

LOCALIZED CORROSION OF CAST ZR 702

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ABSTRACT

There have been a few specific services where random, unexplained, localized corrosion of cast zirconium equipment has occurred. This localized attack is more than can be explained by traditional pitting or crevice corrosion mechanisms. The attack appears to be limited to services that are pushing the corrosive limits of zirconium and the damage is exclusively confined to machined or ground surfaces. Rather than refer to this corrosion as pitting like many other papers, the authors will use the term breakaway corrosion. Experiments were conducted to determine what variables influenced this form of localized corrosion on cast zirconium and what could be done to prevent it.

INTRODUCTION

Zirconium 702 has excellent corrosion resistance to all concentrations of hydrochloric acid and to sulfuric acid up to approximately 75% concentration.¹ Because of zirconium's cost, it is only used when other less costly materials are unsuitable, and usually this involves elevated temperature. It is also well known that oxidizing species in these acids can accelerate the corrosion of zirconium in a localized manner.² Therefore, when services contain these oxidizing species like ferric ions (Fe^{+3}) it creates some serious problems for zirconium, the last line of defense for hot hydrochloric and sulfuric acids.

Besides oxidizing contaminants, there also seems to be a relationship with the surface condition of zirconium and its susceptibility to localized corrosion.³ During the past three years there have been two services in particular that have produced localized or breakaway corrosion problems with cast centrifugal pump impellers. Although investment casting produces an excellent surface finish, it is still necessary to machine dimensionally critical surfaces such as the seal ring and the back shroud from which the operating clearance of the pump is set. In addition, due to the high operating speed of the impellers it is necessary to dynamically balance impellers by grinding as shown in figure 1. The ground area is usually on the front shroud as seen on the finished impeller in figure 2. Dynamic balancing reduces vibration and minimizes the likelihood of fatigue in this fatigue sensitive alloy.

Figure 3 shows a portion of a corroded impeller that has undergone failure analysis thus the reason for the missing sections. Notice that the ground area on the left

side is heavily corroded and black in appearance as is the machined seal ring, particularly its edge. The as-cast surfaces appear to be unaffected. While it is recognized that zirconium experiences localized corrosion in acid-chloride solutions that contain oxidizing species, it is also the authors' experience that localized or breakaway corrosion can also appear in non-chloride containing services like sulfuric and concentrated nitric acids. In addition to oxidizing contaminants, it appears that surface condition by itself may also influence this type of corrosion. Some previous work by Yau and Maguire³ on the effect of surface condition on zirconium in hydrochloric acid with oxidizers showed that surface contamination could be a factor.

Figure 4 shows another example of breakaway corrosion on a pump shaft sleeve. Shaft sleeves are made from wrought 702 material and simply machined; there is no need for grinding. However, for whatever reason the customer in this case felt a need to sand the surfaces of the sleeve and as a result severe localized corrosion is evident on the wetted end of this shaft sleeve. This sleeve was in a service of 62%+ sulfuric acid at 260°F.

As a result of these field problems, several experiments were conducted to investigate the effect of surface preparation on the corrosion resistance of cast zirconium 702 and the objective of this paper is to report on the results of this testing.

EXPERIMENTS

To assess the localized corrosion of ASTM A752 grade 702 cast zirconium, mass-loss experiments were conducted in two different services. One condition was 15% hydrochloric acid with 2000 ppm ferric ions added as ferric chloride and run at boiling for 48 hours. This test duplicated field conditions of one particular customer. The other test condition was 65% boiling sulfuric acid without any oxidizing ions added. Based on other field experiences it was thought that this marginal application for zirconium could also produce localized corrosion simply from a difference in surface condition.

Samples were prepared from Hipped (hot isostatically pressed) gates and runners of a production heat of cast zirconium 702. The composition of this heat can be seen in Table I. Samples were wet cut with a new silicon carbide blade which is the method used for production castings. Samples identified as "dirty" were contaminated by first grinding on a piece of CF8M stainless steel and then grinding one of the surfaces of a zirconium test coupon. This method of contaminating the zirconium samples was used to duplicate what was thought to be production practice for balancing impellers. In other words, a dedicated grinding wheel was not always used for zirconium impellers so iron contamination was likely from previously balanced stainless impellers.

Samples identified as having been heat treated were given a traditional stress relieve heat treatment per ASTM B752 at 1050°F (565°C) for a half hour in an air atmosphere. This was done to try and reestablish a thicker oxide layer on any machined or ground surfaces. Pickled samples were cleaned in a solution of 43% nitric acid and 3% hydrofluoric acid at room temperature for 2 minutes. This was done in an attempt to

remove any contamination from the machined or ground surfaces. Any iron contamination on the surface would be extremely anodic to the zirconium and should be quickly removed in this aggressive chemical cleaning solution.

RESULTS & DISCUSSION

The results for the corrosion testing in 15% hydrochloric acid with 2000 ppm ferric ions can be seen in Table II. Although the results vary widely there do appear to be some discernible trends. Looking at the rates for samples just ground or tested as-cast, conditions A, C and D, the rates are all unacceptably high, ranging from 8 to 11.9 mm/y. Adding heat treatment as a processing step as represented by samples AH, CH and DH, the rates drop by at least a factor of 5, implying that developing a thicker oxide layer has some beneficial effect.

The next processing parameter tested was to look at pickling the ground or as-cast surfaces without the benefit of heat treatment. These samples are represented by the codes AP, CP and DP. Again the rates drop dramatically, particularly for the sample ground with a clean wheel which gave a rate of 0.2 mm/y. The rate for the as-cast and pickled sample decreased the same as the as-cast and heat treated sample which was 1.5 mm/y. The sample ground with the “dirty” wheel and pickled improved but not as much as it did with heat treatment alone. Its rate was 4.1 mm/y.

Next, the benefits of combining pickling and heat treating were evaluated. These rates represented by samples APH, CPH and DPH were 0.08, 0.46 and 0.28 mm/y, respectively. Except for the sample ground with a clean wheel, pickled and heat treated, these rates were the lowest of any of the conditions tested. While the rate for the clean, pickled and heat treated sample was not quite as low as the clean and pickled sample it was still an acceptable rate for cast zirconium equipment. This data suggests that there is a synergistic and beneficial effect with pickling and heat treatment of the ground or as-cast surfaces.

A similar experiment was conducted for 65% boiling sulfuric acid which was another service where unexplained localized/breakaway corrosion occurred. Zirconium 702 samples from the same heat were used and finished in a similar manner as previously discussed above for the hydrochloric acid testing. These results can be seen in Table III. These results in general did not produce the significant differences seen in the hydrochloric acid testing with an oxidizer. Obviously, plain 65% sulfuric acid at boiling has not exceeded the electrical potential of zirconium's passive range nor produced the results experienced in the field. However, the data does point to some benefit of pickling, particularly for the as-cast samples. Pickling of the as-cast sample reduced the corrosion rate 36% while adding pickling and heat treatment reduce it 69%. While not as dramatic, the clean and dirty ground samples that were pickled did show improvement but the stress relieve heat treatment did not produce any real change.

Since the sulfuric samples were given the same stress relieve heat treatment at 1050°F as the hydrochloric samples, it was decided to see whether the higher

recommended heat treatment of 760°C for zirconium used in sulfuric acid would produce lower rates.¹ For this testing only as-cast, clean and dirty ground samples with the optimum processing steps of pickling and heat treating were tested. In addition, another three samples prepared in the same manner were tested in 65% boiling sulfuric acid with 2000 ppm ferric chloride in hopes of pushing the zirconium samples' corrosion rates into the transpassive range. These results can be seen in Table IV.

This additional testing did not produce the expected results. First, the preferred heat treatment at 760°C for zirconium did not produce the overall lower rates as anticipated for sulfuric acid. Secondly, the rates in pure sulfuric acid were slightly higher than the samples tested with 2000 ppm ferric ions. These results suggest that additional testing is needed in sulfuric acid with an oxidizer added.

Obviously something is being changed on the surface of ground zirconium samples to cause accelerated corrosion in these areas. To further investigate this another zirconium 702 sample was ground with a contaminated wheel and cut into three pieces. One piece was left as ground, one was pickled for 2 minutes and one pickled for 4 minutes. The samples were then submitted for scanning electron microscopy (SEM) to analyze the ground areas for surface contamination. The scans can be seen in figures 5, 6 and 7, respectively.

SEM examination of the sample ground with a contaminated wheel did not reveal any visual evidence of chromium or iron particles on the surface. There were patches of organic material that contained carbon, oxygen, nitrogen, sodium and potassium. These elements appeared less prevalent on the two pickled samples. There were changes in the trace iron level which could be related to the organics or a very thin iron layer. The trace iron levels on the two pickled samples were about one-third the level of the as contaminated sample which confirms the expected beneficial effect of pickling. There was not any significant difference in iron level of the sample pickled for 2 minutes versus 4 minutes.

As part of this investigation a copy of the material safety data sheet for the production grinding wheel was obtained and it contained a few surprises. The wheel was basically an alumina oxide ceramic with a resin binder. The organics detected by SEM most likely came from the resin binder. The one surprise was the fact that the wheel was composed of 3 to 15% iron disulfide, thus another source of iron contamination. However, the biggest surprise was the fact that the wheel contained 1 to 25% inorganic fluorides and it is well documented what fluorides do to the corrosion resistance of zirconium.⁴

CONCLUSIONS

- The high corrosion rates experienced by the samples in hydrochloric acid with ferric ions are more than can be explained by a classical pitting mechanism. It seems more appropriate to categorize this corrosion as breakaway or severe

galvanic corrosion due to anodic areas being created on the casting surface by either contamination or simply differences in surface finish.

- Using dedicated grinding equipment for zirconium is desirable but one needs to make sure that the composition of the grinding devices themselves are not the source of contaminants.
- Heat treating and pickling produce a significant reduction in corrosion rates of intentionally contaminated samples. Heat treating and pickling also seem to provide a similar benefit to as-cast surfaces suggesting that this should be standard practice for cast zirconium equipment, particularly if services are marginally acceptable for zirconium.



FIGURE 1
Dynamically Balancing a Zr Impeller



FIGURE 2
Finished Zirconium Impeller Showing Machined and Ground Areas



FIGURE 3
Portion of Returned Impeller



FIGURE 4
Zirconium Shaft Sleeve

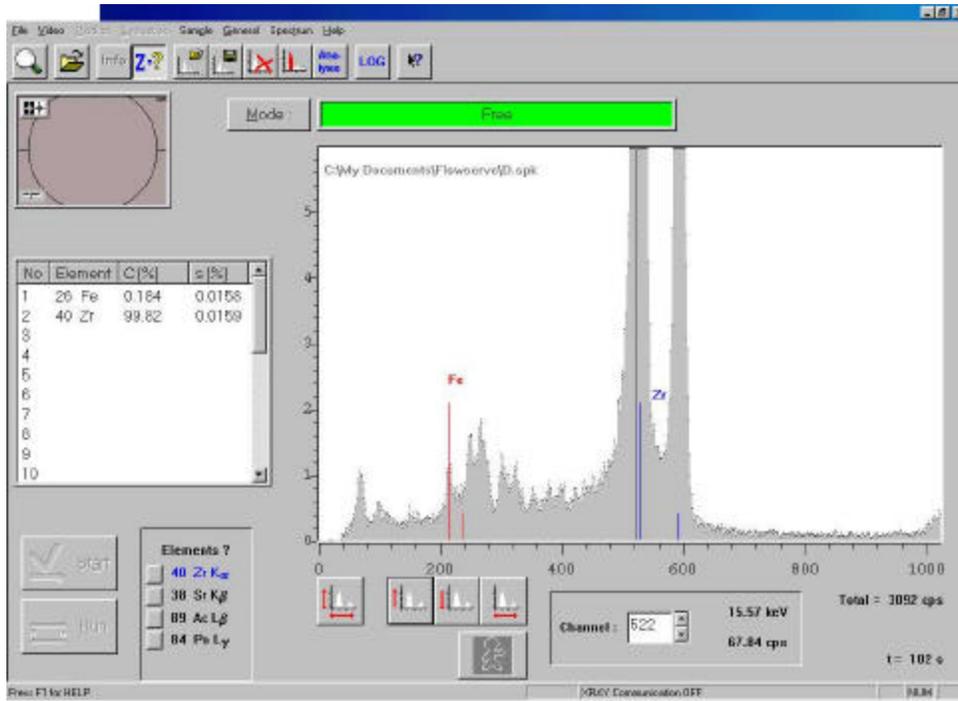


FIGURE 5
Scan of Contaminated Surface

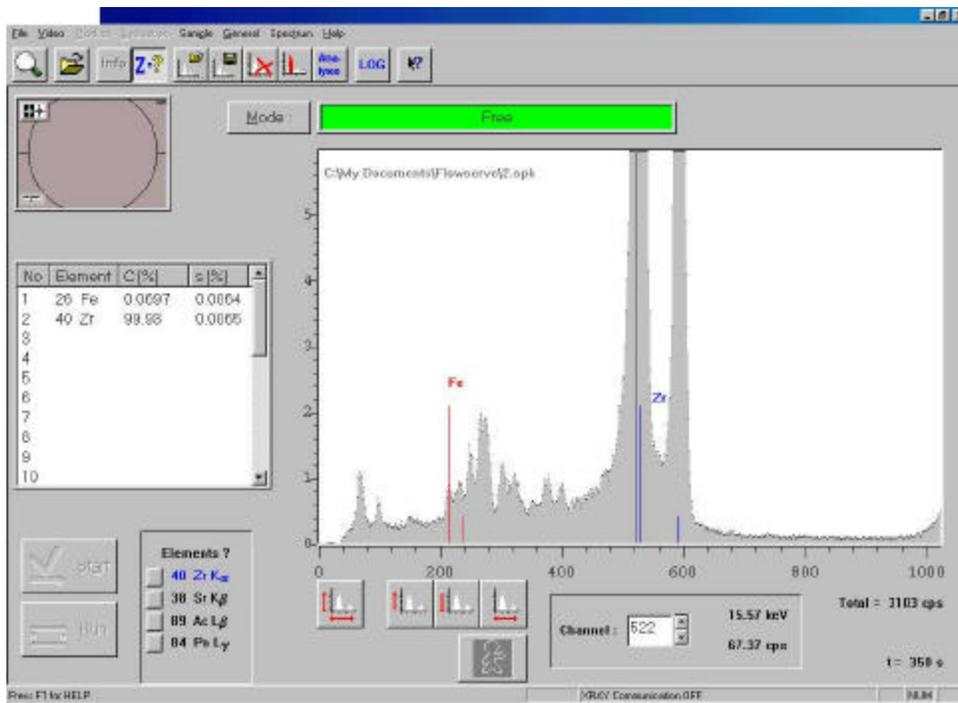


FIGURE 6
Scan of Surface After Pickling for 2 Minutes

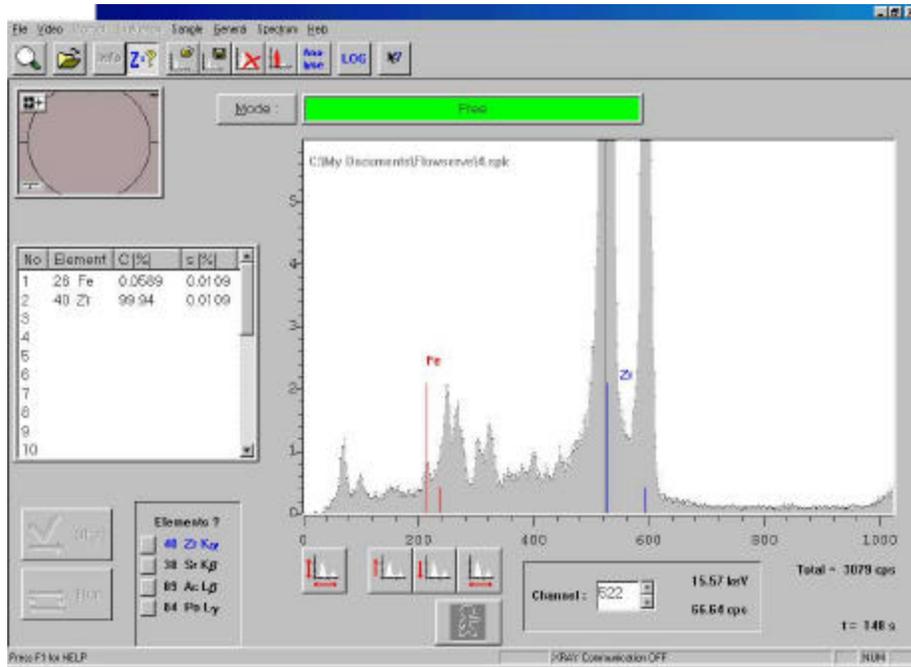


FIGURE 7
Scan of Surface After Pickling for 4 Minutes

**TABLE I
CHEMICAL COMPOSITION**

HEAT	P	Hf	Fe	Cr	Sn	Zr	H	O	C	N	Other
80233	<0.01	0.55	0.06	<0.01	0.2	Bal.	0.002	0.19	0.02	0.01	<0.4

**TABLE II
15% HCL + 2000 ppm Fe⁺³ TEST RESULTS AT BOILING 48 HOURS
MPY (MM/Y)**

CONDITION	RATE	CONDITION	RATE	CONDITION	RATE
A	315 (8)	D	451 (11.5)	C	467 (11.9)
AH	60 (1.5)	DH	49 (1.2)	CH	79 (2)
AP	60 (1.5)	DP	161 (4.1)	CP	8 (0.2)
APH	18 (0.46)	DPH	11 (0.28)	CPH	3 (0.08)

A- as cast
D- contaminated wheel
C- clean wheel
H- heat treated
P- pickled

**TABLE III
65% BOILING H₂SO₄ 48 HOURS
MPY (MM/Y)**

CONDITION	RATE	CONDITION	RATE	CONDITION	RATE
A	42 (1.1)	D	27 (0.7)	C	34 (0.86)
AH	36 (0.9)	DH	43 (1.1)	CH	37 (0.9)
AP	27 (0.7)	DP	28 (0.7)	CP	7 (0.18)
APH	13 (0.33)	DPH	28 (0.7)	CPH	34 (0.86)

**TABLE IV
SAMPLES HEAT TREATED AT 760° C FOR 1 HOUR**

	65% H ₂ SO ₄ , 96 HOURS	65% H ₂ SO ₄ + 2000 ppm Fe ⁺³
APH	56 (1.4)	39 (1)
DPH	48 (1.2)	33 (.8)
CPH	64 (1.6)	30 (.7)

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