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Tempering of Dual Phase steels: Microstructural evolutions and mechanical properties

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ABSTRACT

Modelling the microstructural evolutions and mechanical properties during the tempering of Dual Phase steels is a key objective for industrials as this phenomenon has a strong impact on the final properties. After having determined the tempering kinetics of fully martensitic steels between 100 °C and 550 °C using thermoelectric Power and hardness measurements, time-temperature equivalences were applied to determine the activation energies of the mechanisms controlling martensite tempering. Two tempering stages were clearly identified and thanks to the use of TEM, SEM and tomography techniques, they could be attributed to cementite precipitation, its spheroidization and recovery phenomena. The second stage was found to be retarded with increasing the manganese content of the steel contrary to the first stage. From these studies, a JMAK model was developed to predict the microstructurals evolutions during tempering. Then, an extension of the Hybrid-mean Field Composite model developed in a previous paper to predict the tensile curves of fresh martensite was proposed to take into account the microstructural evolutions of martensite during tempering. The model was tested for a wide range of physical parameters of the microstructure (phase fraction and chemical composition) and for different tempering heat treatments and gave good agreement with experimental tensile curves.

1. Introduction

Dual-Phase (DP) steels are classically produced by austenitization followed by controlled cooling with quenching of remaining austenite to form martensite in various fractions from 5 to 80% depending on the composition and cooling pattern. Additional treatment to galvanize¹ the steel or to improve the formability properties may lead to microstructural evolutions, in particular within martensite, which result in a marked decrease in the steel ultimate strength while strongly increasing its toughness. Consequently, from an industrial point of view, it is very important to accurately model the tensile curve of tempered DP steels for a wide range of microstructural features (grain size, phase fraction and chemical composition) and for different tempering heat treatments (including different tempering times and temperatures) taking into account the microstructural evolutions occurring during tempering [1–4].

From a microstructural point of view, Speich et al. [5,6] distinguished several tempering stages for Fe–C alloys (without residual austenite in the initial microstructure):

- **Stage 0** (between 60 and 120 °C): Carbon segregation towards lower energy sites (such as dislocations or lath boundaries) is expected. This phenomenon may even occur during cooling if the M_S temperature is sufficiently high leading to the so-called auto-tempering.
- **Stage 1** (between 100 and 250 °C): Various intermediate metastable carbides (ϵ , η , Hägg) may precipitate for carbon contents higher than 0.2wt%.
- **Stage 2** (between 300 and 400 °C): Cementite precipitation (θ , Fe₃C, orthorhombic) occurs simultaneously with the dissolution of the intermediate carbides. Initially, cementite precipitates with a plate-like morphology inside martensite laths or interfaces. Then, at higher temperatures, cementite spheroidizes and coarsens to reach its equilibrium state [7].
- **Stage 3**, Recovery/Recrystallization: Recovery takes place for temperatures higher than 400 °C and ferrite recrystallization may occur above 600 °C depending on steel chemistry. According to Marceaux et al. [8], a part of carbon is trapped in the defects of the microstructure up to very high temperatures.

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¹ Hot dip galvanization is a process consisting in immersing the steel in a liquid zinc bath at 460–470 °C in order to coat and protect it from corrosion.

Kinetics of the different phenomena occurring during the martensite tempering can be modified when adding alloying elements [9,10]. In particular, cementite precipitation is expected to be greatly influenced by the addition of substitutional elements (such as Mn, Cr and Si), as these elements are known to retard and/or prevent the growth and coarsening of cementite [10]. This leads to a delayed softening of the mechanical properties (hardness, yield strength, ultimate tensile strength (UTS)) of martensite compared to those of the corresponding binary alloys [9] as the finer and more numerous cementite carbides observed in the microstructures due to this addition are responsible for a higher resistance to grain growth in the ferritic matrix. This retardation in the growth and coarsening of cementite is considered to be mainly due to the partitioning of the substitutional elements (Mn, Cr) between ferrite and cementite which is managed by the slow diffusion of substitutional elements in ferrite.

Microstructural evolutions occurring during martensite tempering are usually investigated using classical techniques such as microscopy [11], resistivity [12], internal friction [13], thermal and dimensional analysis [14]. Another very convenient technique is ThermoElectric Power [15], thanks to its high sensitivity to martensite C content.

Tempering of two-phase steels seems to be similar to the one occurring in purely martensitic steels [16] and is mainly governed by martensite tempering as the evolution of ferrite microstructure and mechanical properties is negligible compared to the important softening observed in martensite. However, it is important to note that the composition and morphology of martensite in the case of two-phase steels are strongly influenced by the intercritical process defining the ferritic and martensitic phase fraction and the martensite carbon content.

For the modelling of the mechanical properties (hardness, Yield Strength (YS), Ultimate Tensile Strength (UTS)) of tempered martensite, different approaches were used in the literature. The simplest ones are more or less empirical and rely on the use of Johnson–Mehl–Avrami–Kolmogorov (JMAK) [17–19] laws or Hollomon and Jaffe relations [20] to predict, for example, the evolution of hardness as a function of time and tempering temperature. This type of approach was used with success by Grange et al. [9] to predict the hardness variations of martensite for steels with different carbon contents [21].

Modelling the whole tensile curve of tempered DP steels is much more complex. A Continuous Composite Approach was used by Cupertino et al. [22] to reproduce the tensile curves of fully martensitic steels after various tempering times and temperatures. In this type of approach, martensite is considered to be composed of regions with variable local yield strengths and it is assumed that after having reached its microscopic yield strength (of about 400 MPa), the martensite mechanical behaviour is governed by an interaction between elastic and perfectly plastic domains. This interaction is described thanks to a function $F(\sigma_1)$ which gives the cumulative probability density to have a domain with a yield strength lower than σ_1 . This function depends on the width of the local distribution of yield strength (noted Δ) which is related to the chemical composition of the steel (especially, its carbon content in solution which is assumed to evolve during tempering). To take into account the martensite softening during tempering and its effect on the tensile behaviour, Cupertino et al. [22] used a Hollomon-Jaffe law to describe the decrease in the carbon concentration in solid solution (C_C^{ss}) due to the carbon departure from the solid solution resulting from cementite precipitation.

They showed that their approach is likely to reproduce rather well the decrease in mechanical properties of tempered martensite resulting from the decrease in the carbon content in solid solution and subsequently in the width of the yield strength local distribution as long as the tempering temperature is lower than 400 °C. For higher temperatures (above 400 °C), these authors highlighted that a second mechanism has to be considered to account for the acceleration of the mechanical property decrease observed in this temperature range and that it could be associated with the martensite recovery

phenomenon observed in Fe–C binaries. To this end, they defined a second Hollomon–Jaffe law and applied it to another parameter σ_{\min} controlling the beginning of the elasto-plastic transition.

As a conclusion, the preceding results suggest that the martensite mechanical properties depend mainly on its carbon content in solid solution which will evolve as a result of three phenomena (carbon segregation on defects, cementite precipitation and recovery) according to the study of Speich et al. for low carbon steels. If no carbide forming elements (such as Nb or Ti, for example) are present, the carbon concentration after tempering for a time t at a temperature T can therefore be expressed as follows:

$$C_{\rm C}^{ss}(t) = C_{\rm C}^0 - C_{\rm C}^{\perp}(t=0) - \Delta C_{\rm C}^{ss \to \perp}(t) - \Delta C_{\rm C}^{ss \to \theta}(t)$$
(1)

where $C_{\rm C}^{ss}(t)$ is the martensite carbon mass fraction in solid solution during tempering, $C_{\rm C}^0$ is the initial carbon content of martensite (which corresponds to the nominal composition of the steel) and $C_{\rm L}^1(t=0)$ is the amount of carbon atoms which segregated to the martensite defects (dislocations, lath boundaries...) during cooling due to auto-tempering. $\Delta C_{\rm C}^{ss \to \perp}$ and $\Delta C_{\rm C}^{ss \to \theta}$ represent respectively the carbon content which left the solid solution during tempering: (i) to segregate to the martensite defects and (ii) to form precipitates in the form of cementite.

The main drawback of the preceding approaches is their lack of physical basis to describe the different stages of the tempering and their kinetics.

In the aforementioned context, the aim of the present paper is to: (i) characterize the microstructural evolutions and mechanical properties of fully martensitic steels during isothermal treatments between 100 °C and 550 °C in order to determine the activation energies of the phenomena responsible for the different tempering stages observed in steels with different carbon and manganese contents; (ii) to model the evolution of the carbon content from the solid solution according time and temperature using JMAK laws calibrated on the experimental kinetics determined in the preceding step and (iii) to model the mechanical properties of tempered fully or partially martensitic steels by introducing the predicted evolution of the carbon content in the Hybrid-Mean Field Composite (Hy-MFC) model recently presented in [23].

Here, it has to be pointed out that in the present approach, the evolution of the carbon content in solid solution during tempering is modelled using JMAK laws calibrated on experimental kinetics. Consequently, this allows to introduce an additional physical basis in the model for predicting martensite properties compared to Cupertino et al. [22].

2. Materials and experimental procedures

2.1. Materials

The experimental investigations presented in this chapter were carried out on four ternary model Fe–C–Mn steels, with various C and Mn contents and with an initial ferritic–pearlitic structure.

Table 1 gives the chemical composition and an estimation of the M_S temperatures of the ternary steels after a full austenitization followed by a water-quench. These temperatures were calculated using different empirical relations for the M_S prediction [24–33]. For each steel, the average calculated value and the corresponding standard deviation are reported in Table 1.

The tempering treatments were performed in salt baths after full or partial austenitization of the steels. Due to the small thickness of the samples (less than 1 mm) and due to their immersion in a liquid, the heating stage to the tempering temperature is very rapid (less than 5s for T < 550 °C), thus enabling to neglect the heating time for most conditions. For these reasons, the shortest tempering time was set at 30 s.

The full autenistization was obtained by a $3 \min$ salt bath heat treatment at 850 °C followed by a water quench. For partially austenitized microstructures, the Fe-0.17C-1.7Mn and Fe-0.17C-0.5Mn steels were

Table 1

Chemical composition and M_S temperature of the ternary steels investigated in this paper. M_S temperatures were calculated using different empirical relations [24–33]; for each steel, the average and standard deviations were calculated.

Steel grades	Chemical (in wt.%)	composition	<i>M_s</i> temperature (°C)
	С	Mn	_
	0.17	0.5	$440~\pm~20$
Ternary	0.17	1.7	395 ± 21
steels	0.17	2.5	$366~\pm~20$
	0.08	1.7	$430~\pm~26$

heat treated for 3 min in a salt bath at 780 °C and at 820 °C resp., and then water-quenched, in order to obtain a mixture combining about 30% of ferrite and 70% of martensite for both steels. Optical quantification of the martensite fraction obtained after water-quench was performed after a Bandoh etching (2.3 mL picral + 2.3 mL metabisulfite + 1 mL Nital - 30 s) at room temperature and a thresholding performed using Otsu's method with ImageJ [34,35]. With this etching, ferrite is usually coloured in brown/blue while martensite appears white/yellow and the quantification is performed at \pm 5%. As Bandoh etching is sensitive to steel oxidation, it has to be carried out directly after the final polishing. In addition, rinsing should be carried out by immersion in water followed by an ethanol rinse near the etched surface.

The tempering kinetics of the fully martensitic steels were followed using Vickers hardness and ThermoElectric Power (TEP) measurements during isothermal heat treatments in the range 100-550 °C. This was done in order to identify the mechanisms involved in the martensite tempering and to determine the associated activation energies for various steel compositions.

Microstructural characterization (FIB tomography) and tensile tests were also performed for a more in-depth analysis of the results obtained with the other techniques.

2.2. TEP kinetics during tempering

The principle of the TEP technique is to measure the voltage (ΔV), arising from the Seebeck effect between two junctions of the studied sample with pure metal blocks (here, pure copper blocks). The temperature of the blocks is *T* and *T* + ΔT with *T* = 15 °C and ΔT = 10 °C. The relative TEP (noted *S*) of the sample with respect to the TEP of pure iron is affected by the defects present in the lattice of the iron matrix and is the sum of various contributions:

$$S = \Delta S_{ss} + \Delta S_d + \Delta S_{pp} \tag{2}$$

where ΔS_{ss} , ΔS_d and ΔS_{pp} are due to elements in Solid Solution (ss), to dislocations (d) and to precipitates (pp).

The atoms in solid solution may induce a strong TEP variation ΔS_{ss} which leads, for most alloying elements (such as C, N, Al, Mn), to a gradual TEP decrease as they are introduced in solid solution and to a TEP increase when they leave the solid solution to segregate to the defects or to form precipitates. It is important to note that this contribution depends on the nature and concentration of each alloying element in solution and also on the resistivity of the material (that is to say, on its chemical composition) and it is given by the Gorter–Nordheim law [36].

Among all alloying elements, carbon is the one having the greatest influence on TEP. If the amount of C atoms in solid solution is $C_{\rm C}^{ss}$, their contribution to the TEP value is: $\Delta S_{ss} = P_{\rm C} \times C_{\rm C}^{ss}$, where $P_{\rm C}$ is the influence coefficient of carbon in iron (which is negative). Thus, with increasing the C content in solution, TEP will decrease. It has to be noted that with an increase in resistivity of the steel due to the addition of alloying elements (such as Mn), the influence coefficient of carbon on TEP is assumed to decrease.

Furthermore, if the concentration of carbon atoms in solid solution decreases due to precipitation or to segregation on defects (dislocations, interfaces), TEP is expected to present a sharp increase.

With regard to the dislocations, they are known to have a negative effect on the TEP, so that they lead to a TEP decrease when they are introduced in the material and to a TEP increase when their density decreases due to recovery phenomena. However, their impact on TEP is much lower than that of carbon atoms.

Lastly, precipitates are considered to have no significant effect on TEP (ΔS_p nearly equal to 0), unless they are very small and coherent, which is not usually the case of carbides in steels.

In order to follow the tempering kinetics of fully austenitized steels using TEP measurements, TEP measurements were performed on asquenched samples in order to assess their initial TEP value, S(t = 0), and on tempered samples after different isothermal treatments to evaluate their TEP value after tempering (noted S(T, t)). Thus, the TEP variation induced by the tempering for a time t at a temperature T, $\Delta_t S(T, t) = S(T, t) - S(T, t = 0)$, could be assessed.

2.3. Kinetics of change of hardness during tempering

As for the TEP kinetics, hardness was measured during tempering under various conditions of time and temperature, in order to obtain the kinetics of change of hardness at different temperatures. Vickers hardness measurements were performed on a Buehler machine at quarter thickness with a load of 0.5 kg. An average of 10 measurements was performed to ensure a standard deviation lower than 15 HV on fresh martensite.

2.4. FIB/SEM tomography

3-D FIB/SEM analyses were performed on a Zeiss NVISION 40 microscope to quantify and characterize the volume fraction of precipitated carbides for various tempering treatments. This type of analysis was chosen as the conclusions of the work performed in [7] clearly showed that it is relevant for estimating the mean volume of the iron carbides formed during tempering and their volume fraction, as long as their size is greater than the voxel size. In particular, a comparison between the mean volumes determined by Transmission Electron Microscopy and FIB/SEM showed an excellent agreement. SEM imaging was done in secondary electrons (SE) mode with an accelerating voltage of 1.5 keV and an in Lens detector. Low energy loss BSE images were simultaneously recorded with a detector located inside the column and a filtering grid set to a potential of 800 V.

Two complementary volumes of $10 \times 10 \times 10$ µm were analysed for each FIB acquisition. A voxel size of 5 nm^3 was chosen. Volumes were analysed using ImageJ software. A 2-D Gabor filter with the VSNR2 plug-in was first used to reduce image noise. A 3-D thresholding using a WEKA learning machine plug-in was then performed on sub-volumes to extract the cementite precipitates after tempering.

2.5. Tensile tests

Tensile tests were performed on an Instron machine using an optical extensioneter and with a velocity of 2 mm/min. Tensile specimens were machined by wire-cut electroerosion. The working section measures $4 \times 1.5 \text{ mm}^2$ for a gauge length of 15 mm. Tensile tests were tripled to confirm the mechanical behaviour of a given condition.

3. Microstructural evolutions of fully martensitic steels during isothermal tempering

This section aims at characterizing and quantifying the microstructural evolutions and mechanical properties of the studied ternary Fe– C–Mn steels (treated to be in a fully martensitic state) after tempering treatments performed between 100-550 °C. One important objective is to highlight the influence of manganese and carbon on tempering and to be able to extract the parameters controlling the evolution of the carbon content in solid solution.



Fig. 1. Isothermal tempering kinetics of the Fe-0.17C-1.7Mn steel followed by: (a) hardness and (b) TEP within the tempering temperature range from 150 °C to 550 °C.



Fig. 2. Master curve at 250 °C of the Fe-0.17C-1.7Mn steel obtained by applying a time-temperature equivalence on the tempering kinetics followed by: (a) hardness and (b) TEP. For the lowest tempering temperatures, an activation energy of 80 kJ/mol was used, while at higher temperatures, the activation energy was 210 kJ/mol.

3.1. Tempering of the Fe-0.17C-1.7Mn steel

To start, the procedures and experimental results obtained during the tempering of the Fe-0.17C-1.7Mn steel used in this work as reference material are presented hereafter.

In order to understand and characterize the phenomena involved in the martensite tempering of this steel, its tempering kinetics were followed during isothermal treatments at different temperatures between 150 °C and 550 °C using both hardness and TEP measurements after different treatment times.For the TEP kinetics, the TEP variation between each tempered state and the initial as-quenched state was plotted as a function of time.

Fig. 1 illustrates that the increase in tempering time and temperature leads to a global decrease in hardness (except for the lowest ageing times at 150 °C where hardness slightly increases). This hardness decrease is associated with a gradual TEP increase which can be interpreted, at first sight, by a departure of carbon atoms from the solid solution and/or by a decrease in the dislocation density (mainly for the highest tempering temperatures where recovery phenomena could come into play). Namely, these two phenomena are assumed to lead to a TEP increase. However, one has to keep in mind that in steels, carbon is known to have a predominant effect on TEP compared to the dislocations.

A time-temperature equivalence has been carried out on the hardness and TEP kinetics obtained at different temperatures using an Arrhenius law with an activation energy (*Q*) and a reference temperature of 250 °C (i.e. 523 K). This law was applied with the aim of finding the "equivalent time" at 250 °C (denoted t_{ref}) for all the treatments performed at a temperature *T* different from 250 °C. This time is given by the following relation:

$$t_{ref} = t_T \exp\left[-\left(\frac{Q}{R}\right)\left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right]$$
(3)

In order to be able to match the different kinetics along a single master curve reflecting the microstructural evolutions during tempering, it was necessary to use two different activation energies (see Fig. 2): one of about 80 kJ/mol for the lowest temperatures (T < 300 °C) and another one of about 210 kJ/mol for the highest temperatures. The first activation energy corresponds to that for carbon diffusion in iron, while the second one is close to that for self-diffusion of iron. Here, it has to be pointed out that the same activation energies were obtained using the hardness and TEP kinetics.

These results suggest that tempering in the investigated temperature range involves two distinct stages associated with several metallurgical mechanisms which have to be identified.

3.1.1. Analysis of the first tempering stage

If we consider the kinetics of Fig. 2, the first tempering stage is observed mainly at low temperature (T < 300 °C) and ends after about 1 h at 250 °C. In this stage mainly governed by carbon diffusion, hardness first increases slightly before decreasing while TEP regularly increases and tends to stabilize before the beginning of the second stage. These observations (notably the hardness increase obtained for a treatment of 1s at 250 °C) suggest that tempering in this stage begins with the segregation of a given amount of carbon to the defects of the microstructure (dislocations and/or lath boundaries) as this phenomenon was probably not completed during the cooling step. The corresponding



Fig. 3. (a) TEM micrograph and (b) SEM observation of the cementite precipitation state within martensite tempered for 1 h at 250 °C (Fe-0.17C-1.7Mn steel). (c) 3D view of the cementite precipitate segmentation resulting in a precipitated carbon content of 0.084 wt% (\simeq 50% of total carbon content).

TEP variation (determined for a tempering of 1s at 250 °C) is estimated as being of the order of 0.35 μ V/K.

Then, for tempering times exceeding 1 s, the significant hardness drop supports the beginning of cementite precipitation, as no intermediate carbide precipitation is expected in the present case due to the carbon content of the steel (lower than 0.2 wt%). This precipitation is supposed to be due to the carbon atoms remaining in solution after segregation to the defects and is linked to the carbon diffusion. In order to confirm this interpretation, TEM observations were performed at the end of the first tempering stage (1 h at 250 °C)(see Fig. 3.(a)). They clearly showed an intra-lath precipitation of plate-like cementite particles (θ carbides) as expected and observed in [7].

With the aim of quantifying the carbon content in solid solution which precipitated in the form of cementite after a tempering for 1 h at 250 °C, a FIB/SEM experiment was performed. SEM observations during the FIB experiment show, similarly to TEM observations, an intra-lath precipitation of plate-like cementite (see Fig. 3.(b)). The treatment of the FIB volume allowed the precipitated cementite fraction during the tempering to be quantified. A volume fraction of approximately 1.3% plate-like cementite was detected (Fig. 3.(c)). This result allows us to estimate that the carbon, which left the solid solution during the cementite precipitation is of about 0.084 wt%. This carbon content represents about 50% of the nominal carbon content of the Fe-0.17C-1.7Mn grade.

3.1.2. Analysis of the second tempering stage

For tempering temperatures above 300 °C and less than 550 °C, hardness presents a second sharp decrease while TEP keeps increasing. In this temperature domain, the measured activation energy is much higher (\approx 210 kJ/mol) and indicates that other phenomena have to be considered during tempering. A FIB/SEM experiment on the Fe-0.17C-1.7Mn grade tempered for 1 h at 450 °C provided an opportunity to study and compare the fraction of precipitated cementite with the state tempered for 1 h at 250 °C. Referring to the studies found in the literature above 300 °C, several phenomena are expected to occur more or less simultaneously:

- Substitutional element partitioning leading to a potential cementite enrichment in Mn and Cr.
- Beginning of the recovery phenomena responsible for: (i) the rearrangement of the martensite defects, (ii) a decrease in the dislocation density and (iii) a possible release of the segregated carbon atoms from the defects which could lead to a further cementite precipitation.
- · Start of cementite spheroidization.

The SEM observations of the sample treated for 1 h at $450 \,^{\circ}$ C provided evidence of the presence of two types of precipitates: (i) spheroidized intra-lath cementite precipitates and (ii) inter-lath cementite precipitates.

They highlighted that the intra-lath cementite precipitates observed at $250 \,^{\circ}\text{C}$ had time to spheroidize during tempering at $450 \,^{\circ}\text{C}$ (see Fig. 4.(a)), while keeping a similar volume fraction. Indeed, volume segmentation leads to a volume fraction of 1.1% for intra-lath cementite.

In parallel, inter-lath precipitates, not present at lower temperature, were clearly observed as illustrated in Fig. 4.(b). The formation of these precipitates can be related to the carbon atoms initially segregated to the microstructural defects during quenching or the first tempering stage. At 450 °C, these atoms are assumed to be released from the defects which tend to disappear during recovery. The quantification of this second type of precipitates led to a non-negligible volume fraction of approximately 1%.

As a conclusion, the two types of precipitates allow to reach a precipitated carbon content of about 0.14 wt% representing 85% of the nominal carbon content of the steel (see Fig. 4.(c)). However, it is necessary to underline that a precise quantification of cementite is difficult due to image noises and the possible lack of representativeness of the studied volume compared to the global microstructure. Nevertheless, the FIB/SEM experiments allowed us to observe a precipitation of intra-lath plate-like cementite of the order of 50% of the nominal carbon composition during the first tempering stage. Moreover, the second stage leads to the spheroidization of inter-lath cementite with a proportion of about 50% of the nominal composition.

Fig. 5 summarizes the main conclusions of this study in relation with the carbon distribution after quench and at the end of the first and second tempering stages.

3.2. Analysis of the influence of the Mn content

After having determined the tempering kinetics of the ternary Fe-0.17C-1.7Mn steel between 150 °C and 550 °C and analysed the two tempering stages identified in this temperature domain, the effect of the Mn content for a carbon content of 0.17 wt% is discussed hereafter.

3.2.1. Effect of the Mn content on the tempering kinetics

In order to identify the possible influence of the Mn content on the tempering kinetics, the Fe-0.17C-xMn steels (with x = 0.5, 1.7 and 2.5) were submitted to the same procedure than that used for the Fe-0.17C-1.7Mn steel in the preceding section.

In particular, the same type of time-temperature equivalence was applied leading to the hardness and TEP master curves shown in Fig. 6.(a-b) for the three Mn contents considered in this study. For all steels, two activation energies had to be applied in order to obtain a unique master curve. Table 2 summarizes the activation energies which were used for the two tempering stages of each steel. In the first tempering stage, the same activation energy was determined for



Fig. 4. SEM image within martensite tempered for 1 h at 450 °C (case of the Fe-0.17C-1.7Mn steel): (a) intra-lath cementite precipitation state and (b) inter-lath cementite precipitation state. (c) 3D view of the cementite precipitate segmentation resulting in a precipitated carbon content of 0.14 wt% (\simeq 83% of total carbon content).



Fig. 5. Schematic representation of carbon distribution after quench and at the end of the first and second tempering stage.

Table 2 Activation energy determined for the two tempering stages of the ternary Fe-0.17C-xMn steels.

Steel grades	Activation energy for low tempering (kJ/mol)	Activation energy for high tempering (kJ/mol)
Fe-0.17C-0.5Mn	80 ± 5	199 ± 5
Fe-0.17C-1.7Mn	80 ± 5	210 ± 5
Fe-0.17C-2.5Mn	80 ± 5	$211~\pm~5$

all steels. However, in the case of the second tempering stage, the activation energy was found to increase slightly with increasing the manganese content of the steel. This suggests that tempering seems not to be strongly affected by the Mn content in the first tempering stage, while it is delayed in the second tempering stage with a higher manganese content.

These conclusions are supported by the hardness evolutions shown in Fig. 6.(a). While the hardness curves of the three steels are superimposed in the first tempering stage regardless of the Mn content, this is absolutely not the case in the second tempering stage where the hardness drop is retarded for the steels with a high Mn content (1.7 or 2.5 wt%) compared to the steel with a 0.5% Mn content. These observations are also consistent with the results of the literature which clearly highlighted that the addition of alloying elements (such as Mn) has a marked influence on the loss of mechanical strength during tempering above 200 °C [9] due to the fact that the growth and coarsening rate of cementite is notably affected by the presence of substitutional elements which tend to partition [10]. This is particularly the case of Mn which tends to enrich cementite. This results in much finer and more numerous cementite particles which could retard recovery and recrystallization and thus, martensite softening.

The analysis of the TEP kinetics requires to keep in mind that the measured TEP variations for given tempering conditions depend on the chemical composition of the steels. Increasing the manganese content of the steel leads to a higher electrical resistivity and to a lower influence coefficient of carbon on TEP. This means that for the same amount of carbon leaving the solid solution, the measured TEP variations should be lower for the steel with the highest Mn content. The fact that the measured TEP variations during the first tempering stage are higher in the case of this steel (as shown in Fig. 6.(b)) suggest that the carbon departure from the solid solution during this stage is more important when the Mn content is higher. This could be explained by the fact that the M_S temperature of the three studied steels is not identical (see Table 1) and decreases with increasing the Mn content. This is why, the self-tempering during cooling due to carbon segregation to the defects could be reduced with an increase in the Mn content, leading to a greater amount of carbon atoms in solid solution after quench (not segregated to the defects). Consequently, during the first tempering stage, higher TEP variations could be measured in the steels with a higher Mn content as observed experimentally in Fig. 6(b).

3.2.2. Effect of the Mn content on the mechanical behaviour (hardness, tensile behaviour)

Fig. 7.(a-b) show isochronal hardness curves of the studied ternary steels for two tempering times (30 s and 1 h). They highlight the low influence of the Mn content on hardness after quench and confirm



Fig. 6. Influence of the Mn content on the master curves at 250 °C obtained by applying a time-temperature equivalence on the tempering kinetics followed by: (a) hardness and (b) TEP.



Fig. 7. Isochronal hardness curves for a tempering temperature range between $150 \,^{\circ}$ C and $650 \,^{\circ}$ C on the three Fe-0.17C-xMn steels (with x = 0.5, 1.7 and 2.5) and a tempering time of: (a) $30 \,^{\circ}$ and (b) 1 h. The experimental data from Speich [5] on a binary Fe-0.18C steel were added. Tensile curves of the fully martensitic Fe-0.17C-xMn steels: (c) after quench, (d) after tempering for $30 \,^{\circ}$ at $450 \,^{\circ}$ C and (e) after tempering for 1 h at $450 \,^{\circ}$ C.

that Mn hardly impacts hardness at low tempering temperatures (T < 250 °C) while this element has a rather strong impact at higher tempering temperatures even for a short tempering time. It is particularly noticeable between 0.5 and 1.7 wt% Mn.

The low influence of Mn after water-quench is also observed on the tensile curves of the steels as shown in Fig. 7.(c). It can be attributed to the solid solution strengthening of manganese on the tensile behaviour of quenched martensite.

By contrast, after tempering for $30\,{\rm s}$ and 1 h at $450\,{\rm ^oC},$ manganese has a strong impact on the tensile curves and tend to retard the drop

in mechanical strength as its concentration in the steel increases. This statement is illustrated by Fig. 7.(d-e) which presents a marked difference between 100 and 200 MPa for the steels with 0.5 and 1.7 wt% Mn for a tempering at 450 °C. This difference appears to increase with increasing the tempering time.

An other important point is that hardness is closely related to the tensile behaviour, in particular to the UTS. For all ternary steels, a linear relationship between the UTS and hardness values was found. It can be written as follows:

$$UTS = [2.9 \,\mathrm{MPa}] \times H_v \tag{4}$$



Fig. 8. Influence of the C content on the master curves at 250 °C obtained by applying a time-temperature equivalence on the tempering kinetics of the Fe-xC-1.7Mn steels followed by: (a) hardness and (b) TEP. Tensile curves of the fully martensitic Fe-xC-1.7Mn steels: (c) after quench, (d) after tempering for 30s at 450 °C and (e) after tempering for 1 h at 450 °C.

3.3. Analysis of the influence of the carbon content

The effect of the carbon content on tempering was investigated using always the same procedure as that applied to the Fe-xC-1.7Mn steels (with x = 0.08 or 0.17 wt%).

Fig. 8.(a–b) presents the master curves at 250 °C obtained thanks to a time-temperature equivalence on the tempering kinetics of the two studied steels determined by hardness and TEP. For the two tempering stages, the same activation energies (80 kJ/mol for the first stage and 210 kJ/mol for the second stage) were used for the two steels supporting the idea that carbon (contrary to manganese) has no influence on the tempering kinetics and probably, on the phenomena responsible for tempering in the two tempering stages. Nevertheless, it is interesting to note that as expected and contrary to manganese, carbon has a very marked effect on the hardness of quenched martensite. On the other hand, during tempering, the difference in hardness of the two steels tends to decrease as far as the quantity of carbon in solid solution is reduced, as the two steels tend to reach the same carbon content in solution after a prolonged tempering. As can be seen in Fig. 8.(ce), the same conclusions can be drawn from the tensile curves of the two steels. While they are very different directly after water-quench, they tend to become very similar with increasing the tempering time at 450 °C, as most of the carbon has left the solid solution in the two steels. Concerning the TEP kinetics, the magnitude of the TEP variations is higher with increasing the carbon content. This is consistent with the fact that the TEP kinetics reflect mainly the departure of the carbon atoms from the solid solution.

3.4. JMAK modelling of the TEP kinetics

The preceding investigations highlighted that the mechanical properties of martensite during tempering are greatly controlled by the decrease in the martensite carbon content in solid solution (to form intra-lath cementite precipitates) for tempering temperatures lower than 300 °C and by the release of the carbon atoms from the microstructural defects (to form inter-lath precipitates) at higher tempering temperatures. With regard to the phenomenon of carbon segregation to the dislocations observed below 150 °C, it is not likely to influence strongly the mechanical properties and can be neglected in a first approach as carbon atoms segregated to the defects or in solid solution have almost the same strengthening effect as suggested by Hutchinson et al. [37], so that it is not necessary to distinguish these two populations of carbon atoms.

Considering that the measured TEP variations during tempering are mainly governed by the evolution of the carbon contribution on TEP, the TEP master curve obtained by Time–Temperature-Equivalence at 250 °C for the Fe-0.17C-1.7Mn was modelled using two JMAK laws, denoted $Y_{ss\to\theta}$ and $Y_{\perp\to\theta}$, accounting for the decrease in the carbon content due: (i) to the intra-lath cementite precipitation and (ii) to the inter-lath cementite precipitation. Each law can be written as follows:

$$Y_i(t,T) = 1 - \exp[-(b_i t)^{n_i}]$$
(5)

$$b_i = b_0 \exp\left[-\left(\frac{Q_i}{RT}\right)\right] \tag{6}$$

where Q_i is the activation energy of the considered phenomenon, n_i is the Avrami coefficient and b_0 is a rate constant.

So, after having subtracted the TEP variation due to the segregation of the C atoms to the dislocations (estimated to be of the order of 0.35 μ V/K), the TEP variation $\Delta S(t, T)$ can be expressed as follows:

$$\Delta_t S(t,T) = \Delta_t S_{ss \to \theta}(t,T) + \Delta_t S_{\perp \to \theta}(t,T)$$
(7)

where $\Delta_t S_{ss \to \theta}(t, T) = \Delta S_{ss \to \theta}^{\max} \times Y_{ss \to \theta}(t, T)$ and $\Delta_t S_{\perp \to \theta}(t, T) = \Delta S_{\perp \to \theta}^{\max} \times Y_{\perp \to \theta}(t, T)$ represent the TEP evolution associated with intra-lath cementite precipitation and that with inter-lath cementite precipitation,



Fig. 9. Modelling of the normalized TEP variations with two JMAK laws using the activation energies determined from the Time–Temperature equivalences. Case of the Fe-0.17C-1.7Mn steel tempered at 250 °C.

Table 3

Parameters of the JMAK laws determined in this work and used for the modelling of the TEP kinetics.

JMAK law	$b_i ({ m s}^{-1})$	Activation energy/(kJ/mol)	n _i
$Y_{ss \to \theta}$ low temperature	6×10^4	80	0.75
$Y_{\perp \rightarrow \theta}$ high temperature	1011	$190 + 22 \left\{ 1 - \exp\left[-(\frac{1.3}{\text{wt\%}} C_{\text{Mn}}^0)^{1.3} \right] \right\}$	0.25

respectively. $\Delta S_{ss \to \theta}^{\max}$ is the maximum TEP variation of the first phenomenon and $\Delta S_{\perp \to \theta}^{\max}$ is the maximum TEP variation of the second one.

Considering that the magnitude of the two tempering stages is the same and is associated with half of the total carbon content (as suggested by the FIB/SEM experiment and by the TEP kinetics), one can write that:

$$\Delta_t S(T,t) = \Delta S^{\max} \left[0.5Y_{ss \to \theta} + 0.5Y_{\perp \to \theta} \right]$$
(8)

where $\Delta S^{\max} = \Delta S^{\max}_{ss \to \theta} + \Delta S^{\max}_{\perp \to \theta}$.

Table 3 gives the parameters of the two JMAK laws which were determined in this work to reproduce the normalized TEP master curves at 250 °C of the ternary steels of this study (see Fig. 9). The activation energies were extracted from the hardness and TEP kinetics.

While the parameters of the first JMAK law are not affected by the manganese content, those of the second JMAK law are modified, notably the activation energy which tends to increase with increasing the Mn content.

4. Mechanical properties of fully martensitic steels during isothermal tempering in the range of [100-550] °C

After having characterized the phenomena occurring during the martensite tempering over a wide range of chemical composition and tempering conditions, an extension of the Composite Continuous model for predicting the mechanical properties of fresh martensite presented in paper [23] is proposed hereafter to take into account the tempering phenomena. A comparison of the model with the experimental tensile curves for fully martensitic steels tempered under various tempering conditions is performed here with the objective of validating the ability of the model to reproduce the effect of temperature and time on a wide range of chemical composition.

4.1. Mechanical model for predicting the tensile curve of fresh martensite

This section gives the main equations of the Composite Continuous model, used in this work, to reproduce the elasto-plastic transition of martensite. In this approach, martensite is considered as a composite, combining soft and hard phases, for which the yield properties are described by a continuous distribution of probability density f (σ_l) to find a domain having a local yield stress σ_l .

This model enables to describe the macroscopic stress of martensite using the following relation [38,39]:

$$\frac{d\sigma^m}{d\epsilon^m} = \frac{1}{\frac{1}{E} + \frac{F(\sigma_l)}{\beta}} \left(1 - F(\sigma_l)\right)$$
(9)

where *E* is the Young's modulus and σ_l is the local stress, while σ_m and ϵ_m are the macroscopic stress and strain of martensite. F (σ_l) represents the cumulative probability density to find domains with a yield strength with a value less or equal to σ_l . In the present work, the parameter β which describes the interaction between the different phases of the composite was fixed to 50 GPa (as in Ref. [39]).

In order to capture the Bauschinger effect on martensitic steels, the stress spectrum is defined using an Avrami-like law with three adjustable parameters (Δ , m, $\sigma_{\min} + \sigma_0^m$) [38,39]:

if
$$\sigma_l < \sigma_0^m + \sigma_{\min}$$
 then $F(\sigma_l) = 0$
else $F(\sigma_l) = 1 - \exp\left[-\left(\frac{\sigma_l - (\sigma_{\min} + \sigma_0^m)}{4}\right)^m\right]$ (10)

where:

 σ₀^m is the contribution of Peierls force and that of the friction stress due to solid solution hardening. Its dependence with the chemical composition of the steel is given by the following relation coming from [38]:

- $\sigma_{\min} = 320$ MPa represents the martensite yield strength.
- m = 1.8 is the parameter controlling the rate of martensite strainhardening
- Δ is the parameter governing the width of the local yield strength distribution and thus controlling the magnitude of the strain hardening between yield strength and tensile strength. In paper [23], it was defined as follows:

$$\Delta = K_0 + \frac{K_1}{\sqrt{D_{\gamma}}} + K_2 (C_{\rm C})^{1.34}$$
(12)

where D_{γ} is the diameter of the austenitic grains before quenching and C_C the austenite carbon content after phase transformation during intercritical annealing. The chosen values for the constants of this law are given in Table 4.

4.2. Model modifications to account for the martensite tempering

4.2.1. Implementation of the evolution of the carbon content in solid solution

To take into account the martensite tempering within the mechanical martensite prediction model, two assumptions were included:

• The first one consists in modifying the constant *m* required to adjust the strain-hardening rate according to the tempering conditions. For low tempering temperature ranges below 300 °C where significant hardening is observed, m = 1.8 was applied as in the case of fresh martensite. On the contrary, to reproduce the decrease in hardening for tempering above 300 °C, m = 3 was used.



Fig. 10. Kinetics of the JMAK laws: (a) $Y_{ss-\theta}$ and (b) $Y_{1-\theta}$ for two temperatures. (c) Evolution of the carbon content in solid solution for the two considered temperatures. (d) Comparison between the experimental and modelled tensile curves of the Fe-0.17C-1.7Mn steel with only the introduction of the evolution of the carbon in solid solution in the expression of Δ .

 The second assumption is to include the evolution of the carbon content in solid solution C_C^{ss+⊥} taking into account the experimentally measured JMAK laws defined in Section 3 and based on the JMAK parameters of Table 3. The width of the local yield strength distribution can therefore be expressed as follows:

$$\Delta = K_0 + \frac{K_1}{\sqrt{D_{\gamma}}} + K_2 (C_{\rm C}^{ss+\perp})^{1.34}$$
(13)

where $C_{\rm C}^{ss+\perp}$ represents the carbon content in solid solution and segregated to the defects within the martensite. Namely, as already mentioned, carbon atoms in solid solution or segregated to defects have almost the same role on the mechanical properties. The evolution of the carbon content in solid solution and segregated to defects is thus assumed to evolve according to the following relationship:

$$C_C^{ss+\perp}(T,t) = C_C^0 \left[1 - 0.5(Y_{ss\to\theta} + Y_{\perp\to\theta}) \right]$$
(14)

where $Y_{ss\to\theta}$ and $Y_{\perp\to\theta}$ are the two JMAK laws reproducing the carbon departure from the solid solution during the two tempering stages defined in Section 3.4 with $Y_i = 1 - \exp\left[-(b_i t)^{n_i}\right]$. The coefficient 0.5 has been fixed in relation to the carbon fraction precipitated during each of the tempering stage measured by FIB. This hypothesis is also based on the fact that almost all the carbon is assumed to be precipitated for a tempering of 1 h at 450 °C.

To test the validity of the model, the mechanical properties of the fully martensitic Fe-0.17C-1.7Mn steel were modelled and compared to the experimental tensile curves obtained after quench and after different tempering conditions. Fig. 10.(a–c) shows the evolution of the JMAK laws ($Y_{ss\to\theta}$ and $Y_{\perp\to\theta}$) as well as that of the carbon content in solid solution for the studied steel tempered at two different temperatures: 250 °C and 450 °C.

For short times ($t < 10^4$ s) at 250 °C and t < 10 s at 450 °C, a fast increase in the $Y_{ss \to \theta}$ law is observed (see Fig. 10.(a)). It corresponds to

the first drop of the carbon content in solid solution visible in Fig. 10.(c) which is due to the intra-lath cementite precipitation.

For longer times, an increase in the $Y_{\perp \rightarrow \theta}$ law is detected (see Fig. 10.(b)). It is associated with the second drop of the carbon content in solid solution shown in Fig. 10.(c) and it can be attributed to the inter-lath cementite precipitation resulting from the recovery phenomena occurring in the steel at high temperature.

Fig. 10.(d) shows the ability of the model to reproduce the softening of the mechanical properties of martensite for temperatures below 300 °C. However, at higher temperature, a more important softening than expected by the model is observed experimentally, supporting the idea that the carbon release from the solid solution is not the only phenomenon to consider to explain the tensile behaviour for high tempering temperature. This will be discussed in the next section.

4.2.2. Additional softening term to account for recovery phenomena

In order to take into account the reorganization and disappearance of internal defects of martensite (decrease in dislocation density, lath boundaries), a term was added in the Δ parameter for high temperature tempering.

$$\Delta = K_0 + \frac{K_1}{\sqrt{D_{\gamma}}} + K_2 (C_C^{ss+\perp})^{1.34} - K_3 Y_{\perp \to \theta}$$
(15)

The values of the parameters K_0 , K_1 , K_2 and K_3 are listed in Table 4. As a conclusion, the modification of the mechanical properties due to tempering can be summarized in 3 steps:

- 1. A partial segregation of the carbon atoms on the microstructural defects occurs during quenching and at tempering temperatures below 150 °C. This step is neglected during the simulation as the segregated carbon atoms are considered to have the same hardening role as in solid solution.
- 2. Intra-lath cementite precipitation of the carbon atoms remaining in solid solution is then observed for tempering temperatures below 300 °C leading to a decrease in the intrinsic mechanical

Values of the key parameters used in the Hy-MFC mechanical model for tempered martensite.

	Parameter	Symbol	Unit	Value used
	Young's modulus	Y	GPa	210 ^a
Martensite model	Composite interaction parameter	β	GPa	50 ^a
	Avrami parameter	$\sigma_{ m min}$	MPa	320 ^a
	Avrami parameter	m	-	1.8 ^a
	Local yield strength constant	K_0	MPa	570
	Local yield strength constant	K_1	MPa mm ^{0.5}	24
	Local yield strength constant	K_2	MPa wt% ^{-1.34}	6053
	Local yield strength constant	K ₃	MPa	450

^a Values used by Allain et al. [38].

properties of martensite. The reduction of the carbon content in solid solution $(C_{cs+\perp}^{ss+\perp})$ due to this precipitation taken into account by the $Y_{ss\to\theta}$ JMAK law for low tempering promotes a decrease in the Δ parameter (see Fig. 10.(c)). Since Δ controls the width of the stress spectrum, this leads to a decrease in the mechanical properties and in the heterogeneity within martensite.

3. For higher tempering temperatures, a change in activation energy close to the self-diffusion of iron (210 kJ/mol) is observed, supporting the start of rearrangement of the microstructure. As the density of dislocations and defects within the microstructure decreases, a reduction in the amount of carbon involved in the hardening of the steel, described by the $Y_{\perp \rightarrow \theta}$ JMAK law, for high temperatures is observed (see Fig. 10.(c)). However, the decrease in the amount of carbon involved in hardening is not sufficient to account for the obtained softening, leading to the necessity of an additional term within Eq. (15). This term reflects the effect of the presence of defects and of a high dislocation density on the properties of fresh martensite. This effect tends to be lowered as the microstructure is reorganized.

4.3. Comparison of the experimental and modelled tensile curves for the ternary Fe-C-Mn steels

A prediction capability validation of the mechanical properties for tempered martensite was carried out on all the Fe–C–Mn ternary steels of this study taking into account all the modifications presented in the previous section.

Fig. 11 illustrates the excellent agreement obtained between the tensile curves of the four Fe–C–Mn grades for fresh martensite as well as for the three considered tempering conditions. For each grade, a softening is observed for the mechanical properties of tempered martensite. It increases with increasing the tempering parameters (time and temperature). The tempering temperature appears here as the key parameter with a very important effect on the martensite properties when the temperature is above 300 °C.

The dependence of the activation energy $Q_{\perp \rightarrow \theta}$ (for the second tempering stage) with the manganese content enables to reproduce the mechanical properties of all the studied steels and in particular the marked softening of the Fe-0.17C-0.5Mn steel.

It is also important to point out the fact that the treatment for 30 s at 450 °C, which is more or less representative of the galvanization step of industrial lines in a zinc bath leads to an important softening of the mechanical properties which is properly reproduced by the model.

The role of each element on the final properties of the steel is discussed hereafter.

Fig. 12.(a) highlights that the mechanical properties of fresh martensite are slightly increased with increasing the manganese content of the steel due to the manganese strengthening effect by solid solution. After a tempering for 1 h at 450 °C, the influence of the manganese content is much more marked since a significant difference of 150 MPa is observed between the steels containing 0.5 wt% Mn and 1.7 wt% Mn as evidenced in Fig. 12.(b). It can be attributed to a potential solute drag effect of manganese within the microstructural defects (dislocations, lath boundaries) slowing down their rearrangement or to a decrease in the growth and coarsening rate of cementite due to manganese partitioning, leading to finer precipitates which can retard the recovery phenomena and subsequently, the martensite softening.

With regard to the carbon effect, Fig. 12.(a) shows that it is very marked in the case of fresh martensite and it is mainly responsible for the martensite intrinsic heterogeneity. For a tempering time of 1 h at 450 °C (see Fig. 12.(b)), the martensite heterogeneity is reduced during carbon precipitation and defect rearrangement. The role of the carbon content on the properties of tempered martensite thus regularly decreases with the progress of the martensite tempering phenomenon.

5. Mechanical properties in a two-phase state during isothermal tempering in the range [100–550] °C

The aim of the present section is to introduce the results of the model for tempered martensite in the recently developed Hybrid Mean Field Composite (Hy-MFC) model [23] used for the prediction of the tensile curves of two-phase steels. This model takes into account the interaction between ferrite and martensite thanks to the addition of GND (geometrically necessary dislocations) within the ferrite due to the martensitic volume variation and the deformation incompatibility between the two phases. Moreover, a particularity of this model is that a linear transition between an iso-strain law and an iso-work law is proposed to describe the strain hardening behaviour of the composite for low deformations.

In the case of tempered martensite, the model is applied by considering that the carbon content of martensite is that of austenite calculated with the following equation:

$$C_{\rm C} = \frac{C_{\rm C}^0}{f_{\gamma}} \tag{16}$$

where f_{γ} is the volume fraction of austenite (and thus of martensite).

Fig. 13 shows the mechanical properties and the good agreement obtained on two DP steels containing globally 70% of martensite for two different manganese contents. In both cases, a decrease in the mechanical properties of the DP steel is noted with the increase in tempering temperatures, due to the softening of the mechanical properties of martensite. Here, it is important to note that once the calibration of the model for the prediction of the mechanical properties of tempered martensite has been completed, its extension in the case of a two-phase steel using the Hy-MFC model is possible without any modification of these parameters.

6. Conclusions

A characterization of the microstructural evolutions and mechanical properties of fully martensitic steels with different chemical compositions was performed during isothermal tempering (100–550 °C) before proposing a modelling of the tensile curve of these steels and of partially martensitic microstructures. The following conclusions could be drawn:

1-Using a monitoring of the microstructural property evolutions of tempered martensite by hardness and TEP at different tempering temperatures, three main mechanisms during the tempering stage were



Fig. 11. Experimental and modelled tensile curves for a fully martensitic steel water quenched or tempered at different temperatures and times: (a) Fe-0.17C-1.7Mn, (b) Fe-0.17C-0.5Mn, (c) Fe-0.17C-2.5Mn and (d) Fe-0.08C-1.7Mn.



Fig. 12. Comparison of the carbon and manganese content effect on the experimental and modelled tensile properties of fully martensitic Fe-xC-yMn steels (a) after water quench and (b) after tempering for 1 h at 450 °C.

identified using a time–temperature equivalence. At very low temperature (<150 °C), a segregation of part of the carbon atoms remaining in solution after quench takes place on the intrinsic defects of martensite without significant effect on the mechanical properties. Thereafter, the first drop in mechanical properties results from the intra-lath cementite precipitation with an activation energy of 80 kJ/mol. Lastly, the second drop in mechanical properties (observed mainly at tempering temperatures higher than 300 °C) was attributed to a rearrangement of the microstructural defects present in fresh martensite leading to a decrease in their density and to a progressive release of the carbon atoms trapped by the defects. As highlighted by FIB/SEM tomography, these phenomena are concomitant with an inter-lath cementite precipitation not observed at tempering temperatures lower than 300 °C. At the end of this stage, almost all the carbon atoms are assumed to be precipitated.

2- The TEP master curve obtained by Time–Temperature-Equivalence at 250 $^{\circ}\mathrm{C}$ was modelled considering that the measured TEP variations

during tempering are mainly due to the carbon contribution on TEP. The modelling was based on two JMAK laws determined from the experimental study and accounting for the decrease in the carbon content in solution due to the: (i) intra-lath and (ii) inter-lath cementite precipitation.

3- From the JMAK laws, the influence of the evolution of the carbon content in solution on the tensile properties of martensite could be taken into account in the mechanical model for martensite presented in paper [23], in which the carbon content influences the width of the yield strength distribution. The model was first tested on fully martensitic steels tempered under various conditions. It was found to reproduce very well the experimental tensile curves as long as the tempering temperature is lower than 300 °C. At higher temperature, in order to obtain a better prediction of the tensile properties during tempering, an additional term had to be introduced in the width of the yield strength distribution to account for the recovery phenomena



Fig. 13. Experimental and modelled tensile curves for a DP steel with $70\%\alpha'$ water quenched or tempered at different temperatures and times: (a) Fe-0.17C-1.7Mn, (b) Fe-0.17C-0.5Mn.

which may take place in the range 300-500 °C and contribute also to the martensite softening.

4- After having validated the model on fully martensitic steels, it was introduced in the "composite" mean-field model for the prediction of the tensile behaviour of Dual-Phase steels. It was applied with success on different two-phase microstructures tempered under various conditions, thus validating the ability of the model to predict mechanical properties for several tempered two-phase steels.

5- In future work, with the ultimate aim of modelling the mechanical properties of industrial DP steels after tempering, the objective will be to analyse the influence of alloying elements (Cr, Si, Mo...) other than manganese on the tempering kinetics and to take into account their impact in the JMAK law used for predicting the carbon departure from the solid solution. The use of a Kampmann–Wagner-Numerical model to predict precipitation during tempering could be also an interesting challenge.

CRediT authorship contribution statement

Alexandre Mathevon: Writing – original draft, Investigation. Véronique Massardier: Writing – review & editing, Supervision, Methodology. Damien Fabrègue: Writing – review & editing, Supervision. Thierry Douillard: Visualization, Investigation. Philippe Rocabois: Validation, Supervision. Arnaud Ollagnier: Validation, Supervision. Michel Perez: Writing – review & editing, Supervision, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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