

Pressure-induced Phase Transitions in $\text{Ti}_{1-x}\text{V}_x\text{C}$ Solid Solution

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Abstract: In present paper we have analyzed the relative structural stability and pressure dependent B1→B2 structural phase transformations in $\text{Ti}_{1-x}\text{V}_x\text{C}$ solid solution. For the present work, we have used three-body force potential model which includes the long range as well as short range interactions, where Coulomb and three body interactions are the contents of long range part and the van der Waals multipole interactions and the Hafemeister and Flygare overlap repulsive interactions (effective up to the next nearest neighbors) makes the short range part. The calculated transition pressures are 490, 511, 531, 552 and 572 GPa for TiC, $\text{Ti}_{0.75}\text{V}_{0.25}\text{C}$, $\text{Ti}_{0.50}\text{V}_{0.50}\text{C}$, $\text{Ti}_{0.25}\text{V}_{0.75}\text{C}$, and VC compounds respectively. The Born criterion for stability is found to be valid in $\text{Ti}_{1-x}\text{V}_x\text{C}$ solid solution.

Keywords: Phase transition, Transition metal carbides, High pressure, Three body interaction, Rocksalt, CsCl

1. Introduction

The refractory metal compounds, especially carbides are of great importance to the scientific community, which determines their scientific, technological, and commercial importance. Because of their effective use in variety of industries such as petroleum, electronics, aerospace, high power, high-temperature engineering, mechanical engineering, nuclear industry, and chemical industry^{1,2} but also for technological applications in low temperature fuel cells, cutting tools, information storage technology and optoelectronic devices, hard coatings, thin films for electronic devices. Refractory carbide materials have special characteristic, such as high melting temperature, extreme hardness, electrical resistivity, magnetic susceptibility, superconductivity and chemical resistance. These are brittle, show metallic

lustre; metallic conductivity and few of them are of superconducting nature. Some experimental and theoretical work indicates that the refractory metal compounds combine covalent, metallic as well as ionic type bonding due to some charge transfer and shows unique properties as ultra hard in nature because of the great degrees of covalency³. The structural, electronic, mechanical and thermal properties of some transition metals and their carbides have been investigated through different theoretical methods⁴⁻⁷. The high pressure behavior, interatomic interaction potentials, P-V diagrams and phase transitions under pressures of transition metal carbides are investigated by using different approximations^{11,12,13,14}. Srivastava et al.⁹ and Singh et al.¹⁰ have recently reported the structural properties and the pressure induced structural phase transition of transition metal carbides (TMCs) by ab initio method using the SIESTA code and rigid ion model, respectively. Ahuja et al.¹⁴ have predicted NaCl (B1) to CsCl (B2) type phase transitions in TiC, TiN, and TiO using the FPLMTO method. The different properties of ternary compounds of transition metal carbides have also been studied by many workers through different models¹⁵⁻¹⁶.

1. Theory and Method of Computation

The classical understanding on the phase stability of solid shows that as the pressure is applied, particular phase of the solid becomes unstable, causes a change in the density, so the volume and consequently leads to the overlapping of the electron shells of the adjacent ions and so the phase transition takes place. Thus, as the pressure increases, these NaCl (B1) type materials are expected to transform into the CsCl (B2) structure. The Gibbs free energy ($G = U + PV - TS$) describes the stability of the system at a given set of thermo dynamical condition. The phase transition is a phenomenon where the parental structure transforms to the most stable structure at elevated pressure and/or temperature and the stability of any system can be explained on the basis of minimization of the total energy. Internal energy of the system can be expressed as

$$U(r) = -\frac{\alpha_m e^2 z}{r} [z + 2nf(r)] - \frac{C}{r^6} - \frac{D}{r^8} + nb\beta_{+-} \exp \frac{(r_1 + r_2 + r)}{\rho} \\ + n' \frac{b}{2} \beta_{++} \exp \frac{(2r_1 - kr)}{\rho} + n' \frac{b}{2} \beta_{--} \exp \frac{(2r_2 - kr)}{\rho},$$

where the first two terms are the potential energies due to long range coulomb and three body interactions⁹, third term is due to van der Waals interaction governed by dipole-dipole (d-d) and dipole-quadrupole (d-q)

interactions and, the last three terms are the overlap repulsive interactions represented by Hafemeister and Flygare (HF) potential effective up to the next nearest neighbour ions.

2. Result and Discussion

The model parameters ρ , b , $f(r)$ are calculated using the measured values of the equilibrium inter ionic spacing, second order elastic constants reported in Table 1 and following the equilibrium conditions. The calculated values of hardness parameters (ρ), range parameter (b) and three body interaction parameter ($f(r)$) for $\text{Ti}_{1-x}\text{V}_x\text{C}$ solid solution in its each phase B1(B2) given in Table 2 and are utilized to compute the internal lattice energies of B1(B2) type structures for TiC, VC and their compound $\text{Ti}_{1-x}\text{V}_x\text{C}$ at different compressed volume and corresponding pressure. Under compression, the calculation shows that the transition pressure decreases as we increase the V composition at the site of Ti in TiC. The calculated equilibrium inter ionic spacing r_o are given in table 3 shows the present calculated values are close match with the other theoretical¹⁰ and experimental⁸ values. The total energies at difference pressure have been calculated, using the minimization technique to found equilibrium inter ionic separation r_o associated with minimum energies for B1 type and B2 type phases, respectively. Figure 2 and 3 shows the variation of the cohesive energy as a function of the volume for TiC and VC in the two phases: rocksalt (B1) and CsCl (B2). The preference for the rocksalt structure (the cubic symmetry) may be traced back to the ionic character of the C-atoms, seems that the phase transition has become from B1 phase to B2 phase and this is essential condition for relative stability of the two competitive phases¹⁸.

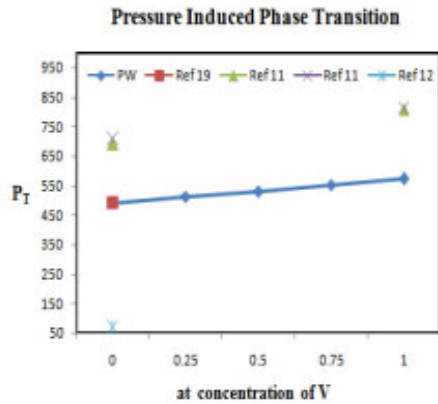


Fig. 1 Pressure Induced Phase Transition of $\text{Ti}_{1-x}\text{V}_x\text{C}$ for both structures B1 and B2; as a function of composition (V).

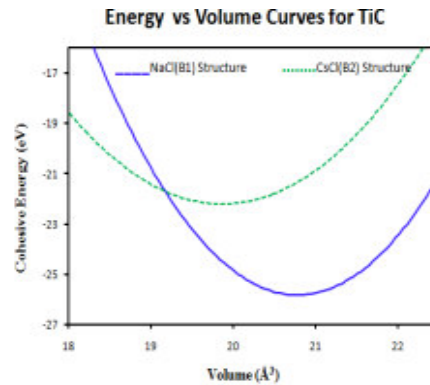
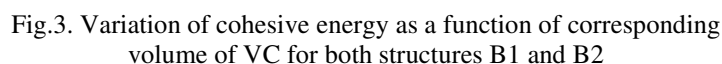


Fig.2. Variation of cohesive energy as a function of corresponding volume of TiC for both structures B1 and B2.



X	r_o	C_{11}	C_{12}	C_{44}
TiC	2.165 ⁸	5.13 ¹⁹	1.06 ¹⁹	1.78 ¹⁹
VC	2.083	5.00 ¹⁹	2.90 ¹⁹	1.50 ¹⁹

X	ρ		b		f(r)		t_{α}		U		P_T
	B_1	B_2	B_1	B_2	B_1	B_2	B_1	B_2	B_1	B_2	
0	0.621 0.200 ¹⁰	0.431	9.764 0.534 ¹⁰	3.74	2.111	4.046	2.164 2.170 ¹⁰ 2.165 ⁸	2.326 2.270 ¹⁰ 2.270 ¹⁰	-25.80 - 25.69 ¹⁰	-22.20 - 24.95 ¹⁰	490 490 ⁹ 691 ⁹ 709 ⁹ 68 ¹⁰
0.25	0.599	0.411	9.761	4.469	0.792	1.589	2.145	2.308	-24.65	-20.75	511
0.50	0.577	0.391	9.757	5.199	- 0.527	- 0.869	2.125	2.290	-23.49	-19.30	531
0.75	0.554	0.370	9.754	5.928	- 1.846	- 3.326	2.106	2.272	-22.34	-17.85	552
1.0	0.532	0.350	9.750	6.657	- 3.165	- 5.784	2.086	2.254	-21.18	-16.40	572 807 ⁹ 813 ⁹

3. Conclusions

Our results predicted that the rocksalt structure is more favorable for TiC and VC than the CsCl one. The calculated phase transitions from rocksalt to CsCl for $\text{Ti}_{1-x}\text{V}_x\text{C}$ solid solutions are in reasonable agreement with the previous calculations. An overall assessment shows that in general, our values are close to experimental data and give a better match than the theoretical data. Since there are less experimental data available for this hypothetical compound, therefore, more experimental measurements and first-principle calculations are needed in order to obtain more accurate and reliable results. Finally, we conclude that the three body potential approach has a reasonable model for more realistic predictions of the relative structural stability, phase transition and high-pressure behavior of $\text{Ti}_{1-x}\text{V}_x\text{C}$ solid solution based on the framework of semi-classical theory. In view of the above results and discussion we hope that the findings of this paper will certainly simulate the work on the mixed systems ($\text{Ti}_{1-x}\text{V}_x\text{C}$ solid solution).

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