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EXPERIENCES WITH ZERON 100 SUPER DUPLEX STAINLESS STEEL IN THE PROCESS INDUSTRIES

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A B S T R A C T

The process industries have used 300 series stainless steels for many years where the corrosion resistance of carbon steel is inadequate. Where stainless steels have proved inadequate there has been a tendency to utilise high nickel alloys with a greatly increased cost. This paper introduces Zeron 100 super duplex stainless steel and shows how its superior corrosion and stress corrosion cracking resistance, plus its high strength, can be utilised to provide a cost effective alternative to both austenitic stainless steels and high nickel alloys. The composition, mechanical properties and corrosion resistance are discussed showing that the combination of high strength and excellent corrosion resistance make it eminently suitable for a wide range of industrial applications.

The wide range of product forms in which Zeron 100 is available means that vessels, piping, valves and pumps can be made from a single alloy with no worries about galvanic compatibility. Zeron 100 has now been in service for up to ten years. The material is readily weldable with over one million joints now in service. The paper reviews examples of the applications of Zeron 100 including service experience in the petrochemical, chemical, fertiliser and mining industries.

The high strength and hardness of Zeron 100 gives it excellent resistance to erosion and erosion-corrosion and it is widely used for pumps and piping in mining and processing applications. The unique composition of Zeron 100 gives it excellent resistance to a wide range of chemicals including non-oxidising acids. This has led to a variety of applications in phosphatic and urea based fertiliser plants and in other chemical industries. The largest super duplex vessel built to date has been fabricated for a chemical company in the UK.

The use of appropriate design codes to reduce wall thickness and fabrication costs is discussed. It is concluded that, with the drive to cut initial capital cost of new plant, there are many more applications for super duplex stainless steel in the process industries.

KEYWORDS: super duplex stainless steel, mechanical properties, design criteria, chemicals, corrosion.

1. INTRODUCTION

Stainless steels have been used by the chemical industry for many years in applications requiring corrosion resistance better than carbon steel. Where alloys such as 304L and 316L have proved inadequate, there has been a tendency to choose nickel base alloys such as C-276 (N10276) and alloy 625 (N00625). These alloys have superior corrosion resistance to the 300 series austenitic stainless steels, but at a greatly increased cost.

In the late 1970's and 1980's the current generation of duplex stainless steels were developed. These alloys have a 50/50 austenite - ferrite structure with higher levels of chromium and molybdenum than the 300 series austenitic alloys. Their combination of high strength and corrosion resistance has led to the widespread use of duplex stainless steels by the oil and gas industry, particularly for corrosive, offshore environments. The use of duplex stainless steels by the chemical industry has been more limited, but there are now numerous applications where their combination of properties has led to the selection of duplex stainless steels in chemical plants.

Zeron 100 was the first of the "super" duplex stainless steels, characterised by its high content of molybdenum and nitrogen, compared with earlier duplex stainless steels, and having a pitting resistance equivalent number (PREN) guaranteed to be greater than 40. (PREN = %Cr + 3.3%Mo + 16% N). The composition of Zeron 100 is shown in Table 1, and some commonly used stainless steels are shown for comparison. The high PREN value of Zeron 100 compared with other alloys indicates its high resistance to localised corrosion in the presence of chlorides.

The present paper will briefly review the important properties of Zeron 100, and then discuss some of the applications over a wide range of industries. The composition of Zeron 100 falls within the range of UNS S32760.

2. PROPERTIES

Zeron 100 is available in a wide range of product forms. These include castings (principally for pumps and valves), pipes, fittings, plate, fasteners, bar and forgings. The alloy is fully weldable by most commonly used processes and suitable welding consumables are readily available both for use in the as-welded condition and also for subsequent heat treatment.

2.1 Mechanical Properties

The mechanical properties of Zeron 100 are shown in Table 2, and the properties of some commonly used austenitic alloys are shown for comparison. The superior 0.2% proof stress of Zeron 100 is clearly shown. Utilising this strength to decrease the wall thickness of pipe and vessels can offset the slightly higher cost of Zeron 100 compared with, say, 316L.

The high strength of Zeron 100 combined with its high resistance to localised corrosion and chloride stress corrosion cracking, makes it very attractive for vessels and pipes operating at high temperatures and/or pressures. To take maximum advantage of the properties it is advisable to use a code which calculates design stresses based on 0.2% proof stress values rather than tensile strength, e.g., BS 8010 Pt 3 for subsea pipelines, ASME B31.3 chapter IX for high pressure pipes and BS5500 for pressure vessels.

Zeron 100 (S32760) is listed in the 1998 addenda to ASME B31.3 (pipes) and as Enquiry Case 5500/111 Jan ’98 in BS5500 (vessels). It is also listed as code case 2245 in ASME VIII div 1. The design stresses from 20° to 300°C to all three codes are shown in Table 3, which shows the higher design stresses permitted by BS5500. Zeron 100 has good strength at high temperature and this is reflected by the almost constant design stress to both ASME codes at temperatures from 150°C to 300°C. Other alloys, such as austenitic stainless steels and 22 Cr duplex show a substantial loss of strength over this temperature range.

By utilising suitable design codes such as BS5500, it is possible to make substantial wall thickness reductions for duplex stainless steels compared to 316L and hence offset the somewhat higher cost of the duplex material. The use of a thinner wall means that there will also be a reduction in fabrication costs and time, leading to overall savings. The greater strength of ZERON 100 compared with 22% Cr duplex, particularly at high temperatures also presents opportunities for wall thickness and cost savings.

Table 4 shows the maximum design stress at room temperature and 150°C for some stainless steels using ASME VIII and BS5500. The figures clearly show the much higher stresses permitted by BS5500. This code is widely used by the UK chemical industry, and in many countries application to the national pressure vessel authority will permit the use of internationally recognised standards such as BS5500.

2.2 Corrosion Resistance

The relative pitting resistance of stainless steels and nickel alloys is often compared using the ASTM G48-A test in ferric chloride. The high chloride content, low pH, and highly oxidising nature of this solution is not dissimilar to a number of solutions in use by the chemical industry. The temperature at which pitting is first observed is known as the critical pitting temperature (CPT). Figure 1 shows the CPT for a number of stainless steels.

It can be seen that the CPT of Zeron 100 is superior to both 316L, 22 Cr duplex and 904L and, while not so great as that of C-276, the value of 70°C for Zeron 100 is adequate for many applications.

One recurring problem in chemical plants is chloride stress corrosion cracking (SCC) of 304L and 316L stainless steels. The duplex stainless steels are much more resistant to chloride SCC than the austenitic alloys, as shown in Figure 2.

Zeron 100 has shown no indications of cracking in 3% sodium chloride solution up to 250^{0}C. Thus Zeron 100 offers the chloride stress corrosion cracking resistance of alloy C-276 at a much lower cost.

Zeron 100 was originally developed for service in seawater, but it has subsequently found applications in many other environments. This is because of its exceptional resistance to hydrogen sulphide, acids and alkalis.

Figure 3 shows the resistance of Zeron 100 to sulphuric acid, compared with 316L, alloy 20 and S32750. The latter is another super duplex stainless, but without additions of copper and tungsten. It is these latter two elements which are believed to contribute greatly to the resistance of Zeron 100 to sulphuric acid. Even when there are chlorides in the sulphuric acid, Zeron 100 has very good corrosion resistance compared to many other stainless steels, as shown in Figure 4.

Hydrochloric acid is widely used commercially and is a by-product in many processes. Figure 5 shows the resistance of Zeron 100 to hydrochloric acid compared with 316L, S31254 (a 6Mo austenitic stainless steel) and S32750 (a super duplex alloy). As for sulphuric acid, it is the combination of copper and tungsten in Zeron 100 that is believed to give its good corrosion resistance.

Zeron 100 also has very good resistance to commercial grades of phosphoric acid (containing fluorides and chlorides) and acetic acid (containing formic acid and/or halides) as described in Section 3, below.

Zeron 100 also has excellent resistance to alkalis. The corrosion rate is $\leq$ 0.1mm/y up to 50 wt% caustic soda at 120^{o}C. This good corrosion resistance is not significantly affected by the presence of chlorides. Some applications in caustic environments are described below.

2.3 Limits of Use

Above 300^{0}C all duplex stainless steels will precipitate the alpha prime phase, which produces a substantial loss of impact toughness. This takes thousands of hours at 330^{o}C but only 6 hours at 475^{o}C, and generally prevents the use of Zeron 100 above 300^{0}C.

Zeron 100 is frequently used in applications where good impact toughness is required in fabricated units down to -46^{0}C. In some cases the alloy has been used at lower temperatures, and two recent applications involved -60^{0}C and -120^{0}C respectively. One of these is described below.

3. APPLICATIONS

Below are some examples of the use of Zeron 100 from a wide range of industries. The list is not meant to be exhaustive, but shows the diverse uses for the alloy.

3.1 Sea Water

Zeron 100 was originally developed as an alloy for sea water service. Sea water lift pumps and firewater pumps have been in service since 1986, with excellent results. Wrought Zeron 100 has been extensively used for sea water and firewater piping, fittings and flanges, as well as heat exchangers and pressure break vessels.

One interesting application concerns a Zeron 100 heat exchanger used as a gas cooler. Because the gas is at high temperature and pressure (180^{0}C and 321 bar) the gas is inside the tubes and sea water is on the shell side. Zeron 100 was used for the tube plates, baffle plates and shell, with the tubes sealed to the tube plate by back-face welding. Zeron 100 was chosen for this application because of its high strength, resistance to sea water and availability in all the forms and thicknesses required. The high-pressure header was fabricated in a single piece by hot isostatic pressing (HIP).

The temperature limit of stainless steels in sea water is very important. Zeron 100 has been used in many piping systems up to 40^{0}C, and in one system in the North Sea up to 55^{0}C for over two years. The sea water discharge temperature on this platform has now been increased to 65^{0}C to improve separator efficiency, and there have been no leaks after a further 2 years.

3.2 Oil and Gas

Zeron 100 has been very successful in the offshore oil and gas industry where the alloy's high strength and good corrosion resistance make substantial weight savings possible. The resistance of Zeron 100 to sour brines has been discussed elsewhere (1,2) as have the applications. The development over the next few years of more high temperature, high pressure wells is going to increase the applications for Zeron 100.

3.3 Petrochemical

Zeron 100 has been used in synthetic rubber production. Winnik et al (3) described the use of Zeron 100 for the pump and pipework in a polymerisation reactor cycle (Methyl chloride plus $Al\ Cl_3$ catalyst). This application involves cycling between - 120^{0}C and + 82^{0}C. Hence the super duplex had to have proven fracture toughness at the lowest operation temperature. The material consistently passed the charpy test specification of 40J minimum and 0.38mm lateral expansion at -120^{0}C. The successful use of Zeron 100 for this application has led to several repeat orders. Zeron 100 was chosen because of its combination of high strength and corrosion resistance. The alternative was a nickel alloy, which would have been much more expensive.

3.4 Desalination

One of the common methods of producing moderate quantities of drinking water from sea water is reverse osmosis (RO). Sea water is filtered and forced at high pressure through a membrane to remove most of the salt. The AGIP Tiffany platform had a requirement to remove sulphate from the sea water used for oilfield injection to prevent scaling and blockage of the oil producing strata. Weir Westgarth designed a compact RO unit using a special membrane to remove sulphate instead of chloride. Zeron 100 was used for both the pumps and pipework. Besides its good resistance to sea water, the high strength of the alloy means that in most RO applications it can be used as schedule 10S pipe, while austenitic alloys (e.g., S31254) must be used as schedule 40S pipe. This results not only in material savings but also fabrication savings. Zeron 100 feed water piping (70bar) has also been supplied to a Spanish RO plant on the island of Tenerife. Further details of Zeron 100 applications in desalination are given by Francis et al. (4) .

3.5 Flue Gas Desulphurisation (FGD)

The removal of SO_x gases from power station flue gases has been an important environmental issue. The sulphur gases are often extracted by passing the flue gas through an aqueous slurry of limestone, producing calcium sulphate. The slurry is very abrasive because of the presence of undissolved limestone and fly-ash. In addition, it can have high chlorides and low pH. Materials for this application must combine a high resistance to localised corrosion with good resistance to erosion corrosion.

Weir Materials have developed a synthetic slurry solution that gives laboratory test results that reflect service performance (5). Table 5 shows the critical crevice corrosion temperatures (CCT) in slurry containing 40,000 mg/l chloride at pH4 for some candidate stainless steels. The high CCT values for both cast and wrought Zeron 100 make it highly suitable for this application where operating temperatures are typically around $50^{o}C$. Tests on welds showed these also to have good resistance to crevice corrosion (Table 4).

Erosion tests have been carried out on a number of alloys in a specially constructed test rig (6). Tests were conducted in simulated FGD slurries containing typically:-

Calcium sulphate	-	10.64 wt%
Calcium carbonate	-	0.26 wt%
Fly-ash	-	0.1 - 0.47 wt%
Chloride	-	5,000 - 40,000 mg/l
pH	-	2.0 - 6.0
Temperature	-	$50^{0}C$.

The results for a number of alloys are shown versus pH in Figure 6. It can be seen that the metal loss increases for 316L and austenitic cast iron as the pH decreases. 25Cr duplex and Zeron 100 were more resistant to erosion, and the metal loss was independent of pH over the range considered. Zeron 100 was the most resistant of the alloys tested over the whole pH range and this prompted its selection for both the slurry circulation pumps and the gas distributor plates in the FGD units at Drax Power Station in the UK. These have been in service now for over 2 years.

The FGD units at the Ratcliffe power station in the UK have tended to use technology based on rubber lined steel and glass fibre reinforced plastic (GRP). However, a number of operating problems has occurred such as in the slurry recirculation lines, where erosion is occurring. Zeron 100 choke restrictors have been fitted to reduce turbulence in the lines. In the most severely attacked areas Zeron 100 spools have been fitted to replace the GRP pipe, and the Zeron 100 is performing well.

The slurry centrifuges at the Ratcliffe power station have used Zeron 100 baskets from start up. These are in excellent condition after more than fourteen thousand hours use with no signs of corrosion or erosion.

3.6 Chemical

Weir Materials delivered in 1995 the largest super duplex vessel built to date (approximately 3.5m diameter and 5.6m long). The vessel operates at 135^{0}C and is used for solvent recovery by a major pigment producer. The environment varies from acid to alkaline and contains chlorides. A previous vessel had been cast-iron, but with the upgrading of the process and the increase in the temperature the corrosion allowance would have resulted in excessively thick castings. Zeron 100 proved to be a cost effective alternative with proven resistance to both corrosion and stress corrosion cracking in the working fluid. The Zeron 100 vessel was fabricated from 20mm plate whereas the cast iron would have been 150mm thick. The weight of the Zeron 100 vessel was 20 tonnes, whereas a cast-iron vessel would have exceeded 100 tonnes. This is an example of vessel design using BS5500 to take maximum advantage of the mechanical properties of Zeron 100. The vessel was inspected after 2 years in service and was found to be in excellent condition. Following this a 316L vessel suffering chloride SCC has been replaced with Zeron 100 at the same plant.

Zeron 100 has been compared with some nickel alloys in an acetic acid plant for two years. The fluid is 42% acetic acid with various impurities, including 10% formic acid at 188^{o}C and 47 bar pressure. Corrosion rates were as follows:

Cast Zeron 100	-	0.045 mm/y
Alloy 20	-	0.075 mm/y
Alloy C-276	-	0.100 mm/y

Alloy 20 has proved unreliable in this application and a Zeron 100 valve is currently being evaluated which it is expected will enable higher reliability to be obtained.

Zeron 100 has also been used for heat exchanger tubing in a Middle East vinyl chloride monomer plant. Sea water is being used to cool hot gases that are normally dry. However, under some conditions water vapour is also carried over and hydrochloric acid condenses on the tubes. Zeron 100 was chosen because of its excellent resistance to both sea water and hydrochloric acid.

3.7 Fertiliser

Nitrophosphate fertilisers have a number of advantages, both economic and environmental, over conventional phosphates. The main ones are that the process is independent of sulphuric acid, and hence the price of sulphur, and also that there are no solid by-products to dispose of.

The process consists of reacting natural phosphate rocks with nitric acid, which produces nitrophosphoric acid and calcium nitrate. The solution is cooled to crystallise the calcium nitrate, which can then be separated, while the liquor is then concentrated as required. The calcium nitrate can be reacted with CO_2 and ammonia to produce calcium ammonium nitrate, which is also used as a fertiliser.

Zeron 100 super duplex is very resistant to hot nitric acid e.g., the corrosion rate is 0.1mm/year in 44 wt% nitric acid at its boiling point (110^0C). The acid is strongly oxidising and so the presence of other oxidising ions from the rocks has no significant effect. The presence of chlorides and fluorides does degrade alloy performance however. The corrosion rate depends on the concentration of halides in the rocks being processed.

Norsk Hydro have used Zeron 100 for recirculation pipework on the primary reaction vessel, where nitric acid and phosphate rocks are reacted. They had previously used 316L, but problems had occurred due to corrosion and erosion. Zeron 100 was chosen because of its high corrosion resistance. This makes it more tolerant of impurities such as fluorides and chlorides and enables the plant to use lower grade rock, which contain high levels of halides. Zeron 100 has extended the life of the pipework by over 500%.

In addition to the pipework the first stage sedimentation tank has also been constructed from Zeron 100 plate, again because of its resistance to corrosion and erosion.

Zeron 100 also has very good resistance to commercial phosphoric acid, containing fluorides and chlorides. For this reason it was used for several components in a phosphate reactor recirculation pump in an East European plant. The environment consists of about 33% phosphoric acid plus fluorides, chlorides and undigested rock at about 100^0C. In this instance Zeron 100 was chosen as a more cost effective alternative to the nickel alloy C-276 (UNS N10276).

3.8 Mining / Extraction

Zeron 100 has been used for pumps in the Canadian Potash fields, where strong solutions of potassium chloride, with some sodium chloride (about 30% concentration) are handled at temperatures around 80^0C Zeron 100 has excellent corrosion resistance and is more cost effective than the alternative nickel alloys. One user now describes his pumps as "BULLET PROOF".

The process for extracting alumina from bauxite ores is based on the Bayer Process, discovered over 90 years ago, in which bauxite is dissolved in caustic solution. Ground bauxite (300 microns) is mixed with caustic soda solution, 120-220 g/l, at 165^0C - 240^0C. The mixture is passed through steam-heated digesters where the alumina is dissolved out of the suspended bauxite. The resulting hot slurry is diluted to help remove insoluble impurities such as sand and iron oxide, and passes through a series of vessels to remove silica. The liquor is passed through pressure filters to remove residual impurities, cooled by evaporation to 50^0C, and is then passed into large capacity vessels where it is mixed with alumina hydroxide (seed) to precipitate the alumina hydrate from the solution. After filtration, most of the alumina hydrate returns to the process as liquor. The hydrate is washed, dried on disc and drum filters and is fed into calcining kilns operating at 1300^0C, producing alumina (Al_2O_3). The spent liquor contains caustic soda, sodium chloride and silica, typically at about 210^0C. Every 10 days or so the piping is cleaned with inhibited sulphuric acid to remove silica scale.

Zeron 100 is currently being used in one alumina plant in Eire for pipework handling the hot slurry. This is both caustic and abrasive and Zeron 100 has proven to have good resistance to this environment. Inspection of a 16" spool after 2 years showed it to be in immaculate condition. Zeron 100 is being used for the J-tubes in the spent liquor circuit, as an alternative to nickel coated steel, which has only a short life (2-3 years).

A titanium dioxide refinery in the Middle East is also using Zeron 100 pipework for the spent acid lines. This plant uses the chloride route and so the spent acid contains hydrochloric acid. Zeron 100 was chosen because of its high resistance to this acid.

Zeron 100 has been very successful in both cast and wrought forms in acid leach mining. There are a range of processes but they all involve treating metal ores with sulphuric acid at elevated temperatures and pressures. These processes are used for extracting gold, nickel, copper and uranium and when the water used for making the slurry contains substantial quantities of chlorides, the fluids are extremely corrosive. Francis et al (7) have described the environments found in acid leach processing of nickel laterite ores and some of the applications for Zeron 100. The uses include the sparge pipes in the reactor at a gold mine, the slurry injection pumps for nickel laterite ore processing, the exposed metal parts on the thickeners at both a uranium mine and a nickel laterite ore project as well as for agitators and stirrers.

Zeron 100 also has uses in the downstream processing area, e.g.vessels and pipework, particularly when pH's are low and/or temperatures and chlorides are high.

3.9 Engineering

Zeron 100 has also found some novel applications in general engineering. Weir Materials has supplied cast Zeron 100 segments for lining a tunnel section of the London Underground Railway. The ground water in this 0.5km stretch consists of dilute sulphuric acid plus chlorides which was causing cracking of the existing cast iron lining. Zeron 100 was chosen because of its strength, corrosion resistance and ready castability. Over 20,000 Zeron 100 fasteners were also supplied for assembling the tunnel lining segments.

Zeron 100 has also found useful applications in concrete constructions. This is because of its high strength and corrosion resistance in the presence of chlorides. The main concern is that the reinforcement should not corrode even when the concrete is damaged. Because of the problems with corrosion of steel reinforcing bars in concrete and the demand for Zeron 100 concrete products, WML is now producing Zeron 100 reinforcing bars. Applications include alignment dowel pins for concrete blocks and special concrete fixings for marine applications. Zeron 100 has also been used for concrete reinforcement bars, support plates and piping in the refurbishment of Devonport Dockyard.

Zeron 100 piping has also been used for carrying electrical cables in aggressive environments such as are found on offshore platforms.

Zeron 100 has excellent resistance to microbial corrosion, particularly SRB's (8), and the alloy is now being considered for several projects for handling sewage and similar waste water in sensitive areas where leakage must be avoided.

4. FUTURE APPLICATIONS

The applications above cover just a few of the potential uses of Zeron 100. Some other possible uses include vinyl chloride monomer plant, Teraphthalic acid plant, and the steel industry. Francis and Bukovinsky (9) reviewed several of these industries and showed where Zeron 100 could be cost effective. It is expected that the combination of high strength and good corrosion resistance will increase the applications of super duplex stainless steel.

5. CONCLUSIONS

Zeron 100 is a super duplex stainless steel with high strength and good corrosion resistance in a wide diversity of environments. Some of the wide range of applications have been described above and the range is expected to increase over the next few years.

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TABLE 1 Nominal composition of some commonly used stainless steels

ALLOY	UNS No.	COMPOSITION (WT %)							PREN *
		Fe	Cr	Ni	Mo	N	Cu	W	
316L	S31603	bal	17	11	2.2	-	-	-	24
904L	NO8904	bal	20	25	4.5	-	1.5	-	35
22 Cr Duplex	S31803	bal	22	5	3	0.15	-	-	34
C-276	N10276	5	15	bal	16	-	-	3.5	67
ZERON 100 (wrought)	S32760	bal	25	7	3.5	0.25	0.7	0.7	>40
ZERON 100 (cast)	J93380	bal	25	8	3.5	0.25	0.7	0.7	>40

bal = balance
*   PREN = % Cr + 3.3% Mo + 16% N

TABLE 2 Typical mechanical properties of some common stainless steels

ALLOY	UNS No.	0.2% Proof Stress (Mpa)	UTS (Mpa)	Elongn. (%)
316L	S31603	210	500	45
904L	N08904	230	530	35
22 Cr Duplex	S31803	450	620	25
C-276	N10276	365	785	40
ZERON 100 (wrought)	S32760	550	750	25
ZERON 100 (cast)	J93380	450	700	25

TABLE 3 Design stresses versus temperature for wrought Zeron 100 to several design codes

CODE	FORM	TEMPERATURE (°C)						
		20	50	100	50	200	250	300
BS5500	Vessels	319	319	300	281	269	250	241
ASME B31.3	Pipes	250	250	246	237	235	234	234
ASME VIII Division 1	Vessels	188	188	185	178	176	176	176

TABLE 4 - Design stresses for some stainless steels to two codes at 20° and 150°C

TEMP (°C)	ALLOY	DESIGN STRESS (MPa)	
		ASME VIII	BS5500
20	316L	115	150
	904L	123	*
	22 Cr Duplex	155	289
	Zeron 100	188	319
150	316L	88	119
	904L	104	*
	22 Cr Duplex	150	209
	Zeron 100	178	281

* not listed

TABLE 5 - Critical crevice temperature for some stainless steels in a simulated anthracite FGD slurry at pH4 (ref 5)

Slurry composition:

CaSO4	10 wt.%
Chloride	40 g/l
Fluoride	50 mg/l
"Dithionate"	200 mg/l
Fe3 +	10 mg/l
Al3 +	30 mg/l

FORM	ALLOY	CCT (°C)
Wrought	Z100	>80
	6Mo aust	64.7
Welded *	Z100	58.5
Cast	Z100	57.8
	25 Cr Duplex	42

* Critical Pitting Temperature