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First-principles analysis of silicon substitution effects on the structural stability, thermal and mechanical characteristics of the Ti_3AlC_2 MAX Phase

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Abstract*— In this study, the pseudopotential method within the framework of density functional theory (DFT) is applied to investigate the impact of silicon (Si) insertion on the structural stability, as well as the thermal and mechanical properties, of the layered ternary Ti_3AlC_2 MAX phase. Our results for cell parameters and bulk modulus values show good agreement with experimental data and previous theoretical studies. The incorporation of Si into the Ti_3AlC_2 MAX phase leads to a notable increase in the lattice parameter c (along the z-axis), attributed to the substitution of Al by Si, which alters the bonding environment, particularly the Ti-Al bonds, resulting in shorter and stronger Ti-Si bonds. This substitution enhances the overall bonding strength within the crystal structure, leading to improved rigidity and thermodynamic stability of the Ti_3AlC_2 MAX phase. Comparatively, the Ti_3AlC_2 MAX phase exhibits greater stability and rigidity within the hexagonal α structure. The insertion of Si further enhances these properties, maintaining structural stability and rigidity even at elevated temperatures and pressures up to 1000 K and 6 GPa, respectively. The pristine Ti_3AlC_2 MAX phase exhibits mechanical stability, brittleness, significant hardness, and low compressibility under uniaxial stress along the <xx> and <zz> directions. Notably, the introduction of Si significantly enhances the thermodynamic stability, rigidity, stiffness, and Vickers hardness of the compound.

***Keywords*— DFT Calculations, MAX Phases, Structural stability, Mechanical Properties, Thermal Properties**

I. INTRODUCTION

MAX phases represent a fascinating class of materials with an exceptional and sometimes unique combination of metallic and ceramic characteristics under various conditions [1, 2]. These remarkable features mainly originate from their distinctive structures, which consist of alternating layers of octahedral MX interleaved with “metallic”, A nano-atomic layers. Additionally, the strong covalent bonding between X atoms and the pronounced repulsion between electrons in the 5d (M) transition metals play a crucial role in shaping their properties. The introduction of alloying elements into these materials can significantly influence their physical properties. Notably, it has been found that the fourth element can stabilize or facilitate the formation of previously non-existent ternary phase. Moreover, it can trigger new properties not observed in the host system and thereby enabling strong correlation between composition and the physical properties of these materials [3].

In this context, the main objective of the present study is to investigate the effects of silicon alloying on the stability, thermal, and mechanical properties of the ternary Ti_3AlC_2 MAX phase using DFT calculations. Silicon atoms were progressively substituted for aluminum ones in the Ti_3AlC_2 alloy to evaluate their impact. The thermal stability of the resulting system, in both alpha (α) and beta (β) structures, were deeply investigated, considering pressure, temperature, and silicon concentration variations. Furthermore, the Quasi-Harmonic approximation was applied to restore the temperature effects neglected by the Born-Oppenheimer approximation on which the first-principles calculations are based. Additionally, the mechanical properties of the $Ti_3(Al_{1-x}Si_x)C_2$ were determined by exploring the strain-stress curves in the small deformation range. The results revealed a strong dependence of the studied properties on the silicon concentration, highlighting its significant influence on the material’s behavior. The

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manuscript is organized as follow: The first section introduces the objectives and significance of the present study. The second section details the pseudopotential method employed in our calculations, including the theoretical framework and computational details. The third section presents the main results, followed by a compressive discussion. Finally, the concluding section summarizes the key findings.

II. COMPUTATIONAL DETAILS

All the results presented in this study are obtained using the pseudopotential method within the framework of density functional theory (DFT) as implemented in the Quantum-Espresso package [4]. The exchange-correlation energy was treated using the Perdew-Burke-Ernzerhof (PBE) [5] functional within the generalized gradient approximation (GGA), and Vanderbilt ultrasoft pseudopotentials [6] were employed. The kinetic energy cut-off was set to 40 Ry, and the Brillouin zone was sampled using a well-converged k-point mesh 8×8×4. Structural relaxations were performed using the Broyden-Fletcher-Goldforb-Shanno (BFGS) [7] algorithm until the total energy converged to less than 10^{-5} eV/atom, and the maximum force was reduced to below 0.004 eV/Å.

III. RESULTS AND DISCUSSION

A. Stability and structural properties

As a preliminary step, total energy versus volume calculations were performed for the Ti_3AlC_2, $Ti_3(AlSi)C_2$, and Ti_3SiC_2 MAX Phases, considering their two structural prototypes, α and β. Details of these prototypes are provided in TABLE I and Fig.1. The energy-volume data were fitted using the universal Birch-Murnaghan equation of state. The resulting lattice parameters (a and c), bulk moduli (B), and heats of formation (ΔH_f) are summarized in TABLE II, alongside theoretical and experimental values from the literature to enrich the discussion and provide comparative context.

TABLE I

CRYSTALLOGRAPHIC DETAILS OF THE A AND B STRUCTURES (SG: $P6_3$/MMC N°194)

	Ti	Al	C
α phase	2*a*, 4*f* (z=0.127)	2*b*	4*f* (z=0.062)
β phase	2*a*, 4*f* (z=0.126)	2*c*	4*f* (z=0.068)

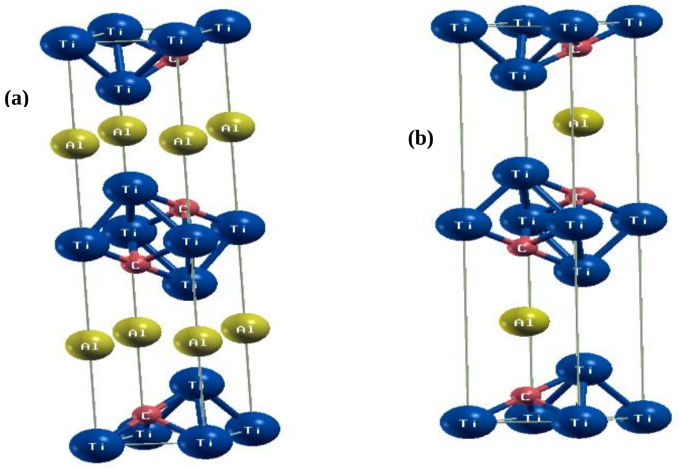

Fig.1: Crystal structures of: (a) α and (b) β MAX Phases.

The predicted cell parameters and bulk modulus of the Ti_3AlC_2, and Ti_3SiC_2 MAX Phases show good agreement with available theoretical [7-9] and experimental [10, 11] data. However, to our knowledge, there are no available results for the $Ti_3(AlSi)C_2$ in the literature for comparison, Nonetheless, our predictions have enabled us to observe the impact of silicon incorporation on the structural properties of Ti_3AlC_2. Specifically, depending on its position within the α or β structures, the incorporation of Si into the Ti_3AlC_2 alloy slightly reduces the *a* parameter, while significantly increasing the *c* parameter. This behaviour is attributed to the elongation of Ti-(Al/Si) bond distances

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along the z-direction. Notably, the presence of Si enhances both the stability and rigidity of the Ti_3AlC_2 alloy. Furthermore, the α structure consistently demonstrates greater stability and rigidity than the β structure across the entire range of Si concentration at 0K.

TABLE III

CELL PARAMETERS, BULK MODULI AND HEATS OF FORMATION OF TI_3ALC_2, $TI_3(ALSI)C_2$ AND TI_3SIC_2 MAX PHASES IN A AND B PHASES.

			a (au)	**c (au)**	**B (GPa)**	**ΔH_f (eV/atom)**
Ti_3AlC_2	α	This work	5.80	35.12	157.5	**-0.8125**
		Theo	5.82[8,9]	35.18[8,9]	145[7]	
		Exp	5.81[10]	35.12[10]		
	β	This work	5.78	35.48	152.9	-0.771
		Theo	5.80[8]	35.59[8]		
$Ti_3(AlSi)C_2$	α	This work	5.75	34.33	168.0	**-0.8182**
	β	This work	5.79	35.58	161.7	-0.7702
Ti_3SiC_2	α	This work	5.75	34.33	180.0	**-0.8489**
		Theo	5.82[8]	33.53[8]		
	β	This work	5.79	35.57	173.9	-0.7933
		Theo	5.76[8]	34.20[8]		
		Exp	5.81[11]	33.52[11]	192.6[11]	

B. *Thermal properties*

The temperature effects neglected by the Born-Oppenheimer approximation, upon which all first-principles methods are based, are accounted for in the present work. Using the quasi-harmonic approximation (QHA), the variations of enthalpy and free energy with pressure and temperature for the Ti_3AlC_2, $Ti_3(AlSi)C_2$ and Ti_3SiC_2 MAX Phases were carried out and presented in Fig.2 and Fig.3 respectively. Detailed data pertaining to this model could be found in the references [12] and [13]. These variations enable a comprehensive investigation of the influence of pressure, temperature and Si concentration on the thermodynamic stability of the three MAX Phases in both their α and β structural prototypes.

The enthalpy of the Ti_3AlC_2, $Ti_3(AlSi)C_2$ and Ti_3SiC_2 alloys increases with rising pressure, while their free energy decreases with increasing temperature. These variations are monotonic, with no intersection of the curves, indicating the absence of an α→β phase transformation across the investigated pressure and temperature ranges. As a result, only the α phase will be considered in the subsequent analysis

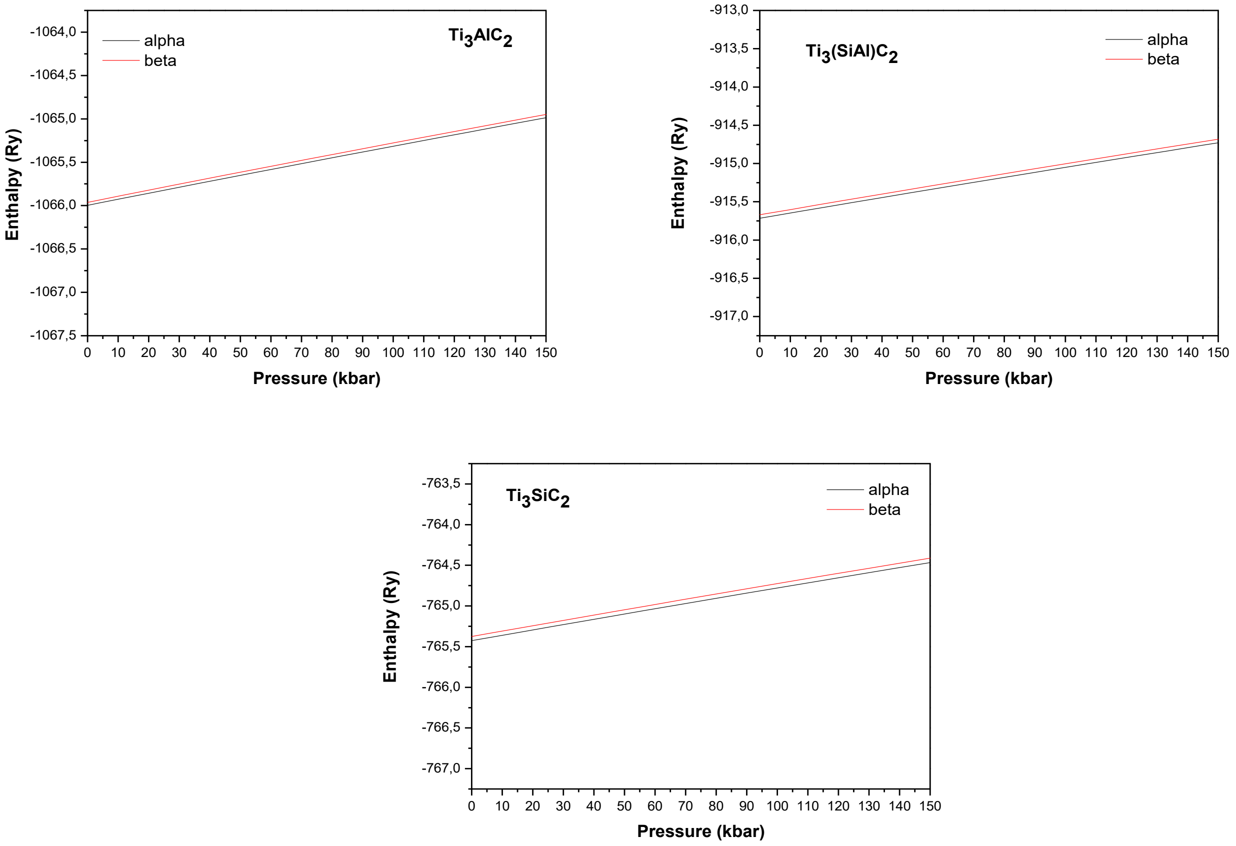

Fig.2: Variation with pressure of the enthalpy of Ti$_3$AlC$_2$, Ti$_3$(AlSi)C$_2$ and Ti$_3$SiC$_2$ in α and β phases.

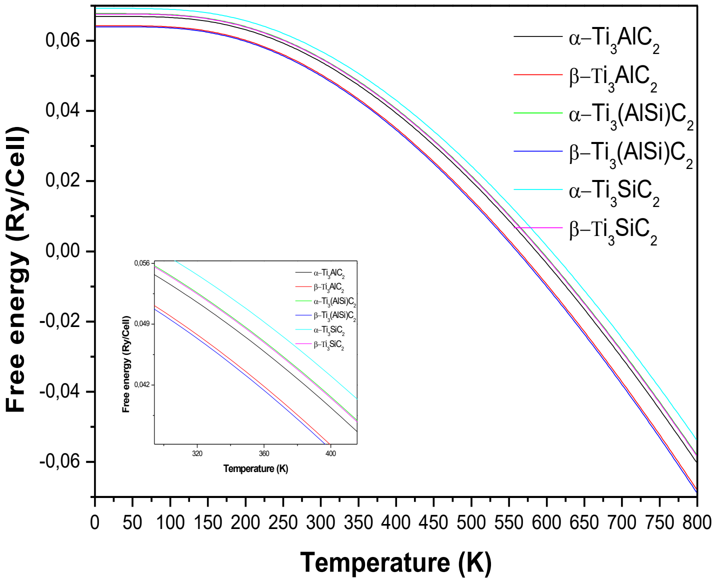

Fig.3: Variation with temperature of the free energy of Ti$_3$AlC$_2$, Ti$_3$(AlSi)C$_2$ and Ti$_3$SiC$_2$ in α and β Phases

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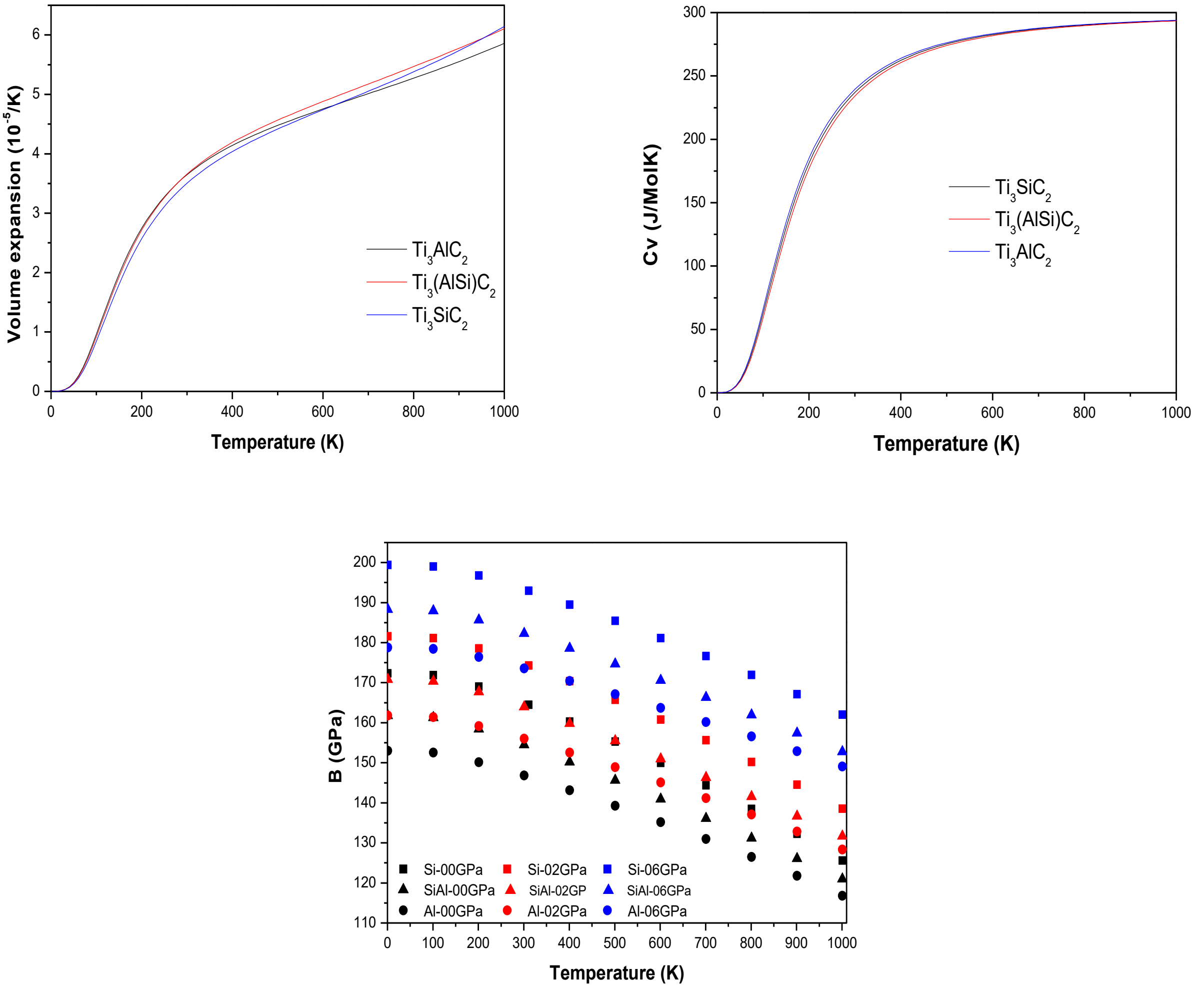

Fig 3: Variation with temperature of: (a) volume expansion, (b) heat capacity of the Ti_3AlC_2, $Ti_3(AlSi)C_2$ and Ti_3SiC_2 and (c) bulk moduli of the Ti_3AlC_2, $Ti_3(AlSi)C_2$ and Ti_3SiC_2 considering various pressure.

The effects of temperature on volume expansion, heat capacity, and bulk modulus of the Ti_3AlC_2, $Ti_3(AlSi)C_2$ and Ti_3SiC_2 Max phases are also analysed in the present study, with the corresponding trends illustrated in Fig.3. Notably, for bulk modulus calculations, three different pressure values; 0, 2 and 6 GPa were considered to examine the combined effect of pressure, temperature, and Si concentration on the rigidity of the Ti_3AlC_2 MAX phase. Due to electronic contributions, the volume expansion of the different alloys increases sharply in the temperature range [0-300 K]. Beyond this range, the expansion follows a linear trend with increasing temperature. The insertion of silicon has a negligible effect on the volume expansion of Ti_3AlC_2 at both low and high temperatures, owing to the strong similarity between Ti-Al and Ti-Si bonds. A similar pattern is observed for the heat capacity, which increases significantly in the range [0-400 K], following a T^3 dependence at low temperatures as stipulated by Debye’s model. At sufficiently high temperatures, however, the heat capacity approaches the classical Dulong-Petit limit. Finally, the rigidity of the three MAX Phases is found to be highly sensitive to both pressure and temperature. Increasing pressure reduces the volume of the alloys and consequently enhances their rigidity, while higher temperatures have the opposite effect, leading to reduced rigidity. Among the alloys, Si-containing phases exhibit the highest rigidity, although this property decreases consistently with temperature, similar to other MAX Phases. Roughly speaking, the rigidity of the different alloys drops by approximately 23% at 1000K, highlighting their potential as promising materials for high-temperature applications.

C. Mechanical Properties

The elastic constants are essential for assessing the structural and mechanical stability of materials. The predicted elastic constants (C_{11}, C_{12}, C_{13}, C_{33}, and C_{44}) for the Ti_3AlC_2, $Ti_3(AlSi)C_2$, and Ti_3SiC_2 MAX Phases are presented in TABLE III. The predicted values show fairly good agreement with the theoretical [7, 11, 14, 16] and experimental results [14-16]. Furthermore, the elastic constants for the Ti_3SiC_2 MAX Phase are significantly higher than those for Ti_3AlC_2, indicating greater stiffness and rigidity. Meanwhile, the $Ti_3(AlSi)C_2$ phase exhibits intermediate values, reflecting its transitional nature between the two end members.

TABLE III:
ELASTIC CONSTANTS C_{IJ} (GPA), BULK MODULUS *B* (GPA), YOUNG'S MODULUS *E* (GPA), SHEAR MODULUS *G* (GPA), PUGH'S RATIO *B/G* AND VICKERS HARDNESS H_V OF TI_3ALC_2, $TI_3(ALSI)C_2$ AND TI_3SIC_2 MAX PHASES IN A AND B PHASES. $H_V = 0.92 \left(\frac{B}{G}\right)^{1.3137} G^{0.708}$

		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	*B*	*E*	*G*	*B/G*	*Hv*
Ti_3AlC_2	**This work**	353.8	71.7	70.1	303.4	126.5	159.6	309.9	131.7	1.21	37.43
	Theo	277[7]	93[11]	70[11]	242[11]	114[11]	165[14]	297[14]	124[14]	1.33[14]	40.28[11]
	Exp	361[15]	75[15]	70[15]	299[15]	124[15]	160[16]	309[16]	131[16]	1.22[16]	-
$Ti_3(AlSi)C_2$	**This work**	364.8	78.3	77.0	315.0	134.7	168.6	322.0	136.3	1.24	39.6
	Theo	365[16]	82[16]	84[16]	338[16]	146[16]	174[16]	333[16]	141[16]	1.23	-
Ti_3SiC_2	**This work**	382.6	82.2	85.0	338.0	145.6	182.8	342.5	144.2	1.27	42.53
	Theo	326[11]	98.3[11]	115[11]	317[11]	143[11]	189[11]	297[11]	121[11]	1.56	46.75[11]
	Exp	365[15]	125[15]	120[15]	375[15]	122[15]	190[14]	341[14]	139[14]	1.37	-

All three MAX Phases are mechanically stable at 0 K in the hexagonal structure, as they satisfy the Born stability criteria for hexagonal phases [17]. Additionally, these materials exhibit low compressibility under uniaxial stress along the <xx> and <zz> directions. Based on the Pugh ratio values [17], it can be concluded that the three studied MAX phases are brittle, with the incorporation of silicon atoms slightly enhancing the ductility of the Ti_3AlC_2 phase. Finally, Ti_3AlC_2 is a relatively hard material, and the insertion of silicon further increases its Vickers Hardness.

IV. CONCLUSIONS

In this study, the pseudopotential method was employed to investigate the effects of silicon (Si) alloying on the stability, thermal, and mechanical properties of the ternary layered Ti_3AlC_2 MAX phase. The results indicate that the α structure is the most stable configuration for Ti_3AlC_2, $Ti_3(AlSi)C_2$, and Ti_3SiC_2 MAX phases. Si incorporation enhances both the thermodynamic stability and rigidity of the Ti_3AlC_2 phase, with the α structure remaining the most stable even at elevated temperatures. All three MAX phases exhibit mechanical stability at 0 K in their hexagonal structures. However, the MAX phases demonstrate brittle behavior and reduced compressibility under uniaxial stress along the <xx> and <zz> directions. Ti_3AlC_2 is identified as a relatively hard material, and Si alloying significantly improves its Vickers hardness.

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