Engineering Journal of Satbayev University
Volume 147 (2025), Issue 4, 1-8

https://doi.org/10.51301/ejsu.2025.i4.01

Thermodynamic calculations and construction of Ellingham and phase stability diagrams for the W-Ti-C-Co system

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Abstract. This study provides a thermodynamic analysis of phase equilibria and compound stability in the W–Ti–C–Co system using ab initio modeling, the Materials Project database, and HSC Chemistry 6. The focus is on identifying stable and metastable phases relevant to composite materials based on refractory metals and carbon with cobalt and titanium as alloying elements. Calculations yielded a list of characteristic phases, quaternary and ternary phase diagrams (Ti–W–C, Co–Ti–C, Co–W–C), Ellingham-type stability diagrams, and interfacial reaction maps. Mechanical properties were assessed via bulk and shear moduli, showing WC as the hardest and TiCo as the most ductile phase. The study predicts the likely formation of ternary carbides (W–Co, W–Ti), which strongly influence material properties. Fourteen interfacial reactions were identified, including carbide and intermetallic formation. Ellingham analysis showed Co_2C is unstable above ~400°C, and Co_7W_6 is unfavorable at all temperatures, while WC remains stable up to ~1400°C, beyond which W2C dominates. These results deepen the understanding of phase behavior in multicomponent metal – carbon systems and support the development of thermally stable, mechanically optimized materials.

Keywords: *thermodynamic modeling, phase diagram, Ellingham diagram, refractory materials, phase stability, bulk modulus, shear modulus.*

Received: 06 May 2025
Accepted: 15 August 2025
Available online: 31 August 2025

1. Introduction

In the context of increasing operational demands on cutting and forming tools, there is a growing need to develop new types of hard alloys with enhanced strength, thermal stability, and wear resistance [1, 2]. Among these, particular attention is given to dual-carbide cemented carbides based on the W–C–TiC–Co system, which are distinguished by their combination of high hardness and thermochemical stability [3]. However, the development of new compositions requires a deep understanding of phase equilibria and interfacial interactions in multicomponent systems, including rare and metastable compounds.

Of special interest is thermodynamic modeling and the construction of phase stability diagrams (Ellingham diagrams) and phase dominance maps for systems involving transition metals and carbon. The application of density functional theory (DFT) methods allows for a quantitative assessment of formation energies and the construction of highly accurate phase diagrams. These approaches have been successfully implemented in systems analogous to W–Ti–C–Co [4, 5], while the Materials Project database [6] offers a comprehensive platform for automated access to thermodynamic and structural properties of compounds based on ab initio calculations.

Previous studies have shown that W–Ti systems exhibit pronounced asymmetry in mixing energies and limited mutual solubility, particularly in the BCC lattice structure [7]. These features significantly affect phase stability and the formation of intermetallic compounds. At the same time, experimental investigations into Co–Ti and Co–W interactions have enabled the construction of isothermal sections and the identification of stable phases at temperatures ranging from 1273 to 1473 K [8].

In the W–C–Ti–Co system, carbide phases such as WC, TiC, and complex carbides of the (Ti,W)C type play a key role. These compounds are characterized by high cohesive energy, low self-diffusion coefficients, and increased metastability, making them especially relevant for high-temperature applications [9]. Furthermore, the stability of phase boundaries critically determines the reliability and service life of cemented carbides. To analyze interfacial interactions, phase reaction and phase dominance diagrams are constructed using computational tools based on the Materials API [6, 10].

The objective of this study is to construct phase diagrams and evaluate the thermodynamic stability of phases in the W–C–Ti–Co system using quantum mechanical modeling, machine learning, and statistical analysis.

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Engineering Journal of Satbayev University. eISSN 2959-2348. Published by Satbayev University

2. Materials and methods

To construct the phase diagram and analyze phase equilibria in the quaternary W–C–Ti–Co system, a comprehensive approach based on ab initio modeling within the framework of density functional theory (DFT) was employed. The primary source of input data was the Materials Project database [10, 11, 5], which contains structural and energetic characteristics for over 100,000 inorganic compounds obtained through standardized DFT calculations.

To improve the accuracy of the electronic state descriptions for the transition metals W, Ti, and Co, formation enthalpy calculations were carried out using a hybrid GGA/GGA+U scheme. The use of GGA+U potentials allowed for correction of d-electron delocalization and ensured a more reliable assessment of compound stability [1]. The U parameters were selected in accordance with semi-empirically calibrated values provided by the Materials Project [10].

Phase diagrams were generated using the PDApp software, a component of the Materials API–a REST-based interface providing access to data on energies, compositions, and crystal structures [2, 7]. The calculations were based on the convex hull method, which made it possible to identify thermodynamically stable and metastable phases at a given temperature. Structural data were primarily sourced from the ICSD database, which contains experimentally validated lattice parameters, symmetries, and atomic coordinates [13].

To predict not-yet-discovered but potentially stable compounds, the modeling incorporated a machine learning–based approach [4]. This method combined data from known phases with DFT results, allowing for an expanded exploration of the phase space in the W–C–Ti–Co system. Probabilistic models were used to evaluate the stability of hypothetical compounds, enabling the prediction of possible stable phases not represented in experimental databases.

The morphology of interfacial boundaries and the evolution of phases under non-equilibrium conditions were studied using phase-field modeling [14], which accounted for kinetic aspects of phase transformations at high temperatures. This was especially relevant for assessing the stability of carbides, known for their high cohesive energy and metastability. According to [9], at 0 K, the median metastability of carbides reaches 144 meV/atom, compared to only about 20 meV/atom for most other compounds.

The methodology applied in this work provides high accuracy in constructing phase stability diagrams, identifying stable phases, and analyzing the behavior of the W–C–Ti–Co system under conditions that closely resemble those of real-world hard alloy synthesis.

3. Results and discussion

3.1. Thermodynamic modeling of phase equilibria and construction of the phase diagram for the W–C–Ti–Co system

The phase diagram of the quaternary W–C–Ti–Co system was constructed based on data obtained using the PDApp software and the Materials Project database. The analysis focused on thermodynamic stability, metastability, and potential decomposition pathways of compounds, carried out through the construction of phase stability diagrams and convex hull projections in composition space.

The resulting phase diagram reflects the thermodynamic stability of compounds in the W–C–Ti–Co system at temperatures up to 1000 K (Figure 1). The diagram's nodes are color-coded according to stability: green indicates thermodynamically stable phases, while yellow and red denote metastable compounds, whose degree of instability is defined by their positive energy deviation from the convex hull surface. The color of the rhombus overlaid on each node represents the magnitude of this deviation, ranging from moderate (yellow) to high (red) metastability.

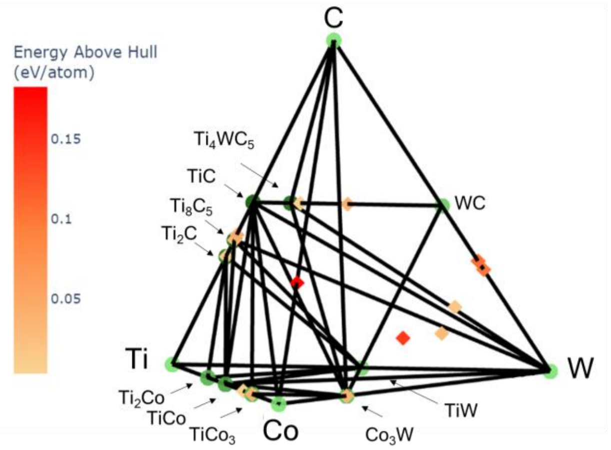

Figure 1. Phase diagram of the W–Ti–C–Co system

The black lines connecting the nodes represent projections of the Maxwell convex hull onto the compositional space. These connections form what are known as Gibbs triangles, with each vertex corresponding to a stable phase. Any point within such a triangle can be described as a mixture of the three phases located at its vertices. The phase composition and ratios of this mixture are determined by the lever rule, applied here in a higher-dimensional compositional space.

Special attention is given to green nodes overlaid with colored rhombuses, which indicate the presence of metastable «satellite» phases that share similar chemical compositions with certain «primary» stable compounds but differ in crystal structure. Examples of such systems include Co_3W, Ti_2C, Ti_8C_5, and $TiCo_3$. The existence of competing structural modifications can have important implications for synthesis conditions and the thermal history of the material.

To assess the potential mechanical properties of the compounds shown in the diagram, Table 1 presents their formation and decomposition energies, shear modulus, bulk modulus, and Pugh's ratio (G/B) [3]. Pugh's ratio serves as an indicator of a material's tendency toward plastic or brittle behavior: values below 0.5 suggest ductility, while values above this threshold indicate brittleness. The elastic modulus values were derived using machine learning algorithms trained on large DFT-based datasets [15].

The TiCo phase exhibits the lowest Pugh's ratio (G/B) among all compounds considered in the W–Ti–C–Co system, indicating its highest propensity for plastic deformation. In contrast, the WC phase displays the highest elastic moduli, reflecting its exceptional stiffness and potential brittleness under mechanical loading. Below are the crystal structures and brief descriptions of the equilibrium and metastable phases identified through the modeling of the system.

Table 1. Stable and metastable phases in the W–Ti–C–Co system

Stable Phases					
Phase		Formation energy, eV/atom	Shear modulus G, GPa	Bulk modulus B, GPa	Pugh's ratio (G/B)
Co_3W		- 0.084	140	179	0.782
Ti_2C		- 0.644	78	139	0.561
Ti_2Co		- 0.285	74	154	0.481
Ti_8C_5		- 0.719	115	170	0.676
TiC		- 0.81	176	253	0.696
TiCo		- 0.401	61	163	0.374
$TiCo_3$		- 0.262	83	194	0.428
TiW		- 0.02	94	206	0.456
WC		- 0.123	279	385	0.725
Co_2W_4C		- 0.067	130	320	0.406
Metastable Phases					
Phase	Decomposition energy, eV/atom	Decomposes into	Shear modulus G, GPa	Bulk modulus B, GPa	Pugh's ratio (G/B)
Co_2C	0.108	C + Co	110	257	0.428
Co_3W_3C	0.089	Co_3W + WC + W	129	308	0.419
$Co_6W_{20}C_7$	0.018	Co_3W + WC + W	141	330	0.427
Ti_3C_2	0.05	Ti_8C_5 + TiC	130	194	0.670
Ti_3WC_4	0.025	WC + TiC	184	280	0.657
Ti_4WC_5	0.019	WC + TiC	183	274	0.668
$TiCo_2$	0.006	$TiCo_3$ + TiCo	90	204	0.441
$TiWC_2$	0.07	WC + TiC	187	304	0.615
W_2C	0.065	WC + W	167	334	0.500
W_9C_4	0.072	WC + W	149	337	0.442

Cobalt carbide Co_2C

The compound Co_2C crystallizes in the orthorhombic crystal system, space group Pnnm, and adopts a hydrophilite-type structure (Figure 2).

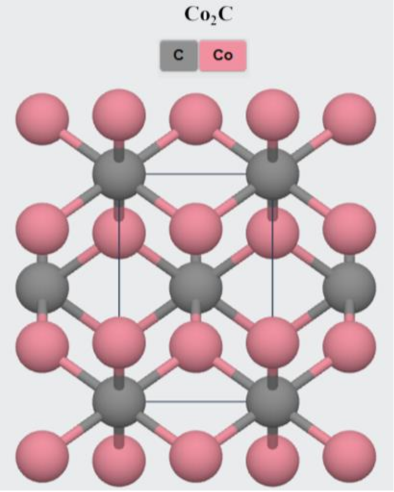

Figure 2. Crystal structure of the Co_2C phase

Its crystal structure is three-dimensional. Co^{2+} ions are in a trigonal planar coordination with three equivalent C^{4-} atoms; all Co–C bond lengths are 1.90 Å. Each carbon atom (C^{4-}) is surrounded by six equivalent Co^{2+} atoms, forming CCo_6 coordination octahedra that share edges and corners. The octahedral tilt angles are approximately 52°, indicating a distortion from ideal geometry and reflecting specific bonding features within this phase.

Titanium-cobalt intermetallics

The Ti_2Co phase crystallizes in the cubic space group Fd-3m and features a three-dimensional crystal structure (Figure 3).

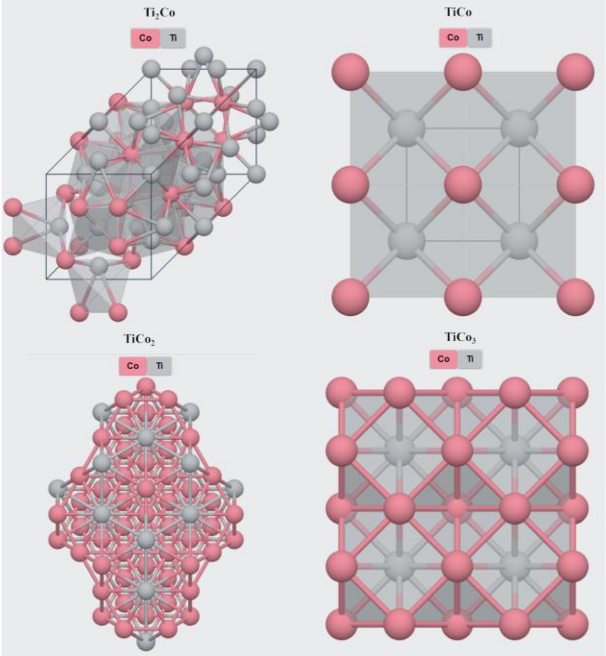

Figure 3. Crystal structures of titanium–cobalt intermetallics: Ti_2Co, TiCo, $TiCo_2$, $TiCo_3$

Two crystallographically distinct Ti positions are present. In the first site, the Ti atom is in a 12-fold coordination with six equivalent Co atoms; all Ti–Co bond lengths are 2.49 Å. In the second site, the Ti atom displays a distorted fourfold coordination with Co, comprising two shorter Ti–Co bonds at 2.53 Å and two longer ones at 2.87 Å. Co atoms are situated in a 9-fold coordination environment, each surrounded by nine Ti atoms.

The TiCo compound adopts the tetraauricupride-type structure and crystallizes in the cubic space group Pm-3m. The crystal structure is three-dimensional. Ti atoms occupy body-centered cubic positions and are coordinated by eight equivalent Co atoms, with uniform Ti–Co bond lengths of 2.58 Å. Likewise, Co atoms are in a body-centered cubic coordination, each surrounded by eight equivalent Ti atoms.

The $TiCo_2$ phase crystallizes in the hexagonal space group $P6_3/mmc$ and adopts a hexagonal Laves-type structure. The structure is three-dimensional and includes five crystallographically distinct titanium atomic sites. At each site, a titanium atom is coordinated in a 12-fold geometry with four titanium atoms and twelve cobalt atoms. In the first site, there is one shorter Ti–Ti bond (2.83 Å) and three longer ones (2.89 Å). The Ti–Co bond lengths range from 2.75 to 2.77 Å. In the second site, the bonding pattern is similar, with one shorter (2.83 Å) and three longer (2.89 Å) Ti–Ti bonds, and Ti–Co bond distances also ranging from 2.75 to 2.77 Å. At the third site, all Ti–Ti bond lengths are 2.89 Å, with Ti–Co distances again falling within 2.75–2.77 Å. In the fourth and fifth sites, all Ti–Ti bonds measure 2.89 Å. The Ti–Co bonds consist of six shorter (2.75 Å) and six longer (2.76 Å) distances.

Cobalt atoms occupy three crystallographically distinct sites. In the first and second sites, each cobalt atom is surrounded by six titanium and six cobalt atoms, forming mixed $CoTi_6Co_6$ cuboctahedra sharing faces, edges, and vertices. In the first cobalt site, there are three shorter (2.36 Å) and three longer (2.37 Å) Co–Co bonds; in the second site, all Co–Co bonds are 2.35 Å. In the third site, the local structure is similar, though the Co–Co bonds include two shorter (2.29 Å) and two longer (2.41 Å) distances, indicating some anisotropy in the coordination environment.

The compound Co_3Ti adopts the uranium silicide structure type and crystallizes in the cubic space group Pm–3m. The structure features a three-dimensional coordination network. Titanium atoms are coordinated by twelve equivalent cobalt atoms, forming $TiCo_{12}$ cuboctahedra. These polyhedra are interconnected: they share vertices with twelve equivalent $TiCo_{12}$ units, edges with twenty-four equivalent $CoTi_4Co_8$ cuboctahedra, and faces with six $TiCo_{12}$ and twelve $CoTi_4Co_8$ units. All Ti–Co bond lengths are 2.55 Å.

Cobalt atoms, in turn, are coordinated by four equivalent titanium atoms and eight cobalt atoms, forming $CoTi_4Co_8$ cuboctahedra. These structures share vertices with twelve similar $CoTi_4Co_8$ units, edges with eight $TiCo_{12}$ and sixteen $CoTi_4Co_8$ units, and faces with twelve $TiCo_{12}$ and four $CoTi_4Co_8$ cuboctahedra. All Co–Co bond distances are also 2.55 Å.

Ternary tungsten–titanium carbides

Ti_4WC_5 adopts the caswellsilverite-type structure ($NaCrS_2$) and crystallizes in the trigonal space group R–3m (Figure 4).

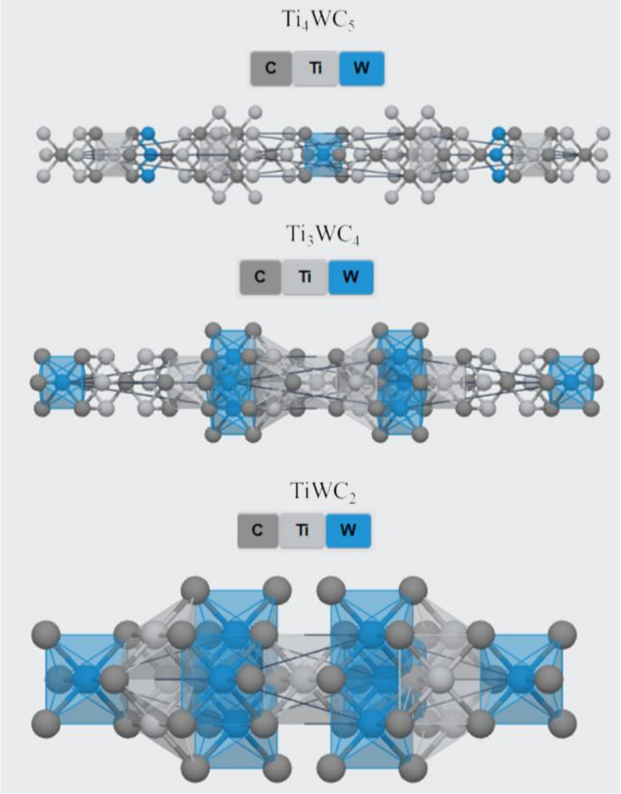

Figure 4. Crystal structures of ternary tungsten–titanium carbides: Ti_4WC_5, Ti_3WC_4, $TiWC_2$

The structure is three-dimensional and features two crystallographically distinct Ti^{4+} sites. In the first site, the Ti^{4+} ion is coordinated by six C^{4-} atoms, forming TiC_6 octahedra. These octahedra are corner-sharing with three equivalent TiC_6 octahedra and three WC_6 octahedra, and edge-sharing with three WC_6 and nine other TiC_6 octahedra. The tilt angles between corner-sharing octahedra range from 0° to 1°. Ti–C bond lengths vary slightly, with three shorter bonds at 2.16 Å and three longer ones at 2.18 Å.

In the second Ti^{4+} site, the ion is also surrounded by six C^{4-} atoms, forming TiC_6 octahedra that are connected via both corner- and edge-sharing. The tilt angles between adjacent octahedra also fall within the 0 e-1° range, and Ti–C bond lengths measure 2.17 Å and 2.18 Å. The W^{4+} ion is coordinated by six equivalent C^{4-} atoms to form regular WC_6 octahedra. These octahedra share corners with six TiC_6 octahedra and edges with six TiC_6 and six WC_6 octahedra. The tilt angles are 0°, and all W–C bond lengths are 2.17 Å.

There are three crystallographically distinct C^{4-} sites. In the first site, the C^{4-} atom is bonded to six Ti^{4+} ions, forming CTi_6 octahedra that share edges and corners. Tilt angles range from 0° to 1°. In the second site, the C^{4-} atom is also coordinated by six equivalent Ti^{4+} ions, forming a similar environment with no observable tilt (0°). In the third site, the C^{4-} ion is coordinated by three Ti^{4+} and three W^{4+} ions, forming CTi_3W_3 octahedra that share both edges and corners, with tilt angles also in the range of 0° to 1°.

$WTiC_2$ also crystallizes in the caswellsilverite-type structure (R–3m) and exhibits a three-dimensional framework. The Ti^{4+} ion is coordinated by six equivalent C^{4-} atoms, forming TiC_6 octahedra. These polyhedra share corners with six WC_6 octahedra and edges with six TiC_6 and six WC_6 octahedra. The tilt angles are 0°, and Ti–C bond lengths are 2.17 Å. The W^{4+} ion is likewise coordinated by six equivalent C^{4-} atoms in WC_6 octahedra. These are corner-sharing with six TiC_6 octahedra and edge-sharing with six TiC_6 and six WC_6 octahedra. The octahedra are nearly ideal, with 0° tilt angles and W–C bond lengths of 2.18 Å. Each C^{4-} ion is bonded to three equivalent Ti^{4+} and three equivalent W^{4+} ions, forming mixed CTi_3W_3 octahedra that are interconnected via shared edges and corners. The tilt angles are 0°, indicating high symmetry and a highly regular crystal structure.

3.2. Calculation of stability and phase dominance diagrams in the W–Ti–C–Co system

To analyze phase interactions at the interface between primary and secondary phases, interfacial reaction diagrams were constructed using the Interface Reaction App software.

Figure 5 shows the interaction diagram between the WC and Co phases. Only a single reaction (Reaction 1) is possible between them. The interaction between tungsten carbide and cobalt can lead to the formation of the intermetallic compound Co_3W and elemental carbon.

$$0.75Co+0.25WC \rightarrow 0.25Co_3W+0.25C \quad (E= -2.222\ kJ/mol). \quad (1)$$

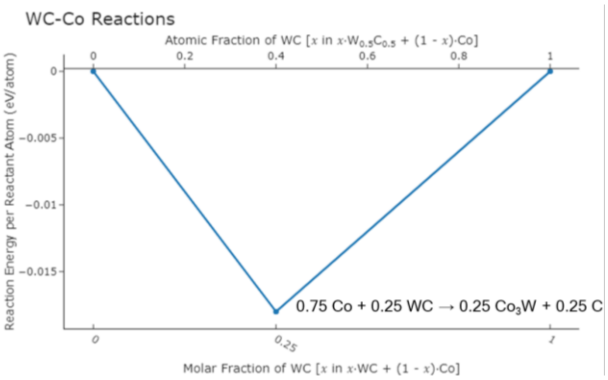

Figure 5. Interfacial reaction diagram between WC and Co phases

Figure 6 presents the interaction diagram between the WC and Ti phases. Four possible reactions (Reactions 2-5) can occur between them. The interaction of tungsten carbide with titanium may lead to the formation of the intermetallic compound TiW, titanium carbides Ti_2C, Ti_8C_5, and TiC, as well as elemental tungsten.

$0.75Ti+0.25WC \rightarrow 0.25TiW+0.25Ti_2C$ (E = -41.64 kJ/mol); (2)

$0.667Ti+0.333WC \rightarrow 0.333Ti_2C+0.333W$ (E = -54.23 kJ/mol); (3)

$0.615Ti+0.385WC \rightarrow 0.077Ti_8C_5+0.385W$ (E = -60.28 kJ/mol); (4)

$0.5Ti+0.5WC \rightarrow 0.5W+0.5TiC$ (E = -66.32 kJ/mol). (5)

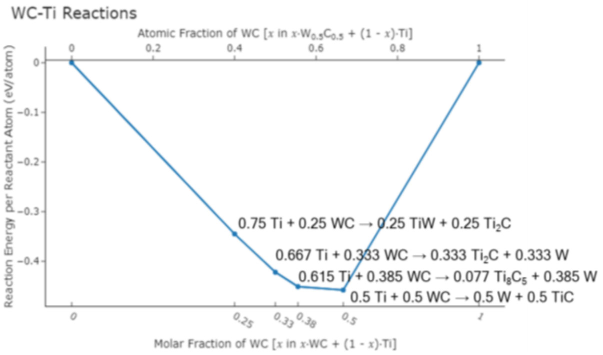

Figure 6. Interfacial reaction diagram between WC and Ti phases

Figure 7 presents the interaction diagram between the Co_3W and Ti phases. Four possible reactions (Reactions 6-9) can occur between them. The interaction between the intermetallic compound Co_3W and titanium may lead to the formation of intermetallics $TiCo_3$, Ti_2Co, TiCo, TiW, as well as elemental tungsten.

$0.125Co_3W+0.875Ti \rightarrow 0.375Ti_2Co+0.125TiW$ (E = -27.34 kJ/mol); (6)

$0.143Co_3W+0.857Ti \rightarrow 0.429Ti_2Co+0.143W$ (E = -30.69 kJ/mol); (7)

$0.25Co_3W+0.75Ti \rightarrow 0.75TiCo+0.25W$ (E = - 49.83 kJ/mol); (8)

$0.5Co_3W+0.5Ti \rightarrow 0.5TiCo_3+0.5W$ (E = -34.22 kJ/mol). (9)

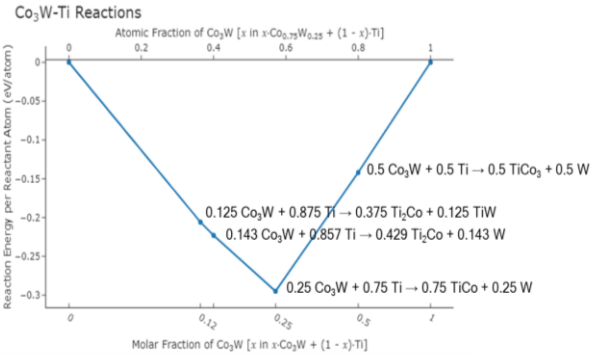

Figure 7. Interfacial reaction diagram between Co_3W and Ti phases

$0.9Co+0.1Ti_8C_5 \rightarrow 0.3TiCo_3+0.5TiC$ (E = -18.26 kJ/mol); (10)

$0.75Co+0.25Ti_8C_5 \rightarrow 0.75TiCo+1.25TiC$ (E= -27.86 kJ/mol). (11)

Figure 8 presents the interaction diagram between the Ti_8C_5 and Co phases. Two possible reactions (Reactions 10–11) can occur between them.

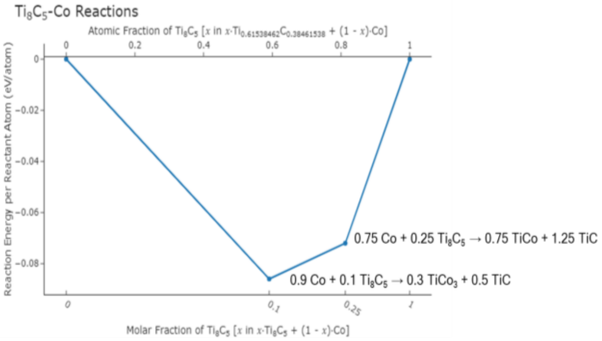

Figure 8. Interfacial reaction diagram between Ti_8C_5 and Co phases

The interaction of Ti_8C_5 carbide with cobalt may lead to the formation of the intermetallic compounds $TiCo_3$ and TiCo, as well as TiC carbide.

$0.9Co+0.1Ti_8C_5 \rightarrow 0.3TiCo_3+0.5TiC$ (E = -18.26 kJ/mol); (10)

$0.75Co+0.25Ti_8C_5 \rightarrow 0.75TiCo+1.25TiC$ (E = -27.86 kJ/mol). (11)

Analysis of the interfacial reaction diagrams indicates that a variety of chemical transformations are possible within the W–Ti–C–Co system, resulting in the formation of intermetallic compounds and carbides. The most energetically favorable reactions occur between WC and Ti (particularly those forming TiC and W), as well as between Co_3W and Ti.

Figure 9 shows the phase stability diagram (Ellingham diagram) for the W–Ti–Co–C system, constructed using the HSC Chemistry 6 software package. The diagram illustrates the change in Gibbs free energy (ΔG) of formation for various compounds as a function of temperature. It should be noted that the diagram includes only those phases for which data are available in the HSC Chemistry 6 database. Specifically, information is lacking on Ti–W and Ti–Co intermetallics, as well as on lower titanium carbides and ternary carbides based on tungsten and cobalt.

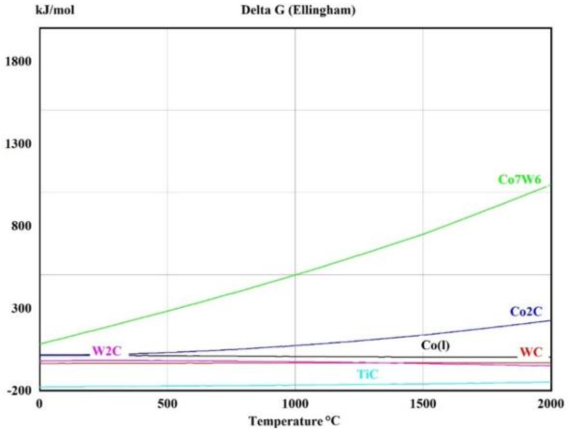

Figure 9. Ellingham-type phase stability diagram for the W–Ti–Co–C system

Based on the phase stability diagram, it can be concluded that Co_2C is thermally unstable at temperatures above approximately 400°C, which limits its applicability in high-temperature processes. Metallic cobalt (Co^0) retains moderate stability but does not form stable carbides at elevated temperatures. Tungsten carbide (WC) remains stable up to ~1400°C; above this temperature, the more stable subcarbide W_2C becomes dominant. The compound Co_7W_6 is thermodynamically unstable across the entire temperature range ($\Delta G > 0$).

The phase dominance diagrams shown in Figure 10 were constructed using the HSC Chemistry 6 software package.

(a)

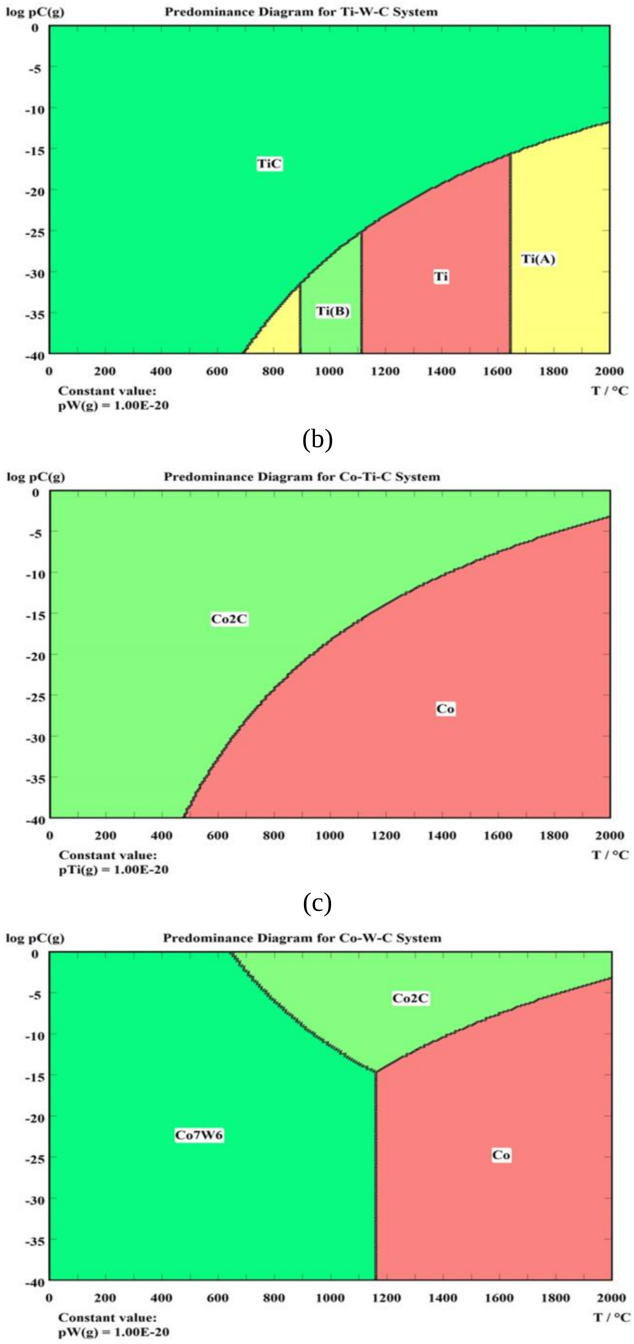

Figure 10. Phase dominance diagrams for ternary systems: (a) – Ti–W–C, (b) – Co–Ti–C, (c) – Co–W–C

These diagrams reflect the thermodynamically most stable phases in the corresponding ternary systems at a given temperature and the partial pressure of one component, assuming the vapor pressure of the second component remains constant. The diagrams were constructed for the Ti–W–C (Figure 10a), Co–Ti–C (Figure 10b), and Co–W–C (Figure 10c) systems. The obtained data enable assessment of the phase stability under conditions approximating real-world processes and contribute to a deeper understanding of phase transformations in multiphase metal – carbon systems.

4. Conclusions

As a result of the conducted research using thermodynamic modeling and the Materials Project ab initio database, a comprehensive analysis of phase equilibria and compound stability in the multiphase W–Ti–C–Co system has been carried out. Based on the calculations, a list of stable and metastable phases characteristic of the system was compiled, and a corresponding quaternary phase diagram was constructed. For each identified phase, bulk and shear moduli were calculated, enabling a comparative analysis of their mechanical properties. It was established that tungsten carbide (WC) is the hardest compound in the system, while the intermetallic TiCo exhibits the highest ductility.

The analysis confirmed the possibility of forming several stable ternary carbide phases, particularly tungsten–cobalt and tungsten–titanium compounds, both in stable and metastable forms. The constructed Ellingham phase stability diagrams, interfacial reaction diagrams, and phase dominance diagrams for the ternary subsystems Ti–W–C, Co–Ti–C, and Co–W–C demonstrated the thermodynamic feasibility of new phase formation at interfaces between components. Fourteen potential reactions were identified, indicating the potential for a wide range of intermetallic and carbide compounds to form as a result of interactions between primary and secondary phases.

Thus, the obtained results not only expand current understanding of phase transformations in refractory metal – carbon systems, but also provide a foundation for the targeted selection of composite materials with tailored mechanical properties, as well as for optimizing synthesis and heat treatment parameters.

Author contributions

Conceptualization: AMA, BTS, NMS; Data curation: AMA, BTS, AAM; Formal analysis: GKM, SAV; Funding acquisition: AZT, GMK; Investigation: AMA, BTS, AAM; Methodology: AMA, SAV, NMS; Project administration: AZT; Resources: AMA, GMK, NMS, GKM; Software: AMA, BTS, AAM; Supervision: AMA, AZT; Validation: SAV, AAM; Visualization: BTS, GKM; Writing – original draft: AMA, BTS, AAM; Writing – review & editing: AMA, BTS, SAV, GMK. All authors have read and agreed to the published version of the manuscript.

Funding

This research received no external funding.

Acknowledgements

The authors express their sincere gratitude to the editor and anonymous reviewers for their constructive comments and valuable suggestions, which have significantly improved the quality of this manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

References

[1] Fal'kovskii, V.A., & Kliachko, LI. (2005). Hard alloys. *Moscow: Ruda i metally*

[2] Andrievskii, R.A., & Ragulia, A.V. (2005). Nanostructured materials. *Moscow: Akademiia*

[3] Pugh, S.F. (1954). XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 45(367), 823-843.* https://doi.org/10.1080/14786440808520496

[4] Hautier, G., Fischer, C.C., Jain, A., Mueller, T. & Ceder, G. (2010). Finding nature's missing ternary oxide compounds using machine learning and density functional theory. *Chemistry of Materials, 22(12), 3762-3767.* https://doi.org/10.1021/cm100795d

[5] Ong, S.P., Jain, A., Hautier, G., Kang, B. & Ceder, G. (2010). Thermal stabilities of delithiated olivine MPO4 (M = Fe, Mn) cathodes investigated using first principles calculations. *Electrochemistry Communications, 12(3), 427-430.* https://doi.org/10.1016/j.elecom.2010.01.010

[6] Ong, S.P., Cholia, S., Jain, A., Brafman, M., Gunter, D., Ceder, G. & Persson, K.A. (2015). The Materials Application Programming Interface (API): A simple, flexible and efficient API for materials data based on Representational State Transfer (REST) principles. *Computational Materials Science, 97, 209-215.* https://doi.org/10.1016/j.commatsci.2014.10.037

[7] Ångqvist, M.A., Rahm, J.M., Gharaee, L., &Erhart, P. (2019). Phase diagram of the Ti–W system from first-principles. *arXiv preprint. arXiv:1904.04814.* https://arxiv.org/abs/1904.04814

[8] Shi, Y., Guo, C., Li, C., Du, Z., & Hu, D. (2022). Experimental investigation of isothermal sections in the Co–Ti–W system. *Frontiers in Materials, (9), 880143.* https://doi.org/10.3389/fmats.2022.880143

[9] Bartel, C.J., Millican, S.L., Deml, A.M., Rumptz, J. R., Tumas, W., Weimer, A.W., & Holder, A.M (2018). Physical descriptor for the Gibbs energy of inorganic crystalline solids and temperature-dependent materials chemistry. *Nature Communications, (9), 4168.* https://doi.org/10.1038/s41467-018-06682-4

[10] Jain, A., Hautier, G., Ong, S. P., Moore, C., Fischer, C.C., Persson, K.A. & Ceder, G. (2011). Formation enthalpies by mixing GGA and GGA+U calculations. *Physical Review B, 84(4), 045115.* https://doi.org/10.1103/PhysRevB.84.045115

[11] Ong, S.P., Wang, L., Kang, B. & Ceder, G. (2008). The Li–Fe–P–O2 phase diagram from first principles calculations. *Chemistry of Materials, 20(5), 1798-1807.* https://doi.org/10.1021/cm702327g

[12] Richards, W.D., Miara, L.J., Wang, Y., Kim, J.C. & Ceder, G. (2016). Interface stability in solid-state batteries. *Chemistry of Materials, 28(1), 266-273.* https://doi.org/10.1021/acs.chemmater.5b04082

[13] Belsky, A., Hellenbrandt, M., Karen, V.L. & Luksch, P. (2002). New developments in the Inorganic Crystal Structure Database (ICSD): Accessibility in support of materials research and design. *Acta Crystallographica Section B: Structural Science, 58(3), 364–369.* https://doi.org/10.1107/S0108768102006948

[14] Folch, R., Plapp, M. (2005). Quantitative phase-field modeling of two-phase growth. *Physical Review E, 72(1), 011602.* https://doi.org/10.1103/PhysRevE.72.011602

[15] De Jong, M., Chen, W., Notestine, R., Persson, K., Ceder, G., Jain, A., Asta, M. & Gamst, A. (2016). A statistical learning framework for materials science: Application to elastic moduli of k-nary inorganic polycrystalline compounds. *Scientific Reports, (6), 34256.* https://doi.org/10.1038/srep34256

W–Ti–C–Co жүйесі үшін эллингемнің фазалық тұрақтылық диаграммасы мен фазалық басымдық диаграммасын құру және термодинамикалық есептеулер

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Андатпа. Осы зерттеуде W–Ti–C–Co жүйесіндегі фазалық тепе-теңдік пен қосылыстардың тұрақтылығына термодинамикалық талдау жасалды. Зерттеу ab initio модельдеу, Materials Project дерекқоры және HSC Chemistry 6 бағдарламалық пакеті негізінде жүргізілді. Негізгі мақсат - кобальт пен титан легирлеуші элементтер ретінде қолданылатын отқа төзімді металлдар мен көміртекке негізделген композициялық материалдарда түзілуі мүмкін тұрақты және метастабильді фазаларды анықтау. Есептеулер нәтижесінде жүйеге тән фазалардың тізімі, төрт компонентті және үш компонентті фазалық диаграммалар (Ti–W–C, Co–Ti–C, Co–W–C), Эллингем типті тұрақтылық диаграммалары мен фазалық өзара әрекеттесу карталары жасалды. Фазалардың механикалық қасиеттері көлемдік және ығысу модульдері арқылы бағаланды: ең қаттысы – вольфрам карбиді (WC), ал ең иілгіш қосылыс – TiCo интерметаллиді. Зерттеу барысында W–Co және W–Ti құрамды үштік карбидтердің түзілу ықтималдығы жоғары екені анықталды, бұл материал қасиеттеріне айтарлықтай әсер етеді. Барлығы 14 ықтимал фазалық өзара әрекеттесу реакциясы анықталды, олардың ішінде әртүрлі интерметалдық және карбидтік қосылыстар бар. Эллингем диаграммасына сәйкес, Co_2C ~400°C жоғары температурада термиялық тұрақсыз, ал Co_7W_6 барлық температурада термодинамикалық тұрғыдан тұрақсыз. WC ~1400°C дейін тұрақты болып қала береді, одан жоғары температурада W_2C басым фазада болады. Бұл нәтижелер металл-көміртек көпкомпонентті жүйелеріндегі фазатүзілуді терең түсінуге және жылу тұрақтылығы мен механикалық қасиеттері жоғары жаңа материалдарды жобалауға негіз болады.

Негізгі сөздер: *термодинамикалық модельдеу, фазалық диаграмма, Эллингем диаграммасы, отқа төзімді материалдар, фаза тұрақтылығы, көлемдік серпімділік модулі, ығысу модулі.*

Термодинамические расчеты и построение диаграмм фазовой стабильности Эллингхема и фазового доминирования для системы W–Ti–C–Co

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Аннотация. В настоящем исследовании представлен термодинамический анализ фазовых равновесий и устойчивости соединений в системе W–Ti–C–Co с использованием ab initio моделирования, базы данных Materials Project и программного комплекса HSC Chemistry 6. Основное внимание уделено выявлению стабильных и метастабильных фаз, характерных для композиционных материалов на основе тугоплавких металлов и углерода с добавками кобальта и титана. Проведенные расчеты позволили определить перечень характерных фаз, построить четвертичную и тройные фазовые диаграммы (Ti–W–C, Co–Ti–C, Co–W–C), диаграммы устойчивости типа Эллингема и карты межфазных реакций. Механические свойства оценивались по значениям объемного и сдвигового модулей: карбид вольфрама (WC) оказался самым твердым, а интерметаллид TiCo – наиболее пластичным. Установлена высокая вероятность образования тройных карбидов (W–Co, W–Ti), существенно влияющих на свойства материала. Выявлены 14 возможных межфазных реакций, включая образование карбидов и интерметаллидов. Анализ диаграммы Эллингема показал, что соединение Co_2C термически неустойчиво выше ~400°C, а Co_7W_6 термодинамически невыгоден во всем температурном диапазоне. WC стабилен до ~1400°C, после чего доминирует W_2C. Результаты исследования способствуют углубленному пониманию фазообразования в многокомпонентных металл-углеродных системах и формируют научную базу для создания термостойких материалов с заданными механическими свойствами.

Ключевые слова: *термодинамическое моделирование, диаграмма фазовых состояний, диаграмма Эллингема, огнеупорные материалы, фазовая стабильность, модуль объёмной упругости, модуль сдвига.*

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