MULTI Alloys

BRIDGING PERFORMANCE LEVELS IN CORROSION RESISTANCE

*The theme of this e-book is the alloys which may bridge the gap between the **corrosion resistance of 316L**, a widely used stainless steel and **Alloy C276** a nickel alloy. **We illustrate some conditions under which 316L may be inadequate and the alternatives that may be available.***

*Aspects of corrosion are explained in order to effectively detail the resistance that some readily available alloys can provide. **However the data presented is intended to illustrate principles and to promote discussion rather than to prescribe a solution.** It is intended that highlighting the role that alloying elements play vis a vis the resistance to specific corrosion mechanisms will assist in more cost effective choices.*

01

CORROSION RESISTANCE EXPLAINED

Corrosion may manifest itself in a number of forms and an early classification focussed on eight. In this review we limit it further to three. They are general/ uniform corrosion, stress corrosion cracking and pitting corrosion and each is explained in subsequent pages.

The corrosion resistance of a metal may be defined as its inherent ability to withstand damage caused by an electro-chemical reaction between the environment with which it is in contact and the metal. Thus corrosion resistance needs to be assessed by knowing the metal and the corrodent. A change of one may give rise to a different result as illustrated below.

Many may say Alloy C276 is more corrosion resistant than 304 stainless steel and this correct in boiling 20% sulphuric acid . But in boiling 20% nitric acid 304 will show a loss of thickness of less than 0.1mm/year whilst for C276 it will be more than 0.5mm/year.

Materials of construction are needed to withstand many, many chemicals and process streams. The anodic reaction in a corrosion cell is the dissolution of the metal, whilst that at the cathode will depend on the corrosive. It is common to categorise the corrosive as “reducing” or “oxidising” relative to that metal. This explains the respective behaviour of 304 and Alloy C276 in the 2 acids. The nickel alloy is not suitable for use in a strongly oxidising acid of which nitric acid is an example.

02 ALLOYS OF INTEREST

There are numerous corrosion resisting alloys that are available: there are old, well established grades and newer, recently developed ones. They may categorised as application specific or general purpose and the alloys selected for this review are some of those that fall in to the latter group since these are the alloys that are more readily available.

Prior to 1992, nickel alloys were defined as alloys nominally containing less than 50% iron with nickel as the highest nonferrous element present. *Since then only alloys containing nickel as the principal constituent have been categorized as a nickel alloy but a legacy of the this is that some high alloy stainless steels have a* ***UNS*** *designation with N as a prefix.* ***eg: 904L, a stainless steel is recorded as UNS N08904***

Table 1. ALLOYS OF INTEREST*

Alloy	UNS	% Cr	%Ni	%Mo	%C	%Cu	Other
304L	S30403	18.0-20.0	8.0-13.0	-	0.03*		
316L	S31603	16.0-18.0	10.0-14.0	2.0-3.0	0.03*		
904L	N08904	19.0-21.0	24.0-26.0	4.0-5.0	0.02*	1.0-2.0	
254SMO	S31254	19.5-20.5	17.5-18.5	6.0-6.5	0.02*	0.5-1.0	N;
Alloy 20	N08020	19.0-21.0	32.0-38.0	2.0-3.0	0.07*	3.0-4.0	Nb+Ta
2205	S32205	22.0-23.0	4.5-6.5	3.0-3.5	0.03*		N;
2507	S32750	22.0-26.0	6.0-8.0	3.0-5.0	0.03*	0.5*	N;
Alloy 255	S 32550	24.0-27.0	4.5-6.5	2.9-3.9	0.04*	1.5-2.5	N;
Sanicro 35	N08935	26.0-28.0	34.0-36.0	6.1-7.1	0.03*	0.4	N
Alloy 825	N08825	19.5-23.5	38.0-46.0	2.5-3.5	0.06*	1.5-3.0	Ti
Alloy 625	N06625	20.0-23.0	58 min	8.0-10.0	0.10*	-	Nb+Ta;Al:Ti
Alloy C276	N10276	14.5-16.5	Bal	15.0–17.0	0.01*		W;Fe;Co

Austenitic St Steel **Duplex St Steel** **Nickel Alloy**

* Composition data from ASTM standards

03

BRIDGING THE GAP: RESISTANCE TO GENERAL CORROSION

*General corrosion, a uniform thinning of the metal, is illustrated in **Fig 1** and in this review the two corrodents considered are sulphuric and nitric acids.*

Collating comparative corrosion data for the alloys of interest in the 2 acids has been done with reference to iso-corrosion curves for the metals and corrosion tables both of which are widely available. These record the temperatures at which a corrosion rate of 0.1mm/year may be expected for various acid concentrations. Above this temperature the corrosion rates will be higher.

Fig 1 Alloy 825 corroded in H_2SO_4 when exposed to extreme temperature.

COMMENT:

Table 2

Temperature (°C) H_2SO_4 and HNO_3 CORROSION DATA Temperature (°C) at which 0.1mm/yr corrosion rate is reached in commercial acid.

Alloy	H_2SO_4 Concentration (%)				HNO_3 Concentration (%)			
	20	40	60	80	20	50	65	80
304L	ns	ns	ns	ns	103	70*	70*	50
316L	35	ns	ns	ns	103	70*	70*	50
904L	70	55	40	35	103	70*	70*	50
254SMO	75	40	25	ns	103	-	70*	-
Alloy 20	70	62	57	58	-	-	-	-
2205	55	ns	ns	ns	103	70*	70*	-
2507	75	30	ns	ns	103	70*	70*	-
Alloy 255	82	75	58	62	103	80	80	-
Sanicro 35	75	55	40	ns	103	110	90	80
Alloy 825	73	55	48	51	103	110	90	-
Alloy 625	89	83	73	48	-	-	-	-
Alloy C276	80	70	70	70	65	58	50	-

Austenitic St Steel **Duplex St Steel** **Nickel Alloy**

***** Intergranular corrosion may occur above these temperatures
ns: not suitable
–: no data found

Table 2 is effectively an ranking of the corrosion resistance of the alloys in the 4 concentrations of the 2 acids – the relative corrosion resistance of the various alloys can be gauged from the fact that those that have a higher 0.1mm/yr corrosion threshold temperature will be the more resistant. Further noteworthy comments relating to this are:

- The effect of the corrodent, illustrated here using sulphuric or nitric acid, may differ markedly and thus selecting a more corrosion resistant alloy needs to be based on full understanding of the environment.
- This extends to the presence of impurities which may accelerate or retard the corrosion process,
- Corrosion resistance in sulphuric acid is aided by the presence of copper in the alloy and whilst it applies to both nickel alloys and stainless steels the effect is more marked in the latter.
- In addition to the general purpose alloys covered in this review there are application specific grades that are often used in demanding applications and this applies to strongly oxidising conditions such as nitric acid and concentrations of sulphuric acid greater than 80%.

04 BRIDGING THE GAP: RESISTANCE TO PITTING CORROSION

Chloride containing solutions are often used in chemical processes or are the byproduct of industrial activity and there are corrosion phenomena that may result from the presence of chlorides and other halides and pitting is one of these. (Fig2)

Because it is so confined and thus difficult to detect, pitting is very damaging. Knowledge that it is taking place may only result when its too late and the metal has perforated and leaks result.

Pitting is normally associated with chlorides or other halide ions with the start of the process being the localised break down of a normally passive film or some other surface imperfection which results in a corrosion cell.

The corrosion process may then be exacerbated by acidic or neutral conditions, temperature and oxygen levels.

There are several standard laboratory tests available to rank the resistance of stainless steel grades to pitting corrosion and the results are reported as the critical pitting temperature (CPT) – the lowest temperature at which pitting takes place.

Years ago a useful indicator of resistance to pitting based on the composition of the stainless steel or nickel alloy was established and this is known as the Pitting Resistance Equivalent (- PRE) and the formula is:

$$PRE = \%Cr + 3.3\%Mo + 16\%N$$

COMMENT:

Table 3 PRE Values

Alloy	PRE
304L	18
316L	24
904L	34
254SMO	43
Alloy 20	28
2205	35
2507	43
Alloy 255	40
Sanicro 35	52
Alloy 825	34
Alloy 625	52
Alloy C276	69

Austenitic St Steel **Duplex St Steel** **Nickel Alloy**

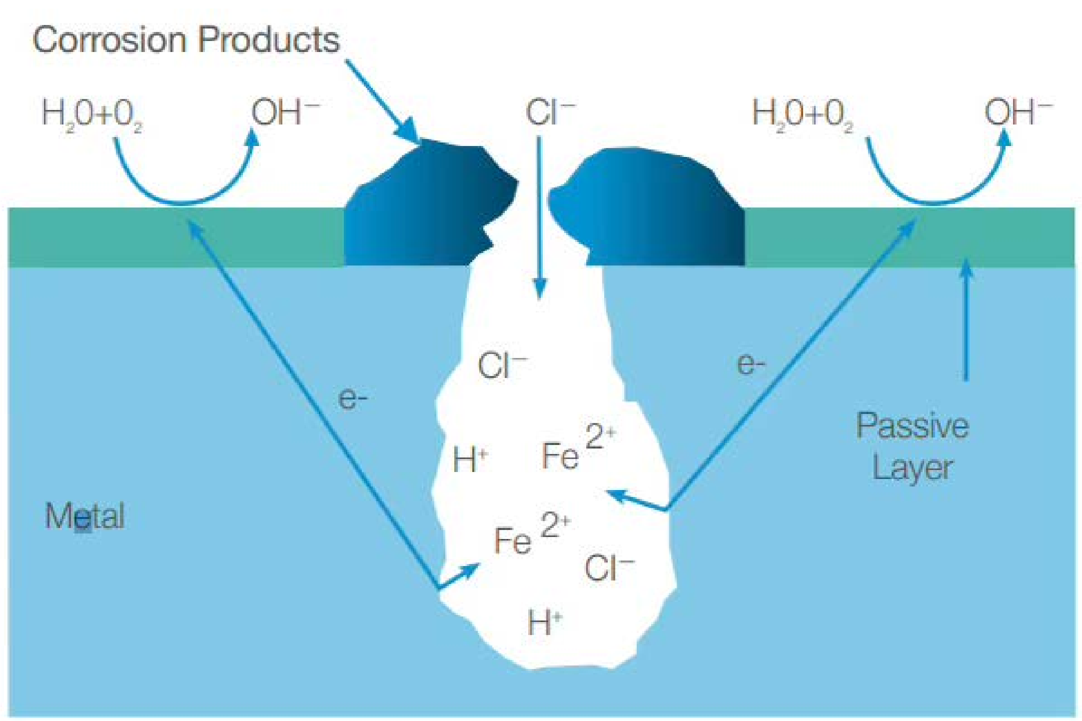

Fig 2 Pitting of Stainless Steel

Although the PRE measure is widely used to compare metals it is not a guarantee of the corrosion performance of any alloy and should only be used as a guide to help the user select potential alloys for further evaluation. There are other parameters that influence the pitting corrosion process and these may play a very significant role as well.

*To illustrate: If **only** pitting of 316L is of concern metals such as Alloy 20 and 825 which may be considered for sulphuric acid service should be overlooked in favour of the duplex range and 254SMO and higher alloy grades if so justified.*

The mechanism for crevice corrosion is closely linked to that for pitting except that for the former initiation occurs in a crevice which may be threaded connections, flange joints, gussets and similar. The PRE number is often used as a gauge for resistance to this form of corrosion as well but again there are standardised test methods to assess resistance to crevice corrosion both on a laboratory scale but also for in-situ testing.

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BRIDGING THE GAP: RESISTANCE TO STRESS CORROSION CRACKING

Stress corrosion cracking is another form of localised corrosion that may take place in chloride containing solutions. There are 3 parameters which, in combination, may give rise to stress corrosion cracking: the one is the environmental parameter and it's the same set of corrosion conditions which result in pitting viz – chlorides / halides, acidic to neutral pH and elevated temperatures.

But importantly a second and overriding parameter needs to also be present and this is a susceptible metallurgical structure. 304L and 316L are most susceptible to this form of corrosion, termed chloride stress corrosion cracking (SCC) whilst Alloy C276 as a nickel alloy may be considered highly resistant. The third factor, a mechanical parameter, is the simultaneous presence of a tensile stress, residual or applied. As can be seen in Fig 3 there is no thinning of the metal. It's a sudden cracking.

Fig. 3 Stress corrosion cracking of 304L

COMMENT:

There are a number of tests used to assess resistance to chloride stress corrosion cracking. They are intended for comparative testing of the metals and vary in severity. Boiling 42% $MgCl_2$ is the harshest of these and was the one used to demonstrate the relationship between the nickel content of stainless steels and the likelihood of SCC. There are tests which are less severe and which may better align with service conditions in a specific application.

The interplay of the 3 parameters as described allow for the prevention of damage by this mechanism by modification of one of these variables. This review has the focus of the metallurgical parameter but it may not be the only one available. It may be possible to change the environment eg treatment to remove the halides or to change the mechanical component by stress relieving or a reduction of operating stress

The high risk grades, 304L and 316L and similar are evident from Fig 4 and if the solution to be followed

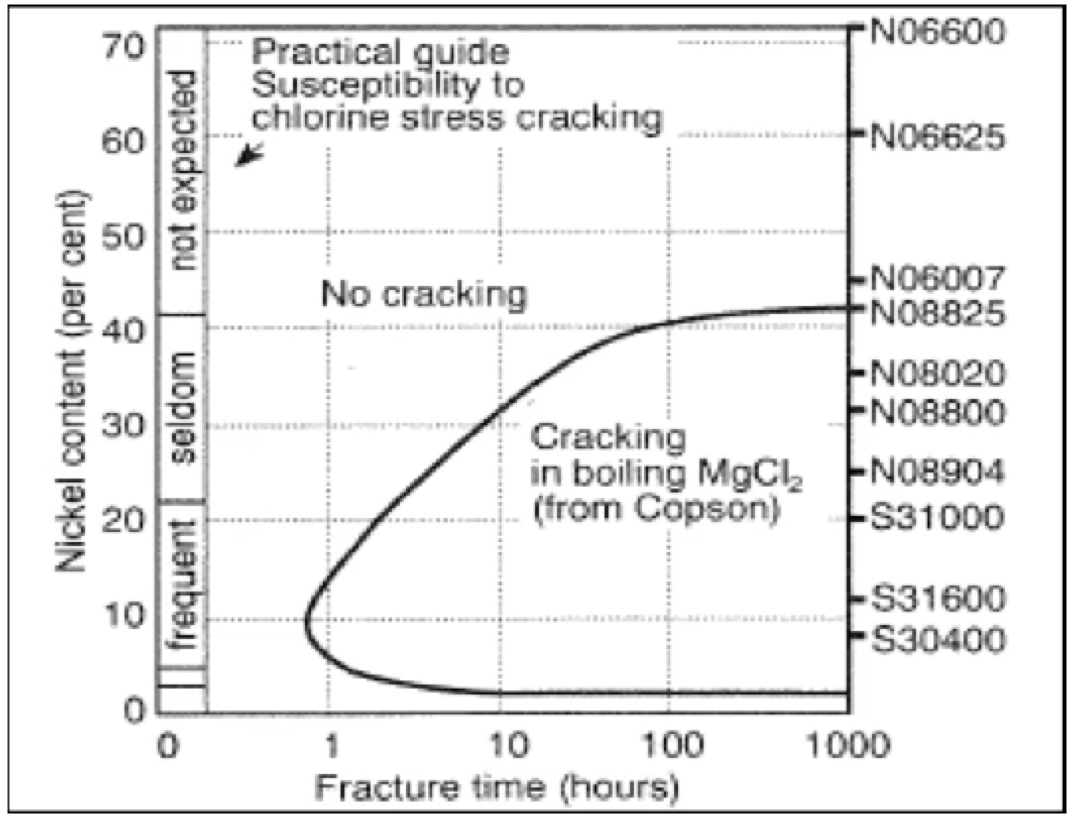
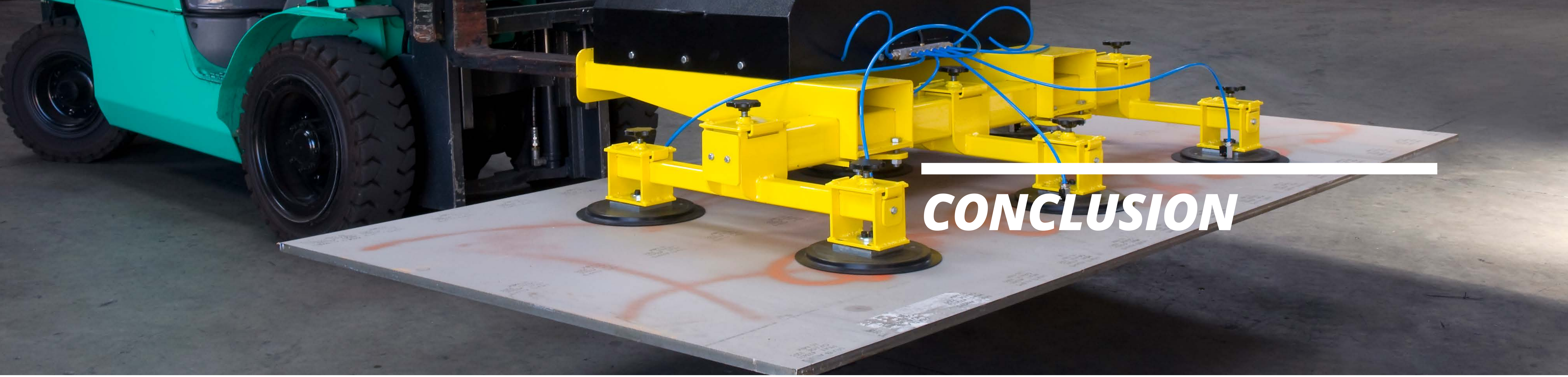


Fig 4 Effect of nickel on resistance t chloride stress corrosion cracking (After Schillmoller and Jasner) (Ref 4)

requires a change of alloy the options may be either lower or higher nickel contents. The duplex stainless steels represent the obvious option in moving in the lower nickel direction. The higher alloyed stainless steel and nickel alloys are the options available if, for other reasons, the problem needs to be addressed by increasing nickel. Importantly both Fig 4 and the statement below indicate that it may be inappropriate to refer to some grades as "immune to stress corrosion cracking" as they may suffer this in harsh conditions.

"The results show that while ferritic, duplex and high performance austenitic stainless steels are not immune under very harsh conditions, such as boiling concentrated magnesium chloride, they withstand stress corrosion cracking under many conditions where conventional austenitic stainless steels are expected to fail"
CORROSION HANDBOOK, 12TH ED, 2023, **OUTOKUMPU**



CONCLUSION

Specifiers and users of corrosion resisting metals may confront material selection decisions when specifying for a new development or when existing materials of construction are inadequate. Of course, in addition to corrosion resistance there are numerous other considerations affecting such decisions (eg mechanical properties) and these may dictate the final selection.

Corrosion is a complex phenomenon with many parameters that may affect it's initiation and progress and thus oversimplifying corrosion resistance is a risk. The atomistic approach taken in this e-book is intended to inform and to illustrate some principles that may assist in identifying a more corrosion resistant alloy than 316L and that is, at the same time not a gross overspecification. Its noteworthy that:

- ***In oxidising conditions the presence of chromium is beneficial.***
- ***In reducing conditions molybdenum and nickel are beneficial.***
- ***Chromium, molybdenum and nitrogen significantly enhance pitting and crevice corrosion resistance.***
- ***304L and 316L and similar austenitic stainless steels have the highest risk of chloride stress corrosion cracking.***
- ***The presence of some copper in the stainless steel or nickel alloy may aid resistance to corrosion by sulphuric acid.***

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MULTI Alloys

CONTACT US

T: + 27 (0) 11 466 2480

F: + 27 (0) 11 466 1692

E: sales@multialloys.co.za

www.multialloys.co.za