Influence of the microstructure of Virgo™38, a 16Cr-4Ni low-carbon supermartensitic stainless steel, on its SCC resistance

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Summary
Within this work, the influence of the microstructure of a 16Cr-4Ni low-carbon supermartensitic stainless steel (SMSS) on its SCC resistance was studied. The work was first focused on the determination of the fraction of retained austenite (austenite stable at room temperature) after tempering heat treatments or after plastic deformation. Indeed, this steel exhibits Strain Induced Martensitic Transformation (SIMT) phenomenon which influences the amount of retained austenite. Different microstructures have been prepared and their resistance to SCC has been studied using Slow Strain Rate Tensile (SSRT) tests in an environment containing Na\textsubscript{2}S. This compound has been chosen in order to reproduce the effect of sulfur/sulphur present in H\textsubscript{2}S-containing environments. These tests have shown that the decrease in initial retained austenite content leads to a diminution of the SCC resistance.

Context
Virgo™38, a 16Cr-4Ni low-carbon supermartensitic stainless steel (SMSS), represents the best stainless steel inside the GE Oil & Gas portfolio. 95% AYS tests were passed according to the standard NACE TM0177 – method A tests with 1 bar H\textsubscript{2}S up to 1 g/L NaCl [1]. It exhibits a good ductility and corrosion resistance [2], combined with high mechanical resistance. Its properties lead it to be used, among others, for the construction of centrifugal compressor's impellers working in sour environments rich in CO\textsubscript{2} and H\textsubscript{2}S. To be safely used, this alloy has to fulfil strict requirement described in the NACE standard MR0175 – ISO15156 [3]. The targeted microstructure of Virgo™38 is composed of tempered α’ martensite containing retained austenite γ\textsubscript{r} in sufficient but not too high volume fraction and located between martensitic laths. The principal role of retained austenite is to improve fracture toughness of the material. After austenitization at high temperature (>1000°C), the alloy is quenched in oil to room temperature. To ensure that no retained austenite subsists after quenching, a sub-zero treatment is applied. Two-stage tempering is then carried out slightly above the Ac1 temperature in order to form the targeted fraction of reverted austenite. The role of second tempering, applied according to NACE guidelines at a slightly lower temperature than the first one, is to transform fresh martensite which might be formed during cooling after the first tempering. After double tempering, the retained austenite fraction is expected to be between 20-30%. Furthermore, double tempering is supposed to increase austenite stability with respect to the martensitic transformation induced by plastic deformation [4].
**Introduction**

Supermartensitic stainless steels are currently used with success for oil & gas applications. Nevertheless, some failures have recently occurred during service in sour environments [5]. In order to improve corrosion properties and prevent any failure, one has to better understand the influence of metallurgy and mechanics on hydrogen assisted cracking phenomena.

Kimura et al. [6] showed that, for a modified 13% Cr steel pipe, the resistance to SSC increases with the increase in retained austenite content. As previously presented [7], in Virgo™38, the retained austenite fraction and its composition are very sensitive to the tempering temperature. Moreover, the retained austenite of Virgo™38 easily transformes to martensite under plastic strain (SIMT). This effect is conditioned by the chemical composition of the austenite, as it was shown by Smirnova et al. [8], and it is therefore supposed to be indirectly related to the tempering temperature.

The sequence of heat treatment applied, according to NACE requirements [3] is shown in Figure 1. On this schematic representation, \( \gamma_{\text{rev}} \) and \( \gamma_r \) correspond to reverted and retained austenite respectively while \( \alpha' \) and \( \alpha'' \) correspond to fresh and tempered martensite respectively. \( \delta \) represents \( \delta \)-ferrite, potentially present in supermartensitic steels.

The motivation of this study is to establish a relation between the retained austenite fraction and the SCC behavior of Virgo™38.

For this, several microstructures with different amounts of retained austenite were prepared using tempering treatments at various temperatures and by applying different amounts of plastic strain prior to SCC testing.

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**Figure 1**: Thermal profile including expected phases at each step, corresponding to the NACE standards
Material and experimental methods

For this work, an industrial heat of Virgo™38, transformed by Forgia Rapida Srl with a composition indicated in Table 1 was chosen.

Table 1: Chemical composition and basic mechanical properties of Virgo™38

<table>
<thead>
<tr>
<th>%C</th>
<th>%Cr</th>
<th>%Ni</th>
<th>%Mn</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>HRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03-0.045</td>
<td>15-17</td>
<td>4-5</td>
<td>max 0.8</td>
<td>min 620</td>
<td>min 780</td>
<td>max 28</td>
</tr>
</tbody>
</table>

Starting from the industrially heat treated grade, an austenitization treatment at high temperature was performed. A purely martensitic state was obtained after sub-zero oil quenching. From this point, several tempering treatments at temperatures between 580°C and 660°C were carried out in order to obtain microstructures with different volume fractions of retained austenite. The retained austenite fractions were measured by X-ray diffraction (XRD) using a Panalytical X’Pert diffractometer. The volume fraction of each phase was then determined by the Rietveld method [9] [10] using the free software MAUD. This technique does not require external calibration and gives accurate austenite content providing its volume fraction is higher than 2 vol%. This technique can be used because the samples have no preferential texture after tempering as determined by XRD. A strict procedure of metallographic preparation was applied in order to ensure that no SIMT occurs at the sample surface during preparation. The reverted austenite fractions (i.e. the amount of austenite at high temperature, at the end of ‘plateau’) were also measured through in situ XRD measurements inside a HTK16 furnace.

Austenite stability at room temperature may be seriously affected in presence of stresses (applied and/or residual), in particular when they induce plastic strains. The martensitic transformation occurring in such conditions, called Strain Induced Martensitic Transformation (SIMT) also depends on austenite composition and it is well documented for different types of stainless steels [4], [8], [11]–[13]. In order to highlight and quantify this phenomenon in an industrially heat treated grade of Virgo™38, successive compression tests interspersed by XRD measurements have been performed on the double tempered state.

Tensile samples with different amounts of retained austenite were prepared either by heat treatments or by straining. Their SSC resistance was then investigated by Slow Strain Rate Tensile (SSRT) tests in a sulfur containing environment (introduced as Na₂S) at a strain rate of $10^{-7}$ s⁻¹. The composition of the solution used is described in Table 2.

Table 2: Composition of the solution used for SSRT tests

<table>
<thead>
<tr>
<th>Component</th>
<th>NaOH</th>
<th>Na₂S</th>
<th>Gas: N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>1M</td>
<td>0.02M</td>
<td>100%</td>
</tr>
</tbody>
</table>

A cathodic potential of -1300mV/ECS was applied after the specimens were fully immersed and during all the tensile test.
**Results and discussion**

The principal motivation of this work is to study the influence of the microstructure of Virgo™38 on its SSC resistance. Firstly, the influence of the tempering treatment on the microstructure and hence the stability of retained austenite regarding SIMT phenomenon for one industrially heat treated grade (double tempered grade) was studied. Then, the relation between the initial retained austenite fraction and the SSC resistance of Virgo™38 was highlighted.

**Influence of the tempering treatment on the retained austenite fraction**

The results of reverted and retained austenite fractions as a function of tempering temperature, after 2 hours treatment, are presented in Figure 2.

![Figure 2: Reverted and retained austenite fractions as a function of tempering temperature](image)

When tempering temperature increases, the amount of martensite transformed into austenite (reverted austenite $\gamma_{rev}$) increases, however a part of it transforms back into fresh martensite ($\alpha'$) on cooling. So that the final austenite content after tempering (retained austenite $\gamma_r$) is smaller than $\gamma_{rev}$. Indeed, during tempering, nickel tends to diffuse into austenite grains [11] so that its average concentration within this phase increases and also depends on its volume fraction. In fact, with high volume fractions of reverted austenite, its enrichment in Nickel is limited. Since the stability of reverted austenite depends on its average Nickel content, the final amount of retained austenite is indirectly function of tempering temperature. For this reason, a maximum of retained austenite fraction is supposed to be observed for an intermediate tempering temperature depending on the composition of the steel [11] and was clearly confirmed by this study. This temperature was determined to be 625°C for this grade of Virgo™38 and results in a retained austenite volume fraction of 15% after the first tempering treatment. This value is lower than the targeted range of 20-30% obtained on an industrially heat treated grade because only a single tempering treatment of 2 hours duration was performed in the present study.
Influence of plastic strain on the retained austenite fraction

The results of retained austenite fraction as a function of applied strain, obtained by uniaxial compression tests, are illustrated in Figure 3.

![Graph showing retained austenite fraction as a function of applied plastic strain](image)

**Figure 3:** Retained austenite fraction as a function of applied plastic strain

When deformation increases, the amount of retained austenite decreases, which means that a non-tempered martensite is formed. No differences between tempered martensite, non tempered martensite and martensite formed by SIMT are observed in XRD patterns, which means that their structure is the same, at least from the crystallographic point of view.

Influence of the retained austenite fraction on the SSC resistance of Virgo™38

Figure 4 illustrates the effect of plastic pre-straining on the plastic deformation at failure obtained in SSRT tests for three different microstructures: not prestrained and pre-strained in air to 3.7% and 8.6%.

![Graph showing plastic deformations at failure obtained after pre-straining in air](image)

**Figure 4:** Plastic deformations at failure obtained after pre-straining in air before the SSRT
Without plastic pre-strain, i.e. for the industrially double tempered grade, the plastic strain obtained in Na$_2$S-containing environment is of about 2%, whereas it is of about 25% in air. The plastic strain at failure decreases with the increase in air-straining before the SSRT. Indeed, during pre-straining in air and as previously observed, retained austenite transformed back into martensite. This transformation induces a reduction in austenite content and thus an increase of fresh martensite content. This phase is known to increase the cracking susceptibility due to hydrogen, especially in sour environments. The reduction of plastic strains could be explained by an increase in hydrogen diffusion [8] due to the newly formed fresh martensite. Furthermore, this pre-straining in air also induces work hardening and dislocation emission so that the hydrogen diffusion is even faster through dislocation assisted transportation (Hydrogen Enhanced Localized Plasticity, HELP mechanism, [14]).

Moreover, the influence of fresh martensite has been studied throughout a tensile specimen in the quenched and non tempered grade. After XRD measurements, we obtained no residual austenite after sub-zero oil quenching. In this heat treatment conditions, failure occurred within the elastic domain, i.e. without any plastic strain at failure. This test confirms the sensitivity of fresh martensite regarding SSC and helps us understanding the decrease in plastic elongations with increase in pre-straining. Indeed, this decrease is probably due to the presence of fresh martensite formed by the transformation of austenite under strains.

**Conclusions and perspectives**

The present study demonstrated the existence of a critical temperature, close to 625°C, beyond which the retained austenite fraction decreases with increasing tempering temperature. The loss of austenite stability for higher tempering temperatures is due to the increase of its $M_S$ point which exceeds 20°C. Moreover, it was shown that, even for the standard heat treatment, retained austenite is not stable under applied stress (SIMT), so that microstructure is likely to evolve in service. To better understand the influence of this possible evolution in service, we performed slow strain rate tensile (SSRT) tests on samples containing different amount of retained austenite, in a sulfur containing environment. This study showed that the transformation of austenite to martensite led to a decrease in the plastic strain at failure, i.e. to a substantial ductility loss.

**References**


