.6, unprotected welded zirconium U bends cracked in all but one case shortly after exposure. Protected U bends resisted cracking for the 32-day test period in all but one acid concentration. From these tests it is obvious that electrochemical protection provides an improvement to the corrosion properties of zirconium in oxidizing solutions.

Forms of Corrosion

The more common forms of corrosion, to which zirconium is susceptible, other than general (uniform) corrosion, include pitting, stress corrosion cracking (SCC), fretting, galvanic, and crevice corrosion.

Pitting

Zirconium will pit in acidic chloride solutions because its pitting potential is greater than its corrosion potential. The presence of oxidizing ions, such as ferric and cupric ions, in acidic chloride solutions may increase the corrosion potential to exceed the pitting potential. Therefore, pitting may occur. However, zirconium does not pit in most other halide solutions. Under certain conditions nitrate and sulfate ions can inhibit the pitting.

One of the critical factors in pitting is surface condition. A metal with a homogeneous surface is less likely to pit and less likely to be vulnerable to other forms of localized corrosion. A common method used to homogenize a metal's surface is pickling. Results of tests show that pickled zirconium may perform well in boiling 10% $FeCl_3$ and even ClO_2, while zirconium with a normal surface finish is unsuitable for handling these solutions.

Stress Corrosion Cracking

Zirconium and its alloys resist SCC in many media, such as NaCl, $MgCl_2$, NaOH, and H_2S, which cause SCC on common metals and alloys. However, zirconium is susceptible to SCC environments such as $FeCl_3$, $CuCl_2$, halide or halide-containing methanol, concentrated HNO_3, 64–69% H_2SO_4, and liquid mercury or cesium.

Stress corrosion cracking of zirconium can be prevented by

1.   Avoiding high sustained tensile stresses
2.   Modifying the environment, e.g., changing pH concentration or adding an inhibitor

3. Maintaining a high-quality surface film (one low in impurities, defects, and mechanical damage)
4. Applying electrochemical techniques
5. Shot peening
6. Achieving a crystallographic texture with the hexagonal basal planes perpendicular to the cracking path

Fretting Corrosion

When the protective oxide coating of zirconium is damaged or removed, fretting may occur. It takes place when vibration contact is made at the interface of tight-fitting, highly bonded surfaces. If the vibration cannot be removed mechanically, the addition of a heavy oxide coating on the zirconium may eliminate the problem. This coating reduces friction and prevents the removal of the passive film.

Galvanic Corrosion

The protective oxide film that forms on zirconium causes zirconium to assume a noble potential similar to that of silver. It is possible for zirconium to become activated and corrode at vulnerable areas when in contact with a noble metal. Vulnerable areas include areas with damaged oxide films and grain boundaries.

     Other, less noble metals will corrode in contact with zirconium when its oxide film is intact.

Crevice Corrosion

Zirconium is among the most resistant of all the corrosion-resistant metals to crevice corrosion. However, it is not completely immune to crevice corrosion in the broad sense. For example, crevice corrosion will occur when a dilute sulfuric acid solution is allowed to concentrate within a crevice.

General Corrosion Resistance

Zirconium is a highly corrosion-resistant metal. It reacts with oxygen at ambient temperatures and below to form an adherent, protective oxide film on its surface. Said film is self-healing and protects the base metal from chemical and mechanical attack at temperatures as high as 662°F (350°C). In a few media, such as hydrofluoric acid, concentrated sulfuric acid, and oxidizing chloride solutions, it is difficult to form this protective film. Therefore, zirconium cannot be used in these media without the use of protective measures previously discussed. Refer to Table Z.7 for the compatibility of zirconium with selected corrodents. The corrosion resistance of all zirconium alloys is similar.

Table Z.7   Compatibility of Zirconium, with Selected Corrodents[a]

Chemical	Maximum temp. (°F/°C)
Acetaldehyde	250/121
Acetic acid, 10%	220/104
Acetic acid, 50%	230/110
Acetic acid, 80%	230/110
Acetic acid, glacial	230/110

Table Z.7 Compatibility of Zirconium, with Selected Corrodents[a] (Continued)

Chemical	Maximum temp. (°F/°C)
Acetic anhydride	250/121
Acetone	190/88
Acetyl chloride	80/27
Acrylonitrile	210/93
Allyl alcohol	200/93
Allyl chloride	200/93
Alum	210/99
Aluminum chloride, aqueous	40%
	200/93
Aluminum chloride, dry	37%
	210/99
Aluminum fluoride	x
Aluminum hydroxide	200/93
Aluminum sulfate	210/99
Ammonia gas	100/38
Ammonium chloride, 10%	210/99
Ammonium chloride, 50%	220/104
Ammonium fluoride, 10%	x
Ammonium fluoride, 25%	x
Ammonium hydroxide, 25%	210/99
Ammonium hydroxide, sat.	210/99
Ammonium nitrate	210/99
Ammonium persulfate	220/104
Ammonium phosphate, 10%	210/99
Ammonium sulfate, 10–40%	210/99
Ammonium sulfide	
Amyl acetate	210/99
Amyl alcohol	200/93
Amyl chloride	210/99
Aniline	210/99
Aqua regia, 3:1	x
Barium carbonate	210/99
Barium chloride, 25%	210/99
Barium hydroxide	200/93
Barium sulfate	210/99
Barium sulfide	90/32
Benzaldehyde	210/99
Benzene	230/110
Benzene sulfonic acid, 10%	210/99
Benzoic acid	400/204
Benzyl alcohol	210/99
Boric acid	210/99
Bromine gas, dry	x

Table Z.7 Compatibility of Zirconium, with Selected Corrodents[a] (Continued)

Chemical	Maximum temp. (°F/°C)
Bromine gas, moist	60/16
Bromine, liquid	60/16
Butyl acetate	210/99
Butyl alcohol	200/93
Butyl phthalate	210/99
Butyric acid	210/99
Calcium bisulfite	90/32
Calcium carbonate	230/110
Calcium chloride	210/99
Calcium hydroxide, 10%	210/99
Calcium hydroxide, sat.	210/99
Calcium hypochlorite	200/93
Calcium sulfate	210/99
Caprylic acid	210/99
Carbon dioxide, dry	410/210
Carbonic acid	210/99
Cellosolve	210/99
Chloracetic acid, 50% water	210/99
Chloracetic acid	210/99
Chlorine gas, dry	90/32
Chlorine gas, wet	x
Chlorine, liquid	x
Chlorobenzene	200/93
Chloroform	210/99
Chromic acid, 10%	210/99
Chromic acid, 50%	210/99
Citric acid, 15%	210/99
Citric acid, conc.	180/82
Copper acetate	200/93
Copper chloride	x
Copper cyanide	x
Copper sulfate	210/99
Cupric chloride, 5%	x
Cupric chloride, 50%	190/88
Dichloroacetic acid	350/177
Ethylene glycol	210/99
Ferric chloride	x
Ferric chloride, 50% in water	x
Ferrous chloride	210/99
Fluorine gas, dry	x
Fluorine gas, moist	x
Hydrobromic acid, dilute	80/27
Hydrobromic acid, 20%	x

Table Z.7 Compatibility of Zirconium, with Selected Corrodents[a] (Continued)

Chemical	Maximum temp. (°F/°C)
Hydrobromic acid, 50%	x
Hydrochloric acid, 20%	300/149
Hydrochloric acid, 38%	140/60
Hydrofluoric acid, 30%	x
Hydrofluoric acid, 70%	x
Hydrofluoric acid, 100%	x
Lactic acid, 25%	300/149
Lactic acid, conc.	300/149
Malic acid	210/99
Manganese chloride, 5–20%	210/99
Methyl ethyl ketone	210/99
Methyl isobutyl ketone	200/93
Nitric acid, 5%	500/260
Nitric acid, 20%	500/260
Nitric acid, 70%	500/260
Nitric acid, anhydrous	90/32
Perchloric acid, 70%	210/99
Phenol	210/99
Phosphoric acid, 50–80%	180/82
Potassium bromide, 30%	200/93
Sodium carbonate	210/99
Sodium chloride	250/151
Sodium hydroxide, 10%	210/99
Sodium hydroxide, 50%	200/93
Sodium hydroxide, conc.	200/99
Sodium hypochlorite, 20%	100/38
Sodium sulfide, to 10%	x
Stannic chloride, 20%	210/99
Sulfuric acid, 10%	300/149
Sulfuric acid, 50%	300/149
Sulfuric acid, 70%	210/99
Sulfuric acid, 98%	x
Sulfuric acid, 100%	x
Sulfurous acid	370/188
Toluene	80/27
Trichloroacetic acid	x
White liquor	250/121

[a]The chemicals listed are in the pure state or in a saturated solution unless otherwise indicated. Compatibility is shown to the maximum allowable temperature for which data are available. Incompatibility is shown by an x. When compatible, corrosion rate is <20 mpy.
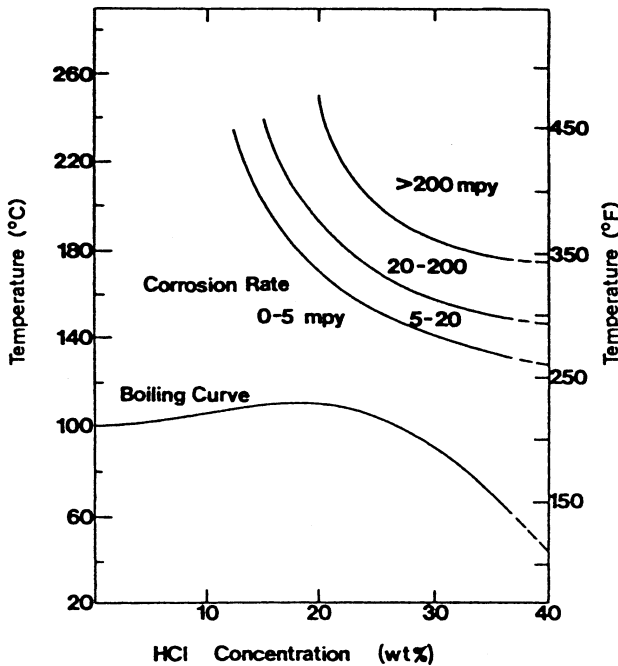*Source:* Ref. 3.

Figure Z.6 Isocorrosion diagram for zirconium in HCl (from Ref. 4).

Zirconium has excellent resistance to seawater, brackish water, and polluted water. It is sensitive to such changes as chloride concentration, temperature, pH, crevice formation, flow velocity, and sulfur-containing organisms.

Zirconium will resist attack by all halogen acids except hydrofluoric, which will attack zirconium at all concentrations. One of the most impressive corrosion-resistant properties is its resistance to hydrochloric acid at all concentrations, even above boiling. The isocorrosion diagram for zirconium is shown in Fig. Z.6.

Nitric acid poses no problem for zirconium. It can handle 9% HNO_3 below the boiling point and 70% HNO_3 up to 482°F (250°C) with corrosion rates of less than 5 mpy. Refer to Fig. Z.7.

The nature of sulfuric acid is complicated. Dilute solutions are reducing in nature. At or above 65%, sulfuric acid solutions become increasingly oxidizing. In Fig. Z.8 it will be noted that zirconium resists attack by H_2SO_4 at all concentrations up to 70% and at temperatures to boiling and above. In the 70–80% range of concentration, the corrosion resistance of zirconium depends strongly on temperature. In higher concentrations the corrosion rate of zirconium increases rapidly as the concentration increases. The presence of chlorides in H_2SO_4 has little effect on the corrosion resistance of zirconium unless oxidizing agents are also present.

Zirconium resists attack in phosphoric acid at concentrations up to 55% and temperatures exceeding the boiling point. Above 55% concentration the corrosion rate may increase greatly with increasing temperature. Zirconium performs ideally in handling dilute acid at elevated temperatures. If the phosphoric acid contains more than a trace of fluoride ions, zirconium may be attacked.
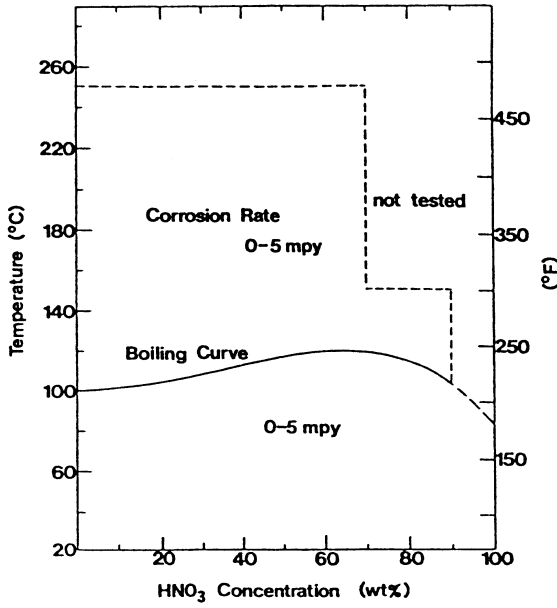
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Figure Z.7   Isocorrosion diagram for zirconium in HNO_3 (from Ref. 4).
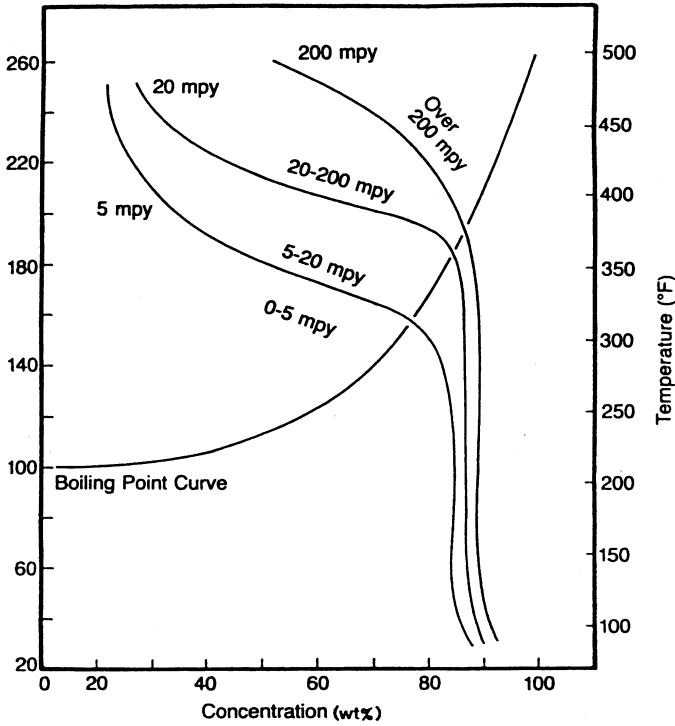

Figure Z.8   Isocorrosion diagram for zirconium in H_2SO_4 (from Ref. 4).

Zirconium is resistant to most alkalies, including sodium hydroxide, potassium hydroxide, calcium hydroxide, and ammonium hydroxide.

Most salt solutions, including halogen, nitrate, carbonate, and sulfate, will not attack zirconium. Corrosion rates are usually very low up to the boiling point. The exceptions are strong oxidizing chloride salts such as $FeCl_3$ and $CuCl_2$. In these media the corrosion resistance of zirconium is dependent on the surface conditions. When the zirconium has a good surface finish, it becomes quite resistant to pitting.

Zirconium possesses excellent resistance to most organic solutions. Corrosion is experienced when halogens are present and there is a lack of water. For example, if water is added to alcohol solutions with halide impurities, zirconium's susceptibility to SCC will be suppressed. Table Z.8 provides corrosion rates of zirconium in selected organic solutions.

ZYMAXX

Zymaxx is the registered trademark for DuPont's carbon fiber–reinforced Teflon. This composite material has outstanding mechanical and corrosion resistant properties. It has an operating temperature range of –350°F to 550°F. At 550°F Zymaxx has four times the flexural strength of filled PTFE at 400°F and with less deflection. Its compressive creep is less than 1% after 100 hours at 500°F and 6000 psi as compared with other polymeric materials that soften and "cold flow." In addition, it offers low friction, low wear resistance, a coefficient of thermal expansion less than that of steel, and virtually no water absorption. Listed in the table (see page 673) is a comparison of the major properties of Zymaxx, filled PTFE, and reinforced PEEK.

Table Z.8   Corrosion Rates for Zirconium in Organic Solutions

Environment	Concentration (wt%)	Temperature (°C)	Corrosion rate (mpy)
Acetic acid	5–99.5	35 to boiling	<0.07
Acetic anhydride	99.5	Boiling	0.03
Aniline hydrochloride	5, 20	35–100	<0.01
Chloroacetic acid	100	Boiling	<0.01
Citric acid	10–50	35–100	<0.2
Dichloroacetic acid	100	Boiling	<20
Formic acid	10–90	35 to boiling	<0.2
Lactic acid	10–85	35 to boiling	<0.1
Oxalic acid	0.5–25	35–100	<0.5
Tartaric acid	10–50	35–100	<0.05
Tannic acid	25	35–100	<0.1
Trichloroacetic acid	100	Boiling	>50
Urea reactor	58% urea, 17% NH_3, 15% CO_2, 10% H_2O	193	<0.1

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Property	Zymaxx	Filled PTFE	Reinforced PEEK
Chemical resistance	E	E	G
Intrinsic mech. properties	G+	P	G+
Impact resistance	E	G	P
Wear performance	G	F	F
Low coeff. of thermal exp.	E	P	G+
Low water absorption	E	E	G+

E = excellent; G = good; F = fair; P = poor.

REFERENCES

1. FC Porter. Corrosion Resistance of Zinc and Zinc Alloys. New York: Marcel Dekker, 1994.
2. I Suzuki. Corrosion Resistant Coatings Technology. New York: Marcel Dekker, 1989.
3. PA Schweitzer. Corrosion Resistance Tables. 4th ed. Vols. 1–3. New York: Marcel Dekker, 1995.
4. TL Yau. Zirconium. In: PA Schweitzer, ed. Corrosion Engineering Handbook. New York: Marcel Dekker, 1996, pp 195–252, 231–281.
5. PA Schweitzer. Atmospheric Degradation and Corrosion Control. New York: Marcel Dekker, 1999.