



McGill University

Department of Mining and Materials Engineering

Project Report

Title: *How do graphite, graphene, and diamond alter the melting point and eutectic features in the Ni–C phase binary diagram?*

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1. ABSTRACT

The Ni–C binary system serves as a model framework for studying fundamental **metal–carbon interactions**, which is crucial in advanced material synthesis processes such as Ni-catalysed graphene growth. This study presents a detailed thermodynamic investigation of the Ni–C phase diagram using **FactSage software**, with an emphasis on the effect of **different carbon allotropes** (graphite, diamond, and graphene) on phase equilibria. The **private thermodynamic databases** were created by manually incorporating these carbon phases, enabling the construction of binary phase diagrams through the **substitution** of the stable graphite phase with the metastable diamond and graphene phases.

The simulations revealed that replacing graphite with diamond or graphene results in a decrease in the **eutectic temperature** by approximately **20–30 °C** and an increase in the eutectic carbon composition. Additionally, significant shifts in the **solvus** and **liquidus lines** were observed, indicating altered carbon solubility and chemical potential in the system. The Ni–C binary phase diagram produces no nickel carbide phases like Fe–C system and the system retained a simple eutectic character across all cases. The phase diagram generated using graphite showed **excellent agreement** with **experimental data**, reinforcing the validity of the thermodynamic modeling approach.

These **findings** underscore the critical role of carbon phase selection in influencing phase boundary locations and equilibrium predictions. The **study** provides meaningful guidance for controlling carbon precipitation behavior in nickel-based systems, which is crucial for applications such as **chemical vapor deposition (CVD)** of graphene, where carbon thickness control is essential. It also informs the **design of carbon material synthesis** strategies, demonstrating how thermodynamic modeling can aid in the optimization of process conditions for emerging carbon-based technologies.

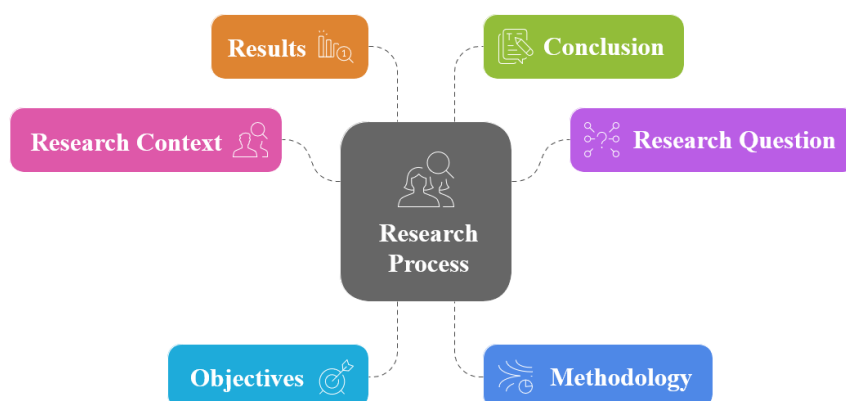


Figure 1.1: Key components of project.

2. LITERATURE REVIEW

2.1 Introduction and Motivation

The Ni–C binary phase diagram is crucial for understanding **metal–carbon interactions** and **synthesising carbon-based materials** [1]. The Ni–C system is characterized by a eutectic reaction and the absence of stable intermetallic carbides. These features make it ideal for both **theoretical** and **experimental studies** [2, 3]. In contrast, the **Fe–C system** is more **complex** because the presence of multiple carbide phases complicates thermodynamic modeling [4]. Nickel (Ni) is widely used in high-temperature applications. It plays a key role in the catalytic synthesis of diamond under high pressure and in the **chemical vapor deposition (CVD)** of graphene [5].

The **primary motivation** for studying is its industrial relevance, theoretical clarity and potential to enable controlled growth of **graphitic** or **diamond structures** [2]. Moreover, the choice of carbon allotrope significantly influences the behavior of the Ni–C phase diagram. Graphite is thermodynamically stable at ambient pressure [6]. Diamond is metastable but becomes stable at pressures above approximately 5 GPa. These allotropes have distinct Gibbs free energies. Their selection in thermodynamic models directly affects the predicted phase boundaries, eutectic compositions, and solubility limits [7].

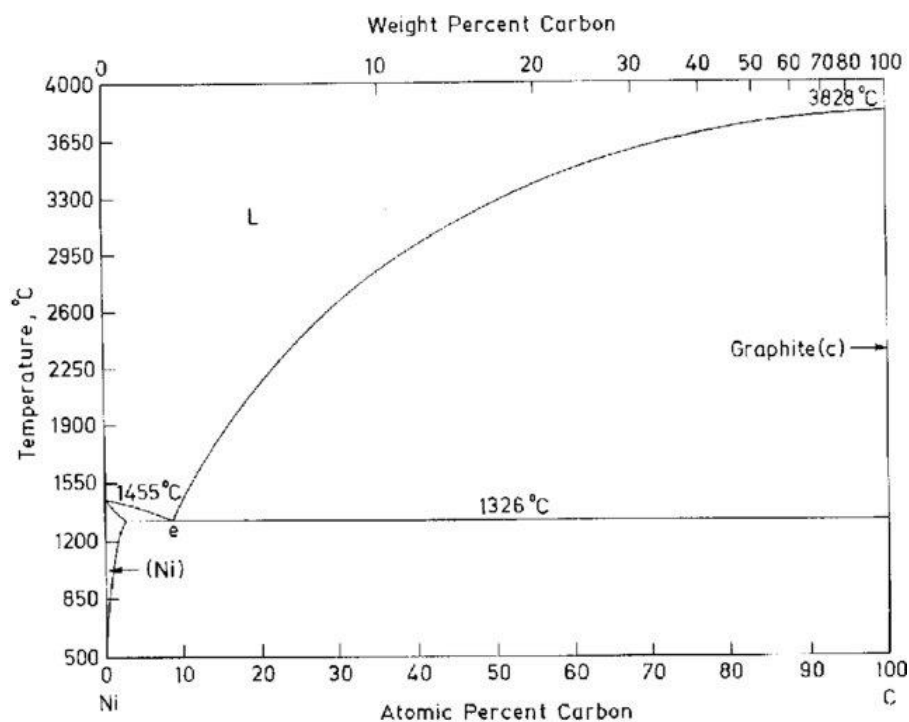


Figure-2.1: The Ni–C (graphite) phase diagram showing a eutectic at 1326 °C and limited carbon solubility in FCC Ni [6].

2.2 Thermodynamic Modeling

Eutectic Behavior: The phase diagram **Figure-2.1** shows a eutectic reaction ($L \rightarrow \text{FCC Ni} + \text{C}$) occurring at about 1326 °C and 9.8 at% carbon for graphite. In this scenario, the carbon solubility in solid Ni is minimal at the eutectic point. It drops sharply as the temperature decreases. The **solvus line** represents the maximum equilibrium carbon content in FCC Ni. It marks the region where carbon begins to **precipitate** as graphite [6, 8].

The **CALPHAD assessments** by accurately reproduce the Ni-rich side of the phase diagram. They apply compound energy formalism and thermodynamic databases. These models reflect the strong negative deviation from ideality in Ni–C solutions, particularly in liquid phase [2]. When diamond is used as the solid carbon phase, theoretical phase diagrams show a shift in eutectic temperature to approximately 1300 °C. They also predict a higher carbon content in the melt. The solvus line also shifts toward higher carbon concentrations. This shift reflects the **metastability** of diamond and the greater **chemical potential** needed for its nucleation [9].

2.3 Carbon Allotropes and Their Influence on Phase Stability

First-principles calculations using density functional theory (DFT) support these findings. Earlier studies confirm that nickel does not form stable carbides under equilibrium conditions. Although Ni₃C has been occasionally observed, it is energetically less favourable than a mixture of elemental carbon and nickel [10]. It also estimates the energy difference between graphite and diamond to be around 2–4 kJ/mol at ambient conditions, consistent with experimental data. These insights help guide the **selection of suitable carbon** phases in simulations and predict behavior under standard conditions. The presence of different carbon allotropes adds complexity to the Ni–C phase diagram [8]. The graphite is composed of **sp²-hybridized** carbon layers and is more stable at low pressure due to its lower Gibbs free energy. In contrast, diamond with its **sp³-hybridized** structure becomes stable only at high pressures and temperatures. The replacement of graphite with diamond in thermodynamic models changes the **chemical potential** of carbon and **shifts the phase equilibria** [11].

2.4 Benchmarking with Experimental Data

In the benchmark study, I studied a paper that presented the Nickel–Carbon (Ni–C) binary phase diagram based on both **thermodynamic modeling** and experimental validation [8]. I used FactSage software to generate my own Ni–C phase diagram and conducted a comparative analysis with the experimental results [6] reported in the literature to assess the **accuracy** of my modeling. In addition to plotting the Ni–C phase diagram, I **extended** the investigation by testing the phase behavior with **different carbon allotropes**, including diamond and graphene.

This approach allowed a **broader evaluation** of how carbon's structural form influences the phase equilibria. These benchmark studies helped establish a strong foundation for validating my methodology and ensured the reliability of the results presented in this project.

3. PROJECT QUESTION

How do graphite, graphene, and diamond alter the melting point and eutectic features in the Ni–C phase diagram?

4. SPECIFIC OBJECTIVES

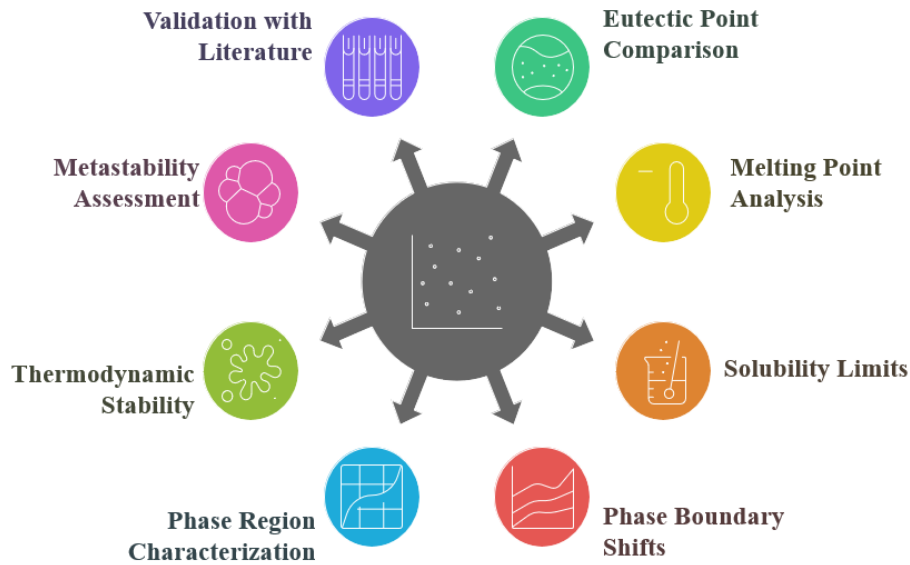


Figure 4.1: Specific Objects of the Project.

- **To construct binary Ni–C phase diagrams** using graphite, graphene, and diamond as the solid carbon phases through thermodynamic modeling (e.g., FactSage).
- **To identify and compare the eutectic points** (temperature and composition) for each carbon allotrope.
- **To determine the changes in the melting point of nickel–carbon alloys** depending on the carbon form used.
- **To evaluate the solubility limits of carbon in solid and liquid nickel** for each allotrope at equilibrium and near-eutectic conditions.
- **To analyse the shifts in the liquidus, solidus, and solvus lines** associated with the substitution of graphite with graphene or diamond.
- **To characterize the phase regions** (e.g., FCC, FCC + C, C + Liquid) that form in each phase diagram.

- To interpret the thermodynamic stability (e.g., Gibbs free energy) of each carbon allotrope and its role in influencing phase behavior.
- To assess the degree of metastability for graphene and diamond in comparison to graphite in the Ni–C system.
- To validate the modeled results by comparing them with existing experimental and literature data on Ni–C systems.

5. METHODOLOGY

5.1 Creation of Private Thermodynamic Databases

5.1.1 Database Initialization in FactSage

The first step involved creating three distinct private databases using the **Compound module** of **FactSage 8.3**. Each database was configured with a specific carbon allotrope:

- **DIAMBASE** – Solid carbon phase: *Diamond*
- **GRAPBASE** – Solid carbon phase: *Graphite*
- **GRIPBASE** – Solid carbon phase: *Graphene*

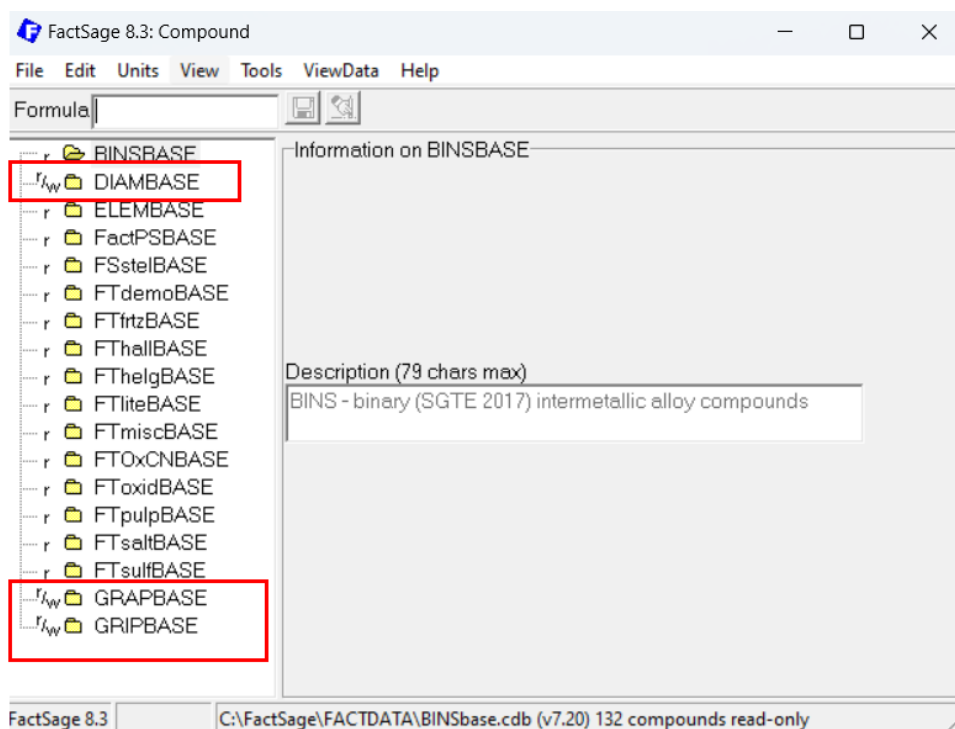


Figure-5.1: This is snapshot of the databases of Ni-C system with different carbon allotropes (graphite, graphene and diamond) in compound module of FactSage Software.

5.1.2 Component Selection

Each database included the same two chemical components:

- Nickel (Ni)
- Carbon (C)

5.1.3 Phases for Nickel

Nickel is defined with three fundamental phases in each database:

- **S1**: Face-Centered Cubic (FCC)
- **S2**: Body-Centered Cubic (BCC)
- **L1**: Liquid Nickel

These phases represent key transformations of Ni. FCC is stable at low temperatures, BCC forms at elevated temperatures and the liquid phase accounts for melting behavior.

5.1.4 Phases for Carbon

Carbon defined with both **solid** and **liquid** phases in all databases. The solid phase (**S1**) changed according to the allotrope under investigation:

- **DIAMBASE**: Diamond
- **GRAPBASE**: Graphite
- **GRIPBASE**: Graphene

This variation in the solid phase was the **core of the study**. It enabled a targeted analysis of how carbon structure affects melting points, solubility limits, eutectic behavior, regions (solid and liquid) and lines (liquidus, solidus and solvus).

5.1.5 Source of Thermodynamic Data

The SGTE ([Scientific Group Thermodata Europe](#)) database used to obtain thermodynamic input parameters for the Ni–C binary system. It provides critically assessed and experimentally validated data essential for modeling.

Limitation of SGTE for 2D Materials: SGTE includes thermodynamic data for three-dimensional (3D) materials such as diamond and graphite, but it does not include data for two-dimensional (2D) materials like graphene.

5.1.6 Manual Entry of Thermodynamic Data:

- **SGTE Database Limitation:** The SGTE database was not available as a built-in component in the installed version of **FactSage 8.3** used for this project.
- **Manual Data Incorporation:** As a result, a manual approach was employed to incorporate the required thermodynamic input parameters (**enthalpy of formation ($\Delta H_{(298)}$)**, **entropy at standard conditions ($S_{(298)}$)**, and **Gibbs free energy expressions $G(T)$**) into private databases.

- **Target Elements and Phases:** These values manually added for Nickel (FCC, BCC, and liquid) and for the carbon (Liquid, solid = diamond and graphite). The enthalpy and entropy values for graphene were taken from published literature [12]. However, since the specific heat capacity (C_p) of graphene above 100 K is identical to that of graphite due to similar interlayer spacing and the diminishing influence of ZA phonons [13]. The C_p values for graphene above 100 K were sourced from the SGTE graphite database due to their close similarity. This ensures consistency and accuracy in thermodynamic modeling [13].

5.2 Binary System Configuration and Phase Diagram Generation

5.2.1 Binary System Setup

In the second step, the **Phase Diagram module** in FactSage was used to simulate binary phase diagrams for the Ni–C system. The primary objective was not just to plot a conventional phase diagram. Instead, the goal was to assess how substituting the solid carbon affects phase equilibria and carbon solubility in nickel. All simulations were performed under standard conditions.

5.2.2 Unit Selection

Temperature set in °C, pressure in bar, and energy in joules (J). Quantity and volume were expressed in grams (g) and litres (dm³), respectively.

5.2.3 Selection of Thermodynamic Databases

Four key databases were selected to ensure accurate thermodynamic input for phase diagram calculations. Each was chosen for its specific purpose and contribution to complete data coverage.

- **FactPS:** This is used for accurate thermodynamic data of pure elements.
- **FTmisc:** This provides access to a variety of **miscellaneous phases and uncommon components** not covered in the core databases.
- **FTstel:** This database is tailored to steels and transition metal alloys.
- **SGTE:** It provides experimentally validated data for elements and compounds.

5.3 Phase Selection for Simulation

5.3.1 Significance of Phase Selection

The third stage of the methodology involved selecting the appropriate phases for the phase diagram simulations. This step was critical, as the chosen phases directly influence thermodynamic predictions.

5.3.2 Selection of Temperature:

- **Temperature Range:** The temperature range selected for the simulations was 298 to 1728 K. This range was chosen to cover both ambient and high-temperature conditions relevant to the Ni–C system.

- **Mole Fraction:**

The mole fraction (X) of a component in a mixture is calculated by this formula:

$$X_C = \frac{n_C}{n_C + n_{Ni}} \quad (5.1)$$

Here, X_C represents the mole fraction of carbon, while ' n_C ' and ' n_{Ni} ' denote the number of moles of carbon and nickel, respectively."

5.3.3. Graphical Representation

- A graph was plotted with **temperature (°C)** on the y-axis and **mole fraction of carbon** on the x-axis (by equation-5.1).
- All relevant **phase regions** (e.g., FCC, Liquid, FCC+C) were clearly labelled.
- Important **phase boundary lines liquidus, solidus, and solvus** were drawn.
- The **eutectic point** (invariant reaction) was marked to indicate the precise temperature and composition where the eutectic transformation occurs.
- The graph was formatted according to standard thermodynamic phase diagram conventions.

In this work, the binary Ni–C phase diagram was first generated using the Phase Diagram module in FactSage software. The calculated diagram was then compared with published experimental results by extracting relevant data points from literature sources [8]. In the next step, the stable carbon phase was systematically substituted with alternative allotropes (diamond and graphene), and two additional phase diagrams were generated to evaluate the effect of carbon phase selection on the overall phase equilibria.

6. RESULTS

6.1 Ni – C (Graphite)

The Ni–C system is a simple binary eutectic with no intermetallic compounds as depicted in **Figure-6.1**. Pure nickel has a melting point of about **1455 °C**, and carbon (as graphite) is the stable solid phase on the carbon-rich side. Because solubility of solid carbon in nickel is extremely limited, the Ni-rich side of the phase diagram is dominated by nearly pure Ni (FCC structure) up to its melting point. The **liquidus line** for Ni drops only slightly with carbon

addition, indicating a **modest melting point** depression due to carbon's low solubility. Essentially, nickel remains almost pure until the eutectic composition is reached.

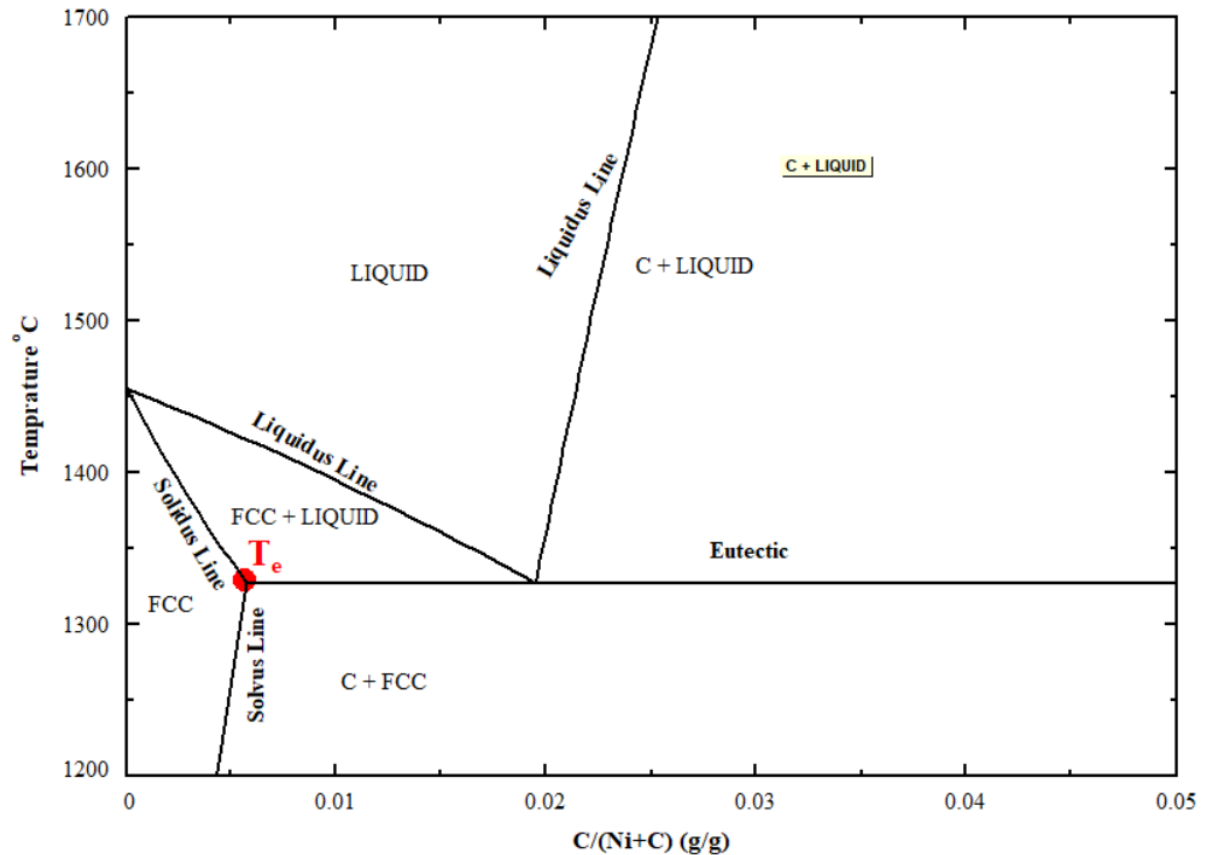


Figure 6.1: Ni–C binary phase diagram showing eutectic point (T_e) near 1326 °C and ~2.8 wt.% C. Key phase boundaries (liquidus, solidus, and solvus) are marked, highlighting regions of FCC, liquid, and graphite coexistence.

6.1.1 Eutectic Reaction

- **Eutectic Reaction Temperature:**

The Ni–C phase diagram features a eutectic reaction where liquid transforms to a mixture of Ni (FCC solid solution) and carbon (graphite) at approximately 1326 °C.

- **Ni-Rich Composition at Eutectic Point:**

This eutectic is at a very Ni-rich composition (~1.9 wt% C in the liquid), reflecting carbon's low equilibrium concentration in the melt.

- **Convergence of Liquidus and Solidus Lines:**

At the eutectic point (marked T_e in the diagram), the liquidus and solidus lines converge into a horizontal invariant line.

- **Solidification Below the Eutectic Temperature:**

This horizontal line at $\sim 1326^\circ\text{C}$ represents the lowest temperature at which liquid can exist in the Ni–C system (the “eutectic temperature”). Below this temperature, any alloy with sufficient carbon will completely solidify as Ni FCC plus graphite.

6.1.2 Solubility Limits

- **Carbon Solubility in Solid Nickel:**

The solid solubility of carbon in FCC nickel is extremely small. At the eutectic temperature, the Ni solid solution can dissolve only on the order of **0.4 wt% C (roughly 2 wt.% C)** before graphite precipitates. This corresponds to the nearly vertical solvus line on the Ni-rich side, barely shifted from the composition axis.

- **Carbon Solubility in Liquid Nickel:**

In contrast, carbon’s solubility in liquid Ni is higher: the liquid can hold about **1.9 wt% C at 1326°C** (the eutectic composition) and significantly more at higher temperatures. The liquidus line on the right side of the diagram (near the carbon-rich end) indicates the carbon saturation limit in liquid Ni, beyond which graphite (solid C) coexists with liquid. For example, at **$1600\text{--}1700^\circ\text{C}$** the liquid can dissolve roughly **2–3 wt% C**, and at still higher temperatures (**$\sim 1800\text{--}1900^\circ\text{C}$**) up to around **4–5 wt% C** is soluble before graphite forms. This steep rise of carbon solubility with temperature is a characteristic feature of Ni–C, and it is captured by the nearly vertical liquidus line on the carbon-rich side.

6.1.3 Phase Boundaries

- **Liquidus Line**

The **liquidus line** on the Ni-rich side slopes down gently from **1455°C at 0%C** to the eutectic isotherm at $\sim 1326^\circ\text{C}$, showing how a small addition of carbon lowers the melting point of the alloy.

- **Solidus Line**

The **solidus line** is almost coincident with the liquidus in this Ni-rich region because the solid solution holds so little carbon. Thus, there is only a narrow (almost negligible) two-phase L+FCC region except very close to the eutectic composition.

At the eutectic composition ($\sim 1.9\%\text{C}$) the liquidus and solidus meet, and beyond that point (higher C) the **primary phase** that freezes from the melt is graphite. On the carbon-rich side, a nearly vertical portion of the liquidus (often called the carbon saturation line) indicates where

liquid Ni is in equilibrium with solid carbon; any further cooling or carbon addition causes graphite to precipitate from the liquid.

- **Solvus Line**

The **solvus line** on the Ni-rich end (marking the boundary between single-phase FCC and FCC + C) is also very steep – it meets the eutectic horizontal at the tiny solubility of carbon in solid Ni (~0.4% C).

6.1.4 Phase Regions

Based on these boundaries, several phase regions can be identified in Diagram 1.

- **FCC Region:**

At low temperatures and very Ni-rich compositions we have a single-phase **FCC** Ni–C solid solution (carbon in solid solution).

- **FCC + Graphite:**

At slightly higher carbon levels (above the solvus limit at a given temperature), the alloy consists of **FCC + C** (graphite precipitates in a Ni matrix).

- **FCC + Liquid:**

Upon heating into the two-phase region between solidus and liquidus, an **FCC + Liquid** region appears (very narrow on the Ni-rich side).

- **Liquid + Graphite:**

At compositions to the right of the eutectic, a two-phase **Liquid + C** region exists when the melt is saturated with carbon and graphite co-precipitates. Finally, above the liquidus for a given composition, the alloy is entirely **Liquid**. Notably, no carbide compound (like Ni₃C) is stable in this diagram.

- **Equilibrium:** The only solid phases are the Ni-based FCC and carbon (graphite). Thus, the equilibrium phases and their boundaries are relatively simple: essentially a binary eutectic between a metal and a non-metallic element.

6.2 Experimental Validation

6.2.1 Eutectic Point

The experimentally determined eutectic occurs at **approximately 1326 °C** with a liquid composition of about **1.8–2.0 wt% C** in **Figure-6.2**, in excellent agreement with the FactSage calculation (**Figure-6.1**) [8]. The Ni-rich solid is nearly pure at the eutectic: measured carbon content in FCC Ni at the eutectic temperature is only **~0.3–0.5 wt%**, confirming the very limited solid solubility. No stable **nickel carbide phase** is detected in experiments (only Ni FCC and graphite are present), consistent with the calculated diagram. The pure Ni end of the

diagram is also confirmed: pure Ni melts at $\sim 1455^\circ\text{C}$, and small carbon additions have minimal effect until the eutectic point is reached. These experimental findings validate that the Ni–C system is a simple eutectic binary with graphite as the carbon precipitate.

6.2.2 Effect of Temperature on Solubility

Some differences appear in the details of the liquidus on the carbon-rich side, but the overall trend is the same. Experimental data show that carbon’s solubility in liquid Ni increases sharply with temperature, going from ~ 2 wt% at $\sim 1320^\circ\text{C}$ to around 3–4 wt% by ~ 1600 – 1700°C . This behavior is captured by the graphite-based calculation: both the measured points and the calculated liquidus line indicate a **steep rise**, meaning the **Liquid + C** two-phase region is confined to a narrow composition range at high temperatures [8].

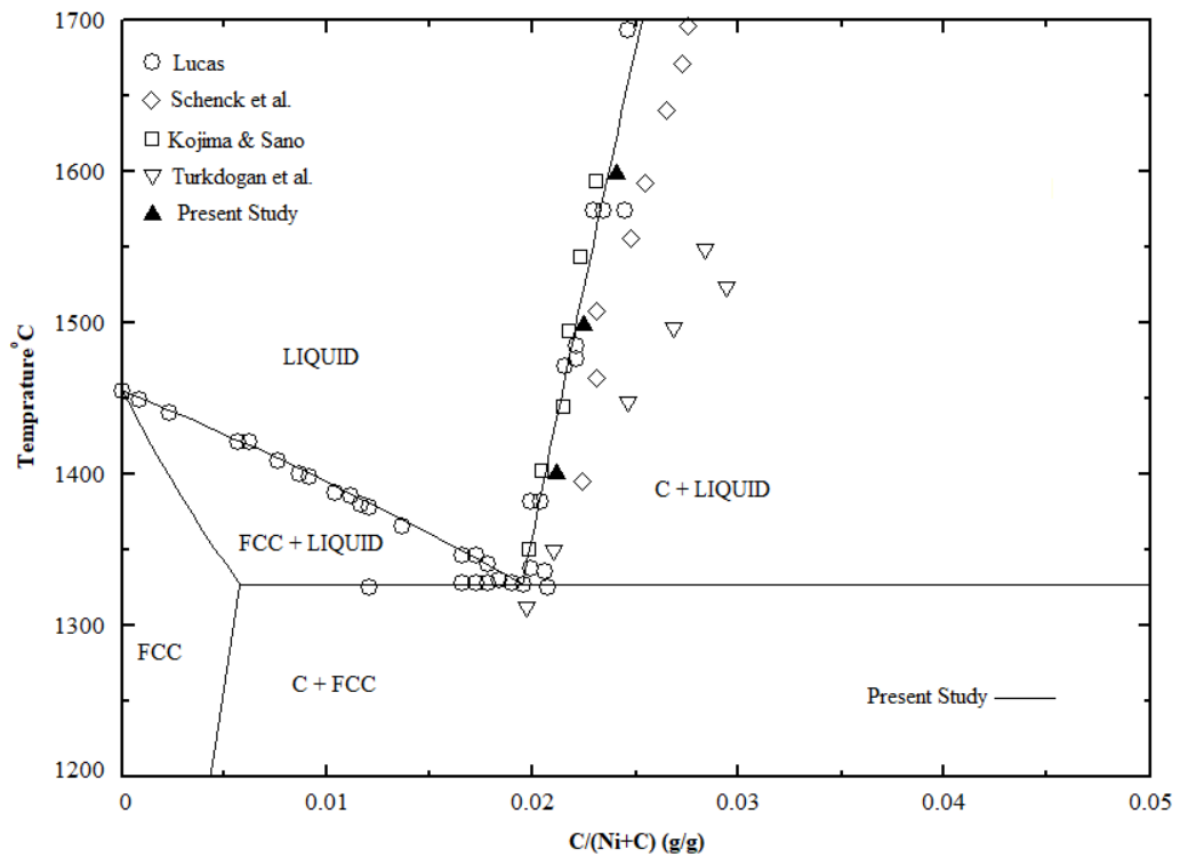


Figure 6.2: Ni–C binary phase diagram generated in the present study by extracting experimental data points from the literature. The diagram is plotted as a function of carbon content ($C/(Ni+C)$, g/g) and temperature ($^\circ\text{C}$). The solid line represents the calculated phase boundaries, while the symbols correspond to experimental data from Lucas (1969), Schenck et al. (1963), Kojima & Sano (1969), and Turkdogan et al. (1956). Phase regions such as FCC, Liquid, FCC + Liquid, and C + Liquid are clearly indicated.

6.2.3 Re-evaluation of Older Data considering Recent Findings

Minor discrepancies in older studies were noted and some early measurements [14,15] suggested a slightly different curvature of the liquidus, implying a stronger temperature dependence of carbon solubility than found in later work. However, more recent experiments [16,8] using rapid quenching and careful analysis show higher carbon solubilities that align well with the calculated equilibrium. The present assessed phase diagram (solid lines in **Figure-6.2**) fits these reliable data, accurately reproducing the eutectic point and the phase boundaries. In summary, the FactSage graphite-based diagram is in **close agreement** with experimental results, with both showing Ni's melting point $\sim 1455^\circ\text{C}$, a eutectic at $\sim 1326^\circ\text{C}$ (1.9% C), negligible carbon in solid Ni, and a steeply rising liquidus as carbon content increases.

6.3 Effect of Carbon Allotrope on the Phase Diagram (Diamond vs. Graphene)

6.3.1 Eutectic Behavior

When carbon is considered in different allotropic forms (**diamond or graphene**) instead of graphite, the phase diagram shifts subtly because the stability of the carbon phase changes. Graphite is the most stable form of carbon at ambient pressure, so using diamond or graphene (which are less stable under these conditions) yields metastable phase equilibria. In practical terms, if carbon were forced to precipitate as diamond or as graphene, the Ni–C eutectic would occur at a different composition (and slightly different temperature) compared to the stable graphite case.

6.3.2 Ni – C binary Phase Diagram (Diamond)

In the **Ni–C (Figure-6.3)** diagram, the eutectic reaction is still Ni (FCC) + C (diamond), but it occurs at a **lower carbon activity** (meaning the liquid needs to be richer in carbon to precipitate diamond). As a result, the **eutectic composition moves to a higher C content** (farther to the right on the diagram) when compared to the graphite-based eutectic. For example, the metastable eutectic with diamond might occur around $\approx 2.5\text{--}3\text{ wt\% C}$ in the liquid (significantly more carbon than the 1.9% in the graphite case). Thermodynamically, diamond has a higher Gibbs free energy than graphite at 1 atm, so the liquid must be more carbon-rich (or at a lower temperature) before diamond can form. The **eutectic temperature** with diamond is therefore slightly **lower** than 1326°C (by a few tens of degrees) because the system stays liquid until further cooling when only the metastable diamond can crystallize.

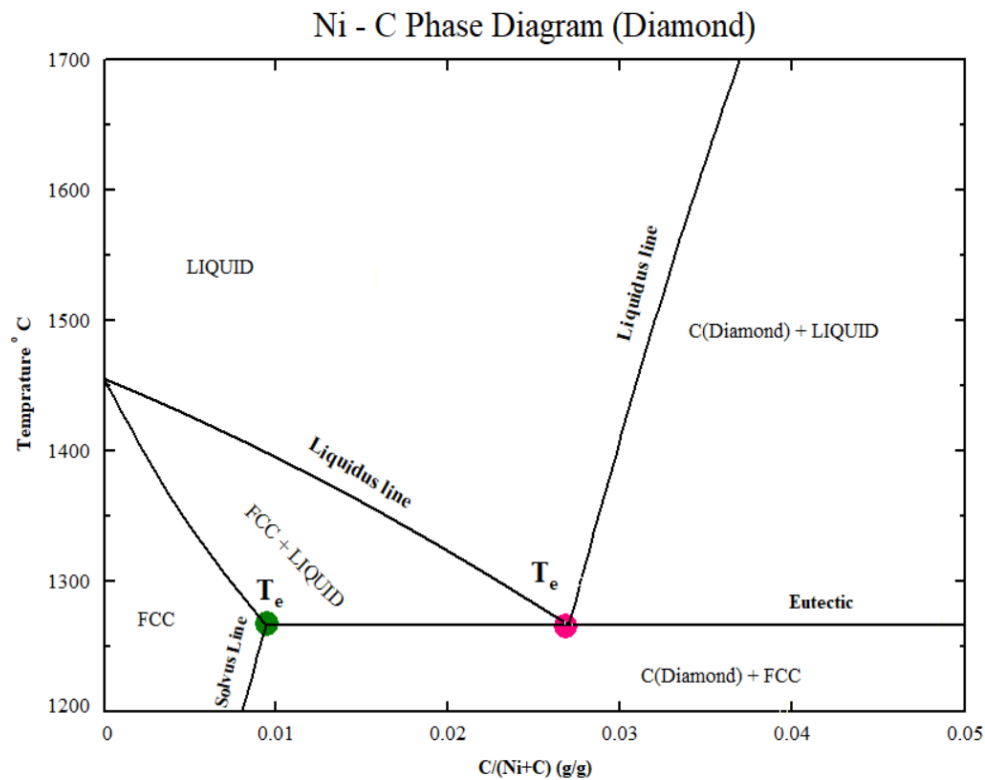


Figure-6.3: Ni–C phase diagram with graphene as the solid carbon phase is calculated by phase diagram module (FactSage).

6.3.3 Phase Boundaries

The overall shape of the phase boundaries in the Ni–C (diamond) diagram is otherwise similar. It remains a eutectic-type diagram. However, every equilibrium involving solid carbon shifts to favour higher carbon percentages.

Notably, the maximum **solubility of carbon in solid Ni** might increase marginally under this metastable scenario (since diamond precipitation is harder, Ni FCC can hold a bit more C in solution before saturation). Nonetheless, even in the diamond-for-carbon case, the solid solubility is still very small (on the order of tenths of a percent) and no new phases appear; we simply observe a Ni–C eutectic at a different location due to diamond’s metastability.

6.3.4 Ni – C (Graphene)

For the Ni–C (Graphene) case, the changes in the phase diagram are relatively small because graphene’s stability is only slightly lower than that of graphite. The **eutectic point** shifts to a marginally higher carbon content possibly around **2.0 to 2.3 wt% C** in the liquid. The temperature remains nearly unchanged or is just slightly reduced. Graphene’s eutectic is likely very close to **1326 °C** differing by only a few degrees at most. The liquidus and solidus lines in the graphene-based diagram remain close to those in the graphite diagram. This similarity is

due to the comparable thermodynamic stability of graphene and graphite. Thus, the Ni–C **phase equilibria** with graphene act as an intermediate case. The eutectic composition and carbon solubility **increase slightly** but not as much as in the **diamond case**. Graphite being the most stable gives the lowest eutectic composition around **1.9 wt% C** and the highest eutectic temperature. Diamond being the least stable at 1 atm results in a higher eutectic composition and a lower temperature. Graphene lies between these two extremes. In all scenarios the diagram retains its eutectic character while only the positions of the lines shift depending on the carbon allotrope.

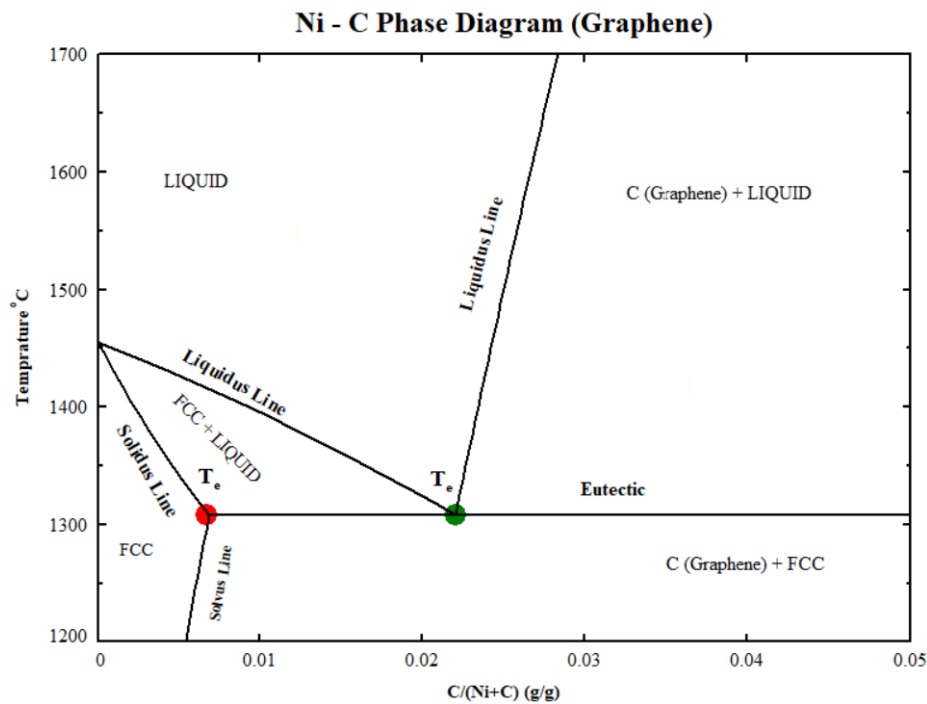


Figure 6.4: Ni–C phase diagram with graphene as the solid carbon phase is calculated by phase diagram module (FactSage).

7. DISCUSSION

7.1 Thermodynamic Impact of Carbon Allotrope on Phase Stability

The Ni–C phase diagram depends on the type of carbon present. Graphite is **sp² carbon** and is stable at room pressure. Diamond is **sp³ carbon** and is only metastable under the same conditions. Graphite has **lower Gibbs free energy** than diamond at **1 atm**. So, it is the favored form in equilibrium. Diamond becomes stable only at **high pressures**. This happens in high-pressure and high-temperature synthesis.

When graphite is used in modeling, it leads to different results. **Carbon** starts to come out of Ni at **higher temperatures**. This is because graphite formation is favored. But if diamond is

assumed as stable, carbon would precipitate at lower temperatures. Or it would need high pressure to form. Diamond has **higher enthalpy** than graphite, so it is less stable at low pressure.

This difference changes the phase diagram. The true equilibrium diagram is with graphite at 1 atm. The diamond-based diagram shows a metastable or high-pressure condition. So, the **phase boundaries shift** depending on the carbon form used.

7.2 Eutectic Behavior and Allotrope-Dependent Shifts

The Ni–C system exhibits a simple eutectic reaction where liquid transforms into FCC Ni and solid carbon, and the eutectic behavior is **highly sensitive** to the form of carbon present. Graphite, being thermodynamically stable at ambient pressure, results in a eutectic point at ~1326 °C with slightly higher carbon content. In contrast, diamond, which is metastable at 1 atm, lowers the eutectic temperature by **20–30 °C** and results in a **leaner carbon composition**, due to its higher Gibbs free energy.

Although these changes shift the temperature and composition values, the reaction remains strictly eutectic, with no compound formation. The stability of the carbon allotrope governs when and how carbon precipitate. The graphite favors higher-temperature precipitation, while diamond requires lower temperatures or high pressure. Thus, the **phase diagram shifts** in both temperature and carbon content based solely on the thermodynamic nature of the carbon phase, without altering the fundamental reaction mechanism.

7.3 Implications for Carbon Material Synthesis

7.3.1 Why Compare Carbon Solubility Across Metals?

How different metals interact with carbon helps explain why certain metals are chosen for synthesizing materials like graphene and diamond. The Ni–C system sits at an interesting balance point offering moderate solubility without forming stable carbides.

7.3.2 Carbon Solubility: Ni vs. Cu, Co, and Fe

The carbon solubility in Ni (**~0.6 wt% at the eutectic for graphite**) is higher than Cu but lower than iron. Importantly, Ni does not form stable carbides. This contrasts sharply with **Cu**, which has extremely low carbon solubility (**~0.008 wt%**). Then, resulting in carbon precipitating directly as graphite with no bulk dissolution. This explains why CVD on Cu produces mostly **monolayer graphene**. On the other hand, Ni allows **dissolution precipitation** and supporting multilayer graphene formation unless carefully controlled. Furthermore, Co behaves similar with slightly higher solubility (**~0.9 wt%**) and no carbide formation, making

it effective in carbon-based synthesis. In contrast, iron can dissolve much more carbon and forms **Fe₃C (cementite)**, especially under non-equilibrium conditions, which diverts carbon away from pure graphite or graphene formation.

7.3.3 Why Ni is a Preferred Metal in Carbon Processing?

The eutectic behavior and lack of carbide formation make it ideal for controlled carbon processing. In CVD, Ni can absorb and release carbon smoothly, allowing control over graphene thickness. In HPHT synthesis, Ni supports **diamond crystallization** by acting as a solvent, with precipitation guided by shifts in **phase boundaries** depending on whether graphite or diamond is the stable phase. The absence of stable carbides ensures carbon remains available for the formation of desired carbon allotropes. Overall, the **Ni–C phase diagram** provides a powerful foundation for tuning carbon material synthesis based on alloy composition, carbon phase, and processing conditions.

7.4: Key Characteristics

Property	Graphite (Calc.)	Diamond (Calc.)	Graphene (Calc.)	Experimental [8]
Ni (pure) melting point	1455 °C (check please)	1455°C (check please)	1455°C (check please)	1455°C (observed)
Eutectic temperature	1326 °C	Slightly lower (1300–1310 °C)	1320 °C (a few °C lower)	1326
Eutectic composition	1.9 wt% C	Higher (2.5–3 wt% C)	Slightly higher (~2.1–2.3 wt% C)	1.8–2.0 wt% C
C solubility in solid Ni	<<1 wt% (≈0.4% at 1326 °C)	Slightly higher (still <<1%, metastable)	Slightly higher (still <<1%)	<<1 wt% (0.3–0.5% at 1326 °C)

Table-7.1: Summary of key thermodynamic characteristics comparing graphite-based and diamond-based Ni–C binary phase diagrams, highlighting differences in eutectic behavior, carbon solubility, and phase stability.

7.3.4. Eutectic Behavior and Composition Shifts with Carbon Allotrope

The thermodynamic comparison of Ni–C binary phase diagrams using different carbon allotropes reveals key differences. When graphite is the solid carbon phase, the eutectic temperature is **1326 °C**, with a **composition of 1.9 wt% C**. This closely matches the experimental range of **1.8–2.0 wt% C**. When **graphene** is used, the **eutectic temperature decreases slightly** to **~1320 °C**. The eutectic composition increases to around **2.1–2.3 wt% C**. For diamond, the temperature drops further to **1300–1310 °C**, with a higher composition of **2.5–3 wt% C**. These shifts result from the metastable nature of graphene and diamond, which influence carbon activity and phase stability.

7.3.5. Carbon Solubility Trends in Solid Nickel

The carbon solubility in solid Ni also changes with the carbon allotrope. In the **graphite-based system**, it remains **below 1 wt%**, around **0.4 wt% at 1326 °C**. With graphene and diamond, the solubility is **slightly higher**, but still **less than 1 wt%**. These results are consistent with experimental data reporting 0.3–0.5 wt% solubility. The increase is linked to the metastability of the non-graphitic phases. Overall, the findings highlight that carbon allotrope selection affects eutectic behavior, solubility, and phase boundaries, which is crucial for thermodynamic modeling and carbon material synthesis.

8. CONCLUSION

This study evaluated the effect of different carbon allotropes (graphite, diamond, and graphene) on the Ni–C binary phase diagram. The analysis demonstrated that substituting graphite with metastable diamond or graphene **decreases the eutectic temperature** by approximately **20–30 °C** and **increases the eutectic carbon content** from ~1.9 wt% C (graphite) to approximately 2.1–2.3 wt% C (graphene) and 2.5–3.0 wt% C (diamond). The solvus and liquidus lines shifted correspondingly, indicating significant **sensitivity of carbon solubility** and chemical potential to carbon allotrope selection. Despite these variations, all calculated diagrams retained a **simple eutectic structure** without nickel carbide formation. The graphite-based simulation showed excellent consistency with **experimental results**, validating the **reliability** of the FactSage-based approach.

Limitations

- Thermodynamic data for graphene were derived from graphite's heat capacity values, potentially limiting the accuracy for precisely modeling 2D materials.
- The databases constructed involved manual data entry, introducing the possibility of minor transcription or interpolation errors.
- The simulations assumed equilibrium conditions, not accounting for kinetic factors that may influence real-world material synthesis.
- High-temperature simulations (>1600 °C) could not be experimentally validated due to limited published data.

Future Work

- Experimental validation of the predicted phase diagrams using metastable diamond and graphene phases under controlled conditions could enhance model accuracy.
- Future studies should incorporate kinetic considerations to better reflect practical synthesis environments.
- Developing comprehensive thermodynamic databases specifically tailored to 2D materials like graphene could refine predictive accuracy.
- Extending simulations to multicomponent alloy systems (e.g., Ni–Fe–C, Ni–Cu–C) would further support industrial applications and material optimization strategies.

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