Abstract: The structural stability and phase transition of osmium and ruthenium carbides (OsC and RuC) were investigated by first principles. Nine structures were considered for each carbide. Zinc blende structure has the lowest energy among the considered structures at ambient conditions for both carbides. For OsC at elevated pressures, the most stable phase is zinc blende structure from 0 to 10 GPa, FeSi from 10 to 32 GPa. In these two structures, Os atom is fourfold coordinated. From 32 to 40 GPa, tungsten carbide (WC) and NiAs are energetically competitive with Os atom sixfold coordinated. NiAs becomes energetically the most stable structure above 40 GPa. For RuC, zinc blende structure is the most stable from 0 to 20 GPa. From 20 to 100 GPa, WC structure is the most stable.

Key words: osmium and ruthenium carbides; structural stability; phase transition; high pressure; first principles

Introduction

Superhard materials are known to be used in many applications, from cutting and polishing tools to wear-resistant coatings. Therefore, the searching for materials with hardness exceeding or comparable to diamond has always fascinated humans and is also a great challenge. In synthesizing and designing new superhard materials, besides the traditional B–C–N–O systems, transition metal carbides, borides, nitrides and oxides are also very attractive due to the relative high bulk modulus of transition metals (in particular 5d metals), but the shear strength is low due to the nondirectional metallic bonding and therefore they have low hardness. For instance, among the transition metals, osmium has the highest bulk modulus (more than 420 GPa), close to 440 GPa of diamond. However, the hardness of osmium is quite small, only 3.5–3.9 GPa, compared with 90 GPa of diamond. Therefore, it is expected that through the insertion of B, C, N, or O atom into the transition metals, superhard materials might be formed by inducing the nondirectional metallic bonding in pure transition metals to highly directional covalent bonding in the corresponding carbides, borides, nitrides or oxides.

Osmium and ruthenium carbides (OsC and RuC) were synthesized in 1960 with tungsten carbide (WC) structure at ambient pressure and high temperature. No further experimental study is available since then. In recent years, theoretical studies have been performed for OsC. In 2005, the compressibility of OsC in WC and NaCl structures was studied by using the ultrasoft pseudopotential (US-PP) method and generalized gradient approximation (GGA). It was found that OsC in WC structure is energetically more favorable than NaCl structure, but the mechanical stability of both structures was not examined. The study of Fan et al. indicated that OsC in NaCl structure is mechanically unstable. In 2007, Chen et al. reported that OsC in WC structure is mechanically unstable. Four reports appeared in 2008. The GGA study by Zemzemi and Hebache indicated that OsC in WC structure is mechanically unstable due to the small C44 value. By using the projector-augmented wave (PAW) method and local density approximation (LDA), Wang studied the OsC in WC, FeSi, and OsSi (CsCl) structures. It was concluded that OsC in FeSi structure is energetically more stable than that in WC structure. Both structures are mechanically stable. Meanwhile, Liang et al. studied OsC in WC and ZnS (zinc blende) structures by US-PP and GGA method. Both structures are mechanically stable, but the relative stability is not shown. In addition, Tian and coworkers studied the OsC in nine assumed structures by US-PP and GGA method, which include NaCl, ZnS (zinc blende), ZnS (wurtzite), CsCl, FeSi, WC, NiAs, CoSn, and MnP. It was found that OsC in FeSi, NiAs, and
CoSn structures are mechanically stable, and the NiAs structure is energetically more favorable among the three structures. OsC in FeSi structure (P2\(_1\), phase, No. 198) transformed into the orthorhombic structure (P2\(_1\)2\(_1\)2\(_1\), No. 19) after geometry optimization. However, the transformation did not occur for FeSi structure in Wang’s study\(^{10}\) (and in our study as well). Therefore, from the above theoretical studies, there are controversial on the structure, mechanical and relative stability for OsC.

For RuC, the only theoretical report in NaCl structure appeared in 2006.\(^7\) The study showed that RuC in NaCl structure is mechanically stable. In this article, OsC and RuC were studied theoretically by considering nine structures, i.e., hexagonal structures NiAs, WC, wurtzite, CoSn, TaN, and cubic structures zinc blende, FeSi, NaCl, CsCl. For OsC, our calculations show that the relative stability obeys the following trend: zinc blende > FeSi > wurtzite > WC > NiAs > TaN > NaCl > CsCl > CoSn, i.e., zinc blende is energetically the most stable. As TaN, NaCl, and CsCl structures lie higher in energy and are mechanically unstable, they are not studied further. Although CoSn structure is mechanically stable, it is the least stable in energy (as also confirmed in the previous theoretical study\(^{12}\)), so further study is not conducted as well. Similarly for RuC, zinc blende, FeSi, wurtzite, WC, NiAs have relative lower energies and were considered in the further study. In addition, although NaCl lies higher in energy, it is also considered in the further study since it is mechanically stable. In our study, it is interesting to note that RuC in FeSi structure converges to zinc blende structure after the geometry optimization. This is interesting because FeSi structure is the distorted form of zinc blende structure.

**Computational Methods**

The calculations were performed by using the CASTEP code,\(^{13}\) based on the density functional theory. For both carbides, the Vanderbilt US-PP\(^{14}\) was used with the same cutoff energy of 600 eV. The k-points of \(8 \times 8 \times 8\) for FeSi, NaCl, and zinc blende structures, \(12 \times 12 \times 11\) for WC structure, \(9 \times 9 \times 6\) for NiAs structure, and \(10 \times 10 \times 6\) for wurtzite structure are generated using the Monkhorst-Pack scheme.\(^{15}\) The exchange and correlation functional were treated by GGA–PBE.\(^{16}\) Formation energy was calculated from \(\Delta E = E(TMC) - E\) (solid TM) – \(E\) (graphite) (TM = Ru, Os). Lattice parameters and atomic positions were optimized simultaneously. For the self-consistent field iterations, the convergence tolerances for geometry optimization were selected as the difference in the total energy, the maximum ionic Hellmann–Feynman force, the stress tensor, and the maximum displacement being within \(5.0 \times 10^{-6}\) eV/Å, 0.01 eV/Å, 0.02 GPa, and \(5.0 \times 10^{-3}\) Å, respectively. The calculated bulk modulus \(B\) and shear modulus \(G\) were from the Voigt–Reuss–Hill approximations.\(^{17–19}\) The Young’s modulus \(E\) and Poisson’s ratio \(\nu\) are obtained by the following formulas:

\[
E = 9BG/(3B + G) \quad \nu = (3B - 2G)/(2(3B + G))
\]

To test the reliability of the our results, the relative stability of the five structures in relative low energy was also studied by the PAW method which implemented in Vienna Ab Initio Simulation Package.\(^{20–23}\) The PAW method is known to be the development of the US-PP method by combining ideas from the US-PP and linearized augmented plane wave methods, and the relationship between the two methods (US-PP and PAW) has been established.\(^{24,25}\) The relative energy and lattice parameters from the PAW method were listed in Tables 1 (OsC) and 2 (RuC) for comparison.

**Results and Discussion**

**OsC**

The calculated results indicate that US-PP and PAW give consistent results (Table 1). All the considered structures are thermodynamically unstable due to the positive formation energies. Similar situation occurs for RuC (Table 2). This suggests that high temperature and/or high pressure are/is necessary for the experimental synthesis. This is in agreement with the high temperature synthesis of OsC in WC structure.\(^5\) In addition, we also noticed that in the synthesis of OsB\(_2\),\(^{26}\) high temperature (1000°C) is used. While OsN\(_2\) was synthesized at high temperature (over 2000 K) and high pressure (over 50 GPa).\(^{27}\) Among the considered structures, zinc blende structure is energetically the most stable (Table 1, see also energy–volume diagram in Fig. 1a), same as OsN.\(^{28}\) OsC–FeSi (i.e., OsC in FeSi structure) is energetically more stable than OsC–WC, in agreement with the previous theoretical study.\(^8\) OsC–WC is only slightly lower in energy than OsC–NiAs (by 0.02 eV in US-PP method, 0.03 eV in PAW method).

OsC–FeSi, OsC–WC, and OsC–NiAs are mechanically stable because they satisfy the mechanical stability criteria.\(^{29}\) This is also confirmed by the PAW method. \(C_{44}\) value of zinc blende structure is very small (8.0 GPa) from the US-PP method. This indicates that zinc blende structure is mechanically unstable or very soft, in agreement with the PAW calculation. Among the mechanical stable phases, OsC–WC has the largest bulk modulus (392 GPa), nearly the same as 393 GPa from the previous GGA method.\(^{11}\) They are all smaller than 438 GPa from the previous LDA calculation.\(^{10}\) This is not surprising because it is known that LDA usually overestimates the lattice constants and elastic constants, while GGA overestimates the lattice constants and underestimates the elastic constants. OsC–FeSi has the largest shear modulus 124 GPa, smaller than the LDA result 158 GPa.\(^{10}\) The calculated \(B/G\) ratio for the mechanical stable phases is larger than 1.75 (1.81 for OsC–FeSi, 4.72 for OsC–WC, 3.77 for OsC–NiAs), the critical value to separate brittleness and ductility.\(^{30}\) This indicates that they are ductile. For instance, diamond has a \(B/G\) ratio 0.8,\(^4\) while aluminum has a \(B/G\) ratio 2.74.\(^{30}\)

It is known that as a fundamental parameter, Debye temperature correlates with many physical properties of solids, such as specific heat, elastic constants, and melting temperature. Therefore, we have calculated the Debye temperature from the bulk modulus, shear modulus, and density of materials.\(^{31}\) OsC–FeSi has the highest Debye temperature of 423 K among the considered structures (Table 1). It is known that the materials possessing higher Debye temperature usually have higher hardness. For instance, the hardest material diamond has the highest Debye temperature 2230 K.
As high pressure might be used in the future synthesis of OsC, it would be interesting to study the behavior of the structures at elevated pressures. By using the PAW method, the energy–volume diagram and the relative energies compared with OsC–zinc blende as a function of pressure were calculated (see Fig. 1). From Figure 1b, it is noted that for OsC–wurtzite structure, the energy goes up with the increase of pressure. From 0 to 10 GPa, OsC–zinc blende structure is the most stable. OsC–FeSi becomes the most stable at pressures from 10 to 32 GPa. OsC–WC and OsC–NiAs are quite close in energy from 32 to 40 GPa. OsC–NiAs becomes energetically the most stable structure above 40 GPa. The crystal structures of zinc blende, FeSi, WC, and NiAs are shown in Figure 2. For zinc blende structure, both Os and C are tetrahedrally coordinated. Although the coordination numbers of Os and C are four for OsC–FeSi, it is structurally different. Os sits in the center of the equilateral triangle formed by three carbon atoms, while another carbon with shorter bond distance lies directly above the Os (giving C$_{3v}$ symmetry, compared with T$_d$ symmetry in zinc blende structure). For WC and NiAs structures the coordination numbers are six for Os and C. The point group symmetry of both atoms is D$_{3h}$. In addition, NiAs structure contains two units of WC structure but with alternating arrangement of carbon atoms (see Fig. 2).

From structural point of view, FeSi structure is the distorted form of zinc blende one. With the increase of pressure, the structure has to be distorted when it transforms from zinc blende to FeSi structure with the increase of the nearest-neighbor bond distances (Os–C) from 1.981 Å to 2.044 Å and 2.011 Å of FeSi structure (Fig. 2e). This suggests that a displacive phase transition occurs, in which the displacement of Os and C in zinc blende structure causes the changes of bond distance, but without the breaking and formation of new bonds. On the other hand, for FeSi structure, besides the nearest coordination for Os (fourfold coordinated, 2.044 Å and 2.011 Å), there are another two next nearest carbon atoms sitting at the distance 3.040 Å (Fig. 2e). With the further increase of the pressure, these two carbon atoms with long bond distance 3.040 Å move toward the Os, meanwhile the four nearest carbon atoms coordinated with Os move away from the Os. Eventually, this

<table>
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<tr>
<th>ZnS, F-43m, zinc blende</th>
<th>FeSi, P2$_1$3</th>
<th>ZnS, P6$_3$mc, wurtzite</th>
<th>WC, P-6m2</th>
<th>NiAs, P6$_3$mmc</th>
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<td>$\Delta E$</td>
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<td>1.77 (1.72)</td>
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<td>4.574 (4.613)</td>
<td>4.443 (4.469)</td>
<td>3.247 (3.262)</td>
<td>2.923 (2.949)</td>
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<td>$c$</td>
<td>5.298 (5.384)</td>
<td>5.382$^b$</td>
<td>2.712 (2.731)</td>
<td>5.482 (5.519)</td>
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<td>$V$</td>
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<td>21.9(22.3)</td>
<td>24.2(24.8)</td>
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<td>336</td>
<td>424$^a$</td>
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<td>86</td>
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<td>188$^e$</td>
<td>83$^c$, 104$^d$, 72$^d$</td>
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<td>237$^a$</td>
<td>383$^a$, 451$^a$, 412$^a$</td>
<td>278$^b$</td>
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<td>$B$</td>
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<tr>
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<td>$\theta_0$</td>
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<td>423</td>
<td>350</td>
<td>383</td>
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Values in parenthesis are from PAW method.
$^a$Ref. 11, theoretical study by GGA method.
$^b$Ref. 12, theoretical study by GGA method.
$^c$Ref. 6, theoretical study by GGA method.
$^d$Ref. 10, theoretical study by LDA method.

As high pressure might be used in the future synthesis of OsC, it would be interesting to study the behavior of the structures at elevated pressures. By using the PAW method, the energy–volume diagram and the relative energies compared with OsC–zinc blende as a function of pressure were calculated (see Fig. 1). From Figure 1b, it is noted that for OsC–wurtzite structure, the energy goes up with the increase of pressure. From 0 to 10 GPa, OsC–zinc blende structure is the most stable. OsC–FeSi becomes the most stable at pressures from 10 to 32 GPa. OsC–WC and OsC–NiAs are quite close in energy from 32 to 40 GPa. OsC–NiAs becomes energetically the most stable structure above 40 GPa. The crystal structures of zinc blende, FeSi, WC, and NiAs are shown in Figure 2. For zinc blende structure, both Os and C are tetrahedrally coordinated. Although the coordination numbers of Os and C are four for OsC–FeSi, it is structurally different. Os sits in the center of the equilateral triangle formed by three carbon atoms, while another carbon with shorter bond distance lies directly above the Os (giving C$_{3v}$ symmetry, compared with T$_d$ symmetry in zinc blende structure). For WC and NiAs structures the coordination numbers are six for Os and C. The point group symmetry of both atoms is D$_{3h}$. In addition, NiAs structure contains two units of WC structure but with alternating arrangement of carbon atoms (see Fig. 2).
leads to the Os sixfold coordinated. The structure thus goes to the WC or NiAs structures. Therefore, the microscopic nature of the pressure-induced phase transition is caused by the change of Os–C bond distance, which leads to the change of coordination numbers, thereby altering the structure.

Recently, Os2C has been studied theoretically by assuming the experimental synthesized structure of Re2C, i.e., the hexagonal space group P63mmc. Therefore, determining the osmium carbide with what kind of composition between osmium and carbide, 1:1, 2:1, or others, could be a challenge to the theoretical study and experimental study as well. This is also true for ruthenium carbide.

### RuC

The results calculated by US-PP and PAW are similar (Table 2). The calculated lattice parameters of RuC–WC match the experimental ones within 1%. For RuC–NaCl, our calculated results are consistent with the previous theoretical study. By using

<table>
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<th>ZnS, P63mc, wurtzite</th>
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<th>NiAs, P63/mmc</th>
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<td>1.44 (1.35)</td>
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<td>2.900 (2.927)</td>
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<tr>
<td>V</td>
<td>23.2 (23.4)</td>
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<td>19.5 (20.0)</td>
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<tr>
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<td>434</td>
<td>299</td>
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<td>488</td>
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\^aRef. 5, experimental study.
\^bRef. 7, theoretical study by GGA method.
the PAW method, the energy–volume diagram and the relative energies compared with RuC–zinc blende as a function of pressure were calculated (see Fig. 3). Similar to OsC, zinc blende structure is the most stable phase at ambient conditions. For RuC, the phase transition is simpler compared with OsC. Zinc blende structure is the most stable between 0 and 20 GPa (Fig. 3b). From 20 to 100 GPa, WC structure is the most stable.

On the other hand, one should remember that the high pressure studies above are conducted at zero temperature. Moreover, we neglect phonon enthalpies arising from the coupling between electrons and nuclei, which can influence the stable structure of the studied carbides.

Based on the relationship between the hardness and shear modulus (shear modulus is regarded as a better indicator of hardness, see refs. 4, 33), the estimated hardnesses of OsC–NiAs and RuC–WC phase are about 13 and 10 GPa, respectively. Thus, OsC and RuC are not superhard.

Conclusions

OsC and RuC were studied by both the US-PP and PAW methods. Our calculations show that all the considered structures are thermodynamically unstable due to the positive formation ener-

Figure 2. Crystal structures of OsC in (a) zinc blende, (b) FeSi, (c) WC, and (d) NiAs structures. (e) Phase transition process from zinc blende to FeSi structures, and from FeSi to WC or NiAs structures. The large (cyan) and small (gray) spheres represent Os and C, respectively.
gies. This suggests that high temperature and/or high pressure are necessary for the experimental synthesis. For both carbides, zinc blende structure has the lowest energy among the considered structures at ambient conditions. For OsC, the most stable phase is zinc blende from 0 to 10 GPa, FeSi from 10 to 32 GPa. From 32 to 40 GPa, WC and NiAs are quite close in energy. NiAs becomes the most stable structure above 40 GPa. The situation is simpler for RuC at elevated pressures. Zinc blende structure is the most stable between 0 and 20 GPa. Above 20 GPa, WC structure is the most stable. The microscopic nature of the pressure-induced phase transition in OsC is discussed based on the structural change.

Acknowledgments

We are grateful to Prof. Z. Pei for proofreading the article.

References