Corrosion Performance and Fabricability of the New Generation of Highly Corrosion-Resistant Nickel-Chromium-Molybdenum Alloys

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ABSTRACT

Key to the development of new chemical products and processes is the demand for materials with improved mechanical properties, metallurgical stability and greater corrosion resistance in aggressive environments. In recent years a number of new highly corrosion resistant alloys combining Nickel, Chromium and Molybdenum have been introduced to combat corrosion in aggressive environments in the chemical, pollution control, marine and oil & gas industries.

INCONEL® alloy 686 (UNS N06686) has been developed as a material offering superior general and localized corrosion resistance compared to the more traditionally used alloy C-276 (UNS N01276) and alloy 22 (UNS N06022). The paper presents data on the performance of the material in resisting general acid corrosion, mixed acid media and to localized attack in both acid and seawater environments. Alloy 686 is shown to have good metallurgical stability and can be readily formed and welded. Results are presented comparing the metallurgical stability of the various Ni-Cr-Mo alloys.

Plant operators are also increasingly using INCO-WELD Filler Metal 686CPT as overmatching filler metal for a wide range of nickel alloy based compositions. The versatility of the welding product and the high alloying content has encouraged the use of the material in severe environments where welding consumables of alloy C-276 and alloy 22 have been found to be unsuitable. Data is shown comparing various welding techniques on the corrosion performance of the nickel-chromium-molybdenum alloys. Examples of the successful application of alloy 686 in industrial environments are described.

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INTRODUCTION

For many years corrosion resistant materials such as INCONEL alloy 625 and C-276 have offered excellent corrosion resistance for equipment in chemical, power production, pollution control, marine and similar applications. Key to the development of new chemical products and improved processes is the demand for new materials. This challenge has been met with the development of the latest Nickel - Chromium - Molybdenum materials INCONEL® alloy 686, HASTELLOY® C-2000® alloy and alloy 59 which are increasingly being used to resist corrosion and safeguard product purity in environments, beyond the capability of stainless steels or other materials. These alloys can offer a number of advantages including improved life cycle cost performance, improved reliability, lower maintenance and reduced downtime costs.

The chemical composition of several highly alloyed nickel-chromium-molybdenum alloys are listed in Table 1. Substantial alloying additions of nickel, chromium, molybdenum and other elements are needed for many applications where a high level of corrosion resistance is required. Chromium provides resistance to oxidizing environments while molybdenum improves resistance to reducing environments. A combination of both chromium and molybdenum increases resistance to localized corrosion (pitting and crevice corrosion). Additions of tungsten may also further increase resistance to localized corrosion. Though nickel provides resistance to caustic and mild reducing environments, its main benefit in alloys containing high levels of chromium and molybdenum is to maintain a stable austenitic single-phase structure. This is important in obtaining optimum corrosion resistance in an alloy capable of being economically produced and fabricated.

Table 1. Compositions of the Ni-Cr-Mo corrosion resistant alloys

Alloy	UNS No.	Werkstoff No.	Fe	Ni	Cr	Mo	W or Nb	Cu	PREN*
686	**N06686**	**2.4606**	**1**	**58**	**20.5**	**16.3**	**3.9**	**-**	**50.8**
59	N06059	2.4607	1	59	23	16	-	-	47.0
C-2000	N06200	2.4675	1	57.4	23	16	-	1.6	47.0
22	N06022	2.4602	2.5	59	21.5	13.6	3.1	-	46.6
C-276	N10276	2.4819	6	57	15.5	16	3.9	-	45.4
625	N06625	2.4856	3	62	22	9	3.6#		40.8
C-4	NO6455	2.4611	2	66	16	16	-	-	40.0

PREN = %Cr + 1.5(%Mo + %W + %Nb)
# - Nb

RESULTS AND DISCUSSION

GENERAL CORROSION RESISTANCE

Table 2 shows a review of published data of the corrosion resistance of alloys C-276, 22, 686, 625, 59 and C-2000 and how they vary with acid temperature, concentration and mixture. INCONEL alloy 686 as well as offering improved corrosion resistance can also be seen to offer greater flexibility and versatility in resisting a wider range of conditions than alloys like C-276 and 22. This kind of data is normally used in selecting a material for a particular service environment, which in the case of the Ni-Cr-Mo alloys normally involves a mixture of corrodents or fluctuating conditions between oxidizing and reducing. When comparing alloys for a particular complex service environment it is usually best practice to test the alloy candidates in the operating environment or in a laboratory test that most closely approximates it.

Table 2. General Corrosion Resistance in acid solutions

Test Medium	Temp °C	625	C-276	22	C-2000	59	686
1.5% HCl	Boiling	-	32	14	5	2	2
2% HCl	Boiling	557	43	52	-	-	6
5% HCl	Boiling	-	146	-	161	158	185
10% H_2SO_4	Boiling	-	23	18	-	8	3
80% H_2SO_4	93	-	24	-	47	88	29
90% H_2SO_4	93	-	18	-	15	72	8
85% H_3PO_4	Boiling	-	10	13	-	20	16
65% HNO_3	Boiling	20	888	53	39	38	231
10% H_2SO_4 + 2% HCl	Boiling	-	138	279	0	0	132
10% H_2SO_4 + 5% HCl	80	-	-	82	0	0	34
50%Acetic acid +1% NaCl	Boiling	-	-	0.8	0	0	.4
3% HF	80	38	16	-	-	-	17
10% HF	80	313	28	32	31	-	26
30% HF	80	-	-	-	29	30	24
40% HF + 10% H_2SO_4	80	-	23	18	-	-	22

Values in mpy, convert to mm/y by multiplying by 0.0254
- No data available

LOCALIZED CORROSION RESISTANCE

Localized corrosion attack is one of the most commonly observed failure mechanisms of stainless steels and high Ni-Cr-Mo alloys. This form of localized corrosion attack being generally less predictable than general corrosion and more limiting to a materials performance. A Pitting Resistance Equivalent Number (PREN) can be calculated, using the alloy chemical composition, to estimate relative pitting resistance of alloys. The PREN calculations for each of the Ni-Cr-Mo alloys are shown in Table 1. The standard PREN equation used for stainless steels cannot be used for the more highly alloyed nickel base alloys with the equation that most closely represents the performance of the high Ni-Cr-Mo alloys in the various media examined being:

PREN = %Cr + 1.5(Mo + W + Nb)

Critical Pitting & Critical Crevice Temperatures

The influence of alloying is demonstrated, in Table 3, by the critical pitting and crevice corrosion temperature results using the acidified $FeCl_3$ test solution of ASTM G48. The higher alloyed materials 22, C-2000, 59 and 686 have sufficient alloying to be completely resistant to pitting and crevice attack up to the tes temperature limit of 85C. At higher temperatures the solution becomes chemically unstable and breaks down **(**1).

Table 3. Critical crevice (CCT) and Critical pitting (CPT) temperatures following testing in the ASTM G48 C and D environments of 6%$FeCl_3$ + 1% HCl for 72 hours.

Alloy	CCT (°C)	CPT (°C)
686	**> 85**	**> 85**
59	> 85	> 85
C-2000	> 85	> 85
22	75	> 85
C-276	45	> 85
625	35	> 85
C-4	37	80
25-6MO	30	70
825	5	30
SS 316	< 0	20

Oxidizing Chloride Solution

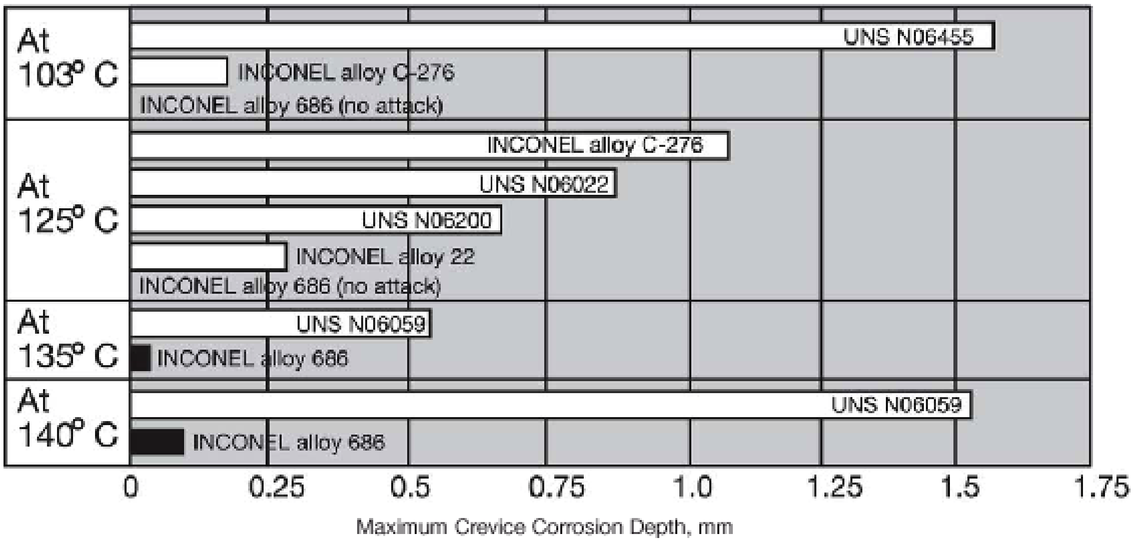
A more aggressive oxidizing chloride environment than the ASTM G48 test is needed to differentiate the effect of alloying on localized corrosion resistance of the latest generation of Nickel alloys. The Green Death solution (11.9% H_2SO_4 + 1.3% HCl + 1% $FeCl_3$ + 1% $CuCl_2$) is commonly used to show the relative resistance of Stainless Steels and Nickel base alloys. Actual maximum crevice corrosion depth of attack and the percentage of sites attacked under multi-crevice washers are shown in Table 4 as a function of temperature.

Table 4. Crevice corrosion resistance for multi crevice specimens tested in green death solution for 24 hours.

Temperature (°C)	Alloy	Max Attack Depth (mm)
103	C-4	1.6
	C-276	0.05
	22	0
125	C-276	1.04
	C-2000	0.508
	22	0.350
	59	0
	686	0
135	C-2000	1.50
	59	0.52
	686	**< 0.025**
140	59	1.51
	686	**0.07**

Figure 1 shows the effect of alloying on maximum crevice corrosion depth for a range of the high Ni-Cr-Mo alloys. Comparison of alloy C-4 and alloy C-276 at 103°C, which have very similar Cr and Mo contents, demonstrates the beneficial effects of alloying with W. At 125ºC alloys C-276, C-2000 and 22 experience significant attack. Alloys 59 and 686 are not attacked at 125ºC but significant attack of the 59 occurs at 135ºC and 140ºC, while the alloy 686 is only slightly affected at these temperatures. At the highest temperature of 140°C the very high localized corrosion resistance of alloy 686 in comparison with alloy 59 also shows the beneficial effect of W.

Figure 1
Crevice Corrosion resistance as a function of temperature in Green Death Solution for 24 hours.



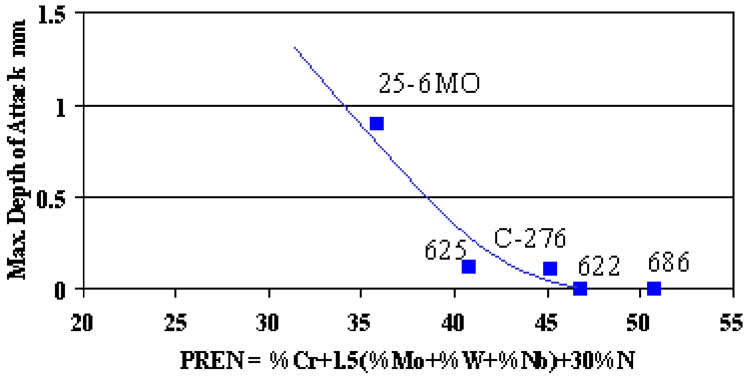
CORROSION RESISTANCE IN SEAWATER

Ambient Temperature

Corrosion rates for the Ni-Cr-Mo alloys in marine environments are very low in flowing and stagnant conditions. The high Nickel alloys are also very resistant to stress-corrosion cracking in waters containing chlorides, which may otherwise affect the lower alloyed 300 series stainless steels.

Nickel alloys with a PREN number greater than 40 are very resistant to crevice corrosion in seawater. However, under very tight crevice conditions, such as in seawater cooled plate heat exchangers which have a multiplicity of very tight crevices, highly alloyed materials like alloys C-276, 22 and 686 are required. Figure 2 shows the maximum depth of attack by crevice corrosion after exposure to quiescent natural seawater at 29°C for 180 days as a function of PREN. Annular crevice washers were used, which have a very severe crevice geometry in order to show the relative performance of these highly alloyed materials. It is important to note that under less severe crevice conditions alloys 625 and C-276 have proved more than adequate for seawater service.

Figure 2
Severe crevice corrosion test results in ambient temperature seawater.



PTFE severe crevice assemblies, 180 days at 29C in quiescent seawater

Weld Overlays in seawater

Alloy 625 with a PREN of greater than 40 is widely used as both a wrought and a weldmetal in resisting seawater attack. This material is commonly used as a weld overlay on carbon steel components as an economical way of improving corrosion performance. However, higher alloyed weldmetals with higher PREN values are also finding applications under some of the more severe seawater service conditions. Table 5 shows results of a comparison between alloy 625 and alloy 686 following exposure in natural seawater at 25°C for 60 days using multi-crevice severe geometry annular washers. Alloy 686 base and weldmetal were found to be completely resistant to the conditions studied, while alloy 625 and the matching filler metal showed crevice attack. In these tests the as-cast structure of the as-welded alloy 625 showed less resistance than the wrought alloy.

Table 5. Crevice corrosion behavior of weld metal deposits compared with the wrought material in natural seawater at 25°C for 60 days using a severe geometry annular crevice washer.

Alloy	Condition	No. of sites attacked/ No of sites available	Max. depth of attack (mm)
INCONEL alloy 686	Wrought	0/6	0
INCO-WELD 686CPT filler metal	Weldmetal	0/6	0
Alloy C-276 (UNS N10276)	Wrought	1/4	0.02
INCONEL alloy 625	Wrought	2/6	0.11
INCONEL 625 filler metal	Weldmetal	1/2	0.49

High Temperature Seawater

Crevice corrosion tests of a number of materials have been conducted in high temperature natural seawater at 60°C for 60 days under nominally stagnant conditions **(2)**. The test medium was chlorinated with 1 to 2ppm free chlorine to simulate service conditions normally employed in offshore oil and gas industry seawater service. The results from these tests are shown in Table 6. All of the materials examined were found to be resistant to general seawater corrosion and to pitting attack, however only alloy C-276, 22 and 686 showed no evidence of crevice attack under these conditions.

Table 6. Crevice corrosion data for duplicate specimens exposed to natural seawater at 60°C for 60 days with 1 to 2ppm free chlorine. Acrylic washers were torqued to 75 in.-lbs

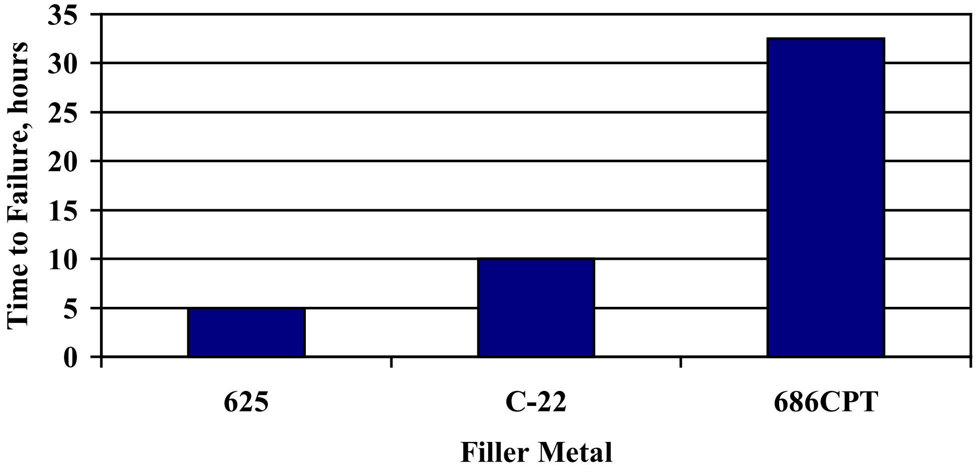
Alloy	Corrosion rate (mm/y)	Max crevice depth (mm)
26-6MO	0	0.075 / 0.075
625	0	0.013 / 0.050
C-276	0	0 / 0
22	0	0 / 0
686	0	0 / 0

Sulfide Stress Cracking Resistance

Sulfide Stress Cracking is considered to be the most severe form of hydrogen embrittlement in the Oil and Gas industry. In general, resistance to stress corrosion cracking (SCC), hydrogen embrittlement (sulfide stress cracking, SSC), increases with increasing nickel, chromium, molybdenum, tungsten and niobium content. Alloy 686, as one of the more recently developed materials is resistant to hydrogen embrittlement in the NACE International TM0177 sulfide stress-cracking test and is listed in the NACE MR0175 document " Standard material requirements – Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment". The maximum permitted hardness for solution annealed and cold worked alloy 686 is 40 HRc compared with alloy C-276 in the same condition, which is approved to 35 HRc.

Corrosion testing of INCO-WELD Filler Metal 686CPT weld overlays has been carried out in simulated oilfield environments using severe conditions that cause general, pitting and crevice corrosion as well as chloride and sulfide stress corrosion cracking. Historically, INCONEL filler metal 625 has been widely used in this type of environment. Figure 3 compares the performance of weld overlays of high Ni-Cr-Mo alloys. The performance is rated in hours to failure for the various weld overlays in a very sour free sulfur containing environment of 25%NaCl + 0.689MPa H_2S + 1.724 Mpa CO_2 + 1 g/liter S at 232°C. INCO-WELD Filler metal 686CPT is shown to offer significantly more resistance to sulfide stress corrosion cracking than other Ni-Cr-Mo filler metals **(3).**

Figure 3
Time to failure in SSR tests in a 25% NaCl + 0.689 Mpa H_2S + 1.724 Mpa CO_2 + 1g/liter S environment at 232°C



THERMAL STABILITY

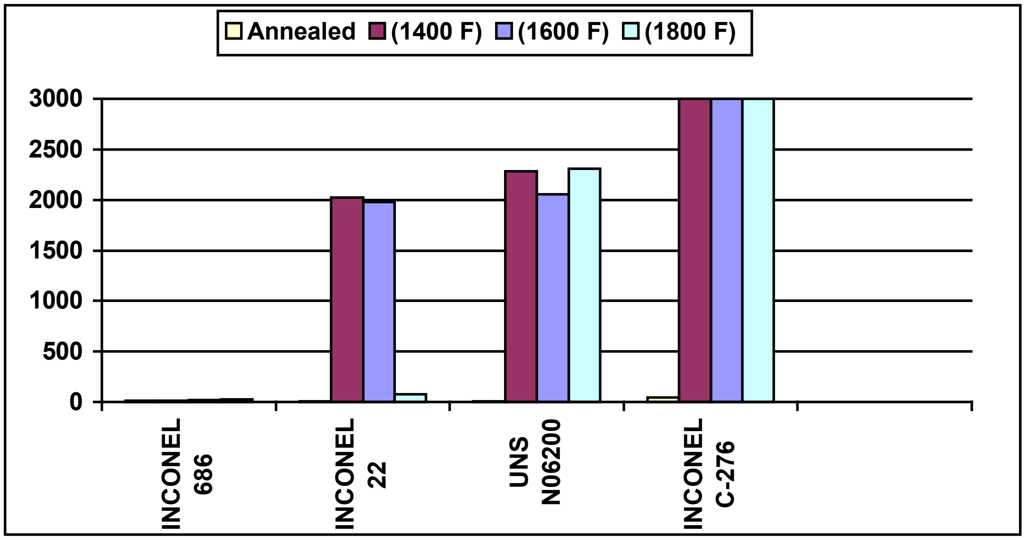
The Ni-Cr-Mo alloys are generally designed to be used in aqueous environments at temperatures up to around 500°C; however, the material may be subjected to high temperatures during welding or possible heat treatment operations of components or vessels where resistance to intergranular attack (IGA) in service can become an important selection issue. High temperature phase formation following welding operations or incorrect heat treatment can lead to accelerated attack, particularly along the grain boundaries, and this phenomenon is known as sensitization.

The ASTM G-28, Method A (600 ml 50% H_2SO_4 + 25g $Fe_2(SO_4)$ 3.H_2O boiling for 24 hours) intergranular corrosion test was developed as a quality control tool to verify that Ni-Cr-Mo alloys have received the proper annealing heat treatment. Base acceptance levels are established for each alloy in Table 7 based on general corrosion rates. Corrosion test rates higher than these values indicate an inadequate or improper heat treatment as a result of accelerated grain boundary attack.

The ASTM G28, Method B test (23% H_2SO_4+ 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$ at boiling temperatures for 24 hours) was developed in the 1970's to detect susceptibility to intergranular attack more accurately than Method A for alloy C-276 and comparable alloys, as the high general corrosion rates of method A masks the initial effects of sensitization. The method B environment being more sensitive to sensitization as the general corrosion rates are significantly lower.

Figure 4 shows microstructural stability of the materials following heating samples for one hour within the sensitization range of the alloys. The test is designed to simulate worst-case conditions during a welding operation of very thick plate material. Alloys C-276, 22 and C-2000 all show the effects of sensitization following this treatment. Alloy 686 and alloy 59 show significantly higher resistance to sensitization than the other materials studied. The low iron content of less than 1%, very low carbon content and a controlled Ti/C ratio help to optimize the stability of alloy 686 and achieve the highest possible alloying of Cr, Mo and W. **(4).**

Figure 4
Effect of heat treatment on resistance of sensitization in ASTM G28, B (24 hr) test.



WELDING

The presence of welds in fabricated components introduces special corrosion considerations and the weld metal can often be a limiting feature in comparison to the base metal in terms of resistance to severely corrosive environments.

Welding of test samples in this study was conducted by Gas Metal-Arc Welding (GMAW) by either spray or pulsed transfer mode and by Gas Tungsten-Arc Welding (GTAW). Welded specimens were tested in the as-welded condition and surface finish, unless otherwise noted. In evaluation of welds made on solid alloy sheet [approximately 0.062" (1.6 mm) thickness] or plate [approximately 0.250" (6.4 mm) thickness], the maximum depth of attack in the base metal or weld metal is reported.

EFFECT OF WELDING ON CORROSION RESISTANCE

Thermal Stability of Welds

In highly oxidizing environments intergranular corrosion of sensitized weld or base metals may result. ASTM G-28, A and B test results for various sheet and plate base metal/weld metal combinations made by two different welding process are shown in Table 7. In ASTM G-28, A only alloy C-276 exhibited evidence of heat affected zone (HAZ) attack in these as-welded specimens. The overall higher corrosion rate for alloy C-276 in this test was typical, and is due to the alloy's relatively low chromium content. In the ASTM G-28, B test severe intergranular weld attack occurred in some cases for C-276 when welded with matching filler metal. This attack was reduced when the overmatching welding product 686CPT was used.

Table 7. Intergranular corrosion test results for welded 6.4mm plate using different base/weld metal combinations.

Base metal	Filler metal	GTAW		GMAW-P	
		G-28A mm/y	G28B mm/y	G-28A mm/y	G28B mm/y
C-276	C-276	8.4**	1.4	12.3**	45.0*
C-276	686	7.9**	1.9	10.7**	4.1
22	22	1.4	0.4	3.3	5.2*
22	686	1.8	0.4	3.6	2.0
686	686	2.3	0.6	2.5	0.5

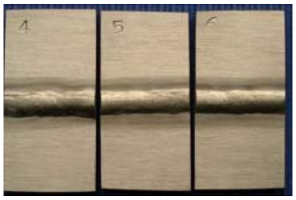
* Accelerated weld attack ** Slight heat affected zone attack

Overmatching Filler Metal

A weld is a small casting and in the unworked condition has a coarse grain dendritic structure with microsegregation of elements through the structure. The detrimental effect of segregation occurs during any fusion welding process. Either autogenous welds or welds made with "matching composition" filler metal will have less corrosion resistance than the base metal. In most applications it is not practical to post weld anneal or cold work and anneal welded structures. In this case the best way to produce a weld with corrosion resistance equal to or better than the base metal is to use an "over matching" filler metal. This concept has been used for some time with austenitic and duplex stainless steels to prevent weld attack 5,6,7. The matching welding product INCO-WELD Filler Metal 686CPT offers an optimum solution to corrosion with the same highly alloyed composition as the matching base material. When pitting

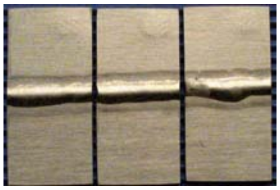
The results of pitting tests in the “Green Death” environment are shown for welded specimens in Figure 5. Welds made on alloys C-2000, 59, 22, C-22, and C-276 base metals using matching composition filler metals were found to pit severely while alloy 686 showed no attack except for pits found on one of the alloy C-22 welded samples. Over matching alloy filler metal 686 welds on the same base metals, however, were found to be resistant to attack. The same beneficial effect of the overmatching filler metal is shown for alloys C-2000 and 59 base metals welded with filler metal 686. Optimum pitting resistance would be realized by use of both alloy 686 base metal and filler metal. The filler metal 686 welding product has the same composition as the base metal. This welding product is more resistant to pitting attack than matching composition filler metals of alloys C-276, C-22, C-2000 and 59.

Figure 5
Welding coupons exposed to boiling green death solution for 72 hours.



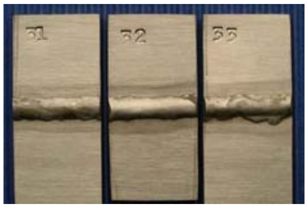
INCONEL alloy 686 w/INCO-WELD Filler Metal 686CPT

Hastelloy alloy C-2000 w/matching filler metal

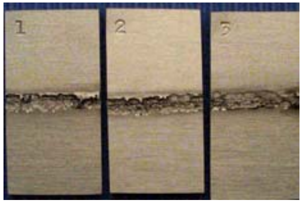


Hastelloy alloy C-2000 w/INCO-WELD Filler Metal 686CPT

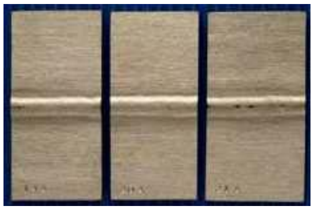
*VDM alloy 59 w/ Matching filler Metal



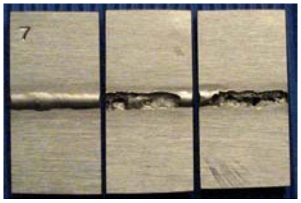
VDM alloy 59 w/INCO-WELD Filler Metal 686CPT



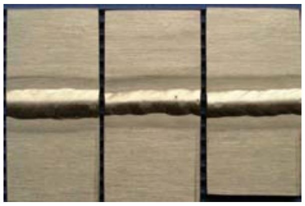
INCONEL alloy C-276 w/Matching filler metal



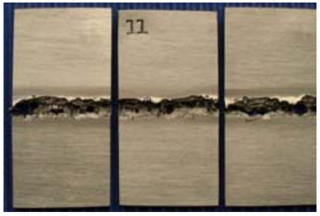
INCONEL alloy C-276 w/INCO-WELD Filler Metal 686CPT



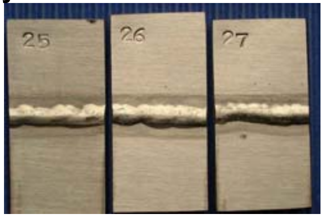
INCONEL alloy 22 w/ Matching filler metal



INCONEL alloy 22 w/INCO-WELD Filler Metal 686CPT



Hastelloy alloy C-22 w/ Matching filler metal



Hastelloy alloy C-22 w/INCO-WELD Filler Metal 686CPT

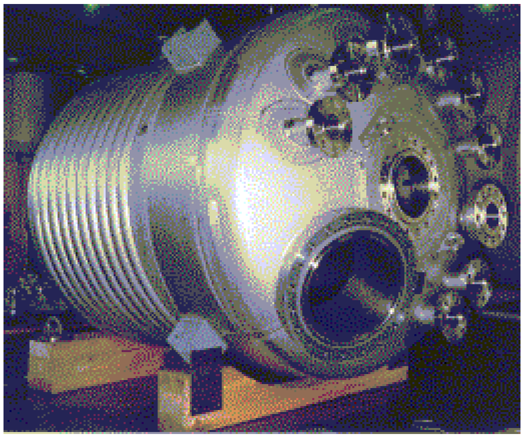
* VDM, is a registered trademark of Krupp VDM.

PLANT PERFORMANCE

Plant designers have become increasingly aware of the higher corrosion resistance of the new generation of Ni-Cr-Mo alloys in a range of aggressively corrosive environments where it is critical to avoid repair of equipment because of operating efficiency or hazardous service issues. The applications of the materials given below demonstrate the materials versatility in resisting aggressive service environments.

INCONEL alloy 686 is used in pharmaceutical production processes requiring resistance to Halogen base catalysts and flexibility to resist batch oxidizing or reducing media, while maintaining product purity. Figure 6 shows a multi-purpose pharmaceutical plant vessel manufactured from 40mm thick alloy 686 plate material. The Tungsten content in alloy 686 was found to be beneficial in resisting microfissuring of the weld metal of the thick plate section when compared with other Ni-Cr-Mo alloys.

Figure 6: Multi-purpose pharmaceutical vessel manufactured in 40mm thick INCONEL alloy 686



Welded tubing in alloy 686 was selected for the closed loop heat transfer system at the VEAG power station at Boxberg in Germany. The system is required to perform in an environment with chlorides, fly ash and sulfuric acid that tests had revealed was too aggressive for lower alloyed C-276 and C-22 compositions.

Alloy 686 has also been used in the handling and manufacture of Hydrofluoric acid. In one case using fluorspar and sulfuric acid to produce HF, alloy C-276 was corroding at a rate of 8mm per month while alloy 686 showed no significant level of attack.

Plate heat exchangers, handling 33% caustic soda and cooled with water containing chlorine and high levels of oxygen, have been manufactured in alloy 686 due to its high general and localized corrosion resistance in devices that contain a multiplicity of tight crevices and where product purity is of very high importance.

INCO-WELD Filler Metal 686CPT has been used to weld overlay carbon steel sour gas wellhead equipment in the North Sea. Alloy 686 was chosen in preference to alloy 625 as the field was a deepwater development requiring very high integrity from the materials used.

CONCLUSIONS

1. Alloy 686 shows good general and localized corrosion resistance in both the base and weld metal.

2. The inherent lower corrosion resistance Ni-Cr-Mo or Ni-Cr-Mo-W alloy weld metal, as compared to the matching composition base metal, can be compensated for by use of an overmatching filler metal such as filler metal 686.

3. The above corrosion and welding advantages represent significant fabrication cost savings as well as reliability improvements for plant and equipment exposed in aggressive environments.

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