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Modelling of Epitaxial Growth of Diamond Crystals in High-Carbon Fe–Al Alloys

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Standard enthalpies of formation of different K-phase unit cells are calculated and compared with formation enthalpy of modified unit cell of K-phase. Spin-polarized calculations are performed to compare electronic structure of carbon atoms in K-phase substrate, diamond, and graphite. An assumption is made on the epitaxial growth of the diamond crystals during the thermobaric treatment of high-carbon Fe–Al alloys.

Розраховано стандартні ентальпії утворення різних елементарних комірок K-фази, виконано порівняння їх з ентальпією утворення модифікованої елементарної комірки. Порівняно електронні структури атомів вуглецю в K-фазі, алмазу та графіту, яких одержано спін-поляризованими розрахунками у пакеті Wien2k. Припущено епітаксіальний ріст кристалів алмазу при термобаричному обробленні високовуглецевих стопів Fe–Al.

Рассчитаны стандартные энтальпии образования разных элементарных ячеек K-фазы, выполнено их сравнение с энтальпией образования модифицированной элементарной ячейки. Сравнены электронные структуры атомов углерода в K-фазе, алмаза и графита, полученные в результате спин-поляризованных расчётов в пакете Wien2k. Предположен эпитаксиальный рост кристаллов алмаза при термобарической обработке высокоуглеродистых сплавов Fe–Al.

Key words: K-phase, diamond, graphite, epitaxy, substrate, Wien2k, electron density, thermobaric treatment, standard enthalpies of formation.

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1. INTRODUCTION

The most common designation for K-phase is Fe_3AlC. Type of crystal

structure of the K-phase is described in reference literature as: $L'1_2$ cubic face-centred crystal lattice with Schoenflies symbol O_h^1 and Hermann–Mauguin symbol of space group $Pm3m$. Average unit cell parameter is $a \approx 3.75$ Å. Coordination number $M \approx 5$. Coordinates of the atoms are as follows: 1Al (O_h): 0 0 0, 3Fe (D_{4h}): 1/2 0 0; ↓ 0.6–0.9 C (O_h) by 1/2 1/2 1/2 [1].

However, actually stoichiometric K-phase has never been observed [2], and real chemical formula is $Fe_{4-y}Al_yC_x$ [2], where $y = 0.4–1.0$, and $x = 0.08$ to 0.66 [2, 3]. Another attempt [4] was made to achieve stoichiometric composition under high pressure (up to 8 GPa) and high temperature (up to 2.2 K). It was unsuccessful; examination has shown that composition of obtained K-phase was $Fe_3AlC_{0.66}$. Besides, in the bulk of compound, which consisted mostly of the K-phase, colonies of diamond crystals of 100–200 micrometres in size were found. Spectral analysis has shown the presence of Fe and Al atoms in these crystals in the ratio of 3 to 1.

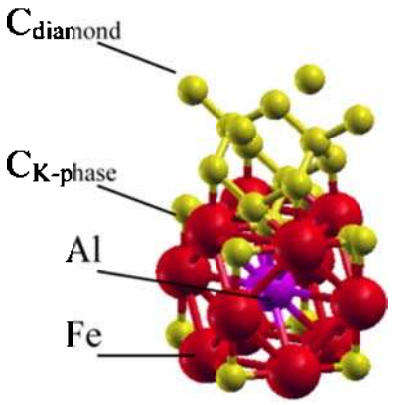

Fig. 1. Scheme of epitaxial growth of a diamond on the K-phase.

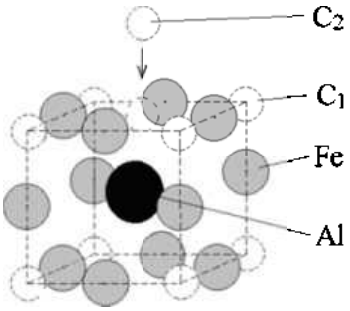

Fig. 2. Octahedral pore, in which carbon is deposited during thermobaric treatment.

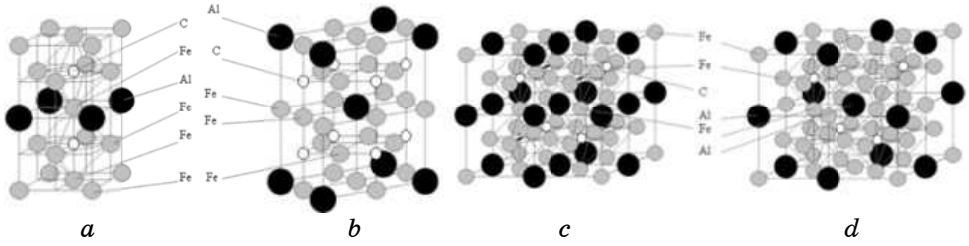

Fig. 3. Calculated crystal cells: (*a*) $Fe_{3.5}Al_{0.5}C$, (*b*) $Fe_{3.5}Al_{0.5}C$ (distinct configuration); (*c*) $Fe_{3.125}Al_{0.825}C_{0.5}$; (*d*) $Fe_{3.5}Al_{0.5}C_{0.5}$; (*e*) $Fe_3AlC_{0.66}$.

This and also the fact that the difference of lattice parameters of the *K*-phase ($\alpha \approx 3.75$ nm) and diamond (3.57 nm) is about 5%, allows to assume that epitaxial growth (or nucleation) of diamonds is possible on the surface (or inside the volume) of *K*-phase (Fig. 1). Increase of pressure during the thermobaric treatment will reduce the difference of parameters even more ($\alpha \approx 3.69$ nm at 7 GPa). The most suitable substrate crystal plane for epitaxial growth of diamonds on *K*-phase is [200]. It contains four atoms of carbon, and it has an octahedral pore in the middle. It is possible that undissolved carbon (*K*-phase can dissolve only up to 2/3 carbon atom per cell) is deposited in this pore during the process of thermobaric treatment (Fig. 2).

As said earlier, *K*-phase composition varies in a broad range, so first we investigated different possible unit cells corresponding to different compositions of *K*-phase. Linearized augmented plane wave method as implemented in Wien2k package is used to perform spin-polarized calculations of the following crystal cells (Fig. 3): Fe_3AlC, $Fe_{3.125}Al_{0.825}C_{0.5}$, $Fe_{3.5}Al_{0.5}C_{0.5}$, $Fe_{3.5}Al_{0.5}C$ (two configurations), $Fe_3Al_{0.66}C_{0.66}$, $Fe_3AlC_{0.66}$. The last one corresponds to the real *K*-phase in terms of composition. Crystal cell parameter is chosen to be 0.375 nm, which corresponds to the optimal volume of stoichiometric *K*-phase according to our calculations. Generalized gradient approximation (Perdew–Burke–Ernzerhof'96) is used as exchange-correlation potential with cut-off energy equal to –7 Ry in all calculations. Atomic radii are chosen as follows: for Al, 2.34 a.u.; for Fe, 1.87 a.u.; for C, 1.66 a.u.

Total energies of corresponding *K*-phase cells and their constituent elements are obtained from calculations and then used to compute enthalpies of formation of these cells. Obtained values are listed in Table 1. Minimum of studied enthalpies of formation corresponds to the $Fe_3AlC_{0.5}$ cell. $Fe_3AlC_{0.6(6)}$ cell also has low value of enthalpy and most probably forms when the melt is oversaturated with carbon. *K*-phase cell of stoichiometric composition Fe_3AlC has higher formation en-

TABLE 1. Standard enthalpies of formation of different compositions of *K*-phase.

Unit cell	Enthalpy of formation, eV/atom
Fe_3AlC	–0.03
$Fe_3AlC_{0.6(6)}$	–0.0328
$Fe_3AlC_{0.5}$	–0.033
$Fe_{3.125}Al_{0.825}C_{0.5}$	–0.0308
$Fe_{3.5}Al_{0.5}C_{0.5}$	–0.0244
$Fe_{3.5}Al_{0.5}C$	–0.0286
$Fe_{3.5}Al_{0.5}C^*$	–0.0275

*Distinct atomic configuration.

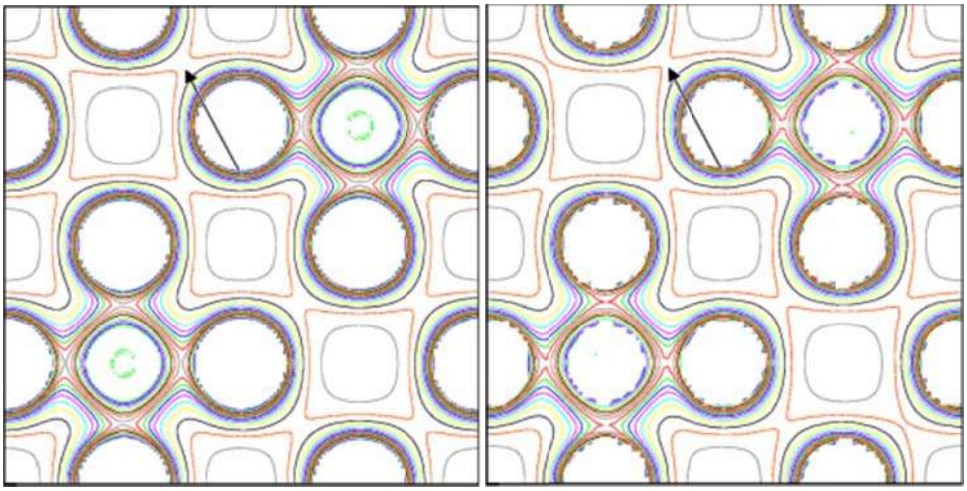

Fig. 4. Spatial distribution of electron densities in plane [200] of $Fe3AlC_{0.5}$ (left) and $Fe_{3.125}Al_{0.875}C_{0.5}$ (right).

thalpy and thus probability of its formation is lower, which corresponds to experimental data: stoichiometric *K*-phase has never been found yet. $Fe_{3.5}Al_{0.5}C$ has even lower probability of formation. Such increase of formation enthalpies with decrease of aluminium contents is caused by the fact that iron atoms embedded instead of aluminium form new bonds with iron atoms from octahedral carcass (that surrounds carbon) and, despite this newly formed bonds are slightly stronger than previous bonds with aluminium atoms, the strength of Fe–Fe and Fe–C bonds of atoms from octahedral carcass is decreased (Fig. 4). As a result, this leads to decrease of stability of *K*-phase structure as a whole.

As for the carbon non-stoichiometry, one can see that structures

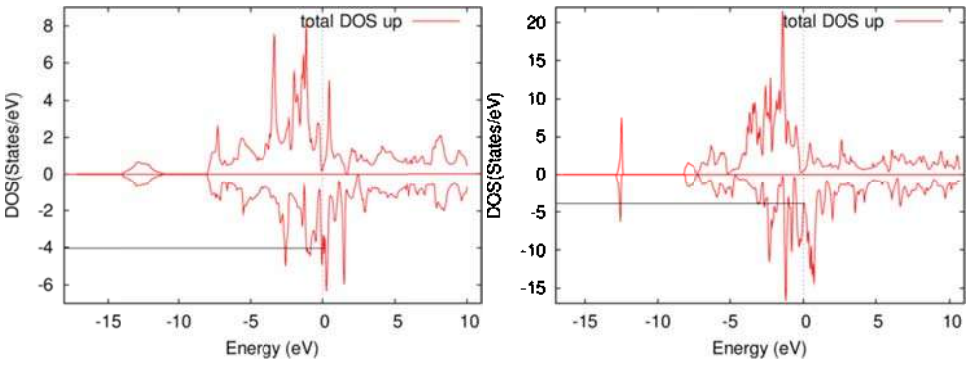

Fig. 5. Total electron densities of Fe_3AlC (left) and $Fe_3AlC_{0.5}$ (right).

with carbon non-stoichiometry have more evident minimum of density of states compared to stoichiometric one, which makes them more thermodynamically stable (Fig. 5).

Despite the experiment and calculations had shown that $Fe_3AlC_{0.5}$ and $Fe_3AlC_{0.66}$ are more thermodynamically preferable than Fe_3AlC, in our further calculations we used the last one, because it is much less computationally expensive. In order to understand whether *K*-phase can be a substrate for a diamond, electron densities of graphite, diamond and modified *K*-phase cell (Fig. 2) (with no pressure and under pressure of 7 GPa) were calculated. They are compared in Fig. 6. The calculation shows that with gradual increase in pressure applied to *K*-phase (and thus, gradual decrease of lattice parameter) electron densities of carbon atoms in *K*-phase become more and more similar to those in diamonds.

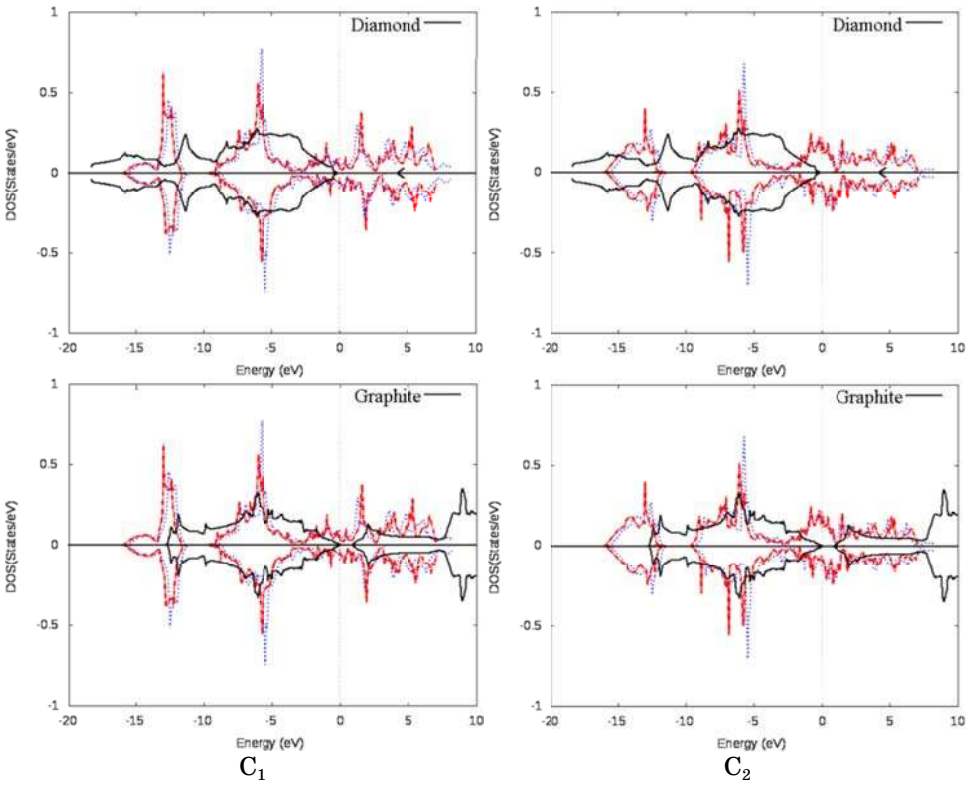

Fig. 6. Comparison of electron densities of graphite/diamond with electron densities of corresponding carbon atoms of modified *K*-phase. On the left, C_1 atom of *K*-phase; C_2 is on the right (see Fig. 2 for atom designation). Dotted lines stand for *K*-phase under no pressure, dashed lines for *K*-phase under pressure of 7 GPa.

Several cells with different number of layers of ordinary (varying from 1 to 4) and modified K-phase were also calculated. Additional layers of K-phase create additional splitting, but the picture mostly remains the same. Enthalpies of formation of such unit cells are close to 0 (varying from –0.008 to –0.01 eV/atom) and are bigger than that of ordinary K-phase, so, these cells require special conditions to form, *e.g.*, abundance of the carbon.

2. CONCLUSION

We have made an assumption that K-phase, because its lattice parameter (0.375 nm) is close to that of diamond (0.357 nm), can be a substrate for a diamond with the substrate plane [200]. We have performed electron densities calculations of K-phase unit cells with additional carbon atom in the octahedral pore of [200] plane. Calculations have shown that with gradual increase of pressure electron densities of carbon atoms from the substrate plane of the modified K-phase become more and more similar to the electron densities of carbon in diamond. We also have performed calculations of standard enthalpies of formation that have shown that $Fe_3AlC_{0.5}$ and $Fe_3AlC_{2/3}$ have the lowest enthalpies and thus have the highest probability of formation. The reasons for this are provided in the article. It is worth mentioning that we have used Fe_3AlC unit cell as a basis for modified K-phase because it has lower computational costs. Formation enthalpies of all calculated modified K-phase unit cells are slightly higher than that of Fe_3AlC, which means that they need special conditions to form, *e.g.*, abundance of the carbon.

REFERENCES

1. K. J. Smittels, *Metals: Handbook* (Moscow: Metallurgiya: 1980) [Russian translation].
2. V. A. Andrushenko, V. G. Gavrilyuk, and V. M. Nadutov, *Fiz. Met. Metalloved.*, **60**, No. 4: 683 (1985) (in Russian).
3. H. G. Goldshmidt, *Interstitial Alloys* (London: Butterworths: 1967).
4. V. A. Andryushchenko et al., *Metallofiz. Noveishie Tekhnol.*, **31**, No. 9: 1257 (2009) (in Russian).