Paper No.
06216

CORROSION NACExpo 2006
61ST ANNUAL CONFERENCE & EXPOSITION

THE PERFORMANCE OF Z100 (UNS S32760) SUPERDUPLEX STAINLESS STEEL IN SULPHURIC ACID.

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ABSTRACT

The history and properties of Z100 superduplex stainless steel are discussed. The corrosion resistance in sulphuric acid is compared with some other common alloys. Four case histories are presented that show the use of Z100 over a range of acid concentrations and temperatures. Most of the applications have been both cost effective and successful. Such problems as have occurred have highlighted the importance of understanding the high influence of minor constituents in the environment in so far as their oxidising nature is concerned and working within the limits of the alloy.

Keywords: stainless steel; sulphuric acid

INTRODUCTION

Sulphuric acid is one of the primary chemicals most commonly used by industry. Because of the high demand for sulphuric acid there are many plants producing this chemical. In addition to being widely used, sulphuric acid is also very corrosive towards many metals and alloys. This has resulted in the development of special alloys to resist corrosion in sulphuric acid. However, many of these alloys are only suitable over a narrow range of acid concentration and/or temperature. One of the earliest attempts to bridge the whole range of acid concentrations was alloy 20 (UNS N08020), developed in the 1930's. In the last quarter of the 20th century, the introduction of AOD refining meant that much improved high alloy stainless steels became available. The present paper describes the performance of Z100 (UNS S32760) superduplex stainless steel in sulphuric acid including some case histories that show the alloy's versatility over a wide range of acid concentrations and temperatures.

THE ALLOY

History.

During the 1970's there was a demand from the oil and gas industry in the North Sea for a stronger, more corrosion resistant alloy, particularly for injection pumps. The author's company further developed the low alloy 25% Cr duplex stainless steels then in use and produced castings in the first superduplex stainless steel, which was called Zeron 100*. The alloy entered service in the early 1980's and was so successful that there was a large demand for a wrought version for piping, vessels etc. This was developed in the late 1980's and first entered service in 1990. Both the cast and wrought alloys have been very successful and they are in all the appropriate ASTM and ASME standards under their UNS numbers, S32760 (wrought) and J93380 (cast). The alloy is widely used and is known by the common name Z100. The alloy has high corrosion resistance, not only in seawater, but also in sour oil and gas fluids and many aggressive chemicals, including sulphuric acid. It should be recognised that the ASME common name for the family of superduplex stainless steels is 2507. This is somewhat unfortunate for the acid industry because some super duplex grades (i.e. UNS S32750) do not contain any copper or tungsten additions, unlike Z100. It is these additions that confer the superior resistance of Z100 to acids, particularly sulphuric, hence use of the ASME common name in this industry should be approached with caution.

Alloy Properties.

Z100 is a superduplex stainless steel with a 50/50 austenite/ferrite microstructure. Its nominal composition is shown in Table 1, along with some common alloys used in the chemical industry. The resistance to localised corrosion by chlorides is often assessed by the pitting resistance equivalent number or PREN, where PREN = %Cr + 3.3x % Mo + 16 x % N. This is an empirical formula, but experience has shown that the higher the PREN, the greater the resistance to attack by chlorides. However, this is relevant to performance in sulphuric acid only when chlorides are present. For stainless steels in sulphuric acid service, alloying elements such as copper are also important[1] and these are not reflected in the PREN. One major advantage of Z100 is its low nickel content, which makes it very cost effective compared with high nickel containing alloys, such as alloy 20 and even 904L. A second advantage of Z100 is its ready availability in all the common product forms.

The minimum room temperature mechanical properties are shown in Table 2. It is clear that Z100 is much stronger that the austenitic alloys and it is also stronger than 22% Cr duplex stainless steel. This is reflected in the design stresses for Z100, shown in Table 3. ASME B31.3 is the widely used code for piping, while ASME VIII, div 1 is the code for vessel design. PD5500 is a European vessel code that allows even higher design stresses and this has been widely used across Europe to reduce costs by reducing wall thickness. This has the additional benefit of reducing welding costs and time.

Z100 can be welded by all the common arc welding processes. It is usually used in the as-welded condition using Z100X filler. This is similar to the parent metal, but contains 2 to 2.5% extra nickel to ensure that the weld metal retains a 50/50 phase balance. Like all high alloy materials, Z100 requires care in welding. It should only be fabricated by qualified welders working to approved procedures. It is recommended that qualification should be as for ASME IX but should include a corrosion test in addition to the usual mechanical and NDE requirements.

CORROSION RESISTANCE.

A common engineering design criterion is that the corrosion rate should not exceed ~0.1mm/y. Figure 1 shows the iso-corrosion curve (0.1mm/y) for a number of alloys in pure sulphuric acid. The curves show that Z100 offers superior performance in both dilute and concentrated acids. Only in the range 50% to 80wt% acid does alloy 20 offer any improvement.

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In many service environments chlorides are also present. These usually reduce the performance of most alloys in sulphuric acid and they can change the nature of the corrosion from general attack to a combination of general corrosion and pitting. Figure 2 shows the iso-corrosion curves (0.1mm/y) in sulphuric acid with 2,000mg/l chloride. Alloy Z100 shows superior performance across a wide range of acid concentrations. Alloy 20 was not included in this graph as it has been observed to pit in acid/chloride solutions[2]. The performance of Z100, along with that of other alloys, improves in the presence of oxidisers in the acid (eg. ferric ions, Fe^{3+}), up to the onset of transpassive corrosion, and decreases as the chloride concentration increases.

CASE HISTORIES

Case History 1.

In the 1990's, London Underground were experiencing problems with two parallel sections of railway tunnel on the Northern Line. The soil conditions were so aggressive that corrosion of the cast iron tunnel linings was occurring and the chemical reaction with the grout sealing the linings was changing the stresses on the linings from compressive to tensile, leading to cracking. The soil was wet and contained pyrites (FeS) and was aerated because of the presence of air from the tunnel. This enabled sulphur oxidising bacteria to become active, producing sulphuric acid. In addition, the ground had a high chloride content because it had been a former salt marsh. The LUL Consultants decided that superduplex stainless steel linings would give the desired 400 year life, because they combined good resistance to sulphuric acid plus chlorides with high ductility and strength. They specified that all castings must have a minimum critical pitting temperature of 70°C at +300mV SCE (saturated calomel electrode) in a solution of $2^{v}/_{v}$% sulphuric acid plus 5g/l sodium chloride. Tests on cast Z100 showed that it passed the test three heats out of four. Hence, an acid grade was developed, still within the compositional limits of J93380, but with improved sulphuric acid resistance, as shown in Figure 3. This variant passed the corrosion test with every heat of the 800 tonnes of castings produced over 18 months. The lining was assembled from sets of 12 castings, bolted into a ring 600mm wide with Z100 fasteners. These rings were bolted together to make the lining, as shown in Figure 4. The castings made two parallel tunnel linings each a quarter of a mile long. These have been in service since 1996 and show no signs of deterioration.

Case History 2.

In the 1990's there was an increasing interest in the extraction of nickel from laterite ores by high pressure acid leaching (HPAL). In this process the crushed ore is mixed with ground water into a slurry that is progressively heated to ~200°C. The slurry is then injected into an autoclave where it is reacted with sulphuric acid at 250° to 280°C and at a pressure of 50 bar to produce nickel sulphate. The reacted slurry is then cooled in stages down to ~ 100°C, and steam from each stage is used to heat the incoming slurry. The reacted slurry then goes through thickeners and separators and the nickel is extracted by one of several processes. A schematic diagram of the HPAL process is shown in Figure 5. This shows two heater and two flash stages, but there could be as many as six, or more, stages in a real plant.

During the conceptual stages of these projects the authors, and others, carried out corrosion tests that showed that titanium alloys would be required for the autoclave. The flash tank environment is also aggressive and the hotter ones need to be in titanium or titanium alloys, while the cooler ones could be in titanium or acid brick lined steel. Only when the reacted slurry temperature was reduced to 100°C or less could superduplex stainless steel be used.

Direct contact steam heating of the slurry was proposed with hypersaline water being used for the slurry make up, as it was the only water available. The design was such that the lowest pH expected in the heaters was 3. Hence, tests were conducted in the following solution:-

NaCl	-	150g/l
$MgSO_4$	-	15g/l
$Fe_2 (SO_4)_3$	-	0.15g/l
pH	-	3
Temperature	-	203°C
Pressure	-	17.7 bar

The customer's initial thoughts were that alloy 20 would be suitable for applications such as the positive displacement (p.d.) pumps. However, these tests showed that alloy 20 could pit in the heater slurry. Z100 showed no indications of pitting, crevice corrosion or stress corrosion cracking in the parent metal, HAZ or weld metal and the general corrosion rate was <0.01mm/ly. These results suggested that Z100 would be an excellent materials choice for this application, providing the necessary corrosion resistance, mechanical properties and foundry characteristics to allow the production of complex shapes for pump parts.

It was estimated that in the steam return lines there would be 1 to 3g/l of acid carry over into the heaters. Z100 has good resistance to sulphuric acid, as shown by Figures 1 & 2. As the acid would be vapour during normal operation, no serious corrosion was expected. Condensation during start up and shut down would give a little corrosion, but this was not expected to be serious as it would only be transient. It was concluded that Z100 would be suitable for the steam return lines.

Three Australian HPAL laterite projects were built and ramp up began in 1999. Problems occurred in a number of areas, not just due to corrosion[3]. Corrosion of superduplex was observed in the steam transfer lines, the heater vessels and the slurry injection pumps. This was not confined to Z100, but was also seen with other superduplex grades, such as UNS S32750. This mostly took the form of pitting, but stress corrosion cracking from the base of the pits was seen in the steam transfer lines and the heater vessels. Details of the attack can be seen in Figures 6 and 7.

A test programme was initiated to try and reproduce the attack in the laboratory. Discussions with project personnel indicated that the pH in the heater vessels may have decreased to 2 or even 1 because of excessive slurry recycling with the steam. Previous tests had shown that Z100 corrodes at a high rate in flash tank slurry at temperatures greater than 100°C, so the attack in the steam return lines was not surprising, occurring presumably where slurry settled on the pipe walls.

Tests in simulated heater slurry were conducted over a range of chloride concentrations at pH's of 1 to 3 and the results are summarised in Table 4. Corrosion rates were still low at pH2, hardly any greater than at pH3, but at pH1 there was a high rate of metal loss. However, there was no pitting and no stress corrosion cracking, and the attack did not appear as in Figure 6.

It was realized that the recycled slurry, entering the heaters with the steam, would also contain substantial quantities of ferric ion. This would make the solution more oxidising. Corrosion tests at pH2 and 200°C with 500mg/l ferric ion showed pitting after 21 days exposure.

The problem in the plants meant that shut downs and start ups were frequent. In the initial corrosion tests it was assumed that the steam would strip the bulk of the oxygen from the incoming slurry. However, with frequent stops and starts it was likely that a significant dissolved oxygen content would be present for much of the time at temperature. A corrosion test was carried out for 30 days at 200°C with a simulated shut down every five days. All the samples showed pitting attack (Figure 8), which was similar to that in Figure 6 and 7[4].

It is clear that the problems arose because the operating conditions in the heaters and steam lines were very different to those suggested at the design stage. Moreover, subtle differences in slurry composition that were not considered in the initial design scope were found to be highly influential on the corrosion process. The main problem appears to have been excessive slurry recycling via the steam return lines. Several authors[5,6] have stressed the importance of correct flash tank design in HPAL plant to offer efficient operation. In the present case, replacement of the flash tanks was not possible, but modifications were made to reduce slurry carryover. The conditions were such that titanium was still necessary for the steam return lines. Now that the plant is under better control, the positive displacement slurry pumps, operating at ~180°C, which utilize both cast and cast and wrought Z100, continue to perform well.

The experiences in HPAL laterite plants were summarized by the authors and recommendations were made for safe operating conditions for Z100 superduplex[4].

Case History 3.

Sulphuric acid is used in the manufacture of explosives. In one UK plant the spent acid is heated to concentrate it in three stages from 70wt% to 94wt%. Nitric acid is then added to remove residual organic chemicals. The main piping material was glass-lined steel, which was susceptible to cracking from either mechanical or thermal shock. Rapid corrosion of the steel then led to a leak. The authors suggested that Z100 would be a suitable replacement if the process was modified and the nitric acid was added prior to acid concentration. Corrosion tests were carried out to simulate the first and third stages of acid concentration. The results are shown in Table 5. It is clear that the presence of an oxidiser greatly improves the performance of Z100 in intermediate strength sulphuric acid.

Case History 4.

The iso-corrosion curve in Figure 1 shows the good resistance of Z100 to strong sulphuric acid (>95wt%). However, the shape of the curve shows a strong dependence of corrosion rate on acid strength. Rodda[7] has described the problems with carrying out laboratory tests in strong sulphuric acid. It is easy to produce data showing lower corrosion rates than would actually occur due to the presence of small quantities of corrosion products. Hence, all the tests on Z100 were conducted by Kvaerner-Chemetics, who design and build sulphuric acid plants.

In the production of sulphuric acid, sulphur dioxide/trioxide is reacted with water. This produces large quantities of heat and the recovery of this heat is important to produce an efficient process. This is currently done with a heat exchanger that may be made of 310 stainless steel (UNS S31000) (Fe/25Cr/20Ni) or a proprietary high silicon austenitic stainless steel. The disadvantage of 310 is its relatively high corrosion rate and short life. The proprietary, high silicon alloys resist corrosion, but are expensive and on long delivery. Z100 offers the potential of a more affordable and more readily available alternative.

Figure 9 shows the corrosion rate of Z100 in 98% sulphuric acid at 200°C as a function of ferric ion content. The results show the corrosion rate to be moderate and ferric ion concentration has little effect. Tests on Z100 seam welded heat exchanger tubes showed a similar rate of corrosion and no preferential attack of the weld.

In the heat recovery system it is common to use filters/strainers made of 310 stainless steel. However, these have a limited life and Mosaic (formerly IMC) reported the successful use of a Z100 strainer, which was in good condition after two years. 310 stainless steel filters required replacement every two years or so. PCS Phosphate utilized a Z100 pipe spool in a heat recovery system to replace 310 stainless and reported minimal weight loss after ~2 years operation. The service experience has shown that the low corrosion rates in the laboratory tests are also realized in service.

CONCLUSIONS

Z100 superduplex stainless steel has excellent resistance to corrosion in sulphuric acid over a wide range of concentrations and temperatures. The case histories show that the alloy can be very successful, provided it is used within the appropriate limits. It is clear that a simplistic assessment of the environment, in terms of pH and chloride only, for example, is not necessarily sufficient to obtain a proper assessment of the corrosion hazard.

ACKNOWLEDGEMENT

The authors would like to thank Kvaerner-Chemetics for sharing the results of their corrosion tests on Z100 in strong sulphuric acid and Weir Lewis Pumps for advice and support.

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**TABLE 1.
NOMINAL COMPOSITION OF SOME ALLOYS
USED IN SULPHURIC ACID.**

Alloy	UNS No.	Nominal Composition (wt%)							PREN*
		Fe	Cr	Ni	Mo	Cu	N	W	
316L	S31603	bal	17	10	2	-	-	-	24
Alloy 20	N08020	bal	20	34	2.5	3.5	-	-	28
904L	N08904	bal	20	25	4.5	1.5	-	-	35
6 Mo aust	S31254	bal	20	18	6	0.7	-	-	43
22 Cr Duplex	S31803	bal	22	5	3	-	0.15	-	35
Z100 (wrought)	S32760	bal	25	7	3.5	0.7	0.25	0.7	>40
Z100 (Cast)	J93380	bal	25	8	3.5	0.7	0.25	0.7	>40

bal = balance
PREN = % Cr + 3.3 x % Mo + 16 x % N.

TABLE 2.
MINIMUM MECHANICAL PROPERTIES AT ROOM TEMPERATURE FOR SOME ALLOYS USED IN SULPHURIC ACID.

ALLOY	UNS. No.	0.2% Proof Stress (MPa)	UTS (MPa)	Elong^n (%)
316L	S31603	170	485	40
Alloy 20	N08020	240	550	30
904L	N08904	220	490	35
6 Mo aust.	S31254	310	655	35
22 Cr Duplex	S31803	450	620	25
Z100 (Wrought)	S32760	550	750	25
Z100 (Cast)	J93380	450	700	25

TABLE 3.
DESIGN STRESS AT ROOM TEMPERATURE FOR SOME ALLOYS USED IN SULPHURIC ACID.

Alloy	Design Stress (MPa)		
	PD 5500 (Vessels)	ASME VIII div 1 (Vessels)	ASME B31.3 (Pipes)
316L	150	115	115
Alloy 20	NL	158	161
904L	NL	140	147
6 Mo Aust	NL	187	207
22 Cr Duplex	289	177	207
Z100	319	214	250

NL = Not Listed

TABLE 4.
CORROSION RATE OF Z100 IN SIMULATED HPAL HEATER SLURRY AT 200°C. (Fe^{3+} = 30mg/l)

pH	Chloride (mg/l)	Corrosion Rate (mm/y)
3	90,000	<0.01
2	90,000	0.014
	90,000	0.005
	10,000	0.014
	10,000	0.014
	1,000	0.017
	1,000	0.059
1	1,000	4.1
	1,000	7.2

TABLE 5.
CORROSION OF Z100 IN SIMULATED ACID RECONCENTRATION PROCESS.

Acid Conc^{n} (wt%)	Temperature (°C)	Corrosion Rate (mm/y)	
		Pure Acid	+0.15% nitric acid
70	125	>>10	0.029
94	225	>1	0.017

FIGURE 1 Iso-corrosion (0.1mm/y) curves for some stainless steels in sulphuric acid

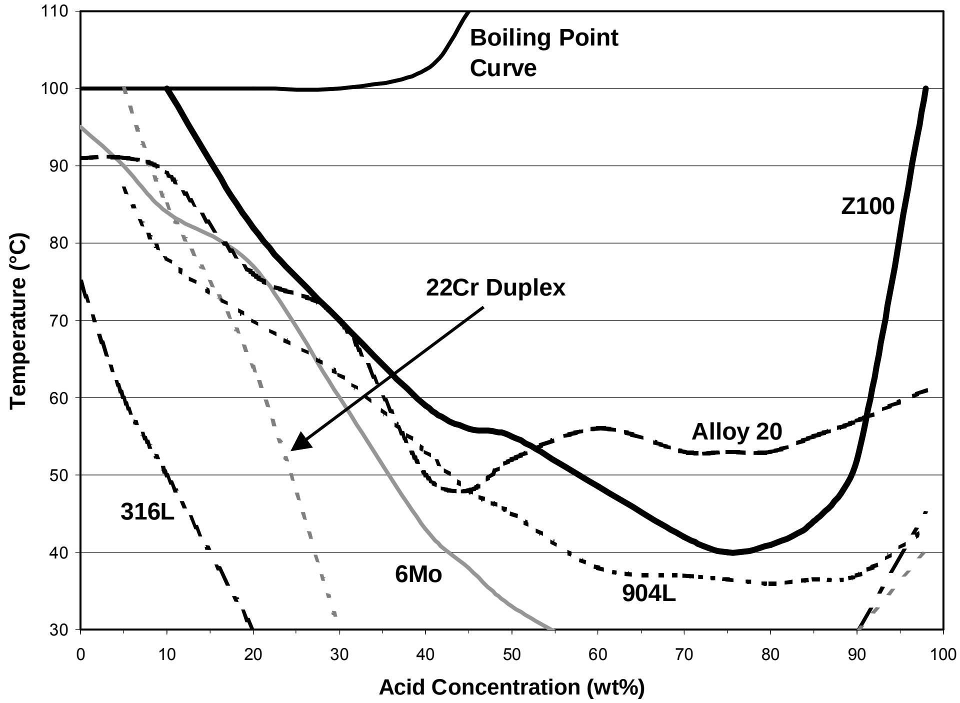


FIGURE 2 Iso-corrosion (0.1mm/y) curves for some stainless steels in sulphuric acid plus 2,000mg/l chloride

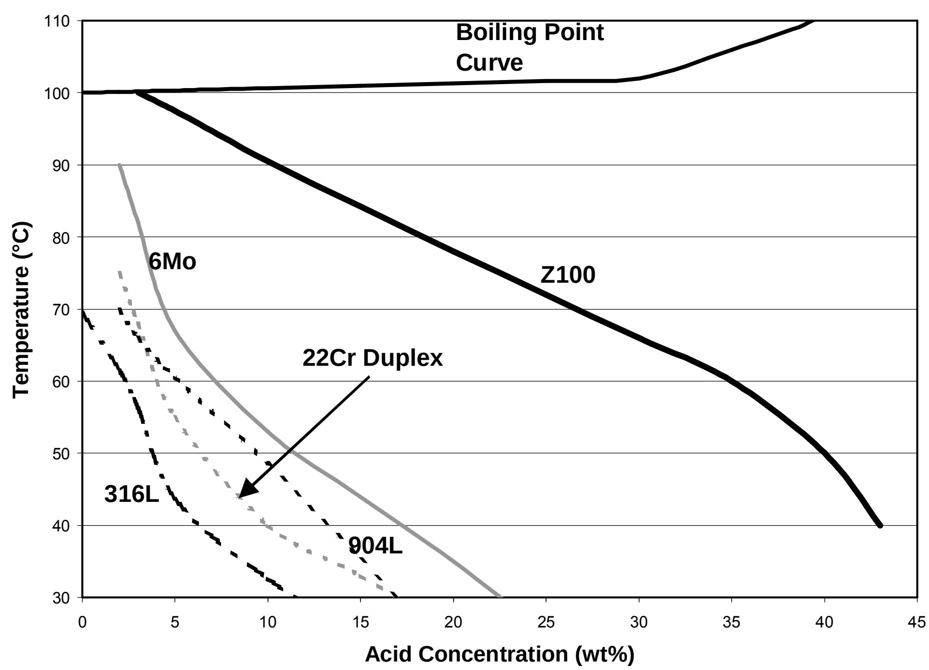
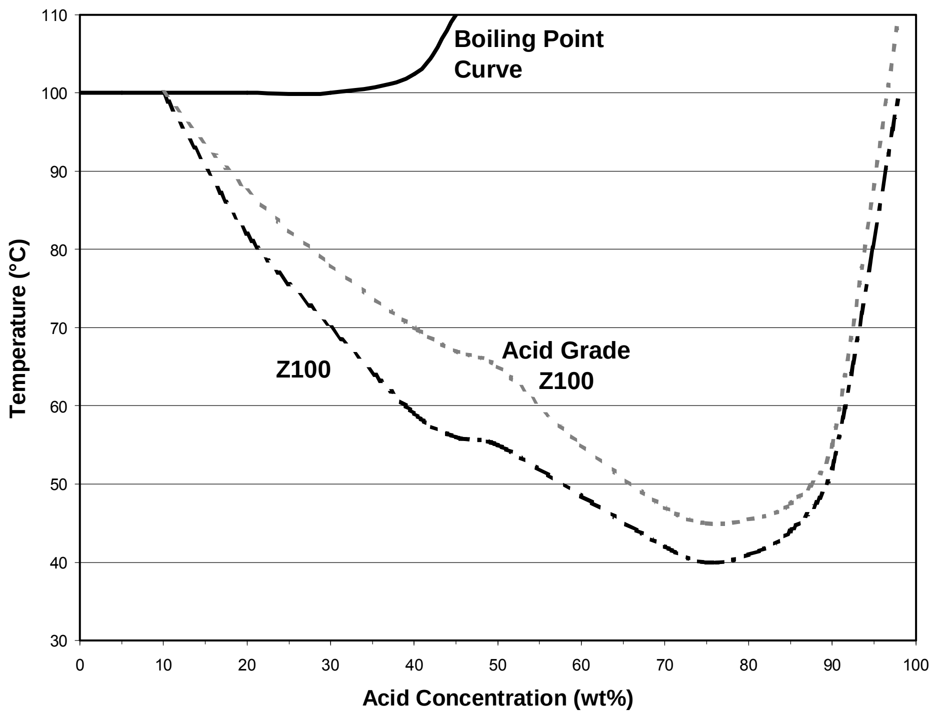


FIGURE 3 Iso-corrosion (0.1mm/y) curves for acid grade Z100 in sulphuric acid



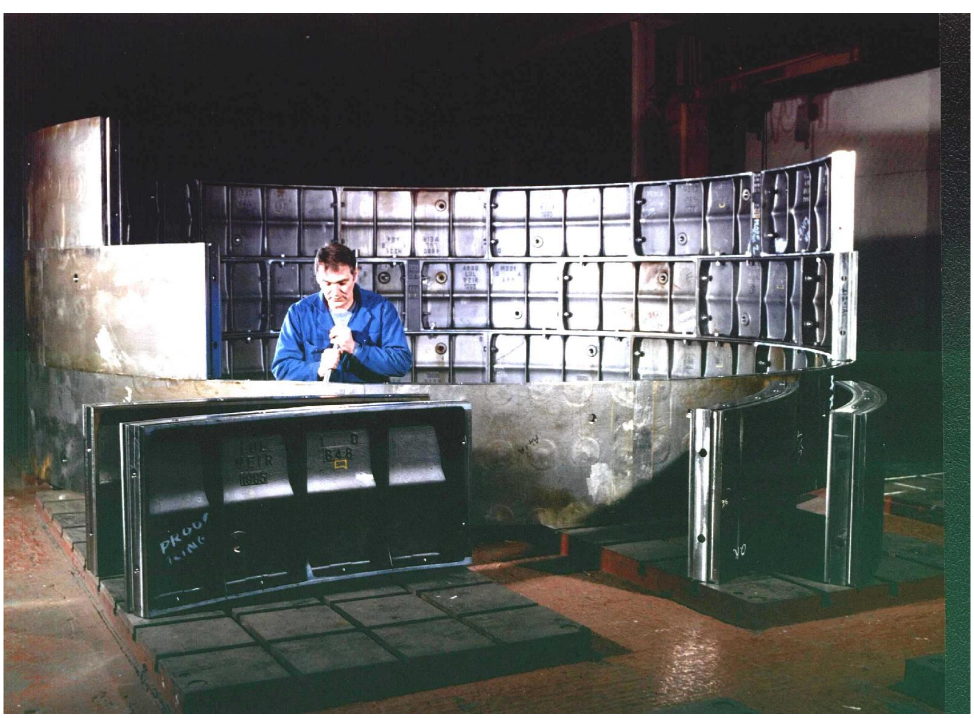


FIGURE 4 Cast Z100 rings being checked for dimensional compliance.

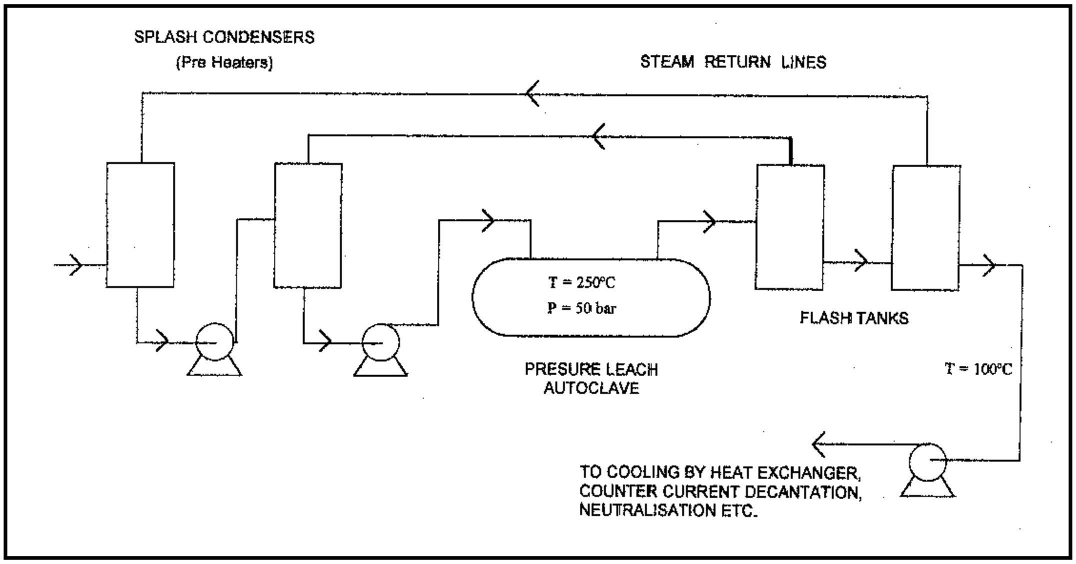


FIGURE 5 Schematic diagram of high pressure acid leach process for nickel laterite ores.

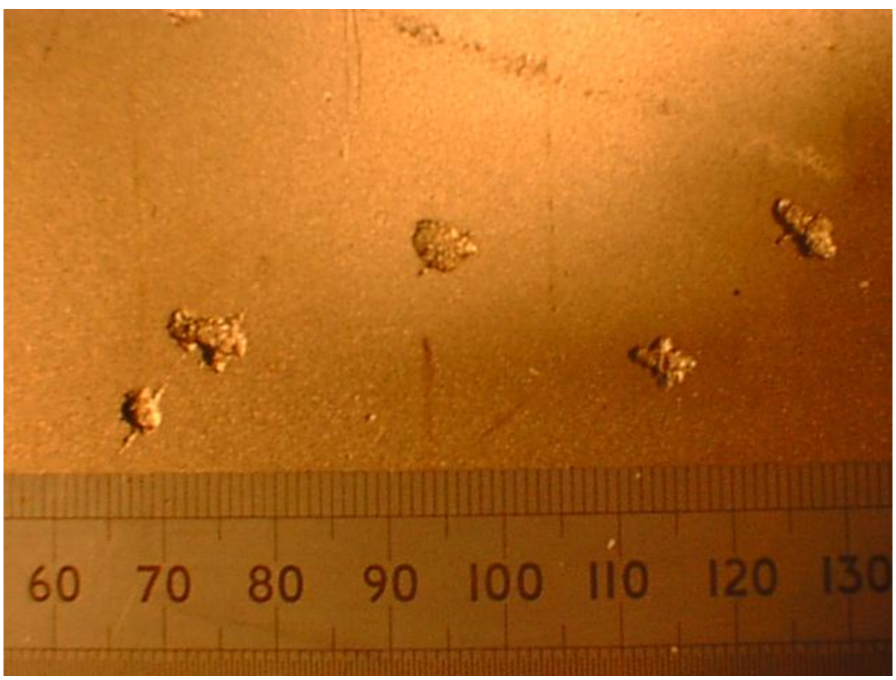


FIGURE 6 Appearance of pits on superduplex stainless steel from a HPAL heater.

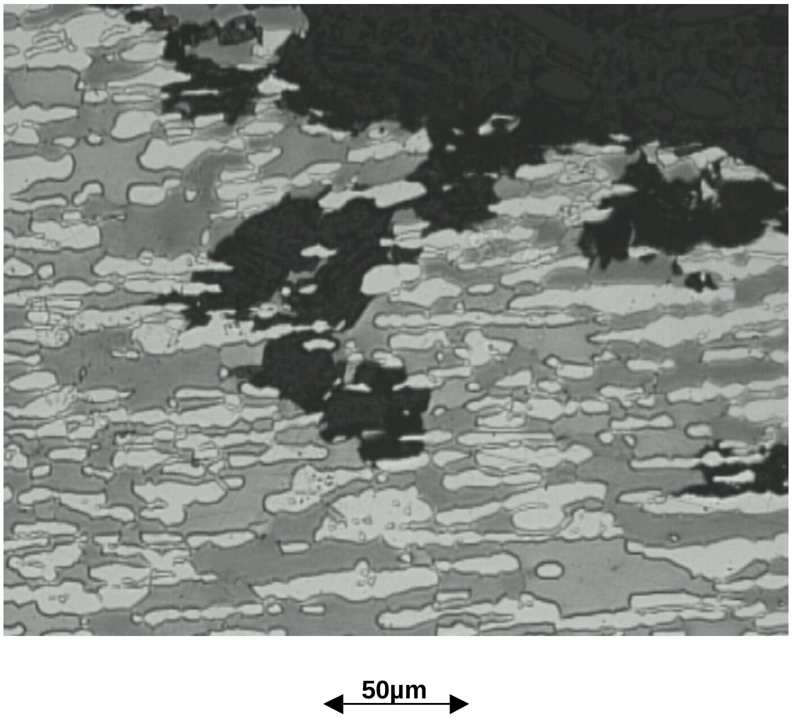


FIGURE 7 microsection through pitting corrosion on superduplex stainless steel from a HPAL heater. (Etchant: Electrolytic 10% oxalic acid & electrolytic 40% KOH).

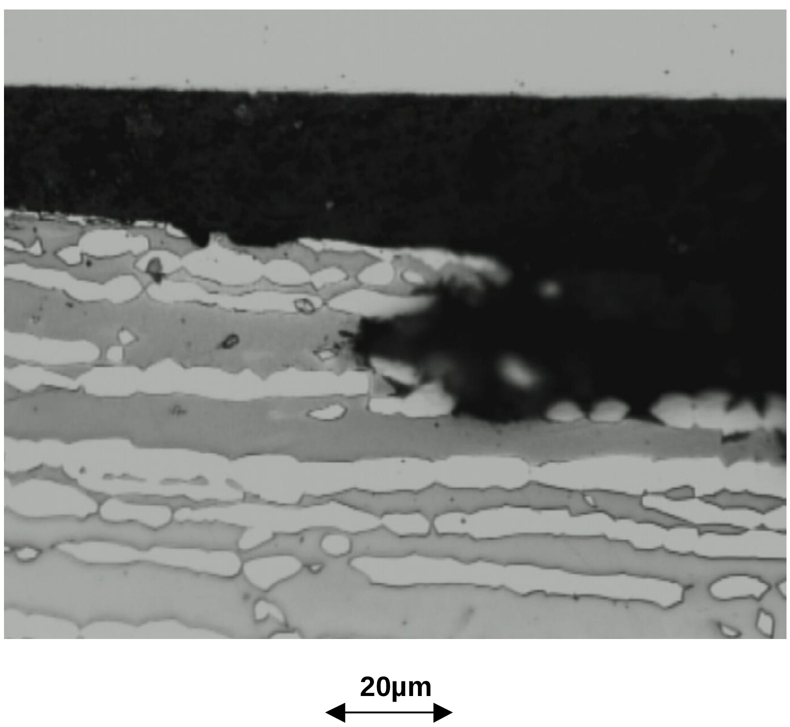


FIGURE 8 Microsection through pitting corrosion of Zeron 100 in 10g/l chloride plus 10mg/l Fe^{3+} at 200°C after repeated start-ups. (Etchant: Electrolytic 10% oxalic acid & electrolytic 40% KOH).

FIGURE 9 Corrosion of Z100 in 98wt% sulphuric acid at 200°C versus ferric iron content