First-Principle Study on the Stability of Lightly Doped (Nb$_{1-x}$Ti$_x$)C Complex Carbides and Their Verification in 1045 Steel

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1. INTRODUCTION

Faced with global warming and environmental issues, there is an urgent need for steel materials to develop in a green direction, which requires steel materials to have better comprehensive mechanical properties and service life. For as-cast steel materials, adding grain refiners to the melt is one of the most effective strengthening methods. By dispersing the particles uniformly in the melt, the concentration fluctuations and the overcooling of the composition formed by the surface melting of the particles make the particles become the nucleation core to refine the grains, which greatly improves the strength, toughness, and fatigue strength of the material. Among them, Nb, Ti, and V carbide nitrides are widely used in steel materials due to their high hardness, high melting point, and excellent thermal and chemical stabilities. Qin et al. prepared nano-NbC particles through mechanical alloying and heat treatment. Also, these particles were successfully added to 1020 steel so that the microstructure of the material was refined and the comprehensive mechanical properties were improved. Park’s research group prepared ultrafine TiC nanoparticles and added them to S25C medium carbon steel to improve the properties of cast steel. Lazarova et al. prepared TiCN particles by self-propagating high-temperature synthesis and successfully added them to P206GH cast steel so that the steel achieved excellent comprehensive mechanical properties. However, when the particles are added to the molten steel, they tend to float or sink because of the density difference between the particles and molten metal, resulting in low utilization efficiency and high cost. For steel materials to have a more uniform microstructure and controllable performance, improving the utilization rate by changing the density of carbides is an important way to reduce costs. However, due to the wide variety of complex carbides, the basic properties and stability usually need to be predicted using the first-principles methods to facilitate reasonable design and development. Jang et al. calculated the stability of (Ti, M)C (M = Nb, V, Mo, and W) complex carbides. The results show that the addition of Mo and W can make the carbides more stable, and it was confirmed by experiment. Adjaoud et al. made a first-principle prediction on the properties of complex carbides in the ZrC–TiC system. They believed that the physical properties of complex carbides could be controlled by the content of Zr or Ti. Liu et al. utilized, the mixing Gibbs free energy and formation enthalpy difference of different Ti-doped (Nb$_{1-x}$Ti$_x$)C complex carbides were calculated using the Cambridge Serials Total Energy Package (CASTEP) module of Materials Studio 2019 software. The calculation results predict that (Nb$_{1-x}$Ti$_x$)C complex carbides have higher stability than pure NbC and TiC. Therefore, three lightly Ti-doped (Nb$_{1-x}$Ti$_x$)C complex carbides with theoretical densities close to that of the 1045 steel were designed for calculations. The calculation results show that the formation energy of (Nb$_{1-x}$Ti$_x$)C complex carbides decreases with an increase in the Ti content. These designed (Nb$_{1-x}$Ti$_x$)C complex carbides have mechanical stability, and their bulk modulus, shear modulus, Young’s modulus, and hardness are all lower than those of pure NbC. The electronic performance results show that these three structures show good conductivity, and the 3d orbitals of Ti atoms and the 4d orbitals of Nb atoms are strongly hybridized with the 2p orbitals of C atoms. The Nb–C and Ti–C bonds exhibit strong covalent bonds. To verify the stability of the (Nb$_{1-x}$Ti$_x$)C complex carbides, the prepared (Nb$_{0.8}$Ti$_{0.2}$)C complex carbide was added to the 1045 steel as a refiner. After observing under a transmission electron microscope (TEM), we found that the (Nb$_{0.8}$Ti$_{0.2}$)C complex carbide could exist stably as a face-centered cubic structure, which provided a method for the design and synthesis of complex carbides used for refriners.
prepared nanocrystalline \((\text{Ti}_{1-x}\text{Zr}_{x})\text{C}_{1-y}\) complex carbides by spark plasma sintering, which confirmed Adjaoud’s prediction, and the results show that the mechanical properties of complex carbides were better than those of pure \(\text{ZrC}\) and \(\text{TiC}\). Hua et al. calculated the mechanical and thermodynamic properties of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) complex carbides, and the results showed that Ti-rich complex carbides have higher stability, while this result has not been confirmed in the experiments.

Based on the previous research studies, three lightly Ti-doped \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) complex carbides were designed and their mechanical and electronic properties calculated after verifying the stability of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) complex carbides. After being synthesized in the experiment, the \((\text{Nb}_{0.8}\text{Ti}_{0.2})\text{C}\) carbides were added to the molten 1045 steel for characterization. The well-dispersed \((\text{Nb}_{0.8}\text{Ti}_{0.2})\text{C}\) carbides were found in the as-cast structure, which verified the prediction of theoretical calculation.

2. CALCULATION METHOD

The Cambridge Serial Total Energy Package (CASTEP) code in Materials Studio 2019 (BIOVIA, San Diego, CA), which is based on density function theory (DFT) and the ultrasoft pseudopotential (USP) method, was used to perform all of the calculations.\(^{24,25}\) The constructed supercell \((2 \times 2 \times 2)\) contains 64 atoms, and the precision of parameter setting is fine, that is, the plane-wave cutoff energy is set to 300 eV, the energy change of each atom is less than 1.0 \(\times 10^{-5}\) eV during constant iteration, and the force on each atom is not more than 0.03 eV/Å, the maximum ion displacement is less than 0.001 Å, the internal stress is not more than 0.05 GPa. The exchange-correlation energy function is described by the Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA). The \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) complex carbides are based on the virtual crystal approximation (VCA) method.

USP is used to describe the interaction potential between ion and electron.

3. RESULTS AND DISCUSSION

The mixing Gibbs free energy \((\Delta G)\) is an important parameter to evaluate the stability of the material structure.\(^{25,26}\) Therefore, to grasp the overall trend of the stability of the complex carbides with the increasing Ti content, the mixing Gibbs free energy at different temperatures is calculated according to eqs 1–3, and the results are shown in Figure 1a.

\[
\Delta G = \Delta H - T\Delta S \tag{1}
\]

\[
\Delta H = E(\text{Nb}_{1-x}\text{Ti}_x)\text{C} - (1-x)E(\text{NbC}) - xE(\text{TiC}) \tag{2}
\]

\[
\Delta S = -R[(1-x)\ln(1-x) + x\ln x] \tag{3}
\]

where \(\Delta H\) is the mixing enthalpy; \(x\) is the atomic fraction of Ti in complex carbides; \(E(\text{Nb}_{1-x}\text{Ti}_x)\text{C}\), \(E(\text{NbC})\), and \(E(\text{TiC})\) are the energies of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\), \(\text{NbC}\), and \(\text{TiC}\), respectively; \(\Delta S\) is a configurational entropy change associated with cation mixing; and \(R\) is the ideal gas constant.

According to the calculation result, the mixing Gibbs free energy of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) decreases with increasing Ti content. When the Ti content increases to 0.375, the value of mixing Gibbs free energy is \(-0.177\) kJ/mol. As the Ti content further increases, the mixing Gibbs free energy gradually increases. However, they are always negative, it indicates that the \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) complex carbides are more energetically favorable. It is worth noting that, at the same doping amount, the mixing Gibbs free energy of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) decreases as the temperature increases, which indicates that the complex carbides are more stable at high temperatures. Especially, the mixing Gibbs free energy of \((\text{Nb}_{0.5}\text{Ti}_{0.5})\text{C}\) at 1800 K is \(-10.54\) kJ/mol. This means that \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) complex carbides have the basic conditions used for structural materials refinement, especially for high-temperature conditions.

The formation energy is an important parameter for evaluating the thermodynamic stability of complex carbides.\(^{27,28}\) Therefore, the formation energy of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) is calculated according to eq 4, and the formation entropy difference of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) is calculated. The result is shown in Figure 1b.

\[
\Delta F = \frac{E(\text{Nb}_{1-x}\text{Ti}_x)\text{C}) - (1-x)\mu_{\text{Nb}}^\text{bulk} - x\mu_{\text{Ti}}^\text{bulk} - \mu_{\text{C}}^\text{bulk}}{2} \tag{4}
\]

where \(\mu_{\text{ Nb}}^\text{ bulk} \), \(\mu_{\text{ Ti}}^\text{ bulk} \), and \(\mu_{\text{ C}}^\text{ bulk} \) are the chemical potentials of Nb, Ti, and C in the form of bulk substances, respectively, i.e., the energies per atom of pure elements. Since there are only two atoms in the complex carbides, the denominator is 2. It can be seen that the formation energy of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) is lower than that of the mechanical mix of pure NbC and TiC. Also, the formation energy of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) decreases first and then increases with the increasing Ti content. When the \(x\) is 0.375, the difference in the formation energy of \((\text{Nb}_{1-x}\text{Ti}_x)\text{C}\) is \(-0.177\) eV/fu, i.e., the stability is the highest. The corresponding structure is inserted in Figure 1b. This result also shows that the stability of Nb-rich complex carbide is...
higher than that of Ti-rich complex carbide. This is inconsistent with the research results of Hua et al. that it is easier to form Ti-rich complex carbides,\textsuperscript{21} which may be caused by the difference in the substitution positions of Ti atoms and the software data packages.

In the method of using carbide particle refiner to promote nucleation, refining grains, and strengthening the mechanical properties of steels, the carbides tend to float or sink due to the density difference between particles and melt, which is inconvenient for the dispersion of carbides.\textsuperscript{29} According to the above calculation, the thermodynamic stability of (Nb\textsubscript{1-x}Ti\textsubscript{x})C is higher than the mechanical mixing of NbC and TiC. Therefore, three kinds of lightly Ti-doped (Nb\textsubscript{1-x}Ti\textsubscript{x}) C complex carbides have been designed to realize the density

Figure 2. (Nb\textsubscript{1-x}Ti\textsubscript{x})C complex carbide models. The black balls denote C atoms, light green denote Nb atoms, and blue denote Ti atoms. (a) NbC, (b) (Nb\textsubscript{0.90625}Ti\textsubscript{0.09375})C, (c) (Nb\textsubscript{0.8125}Ti\textsubscript{0.1875})C, and (d) (Nb\textsubscript{0.71875}Ti\textsubscript{0.28125})C.

Figure 3. (a) Total energy of (Nb\textsubscript{1-x}Ti\textsubscript{x})C and (b) volume of (Nb\textsubscript{1-x}Ti\textsubscript{x})C. (c) Formation energy of (Nb\textsubscript{1-x}Ti\textsubscript{x})C. (d) Theory density of (Nb\textsubscript{1-x}Ti\textsubscript{x})C.
control of complex carbides, and thereby increasing the operability of the experiment.

NbC and TiC have the same space group of Fm3m (225), that is, a typical NaCl-type face-centered cubic structure.30,31 Metal atoms occupy the prismatic and body-centered positions of the face-centered cubic. Six face-centered C atoms form a regular octahedron. With NbC as the parent phase, the density can be controlled by replacing the positions of Nb atoms with Ti to form nonstoichiometric carbides. Also, then, Ti atoms are used to sequentially replace zero, three, six, and nine Nb atoms to form NbC, (Nb0.90625Ti0.09375)C, (Nb0.8125Ti0.1875)C, and (Nb0.71875Ti0.28125)C. The crystal structure models are shown in Figure 2.

The structural stability of the complex carbide can be judged by the total energy of the unit cell after geometric optimization.32 The total energy is negative, and the smaller the absolute value, the greater the structural stability. The relationship between the (Nb1−xTx)xC unit cell energy and the Ti content is shown in Figure 3a. It can be seen that with the increase in the Ti content, the total energy of the unit cell shows a linear downward trend from −54648.2 to −55121.2 eV, or a 0.87% drop. This phenomenon indicates that the replacement of Ti promotes the stability of NbC.

Among the three doped structures, the structure with the highest Ti content has the highest stability. It can be seen from Figure 3b that the unit cell volume first increases and then decreases with the increasing Ti content. This may be due to the larger lattice distortion caused by the lower Ti content. As the Ti content increases, the lattice distortion gradually decreases. Figure 3c shows that the formation energy of (Nb1−xTx)xC gradually decreases with the increasing Ti content. The formation energy is −56.2 kJ/mol for NbC and −58.7 kJ/mol for (Nb0.71875Ti0.28125)C. That is, the thermodynamic stability of (Nb1−xTx)xC gradually increases. The calculation results are consistent with the trend in Figures 1 and 3a. The theoretical densities of the four unit cell structures are calculated, and the results are shown in Figure 3d. It can be seen that the theoretical density of (Nb1−xTx)xC gradually decreases with the increasing Ti content. The density of the designed (Nb0.8125Ti0.1875)C carbide is 7.20 g/cm³, which is the same as the theoretical density of the molten 1045 steel.12

Bulk modulus (B) and shear modulus (G) are important parameters of the macromechanical properties of materials.33,34 Among them, the bulk modulus represents incompressibility, which is the pressure required for unit relative volume shrinkage. The larger the bulk modulus, the stronger the deformation resistance of the materials. The shear modulus is the ratio of the shear stress to the shear strain generated when the materials are subjected to shear stress. The greater the shear modulus, the stronger the rigidity of the materials and the stronger its resistance to plastic deformation. Therefore, they can be used as a measure of whether the material is ductile or plastic. The calculation results of the bulk modulus and shear modulus of the four models are shown in Figure 4a. After doping, the values of both the bulk modulus and shear modulus decrease initially and then increase. In the lightly doped (Nb1−xTx)xC structures, the maximal shear modulus is 212.6 GPa and the maximal bulk modulus is 283.4 GPa for (Nb0.71875Ti0.28125)C. However, the trend of change of bulk modulus is not obvious with the increasing Ti content.

Young’s modulus is used to measure the degree of difficulty of atoms to leave the equilibrium position, and it is a measure of the strength of bonding between atoms in a crystal.35 It is an insensitive parameter of the structure. In engineering, it is a measure of the stiffness of a material. In the case of the same external force, the greater the elastic modulus of the material, the greater the stiffness, and its value can be calculated according to eq 5:

\[
E = \frac{9BG}{3B + G}
\]

where E is the Young's modulus, B is the bulk modulus, and G is the shear modulus.

![Table 1. Calculated Lattice Parameters a, b, and c (Å) and Elastic Parameters (GPa) of Complex Carbides](https://doi.org/10.1021/acsomega.1c02950)
The hardness of a material is one of the basic mechanical properties of a material, which can be derived from an empirical formula. According to the semiemirical formula of hardness and bulk modulus proposed by Hu et al. as below\textsuperscript{37}

\[ Hv = 2(k^2G)^{0.585} - 3 \]

where \( Hv \) is the hardness, \( G \) is the bulk modulus, and \( k = G/\rho \).

The curve of Young’s modulus and hardness is shown in Figure 4b. It can be seen that Young’s modulus and hardness decrease after Ti doping. With the increase in the Ti content, both these values show an upward trend and the trend of change is the same. In the lightly doped (Nb\(_{1-x}\)Ti\(_x\))C\(_2\) structures, the maximal Young’s modulus is 110.2 GPa, and the maximal hardness is 29.9 GPa for (Nb\(_{0.71875}\)Ti\(_{0.28125}\))C. The difference in the hardness can be attributed to the change in the slip system of the complex carbide after doping with Ti\(_2\)\textsuperscript{21,38} where the slip system of NbC is (111)\textsuperscript{′} the maximal hardness is 29.9 GPa for (Nb\(_{0.71875}\)Ti\(_{0.28125}\))C. The elastic parameters for the four models are shown in Table 1.

Through calculation, it can be known that all four models satisfy the Born criterion of mechanical stability. Poisson’s ratio (\( \nu \)) and Pugh’s ratio (\( B/G \)) are used to evaluate and predict the ductility and brittleness of the materials, respectively.\textsuperscript{42} Material with Poisson’s ratio (\( \nu \)) >1/3 are ductile, otherwise they are brittle. The larger the value of \( \nu \), the better the ductility of the materials. Pugh’s ratio (\( B/G \)) >1.75 indicates that the materials are brittle, otherwise they are ductile. Besides, the typical value of \( \nu \) is 0.1 for covalent materials and 0.33 for metallic materials. Therefore, it can be seen that only complex carbides with the Ti doping amount of 9.375 atom % are ductile and the rest are brittle.

Tetragonal stiffness is estimated by eq 8. It can be seen from Table 1 that after Ti doping, the tetragonal stiffness of the complex carbide decreases. However, as the Ti content increases, the tetragonal stiffness shows an increasing trend with the maximal tetragonal stiffness of 254.08 GPa for (Nb\(_{0.71875}\)Ti\(_{0.28125}\))C. Shear stiffness (\( C_{44} \)) shows the same trend as the tetragonal stiffness with the maximal shear stiffness of 190 GPa for (Nb\(_{0.71875}\)Ti\(_{0.28125}\))C. The anisotropy is determined by the ratio of the shear stiffness to the tetragonal stiffness. If the value is close to 1, the structure tends to be more isotropic, otherwise the degree of isotropy decreases while that of anisotropy increases. After doping with Ti, the anisotropy ratio first increased and then decreased with a further increase in the Ti content, with the minimum anisotropy ratio of 0.75 for (Nb\(_{0.71875}\)Ti\(_{0.28125}\))C, indicating that the ductile plasticity of complex carbides decreased.

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Table 2. Calculated Independent Elastic Constants \( C_\nu \) (GPa) of (Nb\(_{0.8125}\)Ti\(_{0.1875}\))C

| \( C_\nu \) (GPa) | \( C_{11} \) | \( C_{12} \) | \( C_{13} \) | \( C_{22} \) | \( C_{23} \) | \( C_{33} \) | \( C_{44} \) | \( C_{55} \) | \( C_{66} \) | \( C_{11} \) |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| (Nb\(_{0.8125}\)Ti\(_{0.1875}\))C | 489 | 501 | 496 | 148 | 151 | 152 | 140 | 140 | 140 | 140 |
| (Nb\(_{0.8125}\)Ti\(_{0.1875}\))C | 489 | 501 | 496 | 148 | 151 | 152 | 140 | 140 | 140 | 140 |
| (Nb\(_{0.8125}\)Ti\(_{0.1875}\))C | 147 | -2.8 | -1.1 | -1.1 | -1.1 | -1.1 | -1.1 | -1.1 | -1.1 | -1.1 |
| (Nb\(_{0.8125}\)Ti\(_{0.1875}\))C | 0.2 | -0.6 | -1.7 | -1.9 | 1.4 | -0.7 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |

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Therefore, Nb/Ti/C = 0.8:0.2:1 was selected to prepare (NbTi)C complex carbide powder in the experiment. Through the vacuum melting method, the prepared complex carbide powder was added to the 1045 steel as a refiner. The transmission electron microscopy (TEM) observations are shown in Figure 7. It can be seen that the (NbTi)C nanoparticles can be uniformly dispersed in the matrix (Figure 7a) without forming agglomerations, with a particle size of about 100 nm (Figure 7b).

The energy-dispersive X-ray (EDX) spectrum analysis was performed on the single (NbTi)C particle in Figure 7b, and the results are shown in Table 3. According to Table 3, Nb/Ti = 31:5.2 ≈ 0.85:0.15, which is almost the same as the experimental design (Nb/Ti = 0.8:0.2). The selected area

Figure 5. Partially enlarged band structures near Fermi level of complex carbides: (a) NbC, (b) (Nb0.90625Ti0.09375)C, (c) (Nb0.8125Ti0.1875)C, and (d) (Nb0.71875Ti0.28125)C.

Figure 6. Total and partial density of states of complex carbides (a) NbC, (b) (Nb0.90625Ti0.09375)C, (c) (Nb0.8125Ti0.1875)C, and (d) (Nb0.71875Ti0.28125)C.
diffraction pattern (SADP) results are shown in Figure 7d. It can be seen that the diffraction patterns are composed of two sets of patterns, one is body-centered cubic α-Fe and the other is face-centered cubic (NbTi)C. It can be observed that the complex carbide has a face-centered cubic structure, and the prepared (NbTi)C nanoparticles can stably exist in the 1045 steel after being smelted at high temperatures.

In summary, through theoretical calculations of the mixing Gibbs free energy and formation enthalpy difference of (Nb1−xTi)xC complex carbides, the Ti-doped NbC was found to show a more stable structure. Also, as the temperature increases, the mixing Gibbs free energy of (Nb1−xTi)xC is reduced, indicating that (Nb1−xTi)xC complex carbides exist stably at high temperatures. To design a complex carbide that can be applied to the 1045 steel, three lightly Ti-doped structures are designed. After calculating the unit cell energy, lattice constant, and elastic constant, it can be observed that the lightly Ti-doped structure satisfies the Bore criterion of mechanical stability. The calculation of electronic properties shows that complex carbides all have conductive properties, and the Nb−C and Ti−C bonds showed covalent bond characteristics. Therefore, it is believed that the complex carbides have the possibility of experimental synthesis, which is consistent with the predicted results in Figure 1a.

In the experiment, the (NbTi)C complex carbide whose theoretical density is close to that of molten steel is selected and added to the 1045 steel. After TEM observation, it was found that (NbTi)C can stably exist in the as-cast 1045 steel, and the ratio of Nb and Ti in the complex carbide is close to the theoretical design. Using first principles calculations to predict the properties of carbides, and then experimental implementation is a feasible method to synthesis the refiner.

### 4. CONCLUSIONS

Through the calculation of mixing Gibbs free energy and enthalpy difference of formation of (Nb1−xTi)xC complex carbides, three lightly Ti-doped models were designed. Also, the experiment of Nb/Ti = 0.8:0.2 complex carbide was carried out in the 1045 steel. The following conclusions were drawn:

1. Compared with pure NbC and TiC, the (Nb1−xTi)xC complex carbides had lower mixing Gibbs free energy and formation energy; also, as the temperature increased, the mixing Gibbs free energy of (Nb1−xTi)xC complex carbides was reduced.

2. Three types of lightly Ti-doped NbC complex carbides were designed. The theoretical calculation results showed that they have thermodynamic stability, mechanical stability, and electrical conductivity. The bonds of Nb−C and Ti−C showed covalent bond characteristics.

3. The complex carbide with Nb/Ti/C = 0.8:0.2:1 was selected to be added to the 1045 steel. The presence of complex carbide was observed in the experiment, which provided a new path for the preparation of the as-cast structural material refiners.

### EXPERIMENTAL DETAILS

Nb powder, Ti powder, and graphite powder were mixed and ball-milled for 8 hours according to atomic ratio Nb/Ti/C = 0.8:0.2:1 using the planetary ball mill and continued to ball-milled for 3 h after adding the same weight of Fe powder. The mixed powder was annealed at 750 °C for 15 min to obtain the (NbTi)C/Fe powder. A vacuum induction melting furnace was used to obtain the modified 1045 steel. The mixed powder is added after holding at 1580−1620 °C for 2 min, and then fully stirred and cast to obtain an ingot of Ø50 mm × 40 mm. Take
the sample at half the radius of the ingot, observe the added (NbTi)C particles with FEI Tecnai G2 F30 TEM, and identify the composition and structure of the particles through the attached energy-dispersive spectrometer (EDS) and selected area diffraction pattern (SADP). The detailed experimental method, process, and conclusion have been published in previous articles.44–46

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**Notes**

The authors declare no competing financial interest.

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