Relationship between microstructure and mechanical behaviour of thermomechanically optimised 9-12% Cr steels

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RELATIONSHIP BETWEEN MICROSTRUCTURE AND MECHANICAL BEHAVIOUR OF THERMOMECHANICALLY OPTIMISED 9-12%CR STEELS

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ABSTRACT

The development of Generation IV fission nuclear reactors and fusion nuclear reactors requires materials able to resist to high temperature (650℃) creep, but also to creep-fatigue. Martensitic 9-12%Cr steels are candidate materials for these applications.
Recent studies on commercial P91 steel showed that cyclic loadings coupled to high-temperature creep loadings lead to a strong softening effect, which affects the steel mechanical strength. This effect is due to the decrease of the dislocations density and the coarsening of martensitic microstructure.
Thermomechanical treatments, including warm-rolling in austenitic phase and tempering, have been applied to P91 in order to refine its microstructure and to improve its precipitation state. The temperature of rolling was set at 600℃, and those of annealing at 650℃ and 700℃, thanks to MatCalc calculations.
Microstructural observations proved that the warm-rolling and the following tempering lead to a finer martensite pinned with numerous small precipitates. In terms of mechanical properties improvement, the hardness of thermomechanically treated P91 is higher than that of as-received P91. The yield strengths are higher than that of P91 (around 400 MPa at 20℃; and more than 200 MPa at 550℃). Preliminary creep resu lts show that these treatments improve the creep lifetime by at least a factor 8.

KEYWORDS

Martensitic steels, 9%Cr steels, high temperature creep, fatigue, thermomechanical treatments, ausforming, microstructural optimization

INTRODUCTION

Advanced 9-12% Cr ferritic and martensitic steels are candidate materials for elevated-temperature applications in Generation IV nuclear reactors, and also envisaged for fusion nuclear reactors [1]. Thanks to a higher thermal conductivity and a lower thermal expansion than austenitic stainless steels, they are less subject to thermal stresses during temperature changes [2].
Numerous studies aim at increasing their high-temperature creep strength by chemical composition optimization. However in service these components will be subjected to high-temperature cyclic loading (fatigue and creep-fatigue). Recent works on commercial P91 steel have shown that cyclic loadings coupled to high-temperature creep loadings lead to a fast and strong cyclic softening effect [3-8]. This effect affects the mechanical strength since it significantly deteriorates the steel creep resistance. This loss of mechanical strength is due

to microstructural evolutions such as the decrease of the dislocations density, the coalescence of precipitates and the coarsening of martensite subgrains and laths [3-8].
In order to improve the mechanical strength, this microstructure degradation should be prevented. It can be achieved by refining the precipitation state within the steel: for example, by "ausforming" [9-12]. Recent studies suggest that it is possible either by cold-rolling [13-14] or warm-rolling [2, 15]. The purpose of these thermomechanical treatments (TMT) is to refine the martensitic microstructure and to improve the precipitation state of the steel in order to reinforce the pinning of the dislocations by the MX particles.

Some parameters of the TMT were chosen thanks to simulations with the software MatCalc [16-17]. A plate of P91 steel was thermomechanically treated and the warm-rolled&quenched P91 microstructure was studied by optical and electronic microscopy. Microhardness measurements and thermo-electrical power measurements were performed in order to choose the final tempering temperature.
The material was then tempered and the effect of the whole treatment on the microstructure and the mechanical strength was investigated.

MATERIALS AND EXPERIMENTAL PROCEDURES

As-received material

The material under study is the commercial P91 martensitic steel under the form of small blanks (100 mm * 40 mm * 30 mm). Its composition is given in Table 1.

C	Cr	N	Mn	Mo	Nb	V	Cu	Ni	S	Si	P	Al
0.088	8.91	0.04	0.363	0.917	0.08	0.198	0.068	0.15	0.001	0.324	0.017	0.18

Table 1: Chemical composition in wt% of P91 steel.

The as-received material was normalized at 1050°C for 30 minutes, then air quenched and tempered at 780°C for 1 hour. It exhibits a fully tempered martensitic microstructure (Figure 1 and Figure 2) made of:
- the former austenitic grains, coming from the normalizing treatment (size : 20-60 µm),
- each grain is made of one or several packets subdivided into blocks of laths (the laths of a block have the same $\{111\}_\gamma$ plane),
- these blocks are made of 5 to 10 parallel martensite laths,
- each lath is composed of subgrains formed during the tempering (mean diameter: 0.372 µm [18]).

The dislocation density of P91-AR is between 1.1 and 1.6×10^{14} m^{-2} [6]. Different kinds of carbide precipitates prevent their motion [3, 4, 8, 13, 15, 19, 20] (Figure 2):
- $M_{23}C_6$: around 100 nm, they are often on prior austenitic grain boundaries,
- MX: around 30-40 nm, they are located homogeneously in the matrix. They are very stable in temperature [20]. These precipitates pin the dislocations and the subgrains boundaries.

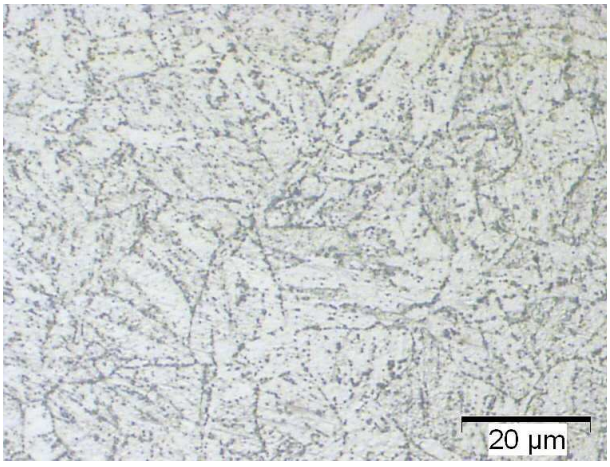

Figure 1: Optical microscopy observations in the as-received state (P91-AR).

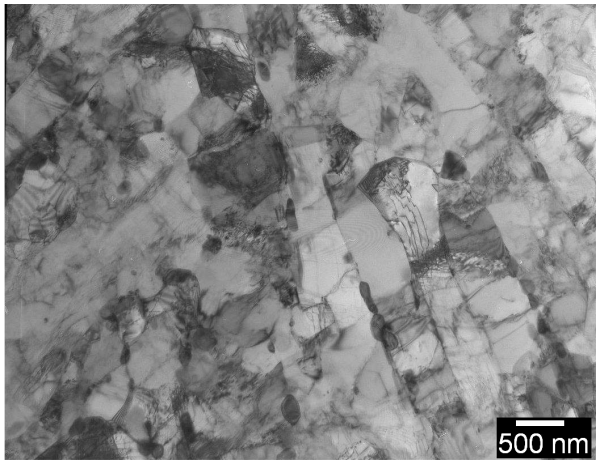

Figure 2 : Bright field TEM observation of P91-AR showing laths, subgrains and dislocations.

Presentation of the thermomechanical treatment

The principle of the thermomechanical treatment is presented in Figure 3. On this figure both the initial thermal treatment and the following thermomechanical treatment are shown.
The steel firstly undergoes a second austenitization. Its temperature is chosen at 1150℃, in order to dissolve all the $M_{23}C_6$ and as much MX as possible, while maintaining the same prior austenitic grains size. The VN particles will indeed dissolve almost entirely in 1 hour at 1150℃ [20]; however the Nb(C,N) will not dissolve at all, according to Klueh and Harris rules [21].

The steel is then air-cooled to the warm-rolling temperature. The choice of its temperature is presented in §3. Warm-rolling in austenitic phase (deformation: 25%, duration about 10 mn) is expected to introduce a high density of dislocations. Therefore the martensitic transformation should be modified: the martensitic laths and subgrains should be finer and the higher density of dislocations should allow a more pronounced precipitation of particles.

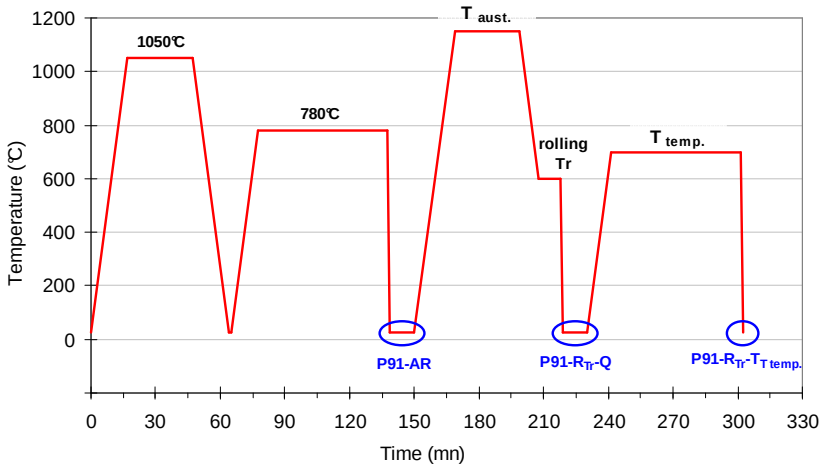

Figure 3: Thermal cycles of the first treatment and the thermomechanical treatment under study. The different states of the material are denoted : AR= as-received, R= rolled, Q= quenched, T= tempered.

Warm-rolling is followed by water quenching. The steel is finally tempered in order to soften the martensite and let precipitate the $M_{23}C_6$ and MX particles.

Thin foils and carbon replicas were examined on a JEOL-2010FEG transmission electron microscope, for both quenched and tempered warm-rolled materials.
Extractive carbon replicas were prepared by the evaporation of carbon onto a polished and etched steel sample, followed by dissolution of the matrix in a solution of 1% tetramethylammonium chloride and 10% acetylacetone in methanol, at a voltage of 1.2V at 20℃.
Thermo-electrical power measurements were used on the quenched warm-rolled material.
Vickers microhardness values were measured under 500g.
Creep tests are being performed on the tempered warm-rolled materials at 650℃ under 120 MPa.
Tensile tests have been performed at a strain rate of 7.10^{-4} s^{-1} at room temperature, 550℃, and 650℃.

RESULTS AND DISCUSSION

Choice of the thermomechanical treatment temperatures

The software MatCalc has been used to test several possible temperatures and durations for each step of the treatment (warm-rolling and tempering). The results given by the numerous simulations have shown that 600℃ is the most relev ant temperature for rolling.
This choice is also constrained by the facts that the rolling temperature must stay above the martensitic start temperature, avoid the ferrite stability domain, and be low enough to avoid dislocations annihilation by dynamic re-crystallization, or recovery.

Tempering tests of one hour were performed every 25℃ between 650℃ and 800℃ on the P91-R600-Q. Thermo-electrical power (TEP) of each tempered sample was measured. The TEP of the warm-rolled&quenched P91-R600-Q is 9.20 $\mu V.K^{-1}$. The annealing treatments induce an increase of the values for the tempered samples, from 10.54 to 10.60 $\mu V.K^{-1}$ (see Figure 4).

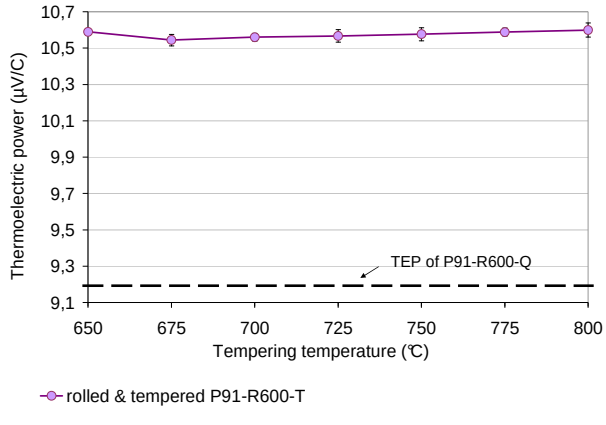

Figure 4 : Thermo-electrical powers versus the temperature of annealing treatments (1h) on the P91-R600-Q (rolled at 600℃ and quenched). Comparison with as-received material.

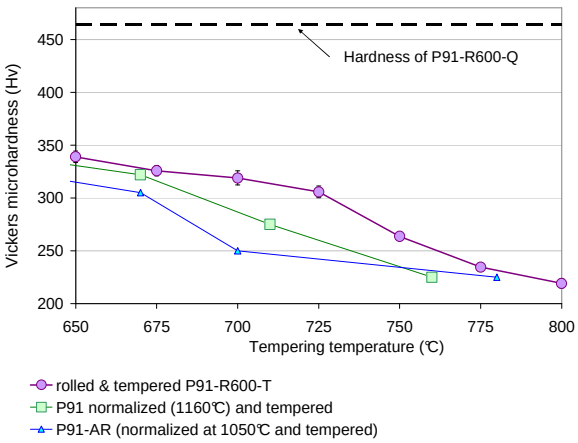

Figure 5 : Vickers hardness (500g) versus the temperature of annealing treatments (1h) on the P91-R600-Q (rolled at 600℃ and quenched).

TEP values are mainly sensitive to solid solution elements (C and N), but also to dislocations density and to coherent precipitates (i.e. the MX). Thus, the $M_{23}C_6$ only have an effect due to the subsequent decrease of solid solution elements, while the MX have this same effect and also an effect due to their own presence. However in the P91 the weight fraction of MX is weak and will not have a very significant effect on the measure.
The increase of the TEP, from 9.20 to 10.54 $\mu V.K^{-1}$ is due to the precipitation of carbides and nitrides and to the decrease of the dislocation density during tempering. A slight increase with the temperature occurs between 650℃ and 800℃ , it might be due to the end of the precipitation of the MX (according to MatCalc: 0.421 wt% after 1 hour at 650℃, 0.427 wt% after 1 hour at 700℃) and to further decrease of the dislocation density.

Microhardness values decrease with temperature, slightly between 650 and 725℃ and more steeply between 725 and 800℃ (Figure 5). The hardening is very pronounced compared to the P91-AR [22] (i.e. normalized at 1050℃ and tempered 1 hour at different temperatures). Moreover, the reason of this hardening can not be due to the difference between our austenitization temperature (1150℃) and that of the P91-AR (1050℃), since even the P91 normalized at 1160℃ and tempered [22] is softer than the thermomechanically treated P91. Therefore this hardening effect is due to the warm-rolling.

MatCalc simulations results showed that tempering 1 hour at 700℃ is sufficient to let precipitate the whole weight fractions of MX and $M_{23}C_6$, and 1 hour at 650℃ lets precipitate all the $M_{23}C_6$ and almost all the MX. In order to have a good compromise between the mechanical strength and the characteristics of the precipitate population, both temperatures of 650℃ and 700℃ have been selected for the annealing treatment.

Microstructure of the rolled&quenched P91-R600-Q and the rolled&tempered P91-R600-T650 and P91-R600-T700

Optical microscopy observations confirmed that the P91-R600-Q material is fully martensitic. Microhardness measurements showed that this rolled&quenched P91-R600-Q is about 60Hv harder than the quenched reference P91 [22] (whatever the P91 was normalized at 1050 or 1160℃); this effect is due to the warm-rolling.

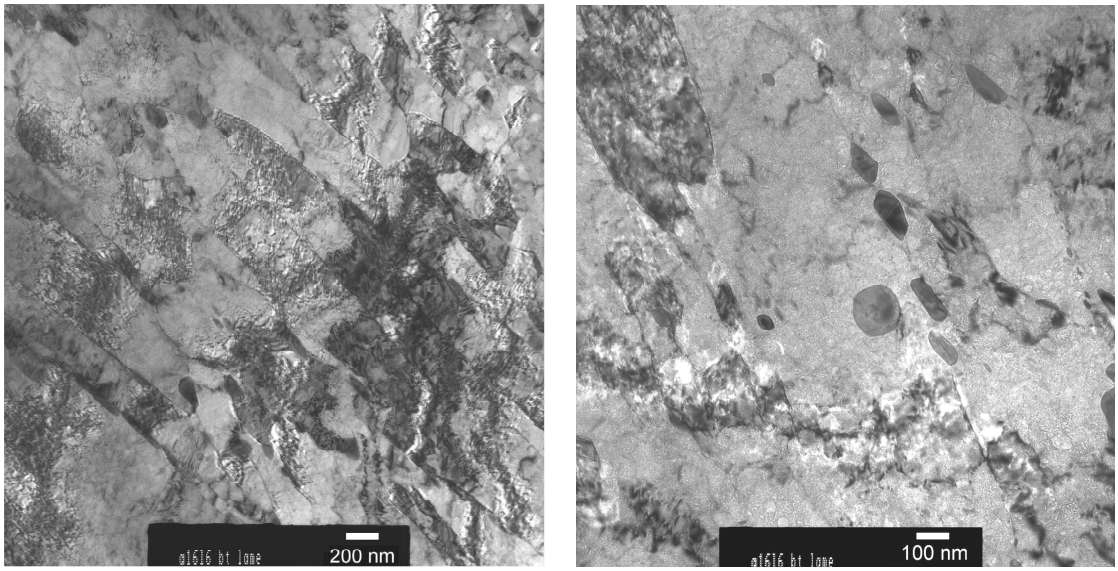

Figure 6: Bright field TEM observations of the P91-R600-Q showing:
a) thin martensite laths and a high dislocation density, and b) some precipitates.

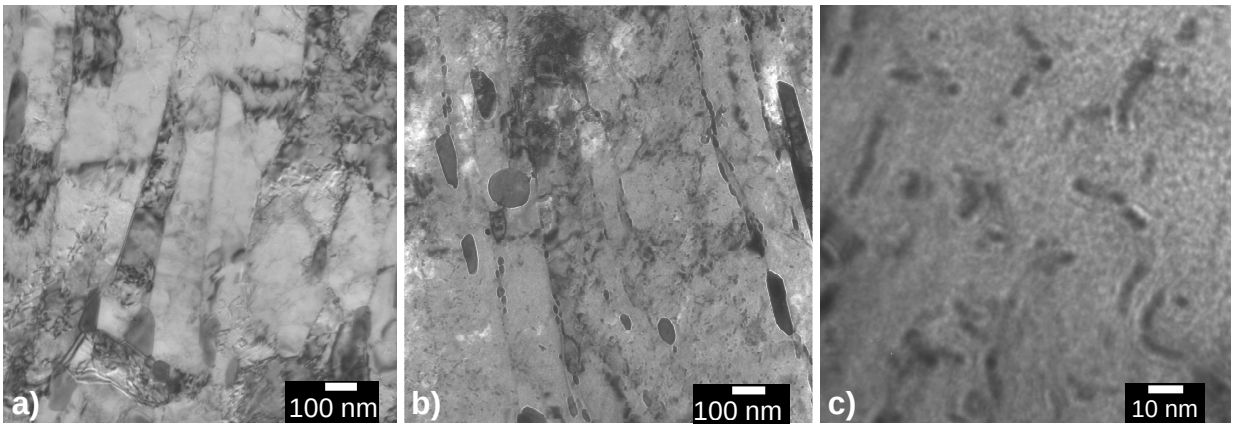

Figure 7 : Bright field TEM micrographs on thin foils of : a) P91-R600-T700 laths, b) $M_{23}C_6$ precipitates, c) small precipitates in the subgrains.

The laths width of both rolled&tempered P91 (Figure 7 a) is smaller than that of the P91-AR (i.e. 100 to 320 nm with a mean width of 180 nm, while mean laths width of P91-AR is 372 nm [18]).
TEM micrographs on thin foils show three kinds of precipitates. Large $M_{23}C_6$ (200nm) did precipitate on triple boundaries and laths boundaries (Figure 7 b); some are even a few hundreds nanometers long.
Inside and along the laths small needle-shaped precipitates (5-20nm) have formed (Figure 7 c), which are smaller than the MX found in P91-AR.
Intermediate size precipitates have also formed on the laths boundaries (around 100nm), these precipitates are $M_{23}C_6$ with a size close to the $M_{23}C_6$ usually found in reference P91.

Mechanical properties of the warm-rolled&tempered P91 compared to the P91-AR

Tensile tests have been performed on both TMT materials at 20℃, 550℃ and 650℃. Figure 8 shows that the TMT of P91 leads to a significant increase of the yield stress (the gain is, respectively for P91-R600-T650 and P91-R600-T700, of 430 and 360 MPa at 20℃; 300 and 200 MPa at 550℃). The treated materials are also m ore ductile than the P91-AR.
At 20 and 550℃, the behaviour of the P91-R600-T650 is better than that of P91-R600-T700 whereas this is the contrary at 650℃. These effect s can be correlated to the fact that the testing temperature, 650℃, is also the annealing t emperature of the P91-R600-T650 steel. Therefore, at 20℃ and 550℃ the finer population o f precipitates of the P91-R600-T650 (compared to the P91-R600-T700) gives a better mechanical strength, while some microstructural evolutions still take place in P91-R600-T650 during the tensile tests at 650℃.

Creep tests (120MPa, 650℃) are currently running. The lifetimes of TM treated materials are already 8 times longer than that of reference P91-AR and, since the deformation values are still low (<1%), the creep lifetimes are expected to be much higher than that of P92-AR (Figure 9).

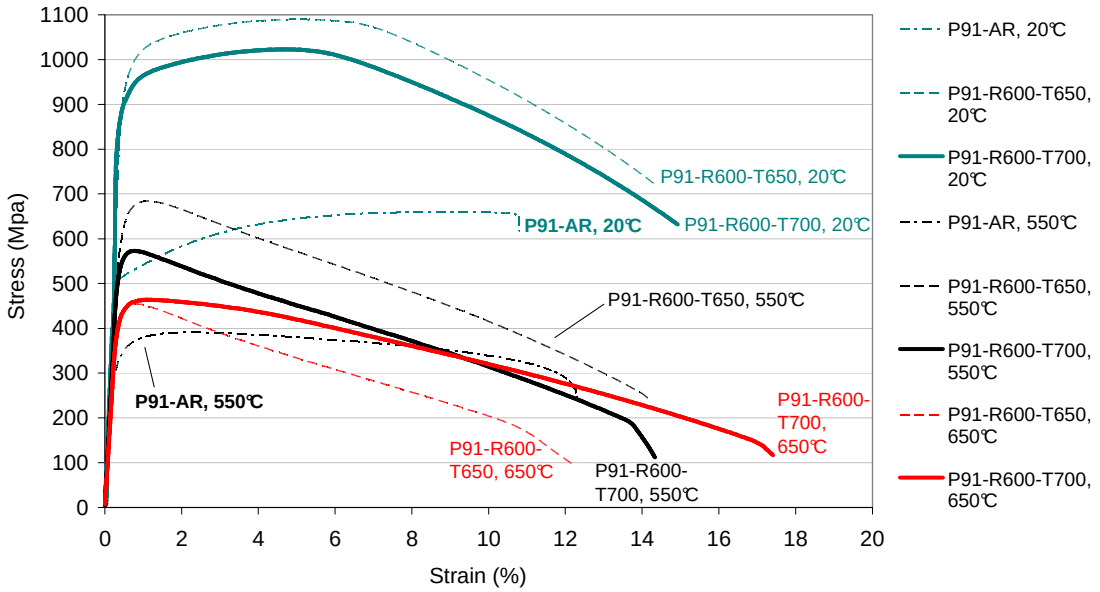

Figure 8: Tensile tests results of P91-R600-T650 and of P91-R600-T700 compared to P91-AR.

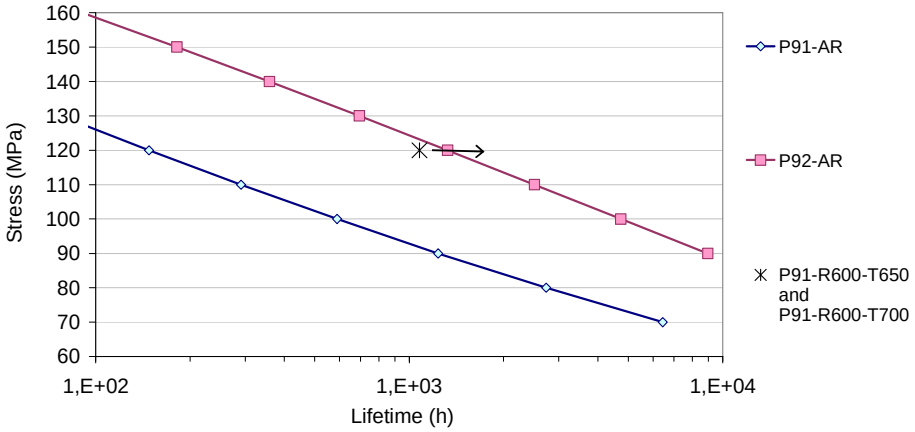

Figure 9: Creep lifetimes vs applied stress at 650°C of P91-R600-T650 and of P91-R600-T700 compared to P91-AR [23] and P92-AR [23].

CONCLUSIONS

Thermomechanical treatments have been applied to the commercial P91 steel. The temperatures of warm-rolling and tempering have been chosen thanks to MatCalc simulations.

The microstructures of the materials have been examined by optical and electronic microscopy after each step of the treatment. The warm-rolling (at 600℃, 25% deformation) induces a hardness increase of 60 Hv compared to the quenched reference P91. The final warm-rolled tempered P91 exhibit a martensitic microstructure with finer laths dotted with smaller precipitates than the as-received P91.

Both warm-rolled tempered P91 samples present a higher microhardness than the as-received P91: the hardness gain is 23 Hv for a tempering at 650℃ and 70 Hv at 700℃. The tensile tests show an important gain in yield strength and in ductility. The ongoing creep tests show a gain of a factor larger than 8 on the creep lifetime at 650℃.

Fatigue tests are currently being performed in order to check whether these thermomechanical treatments also lead to a reduced cyclic softening effect.

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