Thermodynamic Simulation of the Formation of Carbonitrides in Steels with Nb and Ti

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Abstract—Available thermodynamic data on the Fe–Nb–Ti–C–N system have been analyzed and a self-consistent thermodynamic description of the system and its constituent subsystems has been suggested. Using the constructed thermodynamic description, calculations of phase equilibria have been performed for this system and some features concerning the effects of the alloy composition on the phase composition of steels alloyed with niobium and titanium have been considered.

Keywords: thermodynamics, Fe–Nb–Ti–C–N system, CALPHAD method, phase equilibrium, solubility, complex niobium and titanium carbonitrides

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1. INTRODUCTION

In our previous works [1–3], we have suggested a thermodynamic description of the Fe–V–C–N, Fe–Nb–C–N, and Fe–Ti–C–N systems constructed on the basis of the CALPHAD method and, using the algorithm described in [4], have analyzed the solubility of carbonitrides in the austenite of steels with carbonitride strengthening. For the steels of this type, the systems Fe–V–C–N, Fe–Ti–C–N, and Fe–Nb–C–N are basic; therefore, the thermodynamic calculations of the solubility of carbonitrides for these systems help one to understand the main laws of phase transformations in niobium-, vanadium-, and titanium-containing steels. At the same time, in practice, complex alloying with carbonitride-forming elements is frequently employed with a purpose to affect the formation of the steel structure at various stages of thermomechanical treatment. However, upon such alloying not only complex carbonitrides are formed but also the possibility of a simultaneous coexistence, in the equilibrium with austenite, of cubic and hexagonal carbides, nitrides, carbonitrides, and the Laves phase Fe2(Nb, Ti).

This work is devoted to a thermodynamic analysis of a five-component system Fe–Nb–Ti–C–N, which corresponds to steels simultaneously alloyed with niobium and titanium. This thermodynamic analysis was performed on the basis of previously constructed thermodynamic descriptions for the Fe–Nb–C–N and Fe–Ti–C–N systems [2, 3].

2. THERMODYNAMIC MODELS

When constructing a thermodynamic description of the Fe–Nb–Ti–C–N system, one should take into account, apart from the liquid and gaseous phases, also the possible formation of solid solutions based on iron and niobium, cementite, cubic and hexagonal carbides, nitrides, carbonitrides, and the Laves phase Fe2(Nb, Ti).

For the thermodynamic description of the Gibbs energy of the liquid phase, we used the model of a regular solution, according to which its molar Gibbs energy is written as follows:

\[ G^L = \sum_i X_i^{L0} G_i^L + R_Z T \sum_{i=1}^N X_i^L \ln X_i^L + \sum_{Z,IZ} \prod_{LZ} (X) L_{IZ}^L, \]

where \( X_i^L \) is the molar fraction of the \( i \)th component in the liquid phase; \( G_i^L \) is the molar Gibbs energy of the pure component \( i \) in the liquid state; \( R_Z \) is the universal gas constant; \( T \) is the absolute temperature; and \( L_{IZ}^L \) are the parameters of the solution.

For the condensed phases, we used the Hillert–Staffonsson sublattice model [6, 7], according to which the expressions for the Gibbs energy of a phase is written as a function of the molar fractions of each \( i \)th element in the \( s \)th sublattice \( Y_s^i \):

\[ G^f = \sum_{Y_s^0} \prod_Y (Y)^{0i} G_{Y_s^0}^f + R_Z T \sum_{s=1}^N a_i \sum_{i=1}^N (Y_s^i \ln Y_s^i + Y_s^i + Y_s^i \ln Y_s^i) + \mu_{\text{mag}}^f + \sum_{Z,IZ} \prod_{LZ} (Y) L_{IZ}^f. \]
Here V_a stands for a vacancy; \( a_i \) is the number of moles of sites in the sublattice \( s \) per one mole of formula units of the phase; \( Y_i' \) is the molar fraction of the component \( i \) in the sublattice \( s \) of the phase \( f \); \( G_{f0}^{bf} \) denotes the Gibbs energy of one mole \( Y_i' \) of formula units of a compound with the same crystal structure as that of the phase \( f \) corresponding to the element of the array \( I_0 \) which determines one element for each sublattice;
\[
\prod_{f0} (Y)^0_{f0} G_{f0}^{bf} \text{ denotes the product of the corresponding elements of the matrix } (Y)_; \]
\( I_1 \) means an array that defines such variants of the distribution of atoms in the sublattices when one sublattice contains atoms of two elements, while the other sublattices contain atoms of only one element; \( \prod_{I_1} (Y) \) corresponds to the product of the corresponding elements of the matrix \((Y)_I\). The array \( I_1 \) is called a first-order array, in contrast to the zero-order array. The arrays of higher orders, \( IZ \), correspond to various combinations of a greater number of elements from different sublattices.

For magnetic phases, the contribution of magnetic ordering to the Gibbs energy of a phase is usually described, according to [8], on the basis of the Inden model suggested in [9]. According to [8], the contribution to the Gibbs energy due to magnetic ordering is given by the expression
\[
G_{mag}^f = R_s T \ln(\beta + 1) g(\tau), \quad (3)
\]
where \( \tau = T/T_c \), \( T_c \) is the critical temperature of the destruction of magnetic order (Curie temperature for ferromagnetic materials or the Néel temperature for the antiferromagnets); \( g(\tau) \) is a function of \( \tau \); \( \beta \) is the average magnetic moment per atom (in Bohr magnetons). In more detail, the procedure of the calculations of \( G_{mag}^f \) is described in [4]. For the nonmagnetic phases, \( G_{mag}^f \) is equal to zero.

The solid solutions, cubic and hexagonal carbides, nitrides, and carbonitrides were considered as compounds with two sublattices, one of which is occupied by metallic atoms and the other, by interstitial atoms and vacancies. For the Fe–Nb–Ti–C–N system, these phases are described by the formula \((Fe, Nb, Ti)_{a1} (Va, C, N)_{a2}\), the bcc \( \alpha \) solid solution (ferrite) has the sublattice formula \((Fe, Nb, Ti)(Va, C, N)_3\), i.e., \( a_1 = 1, a_2 = 3 \); for the phases with an fcc sublattice of metallic atoms (austenite, cubic carbide, nitride, carbonitride), \( a_1 = 1 \) and \( a_2 = 1 \); for the compounds with an hcp crystal lattice of metallic atoms (hexagonal solid solution, hexagonal carbide, nitride, carbonitride), \( a_1 = 1, a_2 = 0.5 \).

For the intermetallic Laves phase, a two-sublattice model with a formula \((Fe, Nb, Ti)_{a2}(Fe, Nb, Ti)_{a1}\) was used; correspondingly, the expression for the Gibbs energy per one formula unit is written as
\[
G_{Laves} = Y_{Fe}^1 Y_{Fe}^2 0 Y_{Fe}^{12} G_{Fe,Fe}^{bf} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^4 G_{Fe,Fe}^{bf} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 0 Y_{Fe,Fe}^{12} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^4 G_{Fe,Fe}^{bf} (4)
\]
\[
\begin{align*}
&+ Y_{Nb}^1 Y_{Fe}^2 Y_{Fe}^2 Y_{Fe}^{12} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 0 Y_{Fe,Fe}^{12} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^4 G_{Fe,Fe}^{bf} \\
&+ Y_{Ti}^1 Y_{Fe}^2 Y_{Fe}^2 Y_{Fe}^{12} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 0 Y_{Fe,Fe}^{12} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^4 G_{Fe,Fe}^{bf} \\
&+ R_s T [2 \left(Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 \ln Y_{Fe}^1 + Y_{Fe}^{12} \ln Y_{Fe}^{12} + Y_{Fe}^1 Y_{Fe}^2 \ln Y_{Fe}^1 + Y_{Fe}^{12} \ln Y_{Fe}^{12} \right) + \left(Y_{Fe}^{12} Y_{Fe}^1 Y_{Fe}^2 \ln Y_{Fe}^{12} + Y_{Fe}^{12} \ln Y_{Fe}^{12} \right)] + \frac{E}{G_{Laves}}
\end{align*}
\]
where
\[
E_{Laves} = Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} (5)
\]
\[
\begin{align*}
&+ Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} \\
&+ Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} \\
&+ Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} \\
&+ Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} \\
&+ Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe} + Y_{Fe}^1 Y_{Fe}^2 Y_{Fe}^2 L_{Fe,Fe} + Y_{Fe}^{12} Y_{Fe,Fe}^{12} L_{Fe,Fe}.
\end{align*}
\]