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Structural and electronic properties of chromium carbides and Fe-substituted chromium carbides

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Abstract

Chromium carbides are coated over base metal (Fe) to increase wear and corrosion resistance. The electronic structure and bonding properties for chromium carbide bulk phases (Cr$_3$C$_2$, Cr$_7$C$_3$ and Cr$_{23}$C$_6$) and Fe-substituted chromium carbides is investigated using Density Functional Theory (DFT). The bonding in these carbides has been interpreted in the form of partial density of states, electron density distribution and Mulliken population method. Cr$_3$C$_2$ exhibits the strongest covalent character while Cr$_7$C$_3$ displays the highest metallicity. Cr$_3$C$_2$ showed the highest stability among the chromium carbide phases. In the Fe-substituted chromium carbides (Cr$_3$Fe$_2$C$_2$), the site preference of Fe in Cr$_3$C$_2$ system has been reported. In Fe-substituted chromium carbides also show both of metallic and covalent character and Cr$_2$Fe$_3$C$_2$ is found to be the most stable Fe-substituted chromium carbide system.

Introduction

Chromium carbides are materials consisting of different percentages of chromium (Cr) and carbon in the metal carbide system [1]. Stable forms of chromium carbides are known to be good hard-facing alloys. They are used as a coating over metal surfaces due to its resistance towards wear and corrosion. Significance of Fe–Cr–C alloys as precipitated carbides is also well known in several industries, such as drilling [2, 3], mining [4, 5], oil and gas [6, 7] and fuel cells [8, 9].

In literature, experimental findings have reported three stable forms of chromium carbides, Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$. The narrow homogeneity range of structures were assessed through phase diagram reported by Massalski [10]. Several investigators have synthesised and investigated various forms of chromium carbides both experimental [11] and theoretical methods [12–14]. Theoretical investigations using Density functional theory [15, 16] to study the structural and electronic properties of chromium carbides have been conducted successfully. However, these investigations analysed mainly the chromium carbides in their pure form. Often when chromium carbides are deposited in the industry as a surface coating, they are diluted by iron atoms. Inclusion of Fe atoms in chromium carbides would change the physical properties of chromium carbides [17, 18]. The stability of the chromium carbides containing Fe atoms will also be affected in corrosive environments [19]. However, a systematic theoretical report on how the electronic structures of the chromium carbide phases are modified due to the introduction of Fe into the carbides is not yet reported. The intent of this paper is to present a systematic investigation of the transformation of chromium carbides as the concentration of C steadily increases in chromium carbide crystal systems and further investigate the site preference of Fe in the most stable chromium carbide phase. In the present work, we have employed Density functional theory (DFT) to investigate the structural and electronic characteristics for understanding the bonding nature in the three stable chromium carbide phases and the Fe-substituted chromium carbide systems. The theoretical values obtained of various parameters and properties are compared with the available experimental results.
Cell properties, cohesive energies and enthalpies of formation of chromium carbide phases

Results and discussions

Here, $E_{coh}$

Methodology

Computational details

All calculations are performed using DFT as implemented in the Dmol3 code in Biovia Material Studio 2017 [20, 21] computational module. Geometry optimization of Cr, C [graphite], Cr$_3$C$_6$, Cr$_7$C$_3$, Cr$_3$C$_2$ unit cells and isolated Cr, Fe and C atoms are performed with double numerical atomic basis set with a polarization d-function on all non-hydrogen atoms ['dnd']. The generalized gradient approximation [GGA] + Hubbard parameter [$U = 2.50$ eV] in the PWSC_PBE form was used in all the calculations using semi-core pseudo-potentials [22]. For Cr, Fe and C, the valence electrons being considered are $3s^23p^63d^34s^1$, $3s^23p^63d^44s^2$ and $2s^22p^5$, respectively. The experimentally known crystal structures were used as initial geometry for the optimizations. A Monkhorst-Pack grid has been used to select the special k-points necessary to carry out numerical integrations in the reciprocal space [23]. The smearing parameter was set as 0.005 Ha. The energy convergence tolerance, the maximum force and the maximum displacement were selected as $1.0 \times 10^{-5}$ Ha, $0.002$ Ha Å$^{-1}$ and $0.005$ Ha respectively. The quality of orbital cut off was set to ‘fine’ and a global orbital cut off radius of 4.5 Å was used. The crystal structures of Cr, graphite and chromium carbides are represented using MS visualiser and the VESTA software [24].

Stability of chromium carbides

Thermodynamic properties like cohesive energy and enthalphy of formation provide information about the relative stability of the different phases of chromium carbide and Fe-substituted chromium carubides [16]. Theoretically, cohesive energy and formation enthalphy can be calculated using equations (1) and (2) [16]

$$E_{coh}[M_xC_y] = \left[ E_{total}(\text{Cell}) - nxE_{iso}(M) - nyE_{iso}(C) \right] / n$$

(1)

$$[\Delta_rH_m]^x = [E_{coh}(\text{Cell}) - nxE_{coh}(M) - nyE_{coh}(C)] / n$$

(2)

Here, $E_{coh}[M_xC_y]$ is the cohesive energy and, $[\Delta_rH_m]^x[M_xC_y]$ is the formation enthalphy, of chromium carbide phases and Fe-substituted chromium carbides, where $M = \text{Cr/Fe}$ and $x = 3, 7, 26$ and $y = 2, 3, 6$ for chromium carbides. $E_{total}(\text{Cell})$ is the total energy of a unit cell. $E_{iso}(X)$ indicates the total energy of an isolated X atom; finally, ‘n’ refers to the formula number of Cr$_3$C$_2$, Cr$_7$C$_3$, Cr$_{23}$C$_6$ and Fe-substituted chromium carbide units contained in each cell.

Results and discussions

Cell properties, cohesive energies and enthalpies of formation of chromium carbide phases

The optimized geometry of the crystal structures of bcc-Cr [Im-3m], graphite [P63/mmc] are shown in figure 1. Cr has cubic symmetry with $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ and the graphite has hexagonal symmetry with $a = b = c$ and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The three known stable phases of chromium carbides are shown in figure 2. The general formula of crystal structures of chromium carbides is Cr$_{1-x}$C$_x$, $x = \text{amount of C with 0.20 < } x < 0.50 \text{ in Cr (amount of Cr = 1.0)}$. The three phases of chromium carbides that form the stable phases are Cr$_{23}$C$_6$ [Fm-3m], Cr$_7$C$_3$ [Pnca] and Cr$_3$C$_2$ [Pnma] [25, 26] for various values of $x$.

Chemically, the transition of Cr to Cr$_3$C$_2$ with the increasing concentration of C can be represented as

$$\text{Cr}^{15-20\%[C]} \rightarrow \text{Cr}_{23}\text{C}_6^{20-30\%[C]} \rightarrow \text{Cr}_7\text{C}_3^{30-45\%[C]} \rightarrow \text{Cr}_3\text{C}_2$$

(3)

As shown in figure 2, Cr$_{23}$C$_6$ has cubic symmetry with $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ and Cr$_7$C$_3$ and Cr$_3$C$_2$ have orthorhombic symmetry, with $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. Space groups and the calculated cell parameters are listed in table 1. As C atom is introduced, the bcc-Cr bulk phase changes to face-centred crystal...
The fcc crystal structure of Cr$_23$C$_6$ as represented in figure 2 can be thought as a combination of Cr atoms forming cuboctahedral polyhedra and tetrahedral polyhedral with C atoms situated between the two polyhedra. When the concentration of C ($x$) increases from 0.20 to 0.50 (Cr$_7$C$_3$ and Cr$_3$C$_2$), the phases of orthorhombic symmetry with Cr atoms forming triangular prismatic units around the C-atoms are formed. In Cr$_7$C$_3$ (figure 2) the prisms are connected by Cr atoms in the corners of the prisms while in Cr$_3$C$_2$, the prisms are connected by Cr atoms in the edge of the prisms as the number of C atoms per unit cell is higher in Cr$_3$C$_2$.

The calculated cell parameters of all the Cr–C compounds are shown in table 1. The experimental values of the lattice parameters [27–31] shown in parenthesis are in good agreement with our calculated values. The average deviation of our results from the experimental lattice parameters are less than 1%.

Cohesive energy and enthalpy of formation for the stable chromium carbides phases has been calculated using equations (1) and (2) and listed in table 1. The enthalpy of formation is −0.116, −0.109 and −0.105 eV atom$^{-1}$ for Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$, respectively indicating that Cr$_3$C$_2$ is the most thermodynamically stable phase. Our calculated values of enthalpy of formation follow the trend observed in the experimental findings [32, 33]. The calculated formation energy values for Cr$_7$C$_3$ and Cr$_3$C$_2$ are close to the experimental values, whereas for the Cr$_{23}$C$_6$, the deviation is higher. This deviation can be attributed to the different experimental conditions used for obtaining the formation energies reported.

A range of theoretical values for cohesive energies have been reported Cr$_{23}$C$_6$ (−8.404 eV atom$^{-1}$ [12] and −10.10 eV atom$^{-1}$ [16]), Cr$_7$C$_3$ (−8.57 eV atom$^{-1}$ [13] and −10.03 eV atom$^{-1}$ [16]), and Cr$_3$C$_2$ (−9.94 eV atom$^{-1}$ [16]). We find our calculated cohesive energy values of −6.745 eV atom$^{-1}$, −7.084 eV atom$^{-1}$ and −7.415 eV atom$^{-1}$ for Cr$_{23}$C$_6$, Cr$_7$C$_3$, and Cr$_3$C$_2$, respectively follow the trend observed for the three phases are similar to their findings. Hence, based on enthalpy of formation and cohesive energies, the following stability sequence for the three stable chromium carbide phases can be concluded, which is consistent with the stability order reported in experimental findings [32, 33].

Order of chromium carbides stability: Cr$_3$C$_2$ > Cr$_7$C$_3$ > Cr$_{23}$C$_6$

Electronic Properties of Cr, graphite and chromium carbides
In general, the nature of bonding within the chromium carbide phases can be confirmed by metallicity, electron density distribution map, population analysis and partial density of states.
Table 1. Point group [Space group], calculated cell parameters \((a, b, c\ \text{in } \AA)\) of \(\text{Cr, C, and chromium carbide phases. Cohesive energy } (E_{coh},\ \text{eV atom}^{-1})\) and enthalpy of formation \((\Delta H_m,\ \text{eV atom}^{-1})\) for chromium carbide phases.

| Crystal systems | Point group [Space Group] | Lattice parameters (Å) | \(E_{coh}\) eV atom\(^{-1}\) | \(\Delta H_m\) eV atom\(^{-1}\) (at 298 K) |
|-----------------|---------------------------|------------------------|------------------|--------------------------|
| Cr (N = 2)      | Cubic [Im-3m]             | 2.8846 (2.88\(^{\circ}\)) | 2.8846 (2.88\(^{\circ}\)) | 2.8846 (2.88\(^{\circ}\)) | — | — |
| Graphite (N = 4)| Hexagonal [P6\(_3/mmc\)] | 2.4460 (2.464\(^{\circ}\)) | 2.4460 (2.464\(^{\circ}\)) | 6.6480 (6.711\(^{\circ}\)) | — | — |
| \(\text{Cr}_x\text{C}_y\) (N = 116)| Cubic [Fm-3m] | 10.650 (10.659\(^{\circ}\)) | 10.650 (10.659\(^{\circ}\)) | 10.650 (10.659\(^{\circ}\)) | —6.745 | —0.116 (—0.224\(^{vi}\), —0.191\(^{vii}\)) |
| \(\text{Cr}_x\text{C}_y\) (N = 40)| Orthorhombic [Pnca] | 7.0235 (7.01\(^{\circ}\)) | 12.0974 (12.15\(^{\circ}\)) | 4.4182 (4.53\(^{\circ}\)) | —7.084 | —0.109 (—0.125\(^{\circ}\), —0.111\(^{\circ}\)) |
| \(\text{Cr}_x\text{C}_y\) (N = 20)| Orthorhombic [Pnma] | 5.5183 (5.53\(^{\circ}\)) | 2.8163 (2.82\(^{\circ}\)) | 11.4949 (11.48\(^{\circ}\)) | —7.415 | —0.105 (—0.094\(^{\circ}\), —0.088\(^{\circ}\)) |

\(N\) = Number of atoms within the crystal lattice used for calculation.
Experimental values of lattice parameters in parenthesis, i-v [27–31].
Experimental values of enthalpy of formation in parenthesis, vi, vii [32, 33].
Metallicity

The metallicity, $f_m$ of the crystal systems can be estimated by [34]:

$$f_m = \left( \frac{n_m}{n_e} \right) = \left( \frac{k_B T D_f}{n_e} \right) = \left( \frac{0.026 D_f}{n_e} \right)$$

where $D_f$ is the DOS value at the fermi level in electrons/eV, $T$ is the temperature at 298 K, $n_m$ and $n_e$ are the thermal excited electrons and valence electron density, $k_B$ is the Boltzmann constant $=8.617 \times 10^{-5}$ eV.K$^{-1}$.

Here, $n_e = V_E/V_{Cell}$, where $V_E = \text{total number of valence electrons and } V_{Cell} = \text{the cell volume. The metallicity has been calculated as 0.092 99, 0.002 25, 0.015 76, 0.020 62 and 0.015 61 for Cr, C (graphite), Cr}_23C_6, \text{Cr}_7C_3, \text{and Cr}_3C_2 respectively. The calculated results are shown in table 2.}$

Order of metallicity: Cr $>$ Cr$_7C_3$ $>$ Cr$_{23}C_6$ $>$ Cr$_3C_2$ $>$ C (Graphite).

Density of states, electron density distribution and population analysis

In order to take a closer look into the electronic structure of Cr, graphite and chromium carbide phases, their corresponding density of states (DOS) and partial density of states (PDOS) can be used. The DOS allows integration with respect to the electron energy and describes the dispersion of a given electronic band over the space of energy. The positive values of DOS at the Fermi level ($D_f$) indicates the metallicity and electronic conductivity of Cr, C (graphite) and chromium carbide phases.

The projection of the DOS on the atomic components permits to decipher the main contribution to the chemical bonds. For both Cr and graphite the DOS is continuous, with 0.6183 and 0.0603 states/eV-atom (figure 3) at the fermi level respectively.

For chromium carbide phases, the electronic states are discrete in nature, as seen in figure 4. It is observed that first valence band is from $-14$ to $-10$ eV, the main contribution to the electronic states/eV-atom is by the C and Cr-s orbitals. There is no band observed from $-10$ to $-8$ eV. The next valence band starts at $-8$ eV the fermi level is close to top of the valance band. There is no gap observed between the valence and conduction bands. The band extending from $-8$ to 2 eV is composed of C-2p, Cr-3p and Cr-3d orbitals indicating the Cr$_{3d}$-C$_{2p}$ mixing due to covalent bond formation between Cr–C atoms. At the fermi level, the density of states for Cr$_7C_3$, Cr$_3C_2$ and Cr$_{23}C_6$ are 0.9531, 0.7260 and 0.7178 states/eV respectively, which indicates the order of covalence as Cr$_7C_3$ $>$ Cr$_3C_2$ $>$ Cr$_{23}C_6$ due to the differences in Cr$_{3d}$-C$_{2p}$ mixing for the stable chromium carbide phases.

The electron density distribution maps (figure 5) obtained, help us to evaluate the bond character of Cr atoms and the C atoms in their elemental state and also within the three chromium carbide phases. In case of 10Cr–Crystal, from figure 5(i), it is evident that the electrons are proportionally distributed throughout the

| Crystal systems | Element | Charges (e) | $V_E$ (electrons/atom) | $D_f$ (states/eV-atom) | $f_m$ |
|-----------------|---------|-------------|------------------------|------------------------|-------|
| Chromium        | Cr      | 0.000       | 7.00                   | 0.6183                 | 0.092 99 |
| Graphite        | C       | 0.000       | 2.99                   | 0.0603                 | 0.002 25 |
| Cr$_{23}C_6$    | Cr      | 0.253       | 6.16                   | 0.7178                 | 0.015 76 |
|                 | C       | -0.968      |                        |                        |       |
| Cr$_7C_3$       | Cr      | 0.453       | 5.79                   | 0.9531                 | 0.020 62 |
|                 | C       | -1.021      |                        |                        |       |
| Cr$_3C_2$       | Cr      | 0.591       | 5.38                   | 0.7260                 | 0.015 61 |
|                 | C       | -0.886      |                        |                        |       |

Figure 2. Charge (e), Total Valence Electron ($V_E$, electrons/atom), Density of states value at the fermi level ($D_f$, states/eV-atom), metallicity ($f_m$) for Cr, graphite and chromium carbide phases; $f_m$ is the metallicity.

Figure 3. Partial density of states PDOS of Cr and graphite. Fermi level is represented by dashed lines.

Figure 4. Partial density of states PDOS for Cr$_7C_3$, Cr$_{23}C_6$, Cr$_3C_2$ and C (Graphite).
crystal. For graphite, figure 5(ii) a ring structure has been observed with a bond distance of 1.412 Å between the C–C atoms, present around the ring. The C–C bond distance is similar to the bond distances observed for benzene, confirming resonance within the graphite system.

Figure 6(a) shows the electron density distribution maps of slices intersecting both Cr and C-atoms plotted from 0.01 to 1.0 e Å$^{-3}$. The electron density deformation maps (figure 6(b)) help us to determine the amount of distortion in the chromium carbide phases (relative to the
isolated atoms. The electron deformation maps clearly indicate charge-accumulation on C atoms (red areas) and charge-depletion on Cr atoms (blue areas) for all three carbides.

Cr–Cr bond distances are ranged between 2.366–2.626 Å, 2.508–2.756 Å and 2.538–2.727 Å for Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$ respectively (table 3). The Cr–C bond distances are between 2.103–2.149 Å, 1.999–2.522 Å, 2.010–2.120 Å for Cr$_{23}$C$_6$, Cr$_7$C$_3$ and Cr$_3$C$_2$ respectively. In Cr$_{23}$C$_6$, electron densities and bond lengths are closer to the original Cr bulk crystal compared to other chromium carbide phases due to higher concentration of Cr-atoms (80%–85%) within the phase. Thus, the Cr–Cr bonds which are found in Cr$_{23}$C$_6$ are similar to the original Cr bulk crystal. With the introduction of C atoms into the Cr lattice discretely, Cr crystal steadily transforms into various chromium carbide phases. This is indicated by the presence of Cr–C bonds which are observed in Cr$_{23}$C$_6$ phase (figure 6 and table 3).

Since, no C–C bond is found in the Cr$_{23}$C$_6$, the resonant characteristic of graphite is not observed in Cr$_{23}$C$_6$ crystal. Similarly, no C–C bond is observed in Cr$_7$C$_3$ and Cr$_3$C$_2$ which indicate that even with increase in C concentration (30%–45% in Cr$_7$C$_3$ and 20%–30% in Cr$_3$C$_2$) the electronic properties of graphite is not retained
in the chromium carbide phases. In Cr7C3 and Cr3C2, due to increase in C concentration, the distorted contours observed in their electron difference density maps indicate redistribution of electrons between Cr and C atoms. It can also be seen that as the C concentration increases, the distance between Cr–Cr atoms are larger while Cr–C distances are shorter, indicating a move towards covalent nature of the Cr–C bonds in Cr7C3 and Cr3C2 systems. No C–C bond is observed as C atoms are spread with large separation (>3.000 Å) within all the three phases.

Mulliken population analysis is applied to determine the average electron population and the charge calculations [34] and listed in table 3.

\[
\begin{align*}
\text{Average bond length, } L_{\text{avg}} & = \frac{\sum N_{AB}^i \cdot (L_{AB}^i) \sum N_{AB}^i}{N_{AB}^i} \\
\text{Average electron or overlap population, } n_{\text{avg}}^A & = \frac{\sum N_{AB}^i \cdot (n_{AB}^i) \sum N_{AB}^i}{N_{AB}^i}
\end{align*}
\]

where, A and B are arbitrary atoms forming stable bonds in a metal carbide system.

\[N_{AB}^i = \text{ Total number of } i \text{ bonds between A and B in the cell},\]
\[L_{AB}^i = \text{ Bond between A and B atoms},\]
\[n_{AB}^i = \text{ electron population between A and B atoms}.\]

The Mulliken overlap population in Cr metal is 0.6531 e/bond whereas for graphite it is calculated to be 1.5736 e/bond, indicating that the Cr atoms have less than single bond and the C atoms in graphite have 1.5 bond (resonating single and double bond) characters in their respective crystal lattices. The average overlap population for the Cr–Cr bond in Cr23C6, Cr7C3 and Cr3C2 are observed to be 0.0845, −0.0583 and −0.0762 e/bond respectively. This close to zero (negative value) of the overlap population indicate that there is no Cr–Cr interaction in Cr23C6 and Cr7C3 systems. For Cr23C6, the overlap population value is also significantly low, which indicate sparse Cr–Cr interaction. The average overlap population for the Cr–C bond in Cr23C6, Cr7C3 and Cr3C2 are observed as 0.3160 e/bond, 0.2888 e/bond and 0.5347 e/bond respectively. This indicates that the Cr–C binding is the strongest in Cr3C2 compared to Cr23C6 and Cr7C3.

**Electronic properties of Fe-substituted chromium carbides**

Of the three chromium carbide phases, Cr3C2 is found to be the most stable based on cohesive energies and enthalpies of formation (table 1). Based on Mulliken charges in Cr3C2, there are three types of Cr-atoms (Cr1, Cr2 and Cr3) and two types of C-atoms. The Mulliken charges of Cr3C2 are listed in table 4. From experimental findings of Varmaa et al [19] it was observed that the metal alloy carbides exhibited a ratio of 2:1 for Cr:Fe. Hence, in this study the effect of replacing one Cr atom with Fe-atom, out of the three Cr atoms in Cr3C2 will be investigated. This generates three different Fe-substituted Cr3C2. We have represented them as Cr2Fe1C2, Cr2Fe2C2 and Cr2Fe3C2 where Fe-atom replaces Cr1, Cr2 and Cr3 respectively. In the following sections we have discussed the electronic properties, cohesive energies, and enthalpies of formation of the Fe-substituted chromium carbides on substitution of Cr atoms by Fe.

**Metallicity**

Using equation (4), the metallicity of Fe-substituted chromium carbides has been estimated. The metallicity of Cr2Fe3C2 is found to be highest among the Fe-substituted chromium carbides (table 5) and is also higher than that of Cr3C2 and Cr23C6.

### Table 4. List of the Mulliken charges (e) for Cr3C2.

| Crystal system | Mulliken charges (e) |
|----------------|----------------------|
|                | Cr1                  | Cr2                  | Cr3                  | C1                  | C2                  |
| Cr3C2          | 0.194                | 0.864                | 0.713                | −0.831              | −0.952              |
|                | 0.210                | 0.871                | 0.720                | −0.834              | −0.954              |

### Table 5. Total Valence Electron (VE, electrons), Valence electron density (n_e, electrons/Å^3), Density of states value at the fermi level (D_f, states/eV-atom), metallicity (f_m).

| Crystal Systems | V_E (electron or e) | n_e (e/Å^3) | D_f (states/eV-atom) | f_m |
|-----------------|---------------------|-------------|----------------------|-----|
| Cr3C2           | 216.0               | 1.2054      | 0.7260               | 0.015 61 |
| Cr2Fe1C2        | 224.0               | 1.2737      | 0.7578               | 0.015 46 |
| Cr2Fe2C2        | 224.0               | 1.2945      | 0.6973               | 0.014 00 |
| Cr2Fe3C2        | 224.0               | 1.3067      | 0.8209               | 0.016 33 |
Density of states, electron density distribution and population analysis

Figure 7 represents the partial density of states in terms of electronic contribution with regards to Cr, Fe and C atoms for Cr$_3$C$_2$ and the Fe-substituted chromium carbides. At the Fermi level, the total density of states is 0.7260, 0.7578, 0.6973 and 0.8209 states/eV-atom for Cr$_3$C$_2$, Cr$_2$Fe$_1$C$_2$, Cr$_2$Fe$_2$C$_2$ and Cr$_2$Fe$_3$C$_2$ respectively which are significantly dominated by Cr-3d and Fe-3d contribution. It can be seen that from $-14$ eV to $-10$ eV, the main contribution to the electronic states/eV-atom is by the C-2s bands. There is also no band observed from $-10$ eV to $-8$ eV for both for Cr$_3$C$_2$ and the Fe-substituted chromium carbides.

The band extending from $-8$ eV to $2$ eV is composed of C-2p, Cr-3p, Cr-3d, Fe-3p and Fe-3d bands where maximum contribution is from C-2p, Cr-3d and Fe-3d orbitals. At the Fermi level major contributions are from the metal 3d orbitals, typical of transition metals. However, some differences in electronic contributions can be

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Figure 7. PDOS of Cr$_3$C$_2$ and Fe-substituted chromium carbide systems. Fermi level is represented by dashed lines.
observed. In Cr$_2$Fe$_3$C$_2$, the Fe-3d electronic contribution was observed to be higher than Cr$_1$-3d and Cr$_2$-3d states, at the Fermi level. This indicates in case of Cr$_2$Fe$_3$C$_2$, the metallicity is due to Fe and is comparatively higher than in cases of Cr$_2$Fe$_1$C$_2$ and Cr$_2$Fe$_2$C$_2$ systems. In Cr$_2$Fe$_1$C$_2$ and Cr$_2$Fe$_2$C$_2$ systems, the metallic contribution of Cr and Fe is quite similar at the Fermi level. Also, the band between $-8$ to $-2$ eV is composed of C-2p, Cr/Fe-3p and Cr/Fe-3d bands indicating the metal-3d and C-2p mixing forming covalent bonds between metal and C atoms. However, a point to be noted here is the bands in Cr$_2$Fe$_3$C$_2$ are very similar to Cr$_3$C$_2$ and the peak at $-5$ eV are symmetric indicating stronger mixing of C-p and M-d orbitals to from covalent bonds.

In Cr$_2$Fe$_1$C$_2$, Cr$_2$Fe$_2$C$_2$ and Cr$_2$Fe$_3$C$_2$ systems, no significant change is observed in the electron density distribution maps in comparison to the Cr$_3$C$_2$ system. However, the electron deformation density maps (figure 8), shows distinct difference between the four systems. In Cr$_3$C$_2$, Cr$_2$Fe$_2$C$_2$ and Cr$_2$Fe$_3$C$_2$ systems for Cr$_2$Fe$_1$C$_2$, charge-accumulation areas(red) are seen around C-atoms and charge-depletion areas(blue) around the both Cr and Fe atoms. In Cr$_2$Fe$_1$C$_2$ red area around the Fe atoms indicates slight charge-accumulation. This is also reflected in the Mulliken charges of Fe in the in Cr$_2$Fe$_1$C$_2$.

The difference in the Mulliken charges of the Cr and Fe atoms in the three systems in comparison to the original Cr$_3$C$_2$ listed in in table 6 is of significance. The Fe atoms have lesser positive values compared to the Cr atoms they are substituting in each system. In Cr$_2$Fe$_1$C$_2$, Fe atoms flip to negative values, explaining the distortion observed in the electron difference density distribution map (figure 8(ii)).

Using equations (5) and (6), the average bond length and overlap population for the Fe-substituted chromium carbides were calculated. Table 7 summarises the bond distances and electron population per bond for the three Fe-substituted chromium carbides. The average overlap population of the metal-carbon bonds indicates that the Fe–C bond in Cr$_2$Fe$_1$C$_2$ to be the highest at 0.5912 e/bond indicating more covalence than Cr–C bond. The average overlap population of most of the metal-metal bonds is close to zero and similar to the Cr–Cr bonds in Cr$_3$C$_2$ except for two cases. First, the Fe–Cr bond in Cr$_2$Fe$_1$C$_2$ at 0.2642 e/bond and secondly,

Table 6. List of Mulliken charges (e) of Cr and Fe atoms for Cr$_3$C$_2$ and Fe-substituted chromium carbides.

| Crystal systems | Mulliken charges (e) |
|-----------------|---------------------|
|                 | Cr$_1$  | Cr$_2$  | Cr$_3$  | Fe     |
| Cr$_3$C$_2$     | 0.194   | 0.864   | 0.713   |        |
|                 | 0.210   | 0.871   | 0.720   |        |
| Cr$_2$Fe$_1$C$_2$ | 1.140   | 0.928   | $-0.390$|        |
|                 | 1.148   | 0.926   | $-0.367$|        |
| Cr$_2$Fe$_2$C$_2$ | 0.540   | 0.944   | 0.147   |        |
|                 | 0.546   | 0.937   | 0.148   |        |
| Cr$_2$Fe$_3$C$_2$ | 0.442   | 0.995   | 0.131   |        |
|                 | 0.438   | 1.024   | 0.166   |        |

Figure 8. Electron deformation density maps plotted from $-0.02$ to $0.1$ e Å$^{-3}$. 

Mater. Res. Express 7 (2020) 056508 A Ganguly et al
Cr–Cr bond in Cr$_2$Fe$_2$C$_2$. All metal-metal overlap population (Cr–Cr, Fe–Cr and Fe–Fe) in Cr$_2$Fe$_3$C$_2$ are close to zero indicating no metal-metal atom interactions in Cr$_2$Fe$_3$C$_2$ system.

In Cr$_2$Fe$_1$C$_2$ system, the Fe–C bonds are found to be slightly longer than Cr–C bonds whereas in Cr$_2$Fe$_2$C$_2$ and Cr$_2$Fe$_3$C$_2$ systems, the Fe–C bonds are found to be slightly shorter than Cr–C bonds indicating the electronic interaction Fe–C bonds in Cr$_2$Fe$_2$C$_2$ and Cr$_2$Fe$_3$C$_2$ systems is more covalent in nature, thus stating the differences between the Fe-substituted chromium carbides.

Cohesive energies, enthalpies of formation of Cr$_3$C$_2$ and Fe-substituted chromium carbides
Using equation 1 and 2, the enthalpies of formation and cohesive energies for Fe-substituted chromium carbides were calculated and listed in table 8. The cohesive energy values are $-6.966$, $-6.999$ and $-7.029$ eV atom$^{-1}$ and the enthalpies of formation are $-0.009$, $-0.030$ and $-0.048$ eV atom$^{-1}$ for Cr$_2$Fe$_1$C$_2$, Cr$_2$Fe$_2$C$_2$ and Cr$_2$Fe$_3$C$_2$ respectively. The formation enthalpy for Cr$_3$C$_2$ is lesser than any of the Fe-substituted chromium carbides. Of the three Fe-substituted chromium carbides, Cr$_2$Fe$_3$C$_2$ has the minimum value. The lower the formation energy and cohesive energies of the system, the more thermodynamically stable the system is. So, based on the cohesive energies and the enthalpy of formation values, Cr$_2$Fe$_3$C$_2$ is found to be thermodynamically the most stable Fe-substituted chromium carbide.

Conclusions
In summary, we investigated the structural and electronic properties of the bulk phases of chromium carbide in comparison to the Cr metal to study the nature of bonding as Cr is transformed into its various stable phases when C concentration steadily increases within the crystal system by using DFT calculations. The structural and electronic properties of Fe-substituted chromium carbides were also investigated. For chromium carbides, the calculated lattice parameters, cohesive energy and enthalpy of formation are in good agreement with the experimental findings and reaffirmed their order of stability as Cr$_3$C$_2$ > Cr$_7$C$_3$ > Cr$_{23}$C$_6$.

On investigating the Fe-substituted chromium carbide, based on the values obtained for the formation enthalpy and Mulliken charges for the Fe-substituted chromium carbide, it can be concluded that the probability of formation of Cr$_2$Fe$_1$C$_2$ is lower in comparison to Cr$_2$Fe$_2$C$_2$ and Cr$_2$Fe$_3$C$_2$. This is also...
substantiated by the negative Mulliken charge and charge-accumulation on the Fe atoms in Cr$_2$Fe$_3$C$_2$ that could destabilize the system.

Cr$_2$Fe$_3$C$_2$ is found to be the most stable phase amongst the Fe-substituted chromium carbide. Also, the PDOS graphs Cr$_2$Fe$_3$C$_2$ indicate that the mixing of Fe/Cr-d and C-p in the $-8$ to $-4$ eV region to be stronger, stabilizing the metal–C bonds.

Finally, we find that the bonding in chromium carbides and Fe-substituted chromium carbides has a mixed character of metallic and covalent nature. Cr$_7$C$_3$ showed the highest metallicity among the three phases followed by Cr$_3$C$_2$ and Cr$_2$$_3$C$_6$. Through PDOS, it is observed that the Fermi level is at the top of the valence band confirming the metallic nature of the chromium carbides and the Fe-substituted chromium carbides. POS also provide evidence about the covalent bonds formed by the interaction of Cr/Fe-3d and C-2p overlap and metallic interactions between Cr-3d and Fe-3d. We further hope to study the interaction of adsorbents with the chromium carbide and Fe-substituted chromium carbide surfaces using DFT calculations.

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