Effect of grain refinement on mechanical properties of martensitic steel

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Abstract
Microstructure and strength of commercial martensitic steel processed by equal channel angular pressing (ECAP) has been investigated using transmission electron microscopy and tensile tests. Application of ECAP led to significant grain refinement to a grain size of 0.8 µm and precipitation of particles with a size of 90 nm. Impact of annealing on thermal stability of ultrafine-grained structure was investigated. The contribution of various strengthening mechanisms to strength of steel was discussed.

1 Introduction
High strength in martensitic steels at room and elevated temperatures is traditionally ensured by two-stage thermal treatment. At the first stage strengthening takes place due to martensitic transformation as a result of quenching. At the second stage strengthening is provided by dispersion hardening at the expense of precipitation during tempering of the quenched steel [1-4].

It has been recently shown that the strength of steels can be enhanced by grain refinement using severe plastic deformation (SPD) [5-8]. In this case an ultrafine-grained microstructure with grain sizes less than 1 µm can be fabricated allowing additional strengthening in accordance with the Hall-Petch relationship [9,10]:

$$\sigma_y = \sigma_0 + K_y d^{-1/2}$$

(1)

where $\sigma_0$ – the friction stress of a crystal lattice, $K_y$ – the coefficient of strengthening at the expense of grain boundaries, $d$ – the mean grain size.

Usually a grain size depends on the parameters of deformation and thermal treatment, for example, when a deformation temperature increases, grain sizes grow [11]. Therefore, in order to achieve the maximum strengthening effect due to grain refinement, one should reduce the deformation temperature. However, several publications have appeared recently [7,8,12], which demonstrate that the dependence of strength on the deformation temperature is not always decreasing for steels. For example, the maximum strength for carbon steels 10 and 45 was observed after severe plastic deformation at 350 °C [7, 8]. The observed strength in the austenite steel after deformation at 300 °C is higher than that after deformation at room temperature [12]. This is explained by a complex microstructure observed in steels as a result of severe plastic deformation. The deformation temperature affects not only grain sizes, but also such structural features as sizes and distribution of secondary particles, formation of segregations, phase composition, formation of twins [7,8,11,12].
Therefore the influence of temperature on the microstructure and properties of complex-alloyed steels, for which dispersed particles are one of the main factors for strengthening, is especially ambiguous.

This work deals with the possibility of strengthening of martensitic steel as a result of grain refinement by equal channel angular pressing.

2 Experimental procedure

Martensitic steel in the shape of a hot-rolled rod were taken as initial material for investigations. Table 1 displays the chemical composition of the steel under study according to optical emission analysis using Q4 Tasman spectrometer.

Table 1. Composition of the steel, wt.%

| C  | Si  | Mn  | Ni  | S   | P   | Cr  | Mo  | W   | V   |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.14 | 0.31 | 0.32 | 1.63 | 0.009 | 0.02 | 11.53 | 0.45 | 1.66 | 0.18 |

Processing by equal-channel angular pressing (ECAP) was performed using 6 passes on the route Bc with the angle of intersection of the channels equal to 120 degrees at the temperatures of 550°C on samples of 20 mm diameter and 100 mm long.

The microstructure of the alloy was characterized using JEM-2100 transmission electron microscope. Thin foils for TEM investigations were punched from slices of the ECAP-processed samples. Then they were mechanically ground to a thickness of 0.15mm, and finally double-jet electropolished to perforation using an electrolyte based on n-buty alcohol.

The microhardness was measured on a Micromet-5101 device at a load of 100 g for 10 seconds.

3 Results

The microstructure of the steel in the initial state is a ferrite matrix with non-uniformly distributed particles of strengthening phases, which can be clearly seen on the image taken with the SEM (Fig 1a). The average grain size of the matrix phase is 1400 nm. The majority of particles is localized on grain boundaries of the ferrite matrix. The average size of particles is 170 nm, the volume fraction is 5 %. Clear grain boundaries can be observed in the fine structure (Fig. 1b). The majority of grains are free of dislocations. Pile-ups of dislocations can be seen in separate grains.

Non-uniform distribution of particles in the volume, as a rule, decreases the deformability of the material. Therefore, prior to deformation the samples are quenched in oil after heating and holding at 1050°C, for 1 hour, then they are tempered at 800°C for 1 hour.

After quenching martensitic microstructure can be observed (Fig. 1c, d). The average thickness of martensite plates is 518 nm. The martensite is characterized by high dislocation density within a plate. Separate dislocations as well as wide dislocation walls are observed within martensite plates. There are no secondary phase particles, which are typical of the initial state, in the martensitic structure.

After tempering uniform distribution of secondary phase particles in the volume is observed (Fig. 1e, f). The particles precipitate in the boundaries of prior austenite grains and along the boundaries of martensite plates. Only about 25 % of particles are located in martensite plate bodies. The average size of particles is 160 nm, the volume fraction achieves 8.3 %. The plate structure of the martensite retains. The average width of plates is 550 nm.

As a result of ECAP an ultrafine-grained structure with an average grain size of about 0.8 µm has been fabricated (Fig. 2a). The diffraction pattern with numerous spots located around the circle testifies to high-angle misorientations. The dark-field images display the particles of carbides in the body of grains with a volume fraction of 1.5% and a size of 90 nm (Fig. 2b, Table 2).
**Figure 1.** Microstructure of the initial (a, b); quenched (c, d) and tempered (e, f) samples
Figure 2. Microstructure of steel after ECAP: a – bright-field image and diffraction pattern, b – dark-field image of carbides

Table 2. Characteristics of structure after various treatments

| Treatment | Mean grain size, µm | Size of particles, nm | Volume fraction of particles, % |
|-----------|---------------------|-----------------------|---------------------------------|
| Tempered  | 1.4                 | 160                   | 8.3                             |
| ECAP      | 0.8                 | 90                    | 1.5                             |

Transformation of microstructure after ECAP affects considerably the mechanical properties (Table 3). The microhardness in the initial state is 3140 MPa, after quenching and tempering the microhardness increases up to 4820 MPa, and after ECAP it demonstrates the value of 5230 MPa. After ECAP in comparison with tempered sample one can observe the increase of ultimate tensile strength and yield stress up to 1100 MPa and 1040 MPa without visible changes in ductility (Table 3).

Table 3. Mechanical properties of steel

| Treatment | HV, MPa | UTS, MPa | YS, MPa | δ, % |
|-----------|---------|---------|---------|------|
| Tempered  | 3500    | 950     | 790     | 8.0  |
| ECAP      | 5230    | 1100    | 1040    | 8.1  |

4 Discussion

Enhancement of strength in martensitic steel as a result of severe plastic deformation is ensured by formation of a unique microstructure, in which a number of strengthening factors is combined. First of all, it is an ultrafine-grained matrix that ensures grain boundary hardening in accordance with the Hall-Petch relationship [9, 10]. Besides, solid solution hardening of an alloyed ferrite and dispersion hardening at the expense of high-dispersion particles of the strengthening phases take place for the complex-alloyed steel.

Solid solution hardening ($\Delta\sigma_{ss}$) is determined by the content of the alloying element and its strengthening effect [13]:

$$\Delta\sigma_{ss} = k_i c_i$$

where $k_i$ – the strengthening coefficient for ferrite, which is an increment of the yield stress when 1 % (wt) of the $i$-th alloying element dissolves in it; (for carbon $k = 4670$ MPa/ % [14]) $c_i$ – the concentration, % (wt), $i$-th alloying element.

Hardening at the expense of dispersion particles can be determined in accordance with the Orowan’s ratio [15]:

$$\Delta\sigma_{or} = 1.2Gb f^{1/3}d^{-1}$$
where $G=78\ \text{GPa}$ – the shear modulus of the ferrite, $b=0.25\ \text{nm}$ – the Burgers vector for dislocations $\frac{1}{2}<111>$ of the ferrite, $f, d$ – the volume fraction and size of particles.

The dislocation hardening can be calculated via the formula:

$$\Delta \sigma_d = \alpha M b G \rho^{1/2}$$  \hspace{1cm} (4)

where $\Delta \sigma_d$ – the dislocation hardening, where $\alpha$ is the coefficient depending on the character of dislocation interaction in the course of work hardening; $M$ is the orientation multiplier: for $\alpha$ -iron $M = 2.75$, and the product $\alpha M = 0.5$, $b$ – the Burgers vector, $\rho$ - the dislocation density [14].

In general at first approximation the contribution of various mechanisms to the hardening is additive:

$$\sigma_y = \sigma_0 + \Delta \sigma_{ss} + \Delta \sigma_{or} + \Delta \sigma_{gb} + \Delta \sigma_d$$  \hspace{1cm} (5)

where $\sigma_0$ - the friction stress of the $\alpha$-iron lattice; $\Delta \sigma_{ss}$ - solid solution hardening; $\Delta \sigma_{or}$ - dispersion hardening; $\Delta \sigma_{gb}$ - grain boundary hardening; $\Delta \sigma_d$ - dislocation hardening.

The friction stress of the $\alpha$-iron lattice ($\sigma_0$) is determined by the Peierls–Nabarro stress [16]:

$$\sigma_0 = 2 \times 10^{-4} G$$  \hspace{1cm} (6)

Table 4 lists the results of calculation of the contribution of various strengthening mechanisms in the yield stress of steel in accordance with equations (1-6).

The following assumptions were accepted during calculation of solid solution hardening. One-phase structure, namely solid solution of all the alloying elements, is taken for the quenched structure. The carbon content, which most significantly hardens $\alpha$-Fe, in the tempered structure is taken as equilibrium (0.006 % according to diagram “iron-cementite”).

| Treatment | Calculated data | Experimental values |
|-----------|-----------------|---------------------|
|           | $\Delta \sigma_{gb}$, MPa | $\Delta \sigma_d$, MPa | $\Delta \sigma_{ss}$, MPa | $\Delta \sigma_{or}$, MPa | $\sigma_y$, MPa | UTS, MPa | YS, MPa |
| tempered  | 507             | 20                  | 28                  | 295                  | 867                  | 950     | 790     |
| ECAP      | 670             | 33                  | 28                  | 297                  | 1028                 | 1100    | 1040    |

The results listed in the table show that the estimated values are very close to the experimental ones, which proves the possibility of considering the principle of linear superposition when evaluating the contribution of various mechanisms in the yield stress in accordance with (5). Thus, the strength of the tempered steel is ensured mainly by grain boundaries and dispersion hardening. After ECAP the dispersion hardening reduces and contribution of grain boundaries increases whereas solid solution strengthening is not changed.

An interesting fact is that calculated data of the yield stress for the ECAP samples is not coincided with experimental value. One can suppose there are some changes in contribution of strengthening mechanism, for example, at the expense of segregations at grain boundaries [18, 19].

Conclusions
1. As a result of ECAP the ultrafine-grained structure has been produced in martensitic steel. Significant reduction of the volume fraction of secondary phases from 8.3 % in the tempered state to 1.5 % in the deformed state is observed.
2. Evaluation of the contribution of various strengthening mechanisms showed that the strength of ECAP samples ensures mainly by grain boundary hardening, and the combination of various strengthening mechanisms makes it possible producing steels with enhanced mechanical properties.
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