HASTELLOY® C-22HS®: A NEW RISING MATERIAL FOR THE OIL & GAS INDUSTRY

Matteo Bosatra
Fondinox S.p.A.

INDUSTRIALVALVESUMMIT

Summary

- Hastelloy® C-22HS®: Introduction and overview
- Properties for forged and rolled products
- Properties for castings:
    - Tensile
    - Impact
    - Microstructure
    - Corrosion
- Conclusions and future trends

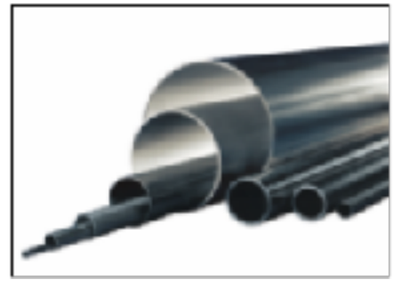
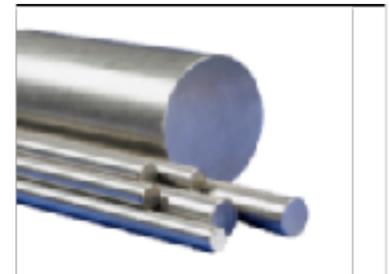
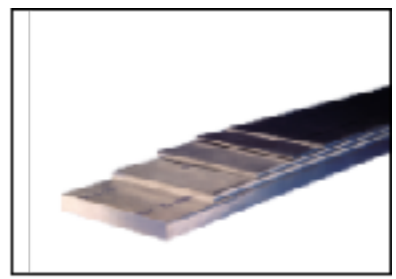
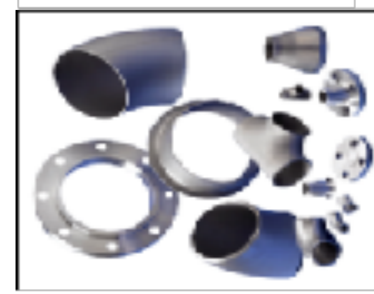
Introduction

HASTELLOY® C-22HS® is one of the most promising Ni-Cr-Mo corrosion resistant alloys for Oil&Gas industry use developed by Haynes International Inc. While the chemistry and corrosion resistance is comparable to that of the most performing among Hastelloy® C-Family alloys, its mechanical strength is almost double of “C-type” alloys in the aged condition with no decrease of its corrosion resistance performance and impact toughness.

- High mechanical strength
- High corrosion resistance: general in oxidizing and reducing media, localized, SCC

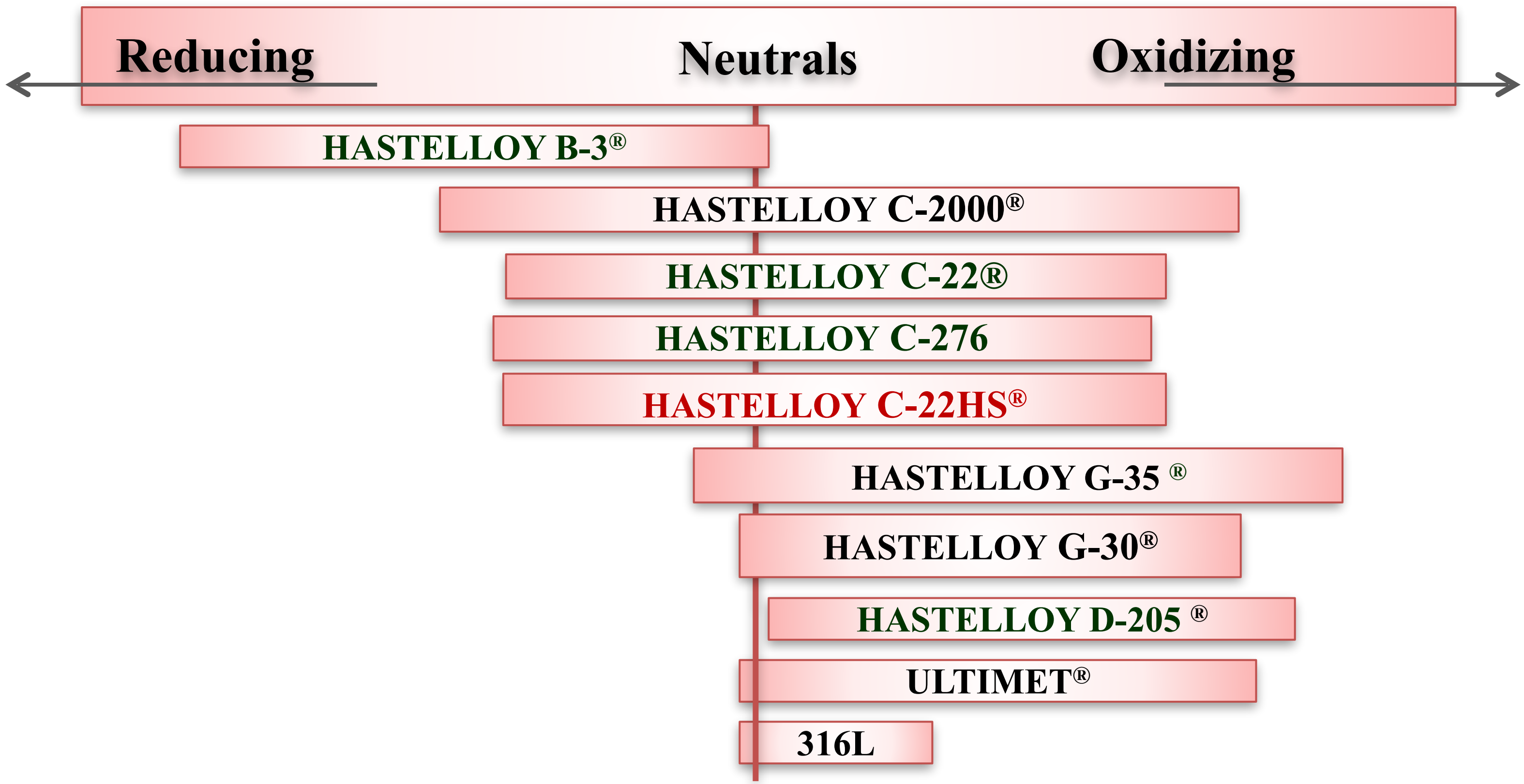
Products form

- Excellent formability and castability: plate, sheet, strip, billet, bar, wire, pipe, tube and castings.
- Suited for any equipment or component intended for sour environments in oil and gas production: hangers, packers, valve stems and tubulars used in wellhead, downhole equipments, Christmas trees, side pocket mandrels and oil country tubular goods.
- Ready for the market and NACE/ISO approved for long and flat products, under development for cast products, which can be produced in the form of valves, pumps, centrifugally cast tubes and flanges.

Hastelloys: overview

In addition to its high uniform corrosion resistance in oxidizing as well as reducing environments, the as-heat treated C-22HS alloy possesses high resistance to chloride-induced pitting and crevice corrosion attack.



INDUSTRIALVALVESUMMIT

C22HS®: Features

Almost all of the Ni-base superalloys which possess high strength also at very high service temperatures are strengthened by Ni_3M type γ' and γ'' phases such as $Ni_3(Al,Ti)$ and $Ni_3(Nb,Ti,Al)$. In some applications the alloy is required to possess both high temperature strength and high corrosion resistance

This new alloy, Ni-21Cr-17Mo, is actually on the base of the ternary Ni-Cr-Mo system. This alloy has corrosion resistance comparable to the well-known HASTELLOY® C-22 alloy and is designed to facilitate the $Ni_2(Cr,Mo)$ precipitation (Figure 1) which promote a sharp strength increase in the aged condition.

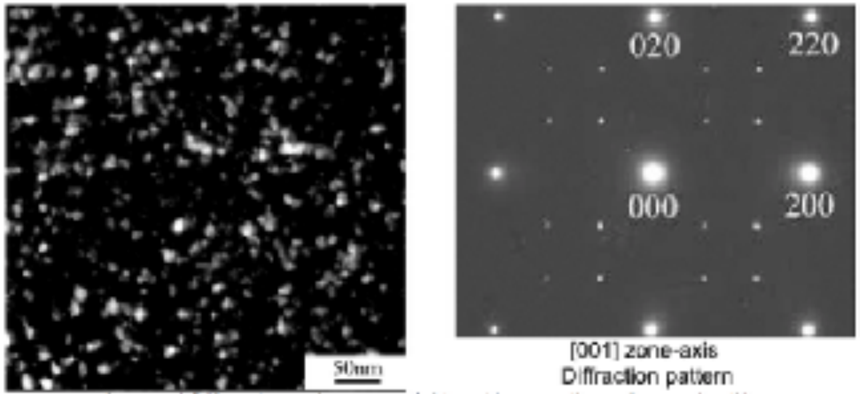


Figure: TEM image and SAD pattern of Ni_2(Cr, Mo) long range ordered particles at heat treated condition (aged)

C22HS®: Features

Early testing of C-22HS® alloy was focused on material in the annealed + age-hardened condition whereas the material was annealed at 1079°C and age-hardened at 705°C/16h/FC to 605°C/32h/AC. In this "standard condition" C-22HS® alloy will typically have strengths around 100 ksi (690 MPa). While this strength level is almost double of "C-type" alloys in the annealed condition, many Oil&Gas applications require even greater strength. For this reason, a considerable development effort has been generated on C-22HS® alloy in three other "very high strength" conditions:

1) Cold Worked

2) Cold Worked + Age-Hardened

3) Low Temperature (LT) Annealed + Age-Hardened

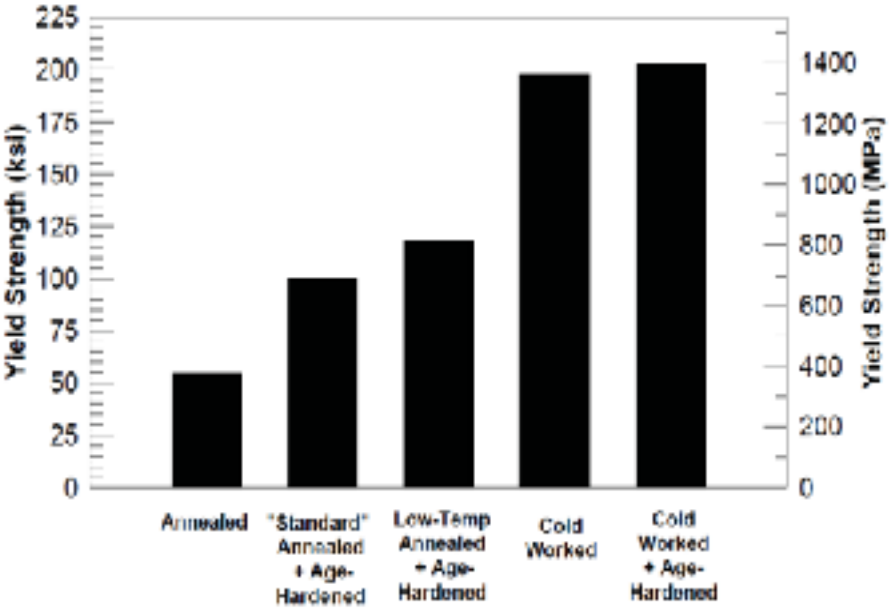


Figure: comparison of yield strengths for the three very high strength conditions is shown below along with that of the annealed and "standard" conditions.

C-22HS®: suitable for foundry process

The lack of cast nickel-based corrosion resistance alloys with high mechanical strength to be used in the Oil&Gas industry has suggested the possibility to reproduce this chemistry also in foundry practice; considering that the only way to obtain an higher strength to a solution annelaed casting is to age hardening the material, being the primary solidification structure also the final one with no changes due to thermo-mechanical processes.

C-22HS®	C	Mn	Si	P	S	Mo	Fe	Ni	Cr	W
Hot rolled products	≤0,01	≤1,0	≤0,08	≤0,025	≤0,025	15,5 - 17,4	≤2,0	Bal	20,2 - 21,4	≤1,0
Castings	≤0,02	≤1,0	≤0,8	≤0,025	≤0,025	15,5 - 17,4	≤1,8	Bal	20,2 - 21,4	≤0,8

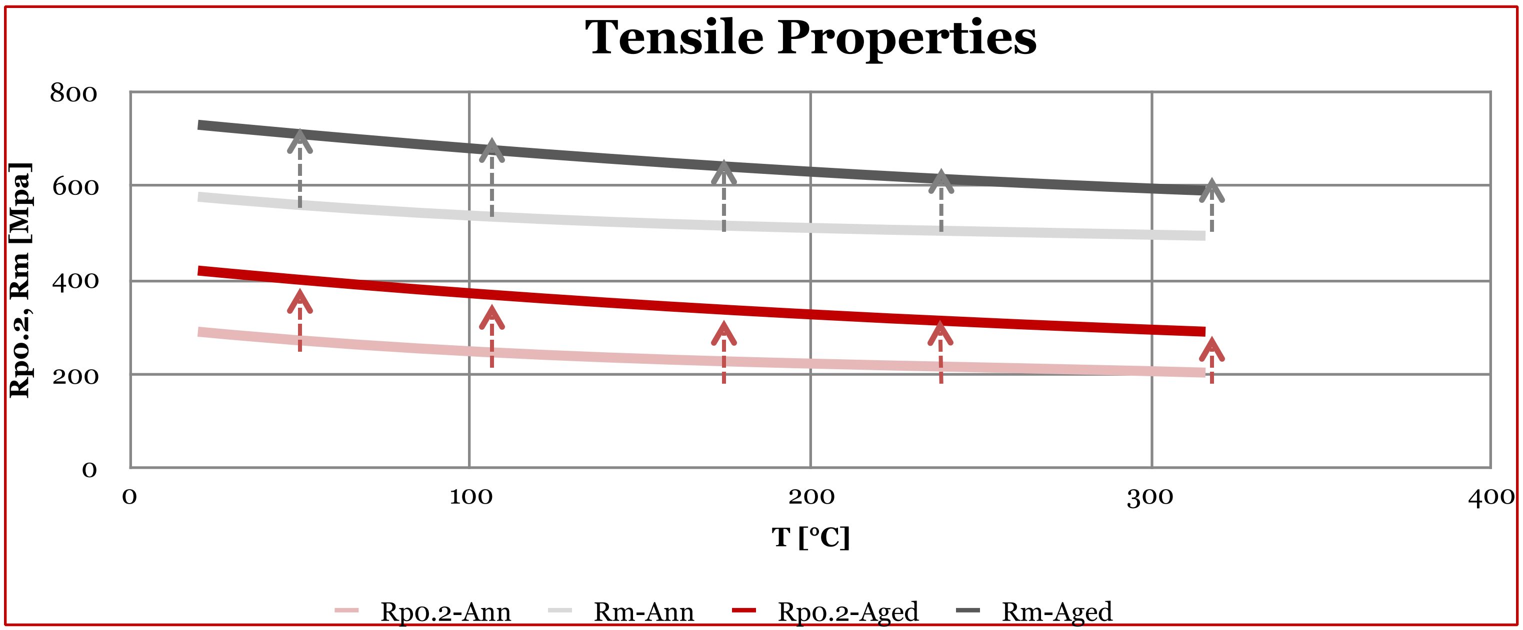
Cast C-22HS®: properties

A test campaign has been carried out in order to evaluate the mechanical behavior and corrosion resistance of C-22HS® cast alloy before and after the ageing heat treatment. Test block models with different wall thicknesses were cast to study the effect of the solidification rate on the final characteristics of the alloy.

Fondinox requested the assistance of Haynes to determine a suitable heat treatment that could be applied to as-cast C-22HS® material. Testing was initiated at Haynes in order to develop a solution annealing and age-hardening heat treatment for C-22HS® cast material that could be suitable applied to the slightly different chemical composition of the cast version of the alloy. Microstructures and phases have been evaluated with the help of Politecnico di Milano.

Tensile properties

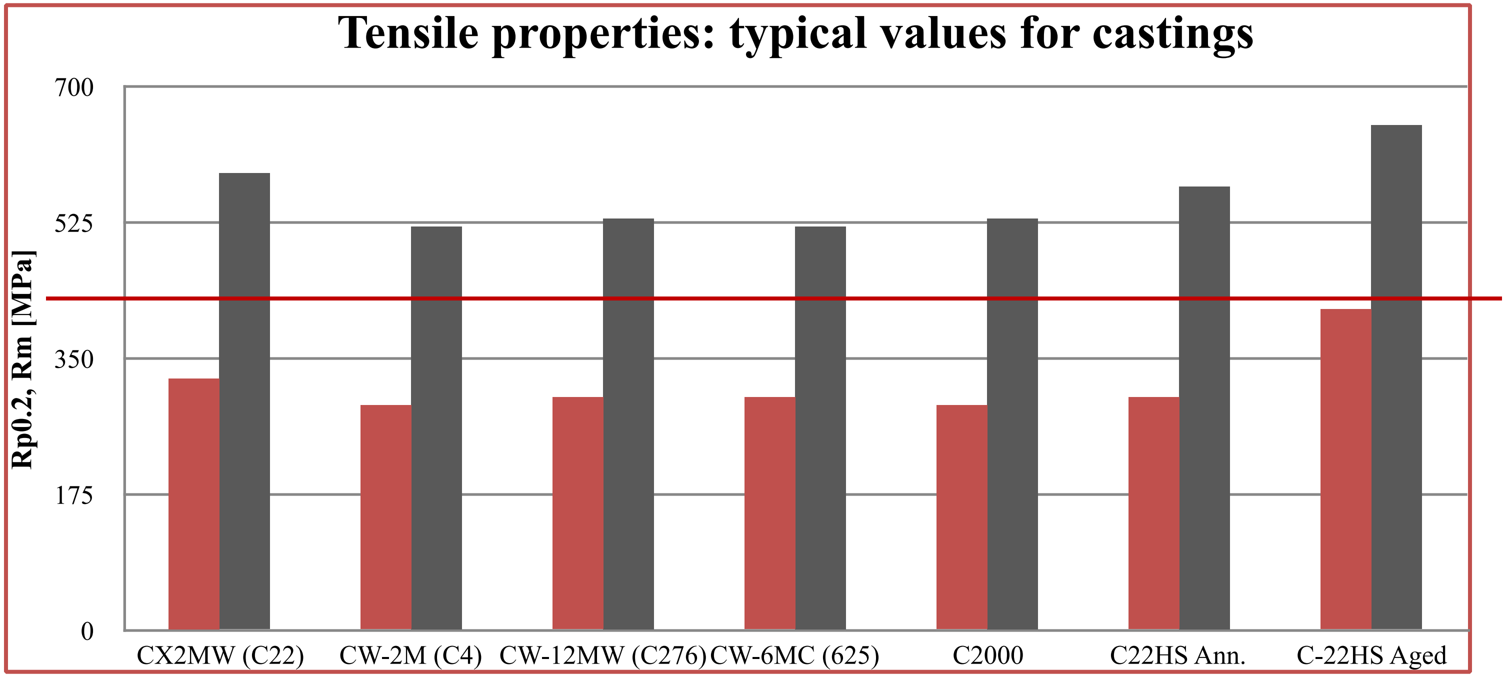
The aged condition show the increase in the UTS associated with a decrease in elongation and reduction of area. Due to the formation of $Ni_2(Mo,Cr)$ nanoprecipitates scattered in the matrix, the mechanical resistance sharply increases and the yield strength becomes 50% higher than in the solubilized condition.



INDUSTRIALVALVESUMMIT

Tensile properties

Tests carried out on cast C-22HS® samples in the solution annealed condition confirms that the alloy has mechanical properties comparable with those of the C-family alloys (C276, C4, C22) and cast 625, with an elongation at 20°C which remains at very high values



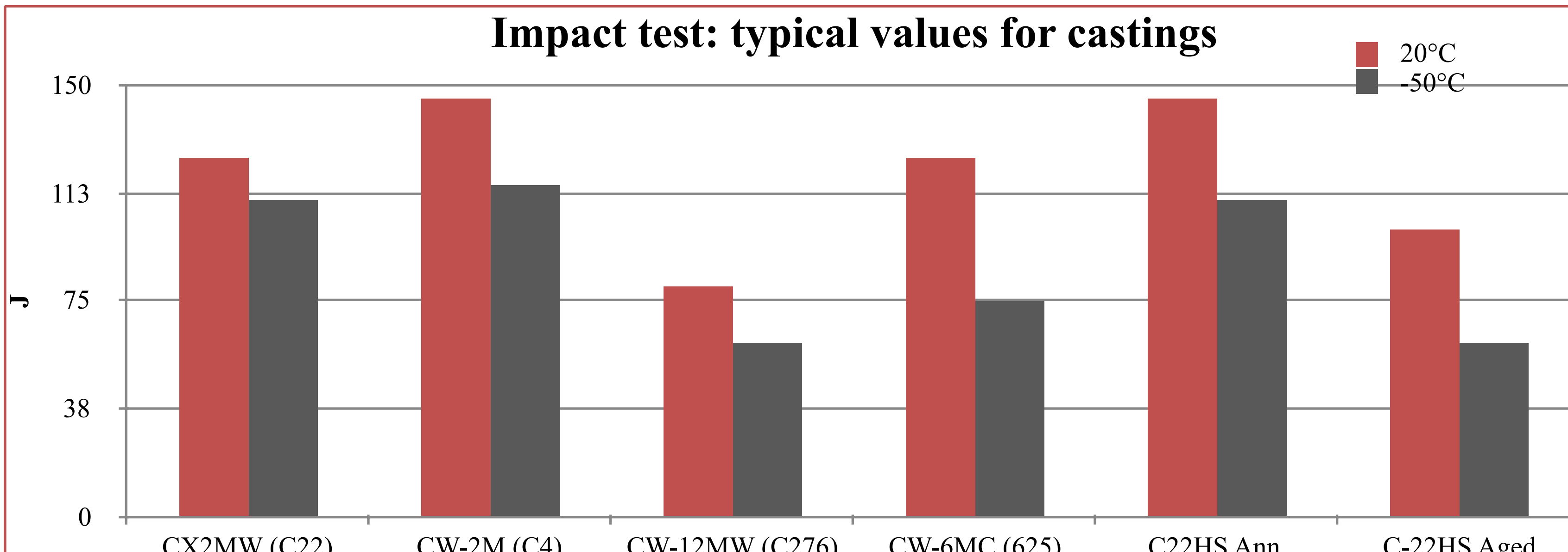
Impact testing

Solution annealed material shows high levels of toughness; in the aged condition impact properties remain above limits imposed by Norsok at -46°C

1" (25.4mm) Diameter Bar, 44% Cold-Worked (CW)

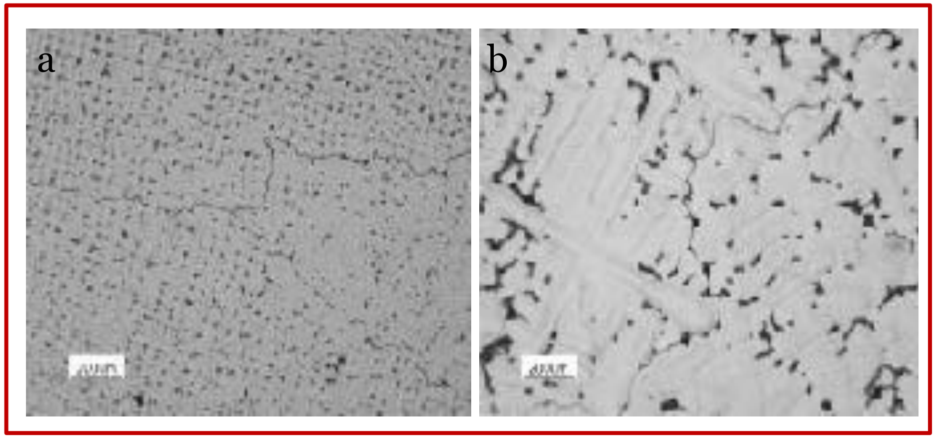
Temperature	LT Anneal – Age-Hardened (ft-lbf)	LT Anneal – Age-Hardened (J)	Cold-Worked (ft-lbf)	Cold-Worked (J)	Cold-Worked + Age-Hardened (ft-lbf)	Cold-Worked + Age-Hardened (J)
RT	75	102	146	198	121	168
-75°F (-59°C)	67	91	153	207	125	169
-320°F (-196°C)	54	73	113	153	102	138

*Average of two tests, all samples were longitudinal



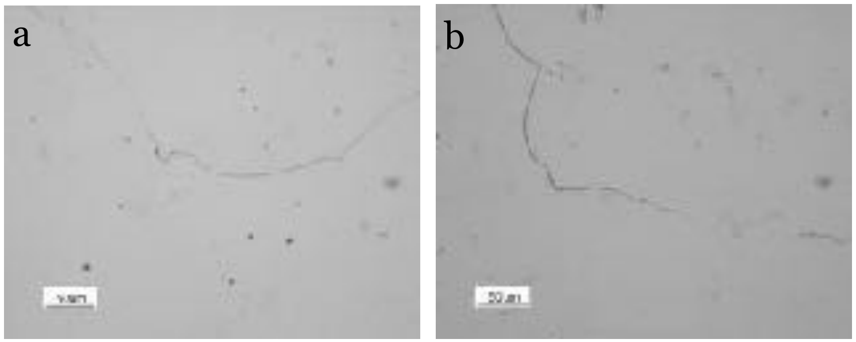
Metallographic examination

Microstructure of cast C-22HS has been analyzed at optical microscope and SEM

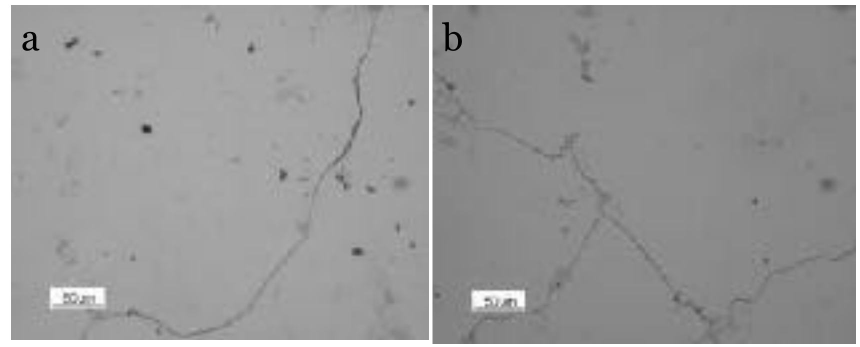


In the "as-cast" condition, the abundant presence of heterogeneously distributed precipitates in the metal matrix is due to the strong segregation behavior of the alloying elements rejected from the solid phase during the solidification process, especially at very high thicknesses (b, 100mm).
The increase in Si concentration with respect to the wrought version makes the alloy more prone to develop precipitation of the intermetallic phases.

Metallographic examination

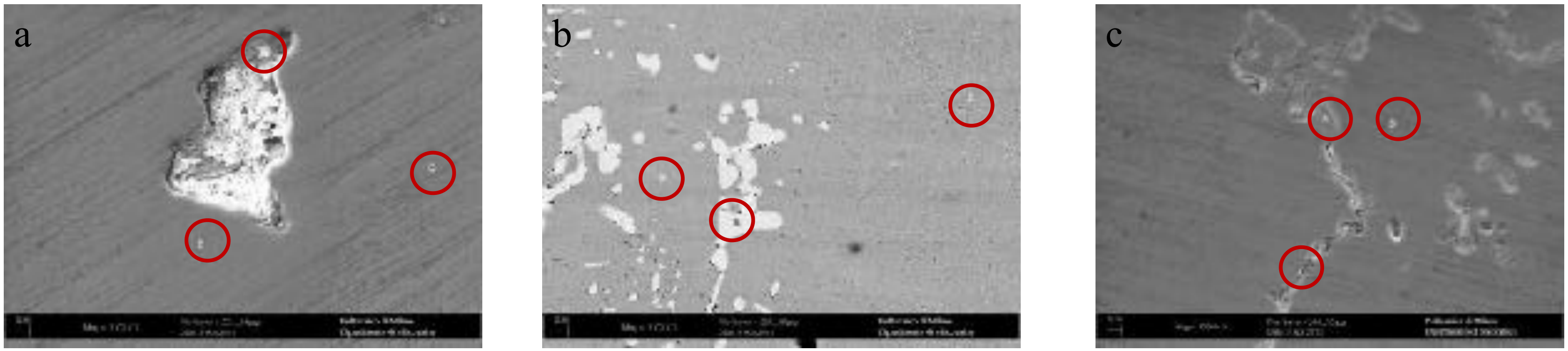


After solution annealing treatment (a 10mm - b 100mm) the microstructure shows absence of interconnected intermetallic compounds or grain boundaries precipitates and carbides. The metal matrix is not featured by the presence of the precipitates aside from the thickest samples where the very slow cooling rates allowed the nucleation of phases enriched in Mo and Si



Also after aging heat treatment (a 10mm – b 100mm) the microstructure shows absence of interconnected intermetallic compounds or grain boundaries precipitates and carbides, meaning that the tailored heat treatment has no influence on precipitation of detrimental phases.

Metallographic examination



SEM-BSE micrographs : (a) as-cast 10mm thk, (b) solution-treated 100mm thk step, (c) aged 100mm thk step.

Figure	Si	Cr	Mn	Fe	Ni	Mo
7a_Matrix	1.11	19.68	0.52	1.32	60.04	17.31
7a_A	3.32	13.89	0.51	0.33	36.11	45.83
7a_B	1.50	19.30	0.62	1.13	56.99	20.45
7a_C	1.03	19.62	0.47	1.23	60.76	16.90
7b_Matrix	0.50	20.94	0.36	1.93	59.01	17.25
7b_A	3.65	12.72	0.17	0.60	24.71	58.16
7b_B	0.54	20.66	0.78	1.93	56.07	20.05
7b_C	0.65	20.32	0.48	1.73	56.07	20.75
7c_Matrix	0.55	20.49	0.41	1.88	59.39	17.29
7c_A	4.00	12.69	0.18	0.53	25.30	57.32
7c_B	0.55	20.85	0.46	1.71	56.08	20.35
7c_C	1.55	24.96	0.49	1.46	43.89	27.65

EDS Analysis

The precipitates formed in C22-HS alloy (Figure a,b,c) are enriched by Si, and a significant chemical difference is pointed out in Si concentration between the metal matrix and the precipitates (from 1% in the metal matrix and 3% in the precipitates). Moreover, in the same samples, a decrease in Cr concentration has been observed as a function of the heat treatment and of the step thickness.

INDUSTRIALVALVESUMMIT

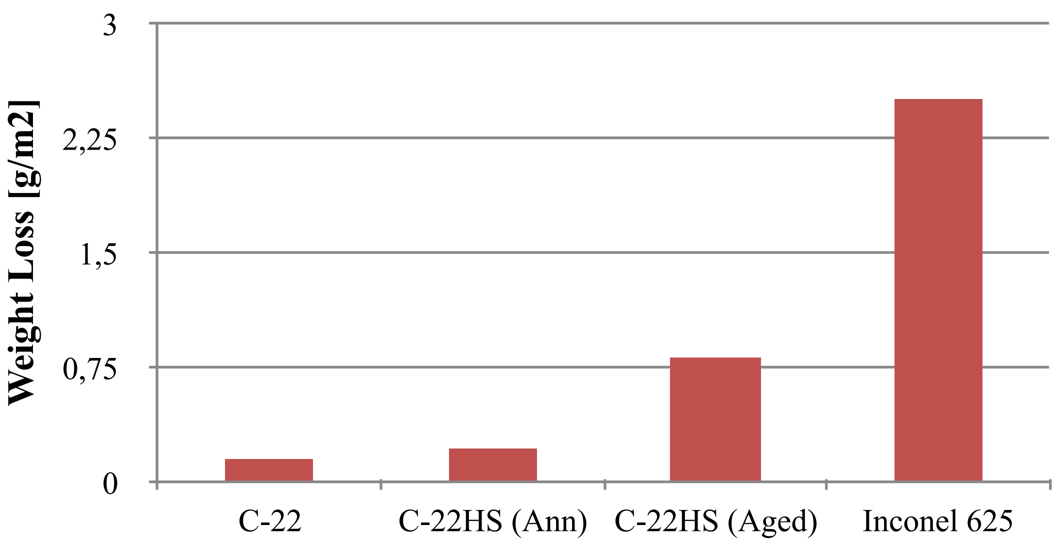
Corrosion resistance

Samples were corrosion tested to estimate their aqueous corrosion resistance The corrosion environment was selected as 20% HCl at 100°F (38°C) for 96 hours, measured every 24 hours. It was suggested that this aqueous corrosion solution would be able to provide the sensitivity necessary to differentiate the samples based on subtle differences in microstructure. The corrosion resistance of wrought C-22HS® alloy was viewed as the benchmark to which cast material in the heat treated condition would be evaluated; a corrosion rate in the vicinity of that for wrought C-22HS® alloy would be considered acceptable.

CONDITION	Hardness HRB	Hardness HRC	Corrosion Rate MPY (mm/yr)
WROUGHT MILL ANNEALED (MA)	90		5.8 (0.15)
WROUGHT MA + AGE-HARDENED		30	8.8 (0.22)
AS-CAST +			8.5 (0.22)
2275F/30MIN/WQ	81.5		7.65 (0.19)
2100F/24HR/WQ	---		8.2 (0.21)
2275F/30MIN/WQ +			
AGING 1	96.7		10.3 (0.26)
AGING 2	97.0		10.0 (0.25)
AGING 3	97.1		6.8 (0.17)
AGING 4	91.7		6.85 (0.17)
AGING 5		28.7	8.75 (0.22)
AGING 6		25.4	9.7 (0.25)
AGING 7		21.6	8.55 (0.22)
2100F/24HR/WQ +			
AGING 1	101.2		12.25 (0.31)
AGING 2	96.1		9.9 (0.25)
AGING 3	95.2		6.05 (0.15)
AGING 4	93.9		6.65 (0.17)
AGING 5	95.7		7.45 (0.19)
AGING 6	93.1		6.55 (0.17)
AGING 7	97.6		6.15 (0.16)

Corrosion resistance

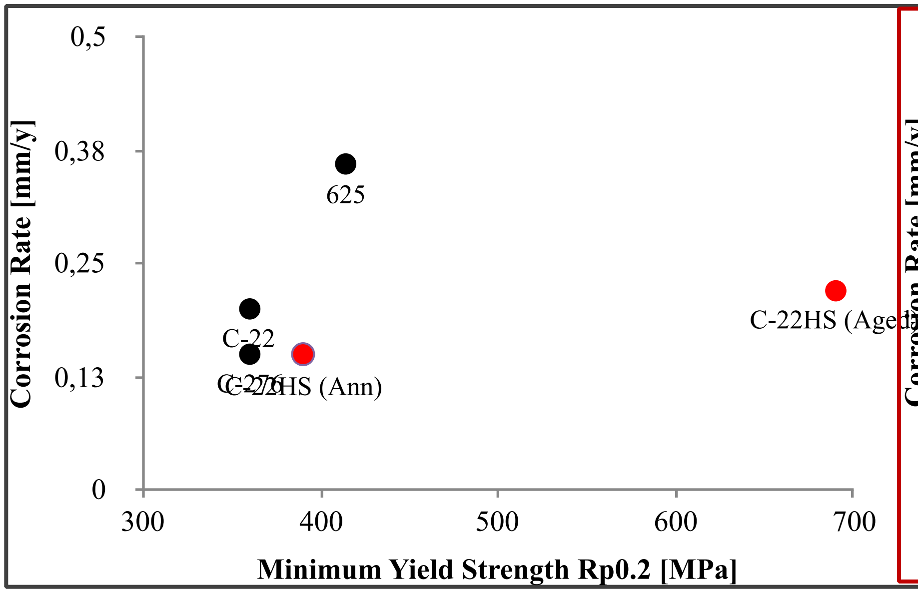
Localized corrosion of cast solution annealed and aged samples is superior compared to cast Inconel 625, due to the less presence of segregations and intermetallic compounds typical of 625 structure. The presence of Niobium in Inconel 625 promotes the formation of carbides and intermetallic compound (Laves phase) which, even in small amounts, worsen the localized corrosion resistance.



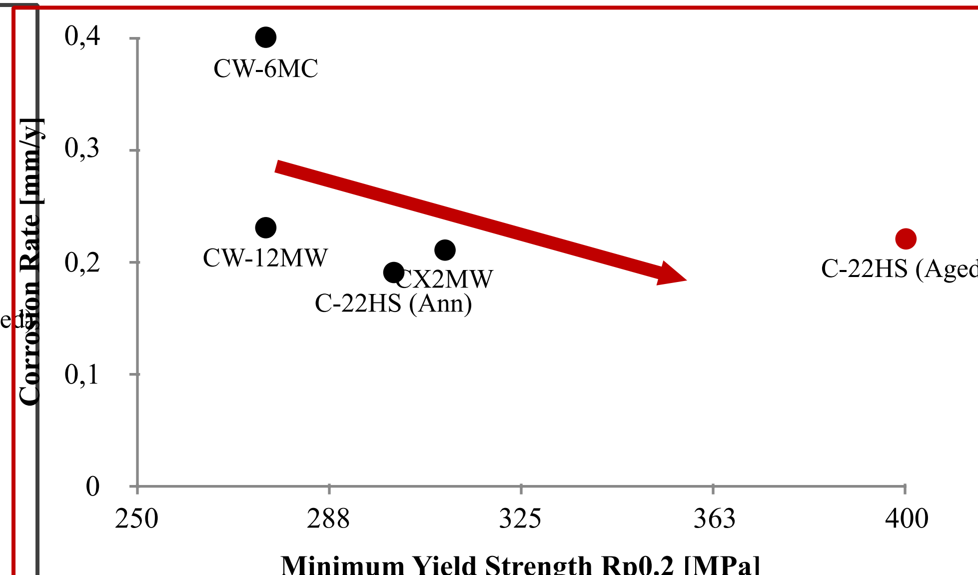
ASTM G48 Met. A: 6%FeCl3 solution, 50°C, 24h

Wrought C-22HS has been tested and approved according to:
- NACE TM0177 Test Levels II and III, Method A, Soultion A, Applied Stress = 100% YS
- NACE TM0198 Slow Strain Rate Tensile, Level VII, With Elemental Sulfur
- C-Ring, Test Level VII, 1 g/L Elemental Sulfur, Applied Stress = 100% YS

Tensile VS Corrosion resistance: comparison



Wrought alloys



Cast alloys

Tests: conclusions and future trends

Aging heat treatment has an effect also on cast structure, increasing the mechanical strength by 1.5 times respect to that of solution annealed condition and maintaining an outstanding corrosion resistance

Due to segregation tendency during solidification chemistry of cast components and their solidification process must be kept under control in order to avoid massive precipitations of intermetallic compounds;

Localized corrosion of solution annealed cast products is comparable to that of the other C-family alloys, and in the aged condition is superior to that of cast UNS N06625

A test campaign to evaluate other aqueous corrosion environment performances will be carried out.

Conclusions

C-22HS® has been developed, tested and put on the market in the form of plates, bars and sheets and is suitable for Oil&Gas and Subsea applications, where very aggressive environments and very high mechanical strength are required;

C-22HS® has corrosion resistance typical of C-Family Hastelloy® alloys but can reach very high levels of strength, typical to that of high temperature service superalloys, in the aged or cold rolled + aged conditions;

C-22HS® has been produced and tested also in the cast form and has been found to possess in the aged condition an outstanding corrosion resistance combined to very high mechanical strength which makes the material a very good alternative to the most diffused Inconel 625 in the Oil&Gas and Subsea services.

IVS
INDUSTRIALVALVESUMMIT