

Article

Applications and Thermodynamic Analysis of Equilibrium Solution for Secondary Phases in Ti–N–C Gear Steel System with Nano-Particles

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Abstract: Thermodynamic analysis and computations of the equilibrium solution for the multivariable secondary phase in steels have been conducted, based on the chemical equilibrium. Solid solution precipitation in the Ti–N–C microalloy steel for the secondary phase was analyzed, and its engineering application in the development of carburizing gear steels was investigated. The complete dissolution temperature increases with more C, N, or Ti in gear steels, and the effects of Ti and N are more significant than C. At a given temperature, the amount of [Ti] increases naturally with more Ti element content, while it decreases with more C or N elements content. It declines rapidly in the complete dissolution temperature range in steels until 1100 °C. The effective activity coefficient k_1 increases with the temperature decreases, and increases with the higher content of Ti or C, while it decreases with the higher N content under the same temperature. Thermodynamic analysis shows that nitrogen has been precipitated largely as TiN micron-particles above 1400 °C in gear steels. Then, titanium precipitated mainly as TiC nano-particles, thus this secondary phase can hinder grain coarsening during heat treatment.

Keywords: gear steels; thermodynamic analysis; secondary phase; nano-particles

1. Introduction

Microalloying elements in steel form solid solutions with the iron matrix and contribute to the formation of carbonitrides, having different effects [1,2]. It is known that the niobium, vanadium, and titanium microalloying elements, in combination with C or N, can form multiple secondary phases and significantly improve the comprehensive performance of the high-strength low-alloy (HSLA) steels through retarding grain growth at high temperature and precipitation strengthening in the iron matrix [3,4]. Thus, it is possible to improve the strength and toughness of steels based on reasonable control of the secondary phase in the solid solution and precipitation in the iron matrix [5]. It is important to conduct a rigorous theoretical analysis of the multiple secondary phases in special steels to effectively control steel microstructure and properties [6–9].

Quantitative computations of the equilibrium solution of complex secondary phases is one of the challenging problems in this area [10–12]. In this paper, according to the thermodynamic analysis

model of the equilibrium solution for the multivariable secondary phases in special steels [13,14] based on the mass balance and solubility product equations—solid solution precipitation of the secondary phase in the Ti–N–C microalloy steel was analyzed, along with analysis of the effects of different elements on the solid solution and precipitation temperature. Taking its engineering application in carburizing gear steels as an example, and combined with heat treatment, the effects of grain coarsening by secondary phase precipitates in 20CrMnTi high quality gear steel at different temperatures were studied, the microstructure of the secondary phase in steel was observed, providing technical support for the enterprise production process development, and optimizing the microalloy composition. In turn, scientific design of the components in multivariate microelements could be conducted based on the specific production process.

2. Thermodynamic Analysis

The microalloying elements in combination with C or N, can form multiple secondary phases; these multiple secondary phases are comprised of carbides and nitrides with similar crystal structure, exhibiting continuous or extended mutual solubility. Therefore, the resulting multivariable secondary phases can be described by the chemical formula $(M_1, M_2)(C, N)$. Valid for small element concentrations, the microalloying elements M_1 and M_2 , as well as the interstitial elements C and N form dilute solutions in the matrix and their activities obey the Henry's law. In this case, the effective activity coefficients of the components M_1C , M_2C , M_1N and M_2N are assumed to be k_1 , k_2 , m_1 and m_2 , respectively, and the total molar fraction of the $M_1(k_1+m_1)M_2(k_2+m_2)C_{(k_1+k_2)}N_{(m_1+m_2)}$ carbonitride formed in the steel is t moles [14,15]. This carbonitride can be seen as a mixture of the following amounts of pure binary carbides and nitrides: k_1t mole M_1C , k_2t mole M_2C , m_1t mole M_1N and m_2t mole M_2N . Therefore, based on the chemical equilibrium, the thermodynamic analysis model and computing method of the equilibrium solution for the multivariable secondary phase in steels have been developed, according to the mass balance and solubility product equations for the quaternary secondary phase, or more. Therefore, the solid solution precipitation of the secondary phases formed in steel is $Ti(C_{k_1}N_{m_1})$ in the Ti–N–C microalloy steel system, and the coefficient of solid solubility of the product is taken as in the reference [14]. Therefore,

$$\log \frac{[M_1] \times [C]}{k_1} = 2.75 - 7000/T \quad (1)$$

$$\log \frac{[M_1] \times [N]}{m_1} = 0.32 - 8000/T \quad (2)$$

$$M_1 - [M_1] = t(k_1 + m_1)A_{m_1} \quad (3)$$

$$C - [C] = k_1tA_C \quad (4)$$

$$\frac{M_1}{A_{m_1}} + \frac{C}{A_C} + \frac{N}{A_N} = \frac{[M_1]}{A_{m_1}} + \frac{[C]}{A_C} + \frac{[N]}{A_N} + 2t \quad (5)$$

$$k_1 + m_1 = 1 \quad (6)$$

where M_1 , C and N are the mass percentages of Ti, C and N, respectively; A_{m_1} , A_C and A_N are the atomic weights of Ti, C, and N, respectively; and $A_{Ti} = 47.9$, $A_N = 14$, $A_C = 12$, $[M_1]$, $[C]$ and $[N]$ are the concentrations (in wt. %) of the respective elements dissolved in the solution; T is the temperature; and t is the total molar fraction of the carbonitride $Ti(C_{k_1}N_{m_1})$ formed in the steel; thus, these ternary secondary phases can be seen as a mixture of the following amounts of pure carbides and nitrides: k_1t mole TiC , m_1t mole TiN . Equations (1)–(6) have six unknowns, which are solved for numerically to determine the equilibrium state. For a given steel at any appropriate temperature, the equilibrium matrix composition, precipitate composition, and precipitate volume fraction can be determined (i.e., $[M_1]$, $[C]$, $[N]$, k_1 , m_1 and t).

It is important to control the combined precipitate in the Ti-bearing gear steels, however, little information is currently available regarding gear steels. In this paper, the numerical iteration method was used for a series of Ti–N–C microalloyed steels with (0.05%–0.35%) C, (0.0025%–0.015%) N and (0.01%–0.08%) Ti composition. The equilibrium solution thermodynamic state, including concentrations of the respective elements in solution [C], [N] and [Ti] from 950 °C to complete dissolution temperature, k_1 and m_1 constants, as well as the total molar fraction of carbonitrides have been investigated. The complete dissolution temperatures for different Ti–N–C system microalloyed steels are shown in Table 1. The carbonitride complete dissolution temperature increases with higher C, N, or Ti levels in Ti–N–C system microalloyed steels. It should be noted that the effects of N and Ti additions on the complete dissolution temperature are expected to be greater compared with C. As is known for microalloyed gear steels, if the complete dissolution temperature is above the liquidus temperature, constitutional liquation of the carbonitrides would occur, so it is important to scientifically optimize the content of Ti, N and C elements in the actual production.

Table 1. Complete dissolution temperature changes with C, N and Ti composition variation in the Ti–C–N system steels.

Variation of C (0.0065N-0.02Ti)		Variation of N (0.20C-0.02Ti)		Variation of Ti (0.20C-0.0065N)	
C (wt. %)	T_{AS} (°C)	N (wt. %)	T_{AS} (°C)	Ti (wt. %)	T_{AS} (°C)
0.05C	1630.69	0.0025N	1470.73	0.01Ti	1507.28
0.10C	1632.35	0.005N	1586.74	0.03Ti	1719.72
0.20C	1635.65	0.01N	1722.56	0.045Ti	1811.57
0.35C	1640.54	0.015N	1812.61	0.08 Ti	1957.49

The thermodynamic analysis results of the Ti–C–N system microalloyed gear steels are shown in Figures 1–3. At a given temperature, the dissolved Ti content increases naturally with the content of microalloyed element Ti increasing, and decreases obviously with the increase in the content of element N, while there seems to be no obvious change with the variation of element C content. The dissolved Ti content ([Ti]) decreases naturally as the temperature decreases, especially in the complete dissolution temperature range until 1100 °C, thus Ti is precipitated easily in the high temperature phase. The coefficient k_1 increases as the temperature decreases, and at a given temperature, the coefficient k_1 increases with the content of C or Ti increasing, while it decreases obviously with the content of N increasing. Therefore, in engineering application, for higher [Ti] dissolved in Ti-bearing microalloyed steels, the addition of N should be decreased during the microalloy composition design, which is significant to control the secondary phase precipitate at the required temperature.

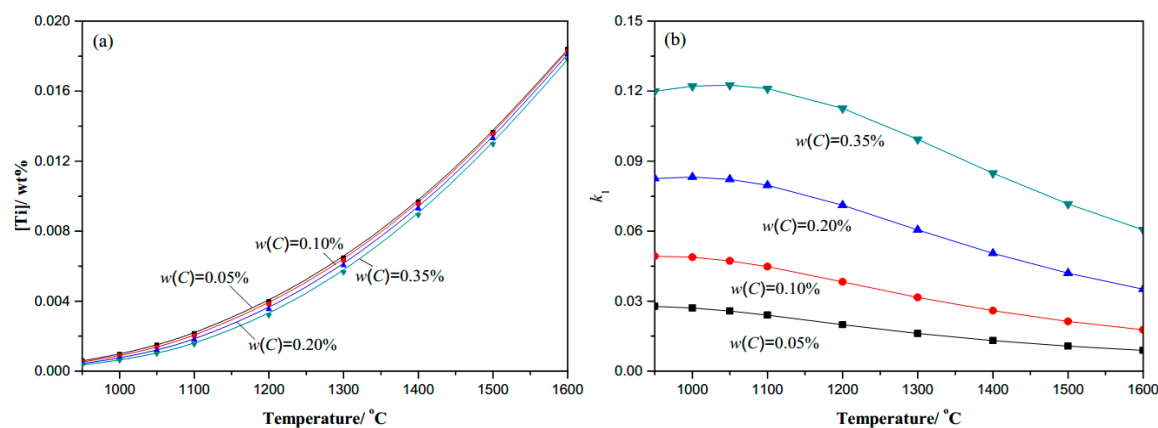


Figure 1. C-0.0065N-0.02Ti microalloy steel: (a) Ti content changes with temperature; (b) k_1 coefficient changes with temperature.

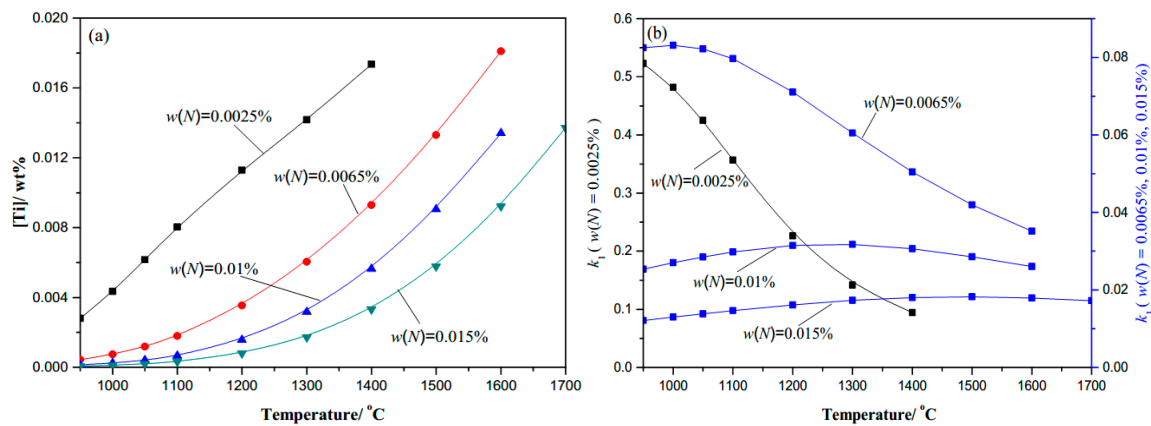


Figure 2. 0.20C-N-0.02Ti microalloy steel: (a) Ti content changes with temperature; (b) k_1 coefficient changes with temperature.

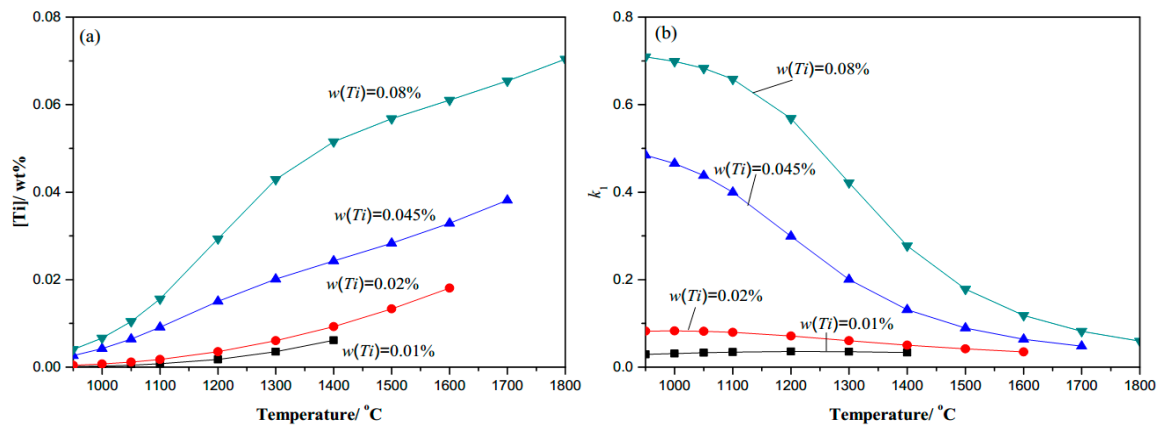


Figure 3. 0.20C-0.0065N-Ti microalloy steel: (a) Ti content changes with temperature; (b) k_1 coefficient changes with temperature.

3. Engineering Applications

At present, the most widely used carburizing gear steel is 20CrMnTi. The main machining process is blanking → heating (950–1150 °C) → hot forging → heat preservation (880 °C for 8 h) → turning → gear milling → carburizing (950–1000 °C for 6 h) → quenching → low temperature tempering → finishing. The steel is required to have lower grain growth tendency at high temperature, which is ensured by keeping the fine matrix grain in the process of carburizing, thereby obtaining good toughness.

To optimize the composition with balanced comprehensive performance of Ti-bearing microalloyed steel, an engineering application of microalloyed gear steel 20CrMnTi was taken as an example here. The 20CrMnTi steel was produced by Fangda Special Steel Technology Co., Ltd (Nanchang, China); the production process of this steel was converter smelting → LF refining → VD vacuum processing → continuous casting → continuous rolling → testing processes. The dimensions of the rolling slab used were 160 mm × 160 mm × 9500 mm, and the rolling temperature was about 1050 °C. After rough rolling, middle rolling and finishing rolling, the steel was rolled into the required product specification (Φ30 mm); the finishing rolling temperature was controlled at about 950 °C. The investigated samples have the chemical composition shown in Table 2. The Ti–N–C system gear steels were heat treated at 850 °C, 900 °C, 950 °C and 1000 °C for 1 h in the intermediate frequency furnace, respectively, then air-cooled to ambient temperature, and the grain coarsening was studied under different temperatures. Metallographic specimens were prepared using conventional grinding,

the polishing method and etched with 3% nitric acid alcohol; microstructures were characterized by 9XB-PC light microscopy (LM) (Shanghai optical instrument factory, Shanghai, China), Zeiss Auriga scanning electron microscope (SEM) (Zeiss, Dresden, Germany) and JEOL JEM-2100 transmission electron microscopy (TEM) (JEOL, Tokyo, Japan). The TEM samples were prepared by cutting 3 mm disks from the hot-rolled bars. The disks were mechanically thinned to a thickness of 100 μm and then the foils were thinned further for electron transparent area using a focused ion-beam, and the hardness was tested by a HB-3000 Brinell hardness tester, etc.

Table 2. Chemical composition of the 20CrMnTi gear steel.

Steel	C	Si	Mn	Cr	Ti	N	P	S
Standard	0.17–0.23	0.17–0.37	0.80–1.15	1.00–1.35	0.04–0.10	≤ 0.01	≤ 0.035	≤ 0.035
Sample	0.22	0.22	0.88	1.14	0.066	0.0067	0.023	0.003

Based on the developed thermodynamic model, the change of the solid solution content of the microalloying elements and the relative content of binary precipitates with temperature can be obtained, as shown in Figure 4. Verified by the thermodynamic model, the amount of precipitates depends on Ti and N content as the temperature is reduced. The actual chemical composition of the carbonitrides as a function of temperature, expressed by the values of k_1 and m_1 , strongly depends on the steel composition. The real content change of the TiC and TiN components with the temperature can be approximated, based on Figure 4b. The thermodynamic analysis shows that the dissolved Ti content is 0.03915%, the dissolved C content is 0.21843%, while the dissolved N content is only 0.00067% in the gear steel, and the coefficient k_1 is 0.23238, and the coefficient m_1 is 0.76762 at 1400 $^{\circ}\text{C}$, thus nitrogen has been precipitated primarily in the TiN micro-particles above 1400 $^{\circ}\text{C}$. The complete dissolution temperature is calculated to be 1915.02 $^{\circ}\text{C}$ by the model, which is 400 $^{\circ}\text{C}$ higher than the corresponding liquidus temperature of 1514.89 $^{\circ}\text{C}$ [16]. It is obvious that constitutional liquation of the strong carbonitrides would occur in this sample.

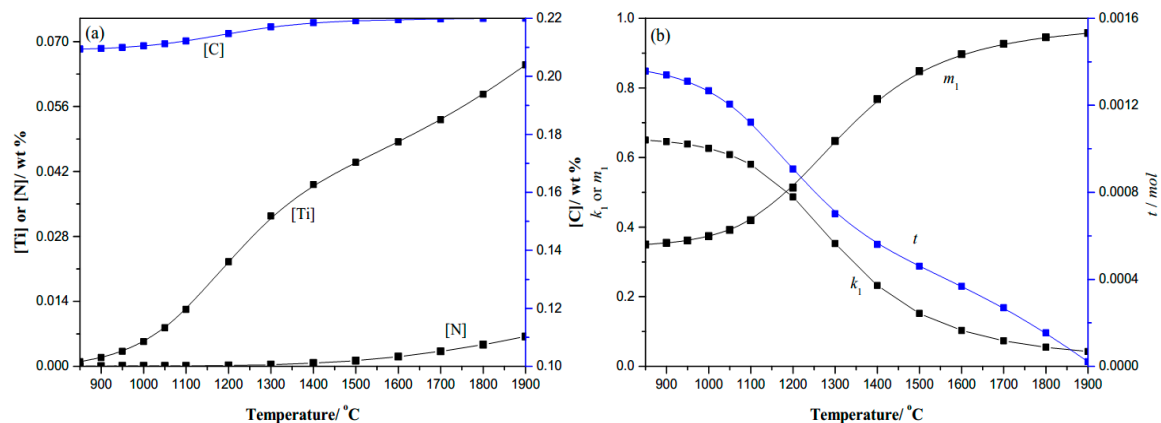


Figure 4. The 0.22% C-0.0067% N-0.066% Ti gear steel: (a) Solid solution contents change with temperature; (b) k_1 , m_1 and t change with temperature.

The carburizing gear steel 20CrMnTi microstructure is shown in Figure 5, where yellow secondary phase in the form of water chestnuts is visible in the etched and un-etched images. The corresponding SEM image is shown in Figure 6a, along with the energy dispersive spectroscopy (EDS) results presented in Figure 6b. The spectral components of the secondary phase are listed in Table 3. The secondary phase precipitation is mainly TiN; this result once again proved that constitutional liquation of the strong carbonitrides has occurred in the sample, which is consistent with the thermodynamic analysis results. In order to accurately control the size and shape of the secondary

phase in steel, the content of each element must be scientifically selected, especially Ti, N and C to ensure that the multivariable secondary phase would precipitate at the required temperature.

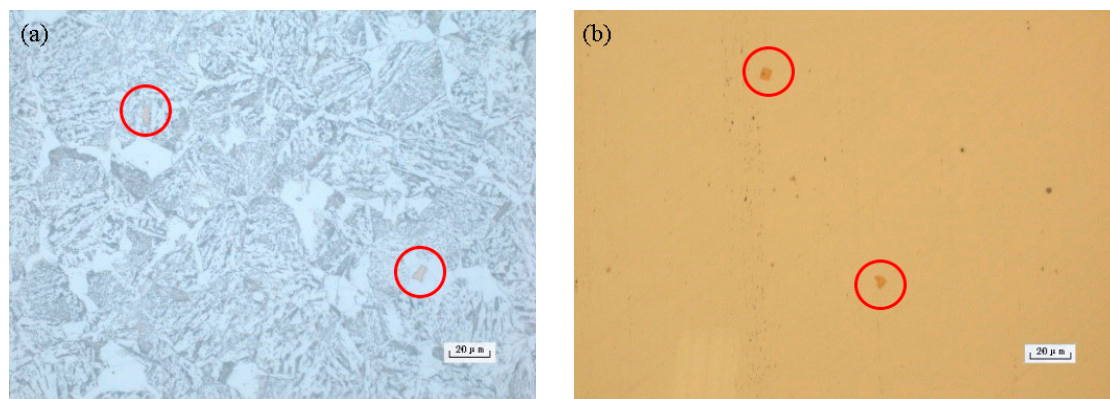


Figure 5. The 20CrMnTi steel microstructure: (a) Optical image after etching; (b) Optical image without etching.

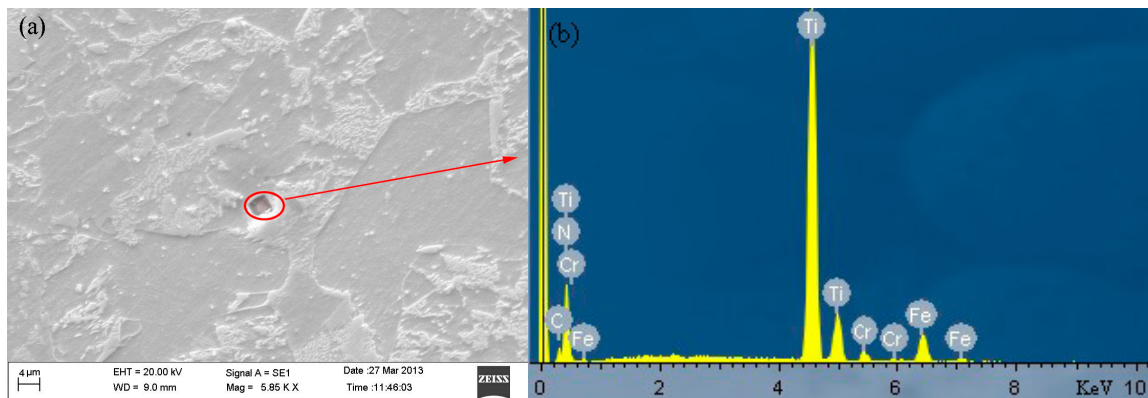


Figure 6. (a) scanning electron microscope (SEM) image of the secondary phase in 20CrMnTi; (b) Energy dispersive spectroscopy (EDS) results.

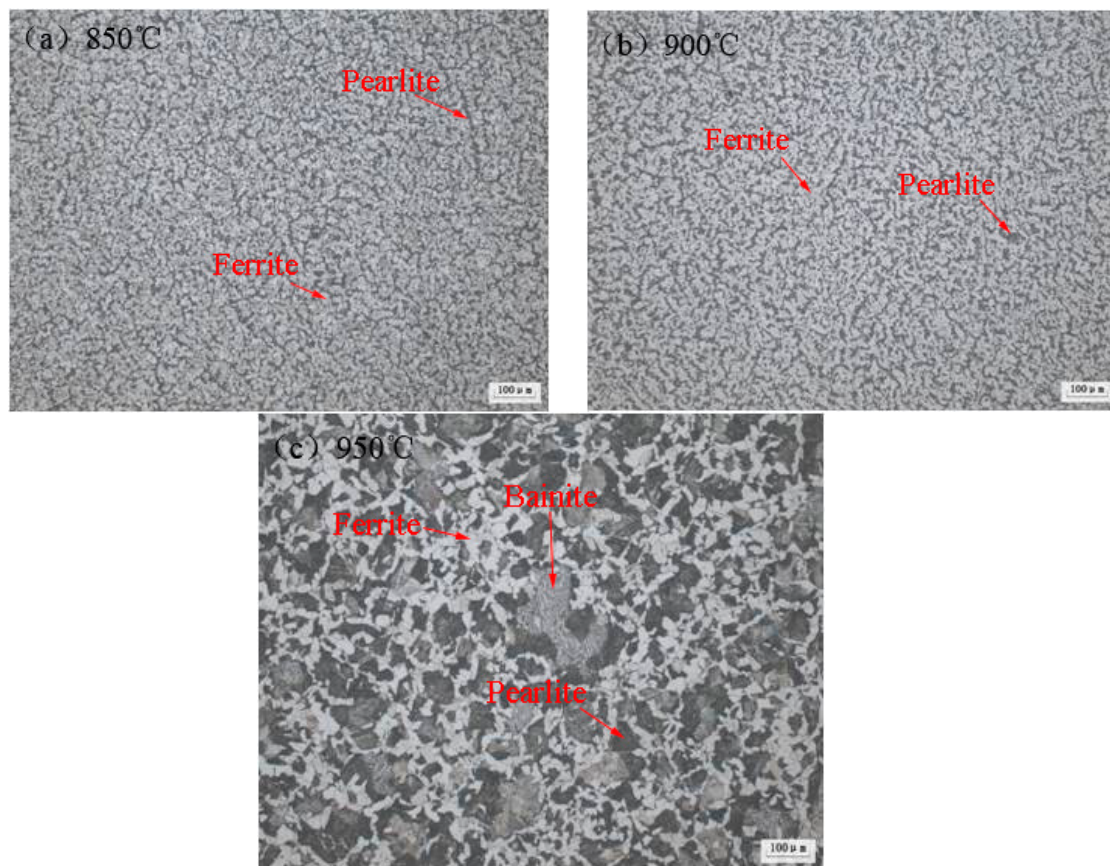
Table 3. Spectral components of the secondary phase in 20CrMnTi.

Element	Weight %	Atomic %
C K1	0.22	0.60
N K1	21.27	48.36
Ti K1	65.22	43.35
Cr K1	2.85	1.75
Fe K1	10.43	5.95

According to the processing schemes, the gear steels were heat treated at 850 °C, 900 °C, 950 °C and 1000 °C, respectively, and the grain coarsening was studied under these treatment temperatures. The microstructure and hardness of the 20CrMnTi steel after heat treatment are shown in Table 4 and Figure 7. The main phases are ferrite and pearlite with the grain size of No. 11.5–12.0 grade at 850 °C and 900 °C. However, when the temperature is 950 °C, the phases are ferrite, pearlite and some bainite, and the material hardness increases. The grain size is further increased to the No. 5.0 grade when the temperature is 1000 °C, and the main phases are ferrite, bainite and a small amount of pearlite with greatly increased hardness. It is known that when the grains begin to coarsen sharply in steel, which increases the stability of austenite significantly, it is advantageous to form the bainite, and the material hardness increases greatly.

Table 4. Microstructure and hardness of the 20CrMnTi gear steel after heat treatment.

Material	Heat Treatment Temperature	Phases	Grain Size	Hardness, (HBW)
20CrMnTi	850 °C	Ferrite, Pearlite	No. 11.5–12.0 grade	172
	900 °C	Ferrite, Pearlite	No. 11.5–12.0 grade	170
	950 °C	Ferrite, Pearlite and Bainite	No. 8.5–10.0 grade	217
	1000 °C	Ferrite, Bainite and a small amount of Pearlite	No. 5.0 grade	234

**Figure 7.** Microstructure of 20CrMnTi under different heat treatment temperatures: (a) 850 °C; (b) 900 °C; (c) 950 °C.

Ti is added frequently in many steels to control the austenitic grain size in the 1200–1250 °C temperature range [16]. However, in this paper, when the temperature is 950 °C, grain coarsening began in the gear steel, so the secondary phase is not effective to control the matrix grain size at this temperature. This is consistent with the thermodynamic analysis results, because nitrogen has been precipitated largely as TiN micro-particles above 1400 °C. However, the larger particles have no effect on precipitation strengthening and hinder grain growth, and in contrast, will seriously affect the fatigue life of gear steel. Then, titanium precipitated mainly as TiC nano-particles, as shown in Figure 8a, along with the energy dispersive spectroscopy (EDS) results presented in Figure 8b, so the secondary phase hinders the grain coarsening mainly due to the TiC during heat treatment. In the practical production process, one should reduce the content of Ti element and control nitrogen. It makes sense to select the content of each element, and then ensure that the multivariable secondary phase precipitated in the required temperature range to accurately control the size and shape of the secondary phase and to improve the comprehensive performance of the product.

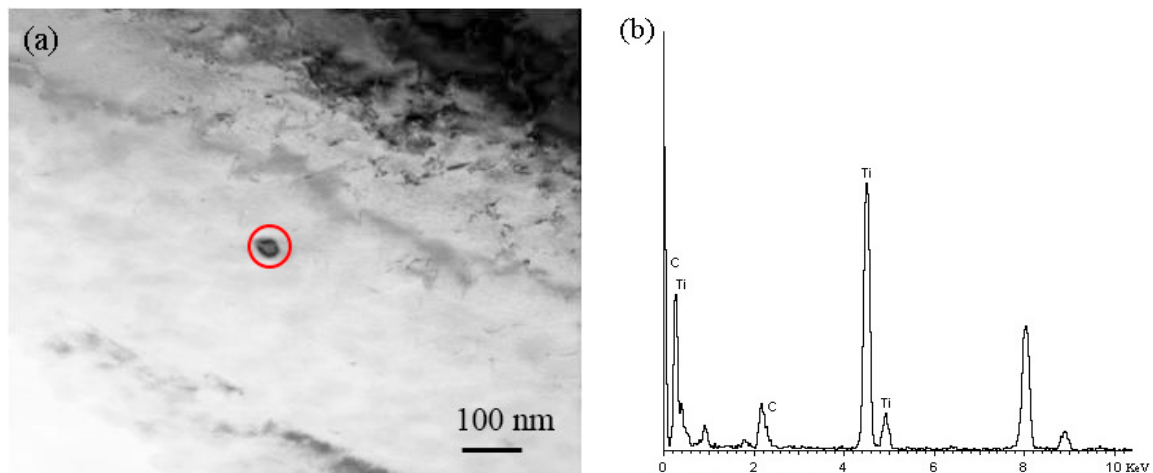


Figure 8. Secondary phase in 20CrMnTi gear steel: (a) transmission electron microscopy (TEM) image; (b) energy dispersive spectroscopy (EDS) results.

4. Conclusions

According to the thermodynamic analysis model and computations, the composition and relative amounts of equilibrium carbonitrides, as functions of steel composition and temperature, are calculated. Taking the Ti–C–N alloy system as an example, the following general trends are predicted and verified:

- (1) Thermodynamic calculation results show that the complete dissolution temperature increases with higher levels of either C, N, or Ti, and the effects of Ti and N are more significant compared with C. At a given temperature, the amount of dissolved Ti increases naturally as the content of Ti microalloyed element increases, while it decreases obviously with more N. It will decline rapidly in the complete dissolution temperature range, until 1100 °C in steels. The coefficient k_1 increases as the temperature decreases, and increases with the higher content of Ti or C, but decreases with the higher N content under the same temperature.
- (2) For the 20CrMnTi gear steels produced by Fangda Special Steel Technology Co., Ltd., the heat treatment shows that when the temperature is above 950 °C, the grains begin to coarsen in this steel. When the temperature is 1000 °C, the grains coarsen sharply, the grain size is No. 5.0 grade, and the phases are ferrite and bainite, containing a small amount of pearlite.
- (3) Thermodynamic analysis shows that the nitrogen has been precipitated largely as TiN micron-particles above 1400 °C in the gear steels, and then the titanium is precipitated mainly as TiC nano-particles, so this secondary phase hinders grain growth during heat treatment, consistent with experimental results.

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Conflicts of Interest: The authors declare no conflict of interest.

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