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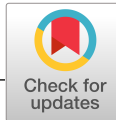
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Influence of microalloying elements (Ti, Nb) and nitrogen concentrations on precipitation of pipeline steels—A thermodynamic approach

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Abstract

A CALculation of PHase Diagrams (CALPHAD) approach was used to study the precipitation of nitrides and carbonitrides in pipeline steels, aligned with new developments of complex chemical compositions and thermomechanical processing of High Strength Low Alloyed (HSLA) Steels. This is in response to growing demand for improved mechanical and chemical properties, manufacturing flexibility and reduced production cost. The calculated results indicated that the precipitation temperatures of nitrides in Ti-Nb microalloyed steels increased by titanium concentration, while the niobium concentration significantly increased the precipitation temperature of niobium carbonitrides. Carbonitride precipitates formed at much lower temperatures ($\sim$100 K) in low carbon steels ($<$0.03 wt%) than the high carbon steels ($>$0.1 wt%), suggesting precipitates larger in size. This is in good agreement with independent experimental data from the literatures, where austenite grain growth was studied in similar steel compositions. Although the dissolution and growth of precipitates are controlled kinetically, these results proved that the thermodynamic calculation can efficiently predict compositions and sequence of precipitation in chemically complex systems, guiding more accurate designs of experiments to identify critical temperatures of grain coarsening during reheating, recrystallisation during hot rolling, and transformation during cooling. This can minimize the number of tests required to obtain optimum chemical compositions and heat treatment procedures.

KEYWORDS
CALPHAD, carbonitrides, microalloyed steel, niobium, nitrides, pipeline steel, precipitates, titanium

1 | INTRODUCTION

Microalloyed high strength steels are widely used as structural materials, specifically for transporting crude oil and natural gas over long distances because of their exceptional mechanical properties, corrosion resistance, and weldability

compared to carbon steels.[1-3] Nitrides,[4,5] carbides,[6,7] and carbonitrides[5,8] of microalloying elements, such as niobium, titanium, and vanadium, precipitate in austenite during thermomechanical processes, pin grain boundaries and consequently improve the mechanical properties of the steels through grain refinement and precipitation hardening.[9]

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.[10-12] 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,[1,4,8,13] the formation of cracks during shaping of steels[14-16] and corrosion resistance due to hydrogen induced cracking[2,13] and microstructural texture.[2,17,18] However, due to the growing demand for improved mechanical properties, environmental resistance, weldability and reduced production cost of High Strength Low Alloy (HSLA) steels, new complex chemical compositions and thermomechanical processing have been continuously developed to advance high-grade pipeline steels for practical applications.[3,19-22] This highlights the needs for better understanding of precipitation behavior including sequence of precipitation in various chemical compositions of microalloyed steels.

Carbides and nitrides precipitate in three main stages in microalloyed steels processing[13]: (i) in the liquid phase or during solidification process; (ii) during controlled rolling by strain induced precipitation; (iii) during or after eutectoid transformation.

Precipitates formed in the first stage are very stable and generally too coarse to influence on austenite recrystallization. Segregation of titanium and nitrogen at the late stages of solidification consumes a substantial fraction of the added titanium to form coarse TiN precipitates; the remaining titanium, precipitates in austenite.[23] Fine titanium nitride precipitates 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 optimize the Ti/N ratio as a major microstructural control factor for a variety of steels.[4,5,24-26] Soluble Nb in austenite reduces the temperature at which Eutectoid transformation occurs and its reduced solubility with temperature in austenite results in formation of niobium carbides and carbonitrides at temperatures lower than precipitation temperature of TiN as a function of Nb concentration.[23] These fine precipitates increase the recrystallisation temperature during hot rolling and refining microstructure along with titanium carbides.[13,23,27]

It should be recognized that the dissolution and growth of 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, their composition and sequence of precipitation can be determined thermodynamically as a function of steels' chemical compositions, identifying critical temperatures of grain coarsening during reheating, recrystallisation during hot rolling and transformation during cooling.[13] This information guides the design of experiments and consequently minimizes the experimental data required to understand the impact of precipitates on grain coarsening, thermomechanical processing and consequently mechanical properties of various HSLA compositions. In the current study, the effect of Ti, Nb and N concentrations are assessed on precipitation behavior of a range of pipeline steels, using CALPHAD (CALculation of PHAse Diagrams) method. The presented phase diagrams in the current work can be directly used to suggest heat treatment processes and assess the austenite grain growth during thermomechanical processes and welding of pipeline steels with similar chemical compositions. The approach presented here can also be applied to various steel compositions for more efficient design of experiments.

2 | METHOD

Several industrial compositions of pipeline steels were selected 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 minimize the number of experiments required to develop new chemical compositions and the optimum thermomechanical processing for microalloyed steels. The ThermoCalc software package,[28] using the thermodynamic databases of TCFE7,[29] was employed to study the composition and formation temperature of nitride and carbonitride precipitates in titanium and niobium microalloyed pipeline 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 thermodynamic database of TCFE7 for steels and Fe-based alloys are used

to calculate the phase fractions, phase compositions and transformation temperatures under thermodynamic equilibrium conditions,[30,31] predicting the equilibrium amount and composition of the stable phases of complex system under a given set of conditions.[32]

3 | RESULTS AND DISCUSSION

Table 1 summarizes the chemical compositions of a number of common pipeline steels with various Ti concentrations. The pipeline steels contain trace elements such as phosphorous, sulfur, calcium and aluminum, which have marginal impact on the composition and temperatures of the precipitates within chosen composition ranges. These elements were disregarded in the CALPHADs to minimize the complexity of calculations and improve the feasibility of obtaining reliable results from the calculated phase diagrams. All calculations were performed above 900 K. According to the diffusion coefficients of Nb[33] and Ti[34] in steel, it takes approximately 12 min and 14 s for Nb and Ti to diffuse 1 μm at 900°C (1173 K), respectively. Therefore, the correlation of calculated phase fractions to the heat treatment and thermomechanical processes should be made cautiously at low temperatures, where the kinetic of precipitation is a predominant factor.

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 concentrations of steels in Table 2.

3.1 | The effect of titanium on precipitates of low carbon, low alloyed steels

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 ~1330 K with carbon concentration up to 0.02 wt% and then gradually increased to ~1440 K with further addition of carbon up to 0.1 wt%. It indicates that the variation in carbon concentrations around 0.03–0.2 (common carbon concentration of pipeline steels) has only a slight effect on the precipitation of nitrides in these steels.

The precipitation of TiN occurs at much higher temperatures than carbonitrides, where the alloying elements of Ti and N diffuse much faster than that at lower temperatures.[28] It suggests that TiN precipitates form larger size precipitates than carbonitrides in the matrix, in agreement with experimental results.[13,35]

Figure 2A 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 N concentration up to 0.002 wt%, and then gradually increased with further N addition. The precipitation temperature of Ti carbonitrides shows only a slight variation with the changes in N concentration, indicating that carbonitride precipitates mainly contain carbon.
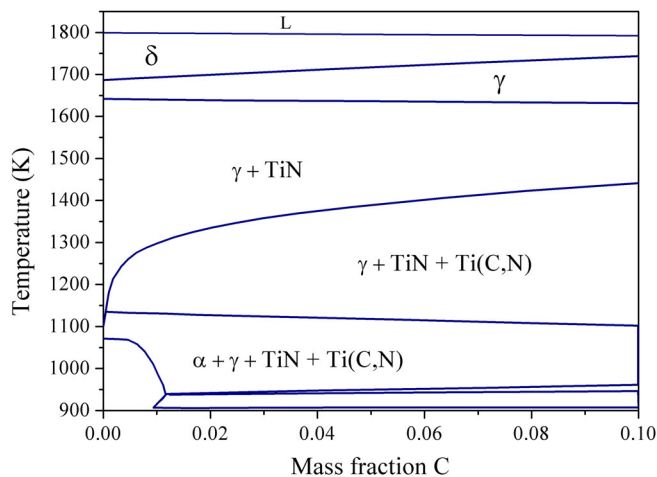
Figure 2B compares the formation temperature of TiN precipitates in Low-Ti (red curves) and High-Ti (blue curves) steels. Higher Ti concentration increases the formation temperatures of TiN precipitates. It should be noted that the Ti/N ratio varies considerably with Ti content. At a given Ti/N ratio, Ti nitrides precipitate in the High-Ti steels at temperatures approximately 70 K higher than that in the Low-Ti steels. Considering the effect of diffusion on the size of precipitates,

**TABLE 1** Chemical composition of common pipeline 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%)

	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

FIGURE 1 Fe-C phase diagram for low-Ti steel showing the composition dependence of the formation temperature of titanium nitrides and carbonitrides
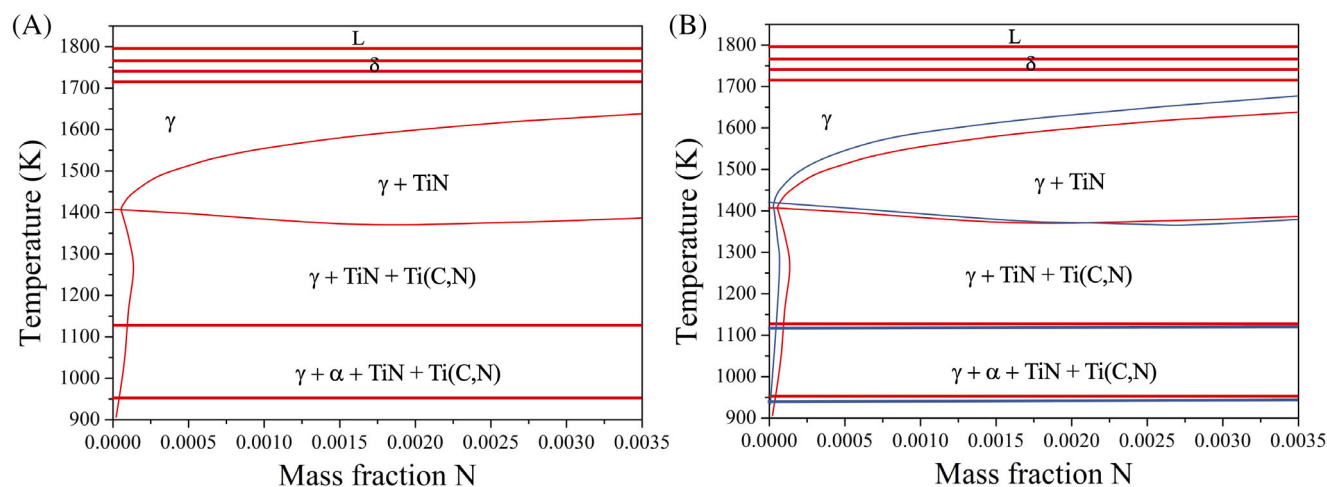
FIGURE 2 (A) Nitrogen dependence transformation temperature of Low-Ti steel; (B) comparison of formation temperatures of precipitates in a Low-Ti (red curves) and a high-Ti (blue curves) steel as a function of nitrogen concentration, demonstrating that titanium nitride precipitates form at higher temperatures and lower nitrogen content in a High-Ti steel

TiN precipitates which form at lower temperatures are anticipated to be smaller in size. A study[36] 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 refined 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.

The optimum Ti/N ratio is found to be around stoichiometry[4,24,26,37]; however, high contents of Ti and N promote the formation of coarse TiN precipitates which deteriorate toughness.[4,37] 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.[4] The presence of nitride forming elements of V, Nb, Molybdenum (Mo), Zirconium (Zr) and Boron (B) in the microalloyed steels might vary the optimum Ti/N ratio due to interaction of N with a combination of these elements.[37] Therefore, calculated Fe-N phase diagrams for these alloys provide guides on the optimum Ti/N ratio.

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

Table 3 presents the chemical compositions of a number of commercial Nb-microalloyed pipeline steels, adopted to study the effect of Nb concentration on the formation temperature and composition of nitride and carbonitride precipitates.

TABLE 3 Example chemical composition of Nb-contained line pipesteels (wt%)

Steel	C	Mn	Si	Nb	Ti	V	Mo	N
1	0.14	1.2	0.27	0.001	0.014	0.006	0.002	0.0020
2	0.085	1.4	0.3	0.033	0.016	0.066	0.01	0.006
3	0.07	1.6	0.25	0.046	0.011	0.027	0.015	0.0037
4	0.05	1.6	0.16	0.11	0.012	0.003	0.002	0.0048

TABLE 4 The chemical composition of Nb-contained steels in mass fraction

| 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

Note: The second row shows the composition range of elements selected to assess the variations.
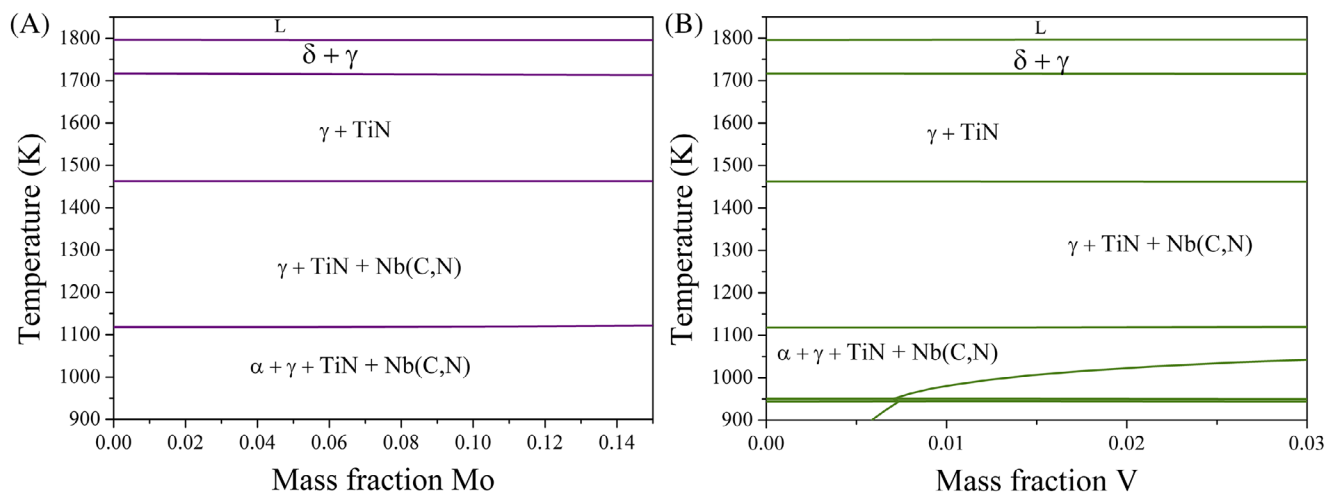
FIGURE 3 (A) Molybdenum; (B) vanadium dependence formation temperatures of carbide and carbonitride precipitates, calculated for High-Nb steel (Table 4)

There is a substantial deviation in the Manganese (Mn), Silicon (Si), Mo and V content of the selected steels. In order to fully realize 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 "High-Nb" steel in Table 4 represents steels 2, 3 and 4 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 3). The precipitation temperatures of nitrides and carbonitrides as a function of Mo content for the High-Nb steel are shown in Figure 3A, as a model of calculated 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, 120–400 nm in size, spherical or plate-like precipitates of (Nb, Ti)C within 10–120 nm and needle-like 3–5 nm (Nb, Ti)C precipitates.[38] Carbide precipitates are believed to be carbonitrides because the method was unable to analyze C and N in small precipitates.[37] Nitride precipitates which form at higher temperatures are larger in size than carbonitride precipitates. The thermal simulation of coiling process for a X90 pipeline steel[1] between 873 and 1073 K demonstrated interparticle spacing increment and growth of (Ti, Nb)CN precipitates from average size of 3.14 nm for treatment at 873 K to 4.83 nm for 1073 K. The mechanical properties of the steel were affected significantly due to the reduced precipitation strengthening effect, however, these precipitates still hindered grain growth to some extent.
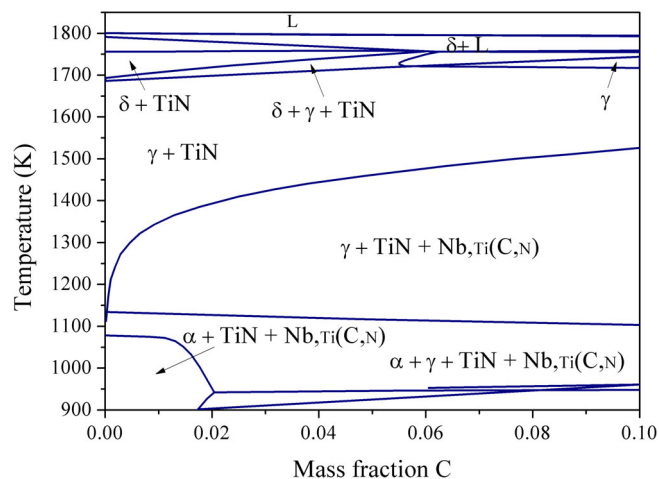
FIGURE 4 Fe-C phase diagram for High-Nb steel, showing the formation temperature of titanium nitrides and carbonitrides varies significantly by carbon concentration

TABLE 5 The chemical composition of precipitates in the High-Nb steel for nominated niobium contents

| Temperature	Nb concentration in the steel (wt%)	Precipitates concentration (at%)				
		Ti	Nb	N	C	Other elements
1400	0.03	48	2	47	-	3
1300	0.11	48	—	45	5	2
		—	47	7	42	4

The changes in V concentration shows no effect on the formation temperature of nitride precipitates (Figure 3B), however, it introduces vanadium carbonitride precipitates to the alloy at temperatures below ~1050 K. 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 during heat-treated processing in the austenite range to a much greater extent. V carbonitride precipitates have a thin, fibrous morphology and contribute to precipitation strengthening.[37]

Figure 4 shows the phase diagram of the High-Nb steel as a function of carbon concentration. The formation temperature of Nb carbonitrides is increased considerably to ~1400 K by carbon concentration up to 0.02 wt% and then increased at lower rate to ~1520 K at 0.1 wt% carbon, demonstrating that niobium carbonitride precipitates form at much lower temperatures (~100 K) in low carbon HSLA steels (<0.03 wt%) than the steels with higher carbon concentrations (>0.1 wt%). It suggests that carbonitride precipitates in pipeline steels with higher carbon contents are expected to be larger in size than in alloys with lower concentrations of carbon (~ 0.03 wt%).

Steel 2 in Table 3 contains 0.085 wt% C and therefore it is anticipated to include higher number of larger carbonitride precipitates than the other alloys in agreement with experimental data.[8] 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.

The variation of niobium and nitrogen concentrations on the transformation and precipitation temperatures, have been assessed for the High-Nb steel. The niobium concentrations up to 0.12 wt% has no influence on the precipitation temperature of nitrides in this steel (Figure 5A), 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 carbonitrides. The calculated chemical composition of precipitates at 1400 K and 1300 K 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 of an X80 microalloyed steel, has shown that the increasing peak temperature from 1223 to 1523 K results in a significant growth of the grain size.[15] 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 5A indicates that the niobium carbonitride precipitates are only partially dissolved at a peak temperature of 1223 K, and therefore remaining precipitates could suppress the austenite grain growth via pinning of the
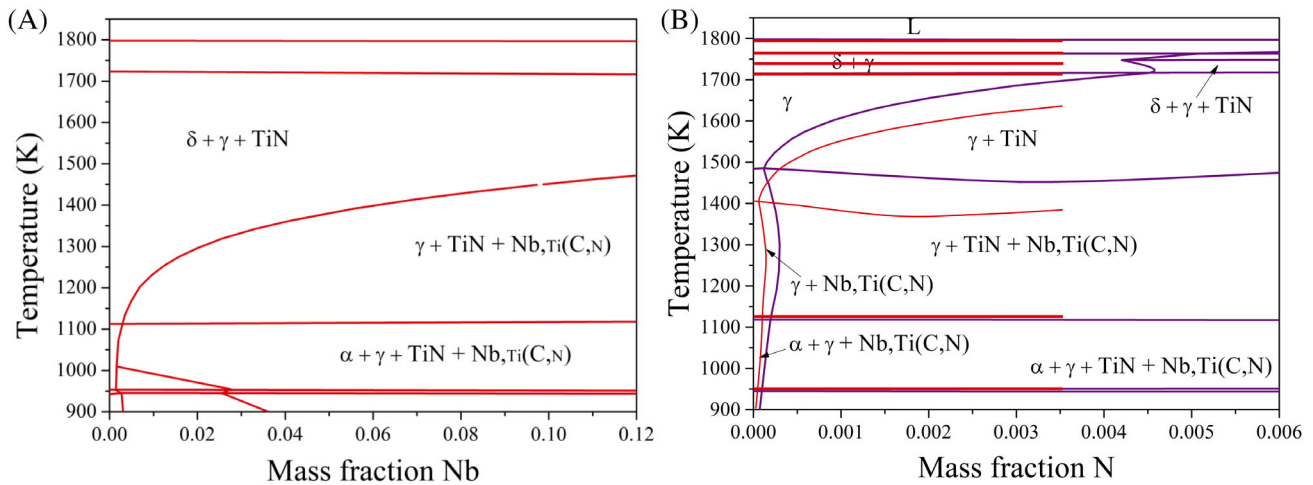
FIGURE 5 (A) The phase diagram of the High-Nb steel as a function of niobium concentration; (B) overlapped phase diagram of the Low-Ti (red curves) and high-Nb (purple curves) steels

FIGURE 6 Comparison of the Fe-C phase diagram for the Low-Nb (red curves) and High-Nb (blue curves) steels, showing that low concentration of nitrogen and niobium in the Low-Nb steel decreases the precipitation temperatures of titanium nitrides
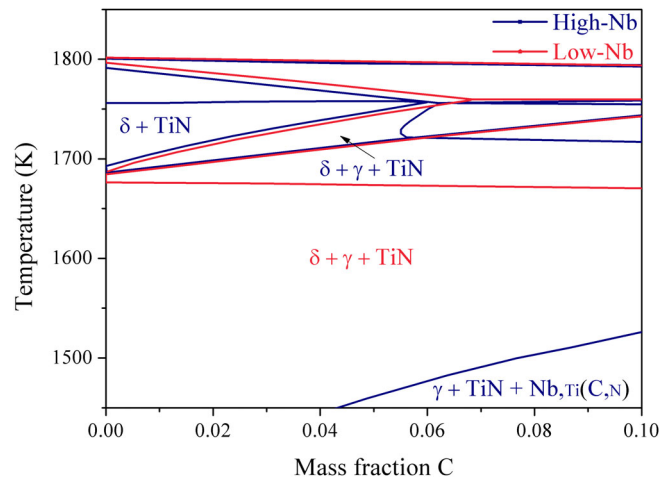
grain boundaries. Whereas austenite grains can grow rapidly at a peak temperature of 1523 K, where niobium carbonitrides are dissolved completely in the matrix. Titanium nitride precipitates are formed at temperatures above 1700 K, and remain undissolved in the austenite matrix at both selected peak 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.[11,12]

The formation temperatures of precipitates in the Low-Ti (red curves) steel are compared with the High-Nb steel (purple curves) in Figure 5B as a function of nitrogen concentration. Figure 2B showed that increasing the concentration of titanium increases only the precipitation temperature of titanium nitrides, however, Figure 5B demonstrates that the addition of niobium has significantly increased the precipitation temperatures of both nitrides and carbonitrides. 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.[14,15,35]

Figure 5B also shows that the precipitation temperature of niobium carbonitrides is almost independent of the nitrogen concentration and the precipitation temperatures are increased with the niobium concentration (Figure 5A), as a result of higher activity coefficient of Nb and Ti in these steels and previously demonstrated experimentally in HSLA steels.[39,40] 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.

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 Fe-C phase diagrams of the low-Nb steel (red) and High-Nb steel (blue) are compared in Figure 6. 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 higher 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 ~1673 K. This will cause a rapid austenite grain growth.

4 | CONCLUSION

A growing demand for improved mechanical and chemical properties of HSLA steels, has inspired development of complex chemical compositions and thermomechanical processing for pipeline steels, which requires better understanding of precipitation behavior. Here, the ThermoCalc software package, using the thermodynamic databases of TCFE7 was employed to study the precipitation of nitrides and carbonitrides as functions of C, N, Ti and Nb concentrations in pipeline steels.

- Higher concentration of titanium increases the precipitation temperatures of titanium nitrides by approximately 70 K, suggesting larger titanium nitrides.
- The niobium concentration up to 0.12 wt% in a Ti-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. Nitride precipitates contain a high concentration of titanium while carbonitrides mostly formed of niobium and carbon.
- Titanium concentration increases the precipitation temperatures of titanium nitrides in a Ti-Nb microalloyed steel. However, the precipitation temperatures of carbonitrides increase significantly with Nb concentration.

It is recognized that the dissolution and growth of precipitates and recrystallisation of grains are kinetically controlled phenomena. However, the results of the current thermodynamic approach are in good agreement with experimental data in the literature, highlighting the suitability of primary calculation approach to identify the critical temperatures of grain coarsening, recrystallisation and transformation, reducing the number of experiments required to design new alloys and heat treatment processes of microalloyed steels.

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