



IMPROVING THE CORROSION RESISTANCE OF DUPLEX STAINLESS STEEL WELDS

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INTRODUCTION

- ➔ Modern duplex stainless steels have been around since the early 1980's.
- ➔ They have high levels of chromium with molybdenum, and deliberate nitrogen additions.
- ➔ Duplex stainless steels have a roughly 50/50 austenite/ferrite content, and combine high strength with ductility.
- ➔ Duplex stainless steels have good corrosion resistance, particularly to stress corrosion cracking.
- ➔ The welding of duplex alloys is well understood and many guidelines for good fabrication have been produced.
- ➔ Despite this, problems with welded joints still occur, and this presentation will describe how to weld for optimum corrosion resistance.

ALLOYS

TYPE	UNS No.	GENERIC NAME	NOMINAL COMPOSITION (wt.%)							PREN*
			Fe	Cr	Ni	Mo	N	Cu	W	
Lean Duplex	S32304	2304	Bal	23	4.8	0.3	0.10	-	-	24
	S32101	2101	Bal	21	1.5	0.3	0.22	-	-	26
	S82011	2102	Bal	21	1.5	0.3	0.22	-	-	26
	S32202	2202	Bal	22	2	0.3	0.2	-	-	26
	S32003	2003	Bal	20	3.5	1.9	0.17	-	-	>30
Standard Duplex	S32205	2205	Bal	22	5	3.2	0.17	-	-	35
Superduplex	S32760	Z100	Bal	25	7	3.6	0.25	0.7	0.7	>41
	S32750	2507	Bal	25	7	3.7	0.27	-	-	>41

Bal = Balance

* PREN = %Cr + 3.3(%Mo + 0.5x%W) + 16x%N

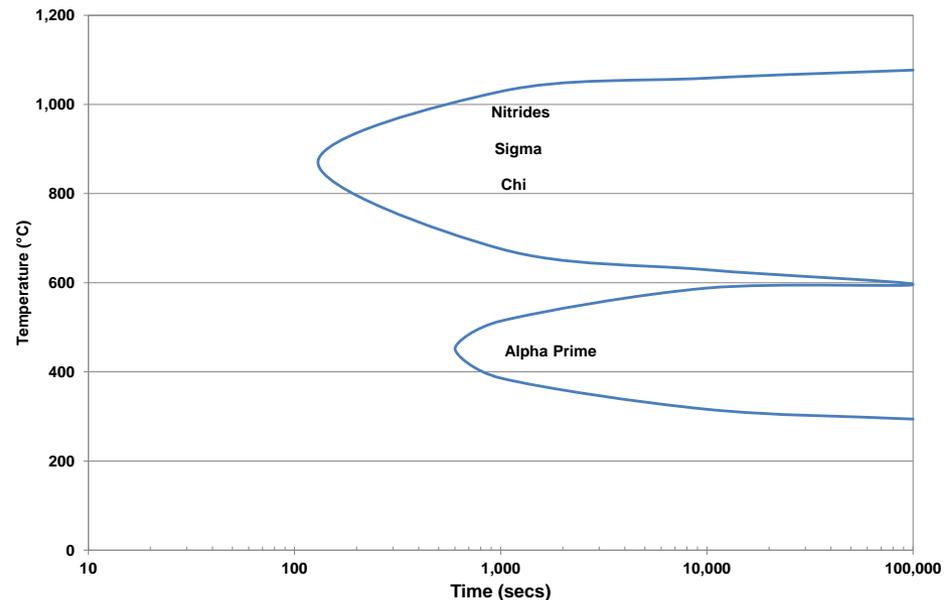
- ➔ All of the alloys have higher strength than their austenitic equivalents.
- ➔ They can all be welded by all the common arc welding methods.

FILLERS

- ➔ Duplex stainless steels can be welded with matching composition filler, but this will produce welds with very high ferrite contents because of the fast cooling.
- ➔ Such welds will require a full solution anneal and a fast water quench after welding to restore the microstructure and the properties.
- ➔ Most welds are used in the as-welded condition and require a matching composition filler with 2 to 3% extra nickel, so that the weld metal is ~50% austenite after cooling.
 - Lean Duplex: 2307 (Fe/23.5Cr/8Ni/0.3Mo/0.14N)
 - Alloy 2003: 2209 (Fe/22.5Cr/8.5Ni/3.0Mo/0.15N)
 - Alloy 2205: 2209 (Fe/22.5Cr/8.5Ni/3.0Mo/0.15N)
 - Superduplex: Z100X (Fe/25Cr/9.5Ni/3.5Mo/0.25N/0.7Cu/0.7W)
 - Superduplex: 2509 (Fe/25Cr/9.5Ni/3.5Mo/0.25N)
- ➔ Note that ASME rules permit welding either superduplex alloy with either filler.

THIRD PHASES

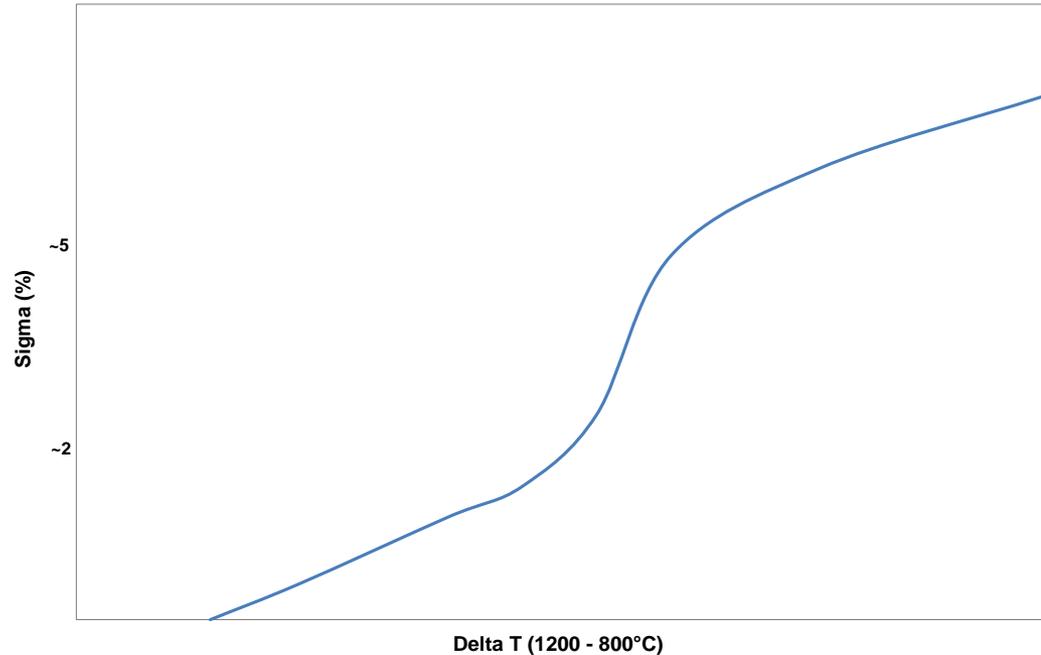
- ➔ The graph shows a typical CCT curve for superduplex stainless steel.
- ➔ When welding, the HAZ passes through the critical temperature zone 750 to 1,000°C, several times for multi-pass welds.



- ➔ It is important that total time in this temperature range does not exceed the limit before entering the sigma “nose”.
- ➔ Sigma, and Chi, are intermetallic phases that are rich in chromium and molybdenum, and reduce the surrounding matrix in these elements, causing a reduction in corrosion resistance.

SIGMA PRECIPITATION

- ➔ There is a welding window of ΔT , when no sigma precipitates.
- ➔ When sigma does precipitate there is a gradual increase in concentration up to ~2%.



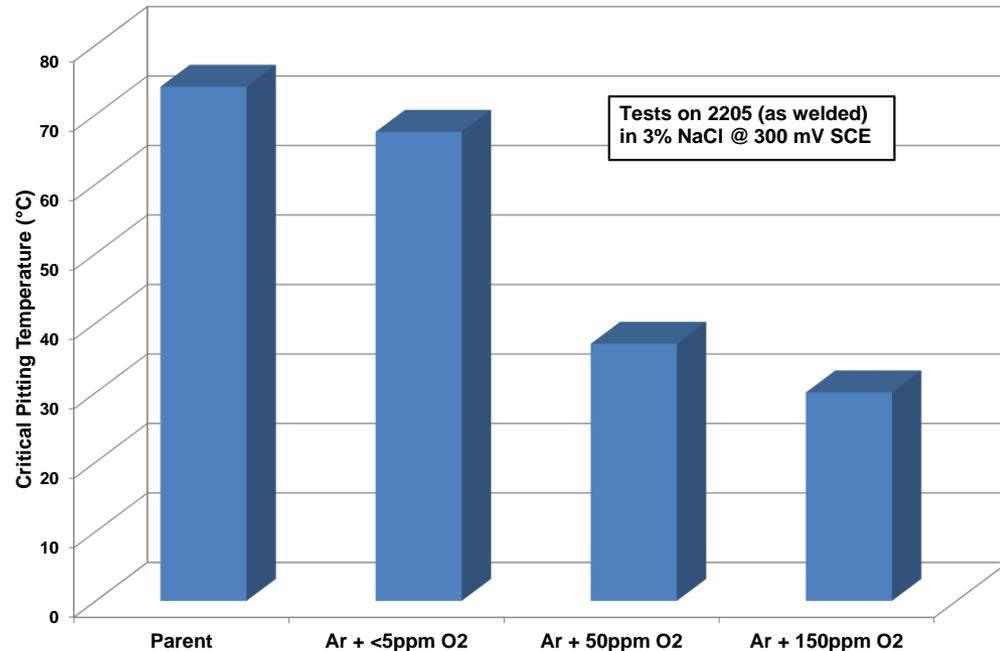
- ➔ Thereafter the sigma concentration rises very quickly to about 5 or 6%.
- ➔ At even greater ΔT the increase is slower as some particles grow, while new ones nucleate.

WELDING CONSIDERATIONS

- ➔ When fabricating it is important to use an appropriate joint design, and suitable heat inputs and interpass temperatures for each pass, to avoid precipitation of third phases.
- ➔ If gas shielding is to be used it is important to use adequate gas flow rates to remove oxygen. This gas is commonly argon (for GTA and GMA), because it is inert, heavy and displaces oxygen easily.

EFFECT OF OXYGEN

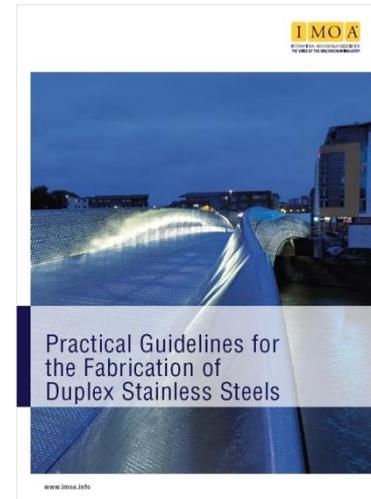
- The graph shows the effect of oxygen content in the welding gases on the CPT in sodium chloride solution @ 300 mV SCE.



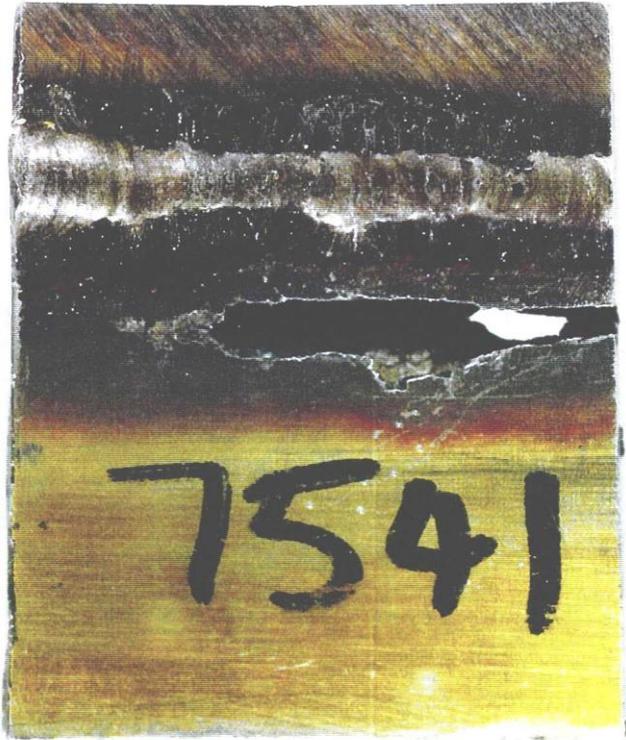
- It can be seen that only with very low oxygen levels can the corrosion resistance be maintained.
- This applies equally to other grades of duplex stainless steel.

WELDING CONSIDERATIONS

- ➔ When fabricating it is important to use an appropriate joint design, and suitable heat inputs and interpass temperatures for each pass, to avoid precipitation of third phases.
- ➔ If gas shielding is to be used it is important to use adequate gas flow rates to remove oxygen and suitable gases. This gas is commonly argon (for GTA and GMA), because it is inert, heavy and displaces oxygen easily.
- ➔ Depending on the welding technique being used, there are other factors that must be considered.
- ➔ Alloy manufacturers usually produce welding guides, and IMOA have a guide to cover welding of all duplex grades.



THINGS THAT GO WRONG 1



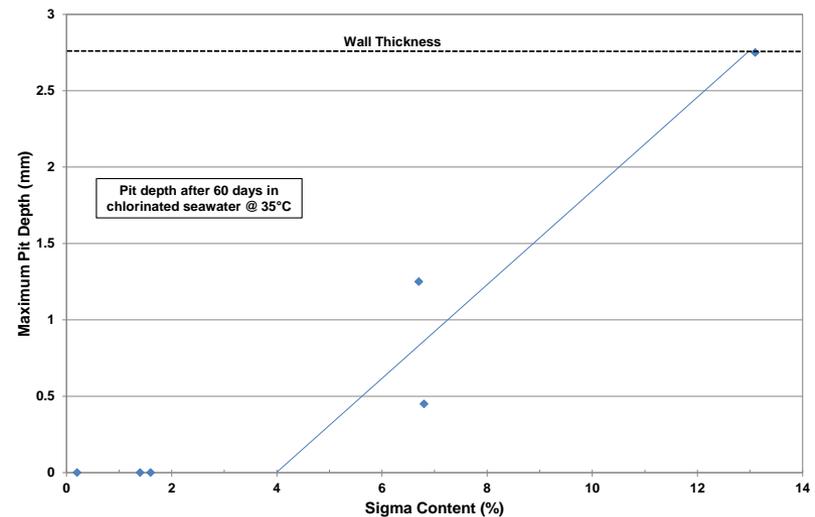
- ➔ This is a very bad weld root that pitted through the HAZ in seawater in a very short time.
- ➔ The black colour shows that there was little or no gas shielding on the root side.
- ➔ In addition there were very high levels of sigma phase in the HAZ (>9%).
- ➔ This shows that the heat inputs and interpass temperatures were too high.
- ➔ All the welds that were like this had to be cut out and replaced, which was both costly and took a long time.

THINGS THAT GO WRONG 2



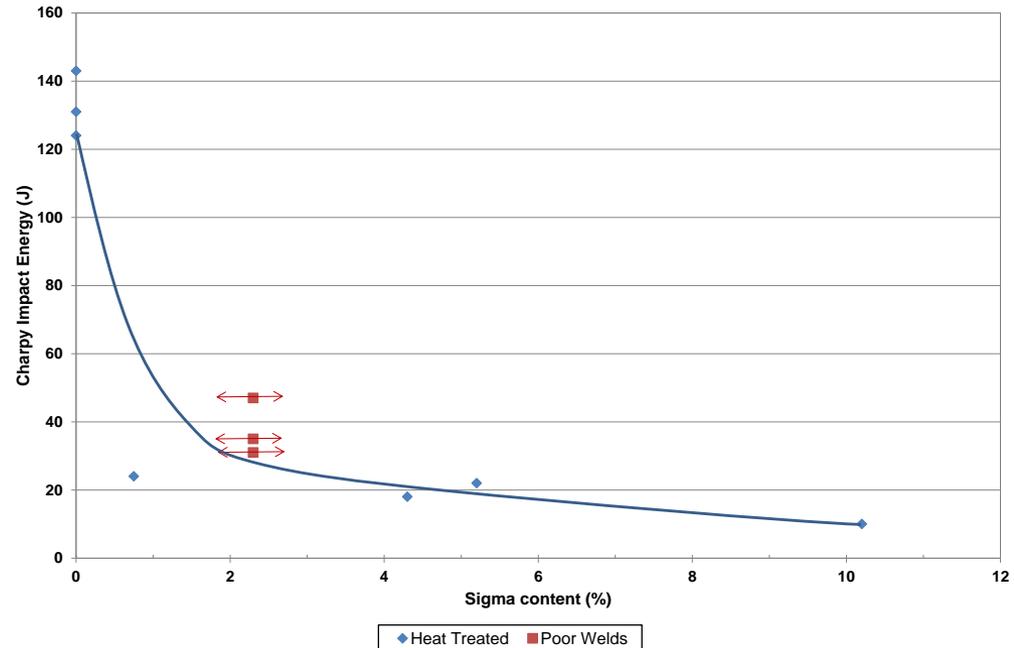
- ➔ This was confirmed by corrosion tests in seawater.
- ➔ The model showed that the threshold was VERY sensitive to the sigma particle diameter, so corrosion testing is essential.

- ➔ This micro shows sigma phase in the HAZ, and this is easily sufficient to reduce the corrosion resistance.
- ➔ A model of sigma phase precipitation in the HAZ of welds predicted a threshold value of ~4%



THINGS THAT GO WRONG 3

- ➔ Sigma also reduces impact toughness.
- ➔ A study by TWI showed that adequate low temperature toughness was retained up to ~2.5% sigma.



- ➔ Hence, sigma phase in the HAZ also has an effect on toughness.
- ➔ The opposite is true for nitrides, which can cause a high weight loss with no pitting, in an ASTM G48 test, long before there is a significant loss of toughness.

QUALIFYING A WELD PROCEDURE 1

- ➔ When qualifying a duplex weld, testing will be required, over and above the requirements of ASME IX.
- ➔ This is to ensure adequate toughness and insufficient third phases to reduce corrosion resistance.
- ➔ There are tests in standards such as NORSOK, as well as company standards.
- ➔ ASTM A923 (for sigma phase) addresses parent metal, but does not adequately address welds.
- ➔ There are test criteria for 2205 welds, but trouble has been experienced when trying to get superduplex welds to pass a G48 test at 40°C.
- ➔ This is difficult to achieve with conventional arc welding techniques and has been judged to be inappropriate for such welds.
- ➔ Corrosion tests should be carried out not just on the PQR, but also on the individual welder qualifications.
- ➔ This ensures that each welder understands what is necessary to produce an acceptable weld.

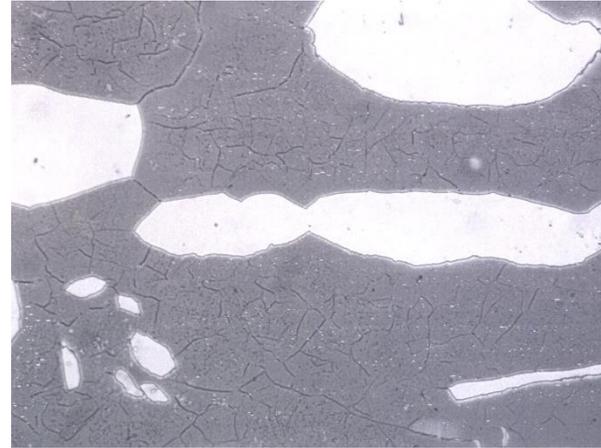
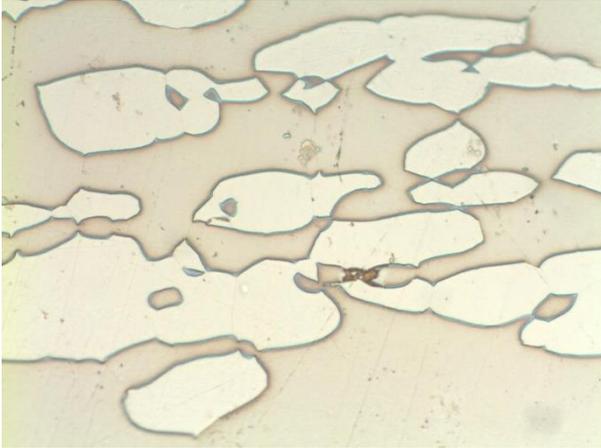
QUALIFYING A WELD PROCEDURE 2

- ➔ The following tests have been suggested for superduplex welds:
 - Impact toughness $\geq 40\text{J}$ average, 35J minimum single value, at -50°C , in the weld metal, fusion line, fusion line + 2mm and fusion line + 5mm.
 - ASTM G48A test for 24 hours at 35°C (no pitting and weight loss $<4\text{g}/\text{m}^2$).
 - Microsection at X500 (electrolytically etched in oxalic acid, then KOH or NaOH). Ferrite to be 35 to 65% and no third phases.
- ➔ For 2205 duplex the tests are the same but the G48A test temperature is 20°C .
- ➔ The impact toughness test guarantees that even after welding there will be adequate toughness.
- ➔ Passing the corrosion test shows that third phases are not present and that there is no Cr denuded layer (wt. loss).
- ➔ It has been suggested that the weld should be pickled, prior to testing, but the side exposed to service fluids should be in the as-welded condition, as it will be in service.

SUITABLE TESTS 1

- ➔ The microsection enables the phase balance to be determined and what third phases if any are present.
- ➔ This can be used to determine what heat treatment is required to restore the properties, in the event of failing the corrosion and/or impact toughness tests.
- ➔ Most of the standard documents are aimed at testing for sigma/chi phases, which are well known to be detrimental.
- ➔ However, it has been shown that nitrides can also reduce both corrosion resistance and impact toughness.
- ➔ Standard etches for duplex stainless steel use NaOH or KOH, which stain the ferrite brown.
- ➔ This etch will not show nitrides, except at very high concentrations.

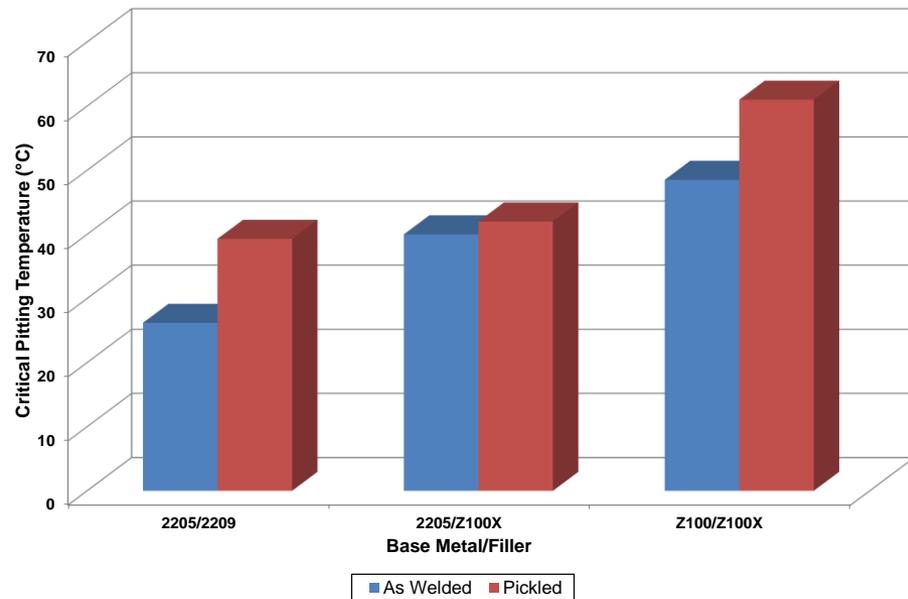
SUITABLE TESTS 2



- ➔ Using a two stage etch in 10% oxalic acid followed by the NaOH/KOH etch enables all the phases to be seen.
- ➔ The photo on the left shows that the two stage etch colours the ferrite brown and sigma orange, making it easy to see.
- ➔ The photo on the right shows nitrides in the ferrite and on the sub-grain boundaries.
- ➔ It is also possible to test the HAZ with a feritscope on production welds. Low readings suggest sigma phase could be present.
- ➔ This can be confirmed with in-situ metallography.

POST WELD CLEANING 1

- ➔ After welding it is customary to clean the weld. The most important face is that wetted in service (usually the root).
- ➔ Wire brushing (with a SS brush) will remove light heat tint and slag (from MMA), but this does not remove the chromium depleted zone below the oxide.
- ➔ It is well documented that pickling welds with a paste or a gel will remove both heat tint and the Cr-denuded layer, to improve corrosion resistance.
- ➔ This data is in seawater at 600 mV SCE.



POST WELD CLEANING 2

- ➔ With piping, particularly smaller diameters, it is difficult to pickle the weld root.
- ➔ If the piping is being spooled, then it is possible to pickle the spools in large commercial pickling tanks before despatch to site for mechanical assembly.

- ➔ This has been common practice for spools for SWRO desalination plants.



POST WELD CLEANING 3

- ➔ After welding customers sometimes complain of rusting around welds.
- ➔ This is usually due to carbon steel contamination, such as cleaning the weld cap with a steel brush rather than a stainless steel one.
- ➔ The steel corrodes in a moist atmosphere and produces rust.
- ➔ Such rusting has caused pitting of 300 series stainless steel.
- ➔ It does not cause corrosion of 2205 or superduplex, but it looks unsightly.
- ➔ It can be removed with a conventional rust removing paste or gel.
- ➔ Alternatively standard heat tint removal pastes can be used.



MORE THINGS THAT GO WRONG

- ➔ It is important that any duplex stainless steel to be welded has a satisfactory microstructure.
- ➔ If third phases are already present it will not be possible to produce satisfactory welds.
- ➔ There are quality tests for duplex, similar to those for welds but with higher Charpy energies and G48A temperatures.
- ➔ In one case an operator was unable to weld thin wall superduplex pipe without getting sigma in the HAZ, even at very low heat inputs.
- ➔ In the end they solution annealed the pipe and then it welded without problems.
- ➔ The problem was the original solution anneal, which had been long enough to dissolve any third phases, but was not long enough to give a homogenous distribution of elements, which reduced Delta T to almost zero.
- ➔ Unfortunately this cannot be detected by any of the tests discussed previously.
- ➔ This is another good reason to do a corrosion test as part of the PQR, and to do Feritscope checks on the HAZ of production welds.

CORRECTING FAULTS

- ➔ If a spool is being fabricated and a weld is faulty then one option would be to fully solution anneal the spool to restore the microstructure.
- ➔ An alternative is to cut the weld out and do a new one, but it is important to cut out the weld metal AND the HAZ. This might mean that a new length of pipe must be inserted, requiring two welds.
- ➔ Castings sometimes require weld repair, and it is important that proper records of any repairs are kept.
- ➔ ASTM A995 requires a full PWHT after any major weld repair of a duplex casting.
- ➔ The photo shows severe pitting at such a repair that had no PWHT.

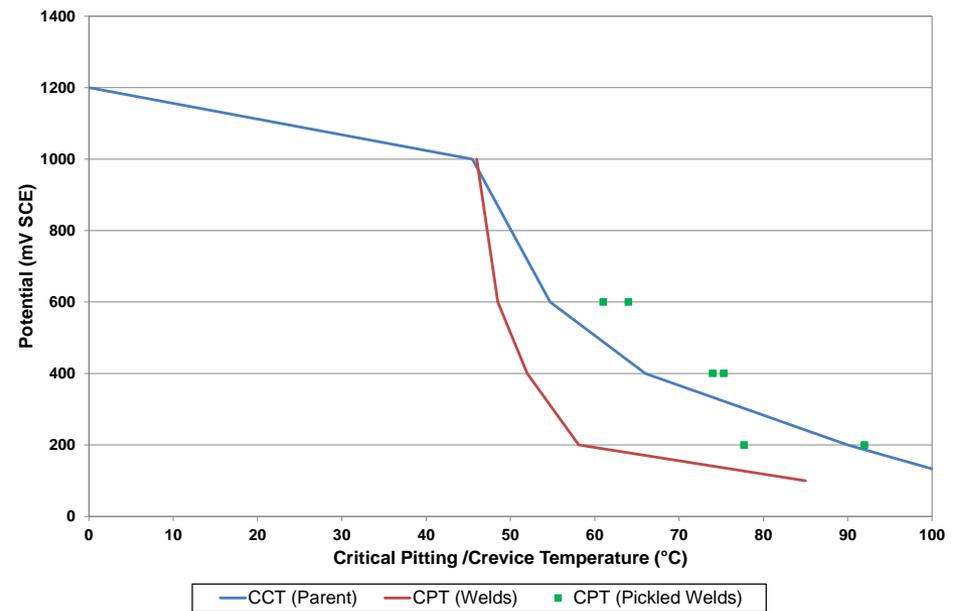


IMPROVING CORROSION RESISTANCE 1

- ➔ The effect of pickling in improving the corrosion resistance of duplex stainless steel welds was discussed earlier.
- ➔ In typical service in seawater the risk of corrosion is crevice corrosion for parent metal, but pitting for welds.

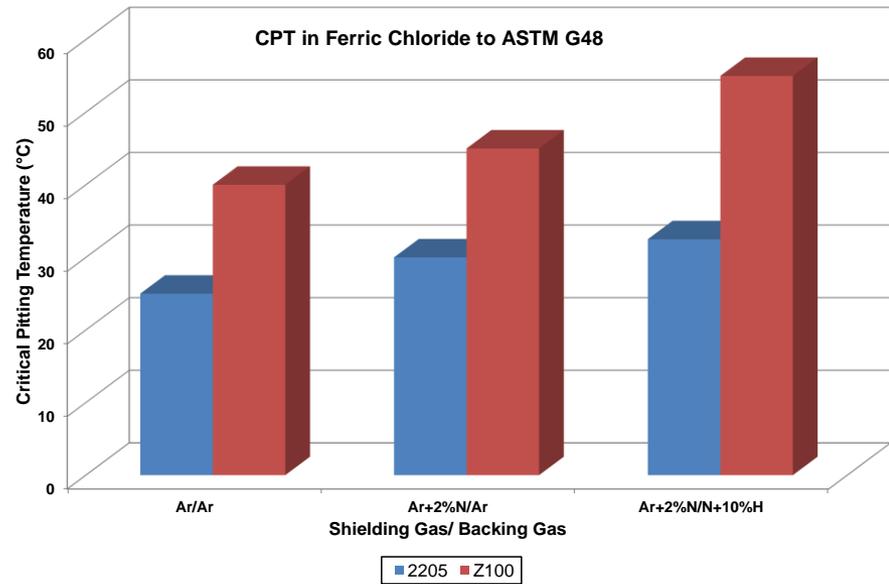
➔ The graph shows that at 1,000 mV SCE the CPT is the same as the CCT, but they diverge at lower potentials.

➔ Pickling gives a weld CPT similar to the CCT of parent metal.



IMPROVING CORROSION RESISTANCE 2

- ➔ For smaller diameter piping, pickling is often not practical and then the option of using alternative welding gases should be considered.
- ➔ When duplex stainless steel is welded, loss of nitrogen from the root will reduce corrosion resistance.
- ➔ Numerous studies have been made using gases containing nitrogen.
- ➔ Gases of argon with 2 to 5% nitrogen have been used, and seem similarly effective.
- ➔ the shielding gas and backing gas was no different to Ar+2%N shielding gas and pure Ar as the backing gas.

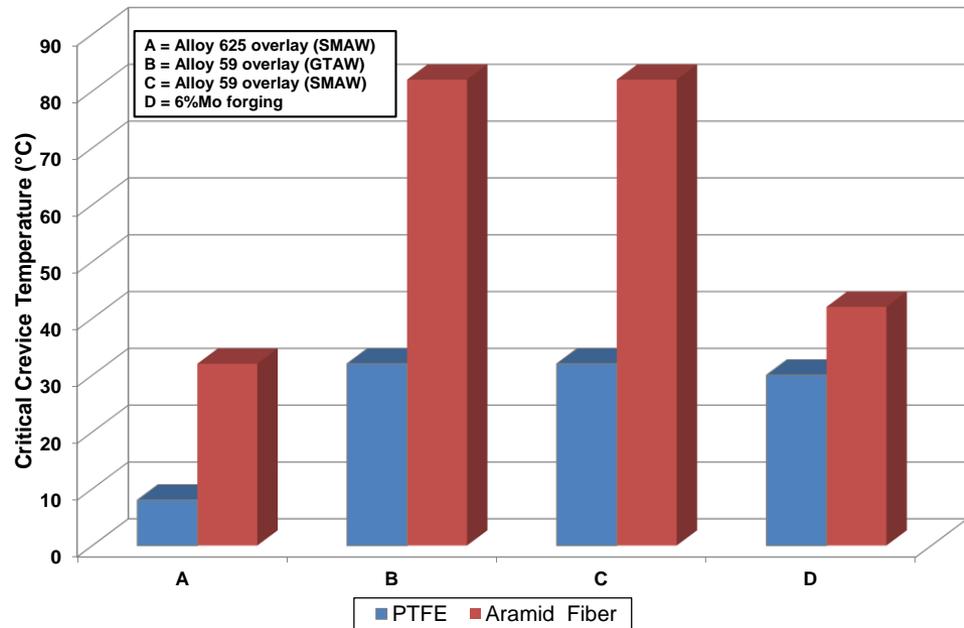


IMPROVING CORROSION RESISTANCE 3

- ➔ Some people have experimented with nitrogen as the shielding and/or the backing gas.
- ➔ While this has stopped nitrogen loss it has resulted in more heat tint on the root than with argon.
- ➔ This is probably because nitrogen is a much lighter molecule than argon, and it is harder for it to displace oxygen.
- ➔ The presence of hydrogen in the backing gas means it reacts with any oxygen and keeps the root side clean.
- ➔ Sometimes a more corrosion resistant weld metal is required and duplex may then be welded with a higher alloyed grade.
- ➔ Lean duplex has been welded with 2209, and 2205 has been welded with superduplex filler.
- ➔ For superduplex a Ni-Cr-Mo filler is required. Alloy 625 is not a good choice because in the as-welded condition the weld has a lot of dendritic segregation.

OVERALLOYED FILLERS

- The graph shows that the CCT of 625 weld overlay is less than that of parent metal.
- This is for 6%Mo but it applies equally to superduplex stainless steel.
- The graph also shows that synthetic fibre gaskets form much less severe crevices than PTFE.
- The data shows that higher alloyed Ni-Cr-Mo alloys are better and successful welds have been made with alloys 59, C-22, 686 and 2000.

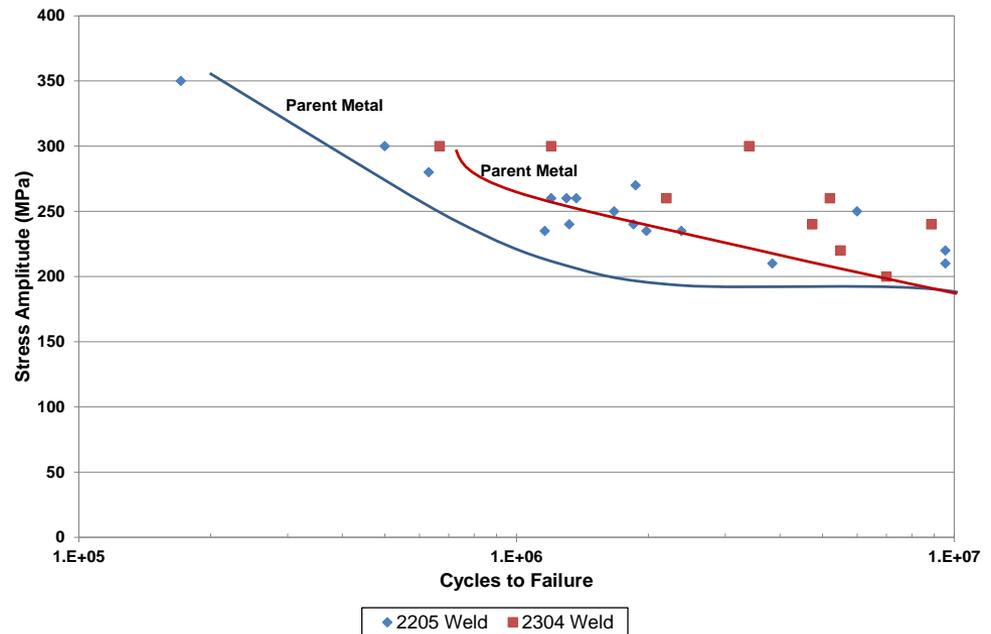


WELDS vs PARENT METAL 1

- ➔ So far we have discussed pitting of welds and shown they can have similar resistance to crevice corrosion of parent metal.
- ➔ However, there are many other sorts of corrosion, and the relative resistance of welds compared with parent metal is important.
- ➔ Duplex stainless steels may suffer SCC in hot, strong chloride solutions, in the presence of H_2S , in caustic soda and by hydrogen.
- ➔ There is now lots of data that shows that duplex welds are no more susceptible to these forms of SCC than parent metal.
- ➔ Gooch commented that the threshold stress for SCC of duplex welds was similar to that for parent metal.
- ➔ As welds are generally a little stronger than parent metal, they are not particularly susceptible to SCC.
- ➔ This applies to all the forms of SCC mentioned above.

WELDS vs PARENT METAL 2

- ➔ There are many instances where duplex stainless steels are exposed to cyclic stresses in a corrosive liquid.
- ➔ One example is the suction rolls in a Kraft pulp mill, which are exposed to white water at ~pH 3.5 at a frequency of 5 Hz.
- ➔ The data show that both 2205 and 2304 welds have superior or equivalent resistance to corrosion fatigue compared with parent metal.



CONCLUSIONS

- ➔ Duplex stainless steels are widely used by industry and can be welded by all the commonly used arc welding processes.
- ➔ With proper attention to joint design and welding parameters it is easy to produce sound, corrosion resistant joints.
- ➔ The corrosion resistance of welds can be increased by pickling or the use of nitrogen-containing welding gases.
- ➔ It is important that all welds are made with good quality parent metal.
- ➔ Additional tests over and above those in ASME IX are required to guarantee the suitability of a PQR.
- ➔ It is important to also carry out tests on individual welder qualifications.
- ➔ The HAZ can be tested by NDT for sigma after production welding.

THANK YOU

ANY QUESTIONS?