**Precipitation strengthening in titanium microalloyed high-strength steel plates
with new generation-thermomechanical controlled processing (NG-TMCP)**

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Abstract

We elucidate here the strengthening mechanisms in titanium microalloyed low-carbon steels, which were rolled into plates of 12 mm thickness using a combination of thermomechanical controlled processing (TMCP) and ultrafast cooling (UFC). The ultrafast cooling combined with thermomechanical controlled processing is referred by us as new generation (NG)-TMCP. Chemical phase analysis, small-angle X-ray scattering (SAXS) and high-resolution transmission electron microscopy (TEM) were used to study the characteristics of nanoscale cementite precipitates and microalloyed precipitates. Besides nanoscale TiC, cementite precipitates of size less than ~35 nm with high volume fraction were observed in Ti-microalloyed steel. Cementite with high volume fraction had a stronger precipitation strengthening effect than nanometer-sized TiC. The precipitation strengthening contribution of nanoscale precipitates of different types and size was estimated together with solid solution strengthening and grain refinement strengthening contribution. The estimated yield strength was consistent with the experimental value.

Keywords: High strength low alloy (HSLA), Thermomechanical controlled processing (TMCP), Nanoparticles, microstructure, High resolution transmission electron microscopy

I. Introduction

Steel is an important structural material and strength is an important property of any structural material. Strengthening mechanisms have been studied for a number of years. Thermomechanical controlled process (TMCP) is a simple and cost effective

method to enhance the properties of ferritic steels ^[1], which consists of controlled hot rolling followed by controlled cooling. This involves complex interaction of chemical composition, temperature, deformation and different metallurgical phenomena. The superior mechanical properties obtained via TMCP is a consequence of refinement of austenite, maximization of austenite boundary area and density of deformation bands, such that there are increased nucleation sites prior to transformation of austenite. The superior mechanical properties of low-carbon microalloyed steels arise from a combination of refined ferrite grain size and precipitation hardening.

In high-strength low-alloy (HSLA) steels containing microalloying elements such as V, Nb, and Ti, nanoscale V, Nb, and Ti carbides provide significant precipitation strengthening effect on the addition of microalloying elements^[2]. Steels industries are currently facing the challenging of reducing alloy costs in steel products, which negatively impacts the strength of steels. In order to meet the requirements of reduction in alloy cost and maintain strength, cementite in steels is viewed as a viable option to partially replace microalloying elements because it is a common second phase constituent in steels^[3-5]. Fu and co-workers, observed nanoscale cementite precipitates in Ti-microalloyed high strength weathering steels during thin slab continuous casting and rolling, which were believed to play an important role in enhancing the strength of steel^[6]. Mao and co-worker studied Ti microalloyed weathering high-strength steel under laboratory and production conditions^[7] and found that TiC precipitation strengthening effect is significantly less than Fe₃C precipitates. Other methods adopted to obtain nanoscale cementites include cold

deformation of pearlitic steels after hot rolling^[8] and static annealing after severe plastic deformation of a low carbon microalloyed steel^[9]. However, little work has been carried out to obtain nanoscale cementites in low-carbon steels plates by ultrafast cooling process after controlled rolling. In order to clearly determine the possible contribution to strength, a detailed characterization of nanoscale compounds is essential. Moreover, it is difficult to determine the volume fraction of different types and size of nanoscale particles, to theoretically quantify their contribution to strength. Only qualitative information can be obtained by TEM.

The present study is focused on studying the effective contribution of nanoscale precipitates to strength during NG-TMCP of microalloyed steel via chemical phase analysis, small-angle X-ray scattering (SAXS) and high-resolution transmission electron microscopy (TEM). Additionally, the crystallography of different types of precipitates is studied.

II. Materials and Methods

A. Materials and Thermo-mechanical Processing

The chemical composition of the experimental steel is listed in Table I. 0.08wt% Ti was added based on the composition of traditional Q345 grade. The steel was melted in a vacuum furnace and cast into ingots of dimensions of $100 \times 100 \times 100 \text{ mm}^3$, and rolled into plates by TMCP process. Schematic illustration of TMCP schedule is presented in Fig. 1. The ingots were heated to 1250°C for 2 h to completely dissolve titanium precipitates in austenite. After removal of the surface iron oxide, the ingots were rolled using $\Phi 450 \text{ mm}$ rolling mill. The rolling process consisted of seven passes

with a total thickness reduction of 88%, and the final thickness was 12 mm. Recrystallization of austenite commences at 1150 °C and consisted of 3 passes of rough rolling. Austenite non-recrystallization region rolling started at 880 °C and final rolling temperature was controlled at 860 °C. This process consisted of four passes. Next, the steels were ultra-fast cooled to isothermal holding temperature with different cooling rate and held for 20 min. Finally, the steels were cooled in air to room temperature. The detailed processing parameters are described in Table II, and the steels with different processing parameters are marked as steel A and B in below.

B. Microstructural Characterization

The steels were mechanically polished to mirror finish and etched with 4 vol. % nital solution at room temperature. Microstructural observations were carried out using a combination of scanning electron microscopy (SEM, ZEISS ULTRA 55) and transmission electron microscopy (TEM, FEI Tecnai G² F20). TEM specimens were produced by cutting slices from the steel plates, thinning them mechanically to 0.06 mm and electrochemically jet polished in a solution of 9 vol.% perchloric acid in ethanol at -30 °C. TEM experiments were carried out using a TEM equipped with an energy-dispersive X-ray (EDX) spectrometer operating at 200 kV. Standard TEM techniques such as bright-field (BF) and dark-field (DF) imaging as well as selected area electron diffraction (SAED) were used to characterize the microstructure. The crystallography and chemical composition of the precipitates were studied by high resolution transmission electron microscopy (HRTEM) and EDX. Furthermore, the precipitates were electrochemically extracted from different steels. The phase

constitution and size distribution were studied using a PANalytical X'pert Pro MPD by using the small angle X-ray scattering method, according to the test standard ISO/TS 13762.

C. Chemical phase analysis and SAXS analysis

It is quite difficult to determine the mass fraction or volume fraction of nanoscale particles in steels with an electron microscope, but the volume fraction of precipitates with different sizes are required for estimating the strength of steel. Chemical phase analysis and SAXS are effective methods to determine the chemical composition, mass fraction, or volume fraction of nanoscale particles with different sizes.

The procedure for chemical phase analysis was as follows:

- (1) Electrolytic dissolution of steel sample to obtain electrolyzed powders containing iron carbide, alloy carbide, sulfides and nitrides.
- (2) Elimination of iron carbides, sulfides, and AlN to obtain alloy carbides and oxide.
- (3) Removal of alloy carbides to get stable oxide.

After the above separation procedure, the electrolyzed powders were dissolved and the content of Fe, Mn, N, and C was analyzed; and then the mass fraction of cementite based on formula $(Fe_aMn_b)_3(C_xN_y)$ was calculated. According to GB/T 1322191 (ISO/TS 13762 2001) the particle size distribution of precipitate powders was analyzed by SAXS with a Kratky small-angle X-ray scattering (Rigaku Corporation, Tokyo, Japan). Using this approach, the analyzed error was less than 10 pct.

D. Tensile and Impact Toughness tests

Standard cylindrical tensile test samples with a gage length of 25 mm and diameter of

5 mm were prepared from the heat treated steel plates transverse to the rolling direction. Tensile tests were conducted at room-temperature to measure the yield strength, tensile strength and elongation using a SANS-5000 tensile tester with a computerized tensile testing system at room temperature at a crosshead speed of 1 mm/min. Standard Charpy v-notch (CVN) impact samples of dimensions $10 \times 10 \times 55$ mm³ were prepared to determine impact toughness at -20 and -40 °C using an Instron 9250 impact tester.

III. Results

A. Microstructural Evolution

Fig. 2 shows SEM and TEM micrographs corresponding to the surface and mid-thickness in steel A. Fig. 2(a) and (c) illustrate the microstructure of the surface and Fig. 2(b) and (d) describe the microstructure of mid-thickness region of the plate. The microstructure at both locations consisted of a fully bainite structure because of low finish cooling temperature and low cooling rate. TEM micrographs were indicative of upper bainite structure. The width of bainite lath at the surface was less compared to the mid-thickness. Fig. 2(d) shows typical morphology of martensite-austenite (M/A) constituent of ~ 400 nm width. The M/A constituents were systematically studied by Misra and co-workers^[10]. During the slow cooling process, the undercooled austenite first transformed to ferrite and the untransformed austenite becomes rich in carbon. When C-rich austenite is cooled to a temperature below M_s , it is partially or totally transformed to martensite and forms M/A constituent. In the present study, the M/A constituent in sample A consisted of alternative layers of

retained austenite and martensite. The SAED pattern obtained from the area marked by white circle in Fig. 2(d) is illustrated in the inset in Fig. 2(d), suggesting Kurdjumov-Sachs (K-S) orientation relationship: $[11\bar{1}]_{\alpha} // [10\bar{1}]_{\gamma}$, $(101)_{\alpha} // (111)_{\gamma}$ ^[11].

Fig. 3 is a schematic diagram of precipitation during different stages in the experimental steel. During solidification and reheating stage, TiN and Ti₂CS are nucleated and redissolved, respectively. The typical morphology and EDS of TiN and Ti₂CS are presented in Fig. 4(a) and (b). It is well known that precipitation of TiN occurs in two temperatures regimes: during solidification of steel and in supersaturated austenite after solidification. Coarse TiN precipitates are formed at liquid iron temperatures of ~1540 °C during solidification^[12]. In the δ - γ (austenite) transformation regime (around 1400 °C), the coarse TiN precipitates dissolve, leading to Ti enrichment in δ - γ solid solution. At temperatures between 1400 and 1200 °C, precipitation of TiN and Ti₂CS precipitates takes place in supersaturated austenite^[12].

Given that both TiN and Ti₂CS have higher dissolution temperatures, they are expected to pin the grain boundaries during hot rolling, leading to refinement of final ferritic grain size^[13]. In the austenitization stage, both coarsening and redissolution of partial TiN and Ti₂CS can occur. During deformation of austenite, precipitation occurs at heterogeneous nucleation sites (e.g. dislocations) and/or at grain boundaries and deformation bands. These precipitates are referred as strain-induced precipitates. In the ultrafast cooling stage, the growth of strain-induced precipitates is inhibited and precipitation in ferrite is promoted. Subsequently, during isothermal holding and air cooling stage, TiC and Fe₃C are nucleated and coarsened in supersaturated ferrite or

during γ - α transformation, as shown in Fig. 4(c) and (d).

It is known that the precipitates can be clearly observed in the matrix, when the contrast of dislocations completely disappears. Thus, we tilted the specimen in TEM to satisfy the condition that the reciprocal vector of diffraction plane is perpendicular to the Burger's vector of dislocation^[14]. Fig. 5(a) shows the morphology and distribution of nanometer-sized carbides precipitated in lath bainite in the mid-thickness of the plate. Random dispersion of carbides of size range of ~2-10 nm was observed. Representative HRTEM image of nanometer-sized carbide is presented in Fig. 5(b). As illustrated in the figure, the carbides were very fine and within the thickness of foil. This led to the development of Moiré fringe contrast because overlapping carbide and ferrite lattices, which provide a clear contrast with the carbide and can be used for accurate measurement of the size of the carbide. The size of the carbides in Figure 5b were determined to be ~5.49 nm along the direction of the Moiré fringe (length) and ~5.26 nm perpendicular to the direction of the Moiré fringe (thickness), and the aspect ratio (length/thickness) is close to 1. Thus, it can be concluded that the morphology of the carbide was close to spherical. The average value of length and thickness of carbide was ~5.38 nm. In order to identify the crystal structure and orientation relationship, the fast Fourier transformed (FFT) diffractogram is presented in Fig. 5(c). Extra diffraction spots are related to iron oxide on the surface and double diffraction from oxide and ferrite. The orientation relationship of carbide with respect to ferrite matrix is $[110]_{\text{carbide}} // [100]_{\text{ferrite}}$, and the angle of the reciprocal vectors $(0\bar{1}\bar{1})_{\text{ferrite}}$ and $(\bar{1}0\bar{1})_{\text{carbide}}$ is $\sim 27.9^\circ$, which does

not obey any specific orientation relationship such as Baker-Nutting (B-N) and Nishiyama-Wassermann (N-W) orientation relationship. This result is inconsistent with previous studies which indicated that carbides obey B-N or N-W orientation relationship to have lowest lattice misfit and maintain coherency at the interface with the ferrite matrix ^[15-22]. Along the zone axis $[110]_{\text{carbide}} // [100]_{\text{ferrite}}$, the double diffraction was found to operate due to strong interaction between $(\bar{2}20)_{\text{carbide}}$ and $(0\bar{1}\bar{1})_{\text{ferrite}}$. The difference vector of the reciprocal vectors from $(\bar{2}20)_{\text{carbide}}$ and $(0\bar{1}\bar{1})_{\text{ferrite}}$ is illustrated in Fig. 5(c). The spacing of a set of parallel Moiré fringe was determined by the reciprocal of the magnitude of the corresponding difference vector, and the Moiré fringe is perpendicular to the difference vector. The spacing for the produced Moiré fringes is given by the following equation:^[14]

$$D = \frac{d_{\bar{2}20_{\text{carbide}}} \times d_{0\bar{1}\bar{1}_{\text{ferrite}}}}{[(d_{\bar{2}20_{\text{carbide}}} - d_{0\bar{1}\bar{1}_{\text{ferrite}}})^2 + (d_{\bar{2}20_{\text{carbide}}} \times d_{0\bar{1}\bar{1}_{\text{ferrite}}} \times \varepsilon^2)]^{\frac{1}{2}}} \quad (1)$$

$$a_{\text{carbide}} = d(\bar{2}20)_{\text{carbide}} \times 2\sqrt{2} \quad (2)$$

Where D is the interplanar spacing of the Moiré fringe, $d_{\bar{2}20_{\text{carbide}}}$ and $d_{0\bar{1}\bar{1}_{\text{ferrite}}}$ are the interplanar spacings of $(\bar{2}20)_{\text{carbide}}$ and $(0\bar{1}\bar{1})_{\text{ferrite}}$, ε is the angle of reciprocal vectors $(\bar{2}20)_{\text{carbide}}$ and $(0\bar{1}\bar{1})_{\text{ferrite}}$. The value of ε is 4.73° (0.0825 rad). The value of $d_{0\bar{1}\bar{1}_{\text{ferrite}}}$ was determined to be 0.202 nm by using the lattice parameter of ferrite ($a_{\text{ferrite}}=0.287$ nm). Given the measured D (0.643 nm) and ε (0.0825 rad), the lattice parameter of carbide determined from equation (2) was 0.433nm.

It is known that Ti microalloying can result in precipitates in the ferrite matrix. Surprisingly, not only TiC precipitates were observed but also new type of fine

precipitates was observed in Fig. 5(d). To the best of our knowledge, these precipitates have not been reported before in conventional HSLA steels plates. Thus, a detailed TEM study was carried out on these precipitates. The selected area diffraction (SAD) pattern showed precipitates with [001] orientation as seen in Figure 5f. It follows that these precipitates have an orthogonal structure. The lattice parameters a and b of the precipitate were calculated to be 4.525 and 5.089. The precipitates with these lattice constants and orthogonal structure has been determined to be cementite with certainty. A DF image using the (210) reflection in the [001] projection of the precipitates is shown in Fig. 5(e). Here, all the precipitates that have same orientation are visible. Furthermore, one can see in Fig. 5(b) that the size distribution of these cementites was in the size range of ~10-25 nm. The shape of the observed cementites in Fig. 5(d) (identified by the circle) and the streaking of precipitate reflections in the SAED pattern in Fig. 5(f), suggested that these precipitates have disk-shaped morphology.

Fig. 6 shows the representative SEM and TEM micrograph corresponding to surface and mid-thickness region in steel B. Fig. 6(a) and (c) indicated that the microstructure at the surface consisted of ~3 to 8 μm fine polygonal ferrite (PF), and ~1 to 2 μm fine pearlite. The percentage of polygonal ferrite and pearlite were 89 % and 11%, respectively. Fig. 6(b) indicated that the microstructure at mid-thickness of the plate consisted of ~5 to 10 μm coarse polygonal ferrite, and ~1-3 μm fine pearlite. The percentage of polygonal ferrite and pearlite were 85% and 15%, respectively. The microstructure at the surface and mid-thickness mainly consisted of polygonal ferrite

and pearlite. Compared to mid-thickness, the polygonal ferrite was marginally refined because of higher undercooling. Moreover, a higher fraction of pearlite was obtained because of relatively low cooling rate, as shown in Fig. 6(a) and (b). The polygonal ferrite first forms at the original austenite grain boundary during phase transformation and rejects C to the surrounding austenite. The undercooled austenite was gradually enriched with C, and pearlite formed during the slowing cooling process. Additionally, Fig. 6(d) illustrates fine lamellar cementite located between ferrite laths in pearlite with interlamellar spacing of ~308 nm.

Fig. 7 shows precipitates in steel B. Two different morphologies of precipitates were observed, interphase precipitation and random precipitates. The majority of interphase precipitates in rows were ~5 nm in size and intersheet spacing was ~10-20 nm, as shown in Fig. 7(a). The random precipitates in ferrite matrix were smaller than ~10 nm and slightly larger than the interphase precipitates. The energy dispersive X-ray (EDX) spectrum of a representative 12 nm precipitate in Fig. 7(b) is presented in Fig. 7(g), showing that the nanometer-sized carbide was TiC. According to the previous studies, the interphase precipitation occurs at relatively higher temperatures, and that interphase precipitation can only occur in some ferrite grains and not in all [23-25]. In our study, interphase precipitation was observed only in some large ferrite grains when the specimen was ultrafast cooled to 700 °C. It is generally agreed that the ledge velocity is inversely proportional to the isothermal aging temperature. The higher isothermal temperature reduces the driving force for γ/α transformation and ledge migration velocity, and increases the possibility of interphase precipitation^[26].

Representative HRTEM micrograph of interphase precipitation of carbides in ferrite is presented in Fig. 7(d). The crystal structure and the orientation relationship were identified by the fast Fourier transformed (FFT) diffractogram, as illustrated in Figure 7(e). Extra diffraction spots are related to iron oxide on the surface and double diffraction from oxide and ferrite. The interphase TiC precipitates have NaCl-type crystal structure and obey the Nishiyama–Wassermann (N-W) orientation relationship with respect to ferrite matrix: $[110]_{\text{carbide}} // [100]_{\text{ferrite}}$ and $(01\bar{1})_{\text{ferrite}} // (\bar{1}1\bar{1})_{\text{carbide}}$ ^[27]. By using inverse fast Fourier transformation (IFFT) for carbides, the lattice images of the carbides along the zone axis $[110]_{\text{carbide}}$ (Fig.7(f)) were obtained, and the lattice parameters of the carbides was estimated to be 0.434 nm.

For fcc precipitates in a bcc matrix, the primary orientation relationships (OR) are BN, NW and Kurdjumov-Sachs (KS). Baker-Nutting (BN) relationship is $\{001\}_{\text{fcc}} // \{001\}_{\text{bcc}}$ and $\langle 110 \rangle_{\text{fcc}} // \langle 010 \rangle_{\text{bcc}}$. On a given $(001)_{\text{fcc}}$ plane, there are two $\langle 110 \rangle$ directions: $[110]$ and $[1\bar{1}0]$. Because these two directions are perpendicular, a symmetry operation on fcc crystal with rotation of 90° about the pole of $(001)_{\text{fcc}}$ plane, would lead to $[110]$ and $[1\bar{1}0]$ being crystallographic equivalent. Thus, three variants of BN ORs can be derived. The NW ORs can be obtained from a rotation of BN ORs. Each BN OR can produce four variants or NW ORs, and therefore three variants of BN ORs can bring about 12 variants of NW ORs. However, in the present study for TiC carbide interphase precipitation, only a single variant of NW OR with respect to ferrite matrix was observed. The result is consistent with interphase precipitation of (Nb, Ti)C^[27].

In recent years, Zhao *et al.* and Fu [6, 28] studied the distribution of nanoscale cementite in 0.15C-1.5Mn ferrite-pearlite steel, and observed less than 100-nm-diameter spherical cementite particles. The distribution of these particles was not homogeneous and the content was high in some regions. In order to study whether the addition of titanium would affect the formation of cementite, TEM studies were conducted. The results indicated that cementite and TiC precipitated simultaneously in the same ferrite grain, as shown in Fig. 7(c). The SAED pattern (Fig. 7(c)) confirmed that precipitates of size range ~10-40 were cementite, with the zone axis of [111]. The representative EDS spectrum of these precipitates in Fig. 7(c) is presented in Fig. 7(h), showing that the relatively larger precipitates are iron carbides.

B. Mechanical Properties

The mechanical properties including yield strength, tensile strength, percentage elongation, and yield ratio obtained from tensile tests of Ti-microalloyed steel are listed in Table III. The data in Table III, is the average value of at least three specimens. In steel A, the yield strength, tensile strength, elongation and yield ratio were 650 MPa, 750 MPa, 19.2%, and 0.87, respectively; and in steel B were 590 MPa, 718 MPa, 18.3 %, and 0.83, respectively.

The CVN impact energy at subzero temperature (−20 and −40 °C) for steel A and B are shown in Table III. For steel A, the CVN impact energy at −20 and −40 °C was 93.4 and 65.7 J, respectively, while for steel B, 24.6 and 17.3 J. The results indicated that the low-temperature impact toughness strongly depends on the cooling rate and the finish cooling temperature. The fracture surface of CVN impact samples tested at

-40 °C were studied and their secondary electron fractograph are shown in Fig. 8. Fig. 8(a) shows fracture morphology at low magnification for steel A. Fig. 8(b) and 8(c) are high magnification images taken from the region marked by marked by blue and pink rectangle in Fig. 8(a). Fig. 8(b) shows numerous small and large deep dimples, indicative of good low-temperature toughness, while in Fig. 8(c) the morphology of fracture surface mainly consisted of quasi-cleavage facets. In addition, some river-like marking on quasi-cleavage facet with some dimples were observed. Fig. 8(e) shows the fracture morphology of steel B. Fracture surface was predominantly cleavage fracture with a small quantity of cracks. Based on SEM analysis of both steels, as shown in Fig. 8(d) and (f), large particles were present. Thus, high stress concentration can occur at the interface due to difference in hardness between ferrite matrix and cementite [29-30], and when the stress is high, microvoids can nucleate. It is known that these microvoids usually nucleate at the second phase particles, i.e. fine M/A constituent, or carbides, by de-bonding of the particle-matrix interface or by particle fracture^[31]. In addition, it was found that the size of particles at the nucleation sites plays a significant role in microvoid initiation^[32]. Based on Griffith theory^[33], for coarse particles in steel B, the crack initiation energy must be low, which is the reason for low toughness of steel B compared to steel A. The difference in mechanical property is due to different cooling schedules. It can be seen that a good combination of strength and ductility can be obtained with cooling rate and finish cooling temperature of 64 °C/s and 580 °C, respectively.

IV. Discussion

A. Chemical phase analysis and SAXS

Chemical phase analysis and SAXS analysis were carried out on steel A and B. Table IV summarizes the structural parameters of precipitates obtained by X-ray diffraction for the extracted particles by electrolysis. From the X-ray results, we can say that the precipitates were mainly composed of $M_3(C,N)$, Ti_2CS , TiC and $Ti(C,N)$. But it was difficult to distinguish between TiC and $Ti(C, N)$, because of similarity in lattice constants.

Table V shows the mass fraction of precipitates in steel. From Table V, it can be seen that the high mass fraction of the precipitated phase was M_3C cementite-based compounds, followed by $Ti(C, N)$. The size distribution of MC type and M_3C type of steel A and B are presented in Fig. 9. It may be noted that the MC carbide mass fraction changed to a small extent in steel A and B, while the M_3C precipitates in steel A and B were significantly different in the size range of ~1-36 nm. The mass fraction of $M(C, N)$ particles of size less than 36 nm was significantly less than $M_3(C_xN_y)$ of similar size in steel. In steel A, the volume fraction of cementite with size less than ~36 nm was ~49 times of TiC of similar size and the corresponding yield strength increment of cementite was ~3.3 times of TiC . In steel B, the volume fraction of cementite with size less than ~36 nm was ~4.8 times of TiC of similar size and the corresponding yield strength increment of cementite was ~1.7 times of TiC .

B. Role of precipitates in strengthening of the steels

An overall objective of TMCP is to enhance the strength of steel by increasing the strength of the ferrite phase through precipitation hardening. It is therefore important

to understand the contribution of the above mentioned precipitates toward effective strengthening. Both TiN and Ti₂CS can be very effective in pinning austenite grain boundaries [12-13, 34] at elevated temperatures during the hot rolling process. This results in reducing the ferrite grain size (grain refinement strengthening) and leading to enhancement of yield strength and toughness. Precipitation strengthening is a strengthening method in which the interaction between dispersed fine precipitation phases and the dislocations in steel obstruct the movement of dislocations, thus increasing the strength of the steel. There are two well-known mechanisms by which the precipitates can retard the motion of dislocation. One is called the shearing (cutting) mechanism where dislocations cut the particles; the other is called the bypass (looping) or Orowan mechanism where the dislocations do not cut the particles, but bypass them, forming a dislocation loop around the particles. The mechanism that requires least energy will be the relevant one for obstructing the dislocation motion. Considering that iron carbides are generally hard and resist cutting, the Orowan mechanism is most likely the dominant mechanism. The precipitation strengthening effect of fine precipitates in steel can be calculated using the simplified equation (3) proposed by Gladman *et al.*^[1] based on Ashby-Orowan's revised model. When the average diameter of particles is greater than 40 nm, the contribution of precipitation strengthening is not significant.

$$\sigma = 10.8 \frac{\sqrt{f}}{d} \ln(1630d) \quad (3)$$

In equation (3), σ represents the precipitation strengthening increment in MPa, f is the volume fraction of the carbides and d is the diameter of the carbide in μm .

When the diameter of precipitates is very small, and the interface tension between them and the matrix is small, the precipitate is coherent or semicoherent [35]:

$$\sigma = \bar{M} \tau_p = \frac{2 \times 1.1}{\sqrt{2AG}} \times \frac{\gamma^{3/2}}{b^2} \times d^{1/2} f^{1/2} \quad (4)$$

Where, τ_p represents the shear stress caused by the dislocations cutting the particles in MPa; $A = \frac{1}{2\pi K} \ln\left(\frac{d}{2b}\right)$, represent the dislocation line tension function; $K=(1-\nu)$ for edge

type dislocation, $K=1$ for screw dislocation, and $\frac{1}{K} = \frac{1}{2} \left(1 + \frac{1}{1-\nu}\right)$ for mixed type

dislocation; ν is the Poison's ratio and equal to 0.291; b is the absolute value of the dislocation Burger's vector and is equal to 0.248 nm; G is the shear elasticity modulus and equal to 80,650MPa; γ is the interface energy between precipitates and matrix and equal to 0.5 to 1 J/m²; d represents the second-phase particle diameter in μm ; f represents the volume fraction of the precipitates; and $\bar{M}$ represents the average Schmid orientation factor and equal to 2 for bcc iron.

From equations (3) and (4), it can be seen that when the second-phase precipitate strengthening is shearing (cutting) type, its strengthening effect is proportional to the half power of particle size d . When it is a bypass mechanism, its strengthening effect is proportional to half power of the volume fraction and roughly inversely proportional to particle size d ; that is, the strengthening effect of the shearing (cutting) mechanism increases with increasing particle size, while the strengthening effect of the bypass mechanism decreases with increase of particle size. The critical transformation size d_c can be calculated by the numerical solution of equation (5): [5,

36].

$$d_c = 0.209 \frac{Gb^2}{K\gamma} \ln\left(\frac{d_c}{2b}\right) \quad (5)$$

The meaning of symbols in equation (5) is same as mentioned above. The critical transformation size of the precipitate depends on the properties of dispersed particles; the smaller the size, smaller is the interface energy between the precipitates and the matrix and larger the d_c . Different types of precipitates have different d_c value.

For HSLA steels, it is generally believed that the precipitation strengthening phase is nanoscale carbides of microalloying elements. In our study, the precipitation strengthening is derived from nanoscale iron carbide and TiC. In considering the contribution of precipitates to yield strength, the combined contribution of precipitates with different types and sizes based on the bypass mechanism and shearing mechanism should be taken into account:

$$\sigma_{sp} = \sum_{i=1}^n \sigma_{sp_{1i}} + \sum_{i=1}^n \sigma_{sp_{2i}} = \sum_{i=1}^n 10.8 \frac{\sqrt{f}}{d_{1i}} \ln(1630d_{1i}) + \sum_{i=1}^n \frac{2 \times 1.1}{\sqrt{2AG}} \times \frac{\gamma^{3/2}}{b^2} \times d_{2i}^{1/2} f^{1/2}; \quad (6)$$

$$d_{1i} \geq d_c \geq d_{2i}$$

where i represents the nanoscale precipitate; $\sigma_{sp_{1i}}$ represents the precipitation strengthening contribution to the yield strength of steel based on bypass mechanism; and $\sigma_{sp_{2i}}$ represents the precipitation strengthening contribution to the yield strength of steel based on shearing mechanism.

The d_c of TiC and Fe₃C were estimated to be ~1.5-6 nm and ~4.7-10 nm. The precipitation strengthening effect of TiC precipitates with different sizes was calculated based on the bypass mechanism and for nanoscale iron carbide with less than 10 nm size, the precipitation strengthening effect of precipitates was calculated based on the shearing mechanism, and for nanoscale iron carbides with size larger

than 10 nm, the precipitation strengthening effect was calculated based on the bypass mechanism. The calculated results are listed in Table VI. It can be seen that the corresponding yield strength increment of cementite is 3.3 times of TiC in steel A, while it is 1.7 times of TiC in steel B.

Comprehensive strengthening mechanism

Yield strength is the minimum stress at which dislocations move and plastic deformation occurs. The greater the resistance to dislocation motion, the greater is the yield strength. It is generally agreed that the strengthening mechanism consists of solid solution strengthening, grain refinement strengthening, precipitation strengthening and dislocation strengthening. While, considering that the original density of dislocation is related to the pinning of the precipitated secondary phase particles; the dislocation strengthening can be ignored. According to Takaki,^[37] ultrafine grain strengthening and dislocation strengthening or precipitation strengthening cannot be added together. The underlying reason is that when the value of ultrafine grain strengthening is calculated, the width of bainite or martensite lath is adopted as the grain size. Accompanying bainite or martensite transformation, a large amount of secondary phase particles and dislocations pinned by nanoscale precipitates in the steel, which means that ultrafine grain strengthening includes or involves dislocation strengthening and precipitation strengthening. If dislocation strengthening or precipitation strengthening is added with ultrafine grain strengthening, it will be added twice. Thus, for low-carbon steel, the yield strength of steel equals the sum of solid strengthening, grain refinement strengthening, and precipitation strengthening,

and is given by

$$\begin{aligned}\sigma_y &= \sigma_g + \sigma_s + \sigma_{sp} \\ &= 600D^{-1/2} + \{46[C] + 37[Mn] + 83[Si] + 59[Al] + 2918[N] + 680[P] + 80.5[Ti]\} + \sigma_{sp}\end{aligned}\quad (7)$$

where, $\sigma_y, \sigma_g, \sigma_s, \sigma_{sp}$ and represents the yield strength, the increased strength due to solid solution strengthening and the increased strength due to solid solution strengthening in MPa, respectively; D is the average grain size in μm ; $[X]$ is the weight percent of alloying elements, the elements in ferrite can be determined to be original chemical composition removing carbide forming elements, as shown in Table VII. The components of the yield strength and the total yield strength calculated by equation (6) are presented in Table VIII. The value calculated by equation (7) agrees with the measured values. The contribution of precipitates to yield strength can be greater than ~ 300 MPa, which clearly indicates that precipitation strengthening primarily contributed to the total yield strength.

V. Conclusions

- (1) The microstructure of steel A with the finish cooling temperature of 580°C and cooling rate of 64°C/s mainly consisted of bainite at surface and mid-thickness because of the low finish cooling temperature and the low cooling rate, and the M/A constituent obeyed the Kurdjumov-Sachs (K-S) orientation relationship. In contrast, in steel B, only ferrite and pearlite were observed.
- (2) Random dispersion of carbides was observed in the size range of $\sim 2\text{-}10$ nm in steel A, and the random precipitates did not obey Baker-Nutting (B-N) and Nishiyama-Wassermann (N-W) orientation relationship. While in steel B, both random and interphase precipitates were observed. The interphase TiC precipitates

had NaCl-type crystal structure and obeyed the N-W orientation relationship with respect to ferrite matrix.

- (3) Besides nanoscale TiC, cementite precipitates of size less than ~35 nm were also observed in Ti-microalloyed steel. The measurement of volume fraction and size distribution of nanoscale cementite and microalloyed carbide in steel were carried out using chemical phase analysis and SAXS. The volume fraction of Fe₃C was significant higher than Ti(C, N) of similar size range.
- (4) A good combination of strength and ductility can be obtained at cooling rate and finish cooling temperature of 64 °C/s and 580 °C. The nanoscale cementite of size less than ~35 nm had remarkable precipitation strengthening effect, and the strength increment was 253 MPa, which were ~3.3 times of TiC. The calculated yield strength was consistent with the experimental value.

Acknowledgements

The research was supported financially by National Science Foundation of China (Grant No. 52134002). RDKM gratefully acknowledges support from University of Texas at El Paso, USA.

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Figure captions

Fig. 1. Schematic diagram of NG-TMCP process at the laboratory scale.

Fig. 2. (a, b) SEM and (c, d) TEM micrographs of surface and mid-thickness of steel A.

Fig. 3. Schematic diagram of precipitation at different stages in the experimental steel.

Fig. 4. SEM micrographs of (a) TiN and (b) Ti₂CS formed during solidification and reheating stage, (c) Ti(C, N) formed during the austenite deformation or air cooling and (d) Fe₃C formed during the isothermal holding or air cooling stage.

Fig. 5. (a) TEM, (b) HRTEM and (c) the corresponding FFT diffractogram of TiC precipitate; (d) BF image, (e) DF image and (f) SAD pattern of Fe₃C at the mid-thickness of steel A.

Fig. 6. (a, b) SEM and (c, d) TEM micrographs of surface and mid-thickness of steel B.

Fig. 7. TEM micrograph of (a) interphase TiC, (b) random TiC, (c) Fe₃C, (d) HRTEM image, (e) corresponding FFT diffractogram, and (f) IFFT lattice image interphase TiC; Representative EDX spectra of precipitates (g) in Fig. 7(a) and (h) in Fig 7(c).

Fig. 8. The secondary electron fractographs of CVN impact samples tested at -40°C of (a-d) steel A and (e, f) steel B.

Fig. 9. Size distribution of (a) MC-type precipitate and (b) M₃C-type precipitate in steels A and B.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Table I. Chemical composition of the tested steel used in this study (wt.%)

C	Mn	Si	Al	Ti	P	S	N	O
0.15	0.98	0.28	0.02	0.08	0.015	0.005	27 ppm	48 ppm

Table II. Thermal mechanical processing parameters of the tested steels

Steel	Plate thickness	Rolled in recrystallization temperature region		Rolled in non-recrystallization temperature region		Cooling rate, °C/s	Final temperature, °C	Type of cooling
		Start, °C	Finish, °C	Start, °C	Finish, °C			
A	12	1150	1096	889	864	64	580	Holding for 20, air cooling
B	12	1150	1135	883	875	36	700	Holding for 20, air cooling

Table III. Mechanical properties of the tested steel

Steel	Yield strength, MPa	Tensile strength, MPa	Elongation, %	Yield ratio	Impact toughness (V-notch, J)	
					-20 °C	-40 °C
A	650	750	19.2	0.87	93.4	65.7
B	590	718	18.3	0.83	24.6	17.3

Table IV. Structural parameters of precipitate.

Phase structure	Lattice constant, nm	Crystal system
M ₃ (C,N)	a ₀ =0.4523-0.4530, b ₀ =0.5088-0.5080, c ₀ =0.6743-0.6772	Orthorhombic
Ti ₂ CS	a ₀ =0.3210-0.3240, c ₀ =0.1.1203-1.1308, c/a=3.49	Hexagonal
TiC	a ₀ =0.431-0.433	Face centered cubic
Ti(C,N)	a ₀ =0.425-0.427	Face centered cubic

Table V. Mass fraction of elements in M₃C and MC in steel, Mass percent

Steel	Phase	Mass fraction in steel of elements			Mass fraction of phase in steel
A	(Fe _{0.984} Mn _{0.016}) ₃ C	Fe	Mn	C*	1.6128
		1.4806	0.0243	0.1079	
	Ti(C _{0.654} N _{0.346})	Ti	C*	N	0.0322
		0.0254	0.0042	0.0026	
	Ti ₂ CS	Ti	S	C*	0.0253
		0.0173	0.0058	0.0022	
B	(Fe _{0.974} Mn _{0.026}) ₃ C	Al	N		0.0017
		0.0011	0.0006		
	(Fe _{0.974} Mn _{0.026}) ₃ C	Fe	Mn	C*	1.6740
		1.5220	0.0400	0.1120	
	Ti(C _{0.768} N _{0.232})	Ti	C*	N	0.0576
		0.0457	0.0088	0.0031	
	Ti ₂ CS	Ti	S	C*	0.0253
		0.0169	0.0021	0.0057	
	AlN	Al	N		0.0008
		0.0005	0.0003		

Note: C* represents calculated value

Table VI. Contribution of Fe₃C and TiC to the yield strength of steel A and B

Steel	Diameter Range, nm	TiC		Fe ₃ C		Total increment, Mpa
		Volume Fraction, Pct	Yield Strength Increment, MPa	Volume Fraction, Pct	Yield strength increment, MPa	
A	1~5	0.0198	47.4	0.712	144.6	331.1
	5~10	0.0013	12.8	0.074	15	
	10~18	0.0016	10.2	0.252	51.2	
	18~36	0.0028	7.4	0.209	42.5	
	Σ	0.0255	77.8	1.247	253.3	
B	1~5	0.0284	57.1	0.123	118.7	279.4
	5~10	0.0064	27.1	0.0014	12.4	
	10~18	0.0015	9.7	0.0014	9.5	
	18~36	0.0036	8.4	0.0654	36.5	
	Σ	0.0399	102.3	0.191	177.1	

Table VII. The solid solution elements content in the experimental steels (wt.%)

Steel	C	N	Mn	Al	Ti	Si	P
A	0.0357	0.0018	0.95	0.019	0.0373	0.28	0.015
B	0.0271	0.0016	0.93	0.02	0.0174	0.28	0.015

Table VIII. Comparison of calculated yield strength values with those actual measured

Steel	Grain Size <i>d</i> , μm	Calculated Yield Strength Values, MPa				Actual Measured σ _s , MPa
		Grain refinement strengthening	Solid solution strengthening	Precipitation strengthening	σ _s	
A	5-6.5	235.3-268.3	78.6	331.1	645-678	650
B	5.5-7.1	223.9-255.8	76.2	279.4	579.5-611.4	590

TEM micrograph of (a) interphase TiC, (b) random TiC, (c) Fe₃C, (d) HRTEM image, (e) corresponding FFT diffractogram, and (f) IFFT lattice image interphase TiC