Influence of Microalloying Elements (Ti, Nb) and Nitrogen Concentrations on Precipitation of Linepipe Steels - A Thermodynamic Approach

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Abstract

A CALculation of PHase Diagrams (CALPHAD) approach was used to study the formation temperatures of nitride and carbonitride precipitates in nominated linepipe steels. The calculated results were in good agreement with relevant experimental data reported in the literatures, where the optimum titanium to nitrogen ratio and austenite grain growth was studied in similar steel compositions. The niobium concentration up to 0.12 wt% showed no influence on the formation temperature of nitrides in a common linepipe steel composition, while significantly increased the precipitation temperature of niobium carbides up to 0.03 wt%. Nitride precipitates contained a high concentration of titanium while niobium contributed mostly to the formation of carbide/carbonitrides. Although the dissolution and growth of precipitates are controlled kinetically, the thermodynamic calculation approach can be used to efficiently predict the equilibrium amount and composition of the stable phases in chemically complex systems. This results in a more accurate design of experiments, to minimise the number of tests required to obtain optimum chemical compositions and heat treatment procedures.

Introduction

Nitride [1, 2], carbide [3] and carbonitride [2] precipitates in steels pin grain boundaries. Depending on the chemical composition of the steel, above certain temperatures during heat treatment, rolling and/or welding, the austenite grains tend to coarsen because the precipitates are taken into solution, leaving the grain boundaries unimpeded [4-6]. Formation and coarsening of nitride and carbonitride precipitates, particularly in microalloyed steels, have been extensively studied experimentally due to their influence on the mechanical properties of products [1] and the formation of cracks during shaping of steels [7, 8].

Titanium Nitride (TiN) precipitates in microalloyed steels extend the temperature range over which the grain boundary pinning is effective, due to a significantly higher solution temperature of these precipitates compared to other precipitates that are known to restrict grain growth [1,2]. Therefore, extensive efforts have been made to optimise the Ti/N ratio as a major microstructural control factor for a variety of steels [1, 2, 9-11]. A high concentration of Ti and N promotes the formation of coarse TiN precipitates that deteriorate toughness. Consequently, a reduced content of Ti and N is suggested while simultaneously retaining a minimum Ti/N ratio to obtain suitable hardenability [1].

It should be recognised that the dissolution and growth of TiN precipitates and austenite grains are kinetically controlled phenomena. Therefore, time is a governing factor for the size and distribution of precipitates. However, the formation temperatures of precipitates can be determined thermodynamically as a function of chemical compositions. This information guides the design of experiments and consequently minimises the

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experimental data required to optimise the Ti/N ratio for various compositions. In the current study, the effect of Ti, Niobium (Nb) and N concentrations are assessed on precipitation of common linepipe steels as a case study using CALPHAD (CALculation of PHAse Diagrams) method. The approach presented here can be applied to various steel compositions for more efficient design of experiments.

METHOD

Several industrial compositions of linepipe steels were adopted to calculate the phase diagrams and study the composition and formation temperature of nitride and carbonitride precipitates, aiming to explore the possibility of calculated methods to minimise the number of experiments required to develop the optimum Ti/N ratio and microalloying element concentrations. The ThermoCalc software package [12], using the thermodynamic databases of TCFE7 [13], was employed to study the composition and formation temperature of nitride and carbonitride precipitates in titanium and niobium microalloyed linepipe steels. This software package is based on minimizing the Gibbs free energy of the individual phases in the equilibrium state. It uses the CALPHAD method to extrapolate thermodynamic descriptions for use in an n-component system, based on the assessment of binary and available ternary and quaternary experimental data stored in the thermodynamic database. The thermodynamics of the liquid phase is described by a regular solution model and the solid phases by sub-lattice models. The phase equilibria are calculated by a free-energy minimization determined by a Newton-Raphson technique. The databases are used to calculate the phase fractions, phase compositions and transformation temperatures under thermodynamic equilibrium conditions [14, 15], providing an efficient calculation technique to predict the equilibrium amount and composition of the stable phases of complex system under a given set of conditions [16]. Phase diagram sections can be determined with up to five independent variables in a very complex multi-component and heterogeneous system (up to 40 elements and 1000 species) [13].

RESULTS AND DISCUSSION

Table 1 summarises the chemical composition of a number of common linepipe steels with various Ti/N ratios. The linepipe steels contain elements such as phosphorous, sulphur, calcium and aluminium in trace levels, which have marginal impact on the composition and temperatures of the precipitates within agreed compositions. These elements were disregarded in the calculation of phase diagrams to minimise the complexity of calculations and improve the feasibility of achieving reliable results from the calculated phase diagrams. All calculations were performed above 900 K where the diffusion of the interstitial elements in the steel matrix is fast enough to reduce the kinetic effect on nucleation and the chemical composition of precipitates. For the Nb and Ti microalloying elements to diffuse one micrometre at 900°C (1173K), it takes approximately 12 minutes and 14 seconds respectively, according to the diffusion coefficients for Nb [17] and Ti [18] in steel. Therefore, the calculated phase diagram should be treated with extra care at lower temperatures.

Two sets of calculations were performed, based on fixed Ti concentrations and varying N contents. The compositions are referred to as Low-Ti and High-Ti, according to the Ti concentration in the steels indicated in Table 2.

Table 1 Chemical composition of common linepipe steels (wt%).

C	Mn	Si	Nb	Ti	V	Ni	Cr	Mo	N	Ti/N
0.05	1.6	0.2	0.055	0.0060	0.02	0.20	0.02	0.15	0.0032	1.88
0.05	1.6	0.2	0.055	0.0087	0.02	0.20	0.02	0.15	0.0027	3.22
0.05	1.6	0.2	0.055	0.0083	0.02	0.20	0.02	0.15	0.0017	4.88

Table 2 The abbreviated chemical composition of the steels (wt%).

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	C	Mn	Si	Nb	Ti	Mo	N
Low-Ti	0.045	1.6	0.22	0.052	0.0060	0.15	0.0032
High-Ti	0.045	1.6	0.22	0.052	0.0087	0.15	0.0017

The Fe-C phase diagram for the Low-Ti steel up to 0.1 wt% C (**Figure 1**) indicates that TiN precipitates form in the austenite matrix of Low-Ti steel at approximately 1650 K regardless of C concentration, while the Ti carbonitride precipitates form at much lower temperatures. The precipitation temperature of Ti carbonitrides has been increased significantly to ~ 1330K with carbon concentration up to 0.02 wt% and then gradually increased to ~1440K with further addition of carbon up to 0.1 wt%. It indicates that the variation in carbon concentration around 0.05-0.2 (typical carbon concentration of linepipe steels) has only a slight affect on the precipitation of nitrides in these steels.

The precipitation of TiN precipitates occurs at much higher temperatures than carbonitrides, where the alloying elements of Ti and N diffuse much faster than at lower temperatures [12]. It suggests that TiN precipitates form larger size precipitates than carbonitrides in the matrix.

3.1. The effect of titanium and nitrogen on the precipitates of low carbon, low alloyed steels

Figure 2 shows the phase diagram of Low-Ti steel as a function of N concentration. Although the Ti concentration remains constant over the whole composition range, the precipitation temperate of titanium nitrides has been increased substantially with up to 0.001 wt% N, and gradually increased with further N addition. The precipitation temperature of Ti carbonitrides shows only a slight deviation with the variation in N concentration, indicating that carbonitride precipitates mainly contain carbon.
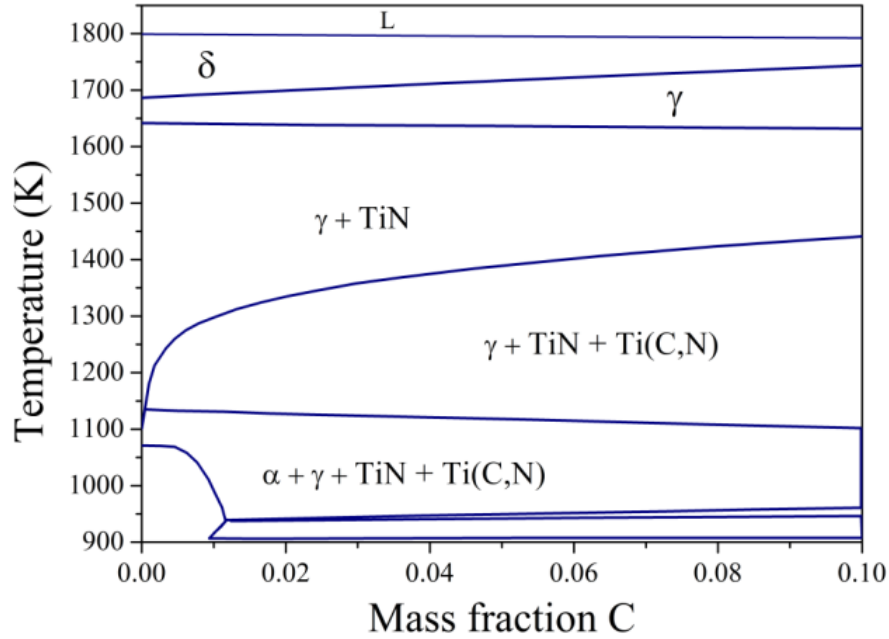

Figure 1 Fe-C phase diagram for Low-Ti steel showing the composition dependence of the formation temperature of titanium nitrides and carbonitrides.

Figure 3 compares the formation temperature of TiN precipitates in Low-Ti (red curves) and High-Ti (blue curves) steels. Higher Ti concentration increases the temperatures of TiN precipitation. It should be noted that the Ti/N ratio varies considerably with the Ti content. At a given Ti/N ratio, Ti nitrides precipitate in the High-Ti steels at temperatures approximately 70K higher than the Low-Ti steels. Considering the effect

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of diffusion on the precipitates size, TiN precipitates which form at lower temperatures are anticipated to be smaller in size. A study [19] on the effect of weld thermal cycles on precipitates of Ti-Vanadium (V)-microalloyed steels with Ti/N ratios of 0.8-1.8, indicated that only TiN precipitates survived high energy weld cycles and determined the Austenite grain size. Smaller, coherent precipitates with a higher concentration of V than Ti formed in these steels, but dissolved during the welding process. This is in agreement with the findings of this study, confirming that carbonitride precipitates which form at lower temperatures, are smaller in size and mostly dissolve during heat treatments, although the time is as limited similar to welding methods.

The optimum Ti/N ratio is found to be around stoichiometry [1, 9, 11, 20]; however, high contents of Ti and N promote the formation of coarse TiN precipitates which deteriorate toughness [1, 20]. Therefore, a reduced content of these elements is suggested while simultaneously retaining a minimum Ti/N ratio to improve the mechanical properties of these steels [1]. The presence of V, Nb, Molybdenum (Mo), Zirconium (Zr) and Boron (B) nitride forming elements in the microalloyed steels might vary the optimum Ti/N ratio due to interaction of N with a combination of these elements [20]. Therefore, calculated Fe-N phase diagrams for these alloys provide advice on the optimum Ti/N ratio.
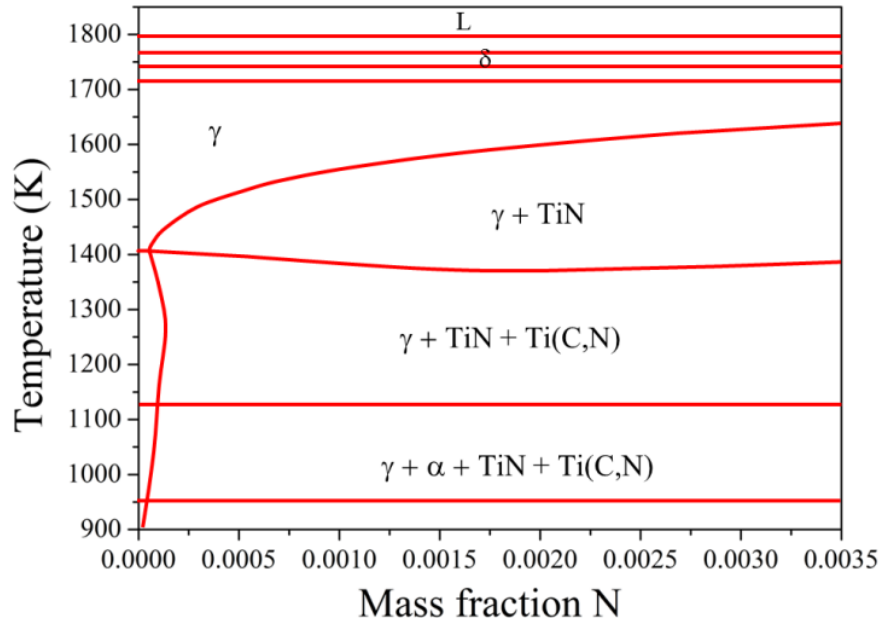

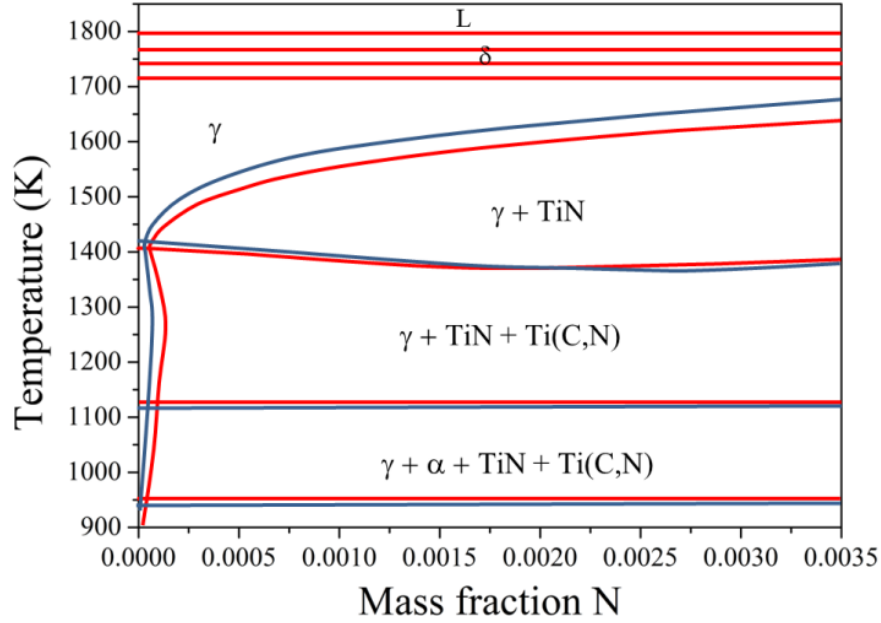**Figure 2** Nitrogen dependence transformation temperature of Low-Ti steel

Figure 3 Comparison of formation temperatures of precipitates in a Low-Ti (red curves) and a High-Ti (blue curves) steel as a function of nitrogen concentration, demonstrating that titanium nitride precipitates form at higher temperatures and lower nitrogen content in a High-Ti steel.

3.2. The effect of niobium on the precipitates of low carbon, low alloyed steels

Table 3 presents chemical compositions of a few Nb-microalloyed linepipe steels fabricated in industries, adopted to study the effect of Nb concentration on the formation temperature and composition of nitride and carbonitride precipitates. There is a substantial deviation in the Manganese (Mn), Silicon (Si), Mo and V content of the selected steels. In order to fully realise the effect of these variations on the nature of precipitates, the phase diagrams of an abbreviated composition of a steel named High-Nb in Table 4, was calculated by varying Mn, Si and Mo composition within the range shown in the second row of Table 4. The steel with chemical composition of "High-Nb" in table 3 represents steels 2, 3 and 4 in table 3 and "Low-Nb" is representative of steel 1 in Table 3.

Interestingly, the deviations of Mn, Si and Mo contents within the designated composition range in Table 4, show no variation in the formation temperatures of carbides and nitrides (**Figure 4a**). The precipitation temperatures of nitrides and carbonitrides as a function of Mo content for the High-Nb steel are shown in **Figure 4(a)** , as a model of obtained phase diagrams for these elements. It is worth noting that nitride and carbonitride precipitates contain both elements of Ti and Nb in these steels, specified by the calculated phase diagrams. Experimental microscopy analysis of rolled Ti-Nb microalloyed steels with similar compositions of the current study, presented ferrite-bainite microstructure which included precipitates of (Ti, Nb)N, 120-400nm in size, spherical or plate-like precipitates of (Nb, Ti)C within 10-120nm and needle-like 3-5nm (Nb, Ti)C precipitates [21]. Carbide precipitates are believed to be carbonitrides because the method was unable to analyse C and N in small precipitates [20]. Nitride precipitates which form at higher temperatures form larger precipitates than carbonitride precipitates.

Figure 4(b) shows that although the variation of V content has no effect on the formation temperature of nitride precipitates, it introduces vanadium carbonitride precipitates to the alloy at temperatures below ~1050K. It indicates that the composition, size and distribution of the carbonitride precipitates in steel 2 and 3 (table 3), is expected to be distinguishable from the rest of the alloys in table 3. The solubility limit of V in austenite is much greater than Ti and Nb in microalloyed steels, and therefore remains in solution

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during heat-treated processing in the austenite range to a much greater extent. V carbonitride precipitates have a thin, fibrous morphology and contribute to strengthening [20].

Table 3 Example Chemical composition of Nb -contained line pipesteels (wt%).

Steel	C	Mn	Si	Nb	Ti	V	Mo	N
High Nb	0.05	1.5	0.16	0.11	0.012	0.003	0.002	0.0048
Composition Ranges		1.2-1.6	0.16-0.3			0-0.03	0-0.03	
Low Nb	0.14	1.2	0.27	0.001	0.014	0.006	-	0.0021

Table 4 The chemical composition of Nb -contained steels in mass fraction. The second row shows the composition range of elements selected to assess the variations.

Steel	C	Mn	Si	Nb	Ti	V	Mo	N
High Nb	0.05	1.5	0.16	0.11	0.012	0.003	0.002	0.0048
Composition Ranges		1.2-1.6	0.16-0.3			0-0.03	0-0.03	
Low Nb	0.14	1.2	0.27	0.001	0.014	0.006	-	0.0021

Figure 5 shows the phase diagram of the High-Nb steel as a function of carbon concentration, demonstrating that titanium nitride precipitates in steels with carbon concentrations <0.06 wt% form at temperatures ˜50K higher than the steels with higher carbon concentrations. Whereas niobium carbonitride precipitates, form at much lower temperatures in low carbon steels. It suggests that titanium nitride precipitates in low carbon steels are expected to be larger in size than in alloys with higher concentrations of carbon (above 0.06 wt%). Steel 4 in Table 3 contains 0.05 wt% C and therefore it is anticipated to include larger TiN precipitates than the other alloys. The formation temperature of Nb carbonitrides is increased considerably to ˜1400K by carbon concentration up to 0.02 wt% and then gradually increased to ˜1520K at 0.1 wt% carbon. The niobium carbonitride precipitates contain higher ratios of carbon to nitrogen and also contain a small amount of titanium. The elemental fractions change by temperature and carbon concentration.
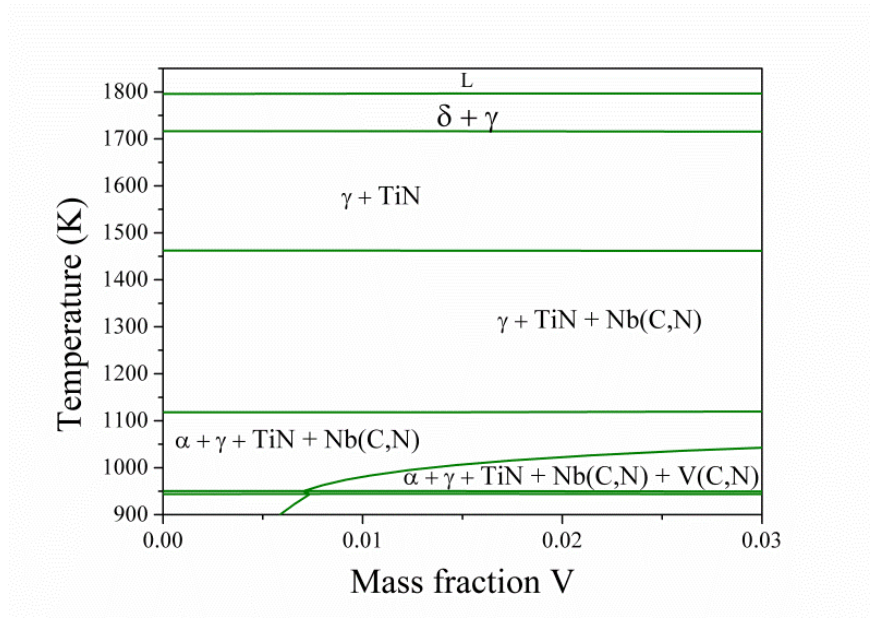
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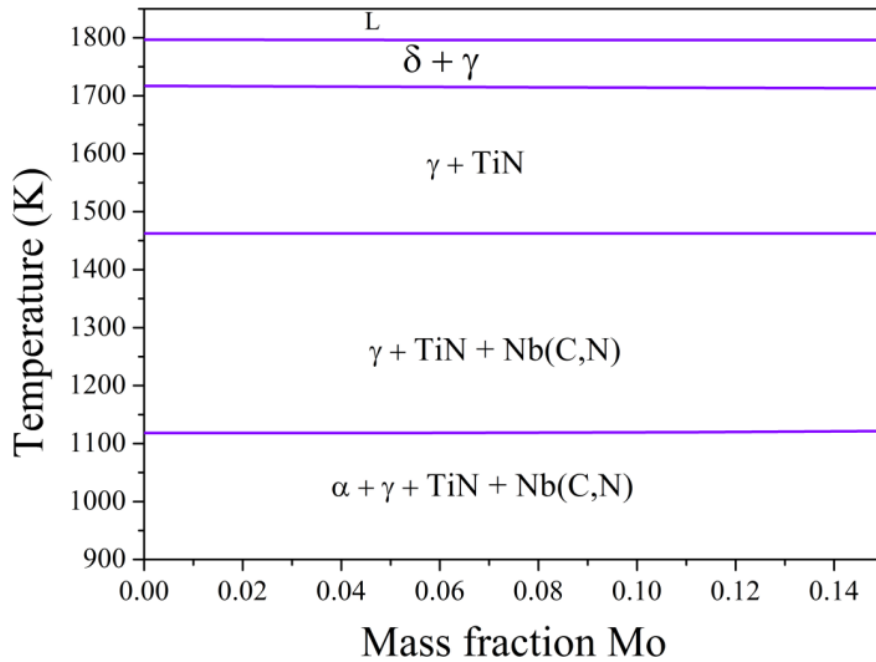
Figure 4 (a) Molybdenum; (b) Vanadium dependence formation temperatures of carbide and carbonitride precipitates, calculated for High-Nb steel (table 4).
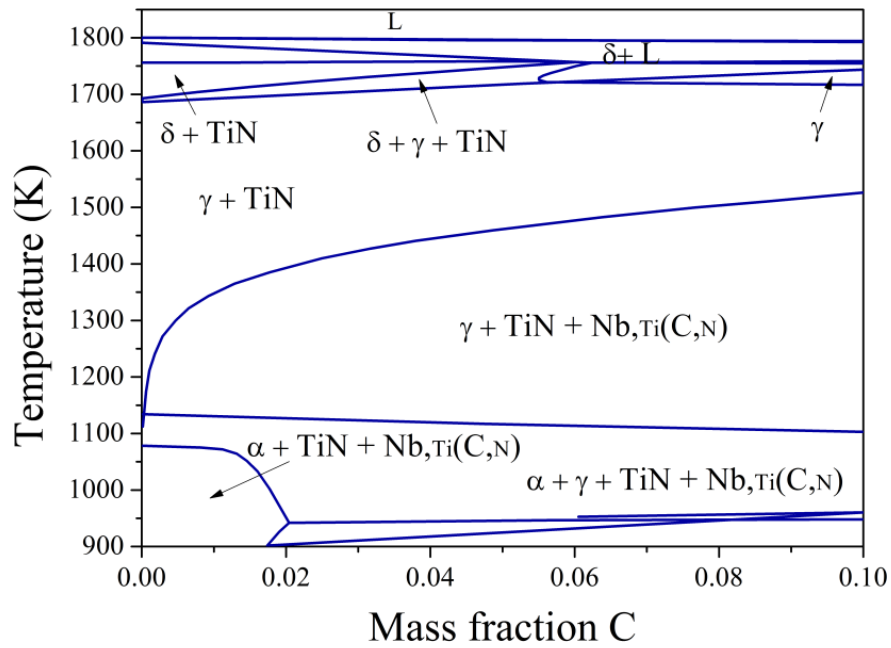

Figure 5 Fe-C phase diagram for High-Nb steel, showing the formation temperature of titanium nitrides and carbonitrides varies significantly by carbon concentration.

The variation of niobium and nitrogen concentrations on the transformation and precipitation temperatures, have been studied for the High-Nb steel. The niobium concentration up to 0.12 wt% has no influence on the precipitation temperature of nitrides in this steel (**Figure 6(a)**), whereas the formation temperature of niobium carbides is increased considerably up to 0.03 wt% Nb. Further addition of niobium gradually

increases the precipitation temperature of carbides. The calculated chemical composition of precipitates at 1400K and 1300K are compared for steels with niobium concentrations of 0.03 and 0.11 wt% respectively in table 5. The nitrides contain mostly titanium, and niobium forms carbides.

A study of non-isothermal austenite grain growth, in the Heat Affected Zone (HAZ) of an X80 microalloyed steel, has shown that the increasing peak temperature from 1223 K to 1523 K results in a significant growth of the grain size [8]. The chemical composition of the studied alloy is similar to the High-Nb steel of the current report with 0.034 wt% Nb. The calculated phase diagram in **Figure 6(a)** indicates that the niobium carbonitride precipitates are only partially dissolved at a peak temperature of 1223K, and therefore remaining precipitates suppress the austenite grain growth via pinning of the grain boundaries. Whereas austenite grains can grow rapidly at a peak temperature of 1523K, where niobium carbonitrides are dissolved completely in the matrix. Titanium nitride precipitates are formed at temperatures above 1700K, and remain undissolved in the austenite matrix at both selected peak temperatures. The nitride precipitates which form at high temperatures are generally large in size and therefore, are not expected to contribute considerably in suppressing the austenite grain coarsening [5, 6].

Table 5 The chemical composition of precipitates in the High-Nb steel for nominated niobium concentrations.

Temperature	Nb concentration in the steel (wt%)	Precipitates concentration (at%)	Precipitates concer
		Ti	Nb
1400	0.03	48	2
1300	0.11	48	-
		-	47

The formation temperatures of precipitates in the Low-Ti (red curves) steel are compared with the High-Nb steel (purple curves) in**Figure 6(b)** as a function of nitrogen concentration.**Figure 3** showed that increasing the concentration of titanium increases only the precipitation temperature of titanium nitrides, however, **Figure 6(b)** shows that the addition of niobium has significantly increased the precipitation temperatures of both nitrides and carbides. This will result in more thermally stable precipitates, which contribute to suppressing austenite grain growth during heat treatments. It can explain the fine grain size distribution in niobium-alloyed steels [7, 8].

Figure 6(b) also demonstrates that the precipitation temperature of niobium carbides is almost independent of the nitrogen concentration and the precipitation temperatures are increased with the niobium concentration (**Figure 6(a)**). Therefore, it is expected that the niobium carbide precipitates which form in steel 2 (Table 3) appear larger in size than the precipitates in steel 4, originated from precipitation at higher temperatures.
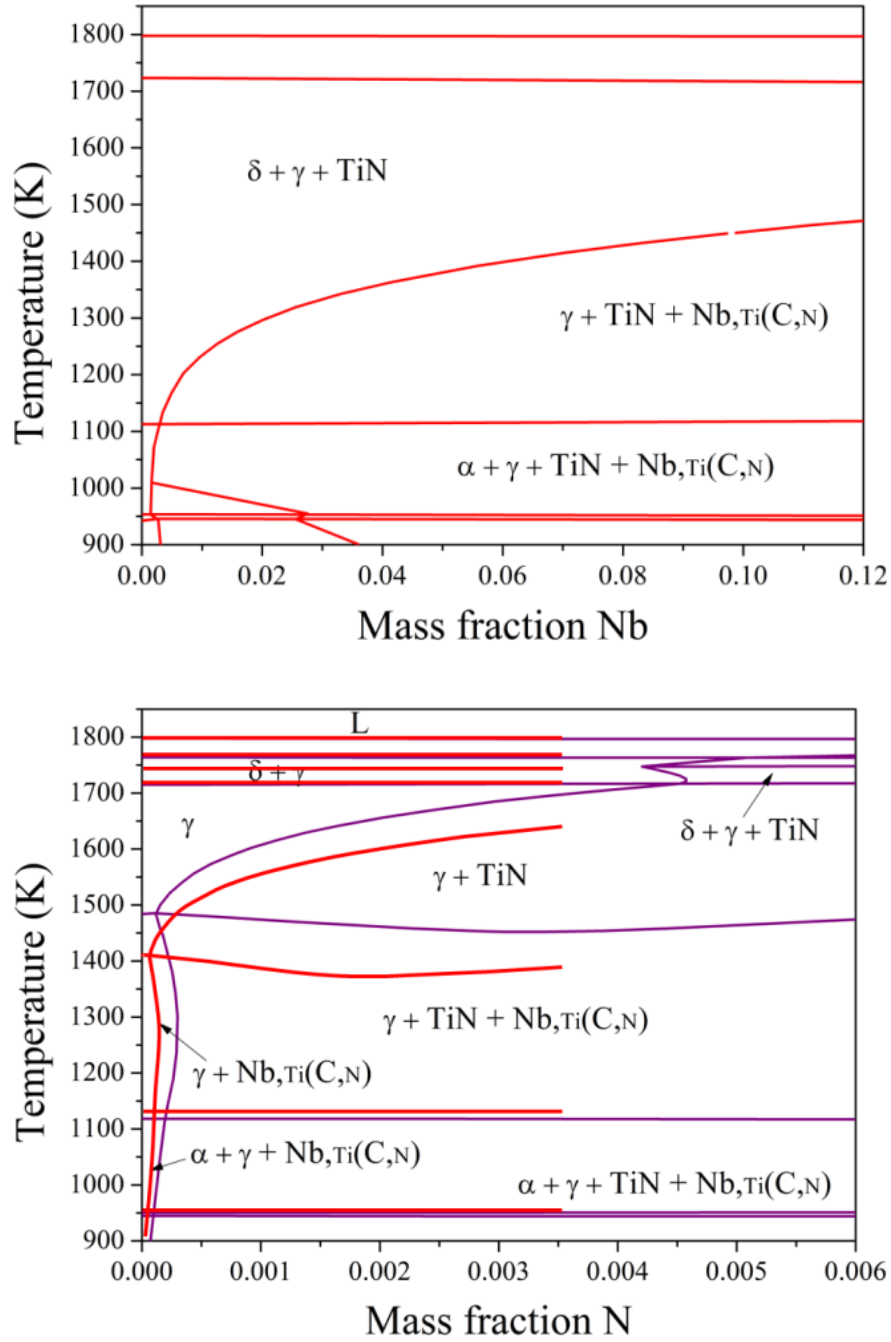
Figure 6 (a) The phase diagram of the High-Nb steel as a function of niobium concentration; (b) Overlapped phase diagram of the Low-Ti (red curves) and High-Nb (purple curves) steels

The phase diagrams were calculated for the Low-Nb steel (**Table 4**) separately due to a much higher concentration of carbon in steel 1 than the rest of the alloys in Table 3. The transformation and precipitation temperature of the Low-Nb steel as a function of carbon and niobium concentration are shown in **Figure 7** . Similar to the High-Nb steel, the precipitation temperature of niobium carbides is increased with niobium concentration.
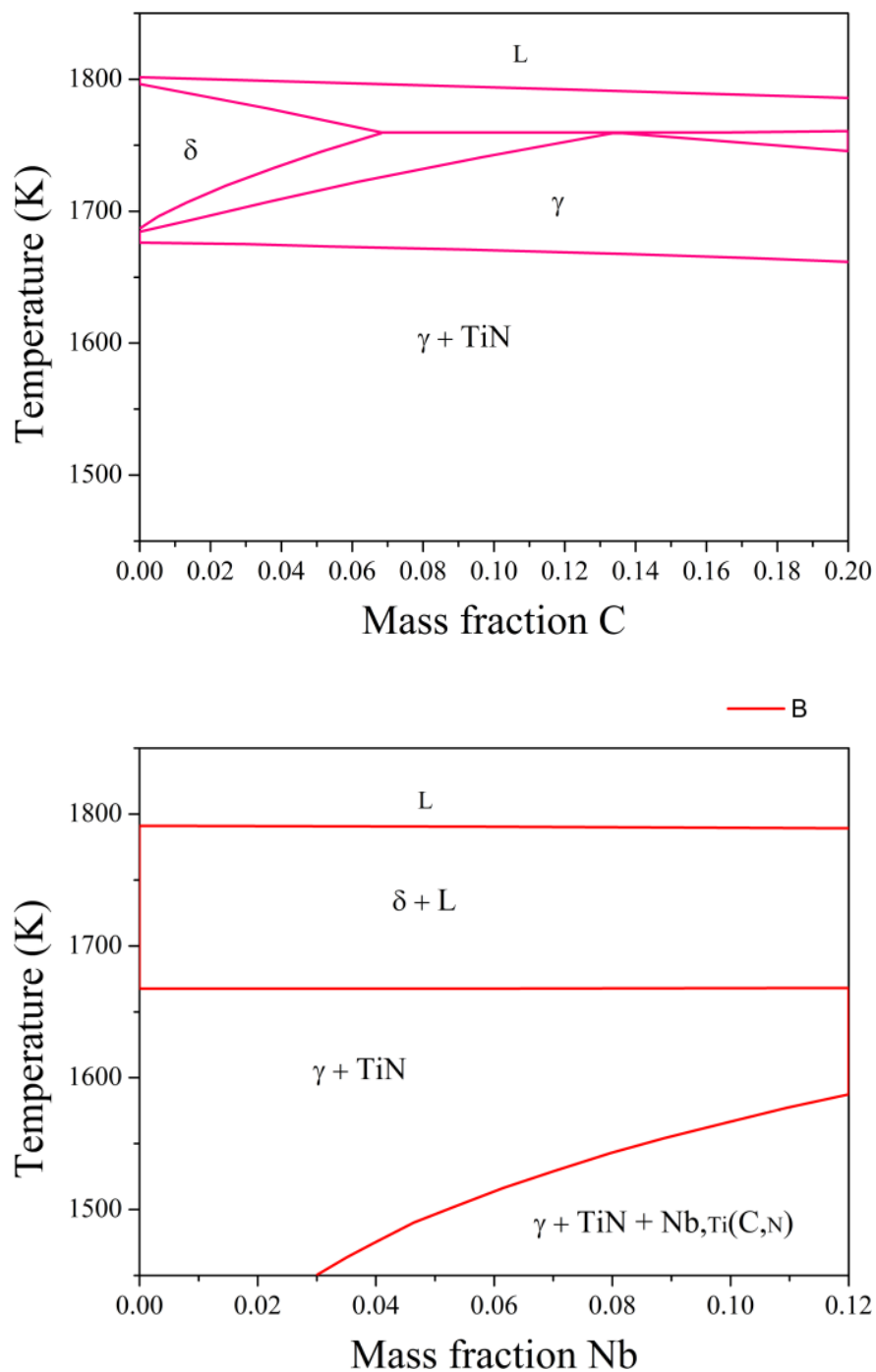
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Figure 7 The phase diagram of the Low-Nb steel as a function of (a) carbon and (b) nitrogen concentration

The Fe-C phase diagrams of the low-Nb steel (pink) and High-Nb steel (blue) are compared in **Figure 8** . The concentration of nitrogen (0.0021 wt%) and niobium (0.001 wt%) in the Low-Nb steel, is lower than High-Nb steel which contain 0.0048 wt% and 0.11 wt% nitrogen and niobium respectively. This results in precipitation of titanium nitrides at lower temperatures in the Low-Nb steel compared to the High-Nb steel with larger nitrogen and niobium concentrations. It suggests that all precipitates including carbides and

nitrides, will dissolve in the matrix where the Low-Nb steel is heat treated above ~ 1673K. This will cause a rapid austenite grain growth.
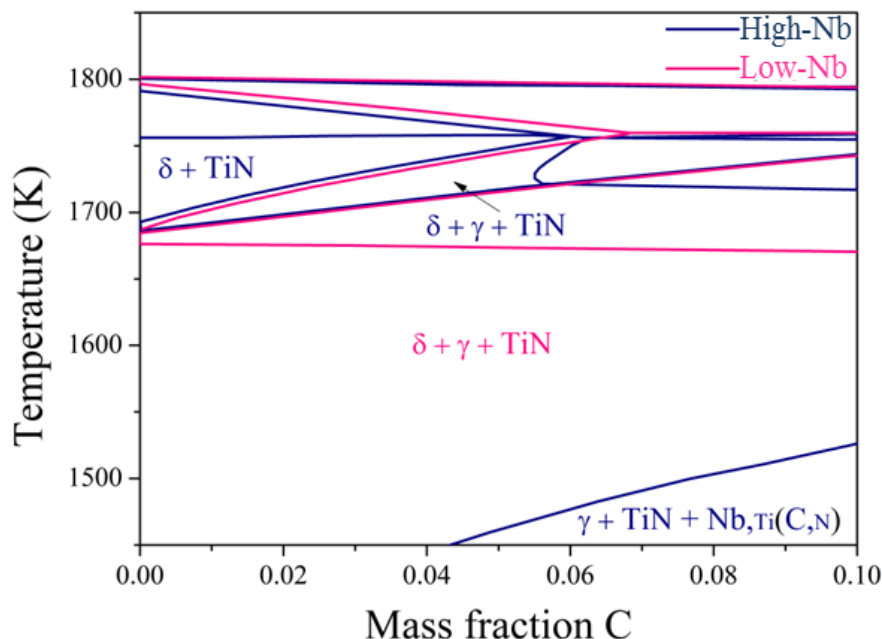

Figure 8 Comparison of the Fe-C phase diagram for the Low-Nb (pink curves) andHigh-Nb (blue curves) steels, showing that low concentration of nitrogen and niobium in the Low-Nb steel decreases the precipitation temperatures of titanium nitrides.

CONCLUSION

The ThermoCalc software package, using the thermodynamic databases of TCFE7 was employed to study the precipitation of nitrides and carbonitrides in common microalloyed line pipe steels.

- Higher concentration of titanium increases the precipitation temperatures of titanium nitrides by approximately 70K, suggesting larger titanium nitrides.

- The niobium concentration up to 0.12 wt% in a Ti and Nb microalloyed steel shows no influence on the precipitation temperature of nitrides, whereas the formation temperature of niobium carbides is increased substantially up to 0.03 wt% Nb. The nitride precipitates contain a high concentration of titanium while carbides mostly formed of niobium.

- Titanium concentration increases the precipitation temperatures of titanium nitrides in a Ti and Nb microalloyed steel. However, the precipitation temperatures of both nitrides and carbides increase significantly with Nb concentration.

The results are in good agreement with experimental data in the literature, highlighting the suitability of primary calculation approach to the design of new alloys and heat treatment processes of microalloyed steels.

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CONFLICT OF INTEREST

The author has no conflict of interest relevant to this article.

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