

EFFECT OF TIN CONTENT ON THE CORROSION OF ZIRCONIUM 702 IN SULFURIC ACID

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ABSTRACT

The effect of Tin content on the corrosion resistance of Zirconium 702 in sulfuric acid was studied. Standard immersion tests including autoclave tests were used to demonstrate the differences in corrosion behavior of typical Zirconium 702 (R60702) containing approximately 2400 ppm Tin, and low-Tin Zirconium 702 containing approximately 1400 ppm Tin. Sample material, both welded and non-welded, was heat-treated at 770°C for 1 hour. Standard immersion and autoclave tests were conducted in 30% to 75% sulfuric acid at elevated temperatures. Updated 5 mpy (0.127 mm/yr) iso-corrosion curves for welded and non-welded Zirconium in sulfuric acid are presented. The effect of heat treatment on corrosion resistance in sulfuric acid applications is discussed.

This study has defined the upper limits of temperature and acid concentration for effective use of Zirconium 702 in processes using sulfuric acid. Current users of Zirconium 702 may also find this information useful. If the chemistry of the Zr702 is known, or can be determined, their process temperature could be increased significantly while still maintaining a corrosion rate of < 5 mpy (0.127 mm/yr). This may allow current users of Zirconium equipment to increase their process efficiency without purchasing new equipment or damaging their existing facility.

KEYWORDS

Keywords: Zircadyne® 702, Zircadyne® 704, R60702, R60704, zirconium, tin, sulfuric acid, heat-treatment, corrosion.

INTRODUCTION

Zirconium has been used for handling sulfuric acid at elevated temperatures for over 35 years. As seen in Figure 1, Zirconium along with Tantalum and its alloys is one of the few materials capable of handling sulfuric acid at temperatures above the boiling point.

With few exceptions, Zirconium has served well in severe sulfuric acid applications. One example of a failure occurred in the late 1960s. Rohm and Haas experienced accelerated corrosion of the weldments in the Zr702 process equipment handling sulfuric acid.^{1,2} In response, Rohm and Haas was among the first to develop a heat treatment for Zr702 welds. The study revealed that heat-treating Zirconium weldments at 774°C for one hour per inch (2.54 cm) of thickness reduced the tendency for preferential corrosion in the weld and heat affected zone (HAZ). Allegheny Technologies Incorporated Wah Chang has continued this study and determined much of the current information available on heat treatments for Zirconium.

Celanese Chemicals contributed to current understanding of the effects of chemistry on the corrosion behavior of Zirconium. In 1996, Celanese found that high tin levels in Zircaloy-2 was detrimental in the production of acetic acid.³

The chemical producing industries (CPI) constantly push for higher efficiencies in production units while at the same time attempting to reduce their resulting waste stream. As a result, acid concentrations and operating temperatures have increased over time. This has taken place while industry has been operating older plants designed for the less severe conditions.

From studies undertaken in the late 1980s, it was known that certain intermetallic compounds, including tin, have an adverse effect on the corrosion resistance of Zirconium in sulfuric acid service.^{4,5} In a paper by Yau, ⁴ Tin distributions in the surface oxide which developed on low tin Zr702 was compared with the distribution of tin which developed on material with a higher level of Tin. This study showed that the Tin concentration is generally lower at or near the surface of the metal which is exposed to the corrosive. However, Tin tends to concentrate in specific areas such as grain boundaries and the oxide-metal interface. Material with a higher Tin content has more and larger tin oxide particles associated with grain boundaries in the near surface oxide layer. Since these areas have enriched tin levels, once the protective zirconium oxide layer is compromised, these areas will suffer the greatest degree of corrosive attack. In the weld and HAZ areas the tin has more opportunity to concentrate in the grain boundaries along with other intermetallic elements. This explains the fact that the HAZ and weld areas suffer accelerated attack once the zirconium oxide layer is broken down in higher concentrations of sulfuric acid and at elevated temperatures.

The effect of Tin on Zr702 is not all bad. Tin gives a more consistent strength, imparts improved corrosion/oxidation resistance in water and steam, and provides a reduction in cost. Reduced cost is accomplished through the use of recycle Zircaloy-2 and Zircaloy-4 (nuclear grades of Zirconium), both of which contain Tin as an important alloy addition. Representative chemical and mechanical property requirements for Zr702 and Zircadyne® 704 (R60704), (here after referred to its generic name of Zr704) are given in Table 1 and 2. Zr704 is the commercial equivalent to either Zircaloy-2 or Zircaloy-4.

Another major reason for the lower corrosion resistance of the weld and HAZ is the physical distribution of intermetallic compounds. These are primarily compounds composed of combinations of Zirconium along with various amounts of Nickel, Chromium, Tin and Iron. During the welding process the intermetallics are concentrated at the grain boundaries in the weld area and the HAZ. These intermetallic compounds are also commonly interconnected in the as-welded condition and serve as anodic sites for the initiation of corrosion. Additionally, since the zones are interconnected in a three dimension array, they allow the corrosion process to propagate deeper into the metal matrix. The

purpose of heat treatment is to disperse the second phase particles and disrupt the interconnected networks. Figure 2 shows a Zr702 welded specimen with a typical Tin level (2400-ppm). Figure 4 shows a Zr702 welded specimen with the lower Tin level (1400-ppm). Notice that the intermetallics (darker stringer areas) are connected. Figure 3 (typical) and Figure 5 (low tin) shows the same material after heat treatment at 770°C for 1 hour. The resulting intermetallics are now smaller and disconnected globules.

There is a special safety concern when using Zirconium. Like some metals, Zirconium may develop a pyrophoric film under very specific conditions. Normally Zirconium corrodes uniformly resulting in a surface corrosion product composed primarily of zirconium oxide. As a result of severe intergranular corrosion, usually associated with the presence of oxidizers, small sub-grain size zirconium particles may be trapped in the surface corrosion product. Sub-grain size particles along with zirconium hydrides are thought to compose the pyrophoric film on zirconium. Generally when the corrosion rate is low, <5 mpy (0.127 mm/y), there is time for the zirconium to corrode uniformly reducing the number of sub-grain size particles. For very high corrosion rates, >200 mpy (5 mm/y), the reaction rate is high enough to again react most of the zirconium particles. Under conditions where the corrosion rate is between these two extremes and usually in the presence of an oxidizer Zirconium may develop a pyrophoric film. To passivate Zirconium, the trapped Zirconium particles contained in the surface corrosion product need to be at least partially oxidized before exposing the equipment to air. This may be achieved by passing steam at 250°C for 20 minutes or alternatively 120°C steam for 3 days through the equipment. This procedure ensures that most of the Zirconium particles contained in the corrosion film are at least partially oxidized. More information concerning the pyrophoricity of Zirconium under these very specific conditions is contained in Materials Testing Institute (MTI)⁶ literature and other publications.⁷

EXPERIMENTAL PROCEDURE

Sample Material:

Tables 3 and 4 provide the chemical composition of the sample material. As seen in Table 3, with exception of Hafnium and Tin levels, the chemistry of the sample material is comparable. The Hafnium levels are not considered significant in this study due to the fact that Hafnium has comparable corrosion resistance to Zirconium. ⁸ In boiling 70% sulfuric acid, for instance, the corrosion rate of Hafnium is <5 mpy (0.127 mm/y), which is comparable to Zr702.

Sample Preparation:

Samples were sheared from nominal .063-inch (.16 cm) thick material. All test sample material was fabricated in similar manner. Samples were sheared from sheet stock, deburred, and then heat-treated at 770°C for 1 hour in air. Welded samples were prepared by use of a Tungsten inert gas (TIG) butt-welding process utilizing no filler material. A mill finish followed by a heat treatment was used for all testing. As-sheared edges were exposed to the test solution in all cases.

Immersion Testing:

A 1000 ml long neck glass-boiling flask containing 1000 ml of test solution was used for testing at the boiling point. Controlled temperature testing below the boiling point was accomplished using 2000 ml resin kettles fitted with a reflux condenser. Liquid volume was monitored daily during the 7day and 30-day test periods. The solution was prepared from reagent grade acid and distilled water. Solutions were mixed in batches to reduce chance of variations in solution concentration. Specific gravity and volume were noted before and after each test period. Samples were suspended in a glass basket to allow solution access to the entire sample surface. Temperature was controlled to within \pm 2°C. Samples were welded and non-welded sheet material with dimensions 1 x 1 x .06 inch (2.54 cm x 2.54 cm x .152 cm) in thickness. ASTM G-2 was used as a guide for immersion testing.

Autoclave Testing:

Autoclaves utilized a fluorinated ethylene propylene (FEP) liner in a 750 ml Zirconium autoclave. Autoclaves were sealed with an FEP O-ring. A solution volume of 600 ml was used for each test. The solution was prepared using reagent grade acid and distilled water. Solutions were mixed in batches and verified with specific gravity to reduce variations in the solution concentration. Specific gravity and volume were noted before and after each test period. Samples were 1-inch (2.54 cm) squares to keep within the 125-ml/square inch (20 ml/ square cm) recommended in ASTM G-31. Temperature was controlled to within ± 2 degrees Centigrade. Heat up time was 8 hours and test period was 7 days. A glass basket was used to suspend samples in liquid phase of each autoclave in such a way that the solution had access to all sides of the sample. Samples were welded and non-welded sheet material with dimensions 1 x 1 x .06 inches. (2.54 cm x 2.54 cm x .152 cm)

RESULTS

Results of Immersion Testing

New data for both non-welded (Figure 6) and welded (Figure 7) Zr702 material indicate that the upper temperature limits, for >30% to 70% acid concentration, are increased when compared to the previously published 5-mpy (0.127 mm/y) line. Iso-corrosion curves for any material are merely a guide for consideration. Factors such as product forms, surface condition, alloy variations, agitation, sparging, and process impurities along with other factors need to be fully considered before specifying any material for a particular use.

As can be seen in Table 5, the corrosion rate does not increase over the longer test period of 30 days for the typical or low tin non-welded samples. The specimens of welded typical Tin material do increase during the 30-day test period, but only in the 70% acid. The corrosion rate for the very low tin material (<50 Sn ppm) increases in the 70% acid, but remains below 2 mpy (0.05 mm/yr). Selected data points for Zirconium with very low Tin levels is included to illustrate the effect on corrosion rate of even lower Tin levels in higher acid concentrations and temperatures. Figure 8 shows the limits for chloride contamination under oxidizing conditions in sulfuric acid. These chloride limits should not substantially change for Zr702 with the lower tin content.

CONCLUSIONS

From the immersion and autoclave data it is apparent that low Tin material shows a significant improvement in Zr702 corrosion rates in sulfuric acid. The only significant variable considered was the Tin level in the material under study.

It is apparent that the effect of Tin content is more discernable in high concentrations of sulfuric acid. The upper limit in 50% sulfuric acid and higher can be raised by 5-8°C by specifying zirconium with tin content controlled at 1400 ppm level. In acid concentrations of 30% or less both typical and low tin material will give the same corrosion performance. Because virtually all fabricated equipment contains at least one weld segment, the iso-corrosion curve for the welded condition is generally a more reliable indicator for corrosion resistance of Zr702 in sulfuric acid. The corrosion rate for the low tin material does not increase over a 30-day test period.

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CHEMICAL COMPOSITION OF COMMERCIAL AND NUCLEAR GRADES OF ZIRCONIUM (Weight %)

	Zr+Hf (min)	Hf (max)	Sn	Fe+Cr (max)	O (max)	
Zr702 (R60702)	99.1	4.5		.2	.16	
Zr704 (R60704)	97.5	4.5	1.0-2.0	.24	.18	

TABLE 2 MECHANICAL PROPERTIES OF ZIRCONIUM ALLOYS ROOM TEMPERATURE

	Minimum Tensile Strength (Mpa)	Minimum Yield strength (.2% offset), (Mpa)	Minimum Elongation % (0.2% Offset)	Bend Test Radius
Zr702	380	207	16	5 T
Zr704	414	240	14	5 T



Figure 1. Materials of Construction for use in Sulfuric Acid



FIGURE 2 Typical Tin Zr702 before Heat-Treatment 760X



FIGURE 3 Typical Tin Zr702 after Heat-Treatment 760X





FIGURE 4 Low Tin Zr702 before Heat-Treatment Low Tin Zr702 after Heat-Treatment 760X

FIGURE 5 760X

TABLE 3 CHEMICAL ANALYSIS OF SAMPLE MATERIALS

Metal	Typical Tin Content	Low Tin Content		
	Zr702	Zr702		
	(ppm)	(ppm)		
Al	330	195		
Cr	<50	64		
Fe	820	790		
Hf	13,100	6,700		
Ni	66	52		
Sn	2500	1400		
Zr	bal	bal		

TABLE 4 GASES AND CARBON IN SAMPLE MATERIALS.

Element	Typical Tin Content Zr702 (ppm)	Low Tin Content Zr702 (ppm)	
Н	17	11	
Ν	47	36	
0	1390	1330	
С	131	144	



FIGURE 6 Iso-Corrosion Diagram for Non-Welded Zr702 in Sulfuric Acid (5 mpy /0.127 mm/yr iso-corrosion lines)



FIGURE 7 Iso-Corrosion Diagram for Welded Zr702 in Sulfuric Acid (5 mpy /0.127 mm/yr iso-corrosion lines)

TABLE 5

Media	Zr702	Time period		
		7-day	30-day	
65% Sulfuric acid	typical tin welded	2.5/0.06	0.1/0.003	
BP (150°C)	non-welded	1.3/0.03	0.1/0.003	
	low tin welded	1.7/0.04	0.5/0.01	
	non-welded	2.7/0.07	0.3/0.01	
70% sulfuric acid	typical tin welded	5.3/0.13	7.8/0.2	
BP (165°C)	non-welded	5.8/0.15	5.4/0.14	
	low tin welded	3.5/0.09	4.2/0.11	
	non-welded	4.0/0.1	3.3/0.08	
	Very low tin			
	Welded	1.2/0.03	1.8/0.05	

CORROSION RATES, 7-DAY VS. 30-DAY TEST PERIOD (mpy / mm/y)



Figure 8. Limits for zirconium in sulfuric acid with oxidizing chlorides.