

EFFECT OF ALUMINIUM (Al) AND NICKEL (Ni) ADDITION ON  
FORMATION OF TITANIUM SILICON CARBIDE ( $\text{Ti}_3\text{SiC}_2$ ) VIA ARC  
MELTING

by

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requirements for the degree  
of Master of Science

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## DECLARATION

I hereby declare that I have conducted, completed research work and written the dissertation entitled “Effect of aluminium (Al) and nickel (Ni) addition on formation of  $Ti_3SiC_2$  (TSC) via arc melting”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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**KESAN PENAMBAHAN ALUMINIUM (Al) DAN NIKEL (Ni) KE ATAS  
PEMBENTUKAN TITANIUM SILIKON KARBIDA (Ti<sub>3</sub>SiC<sub>2</sub>) DENGAN  
KAEDAH PELEBURAN ARKA**

**ABSTRAK**

Ti<sub>3</sub>SiC<sub>2</sub> mempunyai gabungan luar biasa kedua-dua sifat seramik dan logam seperti ketumpatan yang rendah, kekuatan dan modulus yang tinggi, kebolehmesinan yang baik, dan ketahanan terhadap kejutan haba. Malangnya, fasa tunggal Ti<sub>3</sub>SiC<sub>2</sub> sukar untuk disintesis kerana wujudnya fasa titanium karbida (TiC) dan titanium silisida (Ti<sub>x</sub>Si<sub>y</sub>). Serbuk titanium, silikon, grafit, aluminium, dan nikel disediakan mengikut nisbah stoikiometri iaitu Ti:Si:C:Al:Ni = 3:1:2:x:y. Serbuk-serbuk berkenaan dicampur dan dikisar dengan menggunakan mesin pengisar bola selama 24 jam sebelum dipadatkan. Campuran serbuk yang telah dipadatkan telah diarka menggunakan mesin peleburan arka selama 5 saat. Kesan penambahan aluminium yang berbeza dikaji untuk memerhatikan ketulenan Ti<sub>3</sub>SiC<sub>2</sub>. Selain itu, kesan penambahan nikel yang berbeza dikaji untuk menghasilkan Ti<sub>3</sub>SiC<sub>2</sub> dengan ketumpatan tinggi. Kekerasan setiap sampel telah diperolehi daripada ujian kekerasan Vickers. Berdasarkan keputusan yang diperolehi, sampel yang mempunyai Ti<sub>3</sub>SiC<sub>2</sub> dengan ketulenan dan ketumpatan tinggi adalah TSC 0.2Al/0.2Ni. Peratusan Ti<sub>3</sub>SiC<sub>2</sub> dalam produk akhir adalah 90 % berat dan ketumpatan relatif adalah 89.61 %. Walau bagaimanapun, kekerasan TSC 0.2Al/0.2Ni adalah yang paling rendah (3.7 GPa) berbanding dengan yang lain. Di samping itu, produk Ti<sub>3</sub>SiC<sub>2</sub> juga dikaji melalui pemerhatian SEM. TiC dan Ti<sub>5</sub>Si<sub>3</sub> muncul sebagai fasa kedua dalam semua produk.

**EFFECT OF ALUMINIUM (Al) AND NICKEL (Ni) ADDITION ON  
FORMATION OF TITANIUM SILICON CARBIDE  $Ti_3SiC_2$  (TSC) VIA ARC  
MELTING**

**ABSTRACT**

$Ti_3SiC_2$  is a layered ternary carbide that possesses unique properties that combining excellent characteristics of metals and ceramics such as low density, high strength and modulus, good machinability, and good resistance to thermal shock. Unfortunately, it is difficult to synthesize single phase  $Ti_3SiC_2$  material, being often accompanied by unacceptably large amounts of TiC and titanium silicides ( $Ti_xSi_y$ ). Elemental powders of titanium, silicon, graphite, aluminium, and nickel were prepared according to stoichiometric ratio of Ti:Si:C:Al:Ni = 3:1:2:x:y. These powders were mixed and milled using ball milling machine for 24 hours before being compacted. The compacted powder were arced by using arc melting machine for 5 seconds. The effect of different aluminium addition was studied to observe the purity of  $Ti_3SiC_2$ . Besides, the effect of different nickel addition was studied to produce  $Ti_3SiC_2$  with high density. The hardness of each sample was obtained from Vickers hardness test. From the result obtained, the sample that has high purity and density of  $Ti_3SiC_2$  was TSC 0.2Al/0.2Ni. The percentage of  $Ti_3SiC_2$  in the final product was 90 wt. % and the relative density was 89.61 %. However, the hardness of TSC 0.2Al/0.2Ni was the lowest (3.7 GPa) compared to others. Besides,  $Ti_3SiC_2$  were characterized by Scanning Electron Spectroscopy. TiC and  $Ti_5Si_3$  appeared to be the common and dominant second phases in all products.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Jeitschko and Nowotny first discovered titanium silicon carbide in 1967 (Jeitschko and Nowotny, 1967). They synthesized a large number of carbides and nitrides in the 60's, and discovered a series of phases now called Hägg phases. These phases have a chemistry of the form of  $M_2AX$ , where M is an early transition metal, A is an A-group element (usually IIIA and IVA) and X is either C and/or N.

Titanium silicon carbide ( $Ti_3SiC_2$ ) is a unique ceramic that possesses ceramic and metallic characteristics meaning that it is suited to both mechanical and electrical applications.  $Ti_3SiC_2$  has attracted considerable interest because of this unique combination of physical properties. These include a high melting point, good high-temperature strength, resistance to corrosion and oxidation, high Young's modulus, and high electrical/thermal conductivity-characteristics, which are both metallic and ceramic in nature. Furthermore, it has high fracture toughness at high temperatures and can be machined using hardened steel tools. There also some research that revealed that the material has negligible thermoelectric power between 300 and 800 K (Yoo et al., 2000).

These properties make  $Ti_3SiC_2$  a very useful material in fabricating fine ceramic parts and apparatus. It is also a suitable candidate material for many high-temperature structural and functional applications. It also can be used as electrodes in electrochemical cells. Because it has good conductivity, it can be used as conducting films on dielectric and semiconductor devices.  $Ti_3SiC_2$  has a greatest potential in aerospace application since it has good high-temperature strength.

Ti<sub>3</sub>SiC<sub>2</sub> has been prepared by several variety method such as chemical vapor deposition (Gato et al., 1987), hot-isostatic-pressing (Lis et al., 1995), spark plasma sintering (Gao et al., 1999), plasma sprayed coating (Venkata et al., 2009), arc melting (Khoptiar et al., 2003). Recent of years, many researchers prepared using SHS (Lis et al., 1995, Morgiel et al., 1996 and Riley et al., 2003) which utilizes the exothermic heat of formation to promote a self-sustaining reaction. This method has many advantages such as potential of time saving, low energy requirement, and yielding of high-purity products.

Self-propagating high temperature (SHS), a variant of combustion synthesis, is a method for producing substances, materials and items via exothermic auto wave reaction. This combustion-like process is ignited by point-heating of a small part (usually the top) of the prepared sample. The heat should be enough for initial burning of surrounding material, which in turn, generates heat that burns the following part of the material, and in this way a wave of exothermic reaction is generated that covers the rest of material. With this method it is possible to obtain various products both inorganic and organic nature with unusual properties, for example powders, metallic alloys, ceramics with high purity, corrosion-resistance at high-temperature or super-hardnessity. SHS can be performed in fine powders, thin films, liquids, gases, powder-liquid systems, gas suspensions, layered systems, gas-gas systems, etc. The mixture may burn in vacuum, air or inert or reactive gas. In this study, we modify the SHS system by using the arc melting.

Al is an interesting element for the alloy oxidation resistance improvement based on the possible formation of protective Al<sub>2</sub>O<sub>3</sub> scales. In addition, the low melting point (about 660 °C) of Al enables the formation of a melting pool during the arc melting, which may accelerate the corresponding element diffusion and should be

helpful for the  $\text{Ti}_3\text{SiC}_2$  formation. Thus, addition of aluminum in the starting material may improve the synthesis of  $\text{Ti}_3\text{SiC}_2$  via arc melting.

$\text{Ti}_3\text{SiC}_2$  usually contain pores in the final product and this may reduce the density of the product and also decreased the mechanical properties. Ni is an element that believed can assist in densification of  $\text{Ti}_3\text{SiC}_2$ . The low melting point of Ni (about 1455 °C) will melt during the combustion process, flow and solidifies on the surface of TiC impurities. As already know, TiC is one of the major secondary phases that can be observed in the final product of  $\text{Ti}_3\text{SiC}_2$ . Hence, by adding Ni in starting powders, it may increase the TiC density and next increase the  $\text{Ti}_3\text{SiC}_2$  density.

## **1.2 Problem statement**

Over the years, there have been several attempts on fabricating bulk dense and single phase samples of  $\text{Ti}_3\text{SiC}_2$ . However, it is difficult to synthesis single-phase  $\text{Ti}_3\text{SiC}_2$  material, due to large amounts formation of TiC and titanium silicides ( $\text{Ti}_x\text{Si}_y$ ). This problem is due to the high chemical affinity of titanium towards carbon and hence formed the TiC and  $\text{Ti}_x\text{Si}_y$  phases. In previous work that has been done by Julie et al., (2011), they had faced a problem in synthesizing a high purity  $\text{Ti}_3\text{SiC}_2$  via TIG method. The highest percentage (%) of TSC obtained was only 67%. To overcome this matter, Al will be added in the starting powder to increase the  $\text{Ti}_3\text{SiC}_2$  purity. Several groups (Zhu et al., 2003 and Sun et al., 2005) have reported that adding an appropriate amount of Al helped synthesize high-purity  $\text{Ti}_3\text{SiC}_2$  by solid state reaction at relatively low temperature. For example, Zhu et al., (2005) fabricated almost single phase  $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$  by spark plasma sintering (SPS) using a powder mixture consisting of 3Ti/Si/2C/0.2Al at the temperature of 1150-1250 °C. Zhang et al. investigated the mechanism of the facilitating effect of Al on the sintering synthesis of  $\text{Ti}_3\text{SiC}_2$ . They hypothesized that Al

might react with impurities such as TiC, Ti<sub>5</sub>Si<sub>3</sub> and TiSi<sub>2</sub> to form Ti<sub>3</sub>Si(Al)C<sub>2</sub>, thus improving the phase purity of Ti<sub>3</sub>SiC<sub>2</sub> in the final products. In 2005, Li et al., (2005) reported that with an addition of Al into the 3Ti/1Si/2C starting powders, the optimal temperature for the synthesis of highly phase-pure Ti<sub>3</sub>SiC<sub>2</sub> was decreased from 1450°C to 1350°C using vacuum sintering.

Arc melting method usually produced high porosity product as stated by Juliewatty et al., (2011). They have obtained a porous product and this problem will reduce the mechanical properties of Ti<sub>3</sub>SiC<sub>2</sub>. Han et al., (2000) have stated in their study about in-situ combustion synthesis and densification of TiC-xNi cermets that by adding 20 wt. % Ni in the starting powder mixtures, dense TiC can be produced. TiC is a compound that usually exists together with Ti<sub>3</sub>SiC<sub>2</sub> and it contains pores. These pores may affect the mechanical properties of the final product. So, by increased the density of TiC, the density of Ti<sub>3</sub>SiC<sub>2</sub> can also be increased and also may enhance its mechanical properties.

### **1.3 Research objectives**

There are three objectives in this study;

- i. To produce high purity Ti<sub>3</sub>SiC<sub>2</sub> via modified SHS system through arc melting.
- ii. To study the effect of Al and Ni addition on Ti<sub>3</sub>SiC<sub>2</sub> formation.
- iii. To characterize the Ti<sub>3</sub>SiC<sub>2</sub> formation by its microstructure, phase identification, and mechanical properties.

### **1.4 Research approach**

The research was focused on synthesizing Ti<sub>3</sub>SiC<sub>2</sub> through SHS system. Arc melting machine will be used to supply the source of ignition to the sample. In arc

melting, an arc is formed between a nonconsumable tungsten electrode and the metal being welded. Gas is fed through the torch to shield the electrode and molten weld pool.

Powders of Ti, Si, C, Al, and Ni were used as starting materials. Starting powders in molar ratios of Ti:Si:C:Al:Ni = 3:1:2:x:y (x= 0.1, 0.2, 0.3), (y= 0.1, 0.2, 0.3) were weighed and ball mixed for 24 hours. The mixed powders were compacted into pellet form using cold-press machine. The pellet produced is in the size of which fit into the crucible of arc welding machine. Arc melting was performed and conducted in 5 seconds for different ratio of Al and Ni to reveal its effect on the synthesis. The phase composition and the microstructure of the arc sample were analyzed by X-ray diffractometry (XRD) and a scanning electron microscope (SEM). The density was measured according to the Archimedes principle. The hardness of the product will also be measured by using hardness testing machine.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

This chapter consists of three parts. Firstly, the intermetallic will be discussed briefly on their general properties. The second part will discuss on the introduction of titanium silicon carbide ( $\text{Ti}_3\text{SiC}_2$ ) include its system which is Ti-Si-C system. Final part discusses the technique used to synthesize  $\text{Ti}_3\text{SiC}_2$ .

#### 2.2 Intermetallic compound

Intermetallic compound can be defined as a compound of two metals that has a distinct chemical formula. On a phase diagram it appears as an intermediate phase that exists over a very narrow range of compositions (Callister, 2003). They are also known as intermetallic phases. Their properties cannot be transformed continuously into those of their constituents by changing of composition alone, and they form distinctive crystalline species separated by phase boundaries from their metallic components and mixed crystals of these components.

The compounds formed by the transition metals with some nonmetals border on the intermetallic compounds (for example, the transition metal compounds with hydrogen, boron, carbon, and nitrogen). Metallic bonds predominate in such compounds. Intermetallic compounds are produced by direct reaction of their components upon heating or by double decomposition reactions. The formation of intermetallic compounds is observed during the separation of an excess of a component from metallic solid solutions or as a result of positional ordering of the atoms of the components in solid solutions.

Most of the change in character is due to a difference in the chemical bonding that binds the atoms of the phase together. In pure elements and solid solutions, the atoms are bound together with metallic bonds. The chemical bonds binding the atoms together in intermetallic compounds are more covalent in nature. This can profoundly alter the character of the new phase in terms of crystal structure, chemical, mechanical and electrical properties.

Intermetallics have very excellent physical properties which led to the development of functional materials in the past. The early applications as coatings made use of the high corrosion resistance of the respective intermetallics. Besides that, there are also use as an amalgams as dental restoratives. It is also suitable to be used as a structural material at high temperature due to relatively high strengths. However, they are usually brittle when they have such high strength (Berlin-Ferré, 2008). Intermetallics have given rise to various novel materials developments. Some examples include alnico and the hydrogen storage materials in nickel metal hydride batteries.  $\text{Ni}_3\text{Al}$ , which is the hardening phase in the familiar nickel-base superalloys, and the various titanium aluminides have also attracted interest for turbine blade applications (Belin-Ferré, 2008).

A new material which possesses both metal- and ceramic-like properties was successfully fabricated through sintering of metallic elements (early transition metals) together with ceramic materials. One of them is described as MAX phase (accordance to formula:  $\text{M}_{n+1}\text{AX}_n$ ) materials which are belonging to ternary layer carbides and duplicated the merits properties of both metals and ceramics.

## 2.3 MAX phase

The MAX phase gets their name from their composition. These layered, hexagonal carbides and nitrides belongs to the formula  $M_{n+1}AX$  as shown in Figure 2.1 where  $n = 1$  or  $2$  or  $3$ ,  $M$  is a rare-earth transition metal (green),  $A$  is an A-group element (usually IIIA and IVA) in periodic table (yellow) and  $X$  is either carbon (C) or nitrogen (N) (gray) (Khoprtiar and Gotman, 2003). They constitute an exciting new class of materials that is more revolutionary than evolutionary.

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Uun								

M Early transition metal   
 A Group A element   
 X C and/or N

Figure 2.1: Elements in the periodic table that react together to form the MAX phase

Today, more than 50 MAX phases are known whereof the main part belongs to the 211 class as listed in Figure 2.2. The classes of materials characterized naturally form into three groups, based on the number of atoms of the  $M$ ,  $A$ , and  $X$  elements in each molecule. These groups are known as 211, 312, and 413 materials and the completed unit cell is shown in Figure 2.3. At late 1967, the 312 phase of  $Ti_3SiC_2$  is discovered by Jeitschko and Nowothy (1967). The others 312 phases are belonging to  $Ti_3GeC_2$  (Wolfsgruber et al., 1967) and  $Ti_3AlC_2$  (Pietzka and Schuster, 1994). Recently,

the new phase is found which belongs to composition of  $Ti_4AlN_3$  and compatible with formula  $Mn+1AX_n$  (Barsoum et al., 1999). However, this new  $Ti_4AlN_3$  phase is not extensively studied compared to  $Ti_3SiC_2$  phase.

<b>211</b>	$Ti_2AlC^*$	$Ti_2AlN^*$	$Hf_2PbC^*$	$Cr_2GaC$	$V_2AsC$	$Ti_2InN$
	$Nb_2AlC^*$	$(Nb,Ti)_2AlC^*$	$Ti_2AlN_{0.5}C_{0.5}^*$	$Nb_2GaC$	$Nb_2AsC$	$Zr_2InN$
	$Ti_2GeC^*$	$Cr_2AlC$	$Zr_2SC$	$Mo_2GaC$	$Ti_2CdC$	$Hf_2InN$
	$Zr_2SnC^*$	$Ta_2AlC$	$Ti_2SC$	$Ta_2GaC^*$	$Sc_2InC$	$Hf_2SnN$
	$Hf_2SnC^*$	$V_2AlC$	$Nb_2SC$	$Ti_2GaN$	$Ti_2InC$	$Ti_2TiC$
	$Ti_2SnC^*$	$V_2PC$	$Hf_2SC$	$Cr_2GaN$	$Zr_2InC$	$Zr_2TiC$
	$Nb_2SnC^*$	$Nb_2PC$	$Ti_2GaC$	$V_2GaN$	$Nb_2InC$	$Hf_2TiC$
	$Zr_2PbC^*$	$Ti_2PbC^*$	$V_2GaC$	$V_2GeC$	$Hf_2InC$	$Zr_2TiN$
<b>312</b>	$Ti_3AlC_2^*$	$Ti_3GeC_2^*$				
	$Ti_3SiC_2^*$					
<b>413</b>	$Ti_4AlN_3^*$					

Figure 2.2: Currently known 211, 312, and 413 phases

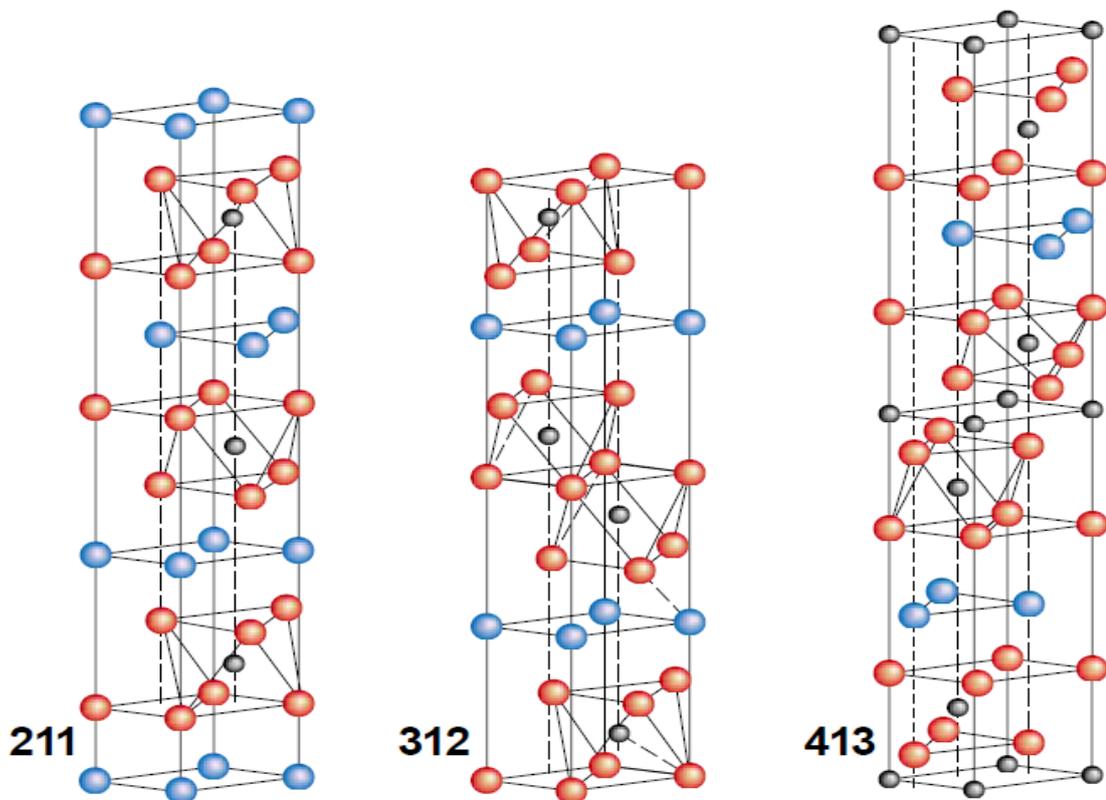


Figure 2.3: MAX phase unit cell (Barsoum and El-Raghy, 2001)

## 2.4 Titanium Silicon Carbide ( $\text{Ti}_3\text{SiC}_2$ )

Nowadays, the advanced materials that possess properties with superior heat-resistant, good thermal and electrical conductivity and adequate machinability have been popular in the aerospace and automotive applications (Barsoum and El-Raghy, 2001). One of them is  $\text{Ti}_3\text{SiC}_2$ , which is belonging to the ternary layered carbide family, whereby  $\text{Ti}_3\text{SiC}_2$  always be at the front line.

In 1996, the ternary compound titanium silicon carbide ( $\text{Ti}_3\text{SiC}_2$ ) was first synthesized (Barsoum and El-Raghy). It was synthesized as a single-phase and fully dense compound. Its characterization revealed a unique combination of properties. For its high fracture toughness, low hardness to elastic modulus ratio and excellent damage tolerance, it was dubbed a soft ceramic. It also displayed a good thermal shock and oxidation resistance.

Initial hints that  $\text{Ti}_3\text{SiC}_2$  was not a typical carbide came as early as 1972, when a German group (Nickl et al., 1972) working on chemically vapor deposited films showed that it was anomalously soft for a carbide. The fabrication of single-phase, bulk samples proved more challenging and several groups had tried and failed. A group headed by Pampuch, (1989) in Poland had come closest. Their best samples were about 85 percent pure by volume. Using these samples, they were the first to show that  $\text{Ti}_3\text{SiC}_2$  was quite a stiff material, almost three times as stiff as titanium metal (with the same density).

$\text{Ti}_3\text{SiC}_2$  has a hexagonal crystal structure consisting of double layers of TiC octahedral separated by a planar Si layer, as shown in Figure 2.4.

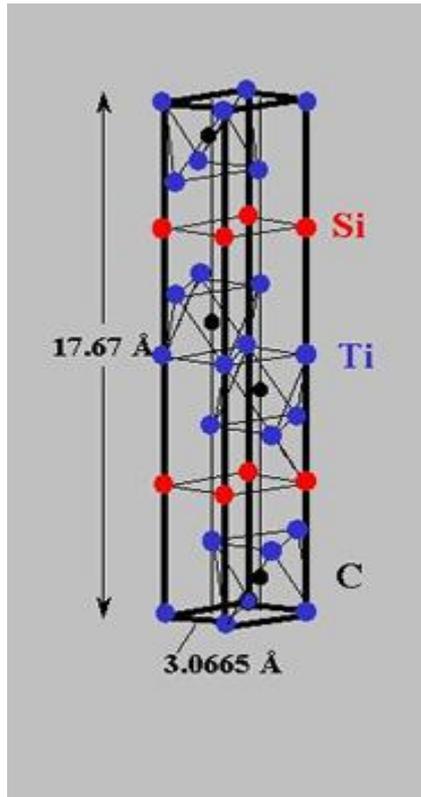


Figure 2.4: Crystal structure of Titanium Silicon Carbide (Ti<sub>3</sub>SiC<sub>2</sub>)

(Jeitschko and Nowotny, 1967)

This layer of ternary carbide combines unusual properties of both metals and ceramics. The c-axis stacking sequence includes double layers of distorted edge-sharing CTi<sub>6</sub> octahedra, reminiscent of the Ti-C structure. The double layers are separated by square-planar Si sheets. Like metals, they are good thermal and electrical conductors and relatively soft. On the other hand, they are elastically stiff and exhibit excellent high temperature mechanical properties, behaving like ceramics. They are resistant to thermal shock and unusually damage tolerant, and exhibit an excellent corrosion resistance. Furthermore, because the layers can slide over each other, the material is not brittle like other ceramics. Above all, unlike conventional carbides, they can be machined by using conventional tools without lubricant, which is of great technological