Influence of the Thermal Deformation Treatment on the Structural State and Properties of Ti-Mo Microalloyed Steels of the Ferritic Class

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Abstract. Investigation on influence of thermal deformation treatment on the special features of structural state, phase precipitates, strengthening mechanisms, and mechanical properties was carried out for low-carbon Ti-Mo microalloyed steel of ferritic class. The following parameters were analyzed: the finishing temperature of rolling and the cooling rate of the steel after rolling end to the coiling temperature. Methods of scanning and transmission electron microscopy, thermodynamic calculation, kinetic analysis, and testing of mechanical properties were used. It was shown that with an increase in the cooling rate from 3 to 22 °C/s, the type of carbide precipitates changes from interphase to ferritic. When fast cooling is applied, mainly mechanisms of dislocation and grain boundary strengthening are realized. When cooling is slowed down, the fraction of precipitation hardening increases. It was established that ferritic precipitates make a smaller contribution to precipitation hardening of steel than interphase ones. To create conditions favorable for the formation of interphase precipitates, the rates of \( \gamma \rightarrow \alpha \) phase transformation and cooling should be close.

1. Introduction

High-strength low-carbon microalloyed steels of a ferritic class are promising for widespread use in transport, construction, engineering, and other branches of modern technology and industry due to a remarkable combination of difficultly-to-combine technological and service properties [1–3]. In particular, they possess simultaneously high strength, ductility, formability, and fatigue and corrosion resistance with good weldability. An effective increase in the strength characteristics of the considered steels having a ferritic structure is achieved as a result of a superposition of various strengthening mechanisms [1]. The main ones, grain refinement and dispersion hardening, in many respects, are controlled by the presence of phase precipitates of different types and dispersion. The dependence of the phase precipitate characteristics on the chemical composition and parameters of the thermal deformation treatment of steel, and their effect on the microstructure and mechanical properties of the metal has been the subject of many studies (see, for example, [4–8]). As a result, hot-rolled Ti-Mo microalloyed steels with a yield strength of up to 700 MPa and satisfactory ductility and other properties were produced [9]. However, in order to stably provide and continue the development and increase of strength characteristics, more precise information is needed on the specifics of the influence of metal
processing parameters and resulting phase precipitates on the implementation of different strengthening mechanisms and properties of rolled products.

Grain-boundary strengthening is facilitated by the carbide, carbonitride precipitation in austenite during hot deformation [10], which inhibit recrystallization and contribute to the formation of a fine-grained microstructure. For dispersion hardening, precipitates from 1 to 3 nm in size are most effective [11]. A as a rule, they are formed during the \( \gamma \rightarrow \alpha \) phase transformation (interphase) and upon further cooling of the steel (ferritic). Interphase precipitates are arranged in layers parallel to the moving front of the \( \gamma/\alpha \) transformation [12]. Their presence leads to an increase in strength of steel not only by the dispersion hardening mechanism, but also contribute to the formation of a fine-grained structure due to inhibition of grain growth. The interconnectedness of various strengthening mechanisms significantly complicates making unambiguous conclusions about the influence of technological parameters of metal processing and the characteristics of phase precipitates on mechanical and other properties. In accordance with the results of studies [13–16], it has been unequivocally established that the maximum strength properties are achieved if the temperature of coiling hot-rolled strip into a roll \( (T_c) \) is 650 °C. However, the effect of rolling end including finishing temperature \( (T_f) \), and especially the cooling rate from \( T_f \) to \( T_c \) on the features of microstructure formation, nanosized carbide precipitates, and the properties of low-carbon Ti-Mo microalloyed ferritic steels have not yet been determined. Their establishment, using the optimum \( T_c = 650 \) °C, has been the subject of this work.

2. Materials and methods
The study was performed using steel of laboratory vacuum induction smelting. The chemical composition was as follows (wt. %): 0.048C, 0.17Si, 1.29Mn, 0.003P, 0.004S, 0.06Cr, 0.06Ni, 0.20Mo, 0.01Cu, 0.09Al, 0.13Ti, 0.0042N. The billets were heated in a resistance furnace to a temperature of 1250 °C, held for 1 hour, and rolled into strips 3 or 8 mm thick. The rolled products were cooled in three ways: in the air-water or air stream created by the compressor, as well as in air to obtain various cooling rates. After cooling to 650 °C, the strips were placed in a furnace heated to the same temperature and held for 30 minutes, then cooled with the furnace to room temperature, thereby simulating cooling of a coiled roll. Samples were prepared from the obtained strips for mechanical tests and microstructure studies. The mechanical properties were determined using HECKERT FP-100/1 tensile testing machine. The results obtained together with the hot-rolling parameters are presented in the table 1.

| Lot No. | Rolled thickness, mm | \( T_f \), °C | Cooling rate to \( T_c \), °C/c | \( \sigma_{0.2} \), MPa | \( \sigma_B \), MPa | \( \delta \), % |
|---------|----------------------|--------------|-----------------|-----------------|-----------------|--------|
| 1       | 8                    | 950          | 6               | 670             | 780             | 20.0   |
| 2       | 8                    | 950          | 5               | 650             | 770             | 20.0   |
| 3       | 8                    | 950          | 3               | 620             | 770             | 20.5   |
| 4       | 3                    | 900          | 22              | 690             | 800             | 18.0   |
| 5       | 3                    | 900          | 10              | 680             | 780             | 16.5   |
| 6       | 3                    | 900          | 7               | 640             | 740             | 15.0   |

The microstructure was studied by scanning electron microscope using a JSM-6610LV (JEOL) instrument equipped with an INCA Energy Feature XT energy dispersive microanalysis system, INCA Wave 500 wave dispersive spectrometer, and transmission electron microscopy (TEM) using a JEM200CX microscope. The type of nanosized precipitates was determined by the original method based on the analysis of their reflections in microdiffraction images [2].

The thermodynamic calculation of the regions of phases existence in the steel under study was carried out using a computer model [17, 18], implemented on the basis of proprietary software. It consisted in
solving the problem of finding the conditions of thermodynamic equilibrium in multicomponent, multiphase systems with given external and internal parameters (temperature, pressure, chemical composition). As a result, the types of equilibrium phases, their quantities and compositions were determined by analysis of the complete possible set for an alloying system of steel. The kinetics of TiC precipitate formation in austenite was simulated using the developed model [19].

3. Results

As can be seen from the table 1, the values of yield ($\sigma_{0.2}$) and tensile ($\sigma_B$) strengths of the rolled products are in the ranges of 620–690 MPa and 740–800 MPa, respectively, and depend on both the cooling rate and $T_f$. Lots of steel subjected to faster cooling (No. 4–6) have higher strength properties. At the same time, in the case of a lower cooling rate, but a higher $T_f = 950 \, ^\circ C$ (No. 1, 2), the values of $\sigma_{0.2}$ and $\sigma_B$ are higher than those of the rolled steel No. 6. At the maximum cooling rate of steel, the highest values were achieved: $\sigma_{0.2} = 690 \, MPa$ and $\sigma_B = 800 \, MPa$. The relative elongation of the obtained samples is higher at $T_f = 950 \, ^\circ C$ and does not depend on the cooling rate. The noted circumstances indicate the preference for using $T_f$ equal to 950 °C compared with 900 °C. With an equivalent cooling rate, in this case, a complex of higher properties of rolled products is achieved. For the highest cooling rate (22 °C/s), the ductility remains quite high - 18%.

The results of thermodynamic calculation of the equilibrium phase composition depending on the temperature for the studied steel in the range of 400–1350 °C are presented in figure 1.

![Temperature dependences of equilibrium fractions of phases in the studied steel.](image)

**Figure 1.** Temperature dependences of equilibrium fractions of phases in the studied steel.

It can be seen that at heating temperatures for rolling, stable phases in austenite are TiN nitride and titanium carbosulfide - Ti$_4$C$_2$S$_2$. The titanium content in the studied steel significantly exceeds its required amount for the complete binding of nitrogen. Therefore, nitrogen is completely removed from austenite at high temperatures. As a result, the precipitation of AlN becomes impossible, and titanium carbide formation below 1100 °C is possible in the region of hot deformation temperatures in austenite and in ferrite. This means that formation of austenitic precipitates can be expected. However, from the kinetic dependences (figure 2) it follows that the reaction of titanium carbide precipitation at the used
high temperatures of finishing rolling will be far from complete, especially for $T_f = 950 \, ^\circ\text{C}$. Therefore, a sufficiently high titanium content will be retained in the steel under study for the further formation of interphase and ferritic precipitates of TiC, including with the participation of Mo [14–17].

Figure 2. Isothermal precipitation of titanium carbide at 900 °C and 950 °C.

According to the calculation, the temperature of $A_{e3}$ is 873.4 °C. The formation of cementite is possible below 683.4 °C. This temperature can be taken as $A_{e3}$. The conditions for the formation of Mo$_2$C and complex iron carbide M$_7$C$_3$ occur at temperatures below 637 and 600 °C, respectively. As a result of the significant consumption of carbon on the titanium carbide formation, including Mo containing precipitates [14–17], and diffusion inhibition, the precipitation of cementite, Mo$_2$C, and M$_7$C$_3$ is almost completely suppressed.

The results of the study using scanning electron microscopy show that the metal matrix of rolled products produced by all modes consists mainly of block ferrite, which has mostly equiaxed block shape, less often elongated. The dislocation density in ferrite varies from moderate to high with increasing cooling rate. Cementite or perlite was not detected in any of the rolling products.

Carbide precipitates of submicron sizes in the studied rolled samples are few (lots No. 4–6) or absent (lots No. 1–3). This indicates that their formation in austenite practically does not occur, as follows from the data in figure 2.

In all studied rolled samples, nanosized carbide precipitates are present (figure 3). Basically, these are precipitates formed in ferrite and of a mixed type (nucleated and partly grown by the interphase mechanism, and then increased their volume in the ferrite region), less often - interphase precipitates. In different areas, in variable proportions, as a rule, simultaneously precipitates of different types are present, including within the same ferrite block. However, there are areas in which precipitates of only or almost only one type are observed. Typical sizes of mixed-type precipitates are 2–3 nm (up to ~ 4 nm); in some areas they are larger: 2-5 nm (up to ~ 8 nm). Their significant part (possibly large) has a size of less than 2 nm. It is seen that with an increase in the cooling rate, the precipitation mechanism shifts more and more towards the realization of a mixed and ferritic mechanism. In rolled products cooled at maximum rate (No. 4), fields are observed where interphase precipitates with a very small distance between layers are visible, followed by sections with pure ferritic precipitates (figure 3b). Interphase precipitates are more common in rolled samples produced by a lower cooling rate.
4. Discussion

An analysis of the obtained results of the study including the mechanical properties and microstructure shows that an increase in the strength characteristics of rolled products is observed with a rise of the cooling rate and is accompanied by an increase in the dislocation density without changing the morphology of the ferrite structure. Moreover, the main role of phase precipitates in strengthening during rapid cooling consists in dispersion hardening due to the formation of ferritic precipitates mainly at dislocations, in the form of randomly located separate or small clusters of precipitates. At the same time, austenitic precipitates are practically absent, and the fraction of interphase particles is quite small.

With a decrease in the cooling rate of rolled products, the mechanism of austenite → ferrite transformation changes accompanying by the formation of a much less dislocation structure, which leads to a decrease in strength properties. In addition, the decrease in the rate of phase transformation taking place in this case contributes to the formation of interphase precipitates and to increase, respectively, the contribution of precipitation hardening to the strengthening of steel.

The dependence of realization of the interphase precipitation mechanism on the cooling rate and finishing temperature of rolling can be explained by analogy with the approach [20, 21] on the basis of an analysis of two following processes: phase precipitation and γ → α phase transformation in steel. The nucleation of a new precipitation layer at the γ/α phase boundary occurs when a certain critical titanium concentration is reached, which is determined from the thermodynamic conditions of TiC nucleation. When the phase boundary moves, titanium diffuses from it to the nucleated precipitates. This diffusing titanium flux is compensated by its transition from the γ phase through the phase boundary. Thus, the titanium concentration at the moving γ/α boundary increases, and the moment of reaching the critical concentration for nucleation determines the distance between the layers. Therefore, the rates of the movement of the interphase boundary and the titanium diffusion, which ensures the nucleation and growth of carbide precipitates, should be comparable. If the metal is cooled too quickly, the rate of the interphase boundary turns out to be too high and the formation of precipitates by the interphase mechanism is violated: after passing through the front of the phase transformation, the ferrite remains supersaturated with respect to the carbide phase, which leads to the disordered formation of precipitates in ferrite. Therefore, there is an optimal combination when the nucleation and growth of interphase precipitates takes place, but the distance between the layers is minimal.

The conclusion made is in good agreement with the results of the analysis of the type and amount of precipitates in the studied steel, depending on the cooling rate. The increase in the cooling rate of rolled products results in the decrease in the distance between the layers of interphase precipitates and their fraction. The maximum cooling rate of rolled lot No. 4, apparently, is almost the limit for the implementation of the mechanism of interphase precipitation at a given $T_f$. 

![Figure 3. Results of the TEM study (dark-field image in the TiC reflection) of carbide precipitates in the samples: a - No. 3, b - No. 4.](image-url)
5. Conclusion
The highest strength properties $\sigma_{0.2} = 690$ MPa, $\sigma_B = 800$ MPa with good ductility $\delta = 18\%$ of rolled products from the studied steel containing wt.%: C-0.048, Mo-0.20, Ti-0.130, were achieved when using a maximum cooling rate of 22 °C/s from the finishing temperature of rolling 900 °C to $T_c = 650$ °C.

Simultaneously higher strength properties and ductility are achieved at a higher finishing temperature of rolling - 950 °C, compared with 900 °C. Strength characteristics also regularly improved with increasing cooling rate of rolled products from $T_f$ to $T_c$.

With rapid cooling of rolled products, high strength characteristics are achieved as a result of the implementation, mainly, of dislocation and grain-boundary hardening mechanisms. This is due to the formation of a higher dislocation structure of ferrite and ferritic carbide precipitates.

A decrease in the cooling rate slows down the phase transformation, which contributes to the formation of interphase precipitates and to increase, respectively, the fraction of precipitation hardening in the strengthening of steel.

References
[1] Lesch C, Kwiaton N, and Klose F B 2017 Steel Research Int. 88 1700210
[2] Zaitsev A, Koldaev A, Arutyunyan N, Dunaev S and D’yakonov D 2020 Processes 8 646
[3] Deng X, Fu T, Wang Z, Liu G, Wang G and Misra R D K 2017 Met. Mater. Int. 23 175
[4] Bai D Q, Yue S, Sun W P and Jonas J J 1993 Metall. Mater. Trans. A 24 2151
[5] DeArdo A J 2003 Int. Mater. Rev. 48 371
[6] Sanz L, Pereda B and López B 2017 Mater. Sci. Eng. A 685 377
[7] Jiao Z B, Luan J C, Miler M K, Chung Y W and Liu C T 2017 Mater. Today 20 142
[8] Zhang K, Wang H, Sun X J, Sui F L, Li Z D, Pu E X, Zhu Z H, Huang Z Y, Pan H B and Yong Q L 2018 Acta Metall. Simica (English Letters) 31 997
[9] Funakawa Y, Shiozaki T, Tomita K, Yamamoto T and Maeda E 2004 ISIJ Int. 44 1945
[10] Jonas J J and Weiss I 2013 Met. Sci. 13 238
[11] Gladman T 1999 Mater. Sci. Technol. 15 30
[12] Lagneborg R, Siwecki T, Zajac S and Hutchinson B 1999 Scand. J. Metall. 28 1
[13] Koldaev A V, Zaitsev A I, Krasnyanskaya I A and D’yakonov D L 2019 Metallurgist 63 487
[14] Zhang K, Li Z, Wang Z, Sun X and Yong Q 2016 J. Mater. Res 31 1254
[15] Park D B, Huh M Y, Shim J H, Suh J Y, Lee K H and Jung W S 2013 Mater. Sci. Eng. A 560 528
[16] Funakawa Y and Seto K 2007 Mater. Sci. Forum. 539-543 4813
[17] Shaposhnikov N G, Koldaev A V, Zaitsev A I, Rodionova I G, D’yakonov D L and Arutyunyan N A 2016 Metallurgist 60 810
[18] Shaposhnikov N G, Mogutnov B M, Polonskaya S M, Kolesnichenko A P and Belyavskii P B 2004 Materials Science 11 2
[19] Koldaev A V, Shaposhnikov N G, 2016 Probl. Chern. Met. Materials Science 3 5
[20] Lagneborg R and Zajac S 2001 Metall. Mater. Trans. A 32 39
[21] Zajac S 2005 Mater. Sci. Forum. Trans. Tech. Publ. 500 75

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