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Optimization of UNS N08034 in the Cold Worked Condition for Use in the Oil and Gas Industry

Philipp Hübner
VDM Metals International GmbH
Kleffstr. 23
58762 Altena
Germany

Julia Botinha
VDM Metals International GmbH
Kleffstr. 23
58762 Altena
Germany

Bodo Gehrmann
VDM Metals International GmbH
Kleffstr. 23
58762 Altena
Germany

Helena Alves
VDM Metals International GmbH
Kleffstr. 23
58762 Altena
Germany

ABSTRACT

UNS N08034, commonly referred to as Alloy 31 Plus(1), is a non-precipitation-hardenable super austenitic stainless steel that is currently commercially available in the solution-annealed state. Compared to its predecessor, Alloy 31(2) (UNS N08031), it has an increased nickel content and the addition of nitrogen and manganese, which serve to stabilize the austenitic phase. The well-balanced chemical composition of UNS N08034 enables excellent machinability in both hot and cold conditions, as well as favorable weldability.

In the oil and gas industry, materials selected for various applications must possess superior corrosion resistance and enhanced mechanical strength, particularly at the expected operating temperatures. UNS N08034 shows promising potential for exploration in this regard. However, to meet the application requirements, an alternative production route must be established, specifically focusing on mechanical strength.

This paper presents two distinct approaches. Firstly, the development of a cold working processing route for UNS N08034 is discussed. Secondly, the influence of specific alloying elements on the response to cold work is examined.

Key words: UNS N08034, Nickel base alloys, Super austenitic stainless steels, Oil & Gas, CPI, Cold work,

(1) Trade name. Alloy 31 Plus is a proprietary alloy of VDM Metals International GmbH
(2) Trade name. Alloy 31 is a proprietary alloy of VDM Metals International GmbH

INTRODUCTION

In the oil and gas industry, as well as in the chemical process industry, the requirements for materials are widely spread. Extraordinary corrosion resistance in a wide variety of media, often including halides, as well as sufficient mechanical strength, are among the main requirements for the materials. Especially in oil wells, a wide spectrum of operating conditions in terms of temperature, depth, pressure and production environments is to be experienced.[1]

UNS N08034 is a super austenitic stainless steel that shows promising material properties to fulfill the requirements for use in the oil and gas sector. It is the successor of the 6-Mo stainless steel UNS N08031. With a slightly modified chemical composition (see Table 1), the manufacturing and its chemical stability have been improved.[1-3]

Table 1
Chemical composition of UNS N08031, UNS N08034 and UNS N08926 in weight-percent.[4-6]

UNS	Chemical composition in wt.%					
	Fe	Ni	Cr	Mo	C	Others
N08031	Balance	31	27	6.5	< 0.01	Cu, N
N08034	Balance	34	26.5	6.5	< 0.01	Cu, N
N08926	Balance	25	20	6.5	< 0.02	Cu, N

The increased nitrogen and manganese content help to improve the stability of the austenitic microstructure of the material. In addition, the higher nickel content leads to enhanced thermal stability as well as greater resistance against stress corrosion cracking.[2, 7] Figure 1 shows the thermal stability of UNS N08034 compared to its precedent UNS N08031, based on Charpy V-notched impact energy (CVN) test results and the combination of annealing temperatures and times. To define the thermal stability, a critical value of 50 J has been used as threshold. The tests have been conducted at -60 °C in the transverse direction.[8]

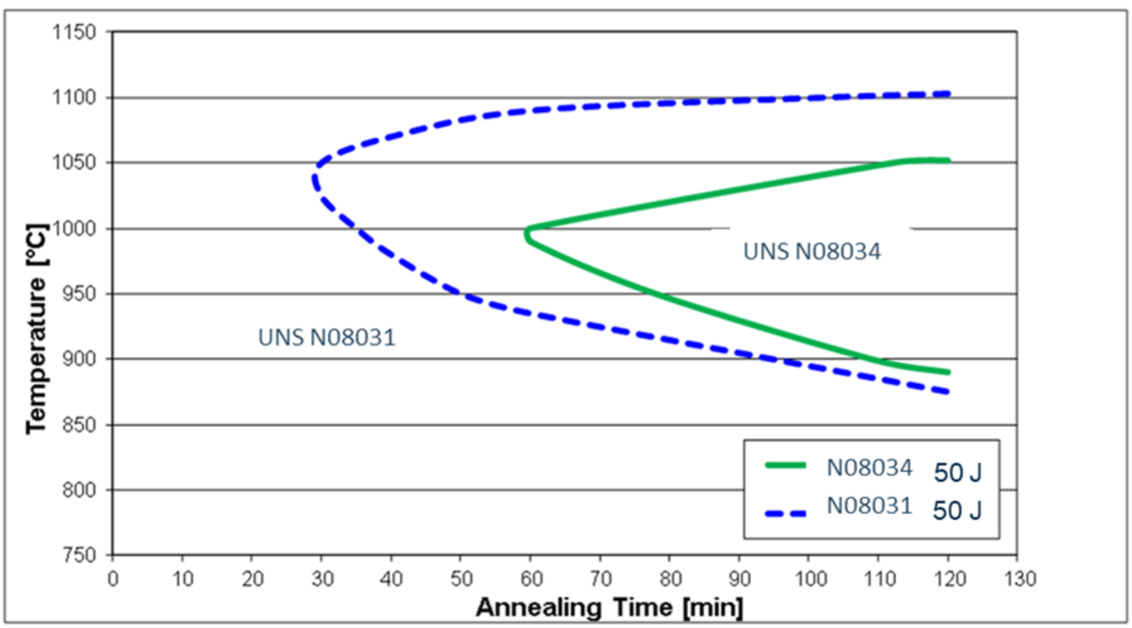

Figure 1: The thermal stability of UNS N08034 compared to UNS N08031. For the tests, different annealing conditions have been set and CVN tests have been conducted at -60 °C. Undercutting the critical value of 50 J equals a sensitized microstructure.[8]

Similarly, the thermal stability of UNS N08034 has been studied by means of microstructural analysis as shown by Figure 2. The alloy shows an increase of the precipitation intensity of sigma-phase in the grains and grain boundaries with increasing annealing time and in the temperature interval between about 800 and 1000 °C. The increased intensity of sigma-phase precipitation leads to a reduction of CVN, which is shown by the results in Figure 1. The nose of the sigma-phase precipitation region in N08034 (characterized by a reduction of CVN) is shifted to the right, increasing the allowance of exposure time to the sigma-phase precipitation temperatures.[2]

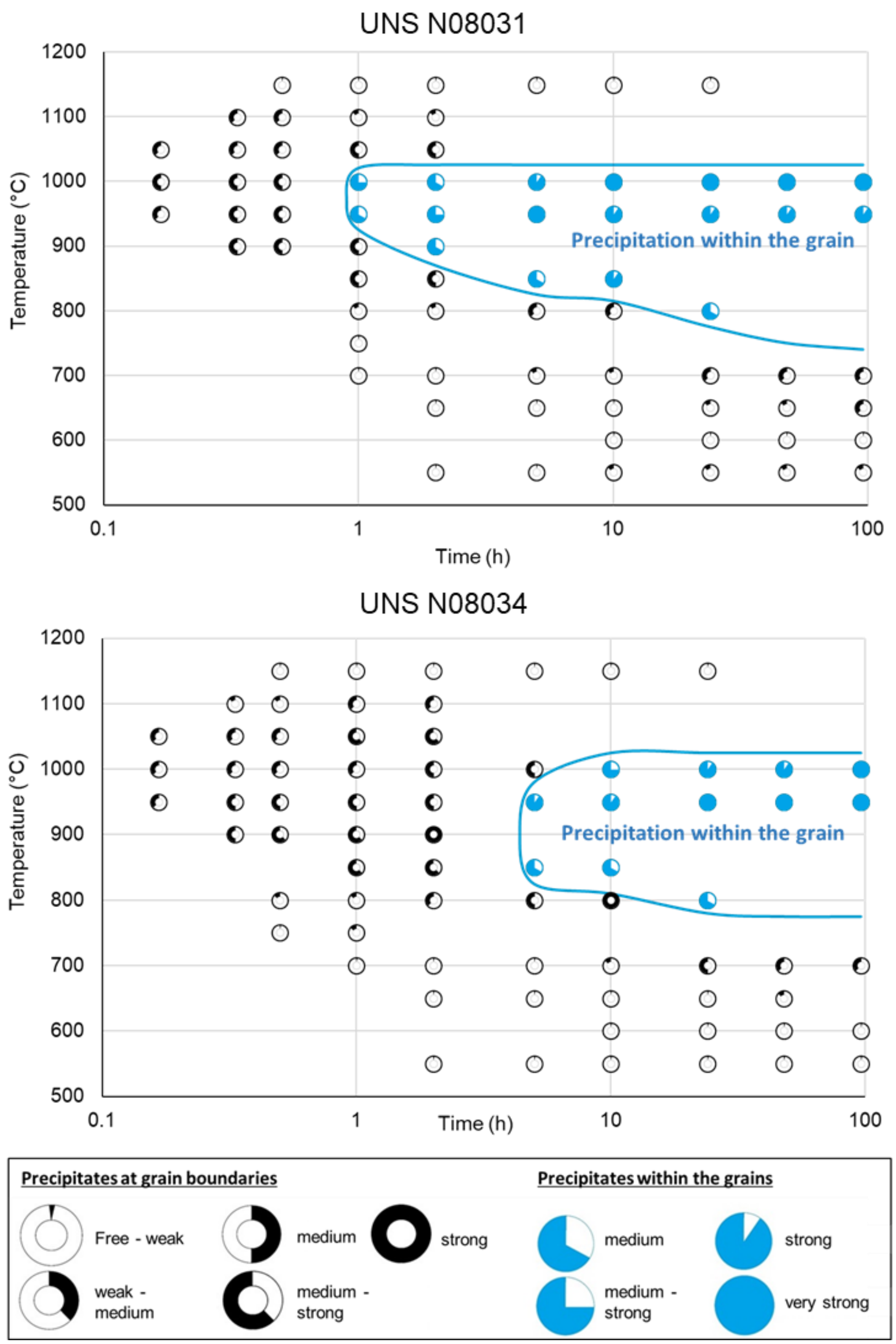

Figure 2: Time-Temperature-Precipitation diagram of UNS N08031 and UNS N08034. For the tests, different annealing conditions have been set and microstructura analysis have been conducted. Sigma-Phase precipitation with the grains have been used as threshold for sensitization.[2]

In the solution-annealed condition, UNS N08034 has a homogeneous microstructure free of continuous precipitation along the grain boundaries and in the grains, as can be seen in Figure 3. The necessary heat treatment to achieve the solution-annealed state could be decreased by 20 °C compared to its predecessor UNS N08031. Thereby, manufacturing costs have been reduced and further processability of the material has been significantly improved.[7]

The material is available in the product types of sheet, strip, bar & wire. Owed to its balanced composition it is suited for welding as matching filler metal or over-alloyed filler metal. Different welding methods can be used such as gas tungsten arc welding (GTAW), also known as tungsten inert gas (TIG) and gas metal arc welding.[2, 7, 9]

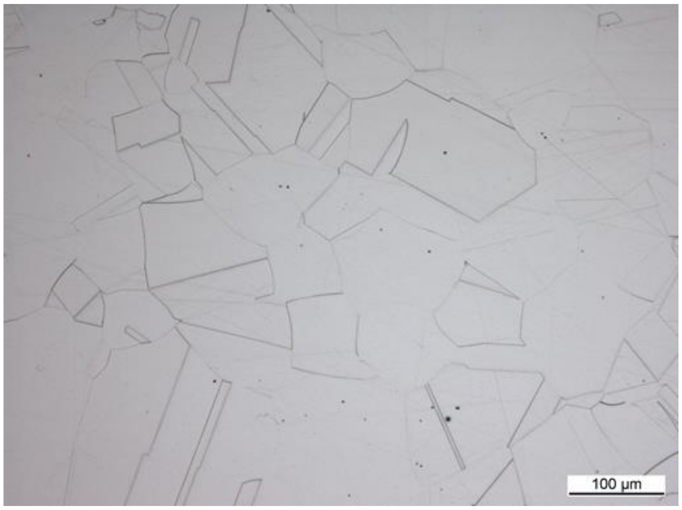

Figure 3: UNS N08034 has a homogeneous austenitic microstructure without precipitations in the grain or on the grain-boundaries in the solution-annealed condition.

UNS N08034, when in the solution-annealed state, has proven rather resistant against corrosion in several aggressive media. Even the presence of oxidizing or slightly reducing agents in the test solutions have little to no influence on the obtained mass loss rates, as shown on Table 2.[10]

Table 2
Mass loss rates of UNS N08034, UNS N08031 and UNS N08926 in different media.[2, 11]

Test medium	Temperature [°C]	UNS N08034	UNS N08031	UNS N08926
		Corrosion loss [mm/a]	Corrosion loss [mm/a]	Corrosion loss [mm/a]
Sulfuric acid 5 %	boiling	0,32	0,36	0,68
Sulfuric acid 10 %	boiling	0,58	0,59	1,6
Huey test (Nitric acid 65 %)	boiling	0,08	0,07	0,36
Hydrochloric acid 5 %	50	0,01	0,01	1,3
Hydrochloric acid 10 %	25	0,58	0,63	0,62
Hydrochloric acid 20 %	25	0,39	0,42	0,42
Phosphoric acid 50 % / 1000 ppm chloride	90	0,003	0,003	0,017

Also, owed to the material's chemical composition, the resistance against localized corrosion is sufficient for use in environments with halides present such as Cl^-. The Pitting Resistance Equivalent Number (PREN) calculated by using the equation below[10] results in 54. The PREN is used to approximate the suitability for applications in media prone to localized corrosion.[6]

$$PREN = wt.\%Cr + 3.3 \times wt.\%Mo + 30 \times wt.\%N$$

Thereby, the material builds a bridge between the so called C-family nickel alloys - which consists of Ni-Cr-Mo alloys with a PREN above 70 - and high alloyed stainless steels with PREN below 50 (Figure 4).[10, 12]

The elevated PREN favors the alloy's performance in testing media of ASTM[(3)] G48 Methods C and D as well as in the "green death" solution with 11.6 wt.% H_2SO_4 + 1.2 wt.% HCl + 1 wt.% $CuCl_2$ + 1 wt.% $FeCl_3$.[2, 9]

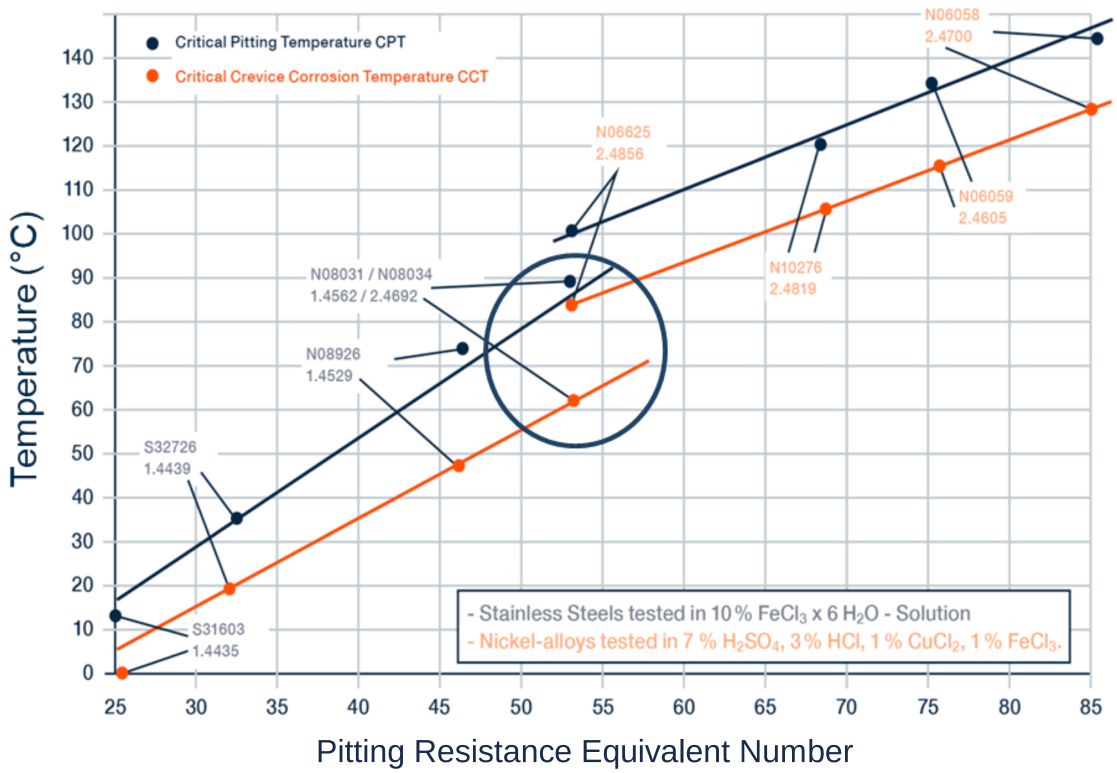

Figure 4: UNS N08031 and UNS N08034 Critical Pitting and Crevice Temperatures in aggressive media compared to other nickel base alloys and stainless steels.[2, 13]

The mechanical properties of UNS N08034 sheet material in the solution-annealed condition are depicted in Table 3.

Table 3
Mechanical properties of the material.[14]

UNS N08034	R_m [MPa]	$Rp_{0.2}$ [MPa]	A [%]
ASTM B 625-21	Min. 650	Min. 280	Min. 40
Average of three heats	705	395	60

Optimal material prerequisites for use in the oil & gas sector would be a yield strength above 120 ksi while also maintaining a sufficient ductility above 10 % elongation.[1]

The conducted research has the goal to increase the yield strength of UNS N08034 while maintaining the good corrosion resistance of the material through the application of cold strengthening. Therefore, two distinct approaches have been performed:

(3) American Society for Testing and Materials

1. Development of a processing route to introduce the required amount of cold work on the standard material in bar product
2. Investigation of laboratory melts with optimized chemical compositions with respect to the influence of certain elements to cold work

In this paper, sample material of the two approaches is going to be compared to solution-annealed material using metallographic investigations, mechanical tests as well as corrosion tests in selected media.

EXPERIMENTAL PROCEDURE

Large-scale production trials

In the attempt to establish a large-scale production route for achieving the mechanical properties required in the oil and gas industry on UNS N08034 bar material, the first priority is to identify a sufficient cold forming ratio. For this purpose, a heat is manufactured using electro furnace (EF) followed by vacuum treatment (VOD) and then the final ingots are produced by means of electro slag remelting (ESR). By hot forging to intermediate dimensions that are calculated based on the final diameter and the degree of cold work wished and subsequent solution annealing, these ingots are then prepared for further production by radial forging, whereby the final degree of cold work is introduced.

Owed to preliminary tests with the material, it is known that introducing cold work to big-dimension products could overload the radial forge. Therefore, the trials are done increasing the amount of effective cold work incrementally but are normalized in this paper for the sake of confidentiality.

Laboratory scale production trials

Building on the initial results with large-scale material, a laboratory scale melting series is conducted to determine the influence of manganese on the material's cold work uptake.

The laboratory melts are produced by means of a mini Vacuum Induction Melting (VIM) furnace. After casting, the blocks are conformed to intermediate dimensions by hot rolling on a laboratory rolling mill. After solution annealing, the cold work is introduced in the material by rolling to achieve the desired final thickness. All laboratory heats are rolled to receive the same amount of cold work that is similar to the final trial of the large-scale approach.

Testing program

The following material properties as well as corrosion resistance are determined via the following testing methods:

- Microstructure
    - Grain size, precipitates
- Tensile test according to ASTM E8[15]
    - Tensile strength, yield strength, elongation at break
- Notched bar impact test according to ASTM E23[16] at room temperature
    - Impact energy
- Hardness measurement according to ASTM E18[17] in the cross-section
    - Hardness readings
- Susceptibility to localized corrosion according to ASTM G28 Method A[18], ASTM G48 Methods C & D[19]
    - Mass loss rate, critical pitting temperature (CPT), critical crevice temperature (CCT)

By taking UNS N08034 in the solution annealed condition as a reference, the large-scale cold work manufacturing routes and the laboratory approach are then evaluated.

RESULTS AND DISCUSSION

The display of the obtained results on the following pages starts with the large-scale production. Subsequently, the results obtained from the material manufactured on laboratory scale are presented. A discussion as well as a comparison of both approaches finalize this chapter.

Large-scale production trials

Tensile test results are shown in Figure 5. For the sake of comprehensibility of the complete development program, trials 1 to 5 are given in the diagram. The incremental work has resulted in a step-wise increase of the yield strength and ultimate tensile strength, while the ductility has decreased, as a result. The yield strength achieved in the final iteration (trial 5) lies at about 160 ksi.

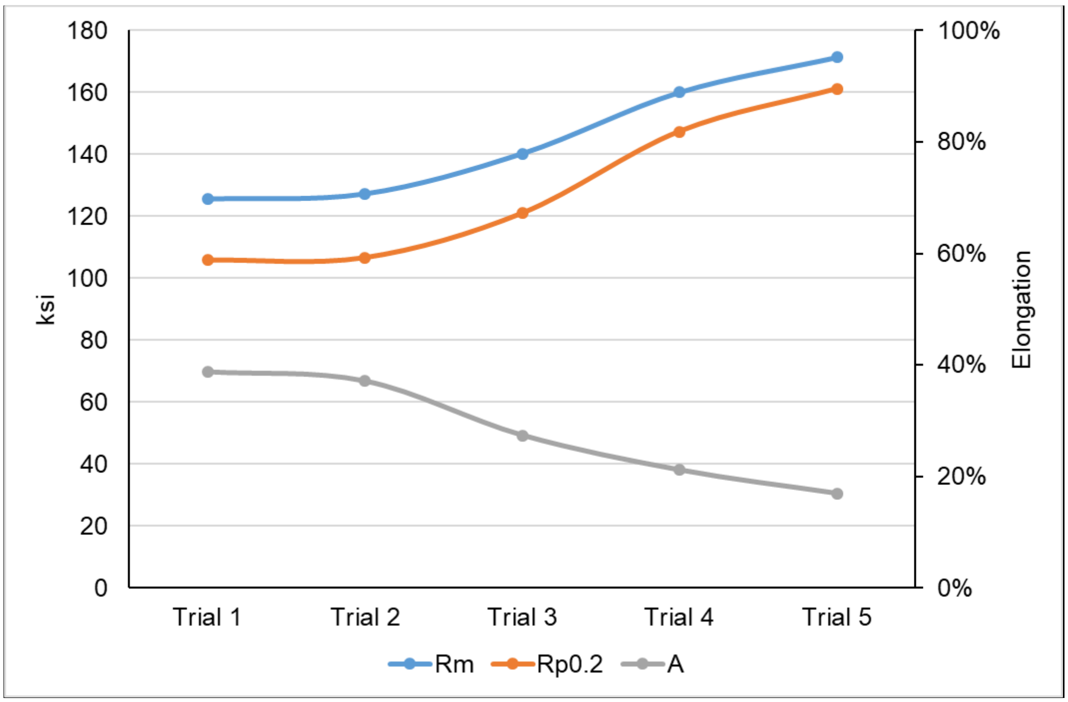

Figure 5: This figure shows the obtained tensile results of the trials. Samples are taken from the position close to the surface.

For the current study, trials 4 and 5 showed to be relevant due to their strength levels and therefore only the corresponding results are shown.

The microstructure is investigated and Figure 6 shows a micrograph of the material in the cold worked condition corresponding to trials 4 and 5. The microstructure is homogeneous. Secondary phases in isolated fields of view that are not representative of the bulk microstructure can be found, as shown in the metallograph of trial 5 in Figure 6. These precipitations can be dissolved using an optimized heat treatment.

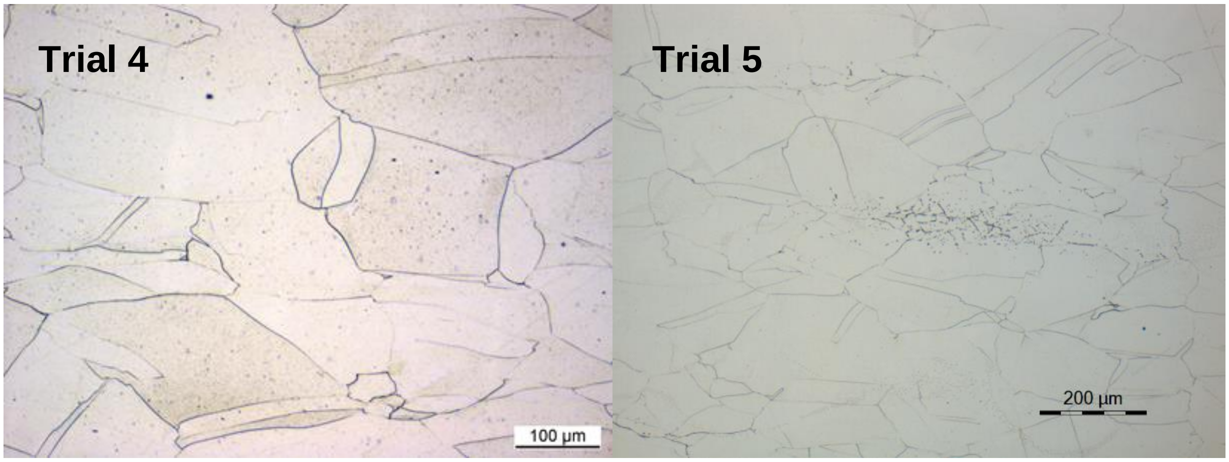

Figure 6: The large-scale production trial resulted in homogeneous austenitic microstructures.

The notched impact and hardness results are shown in Table 4.

Table 4
Notched impact and hardness test results for trials 4 and 5 to be compared with reference values for the solution annealed condition.

	Reference (solution annealed)	**Trial 4**	**Trial 5**
CVN [J]	> 150	199	220
Hardness [HRC]	< 20	30	39

Table 5 shows the obtained values for corrosion resistance according to ASTM G28 Method A and ASTM G48 Methods C & D. For reference, values for the solution annealed condition that are available in the literature are also depicted.

Table 5
This table shows the summary of the obtained mass loss rates or respectively the critical temperatures for localized corrosion.

	Solution annealed	**Cold worked condition**	
	Reference	**Trial 4**	**Trial 5**
ASTM G28, Method A *1	0.22 mm/a 24 h exposure time	0.14 mm/a	0.11 mm/a
ASTM G48, Method C *2	90 °C	90 °C	90 °C
ASTM G48, Method D *3	70 °C	55 °C	55 °C

*1: 50 wt.% H_2SO_4 + 42 g/l $Fe_2(SO_4)_3 \times 9 H_2O$, boiling, 120 h
*2: 6 wt.% $FeCl_3$ + 1 wt.% HCl, 24 h intervals
*3: 6 wt.% $FeCl_3$ + 1 wt.% HCl, 24 h intervals

The investigations using ASTM G28 Method A show no elevated mass loss rates for the cold worked condition. Thus, the microstructure has not been sensitized during the manufacturing process, even if trial 5 shows some minor degree of precipitation. Also, considering the obtained values of the susceptibility to pitting and crevice corrosion in ferric-chloride media of ASTM G48 method C & D, the resistance of the cold worked material against pitting corrosion is similar to the reference material in the solution annealed condition. As expected, the crevice corrosion tends to be somewhat more sensitive to the microstructure's condition. Thus, the critical crevice temperature has decreased slightly and lies at 55 °C. With respect to the intended applications, these values are still acceptable. As a reference, literature values for UNS N07718 lie at <10 °C.[20] As the UNS N08034 in the cold worked condition is intended as a substitute for UNS N07718, we consider that this crevice corrosion resistance is more than sufficient to fulfill the application requirements.

Laboratory scale production trials

For the current study, laboratory melts with a manganese content varying from 1.5 to 3.0 % and subsequently introduced cold work have been manufactured. The investigations on these variants have shown that a manganese content of about 3 % favors a maximized yield strength when introducing cold work, as shown on Figure 7.

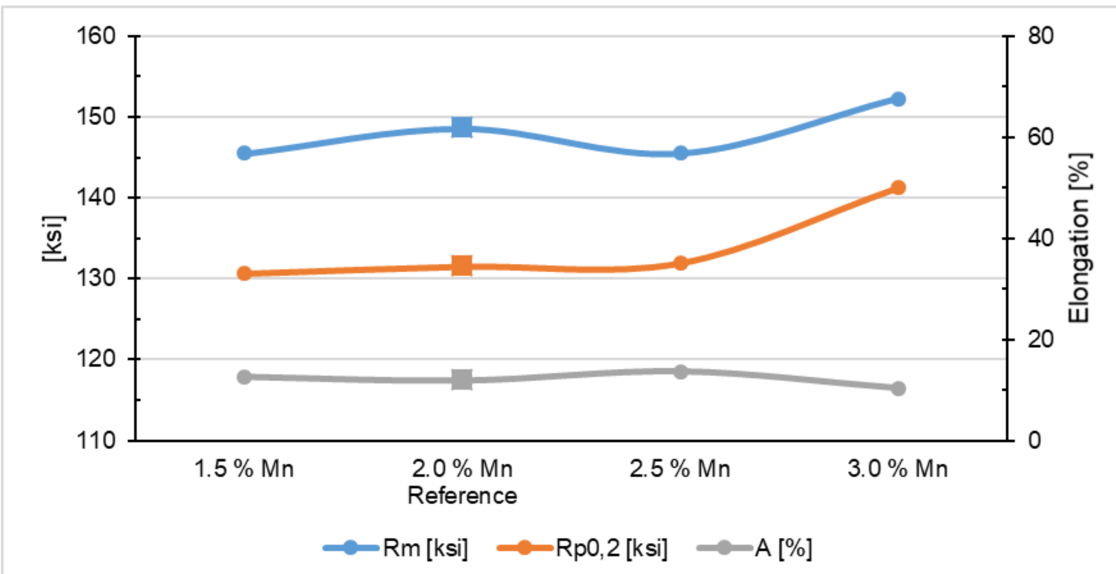

Figure 7: When introducing cold work, a manganese content of about 3 % in the laboratory melts leads to an incresed yield and tensile strength.

Following, only the results from the reference with 2 % manganese and the melt with an elevated content of 3 % manganese are going to be discussed. Owed to the tendency that has been seen frequently on laboratory trials and considering that laboratory-scale material usually presents internal defects that are not present in large-scale production, a laboratory heat, working as a reference for chemical analysis and processing, must always be manufactured to ensure the comparability among the testing matrix.

As it can be seen in the metallographic images in Figure 8, the microstructure of the 3 % manganese variant in the cold worked condition is comparable to the reference melt. Both images show a homogeneous austenitic microstructure with slightly elongated grains, which is to be expected for cold worked materials. The absence of precipitations in the grains or alongside the grain boundaries of both samples indicate the success of the applied manufacturing route. Furthermore, the average grain sizes are comparable.

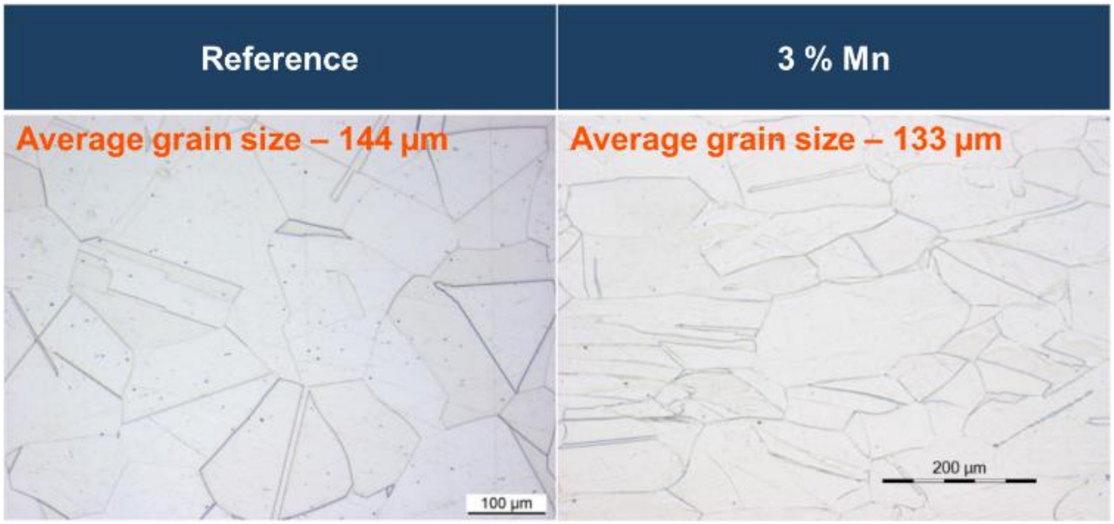

Figure 8: Images of the microstructures of the reference laboratory melt with 2 % manganese and the 3 % manganese laboratory melt both in the cold worked condition.

Looking at the obtained results from the mechanical tests of the laboratory melts from Table 6, a significant increase in yield strength and tensile strength for the variant with 3 % manganese content can be observed. The evaluation of the mechanical results must consider that internal and inherent defects are present in laboratory scale material, causing a reduction of the reference values compared to the ones of the large-scale production.

Table 6
Mechanical properties of the laboratory melts in the cold worked condition.

Laboratory scale		Reference - 2 % Mn (cold worked)	3 % Mn (cold worked)
Tensile test ASTM E/E8M	R_m [ksi]	147	170
	$Rp_{0.2}$ [ksi]	130	141
	A [%]	12	16

One reason for the good response of the material to the introduced cold work is the alloying element nitrogen. It is known from previous studies that an increased level of dissolved nitrogen has a very positive effect on the accommodation of cold work and the resulting mechanical strength. The interstitially dissolved nitrogen provides a strong elastic deformation of the crystal lattice and at the same time reduces the stacking fault energy. As a result, the sliding surfaces of the planes in the crystal become sharper and the internal frictional force is increased. Thus, dislocations introduced via cold work can only move with a comparatively increased energy input and there is an increase in the strength of the alloy. The presence of manganese promotes changes in the lattice, thereby increasing the solubility of nitrogen in the alloy, what drives an enhancement of the hardening mechanism discussed above.[21-22]

Table 7 shows the corrosion results of both laboratory melts, the reference containing 2 % of manganese and with increased manganese content.

The mass loss rates according to ASTM G28 Method A are comparable to solution annealed material as well to the large-scale trials shown above. The reference laboratory melt shows a mass loss rate of 0.11 mm/a, whereas the laboratory melt with increased manganese content shows a mass loss rate of

0.12 mm/a. The difference of 0.01 mm/a between both laboratory heats is not statistically meaningful and cannot be used with the objective of rating both alloy compositions.

Regarding localized corrosion resistance, the results of testing according to ASTM G48 Methods C and D show a reduction of the critical temperatures of both laboratory-produced heats in comparison to solution annealed as well as large-scale cold worked material. As mentioned above, the internal defects inherent of a material manufactured on a laboratory scale can lead to different responses to some corrosion mechanisms - in particular to localized corrosion in the form of pitting and crevice corrosion. Therefore, the discrepancies go well with the authors' expectations. Thus, comparing the ASTM G48 C and D test results of both reference and with increased manganese content heat, they show suitable behaviour with respect to the intended field of use.

Table 7
Corrosion resistance of the laboratory melts in the cold worked condition.

	Reference – 2% Mn (cold worked)	**3 % Mn (cold worked)**
ASTM G28, Method A *1	0.11 mm/a	0.12 mm/a
ASTM G48, Method C *2	65 °C	65 °C
ASTM G48, Method D *3	55 °C	45 °C
*1: 50 wt.% H_2SO_4 + 42 g/l $Fe_2(SO_4)_3 \times 9\ H_2O$, boiling, 120 h *2: 6 wt.% $FeCl_3$ + 1 wt.% HCl, 24 h intervals *3: 6 wt.% $FeCl_3$ + 1 wt.% HCl, 24 h intervals		

CONCLUSIONS

- Large-scale approach
  - The manufacturing route to produce cold worked UNS N08034 has been investigated and proven applicable for the material
  - Yield strength and tensile strength have been significantly enhanced while also maintaining a sufficient level of ductility
  - Microstructure is free of representative deleterious precipitates and a very low level of precipitates seems not to be detrimental to the alloy's corrosion resistance
  - Even in the cold worked condition, UNS N08034 presents sufficient corrosion resistance for oil and gas applications
- Laboratory scale approach
  - Melt with increased manganese content showed elevated mechanical strength when introduced to cold work in comparison to reference composition
  - The microstructure of the elevated manganese lab-melt is homogeneous and comparable to reference material
  - Laboratory scale heats in general show lower mechanical and corrosion resistance when compared to large-scale produced material, what can be explained by the internal defects related to small scale production
  - The corrosion resistance of the laboratory heat with reference composition is similar to the corrosion resistance of the laboratory heat with increased manganese content. Therefore, we conclude that the additional manganese does not influence the corrosion susceptibility of UNS N08034

- A combined approach of manufactured material on the large-scale using the investigated parameters and an elevated manganese content will be investigated with the intention of further increasing the effect of cold working

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