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Theoretical study of the Ni–C system in the pressure range of 0–100 GPa

This work is devoted to the search for stable compounds and structures in the Ni–C system in the pressure range of 0–100 GPa. Based on the density functional theory, a search for stable compounds and structures in the Ni–C system was carried out using modern algorithms for predicting crystal structures. As a result, one stable intermediate compound Ni_3C with the structure of cementite, previously synthesized at 184 GPa, was revealed. Ni_3C nickel carbide is dynamically stable, which is confirmed by the absence of imaginary modes in the phonon spectra. According to the results obtained, Ni_3C is formed by the reaction of $3Ni + C \leftrightarrow Ni_3C$ above 23 GPa and is stable up to at least 100 GPa. Spin-polarized calculations showed that the Ni_3C has no magnetic moment in the entire pressure range. For carbon-rich compounds, performed calculations on the crystal structure prediction did not reveal any phase that would be energetically favorable relative to a mixture of pure nickel and carbon. Also, it was shown that the most energetically favorable modification of metastable carbide Ni_7C_3 is orthorhombic Ni_7C_3-*Pbca*.

Keywords: density functional theory, crystal structure prediction, USPEX, AIRSS, high pressure, phase stability, phonon spectra, nickel carbide.

Introduction

The Ni–C system at high pressure is of interest both from the point of view of Earth sciences and materials science. Nickel carbides are of active interest as catalysts in the chemical deposition of a gas mixture (CVD) to produce high-quality graphene [1]. In addition, nanoparticles of metal carbides, particularly nickel, in the carbon matrix make up nanocomposite thin films, which have a wide profile of application in metallurgy [2]. On the other hand, nickel is the second most common element in the Earth's core after iron [3]. According to cosmochemical data, the core contains 5 wt.% Ni [4]. However, seismic observations show that the core density is significantly lower than that of pure Fe and Fe–Ni alloy under P-T core conditions [5], which suggests the presence of a light element in the core. The question "what exactly are these elements, and what is their number?" remains the subject of active discussions today. Recent estimates of the composition of the inner core indicate a carbon content of up to 2.0 wt.% [4], which makes it a potential candidate for the role of a light element in the Earth's core. Therefore, to study the composition and structure of the Earth's core, it is important to investigate the Fe–Ni–C system at high pressures. To study the ternary Fe-Ni-C system, first, the binary Fe-C and Ni–C systems should be investigated. In the last decade, the Fe–C system has been actively studied at high pressure both theoretically and experimentally [6–9]. To date, there is only one experimental work [10] on the Ni–C system at high pressure and there is no theoretical study on this system. Thus, it is considerable to carry out theoretical study on the Ni–C system.

There are no stable binary Ni–C compounds at atmospheric pressure. In a recent work [10], it was shown that at high pressure (~184 GPa), a stable compound of Ni_3C with the structure of cementite (Fe_3C) is formed. To date, this is the only known stable compound in the Ni–C system.

This work is devoted to the search for stable compounds and structures in the Ni-C system in the pressure range of 0–100 GPa.

Experimental

Calculations implemented by authors on licensed USPEX and AIRSS software allow calculating the electronic structure of periodic systems with the use of the density functional theory.

The search for stable crystal structures in the Ni–C system was carried out using evolutionary algorithms and the random sampling method implemented in the USPEX and AIRSS software packages at pressures of 0, 25, 50, and 100 GPa. The search was conducted using the variable composition method and the USPEX code, while the structures were generated by the AIRSS code for fixed compositions, namely the carbon-enriched part of the Ni–C system.

The number of structures of the initial generation in the calculations by the USPEX method was equal to 50. After their optimization, 60% of the structures with the lowest enthalpy were selected, which were used to generate a new generation in the following percentage ratio: by heredity – 35%, by atomic mutations – 20%, by permutation of lattice parameters – 10% and 35% of all structures of the new generation were generated randomly. In the case of calculations of AIRSS methods, 2000–3200 structures were randomly generated and optimized, from which the most energetically favorable structures were selected. In all calculations, optimization was performed within the framework of density functional theory (DFT), using the conjugate gradient algorithm. The optimization parameters were as follows: the cutting energy of the plane wave basis was 450 eV, the Monkhorst-Pack k-point grid [11] with a point density equal to 0.5 Å-1, the electronic blur was according to the Methfessel-Paxton scheme [12], the parameter σ = 0.05 eV. Calculations of the ground state energies of the most promising of the predicted structures were conducted within the framework of the density functional theory (DFT) by the pseudo potentials method, in the VASP 5.3 software package [13, 14] with higher accuracy: the cut-off energy is 600 eV, the density of k–points is 0.2 $Å^{-1}$, the parameter σ = 0.1 eV. The exchange-correlation interaction was taken into account in the approximation of the generalized gradient according to the Purdue-Burke-Ernzerhof (PBE) scheme [15].

To calculate the phonon spectra, the lattice dynamics method was used in the framework of the quasi-harmonic approximation in the PHONOPY software package [16].

Results and Discussion

Using modern methods of structure prediction, the only energetically advantageous compound Ni_3C was found, as well as a number of metastable structures NiC, NiC_2, and NiC_3 (Fig. 1). Ni_3C stabilizes in the cementite structure (Pnma) above 23 GPa relative to the reaction 3Ni + C ↔ Ni_3C (Figure 2a). The most favorable among the predicted structures of the remaining compounds turned out to be energetically unfavorable relative to a mixture of pure nickel and carbon in the entire studied pressure range (0–100 GPa), with ΔH reaching values of 0.4 eV/f.u. for NiC, NiC_2, and NiC_3 (Figure 1). In the Fe–C system, in addition to Fe_3C, Fe_7C_3 is also thermodynamically stable. Fe_7C_3 iron carbide has two stable modifications: Fe_7C_3–Pbca and Fe_7C_3–P63mc. Similarly, Ni_7C_3 nickel carbide was also considered in the form of two modifications. The structural models Ni_7C_3–Pbca and Ni_7C_3–P63mc were constructed by replacing all iron atoms with nickel atoms in the structures Fe_7C_3–Pbca and Fe_7C_3–P63mc [17]. The calculation of the ground state energy of the obtained structures showed that Ni_7C_3–Pbca is an energetically more favorable structure than Ni_7C_3–P63mc by ~0.42 eV/f. u., however, it is energetically less favorable relative to the mechanical mixture of 7/3Ni_3C + 2/3C in the entire pressure range considered (Fig. 2b).

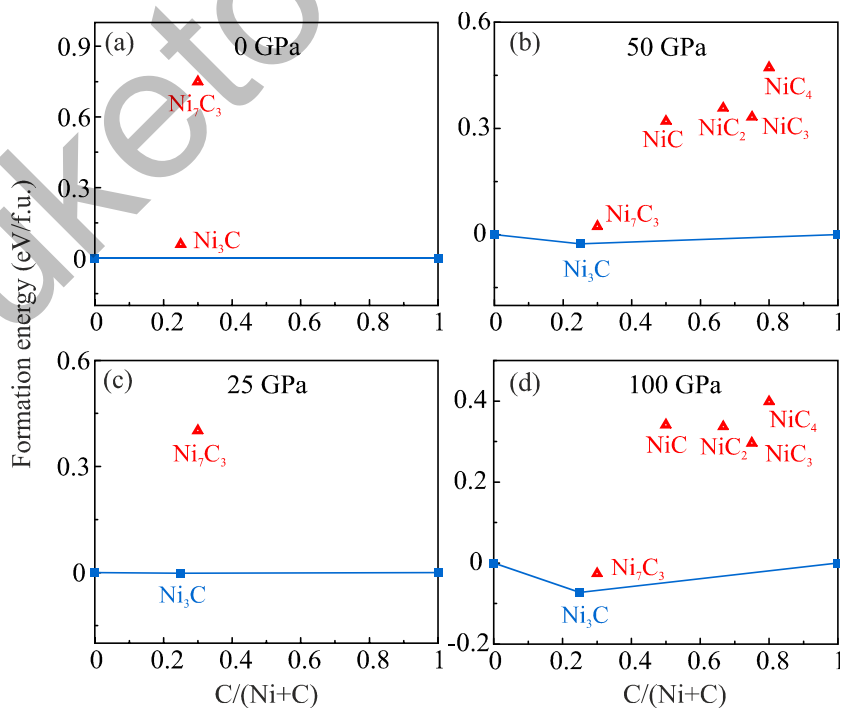

Figure 1. Thermodynamic convex hulls at various pressures and temperatures of 0 K

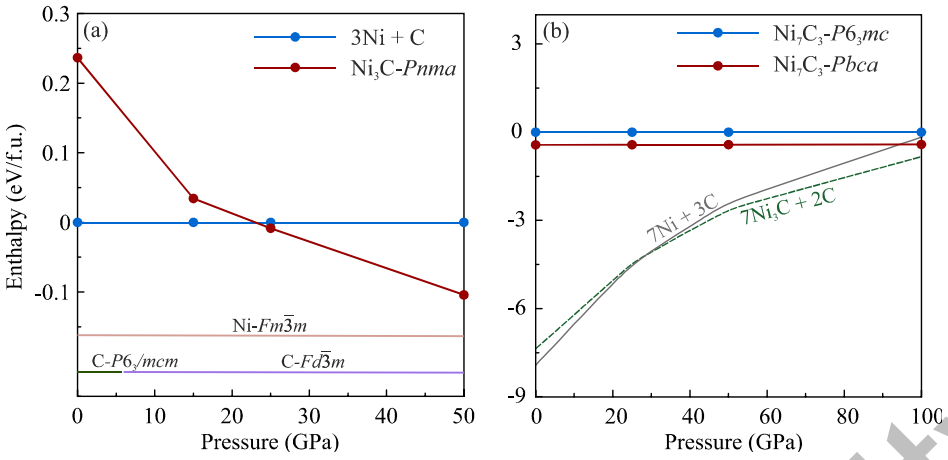

Figure 2. The dependence of the enthalpy on the pressure of Ni_3C–*Pnma* with respect to the decomposition reaction to the association of 3Ni + C (a) and the dependence of the enthalpy on the pressure for modifications of Ni_7C_3 with the application of possible decomposition reactions (b)

Spin-polarized calculations showed the absence of a magnetic moment in the entire studied pressure range. According to the calculations of the phonon dispersion curves, Ni_3C at 25 GPa is characterized by the presence of only real modes, which indicates the dynamic stability of this phase (Fig. 3).

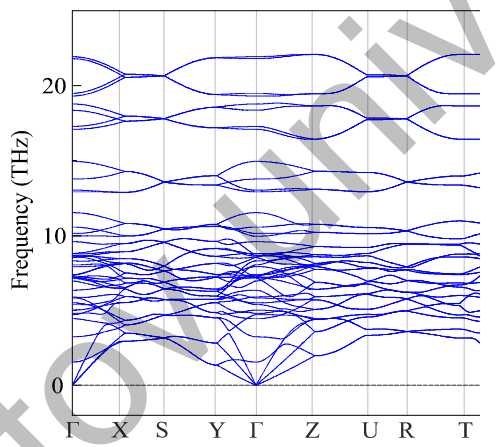

Figure 3. Ni_3C-*Pnma* phonon spectrum at 25 GPa

Also, for comparison with the experimental data [10], the equation of state in the range of 0–200 GPa was calculated. It can be seen from Figure 4 and Table 1 that our results are in good agreement with the experiment.

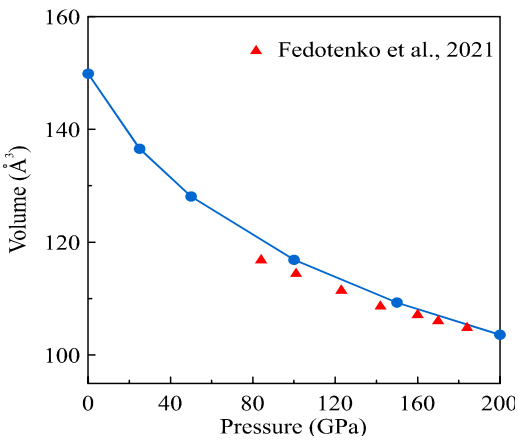

Figure 4. Pressure-volume dependence for Ni_3C–*Pnma*

Table 1

Calculated parameters V_0 and K_0 in comparison with experimental data [10]

	V_0 (Å^3)	K_0 (ГПа)
Experiment	147,7(8)	157(10)
This work	149,88	168

Conclusions

Within the scope of this study, a search for stable structures in the Ni–C system was carried out. It was shown that the Ni–C system in the pressure range of 0–100 GPa is characterized by one intermediate compound NiC. This nickel carbide is stabilized relative to the mechanical mixture of Ni and C above 23 GPa. The dynamic stability of Ni_3C is confirmed by the absence of imaginary frequencies in the phonon spectrum. Also, for comparison with experimental data, the Ni_3C equation of state was calculated in the pressure range of 0–200 GPa. The obtained result is in good agreement with the experiment.

Acknowledgments

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0–100 ГПа қысым диапазонындағы Ni–C жүйесін теориялық зерттеу

Мақала 0–100 ГПа қысым диапазонында Ni–C жүйесіндегі тұрақты қосылыстар мен құрылымдарды іздеуге арналған. Тығыздықтың функционалды теориясының негізінде Ni–C жүйесінде кристалдық құрылымдарды болжаудың заманауи алгоритмдерін пайдалана отырып, тұрақты қосылыстар мен құрылымдар іздестірілді. Нәтижесінде бұрын 184 ГПа синтезделген цементит құрылымымен бір тұрақты Ni_3C аралық байланыс табылды. Ni_3C никель карбиді динамикалық тұрақты, бұл фонондық спектрлерде қиялдық модасының болмауымен расталады. Алынған нәтижелерге сәйкес, Ni_3C 3Ni + C ↔ Ni_3C 23 ГПа-дан жоғары реакция нәтижесінде пайда болады және кем дегенде 100 ГПа-ға дейін тұрақты болады. Айналдыру поляризациясымен есептеулер Ni_3C-де қысымның барлық диапазонында магниттік момент жоқ екенін көрсетті. Көміртекке бай қосылыстар үшін кристалдық құрылымды болжау бойынша есептеулер таза никель мен көміртегі қоспасымен салыстырғанда энергетикалық жағынан қолайлы болатын бірде-бір фазаны анықтаған жоқ. Сондай-ақ, Ni_7C_3 метастабильді карбидтің ең энергетикалық тиімді модификациясы орторомбиялық Ni_7C_3-Pbca екендігі көрсетілген.

Кілт сөздер: тығыздықтың функционалды теориясы, кристалды құрылымды болжау, USPEX, AIRSS, жоғары қысым, фазалық тұрақтылық, фонондық спектрлер, никель карбиді.

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Теоретическое исследование системы Ni–C в диапазоне давлений 0–100 ГПа

Статья посвящена поиску стабильных соединений и структур в системе Ni–C в диапазоне давлений 0–100 ГПа. На основе теории функционала плотности был проведен поиск стабильных соединений и структур в системе Ni–C с использованием современных алгоритмов прогнозирования кристаллических структур. В результате было обнаружено одно стабильное промежуточное соединение Ni_3C со структурой цементита, ранее синтезированное при 184 ГПа. Карбид никеля Ni_3C динамически стабилен, что подтверждается отсутствием воображаемых мод в фононных спектрах. Согласно полученным данным, Ni_3C образуется в результате реакции 3Ni + C ↔ Ni_3C выше 23 ГПа и стабилен по меньшей мере до 100 ГПа. Расчеты со спиновой поляризацией показали, что Ni_3C не имеет магнитного момента во всем диапазоне давлений. Для соединений, богатых углеродом, проведенные расчеты по прогнозированию кристаллической структуры не выявили ни одной фазы, которая была бы энергетически благоприятной по сравнению со смесью чистого никеля и углерода. Также было показано, что наиболее энергетически выгодной модификацией метастабильного карбида Ni_7C_3 является орторомбический Ni_7C_3-Pbca.

Ключевые слова: теория функционала плотности, предсказание кристаллической структуры, USPEX, AIRSS, высокое давление, фазовая стабильность, фононные спектры, карбид никеля.

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