**A Roadmap for Tailoring the Strength and Ductility of Ferritic/Martensitic T91 Steel via
Thermo-mechanical Treatment**

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Abstract:

Ferritic/martensitic (F/M) steels with high strength and excellent ductility are important candidate materials for the life extension of the current nuclear reactors and the design of next generation nuclear reactors. Recent studies show that equal channel angular extrusion (ECAE) was able to improve mechanical strength of ferritic T91 steels moderately. Here, we examine several strategies to further enhance the mechanical strength of T91 while maintaining its ductility. Certain thermo-mechanical treatment (TMT) processes enabled by combinations of ECAE, water quench, and tempering may lead to “ductile martensite” with exceptionally high strength in T91 steel. The evolution of microstructures and mechanical properties of T91 steel were investigated in detail, and transition carbides were identified in water quenched T91 steel. This study provides guidelines for tailoring the microstructure and mechanical properties of T91 steel via ECAE enabled TMT for an improved combination of strength and ductility.

Keywords: T91 steel (9Cr-1Mo steel or Grade 91); ECAE or ECAP; thermo-mechanical treatment (TMT); mechanical properties; microstructure;

1. Introduction

The design of next generation nuclear reactors requires the development of advanced materials that can maintain structural integrity in harsh radiation environments. Structural materials in advanced nuclear reactors need to sustain significant radiation dose, over 100 displacements-per-atom (dpa), cyclic variation of thermal stress, and be resistant to oxidation, corrosion, and radiation creep over 60 years[1]. Ferritic/martensitic (F/M) steels containing 9-12 wt.% Cr are considered as major candidates for advanced nuclear reactors because this family of F/M steels exhibits better resistance to swelling, and irradiation assisted stress corrosion cracking (IASCC), and has less transmutation issues compared to austenitic stainless steels [2-4]. T91 steel is a commercialized F/M steel, which is modified from T9 (9Cr-1Mo) steel by the addition of V, Nb, and N [5]. As a representative of second generation structural materials for the power industry, T91 steel has been used as structural materials for steam generators, pressure vessels, and piping systems [6].

The mechanical properties of these advanced steels are critical for practical applications. Several approaches have been used to enhance the strength of F/M steels [7-9], among which grain boundary induced strengthening is promising. Equal channel angular extrusion (ECAE) is a widely used severe plastic deformation (SPD) technique to refine the grain size of bulk metallic materials [10]. During ECAE, severe shear strain (up to 2-4 mm/mm) is often introduced into a bulk material by extrusion through a channel of constant cross section that contains an abrupt angle. Consequently, the average grain sizes of numerous metallic materials can be refined to several hundred nm [11, 12]. Recently, this technique has been applied to reactor steels and their model alloys, such as F/M T91 [13-15], austenitic Fe-Cr-Ni [16-18], and oxide-dispersion-strengthened (ODS) steels [19, 20]. When the average grain size of T91 steel is refined by over an order of magnitude down to 300 nm, its hardness is increased by 70% [13]. Simultaneously, the refined microstructure shows enhanced radiation tolerance [21-23].

The metallic materials processed by ECAE and similar SPD techniques commonly show high strength, but limited ductility[24]. Thermo-mechanical treatments (TMT) are frequently applied to pure metals or alloys to achieve a combination of high strength and ductility or

microstructural homogeneity. For instance, an ECAREd low carbon steel can regain its ductility while maintaining excellent strength by post-extrusion annealing [25]. By ECARE at high temperature, carbides in T91 steel, which were previously located at prior austenitic grain boundaries (PAGBs), were refined and redistributed throughout the matrix [14]. The tempered EUROFER 97 steel can be strengthened without significant loss of ductility by hot-ECARE [26]. Similar to hot forging and rolling, hot-ECARE (ECARE above the recrystallization temperature of grains) can also be applied to break dendrites in as-cast materials [27].

The evolution of microstructures and carbides in T91 steel during tempering has been studied before [28], and a microstructural scheme was proposed by Abe [29]. However, the transformation products in water quenched T91 steel are more complicated, which may include polygonal ferrite, bainitic ferrite and lath martensite etc as those materials reported previously [30, 31]. Among these derivatives, martensite is of great interest due to the complex microstructure and strengthening effect for industrial application[32, 33]. Lath martensites are commonly observed in low carbon steels, and usually exhibit morphologies of packets and blocks [32, 34]. After examination of their morphology and crystallography, Morito *et al* proposed a hierarchical microstructure for the configuration of these lath martensites [35, 36]. Although efforts were made to correlate between the morphology and crystallography [35-39], some of the austenite (γ)-transformed microstructures are still hard to interpret [37, 39].

In this study, we revisited the phase transformation products of T91 steel subjected to high temperature normalization as well as thermo-mechanical treatment (TMT), and show that dynamic products of the austenite-to-ferrite (γ to α) transformation are size dependent. The microstructures of various phases are characterized in detail and connected to the mechanical properties of T91 steel. Based on the insight of microstructure, a roadmap is developed to achieve various combinations of strength and ductility in T91 steel.

2. Experiments

The chemical composition (in wt.%) of T91 alloy used in this study is shown in Table 1. The as-received (AR) T91 steel was heat-treated by a standard normalization (1038°C for 0.5 h with air cooling) and tempering (760°C for 0.5 h and air cooling) procedure same as described in the literature [40]. Annealing of AR T91 at 800 °C for 1 h, followed by furnace cooling, results

in as-annealed (AA) T91. The AA T91 was fully tempered and contained the predominately ferrite phase. Billets with dimensions of $25.4 \times 25.4 \times (50.8 \sim 127)$ mm were cut from AR materials for further processing. The TMT processes adopted in this study as shown in Fig.1 via a flow chart include: (1) austenitizing at $800 \sim 1200^{\circ}\text{C}$ (with an interval of 100°C) for 1 h followed by quenching in ice water; (2) ECAE process of austenite at 1000°C followed by water quenching, followed by tempering the thus-deformed T91 steel for 1 h at $300 - 800^{\circ}\text{C}$; (3) tempering the water quenched specimens at 500°C for 10 h, followed by ECAE of the tempered specimens at 300°C . The TMT processed materials were then subjected to microstructure characterizations and mechanical testing.

The austenization experiments were performed in a box furnace with a maximum temperature capability of $1300 \pm 10^{\circ}\text{C}$. ECAE processing was carried out on an MTS-controlled hydraulic press with 225 ton (2.22×10^3 kN) force capacity. Prior to the ECAE of T91, billets were heated to 1000°C for 1h to achieve the complete austenite phase, extruded at a rate of 25.4 mm/s, and then quickly water quenched. Although the die was kept at 300°C , the fast extrusion rate was applied to maintain the temperature of the billets close to 1000°C , so that minimum phase transformation occurred during the extrusion. Post-processing heat treatments in a range of $300 \sim 800^{\circ}\text{C}$ were carried out in a quartz tube with the protection of ultra-high purity Ar gas flow, and then cooled by flowing Ar. The identifiers of samples with indication of their TMT history are summarized in Table 2.

Dogbone-shaped tensile specimens with gauge dimensions of $8 \times 3 \times 1$ mm were cut from the inner part of the water quenched or ECAE processed billets using the electro discharge machining (EDM) technique. Samples were electro-polished to remove the porous oxide layer left by EDM, prior to the tensile tests. The electrolyte solution was a 1:1 mixture of sulfuric acid and phosphoric acid. The electro polishing was performed at room temperature at a voltage $8 \sim 10$ V. Tensile tests were performed with an MTS machine at a cross head speed of 0.008 mm/s, equivalent to an initial strain rate of $1 \times 10^{-3} \text{s}^{-1}$. The hardness was measured by an LM 300AT micro hardness tester using a 2.9 N force for a loading time of 13 s by using a pyramidal shape diamond indenter. Scanning electron microscopy (SEM) was performed on an FEI Quanta 600 microscope operated at an acceleration voltage of 20 kV at a working distance of 10 mm. The optical microscopy (OM) and SEM specimens were cut from the tensile specimen away from the deformation zone. Samples were prepared following the standard mechanical polishing process,

and then etched in a 5g FeCl₃, 20ml HCl and 100 ml water solution [41]. Transmission electron microscopy (TEM) experiments were performed using an FEI Tecnai F20 microscope operated at 200 kV equipped with a high angle annular dark field (HAADF) detector and an Oxford instruments energy dispersive X-ray spectroscopy (EDX) detector. The TEM specimens were prepared by mechanical grinding of 3 mm disks down to tens of μm . The disks were then perforated in a twinjet polisher with 10 vol.% perchloric acid plus 90 vol.% methyl alcohol solution with voltage 15 ~ 30 V at -40 °C.

3. Results

3.1 Microstructure and mechanical properties of as-quenched T91 steel

Fig. 2 shows the schematic of phase constitution and morphological feature of the transformation products of water quenched T91 steel heat treated at 800~1200°C for 1h, which is detailed in the following section. The packet is defined as a group of martensite with the same habit plane that can be subdivided into blocks. Blocks are typically identified as a group of martensite with similar orientation or a combination of two variants with different orientations. The definition of various phases of transformation products are based mainly on their morphology or precipitates therein.

OM (Fig.3) and SEM (Fig.4) images were collected simultaneously to examine the microstructure of WQ T91 steel. The interpretation of these images is based on the different morphologies of these phases subjected to the etchant. For instance, ferrite phases typically have a clean blocky appearance in OM micrographs labeled as α_p . The “blocky” ferrite phase is easily etched away and thus appears “deeper” in the SEM images. Examples for this type of ferrite include α_A and α_B . The fine martensites (martensite block) typically have lath morphologies in both OM and SEM micrographs in nearly all the WQ specimens. In what follows, we will discuss the evolution of microstructures of T91 heat treated at different temperatures (from low to high) followed by water quenching, examined by OM (Fig.3), SEM (Fig.4) and TEM (Fig.5) techniques.

The AA T91 steel shown in Fig.3a has typical tempered martensitic lath structure (α'_T) with minor second phases, including retained austenite or martensite (M/A constituent), and/or transformed carbides. The fully tempered T91 is mainly composed of ferrite phase with packet and block boundaries. Prior austenite grain boundaries (PAGBs) and packet boundaries are often

1 decorated by “white” carbide particles (as shown in Fig.4a). Tempered martensite laths in the
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6 AA specimen dominate the microstructures inside a packet as shown in the TEM micrograph in
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8 Fig.5a.

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10 Water quenching of T91 from 800°C leads to fine microstructures as shown in Fig.3b.
11 SEM studies (in Fig.4b) show that this fine structure is a mixture of grain boundary ferrite (α_A),
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13 martensite (α'_M) and ferrite (α_P). Some martensitic blocks within prior austenite grains were
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15 etched as shown in Fig.4b. A prior austenite grain in the 800WQ specimen is surrounded by
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17 adjacent α_A containing undissolved carbides (Fig.5b). The ferrite phase (α_P) and fine martensites
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19 are occasionally separated by a packet boundary highlighted by a red dotted line in Fig.5c.

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21 The microstructures of the water quenched 900 and 1000°C specimens (900WQ and
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23 1000WQ) have primarily martensite α'_M and polygonal ferrite (α_P) shown typically as light clean
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25 grains in OM micrographs in Fig.3c-d. α_A is absent in the 900WQ specimens (Fig.4c). A packet
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27 containing non-etched blocks is highlighted by a red dotted line in Fig.4c. PAGBs are also
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29 observed in the 900WQ specimen (as marked in Fig.4c). The TEM image shows a triple junction
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31 of prior austenite grains in the 900WQ T91 in Fig.5d. Retained γ is identified as the thin layers
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33 between martensite laths with dark contrast in Fig.5d. The α_P ferrite with martensite precipitates
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35 is also observed in the 900WQ specimen as shown in Fig.5e.

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37 Significant coarsening of austenite grains occurs after heat treatment at 1100°C or higher
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39 prior to water quenching as shown in the 1100WQ and 1200WQ specimens in Fig.3e-f. Blocks
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41 are clearly observed in these two specimens. Except for packets around the grain boundaries, no
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43 packet boundaries are identified due to the randomly oriented blocks. Bainitic ferrite (α_B) within
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45 the prior austenite grains in the 1100WQ and 1200WQ specimens was preferentially etched
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47 away as shown in Fig.4d. Auto-tempered martensite (α'_{AT}) is frequently observed as shown in
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49 Fig.5f in the 1200WQ specimen. Carbides are trapped within the martensite laths.

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51 The heat treatment temperature prior to water quenching can change the austenite grain
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53 size and consequent microstructure in water quenched T91. Fig.6a shows the overall martensite
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55 microstructure within a prior austenite grain in the 1000WQ specimen before the austenite grains
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57 coarsen. Single variant blocks are identified within a packet. Fig.6b shows the 1100WQ
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59 specimen, which has the transformed structure after coarsening of the austenite. The blocks are
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61 thicker and longer than those in the 1000WQ specimen. Also no packets can be identified due to
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63 the random arrangement of the blocks.
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Fig.7 shows the average grain size of the prior austenite grains in the WQ T91 steel according to the SEM images. The grain sizes are similar in the AA, 900WQ and 1000WQ specimens. For specimens heated to 1100°C or greater (1100WQ and 1200WQ), the average grain size increased by an order of magnitude from ~ 13 to 150 μm.

Carbides in auto-tempered martensite and bainitic ferrite were studied in detail in Fig.8 and Fig.9. The detection of carbides requires the tilting of TEM specimens to remove contrast from forest dislocations. Fig.8 shows typical microstructures within an auto-tempered martensite (1200WQ). Black needle-shape precipitates are identified in the specimen tilted to the near two beam (TB) condition in Fig.8a. The contrast was reversed in Fig.8b taken at weak beam dark field condition. High resolution TEM (HRTEM) images combined with its fast Fourier transform (FFT) confirm that the precipitates are primarily η-carbide (Fig.8c) and cementite (Fig.8d). The orientation relationship between η-carbide and the matrix follows η-C[010]// α'[011], η-C(001)//α'(200), which is compatible with the orientation relationship proposed by Hirotsu and Nagakura [42]. The growth direction of η-carbide is close to η-C[001]// α'[200]. The satellite diffraction spots in the FFT in Fig.8c stem from the modulation in η-carbide. The cementite has an orientation relationship θ[100] //α'[011], and θ(002)//α'(2̄1 1) with the matrix, which corresponds well to a classic Bagaryatskii relationship [43].

Martensite and carbides are observed within the bainitic ferrite matrix in Fig.9a in the 1200WQ specimen. Precipitates in bainitic ferrite align along nearly the same direction, in comparison to randomly oriented precipitates in auto-tempered martensite in the 1200WQ material. The HRTEM micrograph in Fig.9b reveals a substantial amount of strain contrast around the needle-shape precipitates, which were identified to be ε-carbide as evidenced by FFT analysis. The classic Jack orientation relationship between carbide and ferrite prevails [44], that is α[1̄1 1]//ε-C [1̄2 10], α(011)//ε-C (0002̄). The growth direction of ε-carbide is along the ε-C[101̄0], which is parallel to α[21̄1], consistent with early studies by Murphy et al[45].

Fig.10 provides a comparison of engineering and true stress-strain curves of various WQ T91 steel. In general, the WQ T91 steels show a combination of high strength and ductility. The yield strength (σ_{0.2}) of 800WQ material is 970MPa, ~150MPa lower than those heat treated above 900°C. The uniform elongation is ~ 7% for all of the WQ T91 steel, which is insensitive to austenitizing temperature prior to water quenching. Table 4 summarizes the effect of

austenitizing temperature on phase constituents (before and after water quenching), and mechanical properties.

3.2 ECAE enabled TMT of T91 steel

SEM micrographs of the TMT processed T91 steel (heat treated to 1000°C prior to quenching) are shown in Fig.11. Similar to the 900WQ T91 steel, the 1000WQ specimens shows a predominant martensite phase. Packets containing blocks are commonly observed near the PAGBs. Air cooling of T91 after normalization at 1000°C (1000AC) can also result in a complex transformed structure, which includes α'_M , α'_{AT} , and α_P . More block boundaries are observed presumably because of the auto-tempering process. Further tempering of 1000WQ T91 at 500°C promotes the formation of carbides at the PAGBs, as shown in Fig.11c. Block boundaries can also be observed. The extrusion of tempered T91 at 300°C (1000WQ/500C 10h/1A300) leads to curved (distorted) PAGBs (Fig.11d). The prominent shearing of prior austenite grains is frequently observed in the ausformed T91 steel (via ECAE at 1000°C), as shown in Fig.11e.

Fig.12 shows representative TEM micrographs of the TMT processed T91 steel. Compared to abundant martensite laths and blocks in the 1000WQ specimen (Fig.12a), the 1000WQ/500 10h specimen has a typical tempered martensite structure with large patches of ferrite (Fig.12b). Further ECAE processing of this tempered specimen (1000WQ/500 10h/1A300) leads to deformed martensite with a high density of dislocations (Fig.12c). Fragmented martensite laths containing numerous small grains are also observed as shown in Fig.12c. Ausforming of T91 at 1000°C (1000ECAE) produces a textured martensite structure with much shorter laths (Fig.12d) than those in the 1000WQ specimen.

The thermal stability of T91 produced via different routes was probed by measuring the evolution of the Vickers hardness (at room temperature) after annealing at different temperatures up to 800°C, as shown in Fig.13. The hardness of the AA material remains the same throughout the annealing experiment. In comparison, the hardness of the 2B300 specimen (two pass extrusion following route B at 300°C) is nearly 60% greater up to 500°C and softened afterwards. The hardness of the 1000ECAE material is ~ 2.3 times that of the AA T91 material up to 500°C, followed by rapid softening at higher annealing temperatures.

Fig.14 illustrates the tempering response of 1000ECAE T91 at various temperatures. After tempering at 600°C, tiny carbides precipitate at martensitic lath boundaries as shown in

Fig.14a. Significant coarsening of carbides and the prominent loss of lath structures are evident for T91 steel tempered at 700°C as shown in Fig.14b. The remaining sparsely distributed tempered martensitic laths are coarsened dramatically with “blunted tips” (Fig.14c). The microstructure is fully recrystallized with an average grain size of ~ 660 nm. The martensite structure is rarely preserved after normalization at 800°C, as shown in Fig.14d.

The engineering and true stress-strain curves of TMT T91 steels are displayed in Fig.15. The yield strength of AA material is increased by a factor of ~ 3, from ~ 482 to 1600 MPa after selected TMT processing. Direct quenched T91 steel exhibits a good combination of strength and ductility. TMT of T91 steels further enhances their mechanical strength with moderate loss of tensile ductility as shown in Fig.15b.

4. Discussion

4.1 Microstructure evolution of TMT processed T91 steel

4.1.1 Microstructure of the water quenched T91 steels

In the current study, δ -ferrite was absent in the selected austenization range of 800~1200°C in T91 steel, consistent with earlier studies that show δ -ferrite formed during normalization above 1250°C for 5 min or longer [46, 47]. δ -ferrite is detrimental to the creep strength of T91 [48]. Compared to T9 steel wherein more than 35% δ -ferrite is present at 1200°C or higher temperature [49], the modified T91 steel (with the addition of minor elements, like Nb and V) shows a wider γ -phase region to avoid δ -ferrite. Although there is no δ -ferrite, a full martensite microstructure is not obtained in any of the current water quench specimens.

Martensitic transformation of the γ phase was incomplete in water quenched specimens (preheated to 800,900 and 1000°C), where a polygonal ferrite is observed within the prior austenite grains. The suppression of martensitic transformation could be related to the small austenite grain size [50, 51]. This size dependent martensitic transformation is related to grain size induced strengthening of the austenite matrix [51]. Nucleation of martensite undergoes plastic accommodation due to a geometric strain in the martensite [52]. Fine austenite grains can strengthen the matrix and suppress the nucleation and growth of martensite, thus significantly lower the martensitic transformation temperature. A similar effect will be addressed in ausformed T91 steels described below. In the present study, martensite precipitates are frequently observed in the polygonal ferrites in specimens heated to 1000°C, implying an

insufficient driving force to complete the martensitic phase transformation. The longer martensite lath formed in the larger prior austenite grains in T91 heated above 1100°C follows the same principle. The large austenite grain size produces less plastic constraint on transformed martensite, thus the formation of larger martensite is encouraged.

Bainitic ferrite in the T91 steel quenched from 1100 and 1200°C is a phase commonly observed in some low carbon steels [30, 53, 54], but rarely reported in T91 steel. The larger grain size not only increases the martensitic transformation temperature but also favors the bainitic transformation. The direct impact of the increased martensitic transformation temperature is an auto-tempering effect of martensite. The possibility of bainitic transformation is supported by an early study of time-temperature-transformation (TTT) diagram of low carbon steels [30] or rapid quenching of binary alloys [31], where a bainitic transformation often occurs prior to martensitic transformation if the cooling rate is reduced. Bainitic ferrite is frequently observed within the prior austenite grains rather than at grain boundaries implying a higher local carbon concentration in the vicinity of grain boundaries, supported by the fact that some of the martensite and packets are formed around the boundaries as shown in Figs.3e,6a and 9a. The grain boundaries should have both mechanical (strengthening) and chemical (carbon sinks) effects on the martensitic transformation.

The morphology of transformation products of the water quenched T91 is another subject inviting discussion. As shown schematically in Fig.2, the γ -transformed microstructure is similar among 800WQ, 900WQ and 1000WQ specimens and typically contains a grain boundary packet of the martensite (a packet of martensite close to PAGBs) together with large polygonal or plate ferrite. Within the grain boundary packet, there are usually blocks similar to the previous observation by Morito *et al.* in low carbon steel [35]. The abundant large single variant blocks are separated from other blocks composed of smaller martensite regions. The martensite exists as a precipitate in polygonal ferrite or in between the large ferrite regions. The γ -transformed microstructure is different in 1100WQ and 1200WQ T91. Grain boundary packets are observed frequently, while within the grains, no clear packet boundaries are observed. The blocks within a packet distribute randomly similar to the previous observation in certain high carbon Fe-C alloys [35].

4.1.2 Microstructure after TMT processing

The ECAE enabled TMT of T91 steel (1000ECAE) is an ausforming process. Ausforming can significantly influence the variant selection of the martensite [55, 56]. This phenomena may be qualitatively described by [57]:

$$U = \tau\gamma_0 + \sigma\varepsilon_0 \quad (1),$$

where U is interaction energy, τ is the shear stress resolved on the habit plane of a variant, σ is the stress resolved normal to the habit plane, and γ_0 and ε_0 are the shear and normal component of the transformation strain of the variant, respectively. A greater interaction energy can enhance the formation of that variant. The normal stress σ can facilitate or depress the variant while shear stress often stimulates the formation of a variant. As shear deformation dominates during ECAE, the variants with habit planes close or parallel to the shear plane may form first. The martensite laths formed later are either thinner or shorter due to limited available free space and stress arising from the prior formed thicker martensite laths as shown in early studies [55, 56]. Detailed review of variant selection is given by Kundu recently [58]. Gong *et al.* suggested that a bainite transformation may be accelerated by ausforming [59]. As mentioned previously, this argument could also be applied to the size effect on martensitic transformation, that is, grain refinement (by ECAE) leads to stronger matrix and significantly lowers the martensitic transformation temperature.

After annealing of 1000WQ T91 steel at 500°C for 10 h, the material becomes a moderately tempered martensite because at this annealing temperature, the microstructure evolution is limited to the diffusion of carbon [28]. Thus, more carbides are observed at the block boundaries than in the WQ specimens. ECAE of this tempered martensite structure (1000WQ/500 10h/1A300) does not lead to refinement of martensite laths, but significantly increases the dislocation density. Fragmented martensite laths are observed as well. Small grains are occasionally observed within the martensitic lath with a growth direction perpendicular to the martensite lath.

The heat treatment of 1000ECAE T91 steel is similar to the tempering of martensite [60], which is often controlled by the diffusion of carbon atoms and precipitation of carbides. Carbon is the primary element that can significantly diffuse in T91 steel below 500°C [28]. After tempering at 600°C, the carbides precipitate along the lath boundaries. In the meantime, the residual austenite decomposes to form carbides. At 700°C, the carbides along the lath interphase spheroidize and coarsen significantly. Thinner martensites with the same habit plane and slight

misorientation, produced by water quenching, merge together to form the tempered martensite structure with a typical thickness of 500 nm. After tempering at 800°C for 1h, martensite decomposes followed by significant recrystallization, and thus leads to the formation of equiaxed ferrite with carbides.

4.2 Mechanical properties of TMT processed T91 steel

4.2.1 Strengthening mechanisms

We will use two sets of strengthening mechanisms (SM1 and SM2) to interpret strengthening in T91 steels.

Frist, for steels with primarily martensite and bainite, the yield strength σ_y can be estimated by (**strengthening mechanism one, SM1**) [61]:

$$\sigma_y = \sigma_{Fe} + \sigma_s + \sigma_p + K_L(\bar{L})^{-1} + K_D\rho_D^{1/2} \quad (2),$$

where σ_{Fe} is the strength of annealed pure Fe, $\sim 100\text{MPa}$ [62], σ_s is the solid solution strengthening, σ_p is the precipitation hardening, K_L is the coefficient due to lath size with a value of $115\text{MPa}\cdot\mu\text{m}$ [61], $\bar{L}$ is the average lath size (with units of μm) and is $\sim 0.2\mu\text{m}$ for martensite and $\sim 0.5\mu\text{m}$, K_D is the coefficient due to dislocation strengthening with a value of $7.34\times 10^{-6}\text{MPa}\cdot\text{m}$ [61], and ρ_D is the dislocation density.

The solid solution hardening (in unit of MPa) σ_s can be estimated by [61],

$$\sigma_s = \sum \sigma_{ss} + \sum \sigma_i = 1723\sqrt{[C]} + 5.8[Cr] + 18[Mo] + 105[Si] + 45[Mn] + 37[Ni] + 4.8[V] \quad (3),$$

where all the elements [Z] are in weight percent.

The precipitation hardening is estimated by using the Ashby-Orowan relationship [63],

$$\sigma_p = (0.538Gbf^{1/2} / X) \ln(X / 2b) \quad (4),$$

where G is the shear modulus of Fe, $\sim 82\text{ GPa}$, b is the Burgers vector, $2.49\times 10^{-10}\text{m}$ for the present alloy, f is the volume fraction of particles, and X is the diameter of the particles.

Next, the combinational strengthening from various mechanisms in steel can also be estimated by another equation given by Krauss (**strengthening mechanism two, SM2**)[33],

$$\sigma_y = \sigma_{Fe} + \sigma_{ss} + k_D D^{-1/2} + k_d d^{-1/2} + \alpha G b \rho^{1/2} \quad (5),$$

where D is the packet size, d is the lath width, k_D and k_d are Hall-Petch coefficients for packets and laths, α is 0.4 for BCC metal [62], ρ is the dislocation density in martensitic lath, and the other terms have the same meaning as defined previously. The Hall-Petch strengthening

coefficient is $\sim 100\text{MPa}\cdot\mu\text{m}^{1/2}$ for prior austenite grains in low alloy carbon steels [64], because the packet size shows a linear dependence on the prior austenite grain size with a coefficient of $\sim 1/3$ [65]. A k_D value around $170\text{MPa}\cdot\mu\text{m}^{1/2}$ is achieved. The k_d value is not well documented. However, the importance of block size is realized by Morito et al [65]. Here we use the block size d instead of lath width, which is around $\sim 2.5\mu\text{m}$. Thus the previously reported k_d value of $\sim 700\text{MPa}\cdot\mu\text{m}^{1/2}$ is used for block boundary in low carbon steels [65].

Morito et al [66] also studied the influence of carbon concentration on the dislocation density in martensite lath. A linear relationship is extracted by Hutchinson *et al.* as follows[67],

$$\rho = \rho_0 + K(\%C) = (0.7 + 3.5\text{wt.\%}C) \times 10^{15} \quad (6),$$

where ρ_0 is the dislocation density in martensitic pure iron, K is the increase in dislocation density caused by carbon (in wt.%). The values of K and ρ_0 in equation (6) can be obtained from the same reference.

The solid solution strengthening induced by C is well addressed in martensitic steels [33, 68]. However, the strengthening induced by N is limited to austenite steels [69-71]. In martensite, the role of N in strengthening is not well understood. Here, we assume that the efficiency of N on strengthening of martensite is nearly equivalent to C.

As summarized in Table 5, the 3 major strengthening terms in SM1 are σ_i (610MPa), σ_{H-P} (560MPa), and $\sigma_{\text{disl.}}$ (250MPa). In comparison, the SM2 method has two major strengthening contributors, σ_{H-P} (440MPa) and $\sigma_{\text{disl.}}$ (250MPa). Both mechanisms have similar values of σ_{Fe} (100MPa) and σ_{ss} (130MPa). In SM1, the strengthening arising from C and N appears substantial, because they can both distort the lattice and block dislocations through Cottrell atmospheres [72].

Comparisons with experimental results show that the SM1 approach overestimates the yield strength by $\sim 440\text{MPa}$. The influence of C or martensite lath size on strengthening may have been overestimated. For example, in the term that accounts for carbon induced strengthening in eq. (3), the coefficient is calculated by considering the thickness of the martensitic lath, $\sim 0.25\mu\text{m}$ [33]. While in the eq. (2), the size of lath boundaries is considered again in the size effect term.

Meanwhile, the SM2 method underestimates the yield strength by $\sim 280\text{MPa}$. This could be due to the lack of several coefficients, such as k_D or k_d for the T91 steel. The use of the coefficient for low carbon steel may not be well suited for the current study. Also the influence of interstitials on strengthening was not considered and may lead to underestimate of the yield

strength. Additional discrepancy may arise from the fact that a full martensite structure is not achieved. For instance, a small amount of bainitic ferrite is observed in the 1100WQ specimen. The linear superposition rule adopted in both methods may also require revisions as the strengthening contributions from various terms may be convoluted to some extent.

A dislocation based method derived from strain hardening could be another approach to interpret strengthening [73]. In this case, the dislocation mean free path is a key link between the dislocation-barrier interaction and strain hardening [74]. The different strengthening terms in eqs.(2) and (5) arise from various barriers for the movement of dislocations and thus can be affected by the mean free path of dislocations. Although different attempts have been made[75, 76], the determination of dislocation mean free path for various barriers remains an open question.

Also it is worth mentioning that the softening in the 1000ECAE and 2B300 specimens after annealing, though occurring both at 600°C (as shown in Fig.13), may have different underlying mechanisms. As the 1000ECAE specimens have primarily martensite, its softening after tempering is due to the decomposition of martensite. In contrast, the 2B300 specimen has mostly ferrite, and the softening after annealing is primarily due to grain coarsening.

4.2.2 The influence of TMT on work hardening capability and ductility of T91 steels

The ductility is characterized through a key parameter, known as uniform elongation. It is determined by the Considère criterion [77],

$$\left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{\dot{\varepsilon}} = \sigma \quad (7),$$

where σ and ε are true stress and true strain, $\dot{\varepsilon}$ is strain rate, and $\partial \sigma / \partial \varepsilon$ is the work hardening rate. When a material is subjected to a strain at the onset of necking, its work hardening cannot sustain the geometrical weakening of the deformed region[78, 79]. The strain achieved up to necking is considered as true uniform elongation.

Fig.16 compares the true stress-strain and work hardening rate of several representative cases of the TMT processed T91. The AA specimen has a high work hardening rate and large uniform elongation as the large grains can accommodate a rapid increase of the density of mobile dislocations during deformation. In contrast, the 1000WQ specimen has less work hardening capability and uniform strain as its smaller martensite laths already contain a high density of dislocations.

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4 Finally we examine the yield strength-uniform elongation paradox in T91 steels. A
5 majority of metallic materials, such as those processed by cold working, follow the general
6 syndrome: the strengthening of a material accompanied by a reduction in ductility[24].
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10 As shown in Fig.17, the TMT processes enable us to tailor the mechanical properties of
11 T91 steel over a broad range. Three distinct groups are highlighted on this plot. First, the light
12 blue band outlines T91 steel with primarily ferrite phases. These steels were processed via ECAE
13 at low-to-intermediate temperatures (room temperature to 700°C). The higher strength of ferritic
14 T91 steels originates mostly from grain refinement. The highest strength achieved in ferritic T91
15 steel in this study is 1000MPa with a mere 2% uniform elongation. In the second category
16 (dominated by martensite shown as red band in Fig.17), TMTs via austenitizing at 900°C or
17 greater (followed by water quenching) and ECAE at 1000°C induce primarily martensite. The
18 yield strength of 1000WQ/500 10h/1A300 T91 exceeds 1600 MPa with, however, only ~1.5%
19 uniform elongation. Heat-treatment of the ECAE specimens leads to an improvement of uniform
20 elongation, to ~4%, with a yield strength of 1400 MPa. The third category includes T91 steels
21 processed by water quenching at 800°C or water quenching at 900~1200°C followed by a 600°C
22 tempering procedure as shown in the purple band. T91 processed by this route is composed of
23 both ferrite and martensite. The formation of ferrite reduces the yield strength by ~150MPa.
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27 It is noteworthy that when the austenitizing process is performed above 900°C, water
28 quenching leads to the production of F/M T91 steel composed primarily of martensite. The as-
29 quenched martensite results in a high yield strength, ~1200MPa, as well as a reasonable uniform
30 elongation, ~6-8% as shown by the yellow triangles. The retention of good ductility may be
31 related to the low C concentration in T91 steel as well as auto-tempering of martensite during the
32 cooling process. The accomplishment of high strength with good ductility via such a simple
33 water quenching process is a very encouraging observation.
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37 While the strength and ductility of martensitic T91 (red band) and ferritic T91 (light blue
38 band) may still follow the paradoxical relationship, ductile martensite can bring the coordinates
39 of the strength and ductility to a greater level beyond the ferrites. The F/M T91 (in the purple
40 band) bridges the mechanical behavior between the two distinct groups (red and light blue band).
41 This TMT roadmap thus permits the tailoring of T91 steels with various combinations of strength
42 and ductility for different industrial and nuclear applications.
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5. Summary

The microstructure and mechanical properties of T91 steels subjected to various TMT processes were systematically investigated. The major findings are summarized as follows:

- (1) Ausforming or austenitizing of T91 steels at 900°C or greater produces primarily martensite. These transformed martensites coupled with auto-tempering leads to materials with good ductility. Furthermore, bainitic ferrite is formed during the transformation.
- (2) Transition carbides (ϵ - and η -carbides) are, probably for the first time, observed in water quenched T91 steel. Both orientation relationships of these carbides follow the classical orientation relationships.
- (3) The strengthening mechanisms of thus processed T91 mainly involve the Hall-Petch type of strengthening, dislocation strengthening, and solid solution strengthening.
- (4) A roadmap for tailoring the strength and ductility of T91 steel via TMT has been developed.
- (5) Ductile martensite possesses much greater strength than fine grained ferrites.

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Figures

Fig.1. Flow chart of thermo-mechanical processing of T91 steel with microstructure features and mechanical performance after each treatment. Notation: C - major phase constitutions, $\sigma_{0.2}$ - yield strength, and ϵ - uniform elongation. Note among multiple phases, the major phases are highlighted in bold fonts.

Fig.2 Schematic illustrations showing morphology of transformation products of T91 steel heating up to different austenization temperatures (800~1200°C) for 1 h. The drawing of tempered martensite structure follows the style of F. Abe [29]. For austenization at 800°C (a→b→e), the T91 is at the two phase zone, so significant amount of the grain boundary ferrite is formed. Packets are formed as group of martensite on the same habit plane. In a packet, blocks are typically identified as group of martensite with similar orientation or a combination of two

different orientations. After quenching, a full martensite structure is not achieved, where polygonal ferrite with undissolved carbides are frequently observed. By austenization at 900-1000°C ($\alpha \rightarrow \gamma \rightarrow \delta$), the T91 steels arrive at gamma phase zone, thus no grain boundary ferrite is observed. Carbide precipitates trapped in martensite lath are identified. By ausforming of T91 at 1000°C ($\alpha \rightarrow \gamma \rightarrow \delta \rightarrow \epsilon$), the T91 suffers from variant selection which is different from the unstrained scenario. Martensite with shorter laths is typical in 1000ECAA T91. By austenization at 1100-1200°C ($\alpha \rightarrow \gamma \rightarrow \delta$), the austenite grain coarsens significantly during heating (noted the scale bar is an order of magnitude larger). Except grain boundary packet, no more packet can be identified within the grains although the grain is much larger. Both auto-tempered martensite and bainitic ferrite are identified. ϵ -carbides align along the same direction in bainite, while η - or θ -carbides can precipitate from all the available habit planes in auto-tempered martensite.

Fig.3. Optical micrographs showing the microstructure of as-annealed (AA) and water quenched (WQ) T91 steel. (a) The AA material is predominantly ferrite with a dispersed equiaxed M/A constituent. Packets are identified as groups of martensite laths with the same habit plane and subdivided blocks. (b) Heat treatment at 800°C for 1h followed by WQ (800WQ) led to a mixture of α'_M and α_P , and GB ferrite (α_A). Heat treatment via (c) 900WQ and (d) 1000WQ resulted in a fully transformed microstructure. The polygonal ferrite (α_P) is identified as clean grains by arrows. (e) 1100WQ and (f) 1200WQ yielded primarily martensite α'_M and the minor bainite phase α_B . A prior austenite grain boundary (PAGB) is identified in the 1100WQ and 1200WQ specimens.

Fig.4. Representative SEM images of AA and WQ T91 steel. (a) The PAGBs are decorated by arrays of carbides (white lines) in the AA condition. Packet boundaries are identified within the PAGBs. (b) Three phases, α_A , α_P and α'_M are identified in the 800WQ sample. The darker phase is allotriomorphic ferrite or grain boundary ferrite (α_A). The block of martensite α'_M shows the etched lath feature. The large block phase is α_P . (c) No allotriomorphic ferrite are observed in the 900WQ T91 specimen. A packet is highlighted with red dots with several blocks inside. (d) Except martensite α'_M , bainitic ferrite (α_B) are also observed in the 1200WQ material.

Fig.5. TEM micrographs of AA and WQ T91 steel. (a) AA T91 steel was fully tempered with predominantly the ferrite phase and carbide precipitates. (b) 800WQ T91 exhibits a complex mixture of grain boundary ferrite α_A and γ -transformed structure ($\alpha'_M + \alpha_P$). The α_A phase is marked following the contours of PAGBs. (c) Some of the α_P phase was strengthened by the α'_M precipitates. Large α_P can serve as a single variant and is separated by the packet boundary from martensite during the transformation. (d) Triple junctions of PAGBs in the 900WQ specimen contain a mixture of α'_M and retained γ phase. (e) The α_P phases with α'_M and carbide precipitates are also identified in the 900WQ specimen. (f) Carbides were observed in the martensitic lath structure in 1200WQ materials. Auto-tempered martensite α'_{AT} formed during the quenching process. Evidence of retained γ phase is present as a thin layer located between two martensitic laths. The inserted selected area diffraction (SAD) pattern reveals the coexistence of the martensite α'_M and γ phases.

Fig.6 (a) Comparison of γ transformed microstructure before and after the coarsening of austenite. (a) A packet was identified at the PAGB in the 1000WQ specimen. A single variant block is noted. (b) No packet can be identified in the 1100WQ specimen. However, blocks are still observed. Both the length and width of blocks increase during the coarsening of prior austenite grains. Auto-tempered martensite (α'_{AT}) (with carbide precipitates inside the lath) is present.

Fig.7 Grain size distributions of prior austenite grains at various WQ conditions show that austenite grains coarsen significantly at 1100°C or higher.

Fig.8 η -carbide and cementite in WQ T91 steel. (a) Bright field TEM images at the near two beam condition and (b) corresponding weak-beam dark-field images revealing the formation of carbide and cementite. High resolution TEM (HRTEM) micrograph of (c) an η -carbide and (d) a cementite precipitate.

Fig.9 (a) TEM micrograph shows that the 1200WQ specimen contains precipitates, including martensite and ϵ -carbides, and bainite. (b) HRTEM micrograph of needle shaped ϵ -carbide with fast Fourier transformation (FFT) inserted in the bottom right corner.

Fig.10 (a) Engineering stress-strain and (b) true stress-true strain curves of WQ T91 alloy tested at room temperature at a constant strain rate of 1×10^{-3} /s. Similar flow stress levels are achieved for 900~1200 WQ specimens, which is ~ 200 MPa higher than that of 800WQ T91.

Fig.11 SEM micrographs of T91 after various thermomechanical treatment procedures. (a) Water quenching after normalization at 1000°C gives a fully γ -transformed structure. Both packets and

blocks are identified. (b) Air cooling after normalization at 1000°C (1000AC) creates a mixture of martensite (α'_M) and polygonal ferrite (α_P). (c) Tempering of 1000WQ at 500°C for 10h yields a tempered martensite structure. The PAGBs become clear due to the formation of GB carbides. (d) ECAE deformation at 300°C of tempered T91 (1000WQ/500C 10h/1A300) induces a deformed martensitic structure and curved PAGBs. (e) Ausforming of T91 steel at 1000°C (1000 ECAE) leads to shearing of PAGBs.

Fig.12 TEM micrographs of T91 processed via various thermomechanical treatments. (a) TEM micrograph of 1000WQ T91 shows a mixture of α'_M laths, carbides and residual austenite γ . (b) Heat treatment of the 1000WQ T91 (1000WQ/500 10h) gives rise to a tempered martensite α'_T structure. (c) ECAE of the tempered T91 at 300°C (1000WQ/500 10h/1A300) leads to a deformed martensitic structure with a high density of dislocations. (d) ECAE processing at 1000°C followed by WQ (1000ECAE) induces a textured fine martensitic structure (examined from the transverse plane).

Fig.13 Probing thermal stability of T91 via measurement of hardness evolution with annealing temperature for two representative ECAE processing procedures. The hardness of ECAE processed T91 remained unchanged up to 500°C /1 h, followed by significant softening at higher annealing temperatures.

Fig.14 TEM micrographs showing microstructure of 1000ECAE T91 tempered at elevated temperatures. (a) After tempering at 600°C, tiny carbides forms at martensitic lath boundaries. (b) At 700°C, carbides coarsen. (c) Tempered martensitic laths around 0.5 μm in thickness form by consuming thinner martensitic laths. (d) After tempering at 800°C, recrystallization and grain growth are evident.

Fig.15 Engineering stress-strain (a) and true stress-true strain curves (b) of T91 alloy after various types of thermomechanical treatments. Compared to 1000WQ T91, high temperature ECAE (1000ECAE) leads to a moderate increase of strength with comparable ductility. ECAE at low temperature (1000WQ/500 10h/1A300) causes a substantial increase in the yield strength with however lower ductility. Heat treatment of the same materials (1000WQ/500 10h/1A300/500 2h) results in a combination of high strength and good ductility.

Fig.16 Plots of work hardening rate (open data) and true stress-true strain (solid data points) for several WQ T91 steels and 1000ECAE T91. The intersections between the two sets of curves imply the initiation of plastic instability. AA T91 has excellent uniform elongation. WQ leads to the reduction of uniform elongation to a few percent. 1000ECAE results in a ductility comparable to that of WQ T91.

Fig.17. Summary of yield strength-uniform elongation (a) and yield strength-elongation to failure (b) maps for T91 steel subjected to various types of thermomechanical treatments. Three distinctive zones are identified based on the primary phase after processing. In the lower ferrite zone with a banana shape (light blue), ECAE of the ferrite phase T91 steel leads to fine ferrite. Heat treatment at various temperatures was applied to tailor strength and uniform elongation. In general, a higher strength is accompanied by lower ductility. In the upper martensite zone (red shadow), including water quenching from 900-1200°C, 1000ECAE or 1000WQ/500 10h/1A300/500 2h leads to martensite with a combination of high strength and reasonable ductility. In the middle ferrite/martensite regime (purple shadow), the T91 is processed primarily by water quenching from 800°C and tempering at 600°C. Water quenching at an onset temperature in the range of 800-1200°C (in yellow triangle) leads to ductile martensite with several percent of uniform elongation because of auto-tempering. Noted: the martensitic region is denoted as a martensite dominated microstructure.

Tables

Table 1. The chemical composition (wt.%) of as-received T91 alloy

Cr	Mo	V	Mn	C	Si	Cu	Ni	Al	Nb	N	P	S	Fe
9.37	0.91	0.18	0.37	0.08	0.33	0.08	0.09	0.03	0.08	0.04	0.01	0.000	Bal
6	1	9	9	5	6	0	7	2	0	2	9	8	.

Table 2. Heat treatments and thermomechanical processing conditions of selected samples

Identifiers	TMT processing condition
AA	annealing of as-received material at 800°C for 1h, followed by furnace cooling
800WQ	normalizing at 800°C for 1h, followed by water quenching
1000WQ	normalizing at 1000°C for 1h, followed by water quenching
1000AC	normalizing at 1000°C for 1h, followed by air cooling
1000ECAE	one pass ECAE at 1000°C and followed by water quenching
1000WQ/500C 10h	annealing of 1000WQ sample at 500°C for 10h
1A300	one pass ECAE at 300°C

Table 3. Microstructural symbols and nomenclature used for different phases

symbol	nomenclature
α_P	polygonal ferrite in grain interiors
α_A	allotriomorphic ferrite/grain boundary ferrite
α'_M	martensite
α'_T	tempered martensite
α'_{AT}	auto-tempered martensite
α_B	bainitic ferrite
M/A	martensite/austenite constituent
δ	delta ferrite
γ	retained austenite
PAGB	prior austenite grain boundary
ε -C	epsilon carbide
η -C	eta carbide
θ	cementite

Table 4. Microstructures and mechanical properties of T91 steel after austenitizing (1 h) and water quenching (WQ)

Temperature (°C)	Initial phase	Phases after WQ	Yield stress (MPa)	Uniform elongation (%)
800	γ + undissolved α + undissolved carbides	$\underline{\alpha}'_M + \underline{\alpha}_A + \alpha_P$ + carbides	972 ± 45	7.2 ± 0.1
900	γ + undissolved carbides	$\underline{\alpha}'_M + \alpha_P$ + carbides	1127 ± 74	7
1000	γ + undissolved carbides	$\underline{\alpha}'_M + \alpha_P$ + carbides	1207 ± 17	7
1100	coarse grained γ	$\underline{\alpha}'_M + \alpha_B$ + carbides	1212 ± 45	6.9 ± 0.6
1200	coarse grained γ	$\underline{\alpha}'_M + \alpha_B$ + carbides	1156 ± 48	6.8 ± 0.7

Table 5. Estimated strengthening contribution (MPa) based on the two models for T91 steel water quenched at 1100°C

Strengthening mechanism	σ_{Fe}	σ_{ss}	σ_i	σ_{H-P}		$\sigma_{disl.}$	$(\sigma_y)_{cal.}$	$(\sigma_y)_{exp.}$
				Lath	Packet			
SM1	~100	~130	~610	~560	N/A	~250	~1650	1210
SM2	~100	~130	N/A	~440	~10	~250	~930	1210

Note: σ_{Fe} is the strength of annealed Fe; σ_{ss} is the strengthening by substitutional atoms; σ_i is the strengthening by interstitials; σ_{H-P} is Hall-Petch type strengthening related to the size effect; $\sigma_{disl.}$ is strengthening by dislocations; $(\sigma_y)_{cal.}$ and $(\sigma_y)_{exp.}$ are the calculated and measured yield strengths respectively.