

Design of Sour Service Material Metallurgy by the Combination of Advanced Techniques

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ABSTRACT

The needs of oil and gas operators are challenging the industry to push the limits in sour service materials always further by finding the best compromise between high strength steels and good resistance to Sulphide Stress Cracking (SSC). It is in this context that materials have been recently developed, so as to respond to increasingly severe service with high level of Specified Minimum Yield Strength (SMYS). This communication presents the combination of computational modeling methods, advanced metallurgical characterization techniques, scale-up methods (from laboratory to mass production) for designing sour service steel grades with improved SSC resistance. Basics, pros and cons of several tools are discussed; namely X-Ray Diffraction from synchrotron beam, Transmission Electronic Microscopy, Electron Back Scatter Diffraction, Thermo-CalcTM. Their efficiency to optimize design has been validated on a selection of lab casted prototypes and applied to the development of a new 125 ksi SMYS material with enhanced SSC resistance, able to sustain 0.1 bar H₂S at ambient temperature. Some results demonstrating the SSC resistance as evaluated with NACE TM0177-2016 Method A of the newly developed steel sampled from pipes already produced at industrial scale will be shown.

Key words: Sulfide Stress Cracking, Advanced Material Characterization, Computational Modeling, Prototyping

INTRODUCTION

During the last decades, low alloyed steels with improved resistance to Sulfide Stress Cracking (SSC) have been developed for covering specific applications as heavy wall casings¹ or expandable tubings² or for reaching higher mechanical properties, such as 125 ksi Specified Minimum Yield Strength (SMYS) materials.³⁻⁶ For the latter, relevant sour environments for developed grades are mild, meaning

TM Thermo-Calc : Trade name

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that all sour applications cannot be covered while a strong interest exists for O&G operators to use high strength materials when designing wells. Consequently, there is an incentive to push the limits of use of high strength sour service steels by enhancing their resistance to SSC. Several recommendations were already published when designing high strength sour service grades: hardness level shall be limited as much as possible and be preferentially below 22 HRC⁷, microstructure shall present a minimum required amount of martensite⁸ which is well known to be ideal for combining high mechanical properties and high resistance to hydrogen. Besides, many authors highlighted some other influencing parameters related to the material or the process; below a short and incomplete review:

- The benefit to increasing the tempering temperature⁹ as much as possible for reducing dislocations densities¹⁰ and for increasing the proportion of transgranular cracking¹¹;
- The benefit to reducing prior austenite grain size^{12,14}. To do so, it has been recommended to apply multiple quenching steps⁹;
- The benefit to reducing the amount of inclusions that affect the plastic elongation¹¹ and specifically to avoid oversized oxide particles⁹. Also, the presence of residual elements such as S affect dramatically the Sour Service performance¹³;
- Upper bainite should be avoided^{9,14} and the addition of boron is known to enhance hardenability of low alloyed steels⁹;
- The beneficial impact of Mo for Sour Service is well established¹⁵ with an optimum content at 1.2% has been proposed¹⁶. The benefit would be due to fine carbide precipitation and to a decrease of the corrosion rate¹⁷;
- The impact of niobium content on SSC resistance has also been investigated. This element would help to decrease hydrogen permeation flux¹⁸. Niobium prevents prior austenite grain size growth during austenitization and allows higher tempering temperature thanks to niobium carbide precipitation¹⁹. It has been observed a reduction of SSC growth rate inside DCB specimens with increasing Nb content²⁰;
- While the maximum content in Ni at 1% given in NACE[†] MR0175/ISO 15156 document⁷ has been agreed as a good compromise²¹, Kappes and his co-authors highlighted that this maximum content in Ni is dubious because based on outdated test practices (NACE TM0177 Method B) and claimed that the most important is to have the appropriate tempered martensite microstructure²².

This knowledge results from decades-long scientific work, and its recent development required to use more and more advanced material characterizations for investigating the material microstructure and how it interacts with hydrogen. With Electron Beam Scattering Diffraction (EBSD), it has been possible to observe a decrease of K_{ISSC} with martensite packet size⁶, meaning that likely the benefit of low prior austenite grain size on SSC could be indirect. Transmission Electron Microscopy is powerful for observing the onset of recrystallization or shape, composition and distribution of carbides²³ while X-ray diffraction can be employed for assessing dislocations densities¹⁰ and Conversion Electron Mössbauer Spectrometry (CEMS) for quantifying residual austenite content²⁴. Finally, thermodynamic / thermokinetic computational software such as MatCalc^(‡) or ThermoCalc^(§) have started to be used for designing Sour Service materials^{25,26}.

A methodology combining Sour Service material design rules, thermodynamic modeling, accelerated material prototyping and advanced material characterizations is exposed and has been applied for the development of a new high strength material with enhanced resistance to SSC.

[†] NACE : National Association of Corrosion Engineers (Now AMPP : Association for Materials Protection and Performance)

[‡] MatCalc : Trade Name

[§] ThermoCalc : Trade Name

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SOUR SERVICE MATERIALS DESIGNING PROCESS

The development of various sour-service steels (proprietary 110ksi sour service, proprietary 125ksi sour service and now enhanced 125ksi sour service) has allowed to define and optimize the process of steel design.

- When proprietary 110ksi sour service was designed (in the early 90s), the design methods relied of the intuition of the metallurgists and the definition of the solution was reasonably easy as long as the key process parameters were identified and controlled. Only few industrial trials were needed.
- The design of proprietary 125ksi sour service (in the mid 2000s) was already more challenging. Laboratory heats were used, and the use of more sophisticated design tools (e.g. thermodynamics) was needed.
- The newly developed enhanced 125ksi sour service (in the last few years) needed to combine many of the available tools, both on the design phase but also for characterization. About 50 laboratory heats were investigated to build the appropriate knowledge and find the “right” answer.

To create high performance materials, a method based on 3 steps is used:

- Material design: to write down potential candidates “on paper” based on established design rules and know how.
- Material prototyping: elaboration via a small-scale casting route while keeping the representativeness of the final production (industrial rolling, heat treatment).
- Material characterization: to check the material final performance (Mechanical properties, SSC resistance) but also check that the aimed microstructural features are indeed met at the prototyping-scale.

Material design: to write down potential candidates “on paper”

A material's performance is linked to its microstructural features like:

- Microstructure at relevant scale levels: prior austenitic grain size, martensite microstructure (packets, laths...), precipitation (primary carbides, inter- and intra-laths, etc)
- Level of segregations
- Presence of inclusions (nature, size, etc.)

Some of those microstructural features can be predicted by Integrated Computational Materials Engineering (ICME)-type approaches, among which CALculation of PHase Diagrams (CALPHAD). Nevertheless, well defined design rules are essential for driving the calculations towards the right direction, especially concerning the following points:

- hardenability: the material must exhibit enough hardenability to enable full martensitic microstructure after quenching, even for thick coupling stock material
- tempering temperature: it is known that a better SSC resistance is linked to high tempering temperatures
- cost: obviously, some alloying elements are expensive (Mo, V...) and their cost must be considered as well

These various contributing factors are assembled in a Figure Of Merit (FOM) approach to enable identifying the best candidates among various ideas. A definition of “Figure of Merit” is “a quantity used to characterize the performance of a device, system or method, relative to its alternatives”.²⁷ In the context of material design, it allows ranking various proposals to decide the most promising ones. It mixes various aspects (e.g. hardenability, tempering temperature, cost, etc.) and the relative weight

(somehow arbitrary) of those different contributions will modify the ranking of the candidates. Despite this arbitrary aspect, it has proven to be effective to select the best candidates.

Once a list of possible candidates is established, some verifications are performed to identify potential risks at various process steps: casting (to limit segregation, to avoid coarse carbides and dissolved gasses, etc.), rolling (forces, ductility, etc.), heat treatment (quench cracks, etc.).

Material creation: from a paper-written candidate to a representative prototyping-scale

Once a set of candidates is defined, several processing routes are available, of which the best compromise was chosen.

- Casting:
 - 200-tonne industrial castings are not an economical way to generate test material
 - Rapid Alloy Prototyping (RAP) approach presents many interests for creating rapidly many different materials.²⁸ However, it may generate too small amount of material for the evaluation of the SSC resistance but even more critically it may fail to represent accurately the industrial rolling process.
 - Therefore, laboratory Vacuum Induction Melting (VIM) that provides 80 to 200 kg castings (ingots) of good cleanliness and soundness are preferred.
- Rolling:
 - industrial rolling is preferred, in a plant able to accept the 200-kg size ingots and process them with an industrial rolling process. This approach allows to avoid any discrepancies induced by the rolling process used.
- Heat treatment:
 - To address the tempering resistance of produced material, it is necessary to apply different heat treatments. That is the reason why heat treatments are performed with laboratory heat treatment furnaces. In addition, it allows the evaluation of the SSC resistance at different yield strengths levels and a comparison between candidates in the same range of yield strength.

Materials

To illustrate the methods described above, this paper will present typical results obtained on following materials: three candidates showing a variation of carbon and vanadium content were produced by following the route described above. Chemical analyses are summarized in Table 1.

Table 1
Chemical analyses (wt%) for the main elements

Steel	C	Si	Mn	Cr	Mo	V	Nb	W
A	0.29-0.30	0.20-0.32	0.31-0.36	0.40-1.0	0.83-1.75	w/o	0.30-0.35	<0.1
B						0.15-0.20		
C	0.43							

Material characterization: selection of the best candidate and verification of its final performance

Once materials have been prepared by the route presented before, microstructure, tensile properties based on ASTM^{**} A370²⁹, and Sulfide Stress Cracking resistance based on NACE TM0177-2016 Method A³⁰ are characterized.

ADVANCED TECHNIQUES FOR MICROSTRUCTURAL CHARACTERIZATION

Cleanliness assessment

The microstructure of the material was checked to verify that the material does not suffer from any quality issue (e.g. presence of macro inclusions, etc.). The samples were tested according to ASTM E45³¹, but also thanks to a coupled method using Scanning Electron Microscopy (SEM) to identify inclusions and Energy-Dispersive Spectroscopy (EDS) to get their chemical composition.

Precipitation analysis

Precipitates can act as hydrogen traps, therefore reducing the instantaneous hydrogen concentration in the material and enhancing its susceptibility to H-embrittlement.

A proper analysis of precipitates in the microstructure should involve cross-measurements by several techniques involving at least one technique using diffraction (precipitates crystallography) and one using EDS (precipitates chemical composition). A first step is the identification of the precipitates in the material using XRD synchrotron analysis (SR-XRD), SEM+EDS for the largest precipitates ($\varnothing > 200\text{nm}$) and TEM+EDS for the smallest ones. Based on this identification, quantification can be performed by SR-XRD with Rietveld analysis.

Various methods are used and combined:

- Classical Light Optical Microscopy (LOM) to identify coarse precipitates (such as primary carbides), but also heterogeneities in precipitates sizes and location at various dimensional scales: segregation, grain boundaries, etc.
- Scanning Electron microscopy (SEM) to analyze finer precipitates and get information about their composition. Observations are performed on massive samples, after polishing and slight etching, that allow to measure the composition of mid-size precipitates ($> 1\mu\text{m}$). To avoid the influence of the matrix, precipitates characterization is performed on carbon extraction replica^{††}. Fast information is obtained on small precipitates ($> 100\text{nm}$) thanks to Energy-Dispersive X-Ray spectroscopy (EDS) mapping (Figure 1). SEM+carbon replica associated with the CALPHAD software enable to obtain a trend about the nature of the precipitates. Still, it has shown some limitation in their quantification by image analysis because of the depth of the layer of material extracted by replica.

^{**} ASTM: American Society for Testing and Materials. ASTM E45: Standard Test Methods for Determining the Inclusion Content of Steel. This standard determines the microcleanliness of a steel by counting thanks to an optical microscope the number of inclusions ranked by type/shape and size classes

^{††} Carbon extraction replica : a method to extract precipitates out of the surface of a polished steel sample to allow their chemical analysis to be measured without being influenced by the composition of the steel matrix

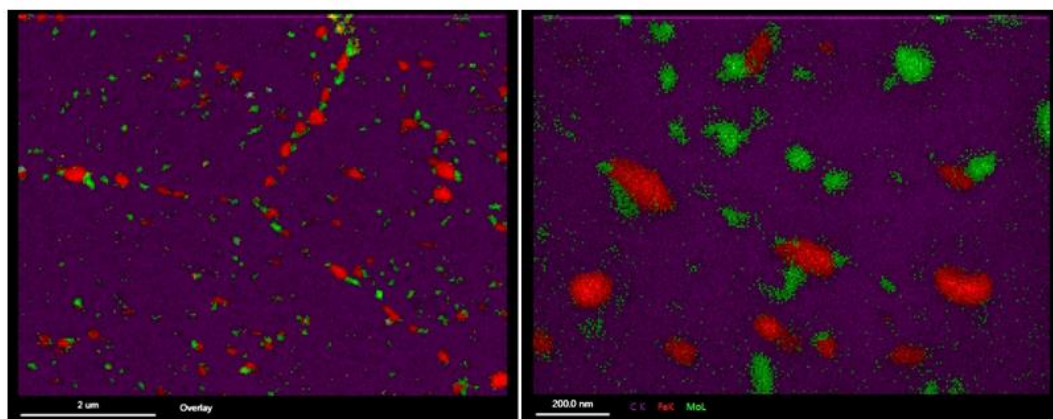


Figure 1 : Steel B - SEM observation of precipitates on Carbon replica. The color of each precipitate is attributed according to their composition determined by SEM (red: Cr-rich, green : Mo-rich). We see alignments of Cr-rich precipitates along a block boundary.

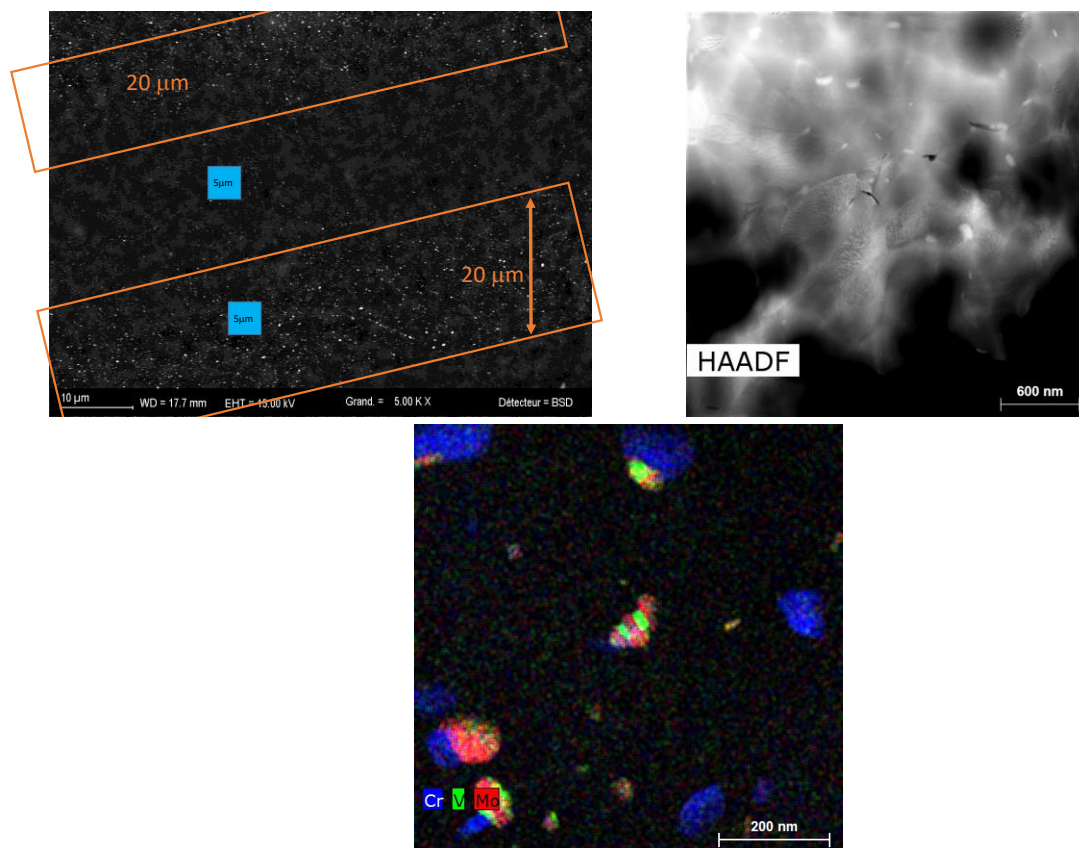


Figure 2 : Steel C –
Top: SEM (left) and TEM (right) thin foil observation of precipitates. In the SEM picture, the blue square shows the size of the TEM picture. We see that the typical size of TEM observation is small with respect to heterogeneities (here: segregations).
Bottom: HR-TEM showing the complex nature of the precipitate (blue : Cr, green : V, red : Mo)