A new type of vanadium carbide \( \text{V}_5\text{C}_3 \) and its hardening by tuning Fermi energy

Wandong Xing\(^1\), Fanyan Meng\(^1\) & Rong Yu\(^2\)

Transition metal compounds usually have various stoichiometries and crystal structures due to the coexistence of metallic, covalent, and ionic bonds in them. This flexibility provides a lot of candidates for materials design. Taking the V-C binary system as an example, here we report the first-principles prediction of a new type of vanadium carbide, \( \text{V}_5\text{C}_3 \), which has an unprecedented stoichiometry in the V-C system, and is energetically and mechanically stable. The material is abnormally much harder than neighboring compounds in the V-C phase diagram, and can be further hardened by tuning the Fermi energy.

Transition metal carbides have attracted continuing interest due to their excellent physical properties and wide engineering applications\(^1\)-\(^6\). Because of the coexistence of the covalent, ionic, and metallic bonding types between the transition metals and carbon, the transition metal carbides usually have various stoichiometries. The flexibility in stoichiometry leads to rich chemical and physical behaviors, and provides a lot of candidates for materials design.

The V-C system is a typical binary system which has many different stoichiometries. \( \text{V}_2\text{C}, \text{V}_4\text{C}_3, \text{V}_6\text{C}_5, \text{V}_8\text{C}_7, \) and \( \text{VC} \) have been synthesized and investigated for many years\(^7\)-\(^11\). \( T_5M_3 \) is a common stoichiometry composed of transition metals \( T \) and main-group elements \( M \). There are several structure types for this specific stoichiometry, including \( D_{8h} \) (\( \text{Mn}_5\text{Si}_3 \), hexagonal, \( \text{P6}_3/\text{mcm}, \text{No.193} \)), \( D_{8l} \) (\( \text{Cr}_5\text{B}_3 \), tetragonal, \( \text{I4/mcm, No.140} \)), and \( D_{8m} \) (\( \text{W}_5\text{Si}_3 \), tetragonal, \( \text{I4/mcm, No.140} \)), with their prototypes and space groups given in the parentheses. For silicides of group VB transition metals, both \( \text{Ta}_5\text{Si}_3 \) and \( \text{Nb}_5\text{Si}_3 \) have the \( \text{Cr}_5\text{B}_3 \)-type structure, and \( \text{V}_5\text{Si}_3 \) has the \( \text{Mn}_5\text{Si}_3 \)-type structure\(^12\)-\(^17\). But carbides with this stoichiometry have never been synthesized nor theoretically studied.

In this work, we take the V-C system as a model system to explore the possibility to design new materials by changing the stoichiometry. The calculations were performed to investigate the crystal structure, phase stability, electronic structure, and mechanical properties of \( \text{V}_5\text{C}_3 \). The results show that the \( \text{Cr}_5\text{B}_3 \)-type \( \text{V}_5\text{C}_3 \) is stable mechanically, dynamically, and thermodynamically, and can be synthesized at high pressures. The hardness of the hard material can be enhanced further through tuning the Fermi energy.

Results and Discussion

As mentioned above, three typical structure types for \( T_5M_3 \), i.e., \( \text{Mn}_5\text{Si}_3, \text{Cr}_5\text{B}_3, \) and \( \text{W}_5\text{Si}_3 \) types are considered in this work, as shown in Fig. 1. For comparison, the known vanadium carbides in the V-C phase diagram, i.e. \( \text{VC} \) (cubic, \( \text{Fm-3m} \)), \( \text{V}_2\text{C} \) (orthorhombic, \( \text{Pbcn} \)), \( \text{V}_4\text{C}_3 \) (hexagonal, \( \text{R-3m} \)), \( \text{V}_6\text{C}_5 \) (hexagonal, \( \text{P3} \)), and \( \text{V}_8\text{C}_7 \) (cubic, \( \text{P4}_3 \)) are also included in the calculations.

The formation enthalpy was calculated using the following equation,

\[
\Delta H = [E_{\text{total}}(\text{V}_5\text{C}_3)] - [(xE_{\text{total}}(\text{V}) + yE_{\text{total}}(\text{C}))]/(x + y)
\]

1Department of Physics, University of Science and Technology Beijing, Beijing 100083, China. 2National Center for Electron Microscopy in Beijing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China. Correspondence and requests for materials should be addressed to F.M. (email: meng7707@sas.ustb.edu.cn) or R.Y. (email: ryu@tsinghua.edu.cn)
The total energies of V₅C₃ as a function of volume for the three structure types are plotted in Fig. 2(a). The Cr₅B₃-type V₅C₃ has the lowest energy at all the volumes. Hereafter, only the Cr₅B₃-type V₅C₃ is considered unless stated otherwise. It is worth noting that the formation enthalpies of these vanadium carbides are all negative at zero pressure. The negative formation enthalpies indicate that the carbides are more stable than the mixture of elemental V and C.

For a compound to be synthesized experimentally, it is more reliable to compare its enthalpy with the known compounds of neighboring stoichiometries. In the V-C phase diagram, V₅C₃ would locate in the two-phase region bounded by V₂C and V₄C₃. Therefore, we need to compare the formation enthalpy of V₅C₃ with the mixture of V₂C and V₄C₃. The formation enthalpies as a function of pressure have been calculated for both V₅C₃ and the mixture of V₂C and V₄C₃, as shown in Fig. 2(b). The mixture is more stable than V₅C₃ under pressures below 9.2 GPa, above which V₅C₃ becomes more stable. It indicates that V₅C₃ is thermodynamically more stable than that of the mixture at high pressures.

The elastic properties of a material are very important as they determine the mechanical stability, strength, hardness, and ductile or brittleness behavior. The calculated elastic constants Cᵢⱼ, the minimum elastic eigenvalue λᵣ, bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio ν and hardness Hₛ of these vanadium carbides are listed in Table 2. The calculated values of V₂C, V₄C₃, V₆C₅, V₈C₇, and VC in this work are in good agreement with the previous calculation values.

Table 1. Calculated lattice parameters a, b and c (Å) and formation enthalpy ΔH (eV/atom).

| Phase   | a   | b   | c   | ΔH  | Ref.  |
|---------|-----|-----|-----|-----|-------|
| V₅C₃(Cr₅B₃) | 5.485 | –   | 10.028 | –0.371 | This study |
| V₅C₃(W₅Si₃)  | 8.323 | –   | 4.361  | –0.188 | This study |
| V₅C₃(Mn₅Si₃) | 6.238 | –   | 4.532  | –0.265 | This study |
| VC       | 4.156 | –   | –     | –0.368 | This study |
| VC       | 4.091 | –   | –     | –0.405 | Ref. 11 |
| VC       | 4.158 | –   | –     | –0.216 | Ref. 8  |
| V₅C₃(Cr₅B₃) | 5.450 | 5.726 | 5.031  | –0.432 | This study |
| V₅C₃(W₅Si₃)  | 4.495 | 5.628 | 4.929  | –0.466 | Ref. 11 |
| V₅C₃(Mn₅Si₃) | 4.551 | 5.735 | 5.032  | –0.164 | Ref. 8 |
| V₆C₅      | 2.918 | –   | 27.907 | –0.421 | This study |
| V₆C₅      | 2.948 | –   | 27.782 | –0.107 | Ref. 8 |
| V₆C₅      | 5.100 | –   | 14.351 | –0.503 | This study |
| V₆C₅      | 5.005 | –   | 14.099 | –0.541 | Ref. 11 |
| V₆C₅      | 5.101 | –   | 14.354 | –0.052 | Ref. 8 |
| V₆C₅      | 8.326 | –   | –     | –0.482 | This study |
| V₆C₅      | 8.181 | –   | –     | –0.522 | Ref. 11 |
| V₆C₅      | 8.329 | –   | –     | –0.036 | Ref. 8 |
The Cr$_5$B$_3$-type V$_5$C$_3$ is tetragonal. For a tetragonal system, the mechanical stability criteria are given by 
\[ C_{11} > 0, \quad C_{33} > 0, \quad C_{12} = 0, \quad C_{13} = 0, \quad C_{44} > 0, \quad C_{55} = 2C_{12} > 0, \quad \text{and} \quad 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0 \].

The elastic constants of the Cr$_5$B$_3$-type V$_5$C$_3$ satisfy these stability conditions, indicating that it is mechanically stable.

The phonon dispersions were calculated to verify the dynamical stability of the Cr$_5$B$_3$-type V$_5$C$_3$. A dynamically stable crystal structure requires that all phonon frequencies should be positive. As shown in Fig. 3 for the Cr$_5$B$_3$-type V$_5$C$_3$ at zero pressure, it is clear that no imaginary phonon frequency can be found in the whole Brillouin zone, indicating that the Cr$_5$B$_3$-type V$_5$C$_3$ is dynamically stable under ambient conditions.

Table 2. Calculated elastic constants $C_{ij}$ (GPa), the minimum elastic eigenvalue $\lambda_1$ (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young's modulus $E$ (GPa), Poisson's ratio $\nu$, and hardness $H_v$ (GPa).

The Cr$_5$B$_3$-type V$_5$C$_3$ is tetragonal. For a tetragonal system, the mechanical stability criteria are given by 
\[ C_{11} > 0, \quad C_{33} > 0, \quad C_{12} = 0, \quad C_{13} = 0, \quad C_{44} > 0, \quad C_{55} = 2C_{12} > 0, \quad \text{and} \quad 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0 \].

The elastic constants of the Cr$_5$B$_3$-type V$_5$C$_3$ satisfy these stability conditions, indicating that it is mechanically stable. The phonon dispersions were calculated to verify the dynamical stability of the Cr$_5$B$_3$-type V$_5$C$_3$. A dynamically stable crystal structure requires that all phonon frequencies should be positive. As shown in Fig. 3 for the Cr$_5$B$_3$-type V$_5$C$_3$ at zero pressure, it is clear that no imaginary phonon frequency can be found in the whole Brillouin zone, indicating that the Cr$_5$B$_3$-type V$_5$C$_3$ is dynamically stable under ambient conditions.
Because the hardness measurement involves complex deformation processes, including elastic deformations, plastic deformations, and fracture, it is difficult to obtain directly the hardness value of a material from first-principles calculations. Therefore, correlations between elastic moduli and hardness have been suggested as indirect indicators of materials hardness. A hard material should have a high bulk modulus to resist the volume contraction in response to an applied load, and a high shear modulus to resist shear deformation. Recently, the softest elastic mode has been shown to correlate better to the hardness number than the other elastic moduli, indicating that elastic anisotropy is essential in determining the hardness. The elastic properties ($B$, $G$, $E$, and $\lambda_1$) of V$_5$C$_3$ and the other previously known vanadium carbides as a function of the V/C ratio are plotted in Fig. 4. For the known vanadium carbides, the general trend is that the elastic moduli decrease with the V/C ratio. An abnormal increase occurs at V$_5$C$_3$, the elastic moduli of which are higher than both the neighboring V$_2$C and V$_4$C$_3$.

Figure 3. Phonon dispersions of the Cr$_5$B$_3$-type V$_5$C$_3$ at zero pressure along high symmetry directions of the Brillouin zone.

Figure 4. (a) The minimum elastic eigenvalue $\lambda_1$, (b) shear modulus $G$, (c) bulk modulus $B$ and (d) Young's modulus $E$ of vanadium carbides as a function of the V/C ratio. The lines are guide to the eye.
In order to explain the origin of the stability and the abnormal mechanical properties of the Cr5B3-type V5C3, the electronic structure of V5C3, V2C and V4C3 has been analyzed. Their densities of states (DOS) are plotted in Fig. 5(a). They are metallic with non-zero DOS values at the Fermi level. There are valleys (sometimes called pseudogap) close to the Fermi level for all the three compounds. In general, the electronic states with lower energies than the valley are bonding orbitals, and those with higher energies are antibonding orbitals. To clarify the nature of the chemical bonding near the Fermi level, we performed the Crystal Orbital Hamilton Population (−COHP) analysis, which gives an idea about the participating orbital pair. The positive value represents the bonding states and negative value represents the antibonding states. As shown in Fig. 5(c) for V5C3, it is clear that the pseudogap separates the bonding and antibonding states appears. A deeper valley means that the bonding orbitals are more stabilized and the antibonding orbitals are more destabilized, forming strong chemical bonds. Among the three compounds, V5C3 has the deepest valley close to the Fermi level. Therefore, the stability and the abnormal mechanical properties of V5C3 can be attributed to the pseudogap effect.

The electronic structure of V5C3 suggests an interesting method to improve its hardness. The Fermi level of V5C3 has a higher energy than the valley, indicating that some antibonding orbitals are occupied. Since the antibonding orbitals would weaken the chemical bonds, once they are made empty, the material could be further strengthened. We consider alloying V5C3 with Ti, which has one less valence electron than V. Since Ti is neighboring to V in the periodic table, it should be relatively easy to enter the lattice of V5C3. According to the rigid band model, the alloying element normally generates small changes in the nature of chemical bond in the host materials. The Cr5B3-type V5C3 with the alloying contents of 5 at.%, 10 at.%, 20 at.%, 25 at.%, and 30 at.% Ti were investigated. The supercells for the calculations are shown in Fig. 6. In order to minimize the interactions between the alloying atoms, they were placed as far as allowed in the supercells.

The DOS curves of V5C3 and its alloys (V5Ci−xTix) were illustrated in Fig. 5(b). As expected, the Fermi level shifts to lower energies with increasing content of Ti from xTi = 0 to xTi = 0.3. The Fermi level is located at the valley for xTi = 0.2. The calculated elastic constants are listed in Table 3. All the alloys are mechanically stable because the elastic constants of these alloys satisfy the mechanical stability criteria and there is no negative elastic eigenvalue. For the Cr5B3-type V5C3, the smallest elastic eigenvalue, represents the shear deformation in xy planes. The smallest elastic eigenvalue, the hardness Hs, shear modulus G and Young’s modulus E are plotted in Fig. 7. A general trend is that λ1, Hs, G and E increase with the content of Ti from xTi = 0.05 to xTi = 0.2, where they reach their maxima, and then decrease as xTi increases further. The trend is exactly what we expect from the electronic structure analysis. At xTi = 0.2, the Fermi level is located at the valley in DOS. In this case, all of the bonding orbitals are occupied and the antibonding orbitals empty, leading to the strongest chemical bonds.
Figure 6. The supercells of (a) V₅C₃, (b) (V₀.9T₀.05)₅C₃, (c) (V₀.9T₀.1)₅C₃, (d) (V₀.8T₀.2)₅C₃, (e) (V₀.75T₀.25)₅C₃ and (f) (V₀.7T₀.3)₅C₃.

Table 3. Calculated elastic constants $C_{ij}$ (GPa), the minimum elastic eigenvalue $\lambda_1$ (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young’s modulus $E$ (GPa), Poisson’s ratio $\nu$ and hardness $H_v$ (GPa) of (V₁₋ₓTₓ)₅C₃.
Conclusions

In summary, the crystal structure, phase stability, electronic structure, and mechanical properties of V₅C₃ have been studied. It is demonstrated that the Cr₅B₃-type V₅C₃ is thermodynamically, mechanically, and dynamically stable, and can be synthesized under pressures above 9.2 GPa.

The elastic properties and electronic structures of (V₁₋ₓTiₓ)₅C₃ alloys have also been investigated. When 20 at.% V is substituted by Ti, the Fermi level is tuned to the valley in DOS, giving the maximum hardness of V₅C₃ alloys. While V₅C₃ itself is not a superhard material, the electronic structure and the hardness optimization based on it suggest an interesting way for searching hard materials. The Fermi energy of a material can be tuned to maximize the occupation of bonding orbitals and minimize the occupation of antibonding orbitals, thus strengthening the material.

Computational Methods

In this work, the density functional theory (DFT) calculations were performed using the projector-augmented wave (PAW) method²⁵–²⁷, as implemented in the Vienna Ab-initio Simulation Package (VASP) code²⁸. The generalized gradient approximation (GGA)²⁹ with the Perdew-Burke-Ernzerhof (PBE) scheme was used to describe the exchange-correlation function. Geometry optimization was carried out using the conjugate gradient algorithm. The plane-wave cutoff energy was 500 eV. The k-points were generated using the Monkhorst-Pack mesh³⁰. Lattice parameters and atomic positions were optimized simultaneously. In order to obtain equilibrium volume of the materials, the total-energies were calculated at several fixed volume with the ionic positions and the cell shape allowed to vary. These total energies were then fitted with the Birch-Murnaghan equation of state³¹–³³. The elastic constants were calculated using the universal-linear-independent coupling-strains (ULICS) method³⁴, which is computationally efficient and has been widely used in calculations of single-crystal elastic constants³⁵–³⁹. Based on the single-crystal elastic constants, the bulk modulus B and the shear modulus G were calculated according to the Voigt-Reuss-Hill approximation⁴⁰. Young’s modulus E and Poisson’s ratio ν were obtained by the following equations:

\[
E = 9BG/(3B + G)
\]

\[
\nu = (3B - 2G)/(2(3B + G))
\]

The hardness (Hᵥ) of V₅C₃ is relative to G and B through the empirical formulabased on the Pugh modulus ratio k = G/B⁴¹,⁴²:

\[
Hᵥ = 2(k^2G)^{0.585} - 3
\]
Phonon dispersions were calculated using the direct supercell method, as implemented in the PHONOPY code\(^{43,44}\). The Crystal Orbital Hamilton Population (−COHP) analysis have been performed to determine the bonding properties of the electronic states close to the Fermi level. Density functional method with LCAO basis sets, as implemented in the SIESTA code\(^{45}\), has been used to calculate the COHP. The PBE parameterization of GGA was used. The DZP basis sets were employed. The norm-conserving Troullier-Martins pseudopotentials\(^{46}\) were used for the core-valence interactions. The mesh cut-off value was set to 200 Rydberg and the Brillouin zone was sampled using Monkhorst-Pack set of \(k\) points.

References

1. Zheng, J. C. Superhard hexagonal transition metal and its carbide and nitride: Os, OsC, and OsN. Phys. Rev. B 72, 052105 (2005).
2. Wang, J. Y. et al. Raman active phonon modes and heat capacities of Ti₅₄AlC and Cr₂₄AlC ceramics: first-principles and experimental investigations. Appl. Phys. Lett. 86, 161902 (2005).
3. Siegel, D. I., Hector, L. G. & Adams, J. B. Ab initio study of Al-Cr interfacial adhesion. Phys. Rev. B 67, 092105 (2003).
4. Fan, C. Z. et al. Low compressible noble metal carbides with rocksalt structure: Ab initio total energy calculations of the elastic stability. Appl. Phys. Lett. 89, 071913 (2006).
5. Gou, H. Y. et al. Pressure-induced incompressibility of ReC and effect of metallic bonding on its hardness. Appl. Phys. Lett. 92, 241901 (2008).
6. Zhao, S. J. et al. Manipulation of electronic and magnetic properties of M₄C₆ (M = Hf, Nb, Sc, Ta, Ti, V, Zr) monolayer by applying mechanical strains. Appl. Phys. Lett. 104, 133106 (2014).
7. Isayev, I. E. et al. Phonon related properties of transition metals, their carbides, and nitrides: A first-principles study. J. Appl. Phys. 101, 123519 (2007).
8. Wu, L. L. et al. Understanding the mechanical properties of vanadium carbides: Nano-indentation measurement and first-principles calculations. J. Alloys Comp. 548, 60–64 (2013).
9. Liu, H. L., Zhu, J. C., Liu, Y. & Lai, Z. H. First-principles study on the mechanical properties of vanadium carbides VC and V₅C₃. Materials Letters 62, 3084–3086 (2008).
10. Rafaja, D. et al. Rietveld analysis of the ordering in V₅C₃. J. Alloys Comp. 269, 60–62 (1999).
11. Chong, X. Y. et al. Electronic structures mechanical and thermal properties of V₆–C binary compounds. RSC Adv. 4, 44959–44971 (2014).
12. Storms, E. K. et al. The Vanadium-Vanadium Carbide System. J. Phys. Chem. 66, 1401–1408 (1962).
13. Tillard, M. The mixed intermetallic silicide Nb₅₃Ta₃Si₃ (0 ≤ x ≤ 5). Crystal and electronic structure. J. Alloys Comp. 584, 385–392 (2014).
14. Romaka, L. et al. Peculiarity of component interaction in Zr–Mn–(Sn, Sb) ternary systems. J. Alloys Comp. 611, 401–409 (2014).
15. Tão, M. X.; Mund, P.; Colinet, C. & Tedenac, J. C. Phase stability and physical properties of Ti₅₄Si₃ compounds from first-principles calculations. Phys. Rev. B 80, 104103 (2009).
16. Mosharivskyj, Y. & Fransen, H. F. High-temperature modification of V₅Sb and its ternary analogue Y₅NiSb₁₋ₓ. J. Alloys Comp. 319, 100–107 (2001).
17. Chen, Y., Kolsuzoglu, A. N., Pettifor, D. G., Shang, J. X. & Zhang, Y. Theoretical analysis of structural stability of TaS₃ transition metal silicides. Phys. Rev. B 82, 184104 (2010).
18. Yu, R., Zhang, Q. & Zhan, Q. Softest elastic mode governs materials hardness. Chin. Sci. Bull. 59, 1747–1754 (2014).
19. Born, M. On the stability of crystal lattices. I. Proc. Cambridge Philos. Soc. 36, 160 (2008).
20. Zhou, L. C. et al. Structural stability and thermodynamics of CrN magnetic phases from ab initio calculations and experiment. Phys. Rev. B 80, 184102 (2014).
21. Hoffman, R. Solids and Surfaces: A Chemist’s View on Bonding in Extended Structures, (VCH Publisher, 1988).
22. Dronskowski, R. & Blochl, P. E. Crystal Orbital Hamilton Populations (COHP). Energy-Resolved Visualization of Chemical Bonding in Solids Based on Density-Functional Calculations. J. Phys. Chem. 97, 8617–8624 (1993).
23. Carlsson, A. E. & Meschter, P. J. Intermetallic Compounds, edited by Westbrook, J. H. & Fleischer, R. L., Vol. 1 (Wiley, 1994).
24. Yu, R., He, L. L. & Ye, H. Q. Effect of W on structural stability of TaAl intermetallics and the site preference of W. Phys. Rev. B 65, 184102 (2002).
25. Blochl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).
26. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector-augmented-wave method. Phys. Rev. B 59, 1758 (1999).
27. Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. Phys. Rev. B 36, 865–867 (1964).
28. Kresse, G. & Furthmuller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169 (1996).
29. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
30. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. Phys. Rev. B 13, 5188–5196 (1970).
31. Murnaghan, F. D. The Compressibility of Media Under Extreme Pressures. Proc. Natl. Acad. Sci. 30, 244 (1944).
32. Birch, F. Elasticity and constitution of the Earth's interior. J. Geophys. Res. 57, 227–286 (1952).
33. Birch, F. Finite Elastic Strain of Cubic Crystals. Phys. Rev. 71, 809–824 (1947).
34. Yu, R., Zhu, J. & Ye, H. Q. Calculations of single-crystal elastic constants made simple. Comput. Phys. Commun. 181, 671–675 (2010).
35. Wei, C., Fan, J. L. & Gong, H. R. Structural, thermodynamic, and mechanical properties of bulk La and A-La₂O₃. J. Alloys Comp. 618, 615–622 (2015).
36. Hu, Y. T. & Gong, H. First principles study of thermodynamic and mechanical properties of Pd₃₀Cu₃₅. J. Alloys Comp. 639, 635–641 (2015).
37. Bartosik, M. et al. Thermal expansion of rock-salt cubic AIN. Appl. Phys. Lett. 107, 071602 (2015).
38. Hole, D. et al. Macroscopic elastic properties of textured ZnN₂AlIN polycrystalline aggregates: Fromab initio calculations to grain-scale interactions. Phys. Rev. B 90, 184106 (2014).
39. Dang, D. Y., Fan, J. L. & Gong, H. R. Thermodynamic and mechanical properties of TiC from ab initio calculation. J. Appl. Phys. 116, 033509 (2014).
40. Karki, B. B., Stixrude, L., Clark, S. J., Warren, M. C., Ackland, G. J. & Crain, J. Structure and elasticity of MgO at high pressure. J. Am. Mineral. 82, 51–60 (1997).
41. Chen, X. Q., Niu, H. Y., Franchini, C., Li, D. Z. & Li, Y. Y. Hardness of Tc-carbon: Density functional theory calculations. Phys. Rev. B 84, 121405 (2011).
42. Chen, X. Q., Niu, H. Y., Li, D. Z. & Li, Y. Y. Modeling hardness of polycrystalline materials and bulk metallic glasses. Intermetallics 19, 1275–1281 (2011).
43. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures. Phys. Rev. B 78, 134106 (2008).
44. Baroni, S. et al. Phonons and related crystal properties from density-functional perturbation theory. Rev. Mod. Phys. 73, 515–562 (2011).
45. Soler, J. M. et al. The SIESTA method for ab initio order-N materials simulation. J. Phys.: Condens. Matter 14, 2745–2779 (2002).
46. Troullier, N. & Martins, J. L. Efficient pseudopotentials for plane-wave calculations. Phys. Rev. B 43, 1993–2006 (1991).

Acknowledgements
This work was supported by National Basic Research Program of China (2011CB606406), the Fundamental Research Funds for the Central Universities (TP-A3:06108170), and NSFC (51371102, 51390475). This work used the resources of Shanghai Supercomputer Center and National Center for Electron Microscopy in Beijing.

Author Contributions
F.M. and R.Y. proposed and supervised the project. W.X. performed the first principles calculations and prepared the figures. All authors discussed the results wrote the manuscript.

Additional Information
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Xing, W. et al. A new type of vanadium carbide V₅C₃ and its hardening by tuning Fermi energy. Sci. Rep. 6, 21794; doi: 10.1038/srep21794 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/