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

by

NORLAILATULLAILI BT MAZUKI

Thesis submitted in fulfillment of the
requirements for the degree
of Master of Science

UNIVERSITI SAINS MALAYSIA
JULY 2012

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.

Name of Student: Norlailatullaili bt Mazuki **Signature:**

Date:

Witness by

Supervisor: Dr Julie Juliewatty bt Mohamed **Signature:**

Date:

ACKNOWLEDGEMENTS

I would like to express my gratitude to all those who gave me the support to complete this thesis. I want to thank the Universiti Sains Malaysia and dean of School of Materials and Mineral Resources Engineering (SMMRE) for giving me the permission to commence this thesis in the first and to do the necessary research work.

I would like to express my deepest gratitude and thankful to my supervisor, Dr Julie Juliewatty bt Mohamed who helped, guided and encouraged me all the time to finish this research. Her guidance through the development of this research thesis had portrayed her patience in enriching me with the research skills that can be used in the future. This thesis may not be completed without her advice and encouragement. I am thankful and honored as well to Prof. Dr. Hj. Zainal Arifin bin Ahmad who guided me through completing my research.

I also offer my sincere gratitude to all technical staff of PPKBSM especially, Mr Azrul, Mr Rashid, Mr Khairi and so on for helping me in the laboratory work, running equipment and analyzing data as well as keeping me stocked with general supplies. I also wish to thanks Mr Johari Abu who always there to advice and support me in my research work.

Finally, I would like to express my gratitude to my family and colleagues for their support, constructive suggestion and also criticism along my master research work.

TABLE OF CONTENT

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULTS AND DISCUSSION

CHAPTER 5: CONCLUSIONS & RECOMMENDATION

LIST OF FIGURES

LIST OF TABLES

KESAN PENAMBAHAN ALUMINIUM (Al) DAN NIKEL (Ni) KE ATAS PEMBENTUKAN TITANIUM SILIKON KARBIDA (Ti_3SiC_2) DENGAN KAEDAH PELEBURAN ARKA

ABSTRAK

Ti_3SiC_2 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_3SiC_2 sukar untuk disintesis kerana wujudnya fasa titanium karbida (TiC) dan titanium silisida (Ti_xSi_y). 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_3SiC_2. Selain itu, kesan penambahan nikel yang berbeza dikaji untuk menghasilkan Ti_3SiC_2 dengan ketumpatan tinggi. Kekerasan setiap sampel telah diperolehi daripada ujian kekerasan Vickers. Berdasarkan keputusan yang diperolehi, sampel yang mempunyai Ti_3SiC_2 dengan ketulenan dan ketumpatan tinggi adalah TSC 0.2Al/0.2Ni. Peratusan Ti_3SiC_2 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_3SiC_2 juga dikaji melalui pemerhatian SEM. TiC danTi_5Si_3 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_3SiC_2 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_2O_3 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 Ti_3SiC_2 formation. Thus, addition of aluminum in the starting material may improve the synthesis of Ti_3SiC_2 via arc melting.

Ti_3SiC_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 Ti_3SiC_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 Ti_3SiC_2. Hence, by adding Ni in starting powders, it may increase the TiC density and next increase the Ti_3SiC_2 density.

1.2 Problem statement

Over the years, there have been several attempts on fabricating bulk dense and single phase samples of Ti_3SiC_2. However, it is difficult to synthesis single-phase Ti_3SiC_2 material, due to large amounts formation of TiC and titanium silicides (Ti_xSi_y). This problem is due to the high chemical affinity of titanium towards carbon and hence formed the TiC and Ti_xSi_y phases. In previous work that has been done by Julie et al., (2011), they had faced a problem in synthesizing a high purity Ti_3SiC_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 Ti_3SiC_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 Ti_3SiC_2 by solid state reaction at relatively low temperature. For example, Zhu et al., (2005) fabricated almost single phase $Ti_3Si(Al)C_2$ 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 Ti_3SiC_2. They hypothesized that Al might react with impurities such as TiC, Ti_5Si_3 and $TiSi_2$ to form $Ti_3Si(Al)C_2$, thus improving the phase purity of Ti_3SiC_2 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_3SiC_2 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_3SiC_2. Han et al., (2000) have stated in their study about in-situ combustion synthesis and densification of TiC-*x*Ni 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_3SiC_2 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_3SiC_2 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_3SiC_2 via modified SHS system through arc melting.
ii. To study the effect of Al and Ni addition on Ti_3SiC_2 formation.
iii. To characterize the Ti_3SiC_2 formation by its microstructure, phase identification, and mechanical properties.

1.4 Research approach

The research was focused on synthesizing Ti_3SiC_2 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 (Ti_3SiC_2) include its system which is Ti-Si-C system. Final part discusses the technique used to synthesize Ti_3SiC_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. Ni_3Al, 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: $M_{n+1}AX_n$) 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) (Khoptiar and Gotman, 2003). They constitute an exciting new class of materials that is more revolutionary than evolutionary.

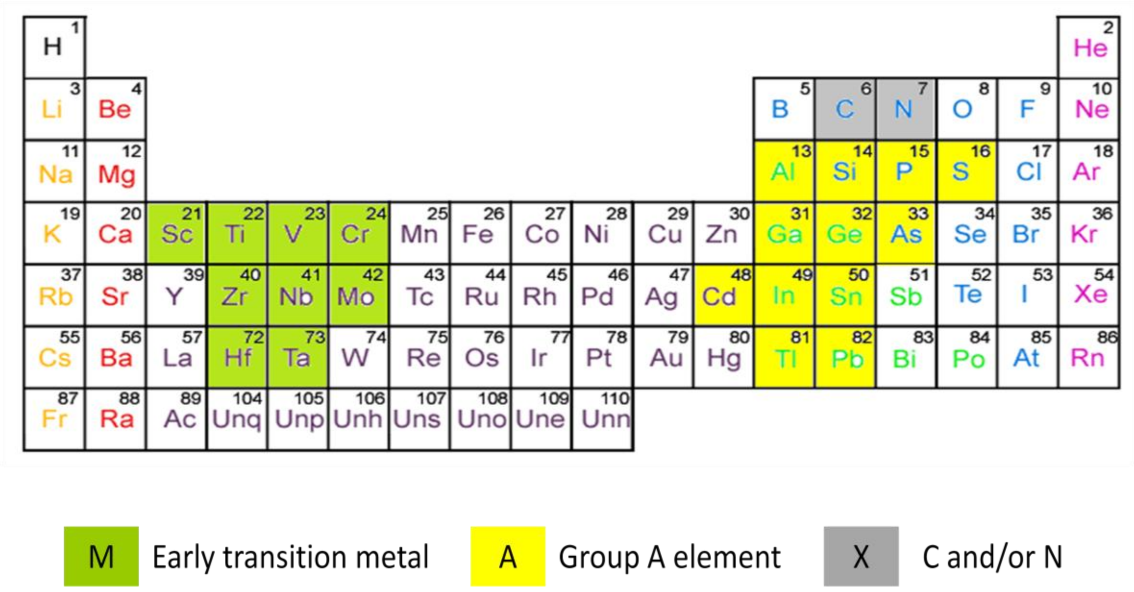
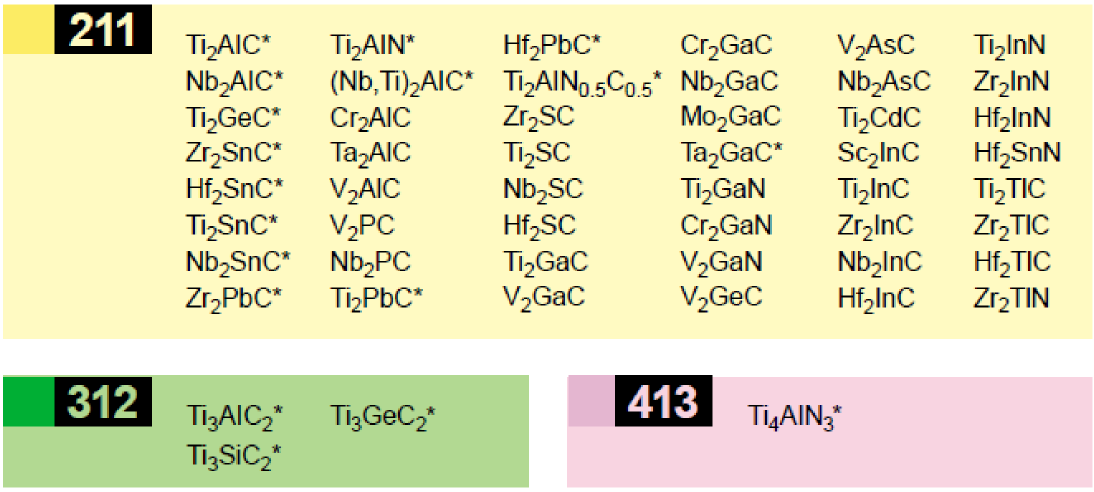


Figure 2.1: Elements in the periodic table that react together to form the MAX phase

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+1AXn (Barsoum et al., 1999). However, this new Ti_4AlN_3 phase is not extensively studied compared to Ti_3SiC_2 phase.



211

Ti_2AlC*
Nb_2AlC*
Ti_2GeC*
Zr_2SnC*
Hf_2SnC*
Ti_2SnC*
Nb_2SnC*
Zr_2PbC*
Ti_2AlN*
$(Nb,Ti)_2AlC$*
Cr_2AlC
Ta_2AlC
V_2AlC
V_2PC
Nb_2PC
Ti_2PbC*
Hf_2PbC*
$Ti_2AlN_{0.5}C_{0.5}$*
Zr_2SC
Ti_2SC
Nb_2SC
Hf_2SC
Ti_2GaC
V_2GaC
Cr_2GaC
Nb_2GaC
Mo_2GaC
Ta_2GaC*
Ti_2GaN
Cr_2GaN
V_2GaN
V_2GeC
V_2AsC
Nb_2AsC
Ti_2CdC
Sc_2InC
Ti_2InC
Zr_2InC
Nb_2InC
Hf_2InC
Ti_2InN
Zr_2InN
Hf_2InN
Hf_2SnN
Ti_2TlC
Zr_2TlC
Hf_2TlC
Zr_2TlN

312

Ti_3AlC_2*
Ti_3SiC_2*
Ti_3GeC_2*

413

Ti_4AlN_3*

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

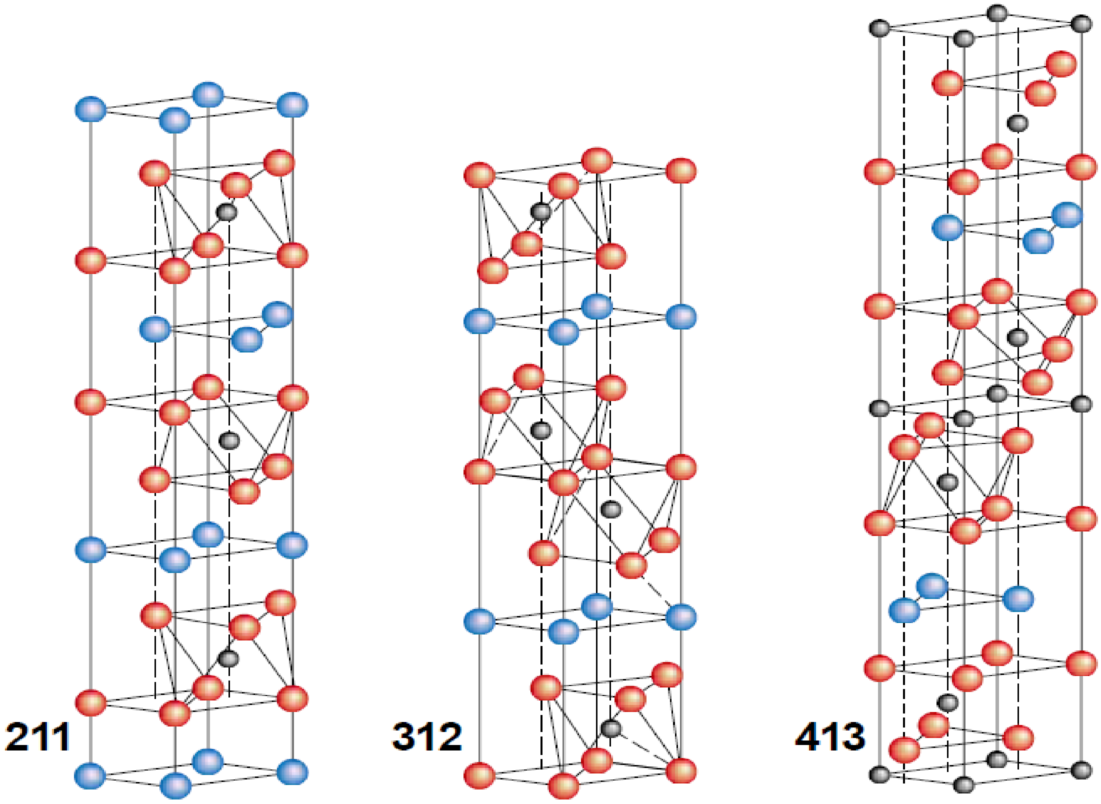


Figure 2.3: MAX phase unit cell (Barsoum and El-Raghy, 2001)

2.4 Titanium Silicon Carbide (Ti_3SiC_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 Ti_3SiC_2, which is belonging to the ternary layered carbide family, whereby Ti_3SiC_2 always be at the front line.

In 1996, the ternary compound titanium silicon carbide (Ti_3SiC_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 Ti_3SiC_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 Ti_3SiC_2 was quite a stiff material, almost three times as stiff as titanium metal (with the same density).

Ti_3SiC_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.

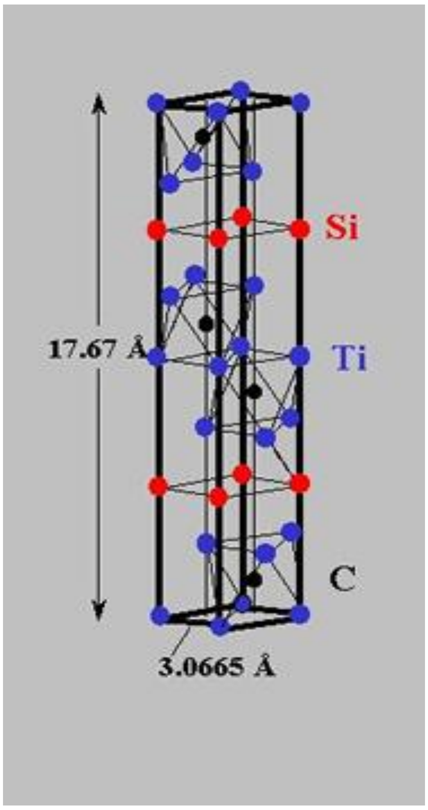


Figure 2.4: Crystal structure of Titanium Silicon Carbide (Ti_3SiC_2)

(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_6 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