Identification of a Potential Superhard Compound ReCN

Xiaofeng Fan^{a,*}, M.M. Li^a, David J. Singh^{c,d}, Qing Jiang^a, W.T. Zheng^{a,b,†}

- a.* College of Materials Science and Engineering and Key Laboratory of Automobile Materials of MOE, Jilin University, Changchun 130012, China
- b.* State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
- c.* College of Materials Science and Engineering, Jilin University, Changchun 130012, China
- d.* Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056, USA

Abstract

We identify a new ternary compound, ReCN and characterize its properties including structural stability and indicators of hardness using first principles calculations. We find that there are two stable structures with space groups $P63mc$ (HI) and $P3m1$ (HII), in which there are no C-C and N-N bonds. Both structures, H1 and HII are elastically and dynamically stable. The electronic structures show that ReCN is a semiconductor, although the parent compounds, ReC_2 and ReN_2 are both metallic. ReCN is found to possess the outstanding mechanical properties with the large bulk modulus, shear modulus and excellent ideal strengths. In addition, ReCN may perhaps be synthesized relatively easily because it becomes thermodynamic stable with respect to decomposition at very low pressures.

Keywords: superhard, ideal strength, compound ReCN

* xffan@jlu.edu.cn

† wtzheng@jlu.edu.cn

1. Introduction

Development of new superhard materials is of importance because of potential uses for cutting tools, abrasives, wear resistant coatings and other applications. This also represents a fundamental challenge as superhardness is a very difficult property to achieve, especially in materials that can be synthesized under moderate conditions¹. Nonetheless, there have been several recent advances particularly for 5d transition metal nitrides. Here we identify a new potential superhard ternary compound, ReCN, and elucidate its properties using first principles calculations.

Transition metal nitrides (TN_x) are of interest because of their high strength and wear resistance as well as for the unusual bonding and resulting physical properties in some of them²⁻⁴. Recently, OsN₂, IrN₂ and PtN₂ compounds having very high bulk moduli have been synthesized under high temperature and high pressure⁵⁻⁸. Re₂N and Re₃N have also been recently synthesized under relatively moderate synthesis conditions and were reported to be ultra-incompressible with bulk moduli of about 400 GPa⁹. However, although ultra-incompressible, ReN₂ and ReN₃ have substantially lower ideal shear strengths. This suggests that they cannot be intrinsically superhard¹⁰. Certain transition metal borides, e.g. OsB₂, show ultra-incompressible hard behavior as well¹¹. OsC has also been predicted to be potentially superhard, and additionally metallic and superconducting¹². Thus superhard materials are found among heavy transition metal borides, carbides and nitrides. While the available data are somewhat sparse, superhardness is possibly more abundant among transition metal borides and nitrides than among the carbides. We note that the elements in the middle of the 5d series, particularly Re and Os, are highly incompressible. Obtaining superhard behavior requires maintaining

and if possible enhancing this incompressibility while adding more directional bonding to increase the shear strength¹³.

The bonding of these materials and their hardness reflects the combination of strong *p*-bonds characteristic of first row *p*-elements and strong covalent *2p-5d* bonds. In this regard, borides, carbides and nitrides may be expected to be rather different. For example, boron *p*-bonding networks are electron deficient, leading to incomplete charge transfer from metal atoms and enhanced metal-B bonding, facts that underlie both the properties of the superhard borides, the metallic nature, as well as for example the superconductivity of MgB₂. This differs from the behavior of carbides and nitrides, which while not having the electron deficient bonding networks do have increasing electronegativity as atoms.

Returning to hardness, it is proposed that the hardness of compounds ReN_{*x*} may increase with increasing nitrogen content, *x*. In this context, ReN₂ is of particular interest and has been studied theoretically and subsequently experimentally synthesized and characterized. Theoretically, a β -BeO₂ like structure with space group *Pbcn* was proposed by Li *et al.*¹⁴, while a rutile structure with space group *P4₂/mnm* was predicted by Zhao *et al.*¹⁵. Du *et al.* then reported that tetragonal ReN₂ with space group *P4/mmm* is more stable at high pressures above ~30 GPa¹⁶. Significantly, this *P4/mmm* ReN₂ reportedly has a high shear modulus of 289 GPa - an important characteristic of a superhard phase. In addition, two hexagonal structures with space groups *P6₃/mmc* and *P-6m2* were proposed by Soto *et al.*¹⁷. Experimentally, Kawamura *et al.* recently reported synthesis of ReN₂ under 7.7 GPa at 1873 K¹⁸. The synthesized ReN₂ material was proposed to have a MoS₂-like structure (space group *P6₃/mmc*)¹⁸. However, Wang *et al.* reported that this MoS₂-like structure is unstable for ReN₂ due to the presence of a negative shear elastic

constant C_{44} , which suggests that the actual structure may be more complex¹⁹. Low shear elastic constants are not compatible with superhardness.

Similar to ReN_x , ReC_x has been proposed as a potential hard material. Recently, Re_2C was synthesized under high temperature (873-1873 K) and moderate pressure (2-6 GPa) and is a novel ultra-incompressible hard material²⁰. ReC_2 has been proposed to have a hexagonal structure with space group $P-6m2$ and large Vickers hardness of 32.2 GPa, which exceeds the hardness of $\alpha\text{-SiO}_2$ (30.6 GPa) and $\beta\text{-Si}_3\text{N}_4$ (30.3 GPa)²¹, although the phase is thought to be only metastable at ambient pressure.

Studies of hard coatings indicate that the electronic and mechanical properties of transition metal nitrides (carbides) are generally expected to be significantly modified by the incorporation of carbon (nitrogen)²²⁻²⁶. Thus transition metal carbonitrides could be potentially useful hard materials. However, relatively little is known about Re carbonitrides.

Here we report first principles calculations done to address some of the properties of a mixed ReCN material. We analyze the structural stability of ReN_2 and ReC_2 under pressure based on bond rules and previously proposed structures. We then construct probable structures for ReCN and analyze the structural stability. Finally, the electronic and mechanical properties including the bulk modulus, shear modulus, Vickers hardness and ideal strengths are investigated.

2. Methods and theoretical models

Our density functional theory based calculations were performed using the projector augmented wave (PAW) method as implemented in VASP code^{27, 28}. We used the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE)^{29, 30}

and a plane wave basis with an energy cutoff of 600 eV. The Brillouin zone sampling for these generally metallic compounds was done with the standard special points method with grids chosen for convergence at the 1 meV/atom level. Γ -centered grids of 17x17x6, 18x18x6 and 17x17x11 were used for $P6_3/mmc$, $P-6m2$ and $C2/m$ structures, respectively. All the structures were optimized until the residual forces were below 0.01 eV/Å. Elastic constants were obtained using calculations of stress under strain. For the calculation of enthalpy about the proposed model, the volume of cell is optimized under the fixed pressure in order to obtain the term PV of pressure effect. In order to perform phonon calculations, the force constants are obtained by the accurate frozen-core full-potential projector augmented-wave (PAW) method implemented in VASP code. With the high-density k mesh, the atomic displacement of 0.01Å is used to calculate the phonon dispersion³¹.

We explored the stability of proposed structures including $Pacn$ ¹⁴, $P4_2/mnm$ ¹⁵, MoS_2 -type¹⁸, $P4/mmm$ ¹⁶, $P6_3/mmc$ ¹⁷, $P-6m2$ ¹⁷ and $C2/m$ ¹⁹ for ReN_2 , as shown in Fig.1. These structures are proposed on the basis of the idea that the nitrogen is incorporated into the interstitial sites of solid rhenium. The proposed structures of ReC_2 are constructed with the same way.

One may obtain bulk modulus (B) and shear modulus (G) of polycrystalline ceramic from the elastic constants. There are two approximations that can be readily used to estimate bulk modulus and shear modulus, namely Voigt model³² and Reuss model³³. For hexagonal phases, the bulk modulus and shear modulus with the Voigt approximation can be expressed by the formulas, $B_V = (1/9)[2(C_{11} + C_{12}) + 4C_{13} + C_{33}]$ and $G_V = (1/30)[(M + 12C_{44} + 12C_{66})]$. With the Reuss approximation, they are expressed as $B_R = C^2/M$ and

$G_R = (5/2)[C^2 C_{44} C_{66}] / [3B_V C_{44} C_{66} + C^2(C_{44} + C_{66})]$. In these formulas, M and C^2 are given by $M = C_{11} + C_{12} + 2C_{33} - 4C_{13}$ and $C^2 = (C_{11} + C_{12}) C_{33} - 2C_{13}^2$. The Voigt scheme yields the upper limit of the actual effective moduli and Reuss scheme is the lower limit. A approximation termed Voigt-Reuss-Hill has been established on the basis of the arithmetic average of Voigt and Reuss bounds³⁴. In this work, the quoted bulk and shear moduli are those given with the Voigt-Reuss-Hill approximations.

We use two phenomenological models based on first principles calculations for the evaluation of hardness. These are the bond-strength model³⁵ proposed by Šimůnek and electronegativity model proposed by Li *et al*³⁶.

With the bond-strength model³⁵,

$$H = (C/\Omega) n \left(\prod_{i,j=1}^n (N_{ij} S_{ij}) \right)^{1/n} e^{-\sigma f_e} ,$$

$$\text{with } f_e = 1 - \left[k \left(\prod_{i=1}^k \frac{Z_i}{R_i} \right)^{1/k} \right] / \left[\sum_{i=1}^k \frac{Z_i}{R_i} \right]^2 \text{ and } S_{ij} = \sqrt{\frac{Z_i Z_j}{R_i R_j}} / (n_i n_j d_{ij}) .$$

Here S_{ij} and f_e are the bond strength and the ionicity indicator. Z_i is the valence electron number of atom i . n_i and n_j are the coordination numbers of atoms i and j , respectively. d_{ij} means the interatomic distance between atom i and j . The radius R_i is defined as the radius of a sphere around atom i can contains exactly the valence electron count, Z_i . n is the number of different binary bonds in the structure. N_{ij} counts the interatomic n -type bonds between atoms i and j in the unit cell and k is the number of different atoms in the system. Ω is the volume per unit cell, while C and σ are constants.

With the electronegativity model³⁶,

$$H_k = \frac{423.8}{\Omega} n \left(\prod_{a,b=1}^n N_{ab} X_{ab} e^{-2.7 f_i^{ab}} \right)^{1/n} - 3.4 ,$$

$$\text{with } X_{ab} = \sqrt{\frac{\chi_a}{CN_a} \frac{\chi_b}{CN_b}} \text{ and } f_i^{ab} = |\chi_a - \chi_b| / 4 \sqrt{\chi_a \chi_b} .$$

Here f_i^{ab} is the ionicity indicator. $\chi_j = 0.481 n_j / R_j$ is defined as the electronegativity. n_j and R_j represent the number of valence electrons and crystalline covalent radius for atom j in Angstroms, respectively. CN_a and CN_b are the coordination numbers of atoms a and b , respectively. Ω is the volume per unit cell. N_{ab} counts the interatomic bonds between atoms a and b in the unit cell.

Physically, tensile and shear strengths are related to the plastic deformation. The ideal tensile and shear strength can be obtained from stress vs. strain curves. These are readily obtained from first principles calculations since the stress can be calculated under any strain as has been described in detail by Roundy and Krenn^{37, 38}. We calculated the ideal tensile and shear strengths of ReCN for *P63mc* (HI) and *P3m1* (HII) structures by this method.

3. Results and discussion

3.1 Structure and formation enthalpy

Thermodynamic stability with respect to decomposition is central for experimental synthesis. The formation energies (formation enthalpy at zero pressure) of ReN₂ and ReC₂ were calculated with the formulas,

$$\Delta E = E_{\text{ReN}_2} - E_{\alpha\text{-N}_2} - E_{\text{Re}} \quad \text{and} \quad \Delta E = E_{\text{ReN}_2} - 2E_{\text{C}} - E_{\text{Re}} , \quad (1)$$

where E_{ReN_2} , $E_{\alpha\text{-N}_2}$, E_{C} and E_{Re} are the energies of the proposed structures of ReN₂, solid $\alpha\text{-N}_2$ ³⁹, graphite and solid rhenium, respectively (note that the interlayer van der

Waals interaction in graphite is not well described by GGA functionals like PBE⁴⁰, but this is less important under pressure and even at ambient pressure has only a small effect on the formation energy). From the calculated results, the formation energies of ReN₂ with different structures have a sequence as follows: $C2/m$ (0.185 eV/atom) < $P4_2/mnm$ (0.272 eV/atom) < $Pbcn$ (0.274 eV/atom) < $P6_3/mmc$ (0.384 eV/atom) < $P-6m2$ (0.391 eV/atom) < MoS_2 -type (0.542 eV/atom) < $P4/mmm$ (0.663 eV/atom). The stability sequences of these structures are consistent with the reports in literatures^{14 15 19}. All these energies are positive, reflecting the high stability of the N₂ molecule. The $C2/m$ structure is the most stable of among those that we investigated and $P4_2/mnm$ is the second most stable. Importantly, the formation energy of the MoS_2 -type structure proposed by Kawamura *et al.* based on the experimental results¹⁸ is clearly higher than that of other structures, such as $P6_3/mmc$ and $P-6m2$. Furthermore, we find calculated elastic constants for this MoS_2 -type structure that implies it is mechanically unstable, similar to the report of Wang *et al*¹⁹.

For ReC₂, the calculated formation energies show that the $P6_3/mmc$ and $P-6m2$ structures are more stable than other structures studied, which is consistent with the previous result²¹. The positive formation energies come from the high stability of elemental C and are consistent with the fact that these materials need to be synthesized under extreme conditions of temperature and pressure. We note that all other things equal pressure in general disfavors incompressible phases with respect to softer phases (note, pressure is a strong driving force towards lower volume phases, so it can stabilize harder phases due to the chemical correlation between low volume and low compressibility, but for phases with similar volume, the higher compressibility phase is favored by pressure).

This is a fundamental challenge for finding the correct set of extreme conditions under which metastable but superhard and incompressible materials can be made. This suggests that superhard materials based on phases with high shear moduli and anisotropic incompressibility may be easier to realize in practice since a single less incompressible direction may greatly facilitate synthesis while not eliminating the possibility of superhardness.

We calculated the formation enthalpies up to high pressure ($\Delta H = \Delta E + \Delta(PV)$) for both ReN_2 and ReC_2 using the ambient elemental structures including solid $\alpha\text{-N}_2$, graphite and solid rhenium as references (note, this is strictly then a lower bound on the formation enthalpy of the compounds as it neglects structural phase transitions of the elements, but nonetheless will maintain the ordering of the different structures studied). Fig. 2(a) shows that for ReN_2 the $P4/mmm$ structure becomes stable at a pressure of 18.8 GPa and is more stable than the $P4_2/mnm$ and $Pbcn$ structures when the pressure is above 33.3 GPa. This is consistent with the previous report of Du *et al*¹⁶. However, the MoS_2 -type configuration does not become more stable than other structures at pressures below the 80GPa. This suggests that the structure of ReN_2 phase synthesized experimentally by Kawamura *et al.*¹⁸ may have a different structure than the proposed MoS_2 -type structure. The two hexagonal configurations, $P6_3/mmc$ and $P-6m2$, become energetically stable at the pressures of 10.1 GPa and 10.4 GPa, respectively. However, their formation enthalpies still are larger than that of $C2/m$. Therefore, although it may be that more than one structure can be accessed experimentally depending on temperature/pressure and the exact N stoichiometry, we conclude the $C2/m$ is the most probable structure of those investigated.

Fig. 2(b) shows the formation enthalpies of different structures of ReC_2 as a function of pressure. It is found that the $P6_3/mmc$ structure is the most stable over the entire pressure range. The enthalpy of the $P-6m2$ structure is slightly higher than that of $P6_3/mmc$. Also, over the entire pressure range, the formation enthalpy of the compound is positive. This implies that ReC_2 will be difficult to synthesize and will require particularly extreme conditions.

Turning to the structures themselves, we observe that ReN_2 and ReC_2 show low energy structures that are layered (on the c -axis as shown) and have apparent N-N or C-C bonds in the structures $P4/mmm$, $P6_3/mmc$ and $P-6m2$. The $C2/m$ structure has N_2 or C_2 substructures, bonded to the metal atoms. This suggests an ansatz for constructing possible ReCN structures. Specifically, we can form structures based on C-N bonds, which is a bonding arrangement that is often very stable and stiff. Several proposed structures based on this ansatz are constructed for the ternary ReCN , as shown in Fig. 3. For the phase $P4/mmm$, three configurations are made and named as T, T-1 and T-2 respectively. The repeated units along c axis for the configurations T, T-1 and T-2 are ABC, AABCC and ABACBC where A, B and C represent nitrogen, rhenium and carbon atoms, respectively. Three types of bonds, Re-N, Re-C and C-N, are present in the T and T-2 structures. The T-1 structure contains four types of bonds Re-C, Re-N, C-C and N-N. Similarly, three $P6_3/mmc$ based structures were constructed and named as HI, HI-1 and HI-2, respectively. One $P-6m2$ based structure, HII, was constructed, while using $C2/m$, four basic alternative ways were used to build ReCN structures and the new configurations are named as C-1, C-2, C-3, C-4, respectively. The configurations C-2 and C-3 have the same space group $C2/m$. In configuration C-2, each carbon atom has three

rhodium neighbors (three Re-C bonds) and one carbon atom (one C-C bond), while each nitrogen atom is fourfold coordinated by rhodium (four Re-N bonds). In configuration C-3, the positions of carbon and nitrogen atoms are reversed. The positions of carbon and nitrogen atoms in both C-1 and C-4 are inversed with each other. In both phases, there are C-N, Re-N and Re-C bonds with space group *Cm*.

The formation enthalpy of ReCN is obtained by the formula,

$$\Delta H = H_{\text{ReCN}} - H_{\text{Re}} - H_{\text{C}} - \frac{1}{2}H_{\alpha\text{-N}_2} \quad , \quad (2)$$

where H_{ReCN} , H_{Re} , H_{C} and $H_{\alpha\text{-N}_2}$ are the enthalpies of ReCN, solid Re, graphite and $\alpha\text{-N}_2$, respectively. As the upper limit, $\alpha\text{-N}_2$ and graphite are chosen to analyze the formation enthalpy/energy. At zero pressure, $\alpha\text{-N}_2$ is more stable than gas N_2 and the energy difference is about 0.046 eV/atom. Graphite is the ground state of the carbon materials as well known and its energy is lower than that of diamond at ambient pressure. From the calculation, the energy difference is about 0.129 eV/atom. The calculated formation enthalpies obtained in this way for the different proposed structures of ReCN are shown in Fig. 4a. It is found that HI and HII are more stable than other configurations. Their formation enthalpies decrease quickly with pressure. Above 3.1 GPa and 3.6 GPa, the formation enthalpies of HI and HII become negative, respectively. It is noticed that diamond becomes more stable than graphite following the increase of pressure. With the calculation, the transition pressure is about 8GPa. Therefore, the analysis about the formation enthalpies of HI and HII doesn't change obviously. Throughout the whole range of pressure, the structure HI is the most stable and its formation enthalpy is slightly lower than the values of HII. If N_2 molecule and diamond are chosen as the reference states, the formation energy of ReCN (ReCN-HI) is 0.011eV/atom. In addition, if the

entropy effect is considered, ReCN can be stable even at room temperature which can afford roughly an entropy contribution of about 25 meV. These indicate that they are likely to be synthesized at the relatively low pressure and temperature. In order to consider the possibility of phase separation during synthesis, we considered different possible separated phases, including the mixture of ReC and α -N₂, that of Re₃N, α -N₂ and graphite, and that of Re₂N, α -N₂ and graphite, since ReC, Re₃N and Re₂N are very stable and have been synthesized experimentally^{9,41}. As shown in Fig. 4b, the mixed phases with Re₃N and that with Re₂N are more stable than ReCN for pressures below 5.6 GPa. Above 5.6 GPa, the ReCN with structures HI and HII may form since ReCN is stable relative to the other possibilities considered. Table 1 gives the calculated lattice parameters, bond distances and formation energies for the HI and HII structures. While GGA often underestimates bond strength (elastic properties) and overestimates lattice parameters, LDA works the other way. In order to compare with the results from PBE, those of LDA are also shown in Table 1 and Table 2. With the LDA results, ReCN can be stable at ambient condition.

3.2 Mechanical stability

The mechanical stability of a structure can be assessed using the elastic constants. Both structures HI and HII belong to the hexagonal crystal system for which the criteria of mechanical stability are⁴²⁻⁴⁴: $C_{44} > 0$, $C_{11} > |C_{12}|$, $(C_{11}+2C_{12})C_{33} > 2C_{13}^2$. The elastic constants are shown in Table 2 and those from LDA due to the overestimation of bond strength are little larger than those from PBE. Clearly both structures are mechanically stable. In order to analyze both structures further, the calculation of phonon spectrum is performed. As shown in Fig. 6c and d, there are no imaginary phonon frequencies in the

spectrum, which means both hexagonal structures are dynamically stable.

From the Table 2, the values of elastic constants C_{33} of both HI and HII are very large, even compared to the equivalent elastic constant of diamond (1076 GPa)⁴⁵. It can be also seen that the values of C_{33} are much greater than those of C_{11} in both structures. C_{11} and C_{33} represent the a - and c -direction resistance to linear compression, respectively, and so this represents a large elastic anisotropy for these directions. The elastic constant C_{44} is one of the most important parameters to govern the indentation hardness indirectly. The C_{44} values of both structures are much higher than those of OsB₂ (73 GPa) and RuB₂ (99 GPa)⁴⁶, and comparable to that of ReB₂ (257 GPa)⁴⁶, while the other related shear C_{66} although lower is still high.

The bulk modulus is often correlated with the valence electron density^{47, 48}. The shear modulus which is relevant with the generation and spread of dislocations can be used to quantify the resistance to shear deformation^{48, 49}. The values of B and G usually are considered as the measures of a hard material. As the mentioned, we used the calculated elastic constants and the Voigt-Reuss-Hill approximation³⁴ $B_H = (1/2)(B_V + B_R)$ and $G_H = (1/2)(G_V + G_R)$ to evaluate the bulk modulus and shear modulus. The calculated B_H and G_H are listed in Table 2. The Young's modulus (E) quantifies the stiffness of materials. It can be obtained in terms of B and G by the formula $E = 9BG/(3B + G)$ and is also shown in Table 2. The both structures are found to possess the large B_H , G_H and E . This manifests that ReCN is an incompressible phase that is expected to have favorable mechanical properties.

3.3 Electronic properties

The electronic density of states (DOS) of ReCN is compared with those of ReC₂ and ReN₂ for the structures HI and HII. As shown in Fig. 5, both ReC₂ and ReN₂ are high density of states metals, while ReCN is predicted to be a semiconductor. Considering the values of the density of states and the covalent, but heavily Re *d* derived nature of the electronic states at the Fermi level for ReC₂ and ReN₂ it seems likely that these may be superconducting as well. It will be of interest therefore to search for superconductivity in these two materials. We note that there are peaks in the DOS around the Fermi energy for both materials, and therefore the superconductivity if present would be sensitive to the N and C stoichiometry.

The band structures of both phases HI and HII for ReCN are calculated and depicted in Fig. 6a and b, respectively. HI ReCN has an indirect band gap of 0.67 eV with valence-band top in H point and conduction-band bottom in K point, while HII ReCN has a direct band gap of 0.73 eV with both the top of valence-band and bottom of conduction-band in the H point. These band gaps may be underestimated as is common in density functional calculations with the PBE functional, but in any case semiconducting character is predicted. This semiconducting behavior is related to the valence electron count, which is 15 for ReC₂, 17 for ReN₂ and 16 for ReCN. As may be seen, there are gaps or near gaps for all the compounds at this electron count - below the Fermi level for ReN₂ and above for ReC₂, as shown. The partial density of states (PDOS) is also shown in Fig. 5. The mixed *p-d* character of the electronic states is evident reflecting the covalent bonding of these compounds. The deep states, below -5 eV, have less metal character than those around the Fermi energy, and are more associated with the *p*-element

bonding, while those around the Fermi energy are then more associated with metal and metal-*p* element bonding, the details of which may be important for the mechanical properties and relative stability of ReCN.

3.4 Mechanical properties

The actual hardness of materials is a very complex property, which is correlated with both intrinsic (including bond direction, strength and density related to the structures) and extrinsic (including defects, dislocations, grain sizes and textures, etc.) factors. The bulk modulus and shear modulus cannot by themselves fully evaluate the real hardness of a structure and provide results to compare directly with experiments. Developing the simple approximate methods to estimate intrinsic hardness is of great value. Several effective semiempirical models have been established⁵⁰, such as the bond-strength model³⁵ and the electronegativity model³⁶. The parameters of these models are based on the effective structural data from first principles calculations. In the both the bond-strength and electronegativity models, the main factors, such as the bond density, bond length and direction of bond, have been taken into account for the calculation of hardness. We estimated the Vickers hardness of ReCN with these models. The results are given in Table 2. The Vickers hardness of both the HI and HII phases are found to be more than 40 GPa, suggesting that could be candidate superhard materials.

In order to better characterize the mechanical properties of ReCN, the ideal stress-strain curves for large strains were calculated. For the structures of hexagonal phase, three tensile directions of $\langle 10\bar{1}0 \rangle$, $\langle \bar{1}2\bar{1}0 \rangle$ and $\langle 0001 \rangle$ and the slip systems of $(0001)\langle 10\bar{1}0 \rangle$, $(0001)\langle \bar{1}2\bar{1}0 \rangle$, $(10\bar{1}0)\langle \bar{1}2\bar{1}0 \rangle$ usually are considered. The calculated stress-strain curves are depicted in Fig. 7. The ideal tensile and shear strengths are taken

from the maximum tensile and shear stresses. The ideal strengths and their corresponding strains are summarized in Table. 3. In addition, we give the ideal strengths of Re_2N^{10} , Re_3N^{10} and ReB_2^{51} from literature along with the ideal strength of ReB_2 calculated here. The calculated anisotropy ratio of tensile strengths for ReB_2 is $\sigma_{\langle 0001 \rangle} : \sigma_{\langle 10\bar{1}0 \rangle} : \sigma_{\langle \bar{1}2\bar{1}0 \rangle} \approx 1.56:1.10:1$, which is consistent with the previous literature result⁵¹. The ideal tensile strengths of ReCN with both structures HI and HII along the $\langle 0001 \rangle$ direction are much larger than that of Re_2N and Re_3N , even larger than that of ReB_2 (93.9 GPa). The anisotropy ratios of tensile strengths (values of $\sigma_{\text{max}}:\sigma_{\text{min}}$) for HI ReCN (2.61) and HII ReCN (2.77) are much larger than those of ReB_2 (1.56), Re_2N (2.11)¹⁰ and Re_3N (1.77)¹⁰. This indicates that ReCN has more anisotropic tensile strength than ReB_2 , Re_2N and Re_3N . However, it cannot be proved that ReCN is intrinsically stronger than ReB_2 based on this. The shear strength is more convincing because plastic deformation is closely related with shear stress. The ideal shear strengths of both HI and HII ReCN along the $\langle 10\bar{1}0 \rangle$ slip direction are the weakest among the three slip directions shown in Fig. 7 and are 27.7 GPa and 27.8 GPa, respectively. The ideal shear strength of ReB_2 along $\langle 0001 \rangle$ slip direction (35.6 GPa) is the weakest. Therefore, the minimal ideal shear strength of ReCN is somewhat lower than that of ReB_2 , but it is much larger than that of Re_2N (12.4 GPa) and Re_3N (15.5 GPa). These results suggest that ReCN under the large shear strain has intrinsically excellent mechanical properties.

4. Summary and Conclusions

We used first principles calculations to study potential low-energy structures of ReN_2 , ReC_2 and ternary ReCN. We found that the structures HI (*P63mc*) and HII (*P3m1*) without N-N or C-C bonds for ReCN are more thermodynamically stable than other

phases. The low energy structures HI and HII of ReCN are mechanical stable with semiconducting electronic structures, while the electronic structure of stoichiometric ReN₂ and ReC₂ are both high density of states metals, with substantial but still covalent transition element character around the Fermi energy, suggesting possible superconductivity. It will be of interest to search for superconductivity in these two materials, especially with control of the stoichiometry.

We find that ReCN possesses the large bulk, shear and Young's moduli, with the excellent ideal strengths. The calculated hardness of about 40 GPa for both structures HI and HII indicate that ReCN is a good candidate for a superhard material. The ultra-incompressible and excellent mechanical properties of ReCN may be attributed to the strong and short covalent C-N bonds with slight ionicity combined with the strong Re-N and Re-C bonds. Both structures HI and HII of ReCN become more thermodynamically stable than other mixed phases above 5.8 GPa. This indicates that ReCN may be relatively amenable to synthesis under less extreme conditions than the binaries, ReC₂ and ReN₂. This suggests experimental efforts to synthesize ReCN.

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Table 1

Crystal	method	ΔH	a_0	c_0	V_0	$d_{\text{Re-C}}$	$d_{\text{Re-N}}$	$d_{\text{C-N}}$
ReCN-HI	GGA	0.069	2.897	7.851	28.54	2.109	2.082	1.401
	LDA	-0.180	2.857	7.786	27.53	2.087	2.057	1.386
ReCN-HII	GGA	0.083	2.891	3.946	28.56	2.108	2.082	1.414
	LDA	-0.163	2.851	3.914	27.55	2.086	2.057	1.399

Table 1. Calculated lattice parameters ($\text{\AA}$), volumes ($\text{\AA}^3$), bond distances ($\text{\AA}$), and formation energies (eV/atom) for both structures HI and HII of ReCN. The results from GGA are compared with that from LDA.

Table 2

crystal	method	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B_H	G_H	E	H_V^1	H_V^2
ReCN-HI	GGA	575	226	221	1021	256	174	378	229	573	40.3	39.7
	LDA	631	252	257	1098	273	190	420	246	618	41.9	40.2
ReCN-HII	GGA	582	217	220	1020	249	182	378	231	576	40.2	42.4
	LDA	640	201	232	1101	266	199	420	248	622	41.8	42.4

Table 2. Calculated elastic constants (GPa), bulk modulus B_H (GPa), shear modulus G_H (GPa) and Young's modulus E (GPa) using the Voigt-Reuss-Hill approximation for ReCN with structures HI and HII. The hardness H_V^1 (GPa) and H_V^2 (GPa) are obtained from the bond-strength model and electronegativity model, respectively. The results from GGA are compared with that from LDA.

Table. 3.

	$\langle 0001 \rangle$		$\langle 10\bar{1}0 \rangle$		$\langle \bar{1}2\bar{1}0 \rangle$		$(0001)\langle 10\bar{1}0 \rangle$		$(0001)\langle \bar{1}2\bar{1}0 \rangle$		$(10\bar{1}0)\langle \bar{1}2\bar{1}0 \rangle$	
	strain	stress	strain	stress	strain	stress	strain	stress	strain	stress	strain	stress
ReCN-HI	0.17	111.0	0.20	54.0	0.24	42.6	0.21	41.8	0.24	45.9	0.34	27.7
ReCN-HII	0.19	117.6	0.20	53.7	0.24	42.4	0.23	46.4	0.25	47.1	0.28	27.8
Re ₂ N ^a		60				28.5		12.4				
Re ₃ N ^a		61.1				34.5		15.5				
ReB ₂ ^b		93.2		63.8		58.5		34.4				
ReB ₂	0.22	93.9	0.20	66.2	0.20	60.2	0.19	35.6	0.23	42.4	0.25	44.6

a, reference¹⁰, b, reference⁵¹

Table 3. Ideal tensile and shear strengths of ReCN with the corresponding strain at the maximum stress (GPa) from first principles calculation. Those of Re₂N, Re₃N and ReB₂ in literatures with our results of ReB₂ are listed for the comparison.

Fig. 1

Fig. 1 Proposed structures of ReN_2 with coordinates and lattice parameters optimized by first principle calculations.

Fig. 2

Fig. 2 Calculated formation enthalpies as a function of pressure for (a) ReN₂ and (b) ReC₂.

The enthalpy differences are per formula unit (f.u.).

Fig. 3

Fig. 3 Proposed structures of ternary ReCN including T ($P4mm$), T-1 ($P4/mmm$), T-2 ($P4/mmm$) on the basis of $P4/mmm$ structure of ReN_2 , HI ($P63mc$), HI-1($P-3m1$) and HI-2 ($P-6m2$) from $P6_3/mmc$ structure of ReN_2 , HII ($P3m1$) from $P-6m2$ structure and C-1(Cm), C-2($C2/m$), C-3($C2/m$) and C-4(Cm) from $C2/m$ structure of ReN_2 .

Fig. 4

Fig. 4 Calculated formation enthalpies of the different configurations proposed as a function of pressure (a) and that of three possible mixed phases as a function of pressure (b) for ReCN.

Fig. 5

Fig. 5 Electronic density of states and partial density of states of ReCN, ReC₂ and ReN₂ with structures HI(a) and HII (b). Vertical black dashed line at 0 eV denotes the Fermi level.

Fig. 6

Fig. 6 Electronic band structure and phonon band structure of HI (a, c) and that of HII (b, d) for ReCN. Notice that Γ , M, K, Z, L and H represent for the symmetry k -points (0, 0, 0), (0, 0.5, 0), (-0.3333, 0.6667, 0), (0, 0, 0.5), (0, 0.5, 0.5), and (-0.3333, 0.6667, 0.5) in Brillouin zone, respectively. Horizontal dashed line at 0 eV denotes the Fermi level (low T , undoped).

Fig. 7

Fig. 7 Calculated stress-strain curves for the structures HI (a) and HII (b) of ReCN.