

Article

Not peer-reviewed version

First-Principles Study of the Mechanical Properties of (Ti,W)C Solid Solutions

[Pavlo Prysyazhnyuk](#)^{*}, Volodymyr Turkevych, Oleksandr Matviichuk, Volodymyr Kotsyubynsky, Myroslav Burda, Andrii Molchanov, Iryna Savchuk

Posted Date: 24 January 2025

doi: 10.20944/preprints202501.1814.v1

Keywords: titanium carbide; tungsten carbide; solid solutions; phase stability; mechanical properties; electronic structure; cluster expansion



Preprints.org is a free multidisciplinary platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This open access article is published under a Creative Commons CC BY 4.0 license, which permit the free download, distribution, and reuse, provided that the author and preprint are cited in any reuse.

Article

First-Principles Study of the Mechanical Properties of (Ti,W)C Solid Solutions

Pavlo Prysyazhnyuk ^{1,*}, Volodymyr Turkevych ², Oleksandr Matviichuk ²,
Volodymyr Kotsyubynsky ³, Myroslav Burda ¹, Andrii Molchanov ¹ and Iryna Savchuk ²

¹ Department of Computerized Engineering, Ivano-Frankivsk National Technical University of Oil and Gas, 076019 Ivano-Frankivsk, Ukraine; andrii.molchanov-a13222@nung.edu.ua; myroslav.burda@gmail.com

² V.M. Bakul Institute for Superhard Materials NAS of Ukraine, 04074 Kyiv, Ukraine; vturk@ism.kiev.ua, o.o.matviichuk@gmail.com, SavchukIV@nas.gov.ua

³ Department of Applied Physics and Material Science, Vasyl Stefanyk Precarpathian National University, 57 Shevchenko Str., 76018 Ivano-Frankivsk, Ukraine

* Correspondence: pavlo.prysyazhniuk@nung.edu.ua; Tel.: +380999163197

Abstract: Titanium carbide (TiC) and tungsten carbide (WC) are essential engineering materials known for their exceptional hardness, wear resistance, and thermal stability. This study investigates the formation, phase stability, mechanical properties, and electronic structure of (Ti,W)C solid solutions. The research employs computational methods, including Density Functional Theory (DFT) and Cluster Expansion (CE), to explore compositional variations and their effects. Results reveal that Ti_{0.5}W_{0.5}C demonstrates superior thermodynamic stability, while intermediate compositions such as Ti_{0.67}W_{0.33}C achieve peak hardness (~33 GPa) due to the synergistic effects of covalent Ti-C and metallic W-C bonding. The electronic structure analysis highlights hybridized bonding characteristics that optimize mechanical resilience and thermal stability. Elastic and vibrational properties show a notable influence of tungsten incorporation, enhancing bulk modulus and enabling tailored properties. These findings provide critical insights for the development of high-performance materials in applications such as machining, wear-resistant coatings, and structural components.

Keywords: titanium carbide; tungsten carbide; solid solutions; phase stability; mechanical properties; electronic structure; cluster expansion

1. Introduction

Titanium carbide (TiC) and tungsten carbide (WC) are critical materials in engineering, renowned for their exceptional hardness, superior wear resistance, and outstanding thermal stability. These attributes make them indispensable for applications such as cutting tools, wear-resistant coatings, and structural components operating in extreme environments. TiC is particularly valued for its high hardness and thermal resistance, while WC is recognized for its excellent toughness and thermal conductivity. The formation of (Ti,W)C solid solutions, which combines the unique strengths of these compounds, offers the potential to achieve enhanced toughness, tunable mechanical properties, and significantly improved hardness [1–3].

Several advanced methods are employed to synthesize (Ti,W)C solid solutions, ensuring optimized properties and microstructures. Self-propagating high-temperature synthesis (SHS) utilizes exothermic reactions to produce dense and defect-free materials with rapid processing and controlled grain size [4,5]. This method has proven effective in producing TiC-WC composites with superior mechanical properties. Plasma transfer arc (PTA) deposition is another prominent technique, enabling the fabrication of coatings with uniform carbide distribution, excellent adhesion, and enhanced wear resistance [6]. Hot-pressing techniques have enabled the fabrication of dense materials with refined grain sizes and enhanced uniformity, while the addition of 5 vol.% WC

increases hardness from 21.5 GPa to 23.5 GPa and flexural strength from 410 MPa to 491 MPa, with the structure characterized by a single NaCl-type phase, indicating the formation of a stable solid solution [7].

The unique properties of (Ti,W)C arise from the substitution of tungsten atoms into the TiC lattice. This substitution reduces the lattice parameter due to the smaller atomic radius of W, increasing atomic packing density and hardness [8,9]. Experimental studies report lattice parameters decreasing from 4.32 Å for pure TiC to approximately 4.27 Å for equiatomic (Ti,W)C [10]. Carbon vacancies, particularly in high-W-content compositions, further stabilize the lattice by reducing strain and improving thermal conductivity. These vacancies also enhance electronic properties, contributing to stronger covalent bonding and improved mechanical properties [11,12].

Despite the progress in understanding (Ti,W)C solid solutions, existing data often focus on isolated compositions and fail to address configurational variations. Experimental approaches are limited in capturing atomic-scale phenomena, such as the role of vacancies and bonding interactions [13,14]. Advanced computational methods, such as Cluster Expansion (CE) [15] integrated within the Density Functional Theory (DFT) framework [16], are robust tools for modeling solid solutions. The CE method excels in determining ground-state structures by systematically evaluating configurational energies, providing a clear advantage over conventional supercell approaches [17], which often struggle with configurational sampling in complex systems. CE method delivers valuable insights into phase stability, mechanical properties, and electronic structures, enabling the exploration of a wide compositional range with unprecedented precision.

The current study employs computational approaches to determine the phase stability and mechanical properties of (Ti,W)C solid solutions. By examining the role of compositional variations in the TiC–WC system, this research aims to address existing knowledge gaps and inform the development of high-performance materials for applications in machining, wear-resistant coatings, and advanced structural components.

2. Computational Details

The structural and mechanical properties of $\text{Ti}_{1-x}\text{W}_x\text{C}$ solid solutions were investigated using density functional theory (DFT) as implemented in VASP [18]. The r2SCAN meta-GGA exchange-correlation functional [19] was selected for its accuracy in modeling transition metal carbides, enabling precise predictions of total energy and electronic structure. The substitutional solid solutions were modeled using the structure inversion method (SIM) within the Alloy Theoretic Automated Toolkit (ATAT) [20,21]. Starting from the TiC lattice (space group Fm-3m), tungsten atoms were substituted in the titanium sublattice across the composition range $0 \leq x \leq 1$ to explore the compositional dependence of mechanical and electronic properties. The β -WC (space group Fm-3m) phase was chosen as the WC end member.

The Brillouin zone was sampled using the Monkhorst–Pack scheme with a k-point density of 1000 points per reciprocal atom, ensuring high-resolution electronic structure calculations. A plane-wave energy cutoff of 520 eV was set to balance computational efficiency and accuracy, and the convergence criterion for the self-consistent field (SCF) iterations was set to 10^{-8} eV. These parameters were optimized to account for the complex electronic structure of transition metal carbides.

The electronic structure, including the density of states (DOS) and projected density of states (pDOS), was analyzed to investigate the underlying electronic interactions in the solid solutions. Gaussian smearing with a width of 0.05 eV was applied for the DOS calculations, with energy values sampled over a range from -20 eV to 20 eV using 2000 points. The pDOS calculations included orbital projections up to $l=2$ (s, p, d orbitals) to capture detailed angular momentum contributions. To gain deeper insights into the chemical bonding characteristics, the Electron Localization Function (ELF) [22], deformation density (DD), and Reduced Density Gradient (RDG) fields were calculated using SSSP-precision pseudopotentials [23] within the Quantum ESPRESSO [24] code, integrated into the

Amsterdam Modeling Suite (AMS). These calculations were performed for TiC, WC, and clusters exhibiting enhanced mechanical properties, specifically in crystal planes containing M–C bonds.

The mechanical properties were determined by calculating the stiffness tensor components using the strain-stress method, which relates applied strain to stress response. This approach was chosen for its direct applicability to materials with complex bonding environments. Elastic moduli were derived using the Voigt-Reuss-Hill (VRH) approximation [25], which averages the elastic constants assuming uniform stress and strain conditions, providing reliable predictions for polycrystalline materials. The Vickers hardness (HV) was determined as an average of predictions from five theoretical models [26–30], ensuring robust and accurate estimates of the material's resistance to local deformation [31].

Vibrational properties were evaluated by calculating the Debye temperature, which provides essential insights into the lattice dynamics, thermal conductivity, and stability of the solid solutions. This parameter was derived from the elastic constants and further analyzed using methodologies integrated into VASPKIT code [32], offering a comprehensive understanding of the thermal and mechanical behavior of $\text{Ti}_{1-x}\text{W}_x\text{C}$ solid solutions.

3. Results and Discussion

3.1. The Cluster Expansion Analysis

The CE results for the TiC-WC system, as depicted in Figure 1, illustrate the pseudobinary energy landscape and provide critical insights into the thermodynamic stability of substitutional solid solutions. The convex hull, derived from the CE calculations, identifies compositions that are thermodynamically stable, corresponding to those that minimize the system energy for specific tungsten carbide mole fractions (x_W). Key intermediate compositions, such as $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$, $\text{Ti}_{0.5}\text{W}_{0.5}\text{C}$ and $\text{Ti}_{0.33}\text{W}_{0.67}\text{C}$, lie on the convex hull, confirming their stability and suggesting their potential as promising candidates for advanced material applications.

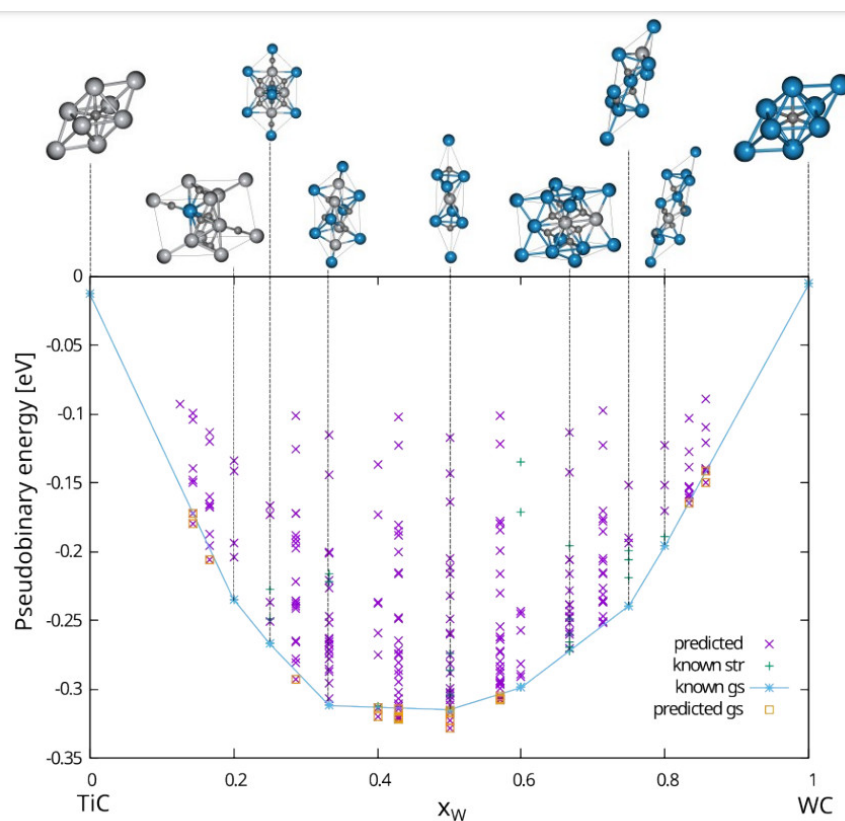


Figure 1. Pseudobinary energy landscape for the TiC-WC system: purple crosses (predicted structures), green crosses (known structures), cyan stars (known ground states), and orange squares (predicted ground states).

The stability of these phases is attributed to the interplay of strong covalent bonding between the transition metals and carbon atoms, as well as reduced lattice strain arising from the optimal atomic arrangement. Among these, $\text{Ti}_{0.5}\text{W}_{0.5}\text{C}$ exhibits the lowest energy along the convex hull, indicating its exceptional thermodynamic stability. This composition benefits from a well-balanced interaction between Ti, W, and C atoms, minimizing the overall energy of the system. In addition to stable phases, the CE results reveal metastable configurations that lie above the convex hull.

3.2. Mechanical Properties

The elastic moduli of (Ti,W)C solid solutions modeled by CE as a function of the mole fraction of tungsten carbide (x_W) reveal significant trends that provide insight into their mechanical properties. As shown in Figure 2, the bulk modulus (B) increases steadily with x_W ranging from 255 GPa for pure TiC ($x_W=0$) to 390 GPa for pure WC ($x_W=1$). This monotonic increase reflects the substitution of weaker Ti-C bonds with stronger W-C bonds, which are known for their higher bonding rigidity and compressive strength. Similarly, the shear modulus (G) and Young's modulus (E) increase consistently with x_W reflecting the influence of tungsten carbide on the stiffness of the solid solutions. Intermediate compositions, such as $x_W=0.5$ and $x_W=0.66$, exhibit bulk moduli of 318 GPa and 346 GPa, respectively, indicating that alloying TiC with WC results in significant strengthening effects. The observed elastic trends are consistent with prior studies. Song et al. [10] reported that the addition of TiC to tungsten composites enhances stiffness, with the elastic moduli increasing linearly as a function of TiC content. This reinforcing effect is attributed to the high stiffness and bonding strength of TiC. Similarly, Ivashchenko et al. [33] validated the elastic properties of TiC and WC, noting their dependence on bond strength and lattice distortion, which corroborates the trends observed in this study.

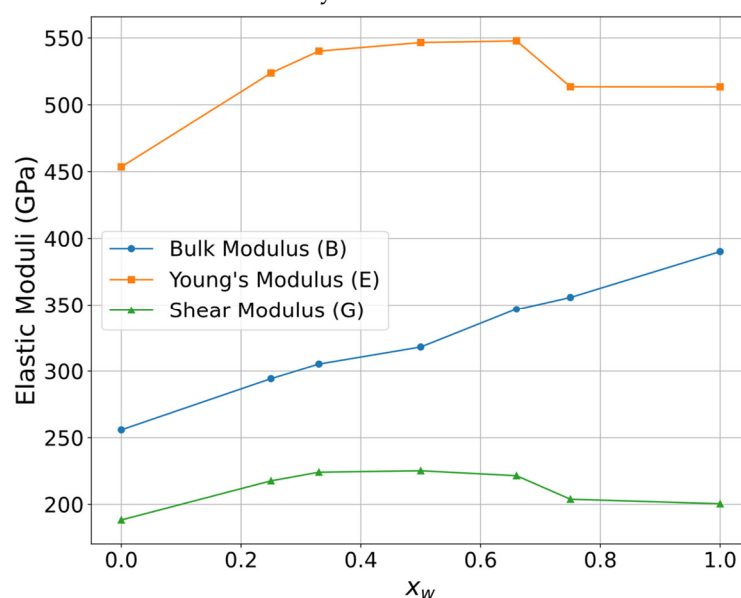


Figure 2. Concentration dependence of the elastic moduli for $\text{Ti}_{1-x}\text{W}_x\text{C}$ solid solutions calculated using VRH approximation.

Figure 3 illustrates the trends in Poisson's ratio (ν) and average Vickers hardness (HV) as a function of the mole fraction of tungsten carbide (x_W) in (Ti,W)C solid solutions. The Poisson's ratio demonstrates a slight increase with increasing x_W , reaching a peak of 0.281 at $x_W=1.0$ for pure WC. This trend reflects the compositional changes in bonding character from predominantly Ti-C to W-C bonds, which contribute to an increase in isotropic compressibility. Conversely, the average HV

exhibits a nonlinear response, peaking at $x_w=0.33$ with a value of approximately 33 GPa before declining to 24 GPa at $x_w=1.0$. This suggests that while intermediate compositions benefit from solid-solution strengthening, the dominance of W–C bonds in pure WC reduces the hardness due to the associated increase in ductility.

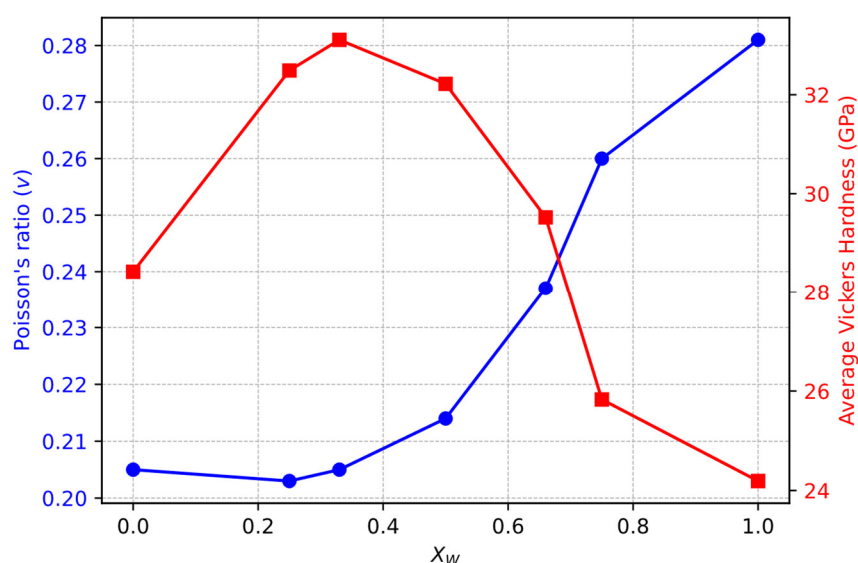


Figure 3. Concentration dependence of the elastic moduli for $\text{Ti}_{1-x}\text{W}_x\text{C}$ solid solutions calculated using VRH approximation.

The observed hardness trends align with the literature, which reports a peak hardness of ~24–25 GPa for dense, binderless WC ceramics at ambient conditions, attributed to their high density and restricted grain growth [34]. Moreover, the hardness of pure WC ceramics at elevated temperatures also approaches ~25 GPa, while that of pure TiC remains lower (~19 GPa) under similar conditions [35]. The intermediate compositions of (Ti,W)C benefit from both the fine-grained microstructure and the synergistic effects of Ti and W bonding, resulting in higher hardness compared to the individual constituents.

The relationship between the Cauchy pressure (P_c) and Kleinman's parameter (ζ) as a function of the tungsten carbide mole fraction (x_w) reveals critical insights into the bonding nature and deformation mechanisms in (Ti,W)C solid solutions. These parameters, depicted in Figure 4, exhibit contrasting trends that reflect the complex interaction of covalent and metallic bonding characteristics with varying x_w .

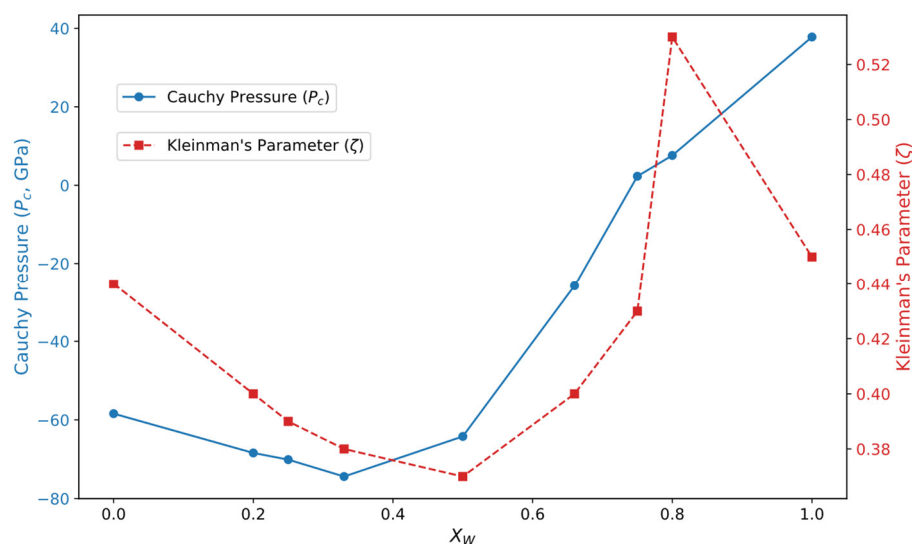


Figure 4. Concentration dependence of the elastic moduli for Ti_{1-x}W_xC solid solutions calculated using VRH approximation.

The Cauchy pressure, P_c exhibits a non-monotonic trend with increasing x_w . Starting at $P_c = -58.4$ GPa for pure TiC ($x_w = 0$), P_c becomes increasingly negative, reaching a minimum of -74.4 GPa at $x_w = 0.33$. This indicates a pronounced dominance of covalent-like bonding in the intermediate compositions, likely due to the synergistic strengthening of Ti-C and W-C bonds. Beyond $x_w = 0.33$, P_c begins to rise, transitioning to positive values at higher x_w with $P_c = 37.8$ GPa for pure WC ($x_w = 1.0$). Positive P_c at these compositions reflects a shift toward metallic-like bonding, typical of WC's bond characteristics. This evolution in P_c highlights the capability to tailor the bonding nature of (Ti,W)C solid solutions by varying the tungsten content. The Kleinman's parameter, ζ , displays a complementary trend, providing further insight into the deformation mechanisms. Initially, $\zeta = 0.44$ at $x_w = 0$, indicating bond-bending dominance in pure TiC. With increasing x_w , ζ decreases to a minimum of 0.37 around $x_w = 0.5$, further signifying the structural anisotropy associated with directional covalent bonding. Beyond this point, ζ increases, peaking at 0.53 for $x_w = 0.8$, before slightly decreasing to 0.45 at $x_w = 1.0$. The rise in ζ at high x_w indicates a transition to bond-stretching dominance, consistent with the more isotropic nature of WC's metallic bonds. The observed trends in P_c and ζ emphasize the duality in the mechanical properties of (Ti,W)C solid solutions. The strongly negative P_c values at intermediate compositions, combined with lower ζ , suggest enhanced hardness and brittleness due to the preponderance of covalent bonding. In contrast, the positive P_c and higher ζ at WC-rich compositions correspond to improved ductility, rendering these materials more suitable for applications requiring toughness.

The variation of longitudinal wave velocity, transverse wave velocity, and Debye temperature as functions of the mole fraction of tungsten (x_w) in the (Ti,W)C solid solutions is presented in Figure 5. These properties provide valuable insight into the elastic and thermodynamic behavior of the material, reflecting the influence of tungsten incorporation on the mechanical and vibrational characteristics of the solid solutions.

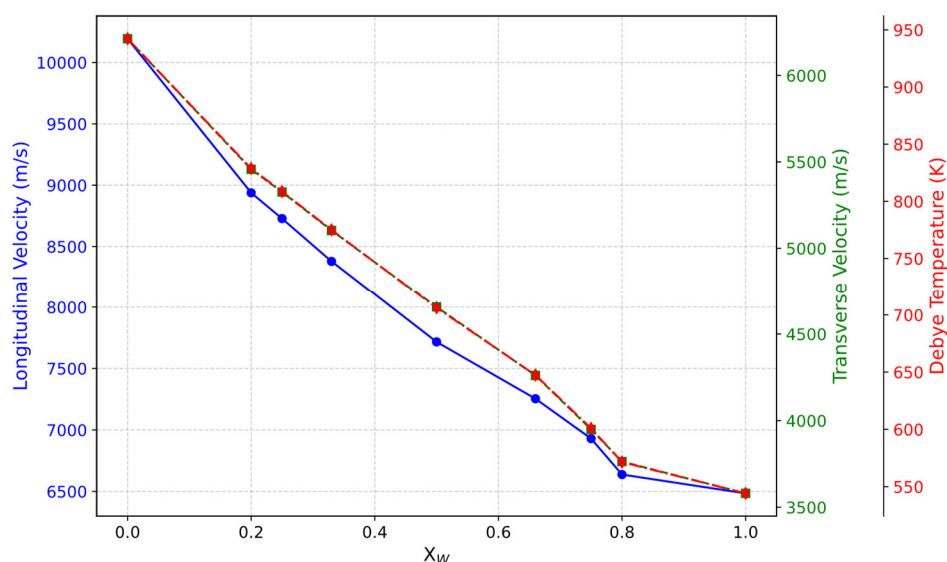


Figure 5. Concentration dependence of the elastic moduli for Ti_{1-x}W_xC solid solutions calculated using VRH approximation.

The longitudinal wave velocity, exhibits a systematic decline from approximately 10200 m/s for pure TiC (x_w) to 6500 m/s for pure WC ($x_w = 1$). This monotonic reduction is indicative of a weakening in the stiffness of the material in the longitudinal direction, which is directly correlated to the substitution of lighter titanium atoms with heavier tungsten atoms. The heavier atomic mass of

tungsten, coupled with the associated changes in bond stiffness, slows the propagation of elastic waves through the material. A similar trend is observed for the transverse wave velocity, which decreases from 6200 m/s at $x_w=0$ to 3500 m/s at $x_w=1$. The transverse velocity reflects the material's shear rigidity, which diminishes as tungsten content increases. This decline correlates with the shear moduli of the solid solution, underscoring the impact of atomic mass and bond strength on the material's shear response. The Debye temperature, decreases steadily from 942 K for pure TiC to 544 K for pure WC. This property, intrinsically related to elastic wave velocities and atomic masses, signifies the vibrational characteristics of the lattice. The introduction of tungsten, with its higher atomic mass, softens the vibrational modes of the material, resulting in a lower Debye temperature. This trend implies a reduced ability of the material to conduct heat via phonons as the tungsten content increases. The observed trends in longitudinal and transverse wave velocities and Debye temperature collectively highlight the impact of tungsten incorporation on the mechanical and thermal properties of the (Ti,W)C solid solution. The simultaneous decline of these properties reflects a reduction in lattice stiffness and an increase in atomic mass, which collectively influence both elastic and vibrational behaviors.

3.3. Electronic Properties

The Density of States (DOS) and Partial DOS (pDOS) analyses for TiC, WC, and the $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster, representing the solid solution with the highest hardness (Figure 6), reveal the intricate interplay between covalent and metallic bonding that governs their mechanical properties.

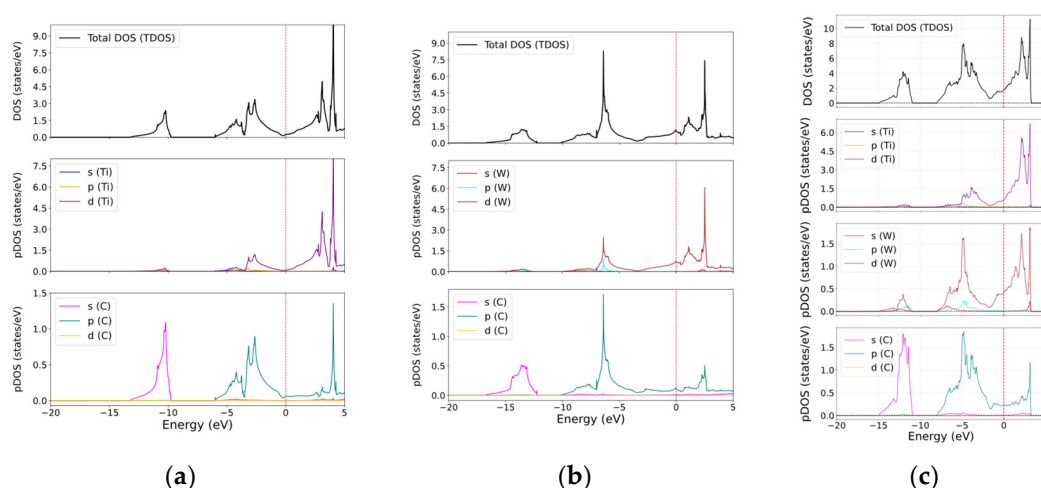


Figure 6. The TDOS and pDOS: (a) TiC; (b) WC; (c) $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster.

The DOS (Figure 6, a) of TiC is characterized by sharp peaks near the Fermi level, primarily dominated by the Ti-d and C-p orbitals. The strong hybridization between these states, observed in the energy range of -6 eV to 0 eV, highlights the robust covalent bonding between Ti and C atoms. This bonding results in high stiffness and significant hardness, as the electronic density is localized in bonding orbitals, resisting deformation. However, the dominance of covalent interactions limits plasticity, making TiC inherently brittle. The localized nature of the C-p states further enhances the bonding rigidity, contributing to TiC's resistance to compression and wear.

The electronic structure of WC reveals a broader distribution of states (Figure 6, b), with W-d orbitals prominently contributing across the energy spectrum, especially around the Fermi level. Unlike TiC, the metallic bonding nature of WC is evident from its delocalized electronic states, which allow for better ductility and toughness. The overlap between W-d and C-p orbitals spans -8 eV to 2 eV, indicating weaker covalent bonding compared to TiC. This results in lower hardness but greater toughness and thermal conductivity, making WC suitable for applications requiring resistance to mechanical and thermal fatigue.

The $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster, exhibits a unique DOS profile (Figure 6, c) that integrates features from both TiC and WC. Ti-d and W-d orbitals show significant hybridization, particularly near the Fermi level, which strengthens covalent bonding in the lattice. This hybridization reduces lattice strain and enhances hardness, exceeding that of WC while maintaining a degree of toughness not achievable in pure TiC. The broad DOS range (-8 eV to 2 eV) demonstrates contributions from both covalent and metallic bonding, offering a balanced mechanical properties. The C-p states, while retaining their localization, interact effectively with Ti and W d-states.

The trends observed in the DOS and pDOS directly correlate with the mechanical properties of these materials. TiC, with its pronounced covalent bonding, achieves superior hardness but at the cost of brittleness. WC, with its metallic bonding, offers exceptional toughness and ductility, making it ideal for dynamic environments. $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ bridges these extremes, delivering a synergistic combination of hardness and toughness. The hybridized bonding in the solid solution also improves thermal stability and electronic conductivity, making it a promising candidate for high-performance cutting tools and wear-resistant materials.

The Electron Localization Function (ELF) provides insight into the bonding nature and its implications for the mechanical properties of TiC, WC, and the $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster, as depicted in Figure 7. The ELF distributions highlight the interplay of covalent and metallic bonding, which defines the unique mechanical behavior of these materials.

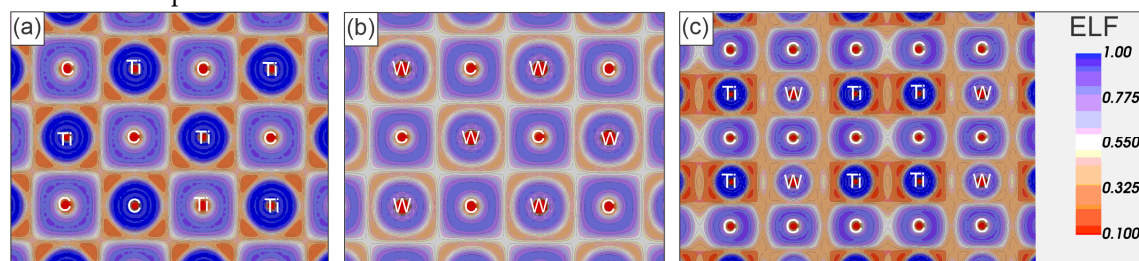


Figure 7. The ELF: (a) TiC; (b) WC; (c) $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster.

In TiC (Figure 7a), the ELF reveals a highly localized electron density between Ti and C atoms, with values nearing 1.0. This strong localization reflects the predominance of covalent bonding, which is responsible for TiC's high hardness as the rigid bonding network resists deformation. However, this strong covalent interaction also leads to inherent brittleness, as the lack of delocalized electrons reduces the material's ability to dissipate mechanical stresses. In contrast, the ELF for WC (Figure 7b) exhibits a more delocalized electron density, with values ranging from 0.550 to 0.775. This distribution indicates a shift toward metallic bonding, where electron delocalization enhances the material's ductility and toughness. The W-C bonds are less localized than Ti-C bonds, allowing WC to accommodate greater plastic deformation under mechanical load. This property, while improving toughness, reduces the hardness of WC compared to TiC, as the delocalized electrons are less effective in resisting localized deformation. The ELF for the cluster representing the solid solution $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ (Figure 7c) demonstrates a hybridized bonding nature, combining features of both TiC and WC. The Ti-C bonds exhibit significant electron localization, while the W-C bonds show delocalization similar to WC. This unique bonding arrangement optimally balances hardness and toughness, where the localized Ti-C bonds contribute to structural rigidity and the delocalized W-C bonds improve ductility. The resulting synergy can minimize lattice strain and enhance the mechanical versatility of $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$.

The deformation density plots for TiC, WC, and the $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster, shown in Figure 8, provide critical insights into the redistribution of electronic charge due to chemical bonding.

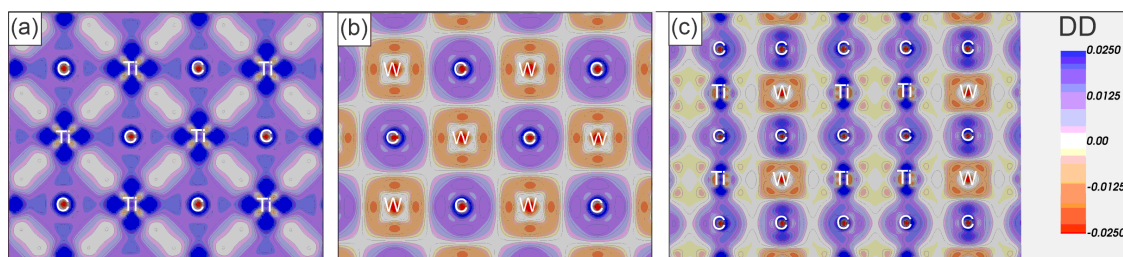


Figure 8. The deformation density: (a) TiC; (b) WC; (c) $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster.

In TiC (Figure 8a), the deformation density exhibits a highly concentrated redistribution of electronic charge between Ti and C atoms, with maximum deformation density values exceeding $0.70 \text{ e}/\text{\AA}^3$. This high charge localization indicates the dominance of covalent bonding, where electrons are strongly shared between Ti and C. The polarized charge around C atoms, directed toward Ti, strengthens the Ti-C bonds, resulting in high hardness ($\sim 24 \text{ GPa}$). However, this strong localization reduces the material's ability to deform plastically, contributing to its inherent brittleness. For WC (Figure 8b), the deformation density shows broader and less intense charge redistribution between W and C atoms, with peak values around $0.40\text{--}0.50 \text{ e}/\text{\AA}^3$. This reduced localization reflects a greater contribution of metallic bonding, where electrons are more delocalized. These characteristics are consistent with its lower hardness ($\sim 20 \text{ GPa}$) compared to TiC. In the $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster (Figure 8c), the deformation density map combines features of both TiC and WC. The Ti-C bonds exhibit localized charge redistribution, with deformation densities reaching $\sim 0.65 \text{ e}/\text{\AA}^3$, preserving the covalent bonding strength. Simultaneously, the W-C bonds display a more delocalized distribution with values around $0.45 \text{ e}/\text{\AA}^3$, introducing metallic bonding characteristics. This hybridized bonding nature balances the mechanical properties.

The Reduced Density Gradient (RDG) shown in Figure 9, provide insights into the nature of bonding and non-covalent interactions within these materials.

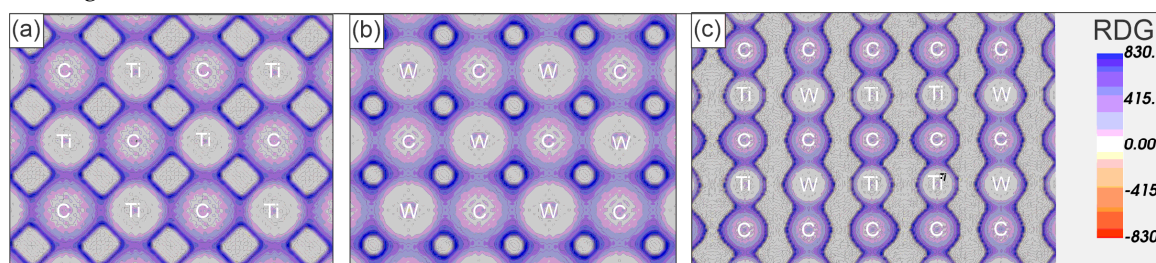


Figure 9. The deformation density: (a) TiC; (b) WC; (c) $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster.

For TiC (Figure 9a), the RDG values highlight strongly localized bonding regions between Ti and C atoms, characterized by low RDG values. These regions correspond to covalent interactions, as evidenced by high electron density and minimal density gradients. This localization results in a highly rigid bonding network, which contributes to TiC's structural hardness and resistance to deformation. However, the lack of significant non-bonding regions in the RDG profile correlates with TiC's limited ability to dissipate mechanical stress, making it brittle. In WC (Figure 9b), the RDG plot reveals broader and less localized bonding regions, with relatively high RDG values. These higher RDG values indicate a mixture of covalent and metallic bonding, where delocalized electrons contribute to WC's toughness and ductility. Additionally, the presence of moderate non-bonding interaction regions in the RDG map corresponds to the material's ability to absorb stress more effectively, even under dynamic conditions. This explains WC's reduced hardness compared to TiC but significantly improved fracture resistance.

For the $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ cluster (Figure 9c), the RDG plot combines features of both TiC and WC. The Ti-C bonds exhibit low RDG values, consistent with strong covalent bonding, while the W-C regions display slightly higher RDG values, indicative of delocalized metallic interactions.

Furthermore, the solid solution exhibits more prominent non-bonding interaction regions around W atoms, enhancing lattice flexibility and stress dissipation. This hybrid bonding nature minimizes lattice strain, balancing rigidity and ductility, and contributes to the material's mechanical versatility.

4. Conclusions

This study demonstrates the potential of (Ti,W)C solid solutions as advanced engineering materials with tailored properties for demanding applications. The computational investigation using Density Functional Theory (DFT) and Cluster Expansion (CE) has provided critical insights into the structural, mechanical, and electronic properties of these materials. The phase stability analysis revealed $\text{Ti}_{0.5}\text{W}_{0.5}\text{C}$ as the most stable composition, benefiting from the optimal interplay of Ti, W, and C atomic interactions. Mechanical evaluations showed that intermediate compositions like $\text{Ti}_{0.67}\text{W}_{0.33}\text{C}$ achieve superior hardness (~33 GPa) due to synergistic effects of covalent Ti-C and metallic W-C bonds, offering an optimal balance of rigidity and ductility. The electronic structure analysis highlighted the hybridized bonding characteristics that contribute to the enhanced mechanical resilience and thermal stability of these solid solutions. Additionally, the elastic and vibrational property trends revealed the influence of tungsten incorporation, which increased the bulk modulus and reduced thermal conductivity, allowing for the customization of properties. These findings provide a foundation for the development of high-performance materials for machining, wear-resistant coatings, and structural applications.

Author Contributions: Conceptualization, P.P., V.T., O.M. and V.O.; methodology, A.M., V.K. and I.S.; software, P.M.; validation, V.T., V.O. and A.M.; formal analysis, O.M., V.T. and V.O.; resources, V.T., V.O. and M.B.; data curation, P.M., M.B. and A.M.; writing—original draft preparation, P.M., O.M., V.O. and A.M.; writing—review and editing, V.T., V.O., M.B. and I.S.; visualization, P.M., O.M., A.M. and I.S.; supervision, V.T. and V.O.; project administration, P.M., O.M. and A.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially supported by the research project of the Ministry of Education and Science of Ukraine 0123U101858 “Development of materials for applying wear-and-impact-resistant coatings in the “high-manganese steel – refractory compounds” system by electric arc surfacing”.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

Acknowledgments: The authors are grateful to the: Ministry of Science and Education of Ukraine for the grant to implement projects 0121U109591 and 0122U002082.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jonsson, S. Assessment of the Ti-W-C System and Calculations in the Ti-W-C-N System. *International Journal of Materials Research* **1996**, *87*, 788–795, doi:10.1515/ijmr-1996-871009.
2. Sara, R.V. Phase Equilibria in the System Tungsten—Carbon. *Journal of the American Ceramic Society* **1965**, *48*, 251–257, doi:10.1111/j.1151-2916.1965.tb14731.x.
3. Park, S.; Jung, J.; Kang, S.; Jeong, B.W.; Lee, C.-K.; Ihm, J. The Carbon Nonstoichiometry and the Lattice Parameter of $(\text{Ti}_{1-x}\text{W}_x)\text{C}_{1-y}$. *Journal of the European Ceramic Society* **2010**, *30*, 1519–1526, doi:10.1016/j.jeurceramsoc.2009.10.022.
4. Mas-Guindal, M.J.; Contreras, L.; Turrillas, X.; Vaughan, G.B.M.; Kvick, Å.; Rodríguez, M.A. Self-Propagating High-Temperature Synthesis of TiC–WC Composite Materials. *Journal of Alloys and Compounds* **2006**, *419*, 227–233, doi:10.1016/j.jallcom.2005.08.079.
5. Lutsak, D.L.; Prysyazhnyuk, P.M.; Karpash, M.O.; Pylypiv, V.M.; Kotsyubynsky, V.O. Formation of Structure and Properties of Composite Coatings TiB₂-TiC-Steel Obtained by Overlapping of Electric-Arc

- Surfacing and Self-Propagating High-Temperature Synthesis. *Metallofizika i Noveishie Tekhnologii* **2016**, 38, 1265–1278, doi:10.15407/mfint.38.09.1265.
6. Yuan, Y.; Wu, H.; You, M.; Li, Z.; Zhang, Y. Improving Wear Resistance and Friction Stability of FeNi Matrix Coating by In-Situ Multi-Carbide WC-TiC via PTA Metallurgical Reaction. *Surface and Coatings Technology* **2019**, 378, 124957, doi:10.1016/j.surfcoat.2019.124957.
 7. Foong, L.K.; Jume, B.H.; Xu, C. Densification Behavior and Mechanical Properties of Hot-Pressed TiC–WC Ceramics. *Ceramics International* **2020**, 46, 28316–28323, doi:10.1016/j.ceramint.2020.07.335.
 8. Chen, K.; Bielawski, M. Ab Initio Study on Fracture Toughness of Ti_{0.75}X_{0.25}C Ceramics. *Journal of Materials Science* **2007**, 42, 9713–9716, doi:10.1007/s10853-007-1930-1.
 9. Zhao, X.; Zhuo, Y.; Liu, S.; Zhou, Y.; Zhao, C.; Wang, C.; Yang, Q. Investigation on WC/TiC Interface Relationship in Wear-Resistant Coating by First-Principles. *Surface and Coatings Technology* **2016**, 305, 200–207, doi:10.1016/j.surfcoat.2016.08.025.
 10. Song, G.-M.; Wang, Y.-J.; Zhou, Y. Thermomechanical Properties of TiC Particle-Reinforced Tungsten Composites for High Temperature Applications. *International Journal of Refractory Metals and Hard Materials* **2003**, 21, 1–12, doi:10.1016/s0263-4368(02)00105-1.
 11. Dang, D.Y.; Fan, J.L.; Gong, H.R. Thermodynamic and Mechanical Properties of TiC from Ab Initio Calculation. *Journal of Applied Physics* **2014**, 116, doi:10.1063/1.4890307.
 12. Filimonenko, V.; Pivovarov, L.K. Tungsten Carbide with an FCC Lattice. *Metal Science and Heat Treatment* **1968**, 10, 732–732.
 13. Cao, Z.; Jin, N.; Ye, J.; Zhuang, D.; Liu, Y. A First Principles Investigation on the Solid Solution Behavior of Transition Metal Elements (W, Mo, Ta, Cr) in Ti(C,N). *International Journal of Refractory Metals and Hard Materials* **2021**, 99, 105605, doi:10.1016/j.ijrmhm.2021.105605.
 14. Jang, J.H.; Lee, C.-H.; Heo, Y.-U.; Suh, D.-W. Stability of (Ti, M)C (M = Nb, V, Mo and W) Carbide in Steels Using First-Principles Calculations. *Acta Materialia* **2012**, 60, 208–217, doi:10.1016/j.actamat.2011.09.051.
 15. Connolly, J.W.D.; Williams, A.R. Density-Functional Theory Applied to Phase Transformations in Transition-Metal Alloys. *Phys. Rev. B* **1983**, 27, 5169–5172, doi:10.1103/PhysRevB.27.5169.
 16. Kohn, W.; Sham, L.J. Self-Consistent Equations Including Exchange and Correlation Effects. *Physical review* **1965**, 140, A1133–A1138.
 17. Prysyazhnyuk, P.; Shlapak, L.; Semyanyk, I.; Kotsyubynsky, V.; Troshchuk, L.; Korniy, S.; Artym, V. Analysis of the Effects of Alloying with Si and Cr on the Properties of Manganese Austenite Based on AB INITIO Modelling. *Eastern-European Journal of Enterprise Technologies* **2020**, 6, 28–36, doi:10.15587/1729-4061.2020.217281.
 18. Hafner, J.; Kresse, G. The Vienna AB-Initio Simulation Program VASP: An Efficient and Versatile Tool for Studying the Structural, Dynamic, and Electronic Properties of Materials. In *Properties of Complex Inorganic Solids*; Springer US, 1997; pp. 69–82.
 19. Furness, J.W.; Kaplan, A.D.; Ning, J.; Perdew, J.P.; Sun, J. Accurate and Numerically Efficient r2SCAN Meta-Generalized Gradient Approximation. *The journal of physical chemistry letters* **2020**, 11, 8208–8215.
 20. Walle, A. van de; Asta, M.D.; Ceder, G. The Alloy Theoretic Automated Toolkit: A User Guide. *Calphad* **2002**, 26, 539–553, doi:10.1016/S0364-5916(02)80006-2.
 21. Walle, A. van de; Tiwary, P.; Jong, M. de; Olmsted, D.L.; Asta, M.; Dick, A.; Shin, D.; Wang, Y.; Chen, L.-Q.; Liu, Z.-K. Efficient Stochastic Generation of Special Quasirandom Structures. *Calphad* **2013**, 42, 13–18, doi:10.1016/j.calphad.2013.06.006.
 22. Savin, A.; Nesper, R.; Wengert, S.; Fässler, T.F. ELF: The Electron Localization Function. *Angewandte Chemie International Edition in English* **1997**, 36, 1808–1832, doi:https://doi.org/10.1002/anie.199718081.
 23. Prandini, G.; Marrazzo, A.; Castelli, I.E.; Mounet, N.; Marzari, N. Precision and Efficiency in Solid-State Pseudopotential Calculations. *npj Computational Materials* **2018**, 4, doi:10.1038/s41524-018-0127-2.
 24. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G.L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *Journal of physics: Condensed matter* **2009**, 21, 395502.
 25. Hill, R. The Elastic Behaviour of a Crystalline Aggregate. *Proceedings of the Physical Society A* **1952**, 65, 349–354, doi:10.1088/0370-1298/65/5/307.

26. Chen, X.-Q.; Niu, H.; Li, D.; Li, Y. Modeling Hardness of Polycrystalline Materials and Bulk Metallic Glasses. *Intermetallics* **2011**, *19*, 1275–1281, doi:https://doi.org/10.1016/j.intermet.2011.03.026.
27. Tian, Y.; Xu, B.; Zhao, Z. Microscopic Theory of Hardness and Design of Novel Superhard Crystals. *International Journal of Refractory Metals and Hard Materials* **2012**, *33*, 93–106, doi:https://doi.org/10.1016/j.ijrmhm.2012.02.021.
28. Teter, D.M. Computational Alchemy: The Search for New Superhard Materials. *MRS bulletin* **1998**, *23*, 22–27.
29. Mazhnik, E.; Oganov, A.R. A Model of Hardness and Fracture Toughness of Solids. *Journal of Applied Physics* **2019**, *126*, 125109, doi:10.1063/1.5113622.
30. Miao, N.; Sa, B.; Zhou, J.; Sun, Z. Theoretical Investigation on the Transition-Metal Borides with Ta₃B₄-Type Structure: A Class of Hard and Refractory Materials. *Computational Materials Science* **2011**, *50*, 1559–1566, doi:https://doi.org/10.1016/j.commatsci.2010.12.015.
31. Prysyazhnyuk, P.; Di Tommaso, D. The Thermodynamic and Mechanical Properties of Earth-Abundant Metal Ternary Borides Mo₂ (Fe, Mn) B₂ Solid Solutions for Impact-and Wear-Resistant Alloys. *Materials Advances* **2023**, *4*, 3822–3838.
32. Wang, V.; Xu, N.; Liu, J.-C.; Tang, G.; Geng, W.-T. VASPKIT: A User-Friendly Interface Facilitating High-Throughput Computing and Analysis Using VASP Code. *Computer Physics Communications* **2021**, *267*, 108033, doi:https://doi.org/10.1016/j.cpc.2021.108033.
33. Ivashchenko, V.I.; Čaplovič, L.; Shevchenko, V.I.; Gorb, L.; Leszczynski, J. Stability and Mechanical, Thermodynamic and Optical Properties of WC Polytypes and the TiC-WC Solid Solutions: A First-Principles Study. *Journal of Physics and Chemistry of Solids* **2023**, *183*, 111652, doi:10.1016/j.jpcs.2023.111652.
34. Nino, A.; Izu, Y.; Sekine, T.; Sugiyama, S.; Taimatsu, H. Effects of TaC and TiC Addition on the Microstructures and Mechanical Properties of Binderless WC. *International Journal of Refractory Metals and Hard Materials* **2019**, *82*, 167–173, doi:10.1016/j.ijrmhm.2019.04.012.
35. Miyoshi, A.; Hara, A. High Temperature Hardness of WC, TiC, TaC, NbC and Their Mixed Carbides. *Journal of the Japan Society of Powder and Powder Metallurgy* **1965**, *12*, 78–84, doi:10.2497/jjspm.12.78.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.