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Precipitation Behaviour of Carbonitrides in Ti-Nb-C-N Microalloyed Steels and an Engineering Application with Homogenously Precipitated Nano-particles

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A thermodynamic model enabling calculation of equilibrium carbonitride composition and relative amounts as a function of steel composition and temperature has been developed previously based on the chemical equilibrium method. In the present work, actual carbonitride precipitation behaviour has been verified in the Ti-Nb-C-N microalloyed steels. The Ti microalloyed steel after refining with 0.012 % Nb exhibited highly improved tensile strength without sacrificing ductility. According to further detailed SEM and TEM analysis, the improved mechanical properties of Ti/Nb microalloyed steel could be attributed to the larger solubility of Nb and Ti, inducing fine dispersion of the carbonitrides with particle size of 2 – 10 nm in the ferrite matrix.

Keywords: microalloyed steel, thermodynamic model, carbonitrides, precipitation.

1. INTRODUCTION

Microalloyed steels have been developed for many years and are widely used in industry today [1, 2]. The microalloying elements, typically niobium, vanadium, and titanium, either individually or in combination, can significantly improve the strength and toughness of high strength low alloy (HSLA) steels through retarding recrystallization and grain growth of matrix at high temperatures and through dispersion hardening both in the matrix [3]. The matrix composition, the amount and composition of the carbonitrides, and heat treatment parameters are essential in determining the optimum composition for the HSLA steels. It is well acknowledged that the quantitative computation of balanced solid solubility of complex carbonitrides is one of the difficult problems in this area. Many experimental and theoretical studies on multicomponent carbonitride compositions based on minimization of Gibbs free energy have been carried out [4 – 6]. However, ideal stoichiometry of the carbonitride was usually assumed, and interstitial or metal vacancies were not considered. In addition, very little work has been done to examine and verify the limited models available. Recently, a thermodynamic model and computing method of solid solution precipitation of the carbonitrides have been developed according to mass balance and solubility product equations, and verified in Ti-V-C-N system by solving the equations through numerical methods [7]. On the other hand, despite the importance of combined precipitate and inclusion control in Ti-bearing microalloyed steels, little information is currently available in the literature on this issue [8]. To investigate this, thermodynamic assessment of carbonitride precipitation behaviour in Ti/Nb microalloyed steels has been evaluated and a concrete engineering application example is presented by the study of mechanical properties and microstructure analysis in this paper.

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2. EXPERIMENTAL

The numerical iteration calculation process was carried out on Matlab 8.1 according to the model developed previously [7]. The sample steels were rapidly quenched to 650 °C after hot rolled at 1100 °C without subsequent heat treatment. Room temperature tensile tests were carried out on a CMT4105 testing machine according to GB/T228-2002. Metallographic specimens were prepared using conventional grinding and polishing method. The phases of the alloy was investigated by 7000S X-ray diffraction (XRD) with Cu Kα radiation. The secondary electron images were obtained on a Carl-Zeiss Auriga scanning electron microscope (SEM) and the highly magnified imaging was carried out on FEI-Tecnai G^2 20 transmission electron microscopy (TEM). The TEM samples were carefully grinded to produce a thin foil, followed by the electropolishing using a solution of 5 % perchloric acid at 30 °C.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic calculation for precipitation of carbonitrides in Ti-Nb-C-N steels

Using numerical iteration method, for a series of Ti/Nb microalloyed HSLA steels of (0.05 % – 0.20 %) C, (0.003 % – 0.015 %) N, (0.005 % – 0.035 %) Nb and (0.005 % – 0.045 %) Ti, the equilibrium thermodynamic state including the concentrations of the respective elements in solution [C], [N], [Nb] and [Ti] from 800 °C to full dissolution temperature, constants k_1, k_2, m_1 and m_2, as well as the total molar fraction of the carbonitrides has been investigated. According to the thermodynamic model [7] and the solubility products [9], the calculated full dissolution temperatures for different microalloyed HSLA steels are shown in Table 1. The carbonitride full dissolution temperature increases with increasing level of either C, N, Nb or Ti for various microalloyed steels. It should also be noted that the effect of N and Ti additions on the full dissolution temperature is expected to be greater compared with C and Nb. As is known for HSLA steels, if the full dissolution temperature is above the liquidus temperature, carbonitrides constitutional liquation would occur, which is helpful to optimize steel composition.

Table 1. Full dissolution temperature of microalloyed HSLA steels with the composition variation of C, N, Nb and Ti in Ti-Nb-C-N systems

Variation of C -(0.006N-0.015Nb-0.012Ti)		Variation of N -(0.1C-0.015Nb-0.012Ti)	
C, wt.%	T_{FD}, °C	N, wt.%	T_{FD}, °C
0.05C	1524.68	0.003N	1419.52
0.10C	1528.30	0.010N	1619.98
0.20C	1535.40	0.015N	1700.55
Variation of Nb -(0.1C-0.006N-0.012Ti)		**Variation of Ti -(0.25C-0.006N-0.015Nb)**	
Nb, wt.%	T_{FD}, °C	Ti, wt.%	T_{FD},°C
0.005Nb	1524.53	0.005Ti	1392.26
0.025Nb	1532.01	0.025Ti	1664.58
0.035Nb	1535.67	0.045Ti	1790.99

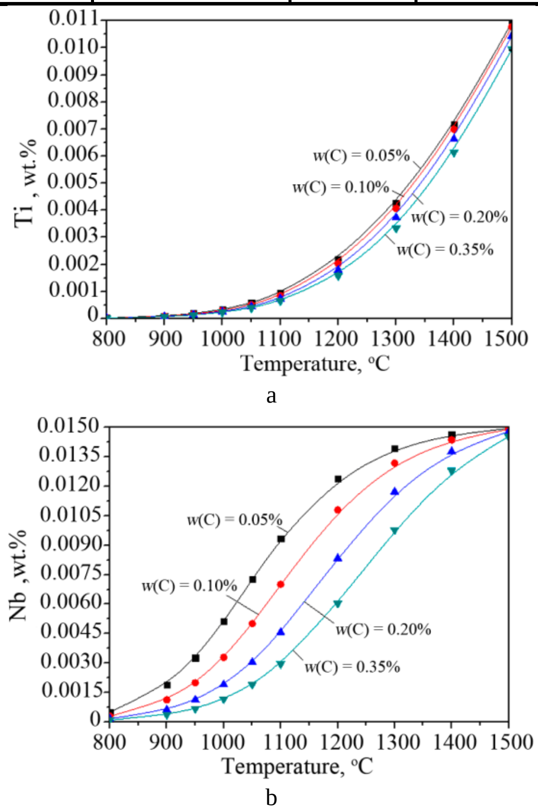


Fig. 1. Change of solid-soluted contents of Ti (a) and Nb (b) with T obtained from thermodynamic analysis of steels 0.012 % Ti-0.015 % Nb-0.006 % N-(0.05% – 0.35 %) C

The calculation results of thermodynamic analysis of the Ti-Nb-C-N steels listed above are shown in Fig. 1 – Fig. 4. At somewhat given temperature, the dissolved Ti content [Ti] decreases obviously with the increase of microalloying elements N, while seems only slight change with the variation of microalloying C and Nb content.

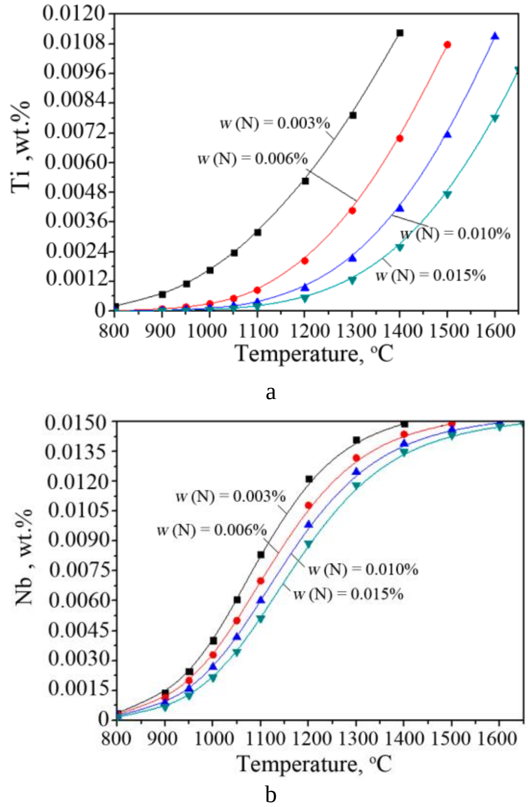


Fig. 2. Change of solid-soluted contents of Ti (a) and Nb (b) with T obtained from thermodynamic analysis of steels 0.012 % Ti-0.015 % Nb-0.10 % C-(0.003 % – 0.015 %) N

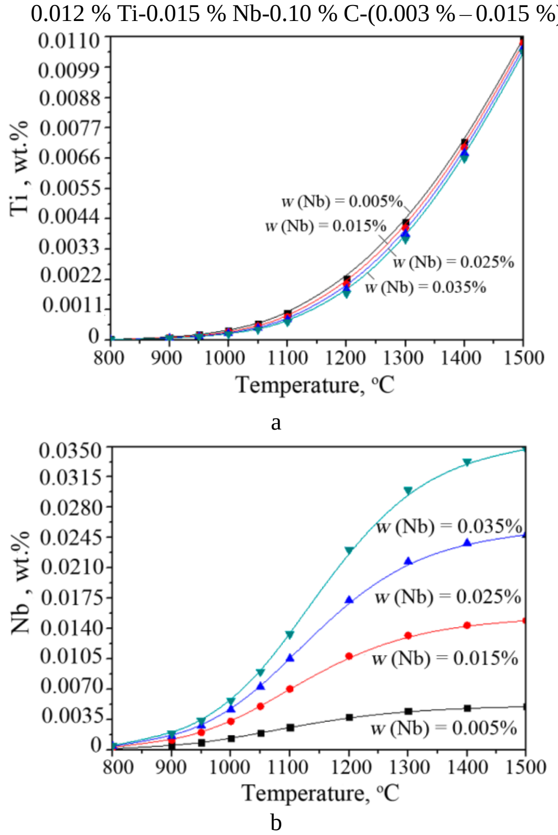


Fig. 3. Change of solid-soluted contents of Ti (a) and Nb (b) with T obtained from thermodynamic analysis of steels 0.012 % Ti-0.10 % C-0.006 % N-(0.005 % – 0.035 %) Nb

In contrast, the dissolved Nb content [Nb] increases reasonably with the content of microalloying Nb, while decreases obviously with the increase of microalloying elements C, N and Ti. Therefore in engineering application, for higher [Nb] and [Ti] dissolved in steels, it is available to decrease the addition of C and N during alloy composition design.

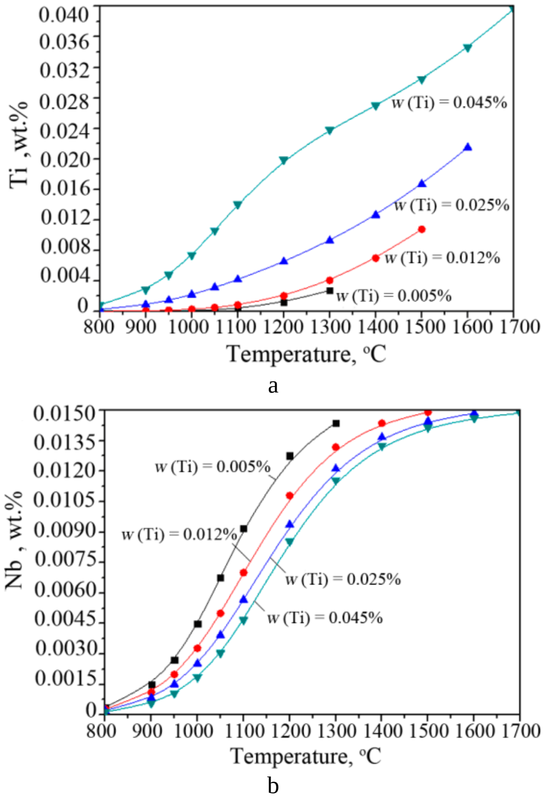


Fig. 4. Change of solid-soluted contents of Ti (a) and Nb (b) with T obtained from thermodynamic analysis of steels 0.015 % Nb-0.10 % C-0.006 % N-(0.005 % – 0.045 %) Ti

Specifically, an engineering application of Ti/Nb-bearing steel was taken as an example here. The investigated samples have the similar composition except for free or bearing of microalloying element Nb, as shown in Table 2.

Table 2. Nominal composition (wt.%) of low carbon steels investigated

	C	N	Nb	Ti	Si	P	S
S1	≤ 0.23	≤ 0.003	0	0.004	0.25	≤ 0.025	≤ 0.02
S2	≤ 0.23	≤ 0.003	0.012	0.004	0.25	≤ 0.025	≤ 0.02

For Ti/Nb bearing microalloyed steel S2, the change of solid-soluted contents of microalloying elements and relative contents of binary precipitates with temperature can be obtained as shown in Fig. 5. As verified by the thermodynamic model, the dissolved [Nb] depends most remarkably on the variation of temperature (Fig. 5 a). The chemical composition of the carbonitrides expressed by the effective activity coefficients of k_1, k_2, m_1 and m_2, strongly depends on the temperature (Fig. 5 b). The total molar quantity of the precipitated carbonitrides (*t* in Fig. 5 c) in S2 at 800 °C is only 2.1004E-4 mol, indicating its minor tendency for precipitation. The real quantities of components NbC, TiC, NbN and TiN with the change of temperature can be approximated as shown in Fig. 5 d. It should be noted that the precipitation of NbC and TiN dominates the whole composition of carbonitrides.

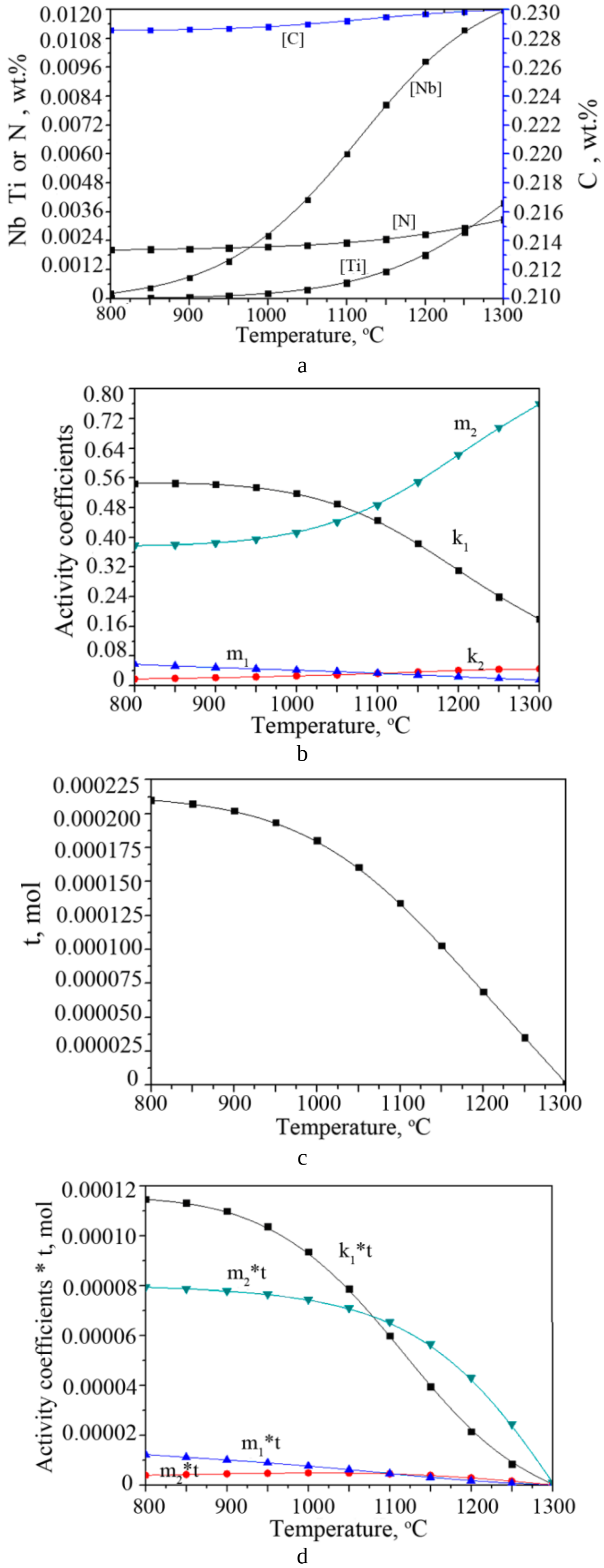


Fig. 5. Change of solid-soluted contents (a), component effective activity coefficients (b), total molar fraction of carbonitrides (c), and constants multiple total molar fraction of carbonitrides (d) with temperature T from analysis of steel S2

In addition, the full dissolution temperature is calculated to be 1301.69 °C by the model, 212.61 °C lower than corresponding liquidus temperature of 1514.30 °C, which implies that no carbonitrides constitutional liquation would occur in the Nb-bearing steels; therefore, improved mechanical properties could be anticipated.

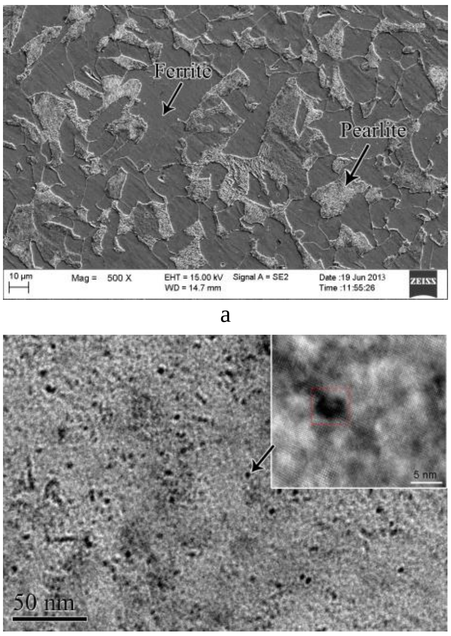
3.2. Mechanical properties and microstructure investigation

The yield strength σ_y, tensile strength σ_t and specific elongation δ for steels S1 and S2 are shown in Table 3.

Table 3. Mechanical properties measured respectively from steels S1 and S2

Samples	σ_y, MPa	σ_t, MPa	δ, %
S1	390	518	24.5
S2	498	625	22.8

For Ti-Nb-C-N microalloyed steels, Ti is employed as matrix grain growth prohibitor and Nb for precipitation strengthening and microstructure refinement, while N is used to enhance the effect of Nb and Ti [10, 11]. The improved tensile strength of Ti/Nb microalloyed S2 without sacrificing specific elongation could be attributed to the more substantial solubility of Nb and Ti, inducing fine dispersion of the carbonitrides in the ferrite matrix, which effectively increases the work hardening rate by promoting the accumulation of geometrically necessary dislocations around the particles [12, 13]. Due to the minor alloying effect and small size of precipitated carbonitrides as investigated above, this has been verified in further detailed SEM and TEM analysis as shown in Fig. 6 a and Fig. 6 b.



a

b

Fig. 6. Secondary electron SEM image (a) and bright field TEM image (b) of steel S2, the inset in (b) shows further magnified TEM image of a carbonitride particle

The homogenously distributed carbonitride particles precipitated in the ferrite matrix with the size range of 2 – 10 nm played a crucial role in the resultant properties. All existing phases have also been confirmed as shown in Fig. 7. Due to the minor alloying effect and small size of precipitated carbonitrides as investigated above, it is hard to detect their existence within the XRD resolution limit.

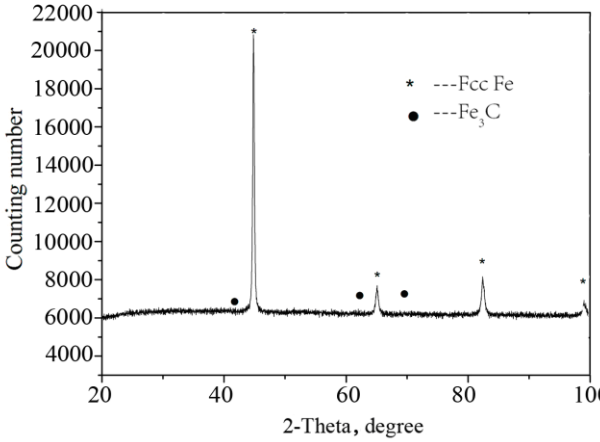


Fig. 7. XRD pattern of Ti/Nb microalloyed steel S2

4. CONCLUSIONS

In this research, the equilibrium carbonitride composition and relative amounts as a function of steel composition and temperature have been calculated in Ti-Nb-C-N microalloyed steels. The results showed that:

1. The carbonitride full dissolution temperature increases with increasing level of either C, N, Nb or Ti for various microalloyed steels. The effect of N and Ti additions on the full dissolution temperature is expected to be greater compared with C and Nb.
2. The Ti microalloyed steel after refining with 0.012 % Nb exhibited highly improved strength without sacrificing ductility. According to SEM and TEM analysis, the improved mechanical properties could be attributed to the more substantial solubility of Nb and Ti, inducing fine dispersion of the carbonitrides with particle size of 2 – 10 nm in the ferrite matrix.

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