

Characterization of Newly Developed High Interstitial Non-magnetic Stainless Steels for Oil And Gas Applications

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ABSTRACT

High interstitial austenitic stainless steels (HIS) contain approximately 18% chromium, 18% manganese and a combined carbon plus nitrogen content between 0.8 and 1.1%. They are non-magnetic and show outstanding mechanical properties and good corrosion resistance. This paper presents test results of two newly developed non-magnetic high interstitial austenitic stainless steels with PREN of 28 and 36. Two variants were produced:

- a Fe18Cr18Mn0.85CN-HIS with 0.85% (C+N) $\Rightarrow$ **CN0.85**
- A Fe18Cr18Mn1.1CN2.2Mo-HIS with 1.1% (C+N) and 2.2% Mo $\Rightarrow$ **CN1.1Mo**

Mechanical and corrosion properties were investigated in solution annealed condition. After solution annealing, both alloys possess fully austenitic microstructure without detrimental phases. They exhibit similar yield strength (> 600 MPa), elongation (> 60 %) and impact energy (> 350 J), while ultimate tensile strength is higher for FeCrMn1.1CN2.2Mo-HIS (> 980 MPa) than for FeCrMn0.85CN-HIS (> 930 MPa). FeCrMn1.1CN2.2Mo-HIS shows better pitting corrosion resistance and higher critical pitting temperature than FeCrMn0.85CN-HIS as well as higher pitting potential in 3.56 % NaCl at RT. The Mo-rich variant did not display cracking or pitting after stress corrosion cracking test. The new non-magnetic high interstitial austenitic stainless steels are promising grades for application in oil and gas industry due to their outstanding combination of high strength, good ductility and excellent corrosion properties.

Key words: Non-magnetic high-interstitial austenitic stainless steel, mechanical properties, corrosion properties

INTRODUCTION

Oil and gas exploration technology is continuously evolving. Directional drilling allows multiple deposits to be drilled and produced using only one rig. Measuring While Drilling (MWD), and Logging While Drilling (LWD) tools use non-magnetic drill collars to perform magnetic inspection of the well trajectory with the help of sensitive measurements tools near the drill bit. The materials used in drill collars must be completely non-magnetic, display yield strength above 758 MPa (110 ksi) or 1000 MPa (145 ksi) for more severe applications, and show high ductility and toughness, anti-galling properties, good wear properties as well as excellent corrosion resistance [1,2]. The first non-magnetic drill collars were made of precipitation hardening NiCu alloys [1]. Subsequently, they were replaced by non-magnetic stainless steels due to their excellent mechanical properties and price-quality ratio. Strain-hardened FeCrMn austenitic stainless steels have been used for directional drilling in the oilfield applications since the 1990s. They have a good combination of mechanical and corrosion properties. However, these steels have shown susceptibility to pitting corrosion and environmentally-assisted corrosion cracking [1,3,4].

High interstitial austenitic stainless steels (FeCrMn-HIS) contain approximately 18% Cr, 18% Mn and in total between 0.8 and 1.1% C+N. Molybdenum can be added to improve corrosion resistance. Carbon and nitrogen contribute to solid solution hardening providing an increase in strength [5]. These FeCrMn-HIS can be produced by conventional steelmaking processes despite the high nitrogen content ($\geq 0.6\%$). After hot deformation, a solution annealing treatment is necessary to dissolve different precipitates. Additionally, a fast quenching is required to avoid grain boundary precipitation of carbides or nitrides which may decrease impact energy and corrosion resistance [6,7]. Cold working of FeCrMn-HIS increases hardness up to approximately 60 HRC. Non-magnetic properties are not affected because cold working processes does not result in the formation of strain-induced martensite [8]. However, the corrosion properties can be slightly deteriorated [9,10,11].

FeCrMn-HIS exhibit an excellent combination of tensile strength and elongation. In the solution annealed condition, they show yield strengths (YS) between 500 and 600 MPa (72 - 87 ksi), an ultimate tensile strength (UTS) higher than 900 MPa (130 ksi), with elongation to fracture above 60%, and notch-impact energy higher than 350 J (258 foot pounds) at room temperature. These steels as well as high nitrogen austenitic stainless steels and FeCrMn austenitic stainless steels demonstrate a ductile-to-brittle transition temperature (DBTT). However, the combination of carbon and nitrogen lower this temperature, which increases the range of possible applications [5,12,13]. These steels present an increased fatigue life, work hardening ability, and good pitting corrosion resistance compared to CrNi austenitics and FeCrMnN austenitic stainless steels [5,12-15].

Pitting corrosion resistance strongly depends on chemical composition of the steel. Elements like chromium (Cr), molybdenum (Mo), nitrogen (N) and tungsten (W) have a positive effect on pitting corrosion resistance, while manganese (Mn) and nickel (Ni) are considered to be detrimental in case of austenitic stainless steels [17,18]. Pitting resistance also is influenced by environmental factors like temperature, pH value, chloride content and the presence of an oxidizing agent. The pitting resistance equivalent number (PREN) is the most common indicator for the resistance of stainless steels and Ni-alloys to localized corrosion in chloride-containing environments. PREN can be calculated with the formula (Equation 1) according to NACE MR0175/ISO15156 [16], as well as modified equations that consider the positive or negative effect of different elements.

$$\text{PREN} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 16 \cdot \% \text{N} \quad (1)$$

The modified PREN (PREN-Mod) formula takes the detrimental influence of Mn (Equation 2) into account, which is one of the main alloying elements in FeCrMn austenitic stainless steels. Sarmiento et al. [19] reported a good correlation between PREN-Mod and pitting corrosion potentials of non-magnetic stainless steels in solutions containing 80,000 ppm Cl^- with near-neutral pH measured at RT.

$$\text{PREN} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 16 \cdot \% \text{N} - 0.5 \cdot \% \text{Mn} \quad (2)$$

Another formula, called MARC (Measure of Alloying for Resistance to Corrosion), is commonly used to estimate pitting corrosion resistance in high nitrogen austenitic stainless steels, (Equation 3). It considers a positive influence of carbon, and the detrimental effects of nickel and manganese [17].

$$\text{MARC} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 20 \cdot \% \text{N} + 20 \cdot \% \text{C} - 0.5 \cdot \% \text{Mn} - 0.25 \cdot \% \text{Ni} \quad (3)$$

These high interstitial austenitic steels (FeCrMn-HIS) exhibit a yield strength and ultimate tensile strength higher than standard austenitic stainless steels and FeCrMn austenitics without losing ductility. They also possess good magnetic permeability of $\mu_{\text{rel.}} < 1.005$ and excellent corrosion properties which are only achieved when nitrogen and carbon are in solid solution. FeCrMn-HIS are nickel-free and can be produced by conventional steelmaking processes [20]. For these reasons, they are a cost-effective option. These steels can be used in different applications, like non-magnetic retaining rings, pump shafts or chain links in the mining industry, or as non-magnetic rolling contact bearings or railroad wheels in cold worked condition.

This paper examines two newly developed non-magnetic high interstitial austenitic stainless steels, with different content of Mo, C and N. Mechanical and corrosion properties were investigated and compared with literature data on materials used in oil and gas applications.

EXPERIMENTAL PROCEDURE

Materials

Two non-magnetic high interstitial austenitic stainless steels were investigated. Their chemical composition is presented in Table 1.

Table 1: Nominal chemical composition of the materials in wt. %

Alloy	C	Si	Mn	Cr	Mo	Ni	N	C + N
CN0.85	0.3	0.28	17.9	18.7	0.06	0.19	0.55	0.85
CN1.1Mo	0.4	0.25	19.2	17.7	2.20	0.14	0.67	1.1

The newly developed materials were produced by conventional steelmaking processes (Electric arc furnace + electroslag remelting + hot forging). The production route is described in a previous paper [13]. The microstructure of the materials obtained after hot forging and cooling in air is shown in Figure 1. A fully austenitic structure without martensite or δ -ferrite was observed in both alloys. They show precipitates at the grain boundaries which are identified as M_{23}C_6 and M_2N [13]. The precipitation of these phases occurs between 700 and 1000 °C (1292-1832 °F) due to the high content of interstitial atoms and slow cooling rate. Additionally, the alloy with higher content of C and N (FeCrMnMo-HIS) shows “pseudopearlite” which consists of carbonitride and austenite layers [13].

After forging, the two HIS were solution annealed between 1075 and 1150 °C (1967-2102 °F) for 30 minutes and water quenched. This solution annealing was performed in the laboratory to determine the optimal temperature to dissolve precipitates and achieve a homogeneous austenitic microstructure with nitrogen and carbon remaining in solid solution. Figure 2 shows the microstructure after solution annealing. Precipitates and the pseudo-pearlitic microstructure are not dissolved at annealing temperatures below 1100°C. The optimal solution annealing temperatures for CN0.85 and CN1.1Mo were found to be 1100 °C and 1125 °C, respectively. Carbon and nitrogen are completely in solid

solution at these temperatures. Higher temperatures are not recommended due to grain growth. The alloys have a magnetic permeability of $\mu_{rel.} \leq 1.003$ in hot forged and solution annealed condition.

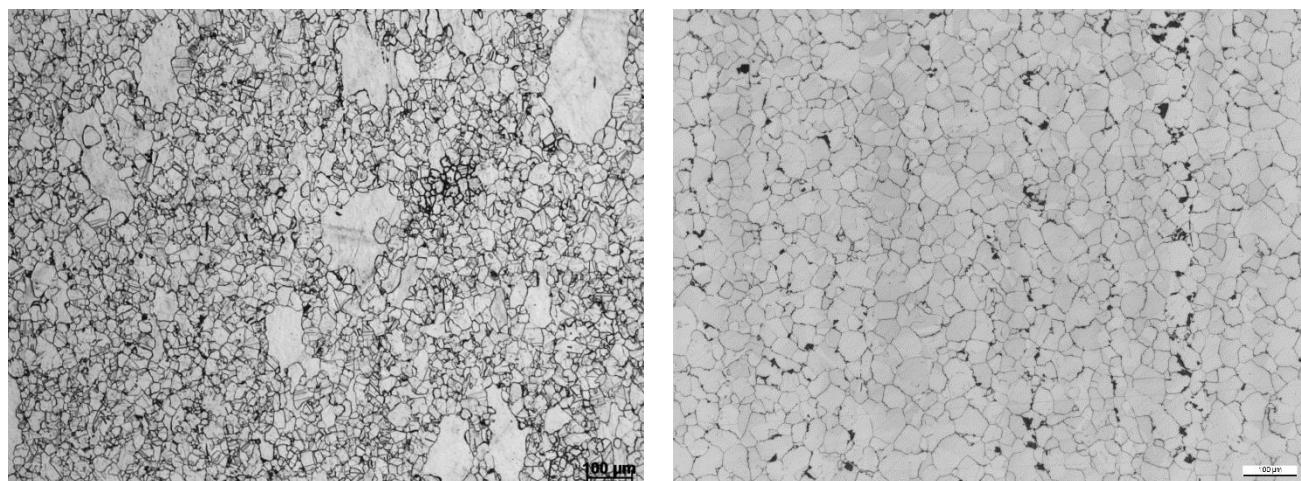
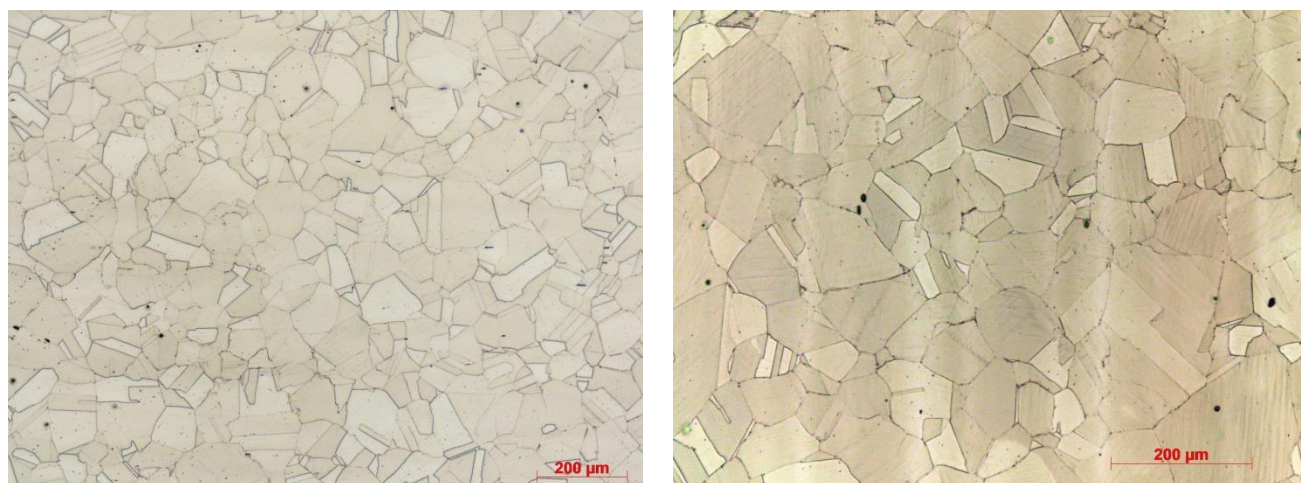


Figure 1: Microstructure of the alloys after forging and air cooling. (a) CN0.85 and (b) CN1.1Mo.



(a) CN0.85: 1100°C/30 min/Water

(b) CN1.1Mo: 1125°C/1h/W

Figure 2: Microstructure of (a) CN0.85 and (b) CN1.1Mo after solution annealing.

Mechanical properties after solution annealing were evaluated according to ASTM A370 [21], i.e. tensile and Charpy-V tests at room temperature. Samples were extracted from the mid-radius position in longitudinal direction.

The influence of the solution annealing temperature on the mechanical properties is shown in Figure 3. Both steels have similar yield strengths around 600 MPa (87 ksi), which does not change significantly with solution annealing temperature. CN1.1Mo shows higher UTS values than CN0.85 for all temperatures due to the higher content of interstitial atoms in solid solution. Elongation A2 and reduction of area increase, while ultimate tensile strength decreases with increasing solution annealing temperature. In the optimal solution annealed condition, both newly developed steels present an excellent combination of elongation, higher than 60%, yield strength and UTS higher than 600 MPa (87 ksi) and 900 MPa (130 ksi), respectively. Similar mechanical properties in high nitrogen FeCrMn-austenitic stainless steel after solution annealing have been reported [5,22]. Impact energy rises with increasing annealing temperature (Figure 4) due to the dissolution of carbide and nitride. The notch-

impact toughness of these steels reaches values higher than 300 J (220 ft-lbs) at room temperature. CN0.85 exhibits higher impact toughness than CN1.1Mo.

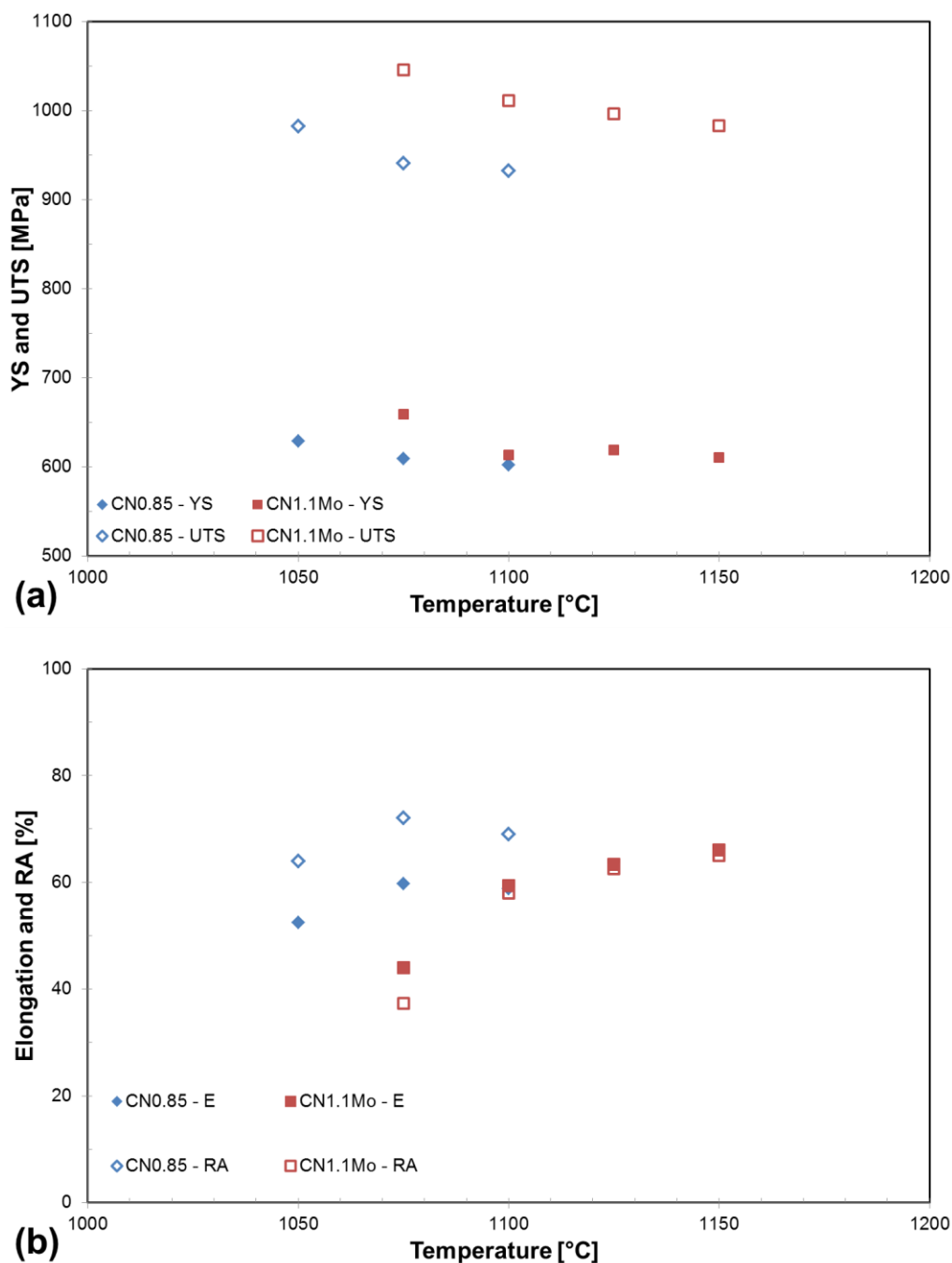


Figure 3: Influence of solution annealing temperature on mechanical properties. (a) Yield strength (YS), ultimate tensile strength (UTS) and (b) elongation and reduction of area (RA).