A NEW HIGH STRENGTH CORROSION RESISTANT ALLOY FOR OIL AND GAS APPLICATIONS

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ABSTRACT

A new Ni-base precipitation strengthened alloy is developed to provide 125 ksi minimum yield strength and an excellent combination of ductility and impact strength. Further, testing in various NACE environments (namely level V and VI) has shown that the alloy has excellent Stress Corrosion and Sulfide Stress Corrosion resistance. A number of commercial heats are melted and processed to establish robust processing. This paper will illustrate alloy development methodology, heat treatment to obtain the target properties, mechanical properties, microstructure, and corrosion properties.

Keywords: Ni-based, Alloy 945, sour environments, precipitation hardenable, high strength,

INTRODUCTION

Material selection is especially critical for sour gas wells -- those containing H_2S (1,2). These wells operate at a high temperature of up to 232°C and may also contain free sulfur. Additionally, these wells generally contain high levels of chlorides and CO_2. Combinations of this type of corrosive media require special care to design an alloy.

Nominal composition of newly developed alloy 945 is Fe-47Ni-20.5Cr-3Mo-2Cu-3Nb-1.5Ti. The relative concentrations of Fe-Ni-Cr-Mo-Cu determine overall corrosion resistance in oil and gas applications. A minimum of 42Ni is needed for aqueous stress corrosion cracking (3) and higher Ni content increases the cost of raw materials. Molybdenum is beneficial for pitting corrosion resistance in reducing acids and alkalies (4). Chromium improves general corrosion resistance in oxidizing media (4). Too high concentrations of Mo and Cr lead to structural instability (5). Copper is found to be beneficial for general corrosion in non-oxidizing corrosion environments. A synergistic affect of Cu and Mo is recognized for countering corrosion in reducing acidic environments which are rich in chlorides (6). Nb and Ti are of course added for precipitation strengthening (7).

Data in the literature shows that alloy 925 has superior corrosion resistance to alloy 718 in certain oil patch environments (8). However, the yield strength capability of alloy 925 is lower than that of alloy 718 (9). The aim of the project was to develop a hybrid of alloys 925 and 718, which has best of both the alloys -- higher strength capability and excellent corrosion resistance.

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ALLOY DEVELOPMENT

The initial development phase consisted of vacuum induction melting of 50 lbs (22 Kg) laboratory heats. These heats were homogenized in the temperature range of 2100°F-2200°F (1149°C-1204°C) and hot-rolled in the temperature range of 1900°F-2100°F (1038°C-1149°C). Subsequently, the billets were annealed in the temperature range of 1900°F-2050°F (1038°C-1121°C) and age hardened in the temperature range of 1150°F-1400°F (621°C-760°C). The heats that showed potential were tested for tensile, impact, hardness, and microstructure. To begin with, a thermodynamic equilibrium based model was used to simulate potential chemical compositions. Table 1 shows selected laboratory scale compositions out of over 100 laboratory heats evaluated in this program.

The S2 series heats containing higher Ti showed a lot of potential to strengthen the material but the addition of Ti degraded microstructural stability. The S3 series containing higher Al decreased the yield strength. Further, higher Al led to higher inter-granular carbide precipitation, which is not desirable for oil and gas applications. Synergistic increase of Nb and Al in S4 heats increased the hardness but decreased the yield strength. Modeling showed that this synergistic increase in Nb and decrease in Ti compared to alloy 925 is required to increase strength and maintain thermal stability, Figure 1.

After optimizing the chemical composition at laboratory scale, three commercial heats of over 50,000lbs (22000 Kg) were melted and re-melted by different melt processes. Melt / re-melt methods used were Electric Arc Furnace (EAF) + Argon Oxygen Decarburization (AOD), vacuum induction melting (VIM), vacuum arc re-melting (VAR) and electroslag re-melting (ESR). The ingots produced by various melt methods were rolled or forged in the temperature range of 1900°F-2100°F (1038°C-1121°C)

MECHANICAL PROPERTIES AND MICROSTRUCTURE

Hot rolled bars were annealed at 1900°F (1038°C) for one hour and water quenched. Then, the material was two step aged as follows: 1325°F (718°C) - 8h, furnace cool at 100°F (56°C) / h to 1150°F (621°C), hold at 621°C - 8h, air cool. Alloy 945 met the target mechanical properties, Table 2. The yield strength was in the range of 133 ksi (917 MPa) to 142 ksi (980 MPa) . The impact strength in the transverse orientation was in the range of 55 to 62 ft-lbs. Impact strength was evaluated at –75°F (23°C). Swab etching by Kallings reagent (10ml Methanol + 5gm Cupric Chloride + 100ml Hydrochloric acid) was found to be suitable to reveal the microstructure of alloy 945. An optical photomicrograph revealing single phase, twinned, equi-axed microstructure is shown in Figure 2. The age hardening treatment precipitates sub-micron $Ni_3(TiAl)$-type gamma prime and $Ni_3(NbTi)$-type gamma double prime phases, which are responsible for higher strength.

CORROSION TESTING

Stress Corrosion Cracking (SCC)

Corrosion testing in MR0175 / ISO 15156-3 (10) NACE level VI and level V were performed on triplicate C-ring specimens for 90 days on three mill heats at 100% of actual yield strength. Testing was done as per TM0177-2004 method C – standard C-ring test. Table 3 shows mechanical properties of the heats tested in this program. The yield strength was in the range of 134 ksi (920 MPa) to 141 ksi (972 MPa) and the hardness was in the range of 42Rc to 43Rc. Specimen dimensions and testing conditions for NACE levels VI and V are given in Tables 4 and 5. No failure was detected on visual observations at 20X, Tables 4 and 5. The samples did show some discoloration.

Galvanically induced Hydrogen Stress Cracking (GHSC)

To fulfill NACE MR0175 / ISO 15156-3: 2003 ballot procedure, triplicate samples of three heats of alloy 945 were tested for 30 days with 90 % of the actual yield strength in acidified NACE solution A at 75°F (24°C). Testing was carried out in accordance with TM0177 - 2004, method A – Tensile tests. Specimen dimensions are given in the table. The samples were coupled to carbon steel via the stressing bolts. No failures were detected on visual observation at 20X, Table 6. The samples did show some discoloration.

Sulfide Stress Cracking (SSC)

Sulfide stress corrosion cracking testing was done on triplicate samples of three heats in acidified NACE solution A at 75°F (24°C) for 30 days using method A (tensile test) in accordance with TM0177-2004. The samples were stressed to 90% of the actual yield strength. Sample dimensions are given in the table. No failures were detected on visual observations at 20X, Table 7. The samples did show some discoloration.

SUMMARY AND CONCLUSIONS

In conclusion, a new alloy is developed for oil and gas applications using thermodynamic modeling and multiple iteration of 22 Kg laboratory heats. The new alloy was scaled up to three 50,000 lbs (22, 000 Kg) mill heats. The material was rolled/forged, annealed + aged, and tested for mechanical and corrosion properties. The material is capable of 125 ksi (862 MPa) min yield strength with excellent ductility and toughness. The alloy passed complete set of corrosion testing required to qualify for NACE approval as per MR0175 / ISO 15156-3. This included SCC in NACE level VI, GHSC, and SSC corrosion testing.

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Table 1. Chemical compositions of the laboratory heats (wt%).

Alloy	Fe	Ni	Cr	Mo	Cu	C	Al	Nb	Ti
Alloy 718	Bal	54	18.5	3.2	-	0.015	0.55	5.0	1.0
Alloy 925	Bal	42.3	20.3	3.2	2.0	0.014	0.2	0.3	2.3
S2-A	Bal	42.5	20.6	3.4	1.7	0.013	0.4	0.3	**2.5**
S2-B	Bal	42.5	20.8	3.4	2.1	0.015	0.4	0.3	**3.0**
S2-C	Bal	42.8	20.4	3.4	1.8	0.021	0.4	0.3	**3.4**
S3-A	Bal	45.0	20.6	3.2	2.0	0.006	**0.6**	0.3	2.3
S3-B	Bal	47.4	20.4	3.2	1.9	0.007	**0.8**	0.3	2.3
S3-C	Bal	46.1	20.5	3.2	2.0	0.005	**1.0**	0.3	2.3
S3-D	Bal	48.0	20.5	3.2	2.0	0.005	**1.2**	0.3	2.3
S4-A	Bal	45.5	20.5	3.3	2.0	0.009	**1.0**	**1.0**	2.3
S4-B	Bal	48.8	20.5	3.3	2.1	0.008	**1.0**	**1.0**	2.3
Alloy 945	Bal	47	20.5	3.3	2.0	0.010	0.2	**3.0**	**1.5**

Table 2. Mechanical properties of annealed + aged alloy 945. YS, UTS, EL, and RA stands for yield strength, tensile strength, elongation, and reduction-of-area respectively. Tensile and hardness testing were done at room temperature. Impact testing was done at –75°F(-23°C) and the reported values are the averages of three data points. The impact strength of the rods larger than 3” (76.2) mm diameter were determined in the transverse orientation.

Rod Size, inch (mm)	Melt Method	YS, ksi (MPa)	UTS, ksi (MPa)	% El	% RA	Impact, Strength ft-lbs (Joules)	Hardness, Rc	Grain Size, ASTM #
1” (25)	VIM +VAR	133.4 (920)	173.2 (1194)	27.8	48.0	76 (103)	40	2
2” (51)	VIM +VAR	132.5 (914)	170.2 (1174)	28.2	47.6	70 (95)	40	3
3.5” (89)	VIM +VAR	135.5 (934)	172.0 (1186)	25.5	40.5	58.2 (79)	43	2
4.5” (114)	VIM +VAR	134.2 (925)	168.6 (1163)	28.6	46.7	62 (84)	42	2.5
6” (152)	VIM +ESR	141.0 (972)	176.0 (1214)	22.0	34.6	55.3 (75)	42	2.5
12” (305)	EAF + AOD + VAR	142.3 (981)	171.7 (1184)	26.3	43.6	61.2 (83)	40	2
Min Target		125 (862)	-	18	25	54	-	-

Table 3 Mechanical properties of the heats used for NACE MR0175 / ISO 15156-3: 2003 qualification.

Heat No.	Yield Strength ksi (MPa)	Ultimate Tensile Strength, ksi (MPa)	Elongation (%)	Reduction of Area (%)	Hardness, Rc
0019PY-12	135.5 (920)	172.0 (1186)	25.5	40.5	43
0019PY-11	134.2 (925)	168.6 (1163)	28.6	46.7	42
0022PK-1	141.0 (972)	171.7 (1184)	22.0	34.5	42

Table 4. C-ring test results in NACE MR017 / ISO 15156 - 3 level VI. Testing was done in accordance with NACE TM0177-2004, method C - C Ring tests. The dimensions of the samples were: 2 inch (51 mm) OD, 0.15 inch (3.8 mm) wall thickness, 0.95 inch (24.1 mm) width. The environment was 3500 kPa (508 psia) H_2S, 3500 kPa (508 psia) CO_2, 20 wt% (121300 mg/l Cl) NaCl, at 175°C (347°F). The applied stress was 100% of the actual yield stress

Sample	Applied Stress *, ksi (MPa)	Results
0019PY-12 (1)	135.5 (920)	No failure, 90 days
0019PY-12 (2)	135.5 (920)	No failure, 90 days
0019PY-12 (3)	135.5 (920)	No failure, 90 days
0019PY-11 (1)	134.2 (925)	No failure, 90 days
0019PY-11 (2)	134.2 (925)	No failure, 90 days
0019PY-11 (3)	134.2 (925)	No failure, 90 days
0021PK-11 (1)	141.0 (972)	No failure, 90 days
0021PK-11 (2)	141.0 (972)	No failure, 90 days
0021PK-11 (3)	141.0 (972)	No failure, 90 days

Table 5. C-ring test results in NACE MR017 / ISO 15156 - 3 level V. Testing was done in accordance with NACE TM0177-2004, method C - C Ring tests. The environment was 700 kPa (101 psia) H_2S, 700 kPa (101 psia) CO_2, 15 wt% (91000 mg/l Cl) NaCl, at 150°C (302°F). The dimensions of the samples were: 2 inch (51 mm) OD, 0.15 inch (3.8 mm) wall thickness, 0.95 inch (24.1 mm) width. The applied stress was 100% of the actual yield stress

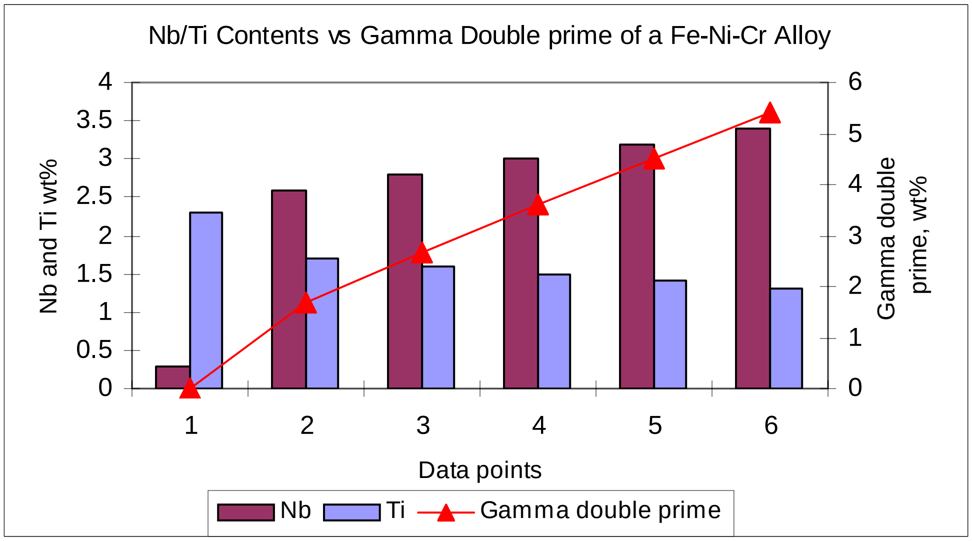
Sample	Applied Stress, ksi (MPa)	Results
0019PY-12 (1)	135.5 (920)	No failure, 90 days
0019PY-12 (2)	135.5 (920)	No failure, 90 days
0019PY-12 (3)	135.5 (920)	No failure, 90 days
0019PY-11 (1)	134.2 (925)	No failure, 90 days
0019PY-11 (2)	134.2 (925)	No failure, 90 days
0019PY-11 (3)	134.2 (925)	No failure, 90 days
0021PK-11 (1)	141.0 (972)	No failure, 90 days
0021PK-11 (2)	141.0 (972)	No failure, 90 days
0021PK-11 (3)	141.0 (972)	No failure, 90 days

Table 6. Galvanically - induced Hydrogen Stress Cracking, GHSC test results. Testing was done in accordance with TM0177-2004, method A - Tensile test, in NACE solution A at 75°F (24°C). The samples were coupled to Steel via the stressing bolt. Samples were nominally of diameter 0.15 inch (3.8 mm) and gauge length 1 inch (25.4 mm). The applied stress was 90% of the actual yield stress.

Sample	Applied Stress	Results
0019PY-12 (1)	122.0 (828)	No failure, 30 days
0019PY-12 (2)	122.0 (828)	No failure, 30 days
0019PY-12 (3)	122.0 (828)	No failure, 30 days
0019PY-11 (1)	120.8 (833)	No failure, 30 days
0019PY-11 (2)	120.8 (833)	No failure, 30 days
0019PY-11 (3)	120.8 (833)	No failure, 30 days
0021PK-11 (1)	126.9 (875)	No failure, 30 days
0021PK-11 (2)	126.9 (875)	No failure, 30 days
0021PK-11 (3)	126.9 (875)	No failure, 30 days

Table 7. Sulfide Stress Cracking (SSC) testing was done in accordance with TM0177-2004, method A - Tensile test, in NACE solution A at 75°F (24°C). Samples were nominally of diameter 0.15 inch (3.8 mm) and gauge length 1 inch (25.4 mm). The applied stress was 90% of the actual yield stress

Sample	Applied Stress, ksi (MPa)	Results
0019PY-12 (1)	122.0 (828)	No failure, 30 days
0019PY-12 (2)	122.0 (828)	No failure, 30 days
0019PY-12 (3)	122.0 (828)	No failure, 30 days
0019PY-11 (1)	120.8 (833)	No failure, 30 days
0019PY-11 (2)	120.8 (833)	No failure, 30 days
0019PY-11 (3)	120.8 (833)	No failure, 30 days
0021PK-11 (1)	126.9 (875)	No failure, 30 days
0021PK-11 (2)	126.9 (875)	No failure, 30 days
0021PK-11 (3)	126.9 (875)	No failure, 30 days



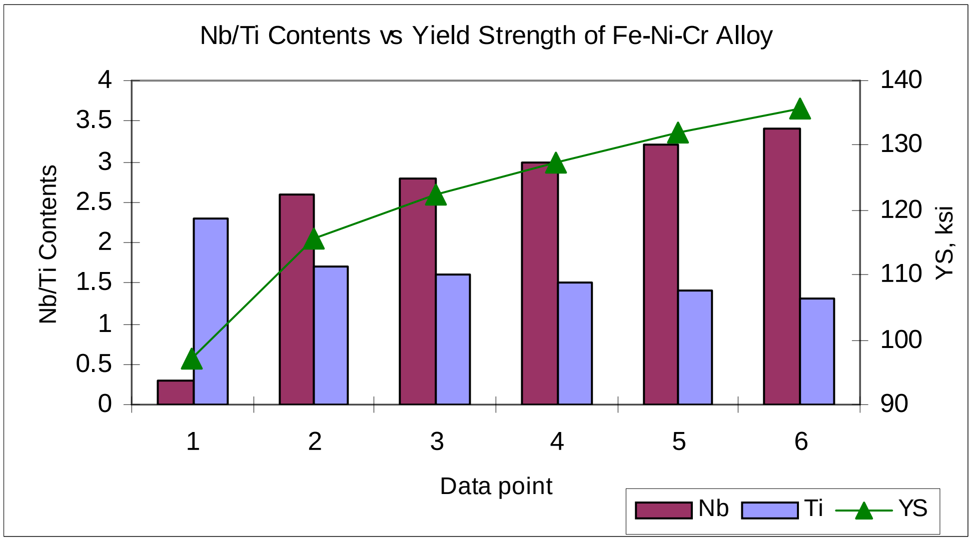


Figure 1. Thermodynamics modeling showing gamma double prime and yield strength variations in alloy 945.

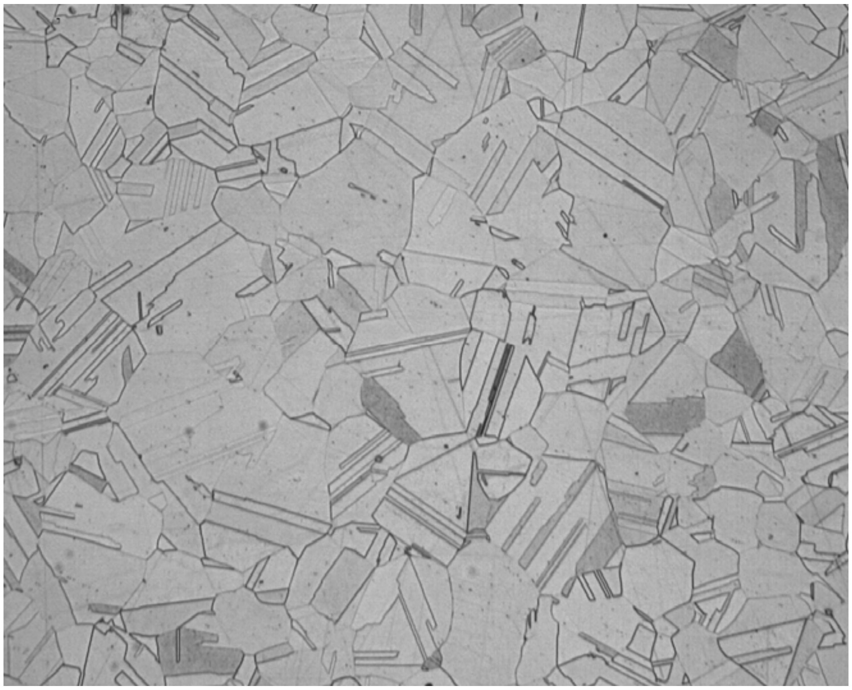


Figure 2. Optical photograph of alloy 945, Magnification = 100X.