

# A NEW NI-BASE SUPERALLOY FOR OIL AND GAS APPLICATIONS

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## Abstract

A new Ni-base precipitation strengthened alloy has been developed to provide 860 MPa minimum yield strength and an excellent combination of ductility and impact strength. Testing in various corrosive environments has shown that the alloy has excellent stress corrosion and sulfide stress corrosion resistance. A number of commercial heats were melted and processed to establish robust mill processing practice. This paper will talk about the overall alloy development methodology including heat treatment studies to optimize microstructure and target mechanical and corrosion properties to obtain the most cost effective solution to the needs of the oil and gas (O&G) industry.

## Introduction

As older shallow and less corrosive O&G wells deplete, higher strength and more corrosion resistant materials are needed to enable deeper drilling into more corrosive environments. The commonly used Ni-base superalloys 718 and 925 do not always offer an adequate combination of strength and corrosion resistance hence the need to develop a new alloy.

Material selection is especially critical for sour gas wells -- those containing H<sub>2</sub>S [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<sub>2</sub>. Combinations of this type of corrosive media require special care when designing 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 O&G applications. A minimum of 42Ni is needed for aqueous stress corrosion cracking [3]. Molybdenum is beneficial for pitting corrosion resistant in reducing acids and alkalies [4]. Chromium improves general corrosion resistance and corrosion resistance in oxidizing media [4]. 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, Ti, and Al 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 alloy 718 [9]. The aim of the project was to develop a cost effective hybrid of alloys 925 and 718, which has best of both the alloys -- higher strength capability and excellent corrosion resistance.

## Laboratory Alloy Development

The initial development phase consisted of vacuum induction melting 22Kg lab heats. These heats were homogenized, hot-rolled, and subjected to annealing and aging studies. First phase of evaluation of laboratory heats was done based on microstructure and hardness of annealed plus aged material. The heats that showed potential were tested for tensile, impact, hardness, and microstructure. To begin with, a thermodynamics based software, JMatPro [10], was used to simulate some of the potential chemical compositions. This software predicts variation of strength with chemical composition. However, it does not give any guidance for inter-granular microstructure. Over 100 lab heats were evaluated in this program. Table 1 shows selected lab heats listed to illustrate the observed trends.

### Effect of Ti

Ti in alloy 925 composition was varied from 2.5 to 3.4 wt% as shown in heats S2-A to S2-C in Table 1. An increase in Ti showed a lot of potential to strengthen the alloys. A plot of hardness versus Ti content is shown in Figure 1. The hardness increased rapidly as Ti content was increased. However, increase in Ti also degraded microstructural stability. Cellular inter-granular Eta phase colonies were observed on age hardening, Figure 2. Based on the limited data reported in the literature, any inter-granular second phase precipitation is likely to degrade corrosion resistance in O&G applications [9].

Table 1. Chemical compositions of the lab heats

Alloy	Fe	Ni	Cr	Mo	Cu	C	Al	Nb	Ti
Alloy 925	Bal	42.3	20.3	3.2	2.0	0.014	0.2	0.3	2.3
Alloy 718	Bal	54	18.5	3.2	-	0.015	0.5	5.0	1.0
S2-A	Bal	42.5	20.6	3.4	1.7	0.013	0.4	0.3	<b>2.5</b>
S2-B	Bal	42.5	20.8	3.4	2.1	0.015	0.4	0.3	<b>3.0</b>
S2-C	Bal	42.8	20.4	3.4	1.8	0.021	0.4	0.3	<b>3.4</b>
S3-A	Bal	<b>45.0</b>	20.6	3.2	2.0	0.006	<b>0.6</b>	0.3	2.3
S3-B	Bal	<b>48.0</b>	20.5	3.2	2.0	0.005	<b>1.2</b>	0.3	2.3
S4-A	Bal	<b>45.5</b>	20.5	3.3	2.0	0.009	<b>1.0</b>	<b>1.0</b>	2.3
S4-B	Bal	<b>48.8</b>	20.5	3.3	2.1	0.008	<b>1.0</b>	<b>1.0</b>	2.3

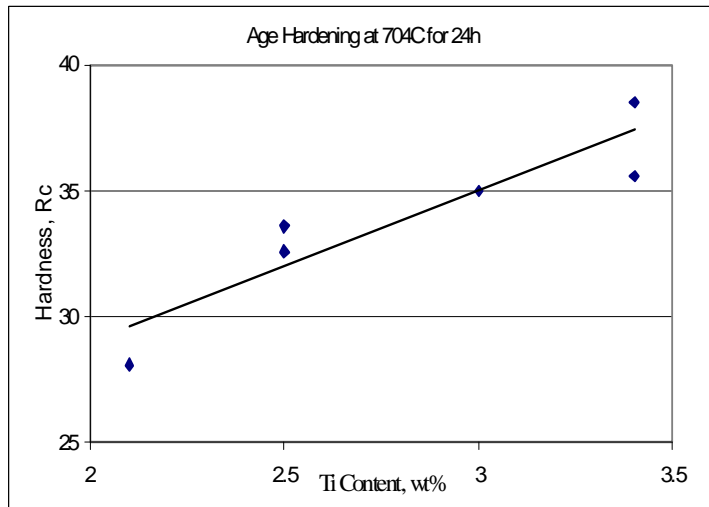


Figure 1. Hardness versus Ti content of S2 series of alloys.

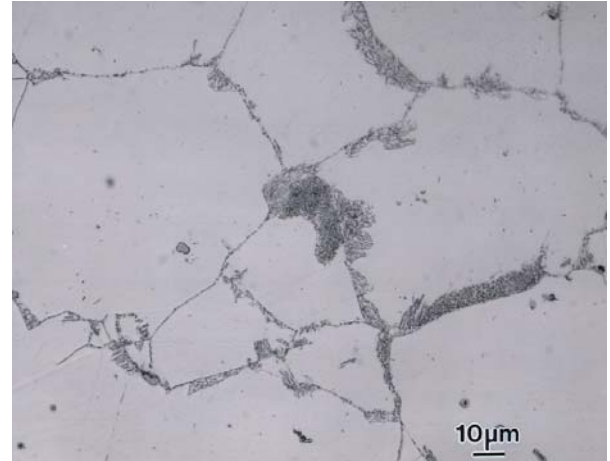


Figure 2. Optical photograph of annealed plus aged S2-C alloy containing 3.4Ti.

#### Effect of Al

Aluminum in the base alloy 925 composition was varied from 0.3 to 1.2 wt% in S3 heats as shown in Table 1. Interestingly, an increase in Al from 0.3 to 0.6 decreased hardness, Figure 3. However, with 1.2Al, the hardness was equivalent to that of 0.3Al. The lower hardness of 1.2Al alloy as compared to 0.6Al alloy in the plot for 24 hours exposure is probably due to over-aging. An increase in Al increases the volume fraction of gamma prime [7], which increases hardness. Further, an increase in Al is also thought to decrease the lattice mismatch / coherency strain [7], which decreases hardness. The observed variations in hardness with Al are combined effects of these two factors. An addition of 1.2Al led to higher inter-granular carbide precipitation, which is detrimental for O&G type aqueous corrosion applications [9]. Based on this data, higher additions than 1.2Al were not studied.

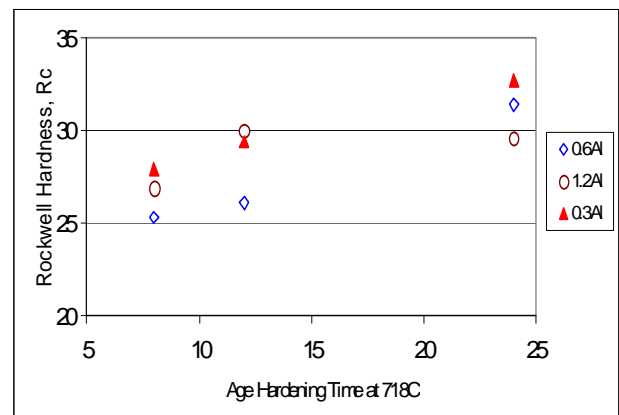


Figure 3. Hardness versus age hardening time at 718°C for S3 alloys.

### Relationship between Nb and Al

Increase in both Al and Nb in alloy 925 increased hardness but marginally decreased yield strength as shown for S4 heats in Table 1 and 2. This is contrary to JMatPro simulations, which suggest an increase in yield strength with this combination of hardeners, Table 2. An increase in hardness but a decrease in yield strength can be misleading because hardness values are typically used as an initial screen during alloys development. Increase in hardness in this set of heats did however increase tensile strength, which is consistent with reported literature, where hardness is correlated to the tensile strength for steel, [11]. These results indicated that increasing Al beyond the levels in alloy 925 would not be beneficial in the new alloy.

### Relationship between Nb and Ti

Once the behavior and optimum level of Al was determined in the alloy, the synergies between Nb and Ti were studied. JMatPro showed that an increase in Nb together with a decrease in Ti in alloy 925 is required to increase strength, Figure 4. Based on this information, a number of lab heats were prepared to study the Nb / Ti effect. The experimental results on yield strength were consistent with JMatPro simulations. Further, these synergistic variations in Nb and Ti resulted in a microstructure, which was essentially devoid of any inter-granular precipitation. A number of lab heats were evaluated for further processing and properties to optimize the final chemical composition of alloy 945 listed in Table 3.

Table 2. Room temperature yield strength of annealed plus two-step aged S4 heats. YS, UTS, EL, and RA stand for yield strength, tensile strength, elongation, and reduction-of-area respectively.

Alloy	Hardness, Rc	JMatPro predicted YS, ksi	YS, ksi	UTS, ksi	% El	% RA
925	34	82	118	173	23	27
S4-A	38	96	112	183	25	25
S4-B	38	99	109	180	26	39

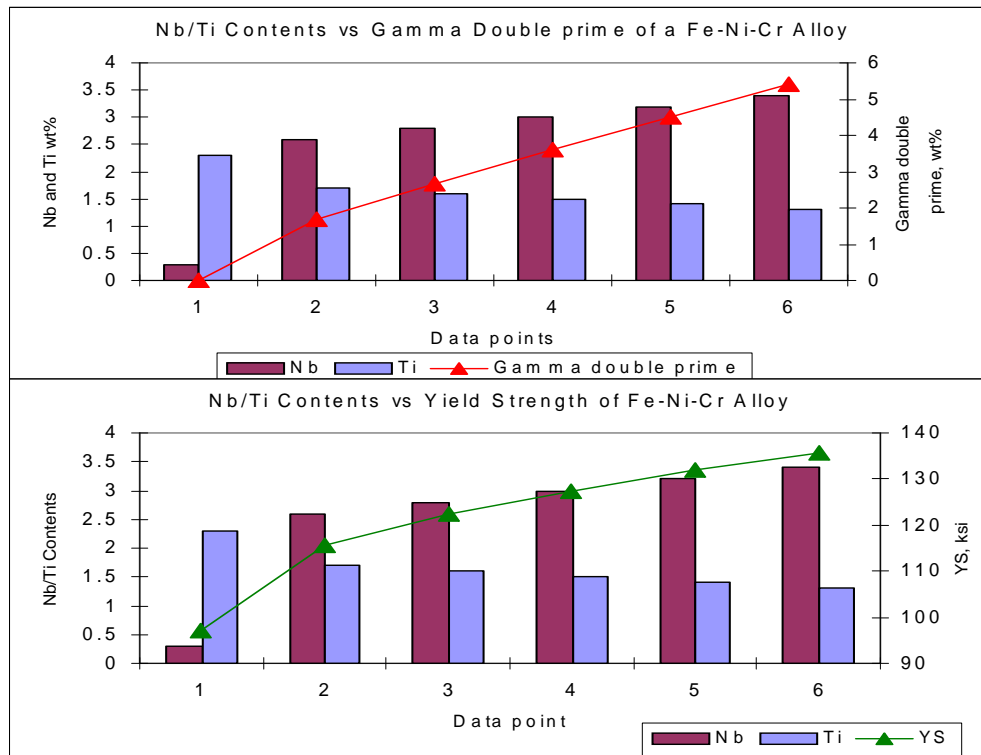


Figure 4. JMatPro simulations showing synergistic increase in Nb and decrease in Ti result in increase in Gamma double prime (upper plot) and increase in yield strength (lower plot).

Table 3. Nominal chemical compositions 925, 945, and 718.

Alloy	Fe	Ni	Cr	Mo	Cu	C	Al	Nb	Ti
925	Bal	42.3	20.3	3.2	2.0	0.014	0.2	0.3	2.3
945	Bal	<b>47</b>	<b>20.5</b>	<b>3.3</b>	<b>2.0</b>	<b>0.010</b>	<b>0.2</b>	<b>3.0</b>	<b>1.5</b>
718	Bal	54	18.5	3.2	-	0.015	0.5	5.0	1.0

## Results and Discussion on Mill Scale Heats

### Processing

An optimized composition of alloy 945 was melted and re-melted in the mill as three commercial heats weighing 22000 to 32,000 kg each. Although a number of variations in electrode / ingots sizes were evaluated, the most common sizes used were 457mm electrode re-melting to 508mm ingot. Melting processes evaluated were vacuum induction melting (VIM) and electric arc furnace (EAF) + argon oxygen decarburization (AOD). The melted electrodes were re-melted using vacuum arc re-melting (VAR) and electroslag re-melting (ESR). The alloy has proved to be process friendly to all the various combinations of primary and secondary melt methods.

Figure 5 shows a 508mm VIM +VAR ingot. The ingots produced by various melt methods were rolled or forged to round bars. Figure 6 shows a 229mm diameter forged bar weighing 2300Kg. Hot rolled bars were annealed at 1038°C for times according to the section sizes and water quenched. Then, the material was two step aged as follows: 718°C/8h, furnace cool at 56°C/h to 621°C, hold at 621°C/8h, air cool.



Figure 5. VIM + VAR ingot of 508mm diameter.



Figure 6. A forged bar of 229mm diameter weighing 2300kg.

#### Mechanical Properties

Rod sizes of diameter ranging from 25mm to 356mm were produced and tested for room temperature tensile, grain size, hardness, and Charpy impact testing. The impact testing was conducted at  $-23^{\circ}\text{C}$ . Impact tests for rod diameters 76mm or less were conducted in the longitudinal orientation, whereas for over 76mm, the tests were conducted in the transverse orientation.

All the tensile testing was done in the longitudinal orientation. Table 4 shows the mechanical properties. The impact values listed are the averages of 3 tests. Being the first scale up heats for the alloy, multiple testing was conducted at extreme ends of a bar or on different bars produced in a lot to ensure uniformity in the material. The listed multiple values for selected sizes represent data generated in this way. The alloy clearly met the target mechanical properties.

Table 4. Mechanical properties of annealed + aged alloy 945. YS, UTS, EL, and RA stand for yield strength, tensile strength, elongation, and reduction-of-area respectively.

Rod Size, mm	YS, MPa	UTS, MPa	% El	% RA	Impact, Joules	Hardness, Rc	Grain Size, ASTM #
25	919.8	1194.2	27.8	48.0	103	40	2
	939.1	1205.2	26.1	46.1	85	40	3
51	913.6	1173.5	28.2	47.6	95	40	3
	942.5	1201.8	25.7	40.1	75	40	3
89	939.8	1201.1	24.9	39.5	77	40	2
	934.3	1185.9	25.5	40.5	79	43	2
114	925.3	1162.5	28.6	46.7	84	42	2.5
	929.5	1171.5	26.6	45.6	84	39	2
152	957.0	1183.9	23.7	35.9	92	40	2
	972.2	1213.5	22.0	34.6	75	42	2.5
305	981.2	1183.9	26.3	43.6	83	40	2
356	967.4	1167	26.6	30.7	105	39	2
Min Target	862	1034	18	25	54	-	ASTM #2 or finer

### Microstructure

An etchant containing one percent bromine in methanol 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 7. The age hardening treatment precipitates sub-micron  $\text{Ni}_3(\text{TiAl})$ -type gamma prime and  $\text{Ni}_3(\text{NbTi})$ -type gamma double prime phases, which are responsible for the higher strength, Figure 8.

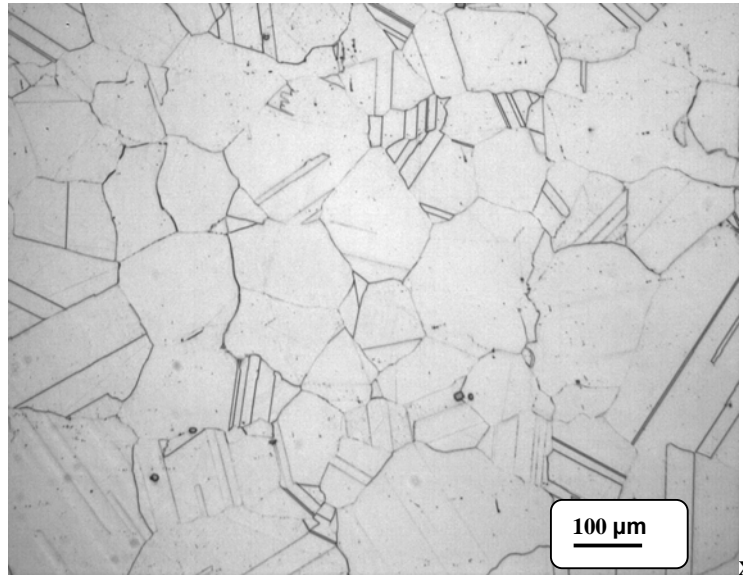


Figure 7. Optical photographs of alloy 945, Magnification = 100X.

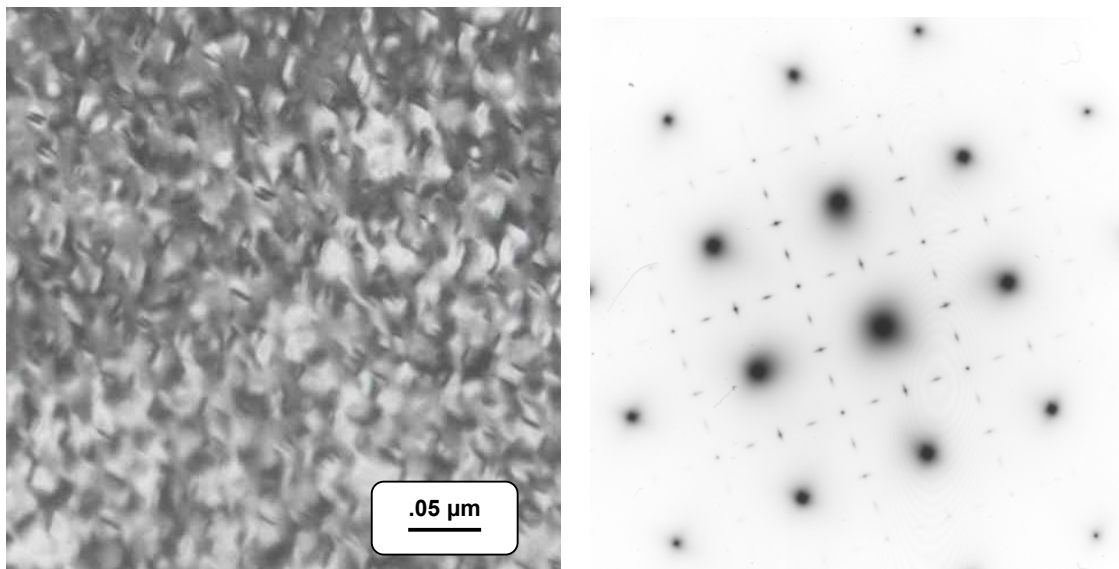


Figure 8. TEM photographs of alloy 945. The left shows gamma prime and gamma double prime distribution and the right shows selected area diffraction pattern of these phases in [001] zone axis.



## Corrosion Resistance

### Stress Corrosion Cracking (SCC):

Corrosion testing in MR0175 / ISO 15156-3 [12] NACE (National Association of Corrosion Engineers) level V and level VI was carried out on triplicate C-ring specimens for 90 days on three mill heats at 100% of actual yield strength. Testing was done in accordance with NACE TM0177-2004, method C - C Ring tests.

In these tests, stressed C-ring specimens were enclosed in a pressurized autoclave under specified partial pressure of gasses. The specimens were immersed in a solution containing specified chloride content at a fixed temperature. The tests were run for 90 days and the specimens were examined with 20X magnifier for cracking after the test. No cracking was observed, Tables 5 and 6. Specimen dimensions were: 51mm OD, 3.8mm wall-thickness and 24.1mm width. Figure 9 shows a C-ring test specimen.

Table 5. C-ring test results in NACE level V. The environment was 700 kPa H<sub>2</sub>S, 700 kPa CO<sub>2</sub>, 91000 mg/l Cl at 150°C. Applied stress was 100% of room temperature yield strength.

Sample	Applied Stress, MPa	Results
EX0019PY-12 (1)	920	No failure, 90 days
EX0019PY-12 (2)	920	No failure, 90 days
EX0019PY-12 (3)	920	No failure, 90 days
EX0019PY-11 (1)	925	No failure, 90 days
EX0019PY-11 (2)	925	No failure, 90 days
EX0019PY-11 (3)	925	No failure, 90 days
EX0021PK-11 (1)	972	No failure, 90 days
EX0021PK-11 (2)	972	No failure, 90 days
EX0021PK-11 (3)	972	No failure, 90 days

Table 6. C-ring test results in NACE level VI. The environment was 3500 kPa H<sub>2</sub>S, 3500 kPa CO<sub>2</sub>, 121300 mg/l Cl at 175°. Applied stress was 100% of room temperature yield strength.

Sample	Applied Stress, MPa	Results
EX0019PY-12 (1)	920	No failure, 90 days
EX0019PY-12 (2)	920	No failure, 90 days
EX0019PY-12 (3)	920	No failure, 90 days
EX0019PY-11 (1)	925	No failure, 90 days
EX0019PY-11 (2)	925	No failure, 90 days
EX0019PY-11 (3)	925	No failure, 90 days
EX0021PK-11 (1)	972	No failure, 90 days
EX0021PK-11 (2)	972	No failure, 90 days
EX0021PK-11 (3)	972	No failure, 90 days



Figure 9. Photograph of a C-ring test specimen.

#### Galvanically induced Hydrogen Stress Cracking (GHSC):

To fulfill NACE MR0175 / ISO 15156-3: 2003 acceptance 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 24°C. Testing was carried out in accordance with TM0177 - 2004, method A – Tensile tests. Samples were nominally of diameter 3.8mm and gauge length 25.4mm. The samples were coupled to carbon steel via the stressing bolts. No failures were detected, Table 7.

Table 7. Test results on triplicate samples for GHSC.

Sample	Applied Stress, MPa	Results
EX0019PY-12 (1)	828	No failure, 30 days
EX0019PY-12 (2)	828	No failure, 30 days
EX0019PY-12 (3)	828	No failure, 30 days
EX0019PY-11 (1)	833	No failure, 30 days
EX0019PY-11 (2)	833	No failure, 30 days
EX0019PY-11 (3)	833	No failure, 30 days
EX0021PK-11 (1)	875	No failure, 30 days
EX0021PK-11 (2)	875	No failure, 30 days
EX0021PK-11 (3)	875	No failure, 30 days

#### Sulfide Stress Cracking (SSC):

Sulfide stress corrosion cracking testing was done on triplicate samples of three heats in acidified NACE solution A at 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. Samples were nominally of diameter 3.8mm and gauge length 25.4mm. No failures were detected, Table 8.

Table 8. Test results on triplicate samples for SSC.

Sample	Applied Stress, MPa	Results
EX0019PY-12 (1)	828	No failure, 30 days
EX0019PY-12 (2)	828	No failure, 30 days
EX0019PY-12 (3)	828	No failure, 30 days
EX0019PY-11 (1)	833	No failure, 30 days
EX0019PY-11 (2)	833	No failure, 30 days
EX0019PY-11 (3)	833	No failure, 30 days
EX0021PK-11 (1)	875	No failure, 30 days
EX0021PK-11 (2)	875	No failure, 30 days
EX0021PK-11 (3)	875	No failure, 30 days

## Applications

Mechanical properties and corrosion resistance of alloy 945 shown in the publication makes it suitable for use in O&G applications for hangers, packers, valve stems and tubulars used in wellhead, downhole equipments, christmas tree, and side pocket mandrels. Figure 10 shows wellhead used for above ground pressure control.

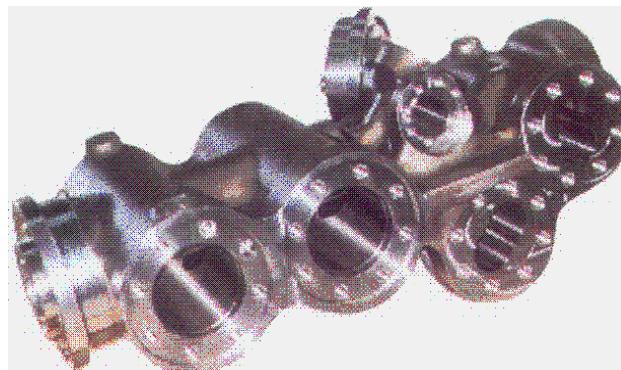


Figure 10. Photograph of a wellhead used for above ground pressure control.

## Summary and Conclusion

A new alloy named INCOLOY\* alloy 945 has been developed for O&G applications using JMatPro simulations and multiple iteration of 22 Kg lab heats. This alloy was scaled up to three 22, 000 to 32,000 Kg mill heats and rolled / forged to 25mm - 356mm diameter rods. Annealed + aged material was tested for mechanical and corrosion properties. The data shows that the material is capable of 860 MPa minimum 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.

\* INCOLOY is a Trade Mark of Special Metals Corporation



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