Study of the Austenitization Process in a P91 Steel

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Abstract. It is well known that two main families of precipitated particles are present in 9Cr1Mo grade 91 steels after a standard manufacturing process that includes, as final stages, normalizing and tempering, i.e., $M_{23}C_6$ carbides (M = Cr, Fe, Mo) and MX carbonitrides (M = V, Nb, Cr). In previous works it was reported that samples of a T91 steel austenized at 1050ºC for times between 0 and 40 minutes following heating at a rate of 50 ºC/s exhibit a heterogeneous austenitic grain size distribution after austenite holding for 20 to 30 minutes from the austenite plateau start. Moreover, $M_{23}C_6$ dissolution and a change in the chemical identity of the MX precipitates (from major V-rich to major Nb-rich) occur during the first 5 minutes of austenite holding at 1050 ºC. In this contribution the detailed evolution of second phase precipitates during the first minutes of holding in the austenite phase field for an ASTM A335 P91 steel, obtained by means of a high speed, high resolution dilatometer is studied and followed by scanning and transmission electron microscopy. $M_{23}C_6$ precipitates were not observed from the first minute of austenitization. MX precipitates change progressively their character from V-rich to Nb-rich. The observed diminution of the M_s, temperature values would be related to the dissolution of $M_{23}C_6$ carbides and V-rich MX carbonitrides.

Keywords: P91 steel, precipitates, austenitization, microscopy

1. Introduction

The challenges posed in the design of structural materials for fission nuclear reactors of the so-called Generation IV are complex and numerous. These include high operating temperatures, exposure to intense fluxes of neutron radiation, extremely corrosive environments and the need to extend the useful life of the material to 60 years or more. Taking into account the microstructural requirements derived from this range of problems for the material in service conditions, the 9Cr-1Mo modified steel, called T/P91 (9Cr1MoNbV) whose maximum operating temperature reaches almost 600 ° C, has been postulated as the primary choice option for various structural components in many of the concepts considered so far in the design of that generation of reactors [1-2].

The normalized and tempered 9% Cr grade 91 steel displays a lath martensitic matrix with a high density of dislocations, carbides of the $M_{23}C_6$ type (M = Cr, Fe) and very fine precipitates denominated MX (M = Nb, V; X = C , N) [3]. During the thermal and thermomechanical treatments to which the material is submitted in manufacturing processes, the precipitates present in the matrix inhibit the growth of austenite grains and stabilize the creep-resistant martensitic structure. The pinning force is governed by the size, size distribution, fraction and thermodynamic stability of the precipitated second phases in the austenite matrix and, when at a certain temperature, this pinning force is exceeded by the

driving force for grain growth, the abnormal growth of some grains begins to appear producing a microstructure of grains with heterogeneous size, thus degrading the mechanical properties of the material [4].

In a previous work [5], austenitic grain growth during austenitization at 1050 °C for 30 minutes was reported as a function of the heating rate to austenite(1, 30 and 50° C/s) and the initial metallurgical state (as-received condition and subsequent tempering at 780 °C for different times up to 6 hours). For the heating rate of 1° C/s and for all of the initial metallurgical states only homogeneous grain growth was observed, whereas for 50 °C/s the growth was only heterogeneous. In contrast, for the heating rate of 30 °C/s, the occurrence of a homogeneous or heterogeneous grain size distribution turned out to be a function of the tempering time prior to austenitizing. Given that the analyzed grain size distributions correspond in all cases to a "snapshot" obtained after 30 minutes of maintenance in austenite, and assuming that the main factors controlling them are related to the pinning particle distribution features, it was considered necessary to study the evolution of the second phase precipitates according to their size and chemical composition for increasing time intervals of austenite maintenance at 1050 °C (0, 5, 10, 20 and 40 minutes) after heating at 50 °C/s, in order to determine the starting time for the austenite heterogeneity development. The results obtained [6] led to conclude that the heterogeneous grain growth begins between 20 and 30 minutes after the start of austenite holding; that all the second phase particles of the material are present at the beginning of that holding and that there is a change in the chemical identity of the MX precipitates and dissolution of the carbides of the $M_{23}C_6$ type within the first 5 minutes of maintenance in austenite.

Taking into account the critical role played by the second phase precipitates, the present work studied the size evolution, size distribution and chemical composition of these precipitates during the first 5 minutes of maintenance at 1050 ° C of a grade 91 steel, after linear heating at controlled speed.

2. Materials and methodology

The study was carried out on an ASTM A335 grade P91 steel manufactured by the Italian steelmaker Dalmine. A piece of seamless pipe, 32 mm thick wall, was supplied with a normalizing at 1060 ° C for 20 minutes and tempering at 780 ° C for 40 minutes heat treatment. The certified chemical composition for this material is shown in Table I.

TABLE I: COMPOSITION OF THE ASTM A335 P91 STEEL.

C	Mn	Si	Cr	Mo	N	V	Cu	Sn	Al	Nb	Ni
0.110	0.360	0.260	8.21	0.90	0.061	0.213	0.15	0.09	0.01	0.085	0.15

Samples 10 mm long and 4 mm in diameter were used to perform different thermal cycles using a Bähr DIL 805 A high speed and high resolution dilatometer. All samples were heated at a rate of 50 ºC/s up to 1050 °C, then maintained at that temperature for times between 0 and 5 minutes, and cooled to room temperature at 50 °C/s. Table II presents the thermal treatments performed and the labeling used for the different samples throughout the work.

TABLE II: AUSTENITIZING TIME AT 1050 ºC (A_t) FOR EACH SAMPLE.

Sample	AR	M0	M1	M2	M3	M4	M5
A_t (min)	-	0	1	2	3	4	5

The martensite transformation start temperatures, M_s, for every treatment were obtained by using the graphical method of extrapolating the linear portion of the contraction curve of the austenitic matrix, in the region close to the martensitic transformation of the dilatometric curve, as indicated by the ASTM 1033-10 standard (see Fig. 1, right).
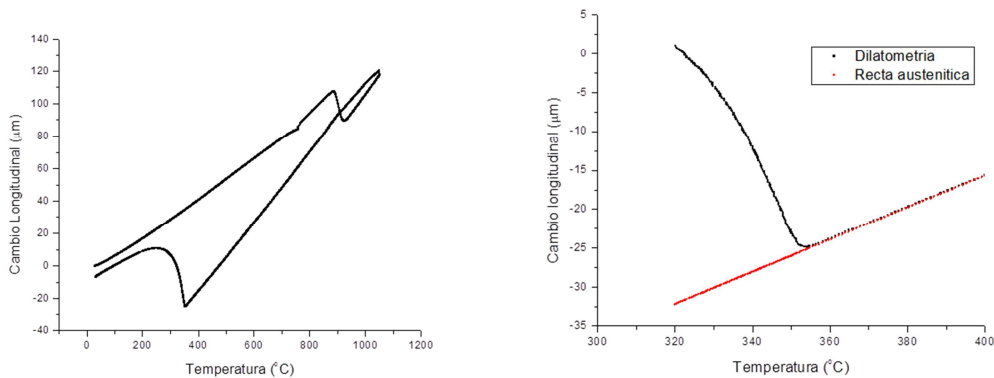
FIG.1. Left: Dilatometric curve of M1. Right: Extrapolation of the austenitic contraction line on the dilatometric curve of M1.

After heat treatments, samples were mounted in a conductive resin, grinded down to the middle plane, polished and etched with Villelas's reagent to be examined by a scanning electron microscope with field emission gun (FEG-SEM) Zeiss Supra 40.

The study of precipitates was carried out by observing carbon replicas with a Phillips CM200 and a FEI TECNAI F20 transmission microscopes, equipped with an EDAX-DX4 system, through which it is possible to study the chemical composition by energy-dispersive X-ray microanalysis (EDS). On the other hand, 40 TEM micrographs were taken in different zones of the replicas for each specimen and particle sizes were measured using image analysis software; then, frequency count histograms were built in order to study the particle size distribution in each case. The same procedure was carried out for the sample in the as-received condition (AR).

3. Results and discussion

3.1. Analysis of dilatometric curves: variations of M_s with austenitization time

Table III presents the M_s values obtained for the different austenitization times studied. M_s shows a significant decrease between samples M0 and M1, an approximate plateau between samples M1 and M3, a new decrease in sample M4 and an increment between M4 and M5.

TABLE III: VALUES OBTAINED FOR M_S.

Sample	M0	M1	M2	M3	M4	M5
M_s (ºC)	365 ± 5	351 ± 5	351 ± 5	353 ± 5	331 ± 5	348 ± 5

3.2. Characterization of precipitates by electron microscopy

Representative SEM and TEM micrographs are presented in Fig. 2. SEM micrographs (*see left column of Fig. 2.*) allow observing the distribution of the precipitates in the matrix. In the as-received condition (MCs) as well as in the M0 sample, a high density of particles is observed, which decreases rapidly with increasing austenitization time. For the M1 sample large particles disappear almost completely.

Precipitates found in each sample are pointed out by arrows in the TEM micrographs shown in the right column of Fig. 2. The precipitates present in this type of steels were identified in a previous work [5] through their electron diffraction pattern and EDS analysis.

In the present work the precipitates were identified mainly through their EDS spectrum. Due to the fact that the chemical composition of the MX precipitates varied gradually as the austenite holding time increased, the criterion was assumed of considering MX particles to be V-rich, MX(V), when the corresponding EDS spectrum displayed a V- K_α line more intense than the Nb-L_α line and vice versa for the Nb-rich particles, MX(Nb).
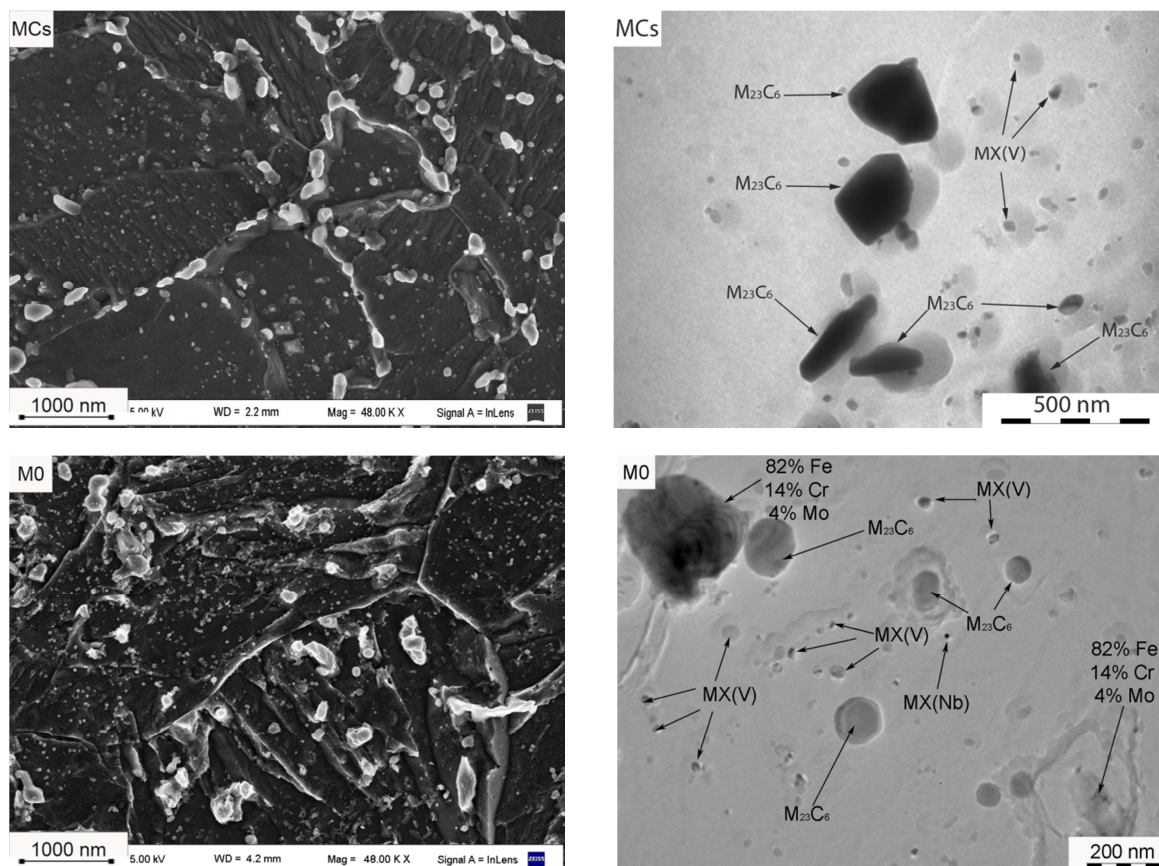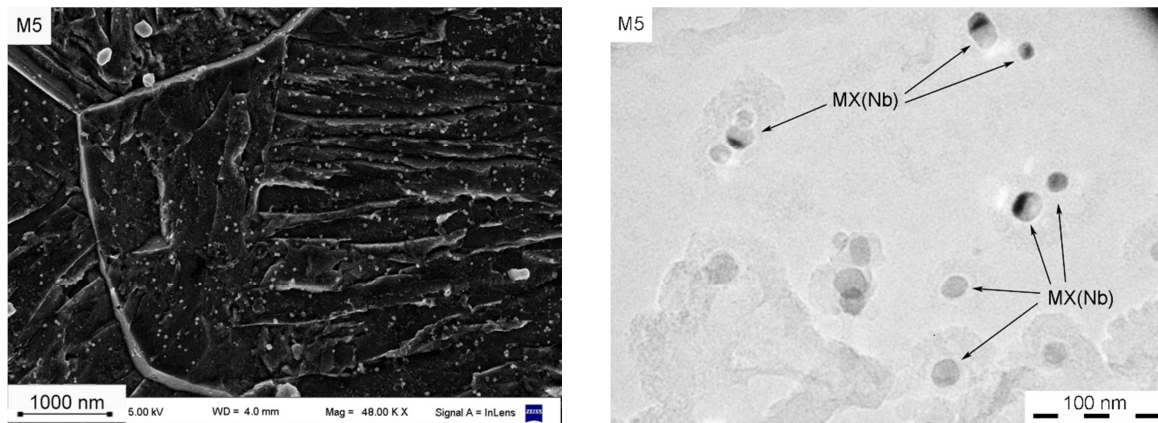
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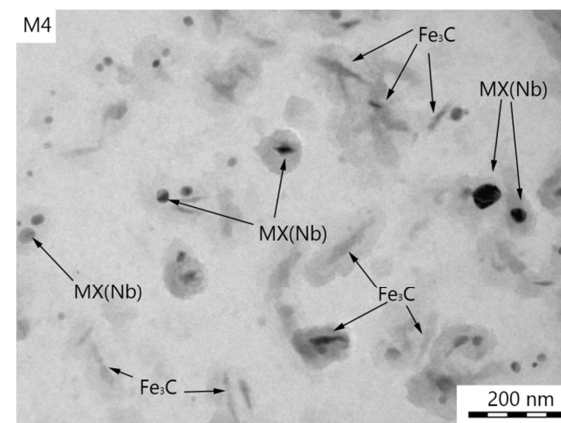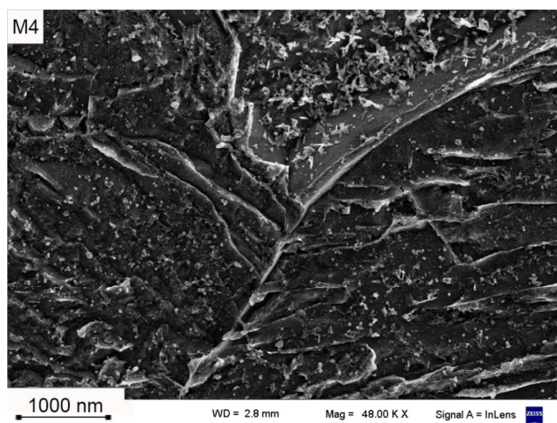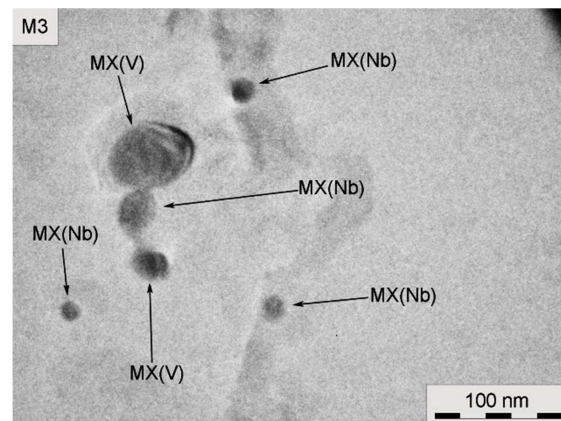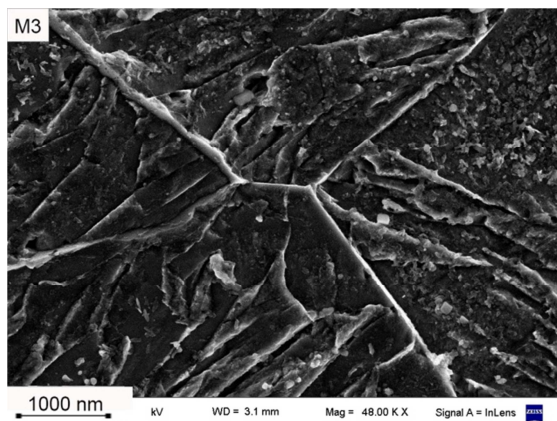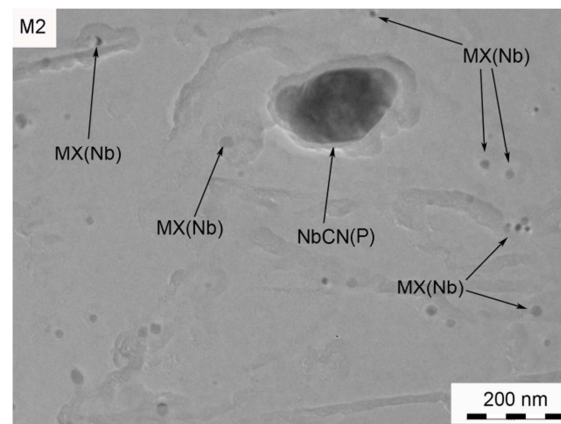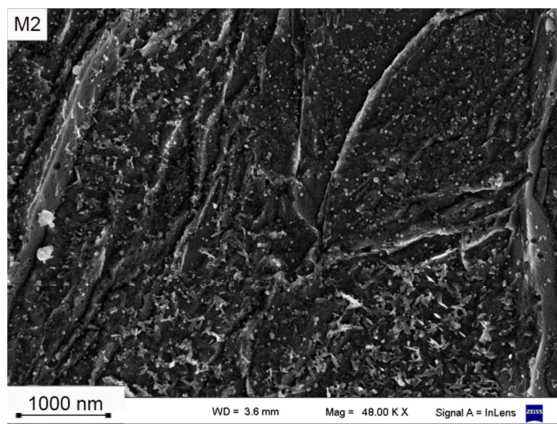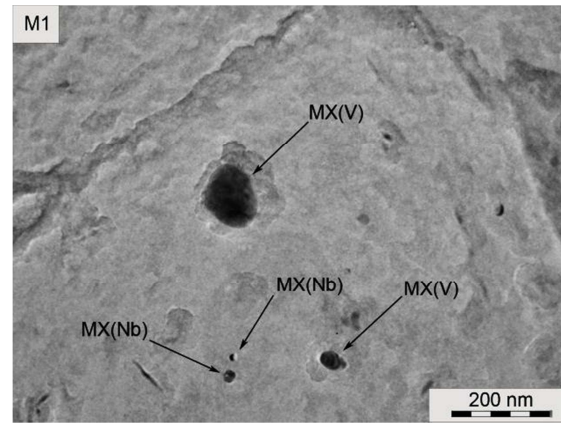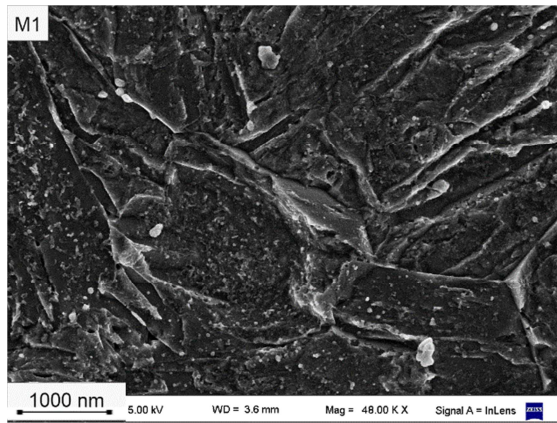
FIG.2. SEM (left) and TEM (right) micrographs.

The following second phases were identified:

- $M_{23}C_6$: they were observed in the as-received condition and in sample M0.
- Primary NbCN: these particles do not dissolve at 1050 ° C, so they are found in all samples. They are characterized by having large sizes, between 200 and 400 nm.
- MX: two characteristic MX types were found:
  - MX(Nb): MX rich in niobium. These particles begin to appear from the sample M0; as the austenitization times are longer, their size increases. In sample M5 some of these particles appear aligned in what could be a former austenitic grain boundary.
  - MX(V): they are V-rich MX particles. As the austenitization times increase, they decrease in size and become richer in Nb.

  Both types of MX particles have sizes smaller than 100 nm for all samples.

- Cementite: these particles have an elongated shape and they are observed from sample M1 onwards. The presence of these precipitates is attributed to the autotempering of martensite, which is very likely due to the high M_s temperature presented by low carbon steels [7].
- Precipitates with high Fe content were observed in sample M0 with a chemical composition 82% Fe - 14% Cr - 4% Mo and sizes between 150 and 400 nm. These particles have not been identified yet.

Because the precipitates that play a critical role in austenitic grain growth are the $M_{23}C_6$ and MX ones, the analysis of the chemical composition and size evolution will be focused on these two families of particles.

3.2.1. Chemical composition of MX and $M_{23}C_6$ precipitates

The composition ternary diagrams obtained by analysis of the EDS spectra particles found in the six samples austenized at 1050 °C and the as-received condition are shown in Fig. 3.
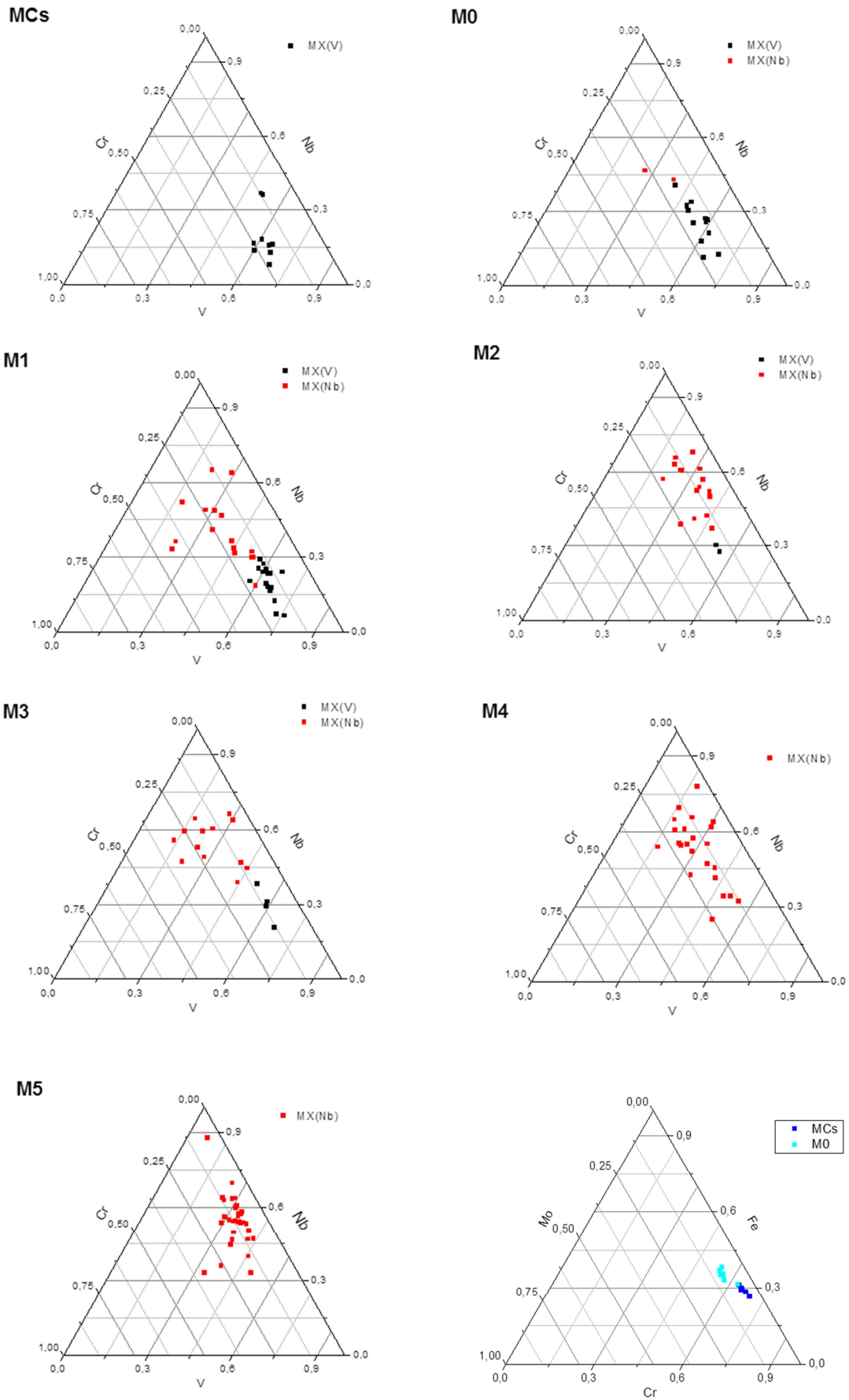
FIG.3. Ternary composition diagrams for MX(V) (black), MX(Nb) (red) and $M_{23}C_6$ (blue).

The amount of precipitates MX(V) decreases with increasing austenitization time, vanishing completely at the fourth minute. On the other hand, MX(Nb) precipitates are observed from minute 1 and increase their amount continuously.

$M_{23}C_6$ carbides of sample M0 have a lower Cr content than those analyzed in the as received condition as observed in Fig. 3. These precipitates would be releasing Cr to the matrix upon dissolution, increasing their Fe/Cr ratio.

3.3. Correlation between the M_s temperature and size of precipitates

To study the trends observed in M_s values and their possible causes we used calculations based on the ThermoCalc software and in M_s value estimation formulas according to chemical composition [8]. The equation used for the calculation of M_s is presented below:

$$M_s = 502 - 810\,x\,C - 1230\,x\,N - 13\,x\,Mn - 30\,x\,Ni - 12\,x\,Cr - 54\,x\,Cu \qquad (1)$$

To determine the fraction of alloying elements released into the matrix during carbide dissolution, the assumption was made that heating was fast enough so as to neglect the dissolution produced during it against that produced during maintenance in austenite. This assumption allows an estimation of the components dissolved in the matrix at the time of quenching, which in turn allows the application of an expression to calculate the value of M_s from the chemical composition of the matrix.

The values of M_s can be related to the mean size of the precipitates for each time (*see FIG.4*). The first observed decrease in M_s can be related to the dissolution of the $M_{23}C_6$ and iron rich precipitates, since both would release carbon and chromium to the matrix. To verify this hypothesis, the THERMOCALC program was used to estimate what would be the amount of chromium and carbon released to the matrix by the total dissolution of $M_{23}C_6$ carbides and equation (1) to calculate what would be the variation in the value of M_s produced by the increase of the concentration of alloying elements in the matrix. The tempering temperature of the as-received condition, i.e. 780 °C, was taken as the initial temperature. This value was chosen because it is assumed that tempering is the stage of the treatment in which most of the samples approached the equilibrium composition.
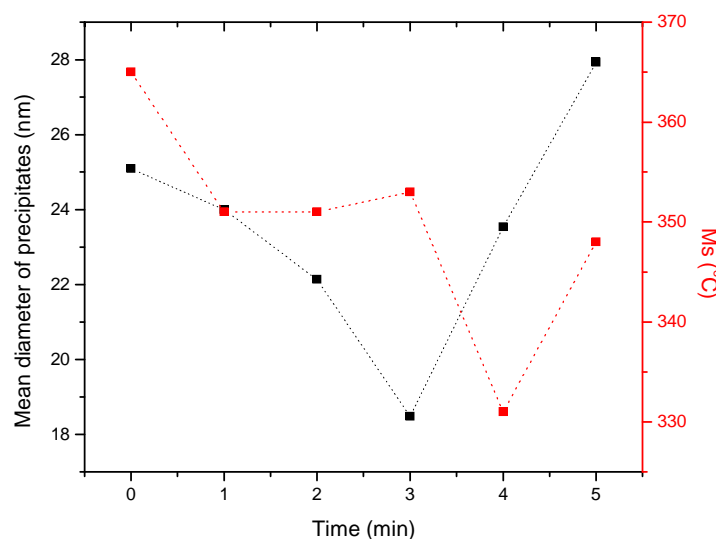

FIG.4. Mean diameter of precipitates and M_s vs. austenitization time.

For the calculations made in this work it was also assumed that the composition does not change significantly during the post-quench cooling at 780ºC in the tempering.

According to the calculations performed with THERMOCALC, the complete dissolution of $M_{23}C_6$ carbides provides 0.1% and 1.05% weight percent of C and Cr, respectively. The change in the M_s value caused by the Cr and C increase was calculated using equation (1), and a decrease of 20 °C was obtained. The value obtained experimentally was 14 °C, which is in the order obtained by equation (1).

The occurrence of cementite in the samples austenitized at times longer than one minute is also consistent with the supersaturation of C and Cr that should contain the matrix after the dissolution of the $M_{23}C_6$ particles. Cementite was found in all samples from the first minute of austenitization, suggesting that the C fraction consumed by the precipitation of other phases during the longer austenitization times is smaller than the one released by the dissolution of $M_{23}C_6$ carbides.

The M_s value displays another minimum around 4 minutes. This decrease in M_s could correspond to the total dissolution of the MX(V) precipitates. To study it, a procedure similar to the one explained above. Volume fractions of this phase were calculated at 780 °C and 1050 °C and the difference between the two was established. Then, the C and N eventually released due to the complete dissolution of the MX(V) to the matrix and the corresponding change in the value of M_s due to this variation in the content of alloying elements was calculated. According to THERMOCALC calculations, dissolution down to the equilibrium composition of the MX(V) releases 2.35×10^{-2} and 4.81×10^{-5} wt. % of N and C, respectively. The change in M_s value obtained with eq (1) was 29 °C. The value obtained experimentally was 22 °C, so it would be plausible to attribute the decrease to the dissolution of the MX(V).

As for the measured particle sizes, it was observed that the largest decrease in particle diameters was found after minute 3. At minute 4 the diameter increased again and the trend continued until 5 minutes. The increase of the average size found at this stage may be due to the possible growth of the MX(Nb). The precipitates MX(Nb) were found from the sample austenitized one minute, with a very small size, and as the austenitization time increased, an increase in the amount of MX(Nb) present was observed.

It may be suggested that the shape of the mean diameter of precipitates vs. austenitizing time curve is due to a combined effect of the behavior of both types of precipitates. Before three minutes of austenitizing time, the dissolution of the MX(V) would have more weight, whereas the growth of the MX (Nb) would prevail from that moment onwards .

Considering that the total dissolution of the MX(V) would decrease the temperature M_s at 29 °C and the decrease observed at 4 minutes was 22 °C - time for which an increase in the size of the precipitates was observed - the minimum value of M_s could be reached between 3 and 4 minutes of austenitization (*see FIG. 4.*). On the other hand, it is striking that M_s does not change between the first and the third minute in spite of the decrease recorded in the size of the precipitates, observing a pronounced change only after 3 minutes. This could be attributed to the fact that the amount of N released by the MX(V) on dissolution in the first minutes is not enough for the dilatometric test to detect it. The corroboration of these hypotheses is in progress.

4. Conclusions

In the present work the evolution of precipitates present in an ASTM A335 P91 steel during the first 5 minutes of austenitization at 1050 ºC was studied, obtaining the following results:

- Carbide type $M_{23}C_6$ is not observed from minute 1 of austenitization. In turn, the Cr/Fe ratio in the composition of these carbides decreases, in the minute 0 of permanence, with respect to the as-received condition.
- The work hypothesis was corroborated quantitatively with respect to the MX-type carbides, that is, the chemical identity of these carbides changes progressively from V-rich to Nb-rich in the first 5 minutes of permanence in austenite.
- Significant variations were observed both in the M_s temperature and in the average particle size of second phases as a function of the residence time in austenite. The decrease found in the value of the M_s temperature would correspond to changes in the fractions of phases present in the steel for the austenitization time studied. The dissolution of the $M_{23}C_6$ carbides would be related to the first decrease in M_s value for the 1 minute austenitization time, while the complete dissolution of the MX(V) would correspond to the decrease observed in the 4 minute austenitization time.

5. Acknowledgments

6. References

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