Characterization of an ASTM A335 P91 ferritic-martensitic steel after continuous cooling cycles at moderate rates

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ABSTRACT

In this contribution some aspects of the behavior of the ASTM A335 P91 (9Cr1MoVNbN) steel subjected to continuous cooling cycles under fixed austenitization conditions are studied. Representative samples of the structures obtained after cooling at moderate rates (i.e. pure martensitic and mixed martensitic-ferritic) were analyzed in order to incorporate information to the Continuous Cooling Transformation (CCT) diagram of this material. The characterization was carried out by means of scanning and transmission electron microscopy (TEM), X-ray diffraction and Mössbauer spectroscopy. For the working conditions here employed, the results showed the existence of retained austenite within both, the pure martensitic and the mixed martensitic-ferritic domains of cooling rates, adding important information to the CCT diagram since retained austenite presence could be detrimental to the mechanical properties of the steel. Second phase precipitates, being relevant to fix the mechanical behavior of the material, were identified by means of TEM on carbon replicas. Mössbauer spectroscopy was very helpful to detect a low volume fraction of cementite-type phase in all of the samples, considering that it could not be conclusively determined by XRD due to orientation effects.

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1. Introduction

Ferritic-martensitic steels of the 9%Cr1%Mo type have been extensively used in conventional power plant components, heat exchangers, piping and tubing, etc., due to an excellent combination of properties such as creep resistance, toughness and corrosion resistance at high temperatures. In the four last decades, 9%Cr1%Mo-based modified alloys have also been designed and studied for applications as structural materials in the new generation of nuclear fission reactors, expected to work at high to very high temperatures (Generation IV reactors) and in fusion reactors as well. These new envisaged applications have raised very exigent requirements, as...
elevated temperatures and aggressive environments in standard service conditions, which must be coupled with the existence of strong irradiation fields [1–3].

Grade P91/T91, P denoting pipes and T tubes, is a ferritic-martensitic 9%Cr1%Mo steel microalloyed with V and Nb. Its enhanced properties enabled steam-plant components to be manufactured with thinner walls, thus minimizing thermally induced stresses. Nb, V and N addition also favored the creep-rupture strength.

The standard manufacturing steps of P91/T91 steels include normalizing at 1050–1060 °C and tempering at 750–760 °C. The resulting microstructure is a lath martensite, and the main type of precipitates are M23C6 carbides (M = Cr, Fe) and MX carbonitrides (M = Nb, V; X = C, N). Although the standard heat treatment ensures the basic sought-after properties of the alloy, the procedure has recently been subjected to review. Some variations have been proposed in order to attain a better performance in the mechanical properties of the material. For instance, two-step tempering treatments (low and high temperature stages, respectively) have been developed to combine a narrow average lath width along with adequate precipitation strengthening [4].

The Continuous Cooling Transformation (CCT) diagrams of these alloys are relatively simple and display basically three phase fields; that is, austenite, ferrite and martensite, with the additional presence of second phase precipitates in all of them [5–7]. The key features of the CCT diagram of P91/T91 steels include two critical cooling rate values: \( c_m \), which represents the maximum cooling rate to achieve a fully ferritic microstructure (on increasing cooling rates), and \( c_m \), which amounts the minimum cooling rate to have a fully martensitic microstructure (on decreasing cooling rates). For cooling rates between these two values, the final microstructure is a mix of martensite and ferrite (with precipitates).

Despite a good knowledge of the CCT diagram of these alloys, some issues still deserve a renewed attention. The existing literature on the characterization of the metallurgical state of 9%Cr steels after continuous cooling at moderate rates is scarce because, traditionally, cooling behavior studies have been directed toward welding or normalizing conditions, however, some differences in the measured transformation temperatures have been found [8]. In this way, novel ideas tend to the design of new heat treatments for these steels, which include the introduction of a non-vanishing ferrite fraction in the final product via isothermal steps or cooling at moderate rates [9,10].

The relevance of microstructural studies on moderate continuous cooling also comes from manufacture processes of thick-walled components. As the wall becomes thicker, the cooling rate of the central section slows down and, as a result, martensite domains or ferrite grain size (if any) may coarse and the precipitation conditions may change [11].

On the other hand, there is also ample evidence of the presence of retained austenite (RA), not reported in the CCT diagrams, in the microstructure of these steels under different experimental or processing conditions [12–16]. In particular, when following the conventional normalization and tempering treatment and depending on the tempering temperature, RA could promote the occurrence of non-tempered or inhomogenously tempered martensite in steel components or parts, producing a negative influence in the mechanical properties of the material during its service life [17]. Even a low fraction of film-like, interlath RA could strongly affect the toughness of some 9Cr steels if a lower-temperature tempering—such as the one used in manufacturing steam turbine rotors [18]—is expected. Hence the importance of assessing the RA content after continuous cooling cycles.

In the present contribution, the microstructure of P91 steel samples tested under continuous cooling conditions at moderate rates is studied taking advantage of the diverse information brought by different characterization techniques.

2. Methods

The starting material is an ASTM A335 grade P91 steel whose chemical composition is shown in Table 1.

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Cu</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.360</td>
<td>0.240</td>
<td>8.370</td>
<td>0.880</td>
<td>0.211</td>
<td>0.160</td>
<td>0.008</td>
</tr>
<tr>
<td>0.009</td>
<td>0.075</td>
<td>0.061</td>
<td>0.004</td>
<td>0.014</td>
<td>0.001</td>
<td>0.010</td>
<td></td>
</tr>
</tbody>
</table>

Specimens ~ 25 mm × 5 mm × 5 mm rectangular prisms – were machined from a seamless pipe 219 mm in external diameter and 32 mm in wall thickness following the rolling direction.

Heat treatments were done in a high temperature furnace Adamel DHT 60 under vacuum better than 10^{-3} Torr. Thermal cycles were chosen – on the grounds of previous information—in order to ensure a fully martensitic or a mixed (martensite + ferrite) microstructure: heating at 300 °C/h up to 1050 °C (that is, austenitization), holding at 1050 °C during 30 min and then cooling at 200, 150, 125 and 100 °C/h. Austenitization temperature was chosen following the standard manufacturing conditions for P91/T91 steels, and holding time was fixed as specified in the reported CCT diagram [5].

Samples were characterized by Field Emission Gun Scanning Electron Microscopy (FEG-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Mössbauer spectroscopy.

2.1. FEG-SEM

The surface of each sample was prepared for examination by the standard metallographic procedures. Grinding with SiC papers (220, 320, 400 and 600 grit) and a final polishing with a 1 μm diamond cloth were carried out. Chemical etching was accomplished with the Villela or Nital reagents, depending on the microstructure expected to be revealed. Observations were carried out in a Zeiss Supra 40 microscope operated at 5 keV accelerating voltage and using a working distance of ~2–3 mm.

2.2. TEM

Replicas were obtained by carbon evaporation in order to identify the various precipitated second phases. The analysis was
carried out in a Phillips CM200 transmission electron microscope (TEM) equipped with an EDAX-DX4 system for energy dispersive X-ray spectroscopy (EDS).

2.3. XRD

Measurements were done on bulk samples using a Panalytical Empyrean diffractometer with the &-2& Bragg-Brentano geometry, a flat graphite monochromator and Ni-filtered Cu-Kα radiation. The mid-plane of each sample was exposed by cutting and the resulting surface was prepared in the same way as described above, adding an electrolytic polishing step. The diffracted radiation was collected between 35 and 120° (2θ) with an ultra-fast PixCell area detector. The step scan angle and step scan time were settled in 0.026° and 939 s respectively. In order to deal with orientation effects, XRD measurements were performed in two configurations, i.e. with the main dimension of the sample parallel and perpendicular to the incident beam. The spectra were processed by the Rietveld refinement method with the software MAUD (materials analysis using diffraction) [19]. Peak broadening was considered by modeling microstrains and crystallite sizes. Texture effects were taken into account considering previous work in literature [20].

2.4. Mössbauer spectroscopy

Powders of the samples were prepared with a diamond file. Measurements were performed at room temperature (RT) in the transmission geometry with a conventional Mössbauer spectrometer set in constant acceleration mode with a ⁵⁷Co source in a Rh matrix. Spectra were recorded at 11 mm/sec and fitted by using the Normos program developed by Brand [21], according to two different procedures; i.e., by decomposition in broadened discrete sextets with a least-squares fit to Lorentzian lines and then by using hyperfine field distributions. Isomer shift (IS) values were referred to that of α-Fe at RT.

3. Results

3.1. FEG-SEM observations

Figs. 1–4 representative FEG-SEM micrographs of the main microstructures found as a result of continuous cooling at moderate rates, i.e., pure martensitic and mixed martensitic-ferritic.

Fig. 1 corresponds to the sample cooled at 200 °C/h. Fig. 1a and 1b evidence a typical lath martensite structure, similar to that obtained after air cooling [13,22], with the presence of second-phase precipitates. Fig. 1c shows details of the precipitates with two different morphologies, some of them look coarser and the others are oriented, needle-shaped ones.

A different pattern for the sample cooled at 150 °C/h can be seen in Fig. 2, where an incipient new constituent is forming at prior austenite grain boundaries. Fig. 2a displays the lath martensitic structure but this time small nodules of ferrite begin to appear. This ferrite includes carbides grown during cooling before the martensitic transformation. The morphology of these second-phase precipitates within the ferrite nodules (Fig. 2b) is different from the morphology of those observed within martensite laths (Fig. 2c).

Micrographs corresponding to the samples cooled at 125 and 100 °C/h are displayed in Figs. 3 and 4 respectively, where

![Fig. 1](image1.png)

**Fig. 1** – FEG-SEM micrographs of the sample cooled at 200 °C/h. Lath martensite microstructure (a, b). Preferred orientation of needle-like precipitates (c).

![Fig. 2](image2.png)

**Fig. 2** – FEG-SEM micrographs of the sample cooled at 150 °C/h. Lath martensite microstructure – including ferrite nodules at prior austenite grain boundaries (a). Precipitates in the ferrite nodules (b). Oriented needle-like precipitates within martensite (c).
a mixed martensitic-ferritic microstructure is seen with an increasing ferrite fraction in lowering the cooling rate. Within the ferritic phase a great quantity of precipitates can be seen with different sizes and morphologies (fibers and faceted) while in the martensitic structure the same type of precipitates described in Fig. 1c are again distinguished.

The size difference in precipitates may be due to nucleation by different mechanisms and in different temperature ranges. Those with larger size were likely nucleated at higher temperatures, having in consequence more time to grow.

3.2. TEM observations

In Figs. 5 and 6 TEM micrographs of the sample cooled at 150 °C/h, chosen as representative to identify the different second phase precipitates mentioned above, are displayed.

In the matrix zone of the sample (Fig. 5a) precipitates with different sizes and morphologies are observed. Needle-shaped particles show an irregular morphology at higher magnifications and were identified as M23C6 (Fe ~ 40 wt%, Cr ~ 53 wt%, Mo ~ 7 wt%) and hexagonal carbonitrides MX (V ~ 4 wt%, Cr ~ 76 wt%, Mo ~ 15 wt%, Fe ~ 5 wt%) (Fig. 6).

3.3. XRD analysis

3.3.1. Peak broadening effects

The major matrix constituents were considered to be bct martensite (space group: 14 mm) and bcc ferrite (space group: Im-3m). This assumption was made in each case on the basis of the FEG-SEM observations introduced in Section 3.1.

The XRD doublets characteristic of the bct martensite structure failed to be resolved in the sample belonging to the fully martensitic domain because they overlapped, yielding a single peak in angular positions very close to those of bcc ferrite. This is an expected consequence of the low carbon content of the steel and of the peak broadening due to the intrinsically deformed character of martensite [23].

Furthermore, martensitic transformation produces a strained matrix which exhibits diffraction domains much smaller than the ferrite ones. Thus, in line with the broadening effects, the width of the matrix peaks diminishes with the cooling rate for the martensitic-ferritic mixed domain samples. This is consistent with the increment of the ferrite content produced by lowering the cooling rate, clearly shown in FEG-SEM micrographs.

As an example, in Fig. 7 the effect of the cooling rate on the width of the (1 1 0) peak of the matrix in the transition from the fully martensitic sample (cooled at 200 °C/h) to the mixed domain sample (cooled at 100 °C/h) is shown.
3.3.2. Phase identification

Fig. 5 shows, as an example, the XRD pattern and the corresponding Rietveld refinement fit for the samples cooled at 200 °C/h (Fig. 8a) and 100 °C/h (Fig. 8b) along with a magnified view of the 37–47° and 47–120° angular regions in order to identify the matrix phases in those samples.

Martensite was identified as the major phase in all of the samples. According to FEG-SEM observations, ferrite was not included in the Rietveld refinement of the sample cooled at 200 °C/h and was refined as a strain-free, minor fraction phase in the sample cooled at 150 °C/h; the ferrite content increased on decreasing the cooling rate as expected.
Fig. 7 – Effect of the cooling rate on the width of the (110) peak of the matrix for the samples cooled at 100 and 200 °C/h.

Besides the main peaks of the martensite, or overlapped martensite-ferrite structures, retained austenite presence was determined in all of the samples. The lattice parameters calculated from Rietveld refinement for the matrix phases in the fully martensitic sample (cooled at 200 °C/h) and the mixed domain samples (cooled at 150, 125 and 100 °C/h) are displayed in Table 2.

At the same time, a few peaks of low to moderate intensity were assigned, tentatively, to cementite – type precipitates (M₃C). No information about other type of precipitates could be

Table 2 – Lattice parameters for the matrix phases. M: martensite, F: ferrite, A: austenite.

<table>
<thead>
<tr>
<th>℃/h</th>
<th>M</th>
<th>F</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a [Å]</td>
<td>c [Å]</td>
<td>a [Å]</td>
</tr>
<tr>
<td>200</td>
<td>2.8747</td>
<td>2.8771</td>
<td>3.5996</td>
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<td>150</td>
<td>2.8859</td>
<td>2.8874</td>
<td>2.9143</td>
</tr>
<tr>
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<td>2.8744</td>
<td>2.8798</td>
<td>2.8749</td>
</tr>
<tr>
<td>100</td>
<td>2.8760</td>
<td>2.8800</td>
<td>2.8768</td>
</tr>
</tbody>
</table>

Fig. 8 – Diffractograms for the samples cooled at 200 °C/h (a) and 100 °C/h (b) with their respective magnified views and their corresponding Rietveld refinement fit. M: martensite, F: ferrite, A: austenite. The A peaks for the 50–120° region are not shown in (b) due to their extremely low intensity.
determined from this analysis; however, it must be mentioned that the peaks identified as the (210) and (102) reflections of the $M_3C$ phase could include a contribution of the (111) and (200) peaks of the VN phase, respectively, in view of their almost complete overlapping in each case.

The intensity of these cementite-assigned peaks showed to be strongly dependent on the direction of beam incidence, denoting a pronounced preferred orientation effect, which would be consistent with the one already noticed by FEG-SEM observations (Section 3.1). To illustrate this point two diffractograms of the sample cooled at 125 °C/h and obtained with the main sample dimension kept perpendicular and parallel to the incident beam are displayed in Fig. 9.

The configuration with the sample parallel to the incident beam gives a noticeably reinforced intensity for the (210) and (102) $M_3C$-assigned peaks. Even so, these peaks were hardly distinguishable in the samples cooled at 200 °C/h and 100 °C/h. This fact becomes evident from the comparison between Figs. 9 and 8; in the former, the possible cementite peak heights reach a significant fraction of the main martensite-ferrite peak, a feature absent in Fig. 8.

The knowledge of the behavior of precipitated second phases and their control throughout the thermal history of the material is relevant to fix its final mechanical properties. Taking into account the difficulties described above for a conclusive determination of cementite, a subsequent analysis by Mössbauer Spectroscopy was necessary to univocally confirm that the cementite-type phase was present in all of the samples.

### 3.4. Mössbauer spectroscopy

#### 3.4.1. General aspects of Mössbauer measurements

Mössbauer spectroscopy was performed on powdered samples. Even if this technique is suitable to distinguish the matrix component phases (martensite, ferrite) from austenite – because the former are ferromagnetic, while the latter is paramagnetic at RT – powdered samples (as an alternative to thin foil samples) could be detrimental in this type of study. Powdering could promote martensitic transformation and, provided the low fraction of retained austenite, information about this phase could be lost. This effect was observed for example in a duplex steel UR45N, in which the difference in the relative abundance of the austenite between bulk (i.e., thin foils) and powder samples was about 25% on the average [24]. A similar transformation due to mechanical stresses was also observed by Skrzypek et al. [25] in hard ball bearing steels. In the same way a reduction in the austenite content was also found due to mechanical polishing with different grain size in an austempered ductile iron by Mercader et al. [26].

However, taking into account that retained austenite phase was already determined from XRD analysis in this work, Mössbauer spectroscopy was carried out on powdered samples resigning eventual information about austenite presence but gaining additional data about cementite-type precipitates (not conclusively identified by XRD in some samples). Powdered samples are easier and less time consuming to prepare than thin foils and give a better final signal to noise ratio in the spectra, key fact when a so minor phase as $M_3C$ has to be detected between the major matrix components. An ulterior, detailed study of thin foils of this steel was also done, determining the retained austenite presence and its content in each sample with more accuracy than XRD; those results will be published elsewhere.

Unfortunately, because of the low carbon content in the steel, a distinction between ferrite and martensite by Mössbauer Spectroscopy is not possible in this case, due to their similar Fe environments. That is why reference in the following text is made to matrix phases (i.e. martensite and/or ferrite) in general.

#### 3.4.2. Sites fitting of Mössbauer spectra

The measured Mössbauer spectra are typical of low carbon steels, showing the presence of several superimposed, magnetically split subspectra. Most of them with IS and quadrupole shift ($\Delta \omega$) near 0.0 mm/s (these values are zero for metallic iron $\alpha$Fe), denoting the matrix elements. In a first attempt spectra were fitted to six sextets with different hyperfine parameters reflecting the influence of the alloying elements. As all the spectra look similar, an example is displayed in Fig. 10 for the sample cooled at 100 °C/h. Fittings were made based on our previous work in a T91 steel submitted to a tempering process at 780 °C during different time intervals [27], in which five sextets were employed to represent the matrix phases. The existence of different neighbors of the Fe atom governed by the concentration of alloying elements.
was analyzed; in particular, the behavior of Cr was studied, as the main substitutional atom.

Thus, the sextet having the highest $B_{hf}$ (~34 T) represents Fe atoms in a pure Fe matrix, i.e. those not surrounded by alloying-element atoms. The successive four sextets, with $B_{hf}$ ~ 31, 29, 27 and 24 T, are associated with Fe atoms surrounded by an increasing number of Cr atoms. A sixth sextet was also added to account for a small contribution at low fields that can be perceived in the recorded spectra. This last sextet with average $B_{hf}$ ~ 15–18 T would represent some iron-bearing precipitates with alloying elements.

It is also worth to mention that the presence of a minute contribution (<1%) seems to arise from at least one incipient doublet in the central part of all the Mössbauer spectra. This contribution could be related to the formation of paramagnetic cementite [28] and/or other types of precipitated iron-containing carbides [29,30] and/or to the presence of retained austenite [31,32]. Due to the scarce content and to the overlap of signals around the weak fields, it is impossible to univocally identify this/these Fe-bearing phase/phases.

### 3.4.3. Further analysis in terms of distributions of hyperfine magnetic field

Being the main purpose of the Mössbauer spectra analysis the differentiation between matrix and precipitated second phases, a detailed study was then performed to deal with the superposition of many magnetically split components of the spectra. Fitting was performed in consequence by considering distributions of hyperfine magnetic fields caused by the multiple local configurations of the alloying elements around the Fe atom.

Two independent hyperfine field distributions were employed. For the sake of simplicity and completeness they are drawn one after the other in Fig. 11, delimited by a dotted line. One of them, ranging from 24 to 38 T, represents the matrix elements and shows a dominant maximum fluctuating around 31 T. The corresponding IS and $2\sigma Q$ values are close to zero. This distribution accounts for the different number of Fe nearest neighbors of the resonant atom. The relatively large alloy-element concentration (especially Cr) found for this steel explains why the maximum $B_{hf}$ value deviates from the one found for $\alpha$Fe (33 T). The broad distribution represents the influence of the main alloying element (Cr), which has a high probability of substituting Fe atoms in the crystal lattice (Cr and Fe atomic radii are similar [33]). It is expected that substitutional non-magnetic atoms, such as Cr, will diminish the hyperfine magnetic field: the higher the number of Cr neighboring atoms, the lower the hyperfine magnetic field [34].

The other hyperfine field distribution instead (ranging from 10 to 23 T), has an average $B_{hf}$ between 17.8 and 19.1 T and an IS value different from zero, suggesting the presence of carbides of the cementite type. The hyperfine fields are slightly lower than those reported for Fe$_3$C ($B_{hf}$ ~ 20.8 T) [28,35]; once again this is due to the presence of alloying elements. As mentioned above for the first hyperfine field distribution, the main alloying element (Cr) would be the responsible for the change in the average $B_{hf}$ value. Analyzing the distribution, two or three main maxima can be distinguished (near 12, 15 and 20 T), corresponding to precipitates of the cementite type - ($\alpha$Fe$_{1-x}$Cr$_x$)$_3$C – with different Cr content.

### 4. Discussion

#### 4.1. Matrix phases and retained austenite

The ferritic and martensitic domain boundaries of the CCT diagram are determined by the critical cooling rates, $c_c$ and $c_n$, which in turn depend both on the chemical composition of the matrix and the austenitic grain size through the austenitization temperature. In the experimental conditions employed in the present work, $c_n$ is near 150 °C/h. This value arises from FEG-SEM observations, considering that tiny nodules of ferrite + carbides begin to come out within the martensitic matrix after cooling at that rate. As the cooling rate lowers from 150 °C/h the ferrite fraction gradually increases; XRD analysis supports this observation as well.

XRD results also showed systematically the presence of retained austenite in low volume fraction in all the samples. This fact suggests that there is a broad range of cooling rates not allowing the complete suppression of austenite; in particular, RA is detected in samples cooled within the martensite-ferrite mixed domain, thus incorporating important information to the CCT diagram of this steel. These data are relevant to identify a potential degradation source of the material properties in certain manufacture processes. A small fraction of retained austenite in a component normalized or subjected to a welding process could imply microstructural heterogeneities at the subsequent tempering stage. Depending on tempering temperature, retained austenite could decompose to non-tempered martensite (below 680 °C), or right to ferrite (above 680 °C) [36]. This means that a tempered martensite matrix could include non-tempered or inhomogeneously tempered isolated regions, which in turn could alter the strength properties of the material. As mentioned before work is in progress with a detailed study of retained austenite in these samples and will be published elsewhere.

Regarding the lattice parameters of the matrix phases obtained by Rietveld analysis it is worth to mention that the
high value determined for the lattice parameter of ferrite after cooling at 150 °C/h, close to the critical rate, could account for carbon supersaturation not released by precipitation. For the other cooling rates, the determined lattice parameters are within the expected values.

4.2. Precipitated phases

The expected precipitation sequence in high Cr steels depends strongly on the chemical composition and the applied thermomechanical treatment. Thus, Kipelova et al. [37] have reviewed various isothermal precipitation sequences as a function of the precise chemical composition and steel generation within high-Cr alloys. For instance, during high (≥750 °C) temperature tempering of 9Cr1Mo steels after quenching or normalizing, the commonly reported sequence for the precipitation of Cr-rich carbides – as a function of tempering time – is [17,22]:

Matrix – M23C – M23C3 – M23C6, where M: (Fe, Cr) (1)

In grade 91 steels, sequences involving carbides, nitrides or carbonitrides of the MX type (M = Cr, Nb, V; X = C, N) should be considered as well. Furthermore, depending on the tempering temperature, hexagonal carbonitrides of the M2X type have also been observed [38]. For the 9Cr steel studied here, Hurtado Noreña et al. [13] provided a thorough discussion of the precipitation sequence as a function of the tempering temperature.

The sequence (1) derives from an isothermal path to equilibrium, instead, a variety of precipitates with different types of structures, morphologies and sizes are expected to be formed during continuous cooling, in different temperature intervals and according to the transformation behavior of the matrix. This assumption is based on previous, detailed studies on the isothermal austenite-ferrite transformation in different temperature ranges and on the anisothermal transformation behavior of 9Cr steels with various compositions [39-41].

In the present work, FEG-SEM and TEM observations introduced in Sections 3.1 and 3.2 allowed to describe the morphology and to estimate the size of the precipitates. Within the martensitic structure mainly two different morphologies of precipitates were distinguished, that is, coarse and needle-shaped. On the other hand, in the ferritic phase of the mixed structure samples, another two different shapes of precipitates were visualized (fibers and faceted).

4.2.1. Cementite and V-rich MX precipitation in the martensitic matrix

The features of needle-shaped precipitates observed in martensite by FEG-SEM agree with those reported by Hurtado Noreña et al. [13] and Jones et al. [22], strongly suggesting that they can be identified as the (Fe,Cr)2C phase. On the other hand, XRD analysis would also indicate the formation of cementite; however, due to the low volume fraction of the precipitates – consequence of the low C content in the steel – and to orientation effects, its identification was not conclusive in all of the examined cases. On the opposite, Mössbauer spectroscopy results unambiguously established the presence of M23C-type precipitates in all of the samples.

Fig. 11 – Distributions of hyperfine fields (Bhf) employed in the alternative fitting of Mössbauer spectra.
In order to confirm these findings TEM analysis was performed in a representative sample, the one cooled at 150 °C/h, where both matrix constituents (martensite and ferrite) were present with their corresponding precipitates. In fact, the needle-shaped second phase was indexed as (Fe,Cr)_{3}C by SAED patterns (Fig. 5b).

Regarding the origin of the cementite particles found within the martensitic regions of the matrix, the most accepted explanation is that they come from an auto-tempering process [22,39]. However, and on the grounds of data obtained by Differential Scanning Calorimetry (DSC), Liu et al. [42] claimed that precipitation of (Fe,Cr)_{3}C particles in T91 steel samples cooled under argon atmosphere after austenitization starts above 750 °C. In other words, they suggest that cementite does not come from an auto-tempering process but that it is completely formed in the γ (austenite) phase before the start of the transformation to martensite. Kirana et al. [43] have in turn criticized this hypothesis, discarding cementite precipitation before reaching the M_{s} temperature. The inhomogeneous feature of cementite precipitation observed in the present work, which seems to follow the lath subdivision of the martensitic matrix (i.e. densely populated laths vs. hardly populated laths of cementite particles, Fig. 3c), could be an element to support the hypothesis of an auto-tempering process.

On the other hand, for the case of cooling rates resulting in a mixed martensite-ferrite structure, Saroja et al. [41] proposed that the supersaturation of carbon in ferrite is relieved by precipitation within the α (ferrite) phase, subsequent to the formation of α grains from γ and not by partitioning of carbon across the α/γ interface. In their work, for a non-stabilized, plain 9Cr1Mo steel, the M_{s}C carbide was proposed as the phase observed to precipitate within the ferrite nodules nucleated and grown during continuous cooling. In summary, in absence of the stabilizing elements Nb and V, previous reports account for cementite precipitation within martensite [39] and -probably- ferrite [41] for cooling rates in the mixed martensite-ferrite domain.

As for the V-rich MX particles, it is worth to mention that previous studies [13,22] report not having found this phase after normalizing (i.e., air cooling) steels of similar composition at 1045–1050 °C. Instead, clusters of fine, elongated V-rich MX particles were detected after 16 min tempering at 760 °C [22] and not detected after 1 h tempering at temperatures up to 600 °C [13]. Another study [44] draws a similar conclusion, i.e., MX particles are found after normalizing a 9Cr1MoVNb steel for 15 min at temperatures ranging from 1050 to 1200 °C, but experimental evidence allows to make sure that they do not precipitate on cooling. The comparison of these observations with the results in the present work suggests that a cooling rate of 150 °C/h is enough to promote V-rich, MX particle precipitation within martensite on cooling.

4.2.2. M_{23}C_{6} and M_{2}X precipitation in ferritic nodules The precipitates present in the ferrite phase nodules were identified by SAED and EDS as M_{23}C_{6} and M_{2}X particles. It is natural to assume that the low solubility of C and N in ferrite promotes the precipitation of these or other carbide, nitride or carbonitride phases. Thus, new thermomechanical processes envisaging the introduction of a ferrite phase fraction in the standard metallurgical state of the material – that is, prior to entering in service – should take into account that a precipitate fraction will be introduced along with it. In this way, ferrite could act as a “carbon sink” via second phase precipitation in it, leaving less carbon available to form the fine MX precipitate dispersion that enhances the creep strength of the martensitic matrix on further cooling and eventual tempering.

The finding of the M_{23}C_{6} and M_{2}X phases within the ferritic nodules in the anisothermal process in this work is fully consistent with the already reported observations on isothermal and anisothermal austenite-ferrite transformation in 9Cr steels with varying composition [39,40]. In the isothermal case, these phases were observed to form early in the transformation, the C/N ratio being the main factor in promoting a higher fraction of one or another [39].

5. Conclusions

The transformation behavior of ASTM A335 P91 steel samples under continuous cooling conditions has been studied in the range of moderate cooling rates. A thorough characterization of the resulting samples showed that retained austenite was systematically identified for all cooling rates, i.e., within the martensitic and part of the mixed martensitic-ferritic domains of the CCT diagram. This fact adds important information to that diagram and opens to debate about what the conditions are for a four-phase metastable state to exist involving austenite, ferrite, martensite and carbides in 9Cr steels.

Among the precipitated second phases observed by FEG-SEM and TEM, (Fe,Cr)_{3}C and V-rich MX were identified in martensite and M_{2}X and M_{23}C_{6} in the ferrite phase. A cooling rate of 150 °C/h was enough to promote V-rich MX particle precipitation on cooling.

Mössbauer spectroscopy showed to be a good tool to differentiate the minor second phases with magnetic character as (Fe,Cr)_{3}C which due to the scarce content and to orientation effects were not conclusively determined by XRD. Mössbauer analysis revealed the presence of ferromagnetic cementite-type precipitates in all of the examined samples. The question about the precise temperature range for cementite nucleation during cooling remains opened, but this work suggests that for the mixed-domain cooling rate range, cementite could nucleate and grow within martensite by an auto-tempering process.

Conflicts of interest

The authors declare no conflicts of interest.

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