On the nature of high-strength state of carbon steel produced by severe plastic deformation

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Abstract. Contributions of different strengthening mechanisms to yield strength of carbon steels C 10 (0.1 % C) and C 45 (0.45 % C) with ultrafine-grained microstructures have been analyzed in this work based on the precision investigation of the microstructure by electron microscopy, 3D atom probe tomography, and mechanical properties. Estimated values of yield stress showed satisfactory agreement with the experimental results. It is shown that significant contribution to strengthening is made by carbides. In particular, as the carbon content increases in carbon steels, the volume fraction of cementite increases and, accordingly, there is a bigger deviation of the yield strength value from the classical Hall-Petch relationship. The relative contribution of grain boundary strengthening into the yield stress is reduced due to an increased proportion of precipitate strengthening.

1. Introduction

The research fulfilled in the recent decade by various scientists demonstrates a variety of processes taking place during severe plastic deformation of steels and alloys. It has been established that various phase transformations take place alongside with grain refinement. Phase transformations have their peculiarities under dynamic conditions and lead to formation of sophisticated microstructures [1]. As a result the strength could be very high, which is typical of nanostructured materials. Considerable deviation of the yield stress of nanostructured materials produced by severe plastic deformation from the Hall-Petch relationship testifies to that as well [2]. Contributions of different strengthening mechanisms to the yield stress of steels and alloys in the nanostructured state can be responsible for this deviation.

The microstructure peculiarities of carbon steels C 10 (0.1 % C) and C 45 (0.45 % C) subjected to SPD processing in the martensitic state have been considered in this paper. The yield stress has been estimated in the first approximation of linear additivity of different strengthening mechanisms.
2. Material and experiment
Carbon steels C 10 (0.1% wt. C) and C 45 (0.45% wt C) were used as materials for study. Severe plastic deformation was performed via high pressure torsion (HPT) at a temperature of 350 °C, a pressure of 6 GPa, and a number of rotations N=5. Water quenching was applied as preliminary treatment prior to deformation. Water quenching was performed from 910 °C for steel C10 and from 800 °C for steel C45.

Samples for atom probe tomography (APT) were cut out from the half radius area of an HPT processed disc and prepared by standard electropolishing. The analyses were performed in UHV conditions, using an energy compensated atom probe equipped with an ADLD detector. Two different configurations were used: a standard reflectron (small field of view) or a curved reflectron (large field of view). Samples were field evaporated using electric pulses (30kHz pulse repetition rate and 20% pulse fraction) at a temperature of 80K [5].

The fine structure of samples was studied with the help of a transmission electron microscope JEM-2100 at an accelerating voltage 200 kV. TEM samples were cut out from the deformed discs at a distance of approximately 3 mm from the disc center and prepared by FIB lift-out method with a 30 kV Ga+ beam. The thinning step was carried out with a 5 kV Ga+ beam. The two-dimensional effective size of carbide particles was defined by \( d_e = (d_L + d_T)/2 \) where \( d_L \) and \( d_T \) are their major and minor axes, and approximately 260 particles were measured per sample. The microstructure was analyzed by automated crystal orientation mapping (ACOM)[3], which can be used for precise determination and localization of a phase on the basis of its diffraction pattern with a nanoscale spatial resolution. Orientation maps with a resolution 300×300 pixels were obtained from an external charge-coupled device fixed on the microscope screen front with a frequency 175 frames per second. A step size was 3-5 nm. Tensile tests were conducted on flat samples with a gauge length 2 mm.

3. Research results
TEM images of the microstructure after SPD processing are displayed in Fig. 1. The average size of structural elements of the ferrite matrix determined via dark-field images (Fig. 1 b, d) was 220± 40 nm for steel C10 (Fig.1, a, b), 120 ± 30nm for steel C45 (Fig.1, c, d). High-dispersed cementite particles with sizes 10-20 nm are uniformly distributed in the ferrite structure. This structure can be defined as a nanocomposite consisting of ferrite ultrafine grains and high-dispersed cementite particles (Fig. 1 a, b and Fig. 1 c, d).

Formation of such a structure provides a high-strength state. Steel C45 has indeed an ultimate tensile strength of 2650 MPa and an elongation of about 3% [4]. Steel C10 has an ultimate tensile strength of 1200 MPa and an elongation of 12%. The obtained strength values significantly exceed the known data for a nanocrystalline structure of steel C45, which is connected with peculiarities of martensite microstructure evolution in the conditions of its decomposition during deformation at elevated temperatures. This process takes place in dynamic conditions, which provide very small sizes of cementite particles.

Besides, the 3D atom probe tomography demonstrated carbon segregations in grain boundaries (Fig. 2a) of the steels structures [5] subjected to SPD at 350 °C. It is seen that the segregations are not homogeneous. Some “nucleus” with a high concentration of carbon surrounded by a cloud with a smaller concentration of carbon is observed.
Such a pattern of carbon distribution allows assuming that deformation-induced transition of carbon takes place during severe plastic deformation independently from temperature. At elevated deformation temperatures in the conditions of diffusion processes, carbon reaches grain boundaries, on which it segregates with subsequent formation of cementite particles.

The ACOM analysis of steel C10 and steel C45 structures [6] after HPT at 350°C revealed distributions of nanostructural precipitates along grain boundaries (light green areas) (Fig. 2b).

The microstructure peculiarities analysis revealed that at least 3 strengthening mechanisms, namely solid solution strengthening, grain boundary strengthening and precipitation strengthening, contribute to strengthening of steels after SPD.

In the first approximation one may consider that these contributions are additive:

\[ \sigma_{\text{total}} = \sigma_0 + \Delta\sigma_{\text{gb}} + \Delta\sigma_{\text{sol}} + \Delta\sigma_{\text{dis}} + \Delta\sigma_{\text{div}} \]  

where:

- \( \sigma_0 = 16.8 \text{ MPa} \) - the constant friction stress of the \( \alpha \)-Fe lattice[9]

- \( \Delta\sigma_{\text{gb}} = k d^{-1/2} \) (2)

- grain boundary strengthening, where \( d \) – the grain size, \( k = 0.39 \text{ MPa} \cdot \text{m}^{1/2} \) [7,8]

- \( \Delta\sigma_{\text{sol}} = k c_i \) (3)

- solid solution strengthening (the strengthening coefficient of the ferrite that is the increment of the yield stress when 1% of i-th alloying element dissolves in it \( k_i = 4670 \text{ MPa/} \% \) for carbon); \( c_i \) – concentration of i-th alloying element (%) [9];
\[ \Delta \sigma_{\text{pr}} = 0.85M \frac{Gb}{2\pi} \Phi \ln \left( \frac{\lambda - D}{2b} \right) \]  \hspace{1cm} (4)

- precipitation strengthening (where \( \lambda \) - the average distance between particle centers; \( D \) - the average size of particles; \( \Phi \) – the coefficient that characterizes the type of dislocations interacting with particles: \( \Phi = 1 \) for screw dislocations, \( \Phi = 1/(1 - \nu) \) for edge dislocations (\( \nu \) - the Poisson’s ratio, \( \nu = 0.33 \) for ferrite), for mixed dislocations
\[
\Phi = \frac{1}{2} \left( 1 + \frac{1}{1 - \nu} \right)
\]  \hspace{1cm} (5)

\( \Phi = 1.25 \) for steel; \( M = 2.75 \) for \( \alpha \)-Fe; 0.85 – statistical coefficient;

\[ \Delta \sigma_{\text{d}} = \alpha M b G \rho^{1/2} \]  \hspace{1cm} (6)

- dislocation strengthening (\( \alpha \) - the coefficient that depends on the character of dislocations interaction during strain hardening; \( M \) – orientation multiplier: \( M = 2.75 \) for \( \alpha \)-Fe, and the multiplication \( \alpha M = 0.5 \); \( b = 0.25 \text{ nm} \) – the Burgers vector; \( \rho \) - the dislocation density) \[9\].

The evaluation results of each mechanism contribution and the total estimated yield stress for steels C10 and C45 after HPT are listed in Table 1 and displayed in Fig. 3. We did not include evaluation of quenched state steel C10, because carbon concentration (0.1%) is not enough for martensite transformation in water cooling.
Table 1. Estimated values of contributions of different strengthening mechanisms into the yield stress of steels

| state                              | $\sigma_0$ MPa (%) | $\Delta\sigma_{ss}$ MPa (%) | $\Delta\sigma_{gb}$ MPa (%) | $\Delta\sigma_{or}$ MPa (%) | $\Delta\sigma_d$ MPa (%) | $\sigma_T = \sum_{i=1}^a\sigma_i$ MPa | Experimental value |
|------------------------------------|--------------------|------------------------------|----------------------------|-----------------------------|--------------------------|------------------------------------------|---------------------|
| C 45 water quenching               | 16.8 (0.7)         | 2102 (90)                   | 137 (5.8)                  | -                           | 128 (4.2)                | 2383                                      | 2000                |
| C 45 water quenching + HPT         | 16.8 (0.9)         | 514 (22.7)                  | 1125 (49.8)               | 497 (22)                    | 105 (5.5)                | 2257                                      | 2397                |
| C 10 water quenching + HPT         | 16.8 (1.3)         | 93 (7.4)                    | 780 (62.6)                | 251 (20.1)                  | 91 (8.4)                 | 1231                                      | 1170                |

The main contribution up to 90% to the martensite state strength is made by a solid solution component, which reduces to 23% after HPT due to martensite decomposition in the deformation conditions at a tempering temperature. After HPT a grain boundary component (50%) makes the main contribution in the strengthening of steel C45, and the precipitation strengthening (22%) becomes more significant. A similar scheme is also typical of steel C10, in which the share of grain boundary strengthening makes 63% and that of precipitation strengthening makes 20%. Besides, the share of solid solution strengthening 23% is rather considerable.

The yield stress experimental values of steels C10 and C45 plotted on the Hall-Petch curve (Fig. 4) show that the experimental values of steel C45 deviate from the Hall-Petch relation to a larger degree than those of steel C10.
This can be explained through analyzing the contributions of different strengthening mechanisms in the yield stress of steels mentioned above. Deviation from the Hall-Petch relationship is connected with other strengthening mechanisms along with a grain boundary one. The precipitation strengthening is determined by the volume fraction of the strengthening phase precipitates, namely by the cementite. The solid solution strengthening is determined by the content of an alloying element (carbon) in the solid solution. When the carbon content in the solid solution increases from steel C10 to steel C45, the contribution of a solid solution component increases as well. Besides, the distribution of cementite in the structure increases, which results in enhancement of the absolute contribution of a strengthening dispersed component.

4. Conclusion

SPD techniques allow producing UFG structures in carbon steels with a grain of 225 nm in steel C10, 120 nm in steel C45 and nanocarbides 10-15 nm in size. The contribution of different strengthening mechanisms in the formation of a high-strength state in steels C10 and C45 has been evaluated. The estimated values of the yield stress demonstrated good correlation with the experimental results. It is shown that the highest contribution (over 40%) is made by the grain boundary component. The precipitation strengthening makes significant contribution, which enhances considerably when the carbon content increases from 0.1% to 0.45%. The above estimates are primary, they only show that the deviation of the yield stress on the Hall-Petch relationship is associated with the contributions of other than grain boundary strengthening mechanisms in the yield stress. Such assessments should continue.

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References
[1] Ruslan Z. Valiev, Alexander P. Zhilyaev, Terence G. Langdon. Bulk Nanostructured Materials: Fundamentals and Application. Wiley. 2013, 456 P.
[2] R.Z.Valiev, N.A.Enikeev, T.G.Langdon. Towards superstrength of nanostructured metals and alloys, produced by SPD. Kovove Mater. 49, 2011, pp.1-9.
[3] Kobler A.,. Kashiwar A, Hahn H., Kübel C. Combination of in situ straining and ACOM TEM: A
novel method for analysis of plastic deformation of nanocrystalline metals Ultramicroscopy Volume 128, May 2013, Pages 68-81

[4] Karavaeva M.V., Nurieva S.K., Zaripov N.G., Ganeev A.V., Valiev R.Z. Microstructure and mechanical properties of medium carbon steel subjected to severe plastic deformation. Metal Science and Heat Treatment. 2012. pp. 1-5.

[5] X. Sauvage, A. Ganeev, Y. Ivanisenko, N. Enikeev, M. Murashkin, R. Valiev, Grain boundary segregation in UFG alloys processed by severe plastic deformation, Adv. Eng. Mater., 2012 Vol 14 (11) pp968-974.

[6] Jiangli Ning, Eglantine Courtois-Manara, Lilia Kurmanaeva, Artur Ganeev, Ruslan Z Valiev, Christian Kubel, Yulia Ivanisenko. Tensile properties and work hardening behaviors of ultrafine grained carbon steel and Armco-iron processed by warm high-pressure torsion, Acta Materialia, 2013. pp8-15

[7] Valiev R.Z., Murashkin M.Y., Ganeev A.V., Enikeev N.A. Superstrength of nanostructured metals and alloys produced by severe plastic deformation. The Physics of Metals and Metallography. 2012. T. 113. № 13. C. 1193-1201.

[8] Malow T.R., Koch C.C. Mechanical properties, ductility, and grain size of nanocrystalline iron produced by mechanical attrition Met.Mater.Trans.A, 29, 1998, p. 2285-2295.

[9] Goldshtein, M.L, Litvinov, V.S., Bronfin, B.M. Metals physics of high-strength alloys. Moscow: Metallurgy(In Russian).1986.