DEVELOPMENT OF A NEW HIGH-PERFORMANCE MARTENSITIC HEAT-RESISTANT STEEL FOR BOILER APPLICATIONS

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ABSTRACT

The realization of advanced thermal power plants with increased efficiencies requires the development of new materials with enhanced capabilities in respect to high temperature strength and steam oxidation behavior. The change in the environmental policy and the increasing contribution of renewable energy sources into the public electric grid has changed the operation mode of the existing power plants in Europe. Instead of quasi stationary operation, for which the conventional thermal power plant fleet was designed, cyclic operation modes will dominate the power plant service lifetime. The creep-fatigue phenomena, however, may be responsible for significant lifetime reductions compared with the original design lifetime. Revamping of the existing power plants by application of “stronger” materials with improved steam-oxidation behavior, allowing wall thickness reduction can be a possible way to address the topic. Recently, Vallourec developed a new high-Cr ferritic-martensitic steel that combines excellent creep rupture strength properties and enhanced steam oxidation resistance of 12%Cr steels such as VM12-SHC or X20CrMoV11-1. Industrial products were successfully manufactured and the creep and steam oxidation properties were validated.

INTRODUCTION

The key factor for the further development of the power plant technology is the increase of the operating efficiency. The realization of elevated steam parameters requires the application and, in case of non-availability, the development of materials with improved capabilities with regard to creep rupture strength and oxidation properties. Over the last decades, a variety of new “stronger” ferritic/martensitic steel grades, such as 9% Cr steel Grade 91 or tungsten modified 9% Cr steels Grade 911 and Grade 92, has been developed and applied as construction materials for components in modern high-efficiency thermal power plants.

A further extension of the temperature application range for ferritic/martensitic steel grades beyond the current limit of approximately 620°C, however, requires new materials with improved steam oxidation properties, which may be achieved by increasing the chromium alloying content from 9 to 12 wt.-%, or application of protective coatings [1]. The tungsten modified 12%Cr steels Grade 122 and VM12-SHC did not reach the creep strength level of Grade 92 due to long-term microstructural instabilities introduced by their elevated Cr contents.

Very recently, Vallourec’s continuous steel development efforts have lead to a new 12% Cr heat-resistant steel that provides improved creep rupture strength and enhanced steam oxidation behavior. The aim of this paper is to describe the alloying design concept for the new steel and to present the first results of validation tests on industrial pipe prototypes.

ALLOYING DESIGN

High chromium martensitic steel grades generally suffer from microstructure instabilities upon long-term creep loading at elevated temperatures. The recovery process, which includes the transformation of the tempered martensite lath microstructure into a subgrain microstructure (as a consequence of dislocation rearrangement due to dislocation climb) and at the later stage the coarsening of the emerging subgrain microstructure, diminishes the number of free dislocations and the strengthening effect of the martensite itself [2,3]. The described microstructure degradation process may be retarded or even delayed by precipitates such as:

- M23C6 carbides (M: Cr, W, Mo, V),
- Laves phase (Fe2W, Fe2Mo),
• MX carbonitrides (M: V, Nb; X: N, C).

However, the coarsening of boundary strengthening precipitates like $M_23C_6$ or Laves phase [4], the transformation of MX carbonitrides into the Z phase with an enhanced coarsening rate [5] and the depletion of W and Mo from the matrix [6] promotes detrimental microstructural changes with increasing exposure times at elevated temperatures. Especially the PAGBs (Prior Austenite Grain Boundary) have been identified as the weak link in the martensitic microstructure, where the preferential recovery takes place [7].

Small additions of B can effectively reduce the coarsening rate of $M_23C_6$ at and in the vicinity of PAGBs, hence strengthen them and consequently, delay the recovery of the subgrain microstructure next to the PAGBs [8]. However, in order to unfold the beneficial effect of B on coarsening of $M_23C_6$ carbides, it is necessary to limit the nitrogen content and to avoid BN formation [9].

The strengthening concept for the new 12%Cr steel, hereafter referred to as Super VM12, relies on:

• Small B additions that stabilize the $M_23C_6$ precipitates at and in the vicinity of PAGBs and suppress there the martensite microstructure evolution processes during creep loading,
• Strict control of nitrogen for improved utilization of boron additions,
• Solid solution hardening by addition of Mo and W,
• Precipitation hardening ($M_23C_6$, MX, Laves phase).

EXPERIMENTAL

Pipe products have been produced with dimensions 457x50mm and 508x50mm from a 60t cast of Super VM12 (12CrCoWMoBN), which was in accordance with the specification for the chemical composition given in Table 1. Typically, Super VM12 steel is used in normalized and tempered condition. The creep qualification test program was launched in the temperature range between 550°C and 700°C. Laboratory steam oxidation tests were performed on specimens of dimensions 20 mm x 10 mm x 2 mm by exposing them in a Ar-50%H$_2$O gas mixture at 600°C, 625°C and 650°C. All specimens were ground with a 1200 grit surface finish on all sides and subsequently, cleaned in ethanol prior to exposure. The mass change was measured every 250h. The reference materials Grade 92 and VM12-SHC were oxidized in parallel.

The strengthening concept for the new 12%Cr steel, hereafter referred to as Super VM12, relies on:

Table 1: Specified chemical composition range for Super VM12 steel in wt.-%.

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Ni</th>
<th>B</th>
<th>N</th>
<th>Co</th>
<th>W</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.30</td>
<td>0.20</td>
<td>10.50</td>
<td>0.10</td>
<td>0.15</td>
<td>max.</td>
<td>0.008</td>
<td>0.002</td>
<td>1.50</td>
<td>1.50</td>
<td>0.02</td>
</tr>
<tr>
<td>0.16</td>
<td>0.80</td>
<td>0.60</td>
<td>12.00</td>
<td>0.60</td>
<td>0.30</td>
<td>0.40</td>
<td>0.015</td>
<td>0.020</td>
<td>2.50</td>
<td>2.50</td>
<td>0.10</td>
</tr>
</tbody>
</table>

RESULTS

Super VM12 in heat-treated condition exhibits a tempered martensite microstructure with a low δ-ferrite amount, typically less than 2vol.-% in average (Figure 1).

Yield and tensile strength at room and elevated temperatures are above the minimum values of Grade 92, as defined in the EN10216-2 standard (Figure 2).

Room temperature Charpy V-notch impact energy for thick-wall pipe products lies typically in the range of 40J in transversal direction (Figure 3).

Figure 4 shows the creep rupture strength results in the temperature range between 575 °C to 675 °C. The maximum test duration currently exceeds 30,000 h. The first estimation of the 100,000 h creep rupture strength indicates a performance improvement compared to Grade 92 of up to 20% and more than 30% when compared with the VM12-SHC steel.
Additional long-term testing is currently in progress to validate the first estimates.

Figure 3: Charpy V notch test results for Super VM12 pipe products compared with minimum requirements for Grade 92 according to the EN10216-2 standard.

Figure 4: Creep rupture strength of the Super VM12 steel compared with the average lines for Grade 92 according to the ECCC material datasheet from 2005 (dashed lines).

Figure 5 shows the steam oxidation results in the temperature range between 600 °C to 650 °C. At 600°C and 650°C, the Super VM12 steel shows similar weight change values as the VM12-SHC steel. These values are significantly lower than those obtained for the typical 9%Cr steels Grades 91 and Grade 92, which are characterized by oxide scale spallation as well. Figure 6 illustrates the metallographic cross sections of Grade 92 and Super VM12 after 5,000h exposure in Ar-50%H₂O at 600°C and 650°C. The Super VM12 steel shows coexistence of a protective Cr-rich oxide scale and some iron-rich oxide nodules at its surface. In contrast, the Grade 92 forms much thicker iron-rich oxide scales which are prone to suffer from spallation by either in-scale gap and pore formation or buckling as illustrated in Figure 6b.

Figure 5: Steam oxidation behaviour of Super VM12 compared to 9%Cr steels and VM12-SHC at a) 600°C and b) 650°C.

Figure 6: Metallographic cross sections of P92 and Super VM12 after 5,000 h exposure in Ar-50%H₂O at a) 600°C and b) 650°C.
First welding trials using a matching filler metal have been accomplished (Figure 7). The results will be reported in a future publication. The induction bend trials were successfully performed as well (Figure 8).

**DISCUSSION**

New materials with enhanced steam-oxidation capabilities are needed for a further increase of the application temperature range for ferritic/martensitic steel grades in modern thermal power plants. Typical 9-12% Cr ferritic/martensitic steels tend, when in contact with steam and/or high water vapor containing atmospheres, to develop thick iron-rich oxide scales [10]. Overheating of boiler tubes [11] and/or oxide scale spallation [12], may have serious implications for the lifetime and the safe operation of the steam conducting boiler components and the associated steam turbine. The steam-side oxidation of boiler heat exchange tubes and steam piping components is strongly related to the chromium content of the corresponding alloy [13]. Cr contents higher than 11 wt.-% are typically required in the ferritic/martensitic steels to form protective scales in steam. In this term, the newly developed Super VM12 steel exhibits similar oxidation behavior as VM12-SHC steel. Both steels show weight change values far lower than typical 9%Cr steels. The gravimetric data were confirmed by the metallographic characterization of the investigated specimens. Specimens of Grade 91 and Grade 92 tend to form non-protective oxide scales. Beneath the original metal surface an inner layer is formed, consisting of Fe₃O₄ and a Fe₃Cr-rich spinel. Above the original metal surface, Fe₂O₃ and Fe₃O₄ layers were present. Close to the steel, an internal oxidation zone is observed. In-scale gap and porosity was presented on the 9%Cr steel specimens at 600°C and 650°C, being more frequent at higher temperatures. The Super VM12 steel, due to its optimized combination of alloying elements, forms a protective Cr-rich oxide scale, which is still present after 10,000h exposure at 600°C and 650°C. These scales are also characterized by the local formation of iron-rich nodules as shown in Figure 6. The composition of these nodules is similar to that being described for the case of the Grade 91 and Grade 92, but with an evidently lower amount of in-scale porosity, and also gap formation was not present. As a consequence, the newly developed Super VM12 steel shows a higher oxidation resistance, but also a better behavior than Grade 91 and Grade 92 against scale spallation under cyclic conditions.

On the other hand, it is repeatedly reported that the high strength high-Cr martensitic steels suffer from unexpected deterioration of their long-term creep properties. Usually, the deterioration is ascribed to preferential recovery of the martensitic microstructure next to PAGBs [7], Z-phase formation and disappearance of MX strengthening precipitates [5], depletion of W and/or Mo due to Laves phase formation [6], and strains induced by the martensitic transformation [14] etc.. The degradation of creep rupture strength due to microstructure evolution processes upon long-term exposure to elevated temperatures and creep load were so far the major challenge for the development of a new high Cr steel with a strength level beyond that of Grade 92. The new Super VM12 steel, however, shows a remarkable long-term stability of the creep rupture strength, so far unmatched in the class of 12%Cr steels and apparently also better than Grade 92. The improvements may be attributed to the beneficial effect of small B additions on the coarsening of M₂₃C₆ at and in the vicinity of PAGBs. On the one hand stable precipitates at boundaries are essential to maintain the tempered martensite lath microstructure for long exposure times and delay its transition into the subgrain microstructure. On the other hand stable precipitates are crucial to suppress the coarsening of subgrains, once they emerge. Enhanced precipitate stability is responsible for the retardation of the onset of the tertiary creep and minimization of the creep acceleration within the tertiary creep region. This is especially noteworthy in view of the fact that the precipitation stabilizing effect, initially described for the 9%Cr MARBN (SAVE12AD/Grade 93) steel [4], was very successfully applied on a 12%Cr steel. Since fabricability characteristics (bending, welding) and the toughness and tensile properties are good, Super VM12 obviously represents a steel grade with an extraordinary balance of properties, which provides superior and stable long-term creep rupture strength, outstanding oxidation performance and good fabricability features at moderate costs united in one material.

**SUMMARY**

Using novel alloying design Vallourec developed a new 12%Cr steel, called Super VM12, with both an excellent creep
rupture strength and also a superior steam oxidation performance.

Industrial prototypes were successfully manufactured and subjected to an exhaustive qualification testing program. Long-term creep data now exceeding 30,000h indicate a creep performance improvement compared to Grade 92 in the range of up to 20%. Long-term steam-oxidation testing at 600°C, 625°C, and 650°C proved a superior behavior of the new steel in steam atmospheres with low oxidation rates and without any tendency to oxide scale spallation. Tensile and toughness properties fulfill the requirements from standards. Induction bending trials were successfully performed and first welding trials with matching filler metal were carried out.

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REFERENCES