Temperature-influenced Substitution of Si in $\text{Ti}_3(\text{Si,Al})\text{C}_2$ Solid Solution

Jun Ji

University of Jinan

Zirun YANG

Yancheng Institute of Technology

Zhenyu ZHANG

university of jinan

Dechun LI

Shandong University

Zhi Wang (✉ wangzhi@ujn.edu.cn)

School of Material Science and Engineering, University of Jinan, Jinan 250022, China

<https://orcid.org/0000-0002-8001-6648>

Liu ZHANG

Yancheng Institute of Technology

Rapid Communication

Keywords: Ti_3SiC_2 , hot-pressing sintering, solid solution, substitution behavior

Posted Date: November 6th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-102637/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

High-pure $\text{Ti}_3(\text{Si},\text{Al})\text{C}_2$ solid solutions were synthesized in the range of 1473 to 1773K. The microstructures and chemical compositions of all samples were characterized by X-rays diffraction (XRD) and scanning electron microscope (SEM). It was worthy noted that experimentally determined lattice parameter c of $\text{Ti}_3(\text{Si},\text{Al})\text{C}_2$ crystal decreased with the increasing of sintering temperature. The contents of Si and Al elements in solid solution were conducted by Vegard's Law. Gibbs energy differences (ΔG) of substitution behaviors of Si at different temperatures were also listed. With the increase of temperature, ΔG of Eq. $\text{Ti}_3(\text{Si}_{0.75}\text{Al}_{0.25})\text{C}_2 + 0.25\text{Si} \rightarrow \text{Ti}_3\text{SiC}_2 + 0.25\text{Al}$ were negative and decreased gradually, which means that the transformation from $\text{Ti}_3(\text{Si},\text{Al})\text{C}_2$ to Ti_3SiC_2 was spontaneous and had a greater tendency in higher temperatures. By analyzing the experiment data, a possible mechanism of the substitution process of Si in various temperatures was determined.

Background

MAX phase compounds (M is an early transition metal, A is an A group element, X is carbon or nitrogen) with the $P6_3/mmc$ space group were initially reported in the 1960s[1]. Due to the excellent combination of metallic and ceramic properties[2-5], including good thermal and electrical conductivity, low coefficient of thermal expansion and superior machinability, they have attracted more attention in recent years[6,7]. To date, more than 150 kinds of MAX phases have been discovered, most of which belong to 211, 312 and 413 phase.

First-principles calculations are valuable to predict the properties and behaviors of crystalline materials[8,9]. By analyzing electron-phonon coupling strengths obtained both in experiments and density functional calculations, it is predicted that Ta_2AlC might be a new superconductive MAX phase [10]. Lane[11] investigated the thermal expansions and temperature-dependent crystal structures of Ti-Al-C phase diagram in the temperature range of 373-1373K and demonstrated that thermal expansions of Ti_2AlC , Ti_3AlC_2 and $\text{Ti}_5\text{Al}_2\text{C}_3$ were higher in the c direction in contrast with a direction. Lu[12] reported the substitution behavior of Si atoms in the Ti_2AlC ceramics and calculated the formation energy of this process to be -0.37 eV.

Solid solution modification method was often used to transform ternary MAX phase to quaternary, or even quinary compounds which at least contain two M, two A or two X elements, such as $(\text{Cr},\text{Ti})_3\text{AlC}_2$ [13], $(\text{Zr},\text{Ti})_3\text{AlC}_2$ [14], $\text{Ti}_2(\text{Al},\text{Sn})\text{C}$ [15], $(\text{Ti},\text{Cu})_3(\text{Al},\text{Cu})\text{C}_2$ [16], $(\text{Zr},\text{Ti})_2(\text{Al},\text{Sn})\text{C}$ [17]. Burr[13] summarized the major advantages of quaternary MAX ceramics, indicating that they had new and outstanding mechanical properties compared with common MAX phases. As Si and Al elements have similar atomic radius, Al atoms often dissolved into Ti_3SiC_2 crystal inevitably, generating $\text{Ti}_3(\text{Si}_x\text{Al}_{1-x})\text{C}_2$ solid solution when Al was added as sintering additive via in-situ synthesis. Although some research[18-21] suggested that adding an appropriate amount of Al to initial powder mixtures can lower the sintering temperature and

improve the purity of Ti_3SiC_2 , the investigation on the temperature-induced transformation of $\text{Ti}_3(\text{Si,Al})\text{C}_2$ solid solution was very limited.

In this study, high-purity $\text{Ti}_3(\text{Si,Al})\text{C}_2$ solid solutions were synthesized at 1473, 1573, 1673 and 1773K. As the increase of sintering temperature, the content of Al decreased rapidly in $\text{Ti}_3(\text{Si,Al})\text{C}_2$ crystal. The phenomenon might be caused by the lower energy of Ti-Al bonds which were more susceptible to higher temperatures compared with Ti-Si bonds, leading to the substitution process of Si atoms.

The $\text{Ti}_3(\text{Si}_x\text{Al}_{1-x})\text{C}_2$ bulk were prepared via hot-pressing sintering using molar ratio 1.0Ti/1.2Si/0.3Al/2.0TiC powders at 1473, 1573, 1673 and 1773K respectively. The pressure was maintained at 30 MPa for 1.5 h at the specified temperatures. Finally, the sintered samples were allowed to cool naturally to room temperature before removing from the furnace. The obtained samples were polished by using SiC powder and then cleaned via ultrasonication. The phase compositions of the obtained samples were determined by XRD (D8 ADVANCE, Bruker). Their microstructures were investigated by SEM (FEIQUANTA FEG 250, USA). First-principles calculations were performed by using the plane-wave CASTEP codes based on the density functional theory (DFT) approach. The electron exchange-correlation was described using the GGA-PBE function. The plane-wave ultrasoft pseudopotential methods were exploited to present the interactions between the electrons and the ion cores and the cut-off energy was 400 eV. The virtual crystal approximation (VCA) and supercell (SC) methods were employed to construct the solid solution crystal model. VCA was introduced by assigning partial occupancies to each atomic site and SC was performed by enlarging $2 \times 2 \times 1$ supercell (48 atoms). All models were relaxed until the forces on each atom were $< 0.03 \text{ eV/\AA}$, and the stress on each atom was converged to 0.05 GPa. The maximum atom displacement was set at $0.001 \text{ \AA}$, and the total energy changes during the optimization finally converged to 10^{-5} eV/atom . Phonon dispersion calculations were performed by using the finite displacement method and the supercell was defined using a cutoff radius of $5.0 \text{ \AA}$. Gibbs energy was evaluated by employing the quasiharmonic approximation (QHA). All the modelling for first-principle calculations were shown in Supplementary materials.

Samples 1-4 were fabricated at 1473, 1573, 1673 and 1773K respectively. The phase compositions of the obtained ceramics were analyzed through XRD (Fig. 1a), where strong peaks corresponding to $\text{Ti}_3(\text{Si,Al})\text{C}_2$ were clearly shown and different crystal planes were also indexed. No obvious peaks of Ti-Si/Al alloy and TiC were discovered, indicating the complete reaction between 1473 to 1773K.

SEM images (see Fig. 2) revealed a significant change of the microstructures as increasing the sintering temperature. Large holes and relatively small grains were presented in fig.2a. As the sintering temperature up to 1573K, the number of holes and small grains reduced obviously (fig.2b). Samples 3 and 4 (fig.2c and 2d) exhibited grown grains with no obvious micropores, as well as grain boundaries were clearer than samples 1 and 2. From the analysis above, it was concluded that sintering temperature plays a significant role in in-situ synthesis of $\text{Ti}_3(\text{Si,Al})\text{C}_2$, that is, high temperature (1673-1773K) would accelerate the growth of crystals and improve densification, which was beneficial for their mechanical properties.

Partial enlarged drawing of (1 0 4), (0 0 8) and (1 0 5) planes were shown in fig. 1b. All the peaks shifted right to a bigger 2 theta degree with the increasing of temperature, which meant that the lattice parameter of $Ti_3(Si,Al)C_2$ declined. Because the radii of the Si atoms were smaller than Al, the cause for this phenomenon is the substitution behavior of Si to replace Al site in $Ti_3(Si,Al)C_2$ solid solution.

To investigate the influence of sintering temperature on the solid solution, the lattice parameters of $Ti_3(Si,Al)C_2$ and contents of Si/Al elements were calculated by using the spectrum fitting method and first-principle calculations. Vegard's law is an empirical rule, stating that the lattice parameters can be calculated from a linear interpolation of its constituent elements fraction. Herein, supercell (SC) and virtual crystal approximation (VCA) methods were used to reveal the relationship between lattice parameters and Si/Al contents. Because of the similar a value in Ti_3SiC_2 and Ti_3AlC_2 crystal, it is unsuitable for calculating Si/Al contents, c value was adopted to further calculate. The lattice parameter c was obtained by optimizing the geometry of $Ti_3(Si_x,Al_{1-x})C_2$ modeling. ($x=0, 0.125, 0.25, 0.5, 0.75, 0.875, 1$). Combined SC and VCA methods, fig. 3 plotted the lattice parameter c as a function of the atomic ratio of Al in $Ti_3(Si,Al)C_2$ solid solution. A good linear relationship was shown for VCA methods. However, when $x=0.125, 0.25$ and 0.5 for SC method, it caused a markedly higher deviation. By summarizing the analysis above, VCA was adopted to fit linear to calculate the contents of Si and Al, which can be shown in Eq.(1),

$$y = 1.1263 x + 17.615 \tag{1}$$

where y represents lattice parameter c and x is the molar ratio of Al, and the results are listed in Tab.1.

Tab.1. The calculated fraction of Al in solid solution at different temperatures.

Temperature/K	1473	1573	1673	1773
$c/\text{\AA}$	17.8256	17.8087	17.7321	17.6837
Al/ at%	18.7	17.2	10.4	6.1

It was found that at 1473K, the fraction of Al in $Ti_3(Si,Al)C_2$ was very close to that in raw materials (20 at%), indicating that almost all of Al element would present in $Ti_3(Si,Al)C_2$ crystal. As the temperature increased, masses of Al atoms will be substituted by Si, causing that Al content reduced rapidly and only 6.1 at% existed in $Ti_3(Si,Al)C_2$ at 1773K. The substitution process of Si atoms can be conducted by the following reactions:

The formation energy can be evaluated according to the following Eq:

$$E_f = E_{Ti_3(Si_{1-x-y}Al_{1-x-y})C_2} + yE_{Al} - E_{Ti_3(Si_xAl_{1-x})C_2} - yE_{Si} \quad (3)$$

To make the calculated process close to the real experiments, we simulated the transformation changed from $Ti_3(Si_{0.75}Al_{0.25})C_2$ to Ti_3SiC_2 . The modeling of $Ti_3(Si_{0.75}Al_{0.25})C_2$ was constructed by $Ti_3(Si,Al)C_2$ unit-cell enlarged by $2 \times 2 \times 1$, containing 24 Ti, 6 Si, 2Al and 16 C atoms in total. One Al atom removed from $Ti_3(Si,Al)C_2$ crystal and left a vacancy, which was then occupied by Si atom. The formation energy of this process was shown in Fig. 4. The formation energy would up to 1.78eV once the Al vacancy emerged in $Ti_3(Si_{0.75}Al_{0.25})C_2$ modeling. Subsequently, it decreased to -0.38eV when Si atom occupied the vacancy to form $Ti_3(Si_{0.875}Al_{0.125})C_2$ structure. The negative formation energy indicated that substitution of Si was spontaneous and could improve the structural stability of the solid solution. Finally, similar to the previous step, the most stable structure Ti_3SiC_2 formed after another Si atom replaced Al atom, and the formation energy value was -0.42 eV. Because the sintering was processed over 1473K, the phonon calculations were used to reveal the Gibbs energy difference of the above transformation:

The results were listed in Tab. 2.

Tab. 2. Gibbs energy difference of reaction (4) at different temperatures.

Temperature (K)	1473	1573	1673	1773
ΔG (KJ/mol)	-13.16	-13.57	-14.23	-15.85

With the temperature increased, the ΔG of reaction (4) decreased from -13.16 to -15.85 KJ/mol, suggesting that Si atoms were more preferred to substitute Al atoms at higher temperatures. Ti-Al and Ti-Si bonds properties were evaluated by calculating single point energy for Ti, Si, Al, Ti-Al, and Ti-Si model, which were shown in Tab. 3.

Tab. 3 Bond length and energy for Ti-Si and Ti-Al bond.

	Bond length (Å)	Bond energy (eV)
Ti-Si	2.6784	3.7146
Ti-Al	2.9011	2.1226

Ti-Al bond has a larger length and lower energy than Ti-Si bond, as the temperature increased, Ti-Al bond is particularly susceptible to break, forming Al vacancy in solid solution. Afterward, Si atoms fill the vacancy to generate a stronger Ti-Si bond. It was worthwhile pointing out that aggregation of Al elements was found in grain boundary (see fig. 5), which was mainly attributed to the segregation.

In conclusion, high-pure $\text{Ti}_3(\text{Si,Al})\text{C}_2$ solid solutions were fabricated at different sintering temperatures. The results demonstrated that sintering temperature not only influence crystal growth, but also determine the contents of Si and Al in $\text{Ti}_3(\text{Si,Al})\text{C}_2$. That is, the mass percentage of Si would increase gradually at higher temperature. Fig. 6 showed the mechanism of this phenomenon. Due to the lower bond energy, Ti-Al bond would prefer to fracture in high temperature, causing dissociative Al atoms and vacancy in the previous site. In order to stabilize the crystal structure, Si atoms would occupy the site to form Ti-Si bonds, which were more insusceptible as the increase of temperature. Finally, the extra Al atoms were likely to segregate in grain boundaries accompanied by Gibbs free energy reduced.

Declarations

Acknowledgements

Authors appreciate the financial supported by the National Natural Science Foundation of China (Grant No. 51872118, 51701081), the Key Research and Development Program of Shandong Province (Grant No. 2019GGX104077, 2019RKB01018), the Shandong Provincial Natural Science Foundation, (Grant No. ZR2018PEM008, ZR2019MEM055).

Reference

- [1] Nowotny H, Strukturchemie einiger verbindungen der ubergangsmetalle mit den elementen C, Si, Ge, S. *Prog Solid State Chem* 1970, **2**: 27-70.
- [2] Cai LP, Huang ZY, Hu WQ, *et al*, Fabrication, mechanical properties, and tribological behaviors of Ti_2AlC and $\text{Ti}_2\text{AlSn}_{0.2}\text{C}$ solid solutions. *J Adv Ceram* 2017, **6**: 90-99.
- [3] Yu W, Guénolé J, Ghanbaja J, *et al*, Frank partial dislocation in Ti_2AlC -MAX phase induced by matrix-Cu diffusion. *Scripta Mater* 2021, **191**: 34-39.
- [4] Yang DX, Zhou Y, Yan XH, *et al*, Highly conductive wear resistant $\text{Cu/Ti}_3\text{SiC}_2(\text{TiC/SiC})$ co-continuous composites via vacuum infiltration process. *J Adv Ceram* 2020, **9**: 83-93.
- [5] Yao P, Qian Y, Li W, *et al*, Exploration of dielectric and microwave absorption properties of quaternary MAX phase ceramic $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$. *Ceram Int* 2020, **46**: 22919-22926.
- [6] Magnus C, Cooper D, Sharp J, *et al*, Microstructural evolution and wear mechanism of Ti_3AlC_2 - Ti_2AlC dual MAX phase composite consolidated by spark plasma sintering (SPS). *Wear* DOI:

- [7] Velasco B, Gordo E, Hu L, et al, Influence of porosity on elastic properties of Ti_2AlC and Ti_3SiC_2 MAX phase foams. *J Alloy Compd* 2018, **764**: 24-35.
- [8] Togo A, Tanaka I, First principles phonon calculations in materials science. *Scripta Mater* 2015, **108**: 1-5.
- [9] Stumpf M, Biggemann J, Fey T, et al, Thermochemical calculations of the oxidation behavior of Nb_2AlC MAX phase in ZrO_2 -matrix composites. *Ceram Int* 2018, **44**: 15747-15753.
- [10] Xiang HM, Wang JM, Chen Y, et al, Prediction of superconductivity of Ta_2AlC : in situ Raman spectrometry and density functional investigations. *J Raman Spectrosc* 2014, **45**: 202-207.
- [11] Lane NJ, Vogel SC, Caspi EN, et al, High-temperature neutron diffraction and first-principles study of temperature-dependent crystal structures and atomic vibrations in Ti_3AlC_2 , Ti_2AlC , and $\text{Ti}_5\text{Al}_2\text{C}_3$. *J Appl Phys* 2013, **113**: 183519
- [12] Lu C, Piven K, Qi Q, et al, Substitution behavior of Si atoms in the Ti_2AlC ceramics. *Acta Mater* 2018, **144**: 543-551.
- [13] Burr PA, Horlait D, Lee WE, Experimental and DFT investigation of $(\text{Cr,Ti})_3\text{AlC}_2$ MAX phases stability. *Mater Res Lett* 2017, **5**: 144-157.
- [14] Solvas EZ, Hadi MA, Horlait D, et al, Synthesis and physical properties of $(\text{Zr}_{1-x}\text{Ti}_x)_3\text{AlC}_2$ MAX phases. *J Am Ceram Soc.* 2017, **100**: 3393-3401.
- [15] Yeh CL, Chiang CH, Combustion synthesis of $\text{Ti}_2(\text{Al,Sn})\text{C}$ solid solutions from Ti/Al/Sn/C samples with addition of TiC and Al_4C_3 , *Ceram Int* 2015,**41**: 6263-6268.
- [16] Nechiche M, Gauthier BV, Mauchamp V, et al, Synthesis and characterization of a new $(\text{Ti}_{1-x}\text{Cu}_x)_3(\text{Al,Cu})\text{C}_2$ MAX phase solid solution. *J Eur Ceram Soc* 2017, **37**: 459–466.
- [17] Tunca B, Lapauw T, Delville R, et al, Synthesis and Characterization of Double Solid Solution $(\text{Zr,Ti})_{(2)}(\text{Al,Sn})\text{C}$ MAX Phase Ceramics. *Inorg Chem* 2019, **58**: 6669-6683.
- [18] Xu X, Ngai TL, Li Y, Synthesis and characterization of quaternary $\text{Ti}_3\text{Si}_{(1-x)}\text{Al}_x\text{C}_2$ MAX phase materials. *Ceram Int* 2015, **41**: 9626-7631.
- [19] Zhang HB, Zhou YC, Bao YW, et al, Intermediate phases in synthesis of Ti_3SiC_2 and $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$ solid solutions from elemental powders. *J Eur Ceram Soc* 2006, **26**: 2373–2380.

[20] Zhu JQ, Mei BC, Xu XW, et al, Synthesis of single-phase polycrystalline Ti_3SiC_2 and Ti_3AlC_2 by hot pressing with the assistance of metallic Al or Si. *Mater Lett* 2004, **58**: 588–592.

[21] Pourebrahim A, Baharvandi H, Foratirad H, et al, Effect of aluminum addition on the densification behavior and mechanical properties of synthesized high-purity nano-laminated Ti_3SiC_2 through spark plasma sintering. *J Alloy Compd* 2018, **730**: 408-416.

Figures

Figure 1

XRD data for samples 1-4 with 2 theta (a) 25-80 degree; (b) 38-43 degree.

Figure 2

SEM images of (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4.

Figure 3

The calculated lattice parameters with various Al content of $\text{Ti}_3(\text{Si}_x\text{Al}_{1-x})\text{C}_2$ modeling by SC and VCA methods.

Figure 4

Formation energy for substitution of Si.

Figure 5

SEM and EDS images of grain boundary.

Figure 6

The mechanism of substitution of Si in $\text{Ti}_3(\text{Si,Al})\text{C}_2$ crystal.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supplementarymaterials.docx](#)