The performance of duplex stainless steels in caustic soda

Caustic soda (NaOH) is widely used in industry, and at lower temperatures and concentrations carbon steel is commonly used. However, at higher concentrations and temperatures the corrosion rate increases, and there is a significant risk of caustic stress corrosion cracking (SCC). In such cases it has been common to switch to nickel alloys, with a significant rise in cost. This paper shows that duplex stainless steels have good resistance to both general corrosion and SCC in caustic solutions over a wide range of concentrations and temperatures. The limits of use and some successful service experiences are presented to show how duplexes may be applied cost effectively.

By Roger Francis, RFMaterials, UK

Caustic soda (NaOH) is widely used in industry for a variety of purposes, including pulp and paper, soap, detergent, catalyst recovery, mineral processing, pH control and many others. As caustic concentrations and temperatures increase, the corrosion rate of carbon steel increases, and also the risk of SCC.

The recommended limits of use to avoid excessive corrosion of carbon steel in caustic soda vary from 50° to 80°C depending on the source[1], but carbon steel is often used at higher temperatures with a corrosion allowance.

The limits of use of carbon steel to avoid caustic SCC are in NACE SP0403 (Figure 1), and it can be seen that the temperatures significantly exceed 80°C where carbon steel is allowed with stress relief[2]. However, there are frequently SCC failures of carbon steel at elevated temperatures and one reason for this is that not all commercial caustic soda is pure. The most common method for caustic production is the diaphragm process and this will always contain chlorides, typically at around 1% concentration, but individual batches maybe 5 or more times this. The presence of chloride significantly affects the corrosion of carbon steel. In addition, diaphragm grade caustic also contains ~0.3% chlorate, which is an oxidizer and can move the potential to a region where SCC is likely. Caustic soda made by the membrane method contains low levels of impurities, but it is more expensive.

It can be seen in Figure 1 that where carbon steel is not satisfactory, nickel alloys are recommended. The most common ones are alloys 400 (UNS N04400), 800 (UNS N08800), 600 (UNS N06600) and nickel 200 (N02200). This alloy change represents a significant increase in the cost of equipment.

What is less well publicised is the fact that duplex stainless steels perform well in caustic soda, and at lower cost, although they do have limits of use, as is discussed below.

General corrosion

The iso-corrosion curves (0.1 mm/y) for duplex (UNS S32205) and superduplex stainless steel (UNS S32760 and S32750) in caustic soda are shown in Figure 2, along with that for 316L austenitic stainless steel. These were compiled by the author from a number of sources[3].

One advantage of corrosion in caustic soda is that a change that moves conditions across the iso-corrosion curve does not cause a massive increase in corrosion rate[3]. For example, this means that a small increase in temperature does not necessarily cause a massive increase in corrosion rate[3].

Figure 3 shows the effect of increasing chlorate concentration on the general corrosion rate of superduplex and nickel 200 in 50% caustic with 7% NaCl at 100°C. It can be seen that the corrosion rate

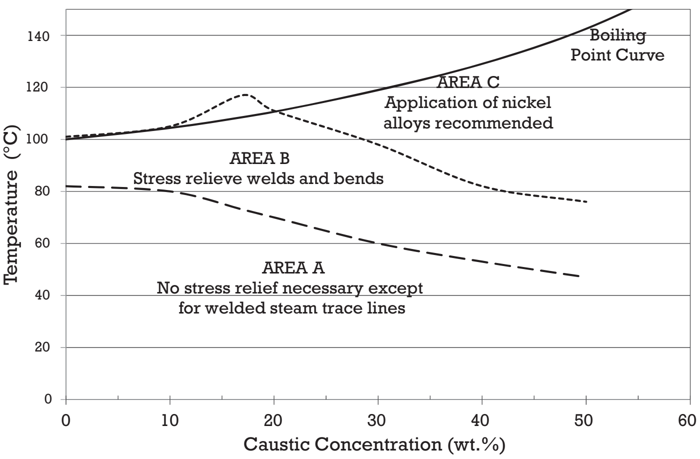

Figure 1. Limits of use of carbon steel in caustic soda to avoid SCC[2].

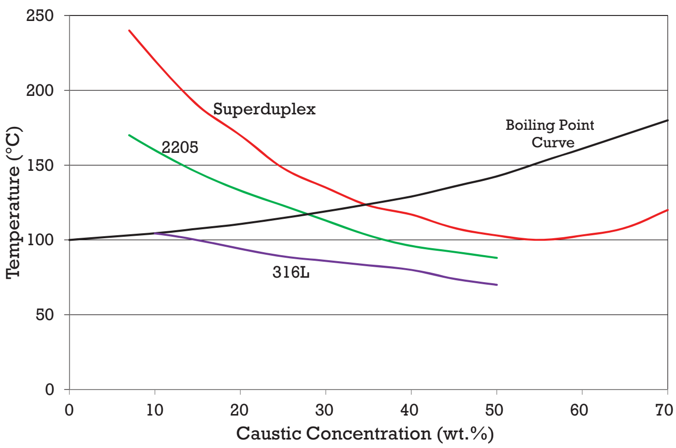

Figure 2. Iso-corrosion curves (0.1mm/y) for some stainless steels in caustic soda[3].

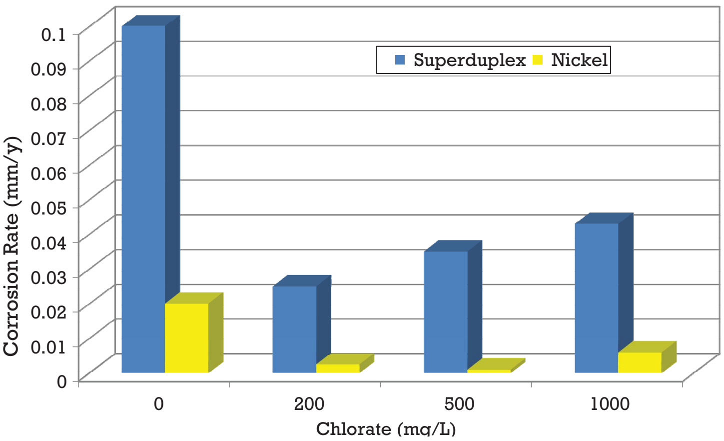

Figure 3. Corrosion rates of superduplex and nickel in 50 wt% caustic plus 7wt% NaCl at 100°C[3].

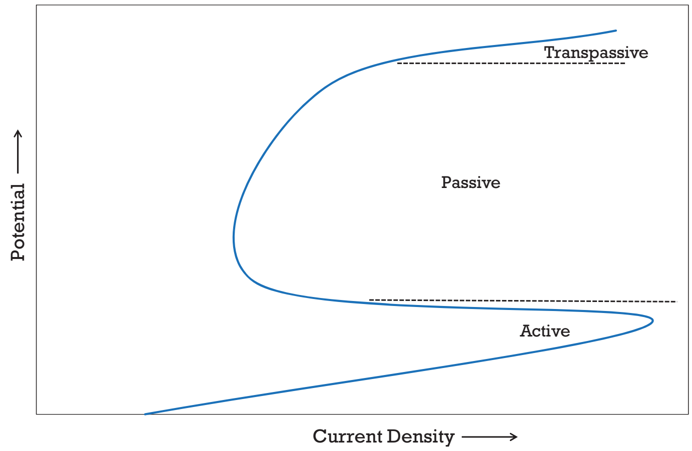

Figure 4. Schematic polarisation curve for duplex stainless steel in caustic soda[4].

decreases at low chlorate concentrations and then slowly increases with chlorate concentration. This is because of the shape of the polarisation curve for stainless steels in caustic soda, as shown schematically in Figure 4[4]. In 50% caustic at 100°C, superduplex stainless steel is in the active region. Small additions of chlorate move it into the passive region with a lower corrosion rate. The corrosion rate increases with further increase of the chlorate concentration, because the passive current increases as the potential increases (Figure 4). When an alloy is in the passive region, the addition of an oxidizer can move the potential into the transpassive region, with a significant increase in corrosion rate. Although the corrosion rate of nickel was lower than that of superduplex, the corrosion rate of superduplex was still very low, and within normal engineering design values.

Crevice corrosion

Crevice corrosion in stainless steels is caused by a build-up of chloride in the crevice and a reduction in the pH by hydrolysis, until the depassivation pH is reached. In caustic soda with chlorides, the high solution pH and its diffusion into the crevice prevents a very low pH being reached. Hence, crevice corrosion has not been observed with duplex stainless steels in caustic soda containing chlorides.

Stress corrosion cracking

Duplex stainless steels are very resistant to caustic SCC and none has been seen in 2205 or superduplex in solutions from 5 to 50 wt% caustic at 100 to 250°C under slightly oxidizing conditions[3]. Even with significant additions of chloride, no caustic SCC was seen under the same conditions.

Caustic SCC of duplex and superduplex stainless steel has occurred under oxidizing conditions, as it has for other grades of stainless steel. Clarke reported SCC of 2205 in 15% caustic plus 10% sodium sulphate with 10 bar oxygen at 160°C, but not at 140°C[3]. Unfortunately further data on 2205 in caustic under oxidizing conditions is not currently available.

The author carried out extensive tests on S32760 superduplex with 10 bar oxygen pressure over a range of caustic concentrations and temperatures. The results in Figure 5 show that SCC only occurred over a limited range of concentrations and temperatures. Further tests in 10% caustic with a range of partial pressures of oxygen showed that the threshold for SCC was about 5 bar of oxygen (Figure 6). This enabled a conservative limits-of-use curve for S32760 in oxidizing caustic to be constructed, as shown in Figure 7 alongside the curve for 316L from Sedriks[5].

Many of the applications for duplex and superduplex in caustic soda are under reducing or slightly oxidizing conditions, and SCC failures are rarely seen. Superduplex piping was handling ~7% caustic plus bauxite at around 230°C in an alumina plant and SCC was detected after two years of operation (Figure 8). The conditions were not thought to be oxidizing, but an analysis of the bauxite showed that it contained

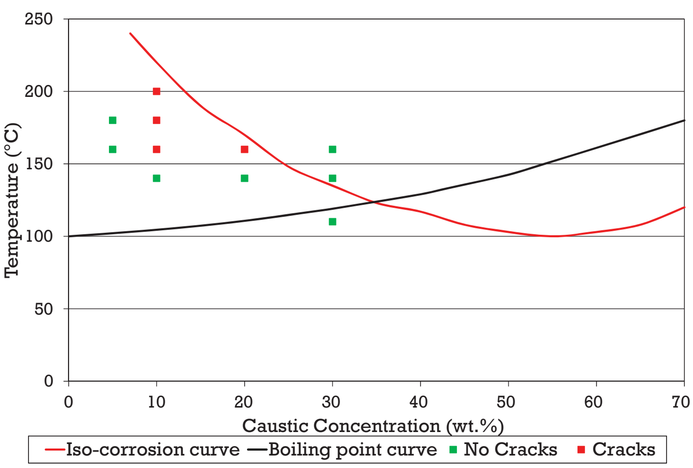

Figure 5. Results of SCC tests on S32760 superduplex in caustic soda with 10 bar oxygen pressure[3].

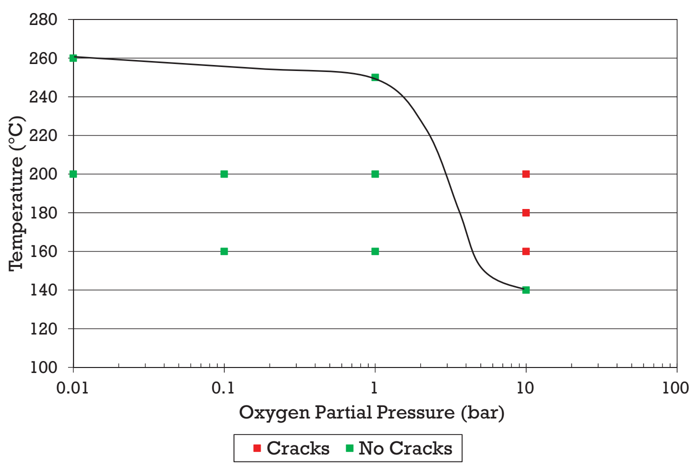

Figure 6. Results of SCC tests on S32760 superduplex in 10% caustic soda with different partial pressures of oxygen[3].

0.5 g/L vanadium, which is a powerful oxidizer in its higher valency states.

Service experience

Duplex (2205) and lean duplex (UNS S32304) have been widely used in the Kraft pulp and paper process for many years with excellent results. The caustic soda is present with a sodium sulphide catalyst, so the conditions are reducing. There have been one or two failures, but these were all on material that was poorly welded or stressed beyond its 0.2% proof stress[6].

In the petrochemical industries it is common to remove the catalyst from some process streams with caustic soda. The author has seen severe SCC of carbon steel piping and valves in this duty at 85°C, where the 25 wt.% caustic soda was diaphragm grade. A change to 2205 duplex for the pipes and valves solved the problem. Other plants have fitted caustic recovery lines in 2205 duplex from new, with good results.

In some processes it is required to remove impurities from caustic soda by oxidation. Provided this is done at temperatures below the limits discussed above, or less than 5 bar oxygen pressure, 2205 duplex and superduplex have given good service for vessels and piping.

The data and service experience show that duplex and superduplex stainless steels can provide a cost effective alternative to nickel alloys in many applications involving caustic soda.

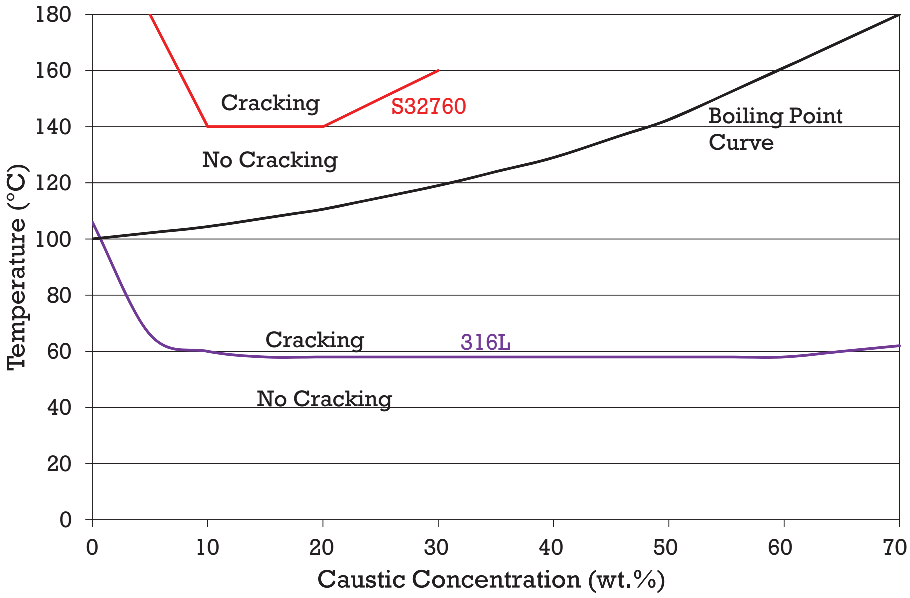

Figure 7. Conservative SCC limits for 316L and S32760 superduplex under strongly oxidizing conditions[3, 5].

Acknowledgement

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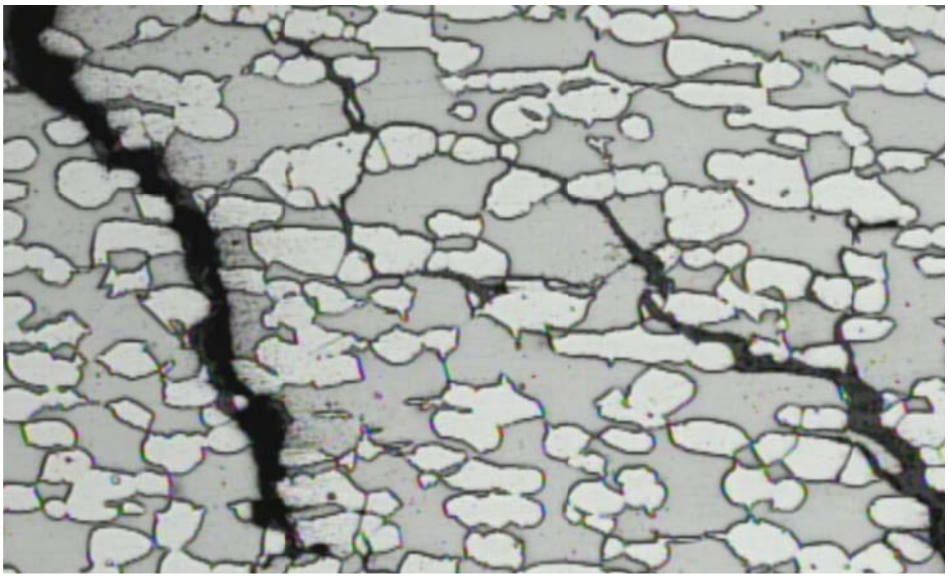

Figure 8. Caustic SCC cracks in a superduplex pipe after two years in ~7% NaOH with 0.5 g/L vanadium at 230°C.

About the author

Roger Francis has been a corrosion engineer for 45 years, with 25 years spent largely on duplex stainless steels. He has published over 90 technical papers, many on corrosion of duplex stainless steels. He has written 6 books and co-edited two more. He has worked extensively in desalination and the corrosion issues that occur in all three types of desalination plant.

He is currently helping to write a guide to avoiding and solving corrosion problems for desalination plant engineers.