Some Applications of Z100 Superduplex Stainless Steel In Marine Heat Exchangers

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Summary
Z100 (UNS S32760) superduplex stainless steel combines high strength with good corrosion resistance in a wide range of corrosive fluids, including seawater. Z100 is particularly resistant to seawater when there are large quantities of suspended solids present and some service experience is presented. The temperature limits of use of Z100 in seawater are described plus methods of extending these limits. The corrosion resistance to some common corrosive fluids that may be found on the process side of a heat exchanger are described. Some service heat exchanger applications are presented that demonstrate the successful extension of the seawater operating limits or the use with very corrosive process side chemicals. A new development is seam welded heat exchanger tubing and a comparison of the corrosion resistance and economics of seamless and seam welded tubing is presented.

Keywords Superduplex stainless steel, crevice corrosion, seawater, welding, erosion corrosion.

Introduction

Many industrial processes require cooling and the most common cooling medium for heat exchangers is seawater. The most common heat exchanger configuration is the tube and shell type and this discussion will be confined solely to this type.

Copper alloys, particularly copper-nickel alloys have been used for heat exchanger tubes for many years but problems can arise when the seawater is very corrosive, for example due to sulphides or a high solids burden. Other problems arise when the process side fluids are very corrosive e.g. acids. For more severe applications titanium has been the main choice for heat exchanger tubes, because of its excellent corrosion resistance in a wide range of fluids. However, in the current economic climate titanium is both expensive and in short supply. The author was recently quoted 2½ years delivery for titanium tubes for a small heat exchanger. This paper examines the properties of superduplex stainless steel and suggests the limits of use where the alloy can be used as a lower cost and more readily available alternative to titanium.

Alloy Properties

Superduplex stainless steels are those with 25% chromium, a roughly 50/50 ferrite/austenite microstructure and a PREN>40, where PREN = % Cr + 3.3 x % Mo + 16 x % N. This is an empirical relationship that shows the connection between alloy content and resistance to localized attack by chlorides. It is generally accepted that a PREN>40 confers a high degree of corrosion resistance and some standards require a minimum PREN of 40 for stainless steels for use in seawater systems.

Zeron 100 is the superduplex stainless steel manufactured by Weir Materials and it has been in seawater service since 1990. The nominal composition is Fe/25Cr/7Ni/3.5 Mo/0.25N/0.7Cu/0.7W and the alloy is covered by UNS S32760 and appears in ASTM standards for all the common product forms. Tungsten acts in a similar manner to molybdenum and if it is added into the PREN equation (usually as 1.65x%W), the minimum PREN of Zeron 100 is 41, with typical values of 42. The alloy is known generically as Z100.

Table 1 shows the mechanical properties of Zeron 100 and the high strength compared with titanium means that fewer baffle plates are required on the shell side to prevent fatigue. Superduplex stainless steel also has a thermal expansion coefficient closer to that of carbon steel than austenitic alloys (Table 2). As carbon steel is often used for the shell of heat exchangers, this minimizes the allowances for differential thermal expansion in design.

Table 1. Minimum Mechanical properties of some common heat exchanger alloys at room temperature.

Alloy	**0.2% Proof Stress (MPa)**	**Tensile Strength (MPa)**	**Elongation (%)**
Zeron 100	550	750	25
Titanium	300	450	15
6% Mo Aust	300	650	35

Table 2. Thermal expansion coefficients of some common heat exchanger alloys.

Alloy	**Linear Thermal Expansion Coefficient (10^{-6} K^{-1})**	
	20 – 100°C	**20 – 200°C**
Zeron 100	12.8	13.3
Titanium	-	8.9
6% Mo Aust	16.8	17.2
Carbon Steel	11.5	12.2

Because of the strength of superduplex stainless steels, they are difficult to roller expand into tube plates. Hence, it is recommended that superduplex tubes be seal welded to tube plates of the same alloy. With modern, multi-head automatic TIG machines this is relatively easy. It is customary to use a filler containing an extra 2 to 2.5% nickel, such as Zeron 100X, so that the phase balance in the fast cooling weld metal remains roughly 50/50 austenite/ferrite.

Corrosion Resistance

Superduplex stainless steels have very good resistance to both pitting and crevice corrosion in seawater. In most applications chlorine/hypochlorite is added to the cooling water to prevent fouling. The concentration in the heat exchanger is typically 0.2 to 0.7 mg/l, which results in an open circuit potential of around +600 mV SCE. Laboratory corrosion tests on both parent metal and welds have been carried out at this potential and the critical pitting temperature (CPT) and critical crevice temperature (CCT) have been determined. The results, Figure 1, show that the limiting factor is the CPT of welds. However, this limit can easily be extended using one of the techniques described in the next section.

Zeron 100 heat exchanger tube is also available as seam welded tube manufactured from strip. This is cost effective and reduces lead time because the strip is in stock and requires only slitting, seam welding and annealing.

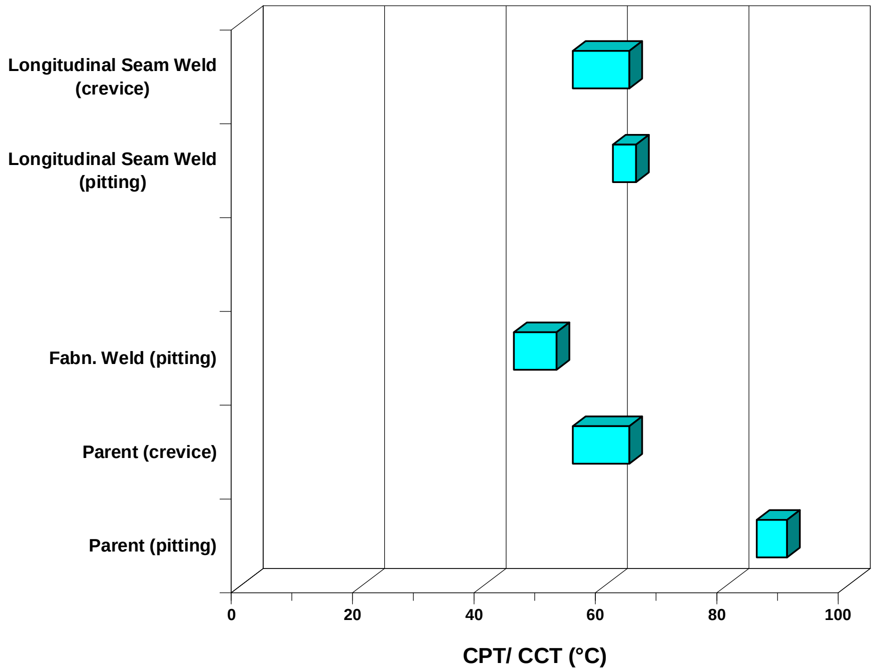

FIGURE 1 Critical pitting and crevice temperature for Z100 in seawater at +600mV SCE

The data in Figure 1 shows that the resistance of seam welded tube to pitting is better than that of an as-welded weld and the CPT and CCT are similar to the crevice corrosion resistance of parent metal. The crevice corrosion resistance of seamless and seam welded materials are almost identical.

The other factor that needs to be considered is galvanic compatibility. Superduplex stainless steels in seawater are compatible with 6% Mo austenitic alloys, titanium and nickel-chrome-molybdenum alloys containing more than 7% molybdenum [1]. When connected to lower alloy stainless steels, copper alloys and carbon steel, superduplex will always be the cathode. Depending on the area ratio and the particular coupled alloy, corrosion of the anode may be increased dramatically, but by the use of some thought in design, these problems can be overcome[1]. One advantage is that Zeron 100 is not only readily available in a wide range of product forms, it is also available as castings, Hence, it is possible to build systems largely from superduplex and thus avoid galvanic corrosion problems.

The fluids on the process side of the heat exchanger can also be very corrosive, but Zeron 100 has very good resistance to a wide range of chemicals. In sulphuric acid, Zeron 100 has a corrosion resistance better than that of most other stainless steels across the whole concentration range (Figure 2). Pilot plant tests by Kvaerner Chemetics[2] have shown that Z100 heat exchanger tubing has a moderate corrosion rate in 98% sulphuric acid at 200°C.

Tests on seam welded tubing showed that the corrosion rate in the same environment was the same as for seamless tube[2]. The alloy is now finding use in the heat recovery section of sulphuric acid plants. In addition the alloy has very good resistance to dilute hydrochloric

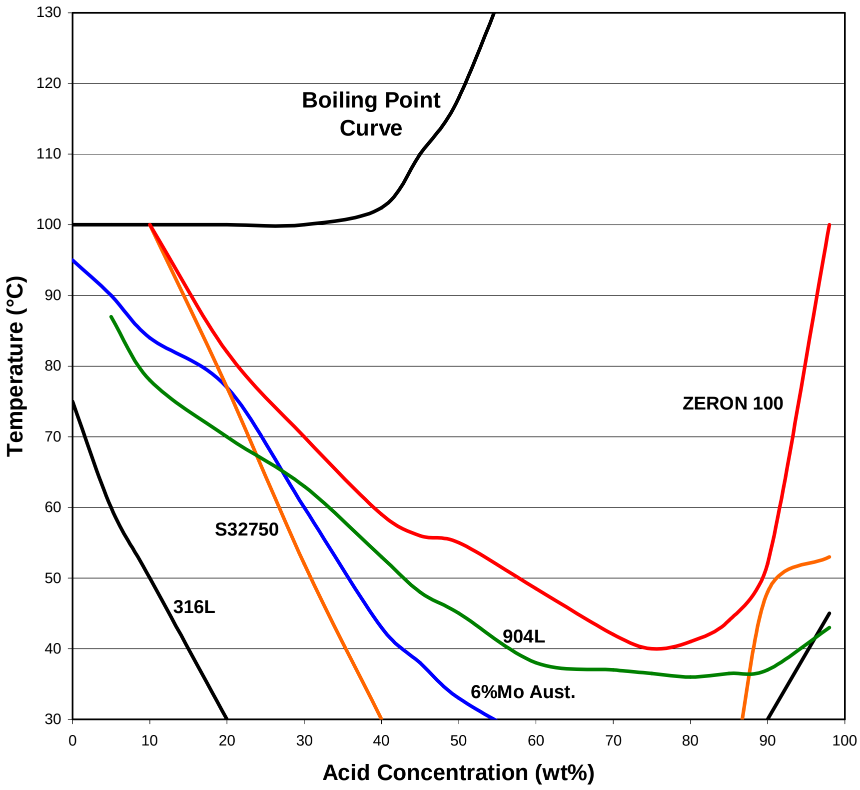

FIGURE 2 Iso-corrosion curves (0.1mm/y) for some common stainless steels in sulphuric acid

acid, organic acids and caustic soda [3]. As with all duplex stainless steels, applications are limited to a maximum of 300°C, because of the precipitation of alpha prime phase at higher temperatures and the consequent loss of ductility.

Optimising Performance

It can be seen from Figure 1 that the factor limiting performance for superduplex stainless steel is the CPT of welds in the as-welded condition. The reduction of corrosion resistance is believed to be mainly due to a loss of nitrogen from the surface, rather than any non-equilibrium distribution of elements between the two phases [4]. There are a number of ways that the corrosion resistance of welds can be improved.

One of these is to weld with argon + 2% nitrogen instead of the normal argon for both shielding and backing gases. Unpublished data from Weir Materials has shown that this can increase the CPT of as-welded Z100 into the range 65° to 80°C (Table 3).

Another alternative is to pickle the welds. On a tube plate with seal welded tubes this is relatively easy to do using a pickling paste or gel formulated for high alloy stainless steels [5]. This technique increases the CPT of Z100 welds by approximately 20°C. (Table 3)

The Piper Bravo platform operated for several weeks initially with a temperature of 20°C at the heat exchanger discharge. This was then increased to 50° to 55°C for two years and then 60° to 65°C for the eleven years since, with no corrosion problems at crevices or welds downstream of the heat exchangers [6]. This experience shows the benefits operating initially at a low temperature to condition the film on the tube service. It is then able to better resist high temperature excursions [7].

Based on these experiences, a soft start up regime has been recommended where maximum operating temperature limits may need to be extended. This is only possible where there is time to flow seawater through the plant before full service conditions are experienced. Weir Materials have recommended the following regime [6]:

cold seawater - 2 days minimum
cold chlorinated seawater - 5 days minimum
heat exchanger operational thereafter.

Table 3. Effect of various treatments on the CPT of Z100 welds in seawater at +600mV SCE.

Condition	**CPT (°c)**	
	Min	**Max**
As welded	45	52
Ar + 2% N	65	80
Immersion Pickle at 55°C	60	65
Pickling Paste/Gel	61	64
Soft Start up	50*	70

**The minimum increases as the length of the soft start increases.*

If improved corrosion resistance at elevated temperatures is required, one of the above options should be used.

Case Histories

Four case histories are described below that show different aspects of the advantages of Z100 for heat exchanger applications.

<u>VCM Plant</u>

Z100 was chosen for the heat exchangers in an Egyptian vinyl chloride monomer (VCM) plant. The cooling water was brackish and the process side was normally an inert gas mixture. However, under upset conditions it was possible to produce HCl, which condensed on the tubes as hydrochloric acid. This caused failure of the original heat exchanger tubes and Zeron 100 was chosen after evaluation of alternatives by the plant operators [8, 9]. The plant has been in operation for ten years with no problems and the alloy has been used for the heat exchanger tubing in the two subsequent plant expansions (Figure 3). This application demonstrates the advantage of Z100 because of its excellent resistance to dilute hydrochloric acid.

FIGURE 3 Heat Exchanger for VCM plant under construction.

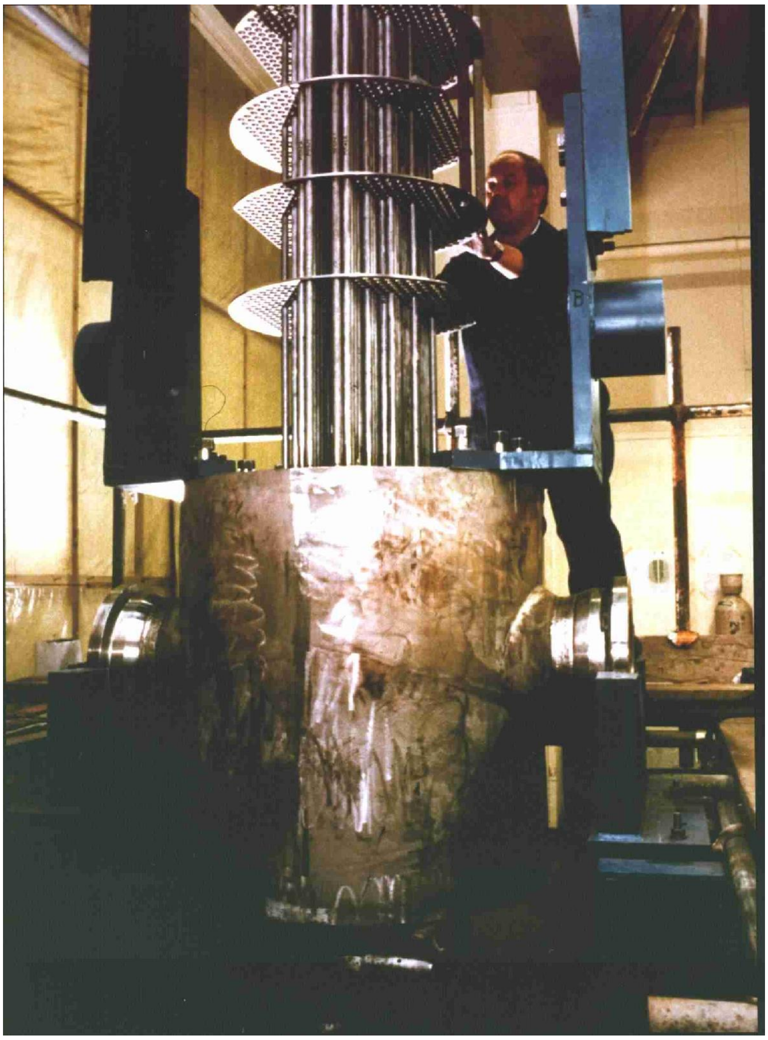

FIGURE 4 High pressure gas cooler with seawater on shell side.

High Temperature Gas Coolers

Some offshore fields produce gas at such high temperatures and pressures that cooling is required before processing. In these cases it is usual to use a tube and shell heat exchanger in reverse mode, i.e. seawater on the shell side. Figure 4 shows a heat exchanger supplied to a North Sea field, where the "water boxes" were made from Z100 by HIP (hot isostatic pressing). Because the seawater was on the shell side, not only was the tube plate superduplex, but so were the shell and baffle plates. The unit in Figure 4 was cooling gas at 200°C and 200 bar pressure and it has now been in successful operation for 9 years.

To prevent any risk of crevice corrosion at the tube/tube plate joint on the seawater shell side, the tubes were attached to the tube plate by back face welding and all the welds were pickled. This application demonstrates that superduplex stainless steel can cope with corrosion even under unusual geometries and arduous operating conditions.

Subsea Heat Exchangers

With some offshore fields it is necessary to cool the wellhead products at the wellhead so that lower cost materials may be used for the pipeline taking the fluids for processing. In this case the sea itself can be used as the cooling medium, with the well fluids inside a pipe that zigzags through the support frame (Figure 5). The first unit of this type that was supplied by Weir Materials was to replace a lower alloy unit that failed by MIC. The Z100 unit has now been in service for more than 8 years without problems.

Figure 5 shows that the heat exchanger has a steel support frame that is coated and also has cathodic protection from sacrificial anodes. These provide some measure of protection to the heat exchanger tubes but not total protection. However, the level of protection means that the wall temperatures can be high without risk of pitting of the welds. The welds shown in Figure 5 were pickled prior to final assembly to increase the corrosion resistance of the welds. This application demonstrates the versatility of superduplex for heat exchangers operating under unusual conditions.

FIGURE 5 Subsea heat exchanger in coated steel frame.

High Temperature Nitrogen Coolers

In the early 2000's a problem arose at a seawater cooled gas compression plant. The nitrogen gas had to be cooled seven times as it was being compressed and there were four trains, making a total of 28 heat exchangers. The original units were tubed with 70/30 copper-nickel and suffered severe erosion due to the high solids burden of the cooling water. The seawater comes from a shallow bay that is stirred up every time there is a tropical storm, with entrained solids levels as high as 50,000mg/l. Zeron 100 was selected for the replacement heat exchangers because of its high resistance to erosion corrosion.

The heat exchangers at this plant presented a number of interesting challenges from a design perspective. The original heat exchangers used a non-standard size of tube and, because the plant is in a conservation area, the footprint of the heat exchangers could not be increased. Secondly, the originally specified operating conditions were for a temperature of 60°C with excursions up to 70°C, but the final specification called for an operating temperature of 70°C with excursions up to 80°C. While Zeron 100 could have coped with the initially specified conditions, the increase in operating temperature created a risk of pitting if any deposits formed in the tubes. To increase plant reliability, resistor controlled cathodic protection (RCP) [10] was installed in each water box.

The tubes were all seal welded to the tube plates with automatic GTA welding and the welds were pickled (Figure 6). The heat exchangers have now been in service for three years and are performing well.

FIGURE 6 Z100 gas cooler for use in seawater with a high solids burden.

Conclusions

1. Z100 superduplex stainless steel offers a cost-effective, viable alternative to titanium for the tubes in seawater cooled heat exchangers.
2. The high corrosion resistance of Z100 superduplex in a wide variety of aggressive fluids makes it a versatile alloy for a wide range of cooling duties.
3. The maximum operating temperature limit of Z100 superduplex can be extended by a number of means, all of which have been demonstrated successfully in service.

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