

Ti-Si-C MAX phase system

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Abstract

In this study, the processing of Ti_3SiC_2 MAX phase was carried out using pure Ti, Si and C powders. The prepared mixture was heat treated at temperature between 1300-1500 °C, for various holding times. There were numbers of peaks on the TG/DTA curves which indicate thermal behavior of the starting composition and the formation of the aimed phase. At temperature 1300 °C and above, titanio-silico-carbide phase was detected as a major phase in the heated samples. It was observed that, the silicon content of the starting mixture was decreased and the formation of 312 phase of the Ti-Si-C system. At lower temperature SiC was formed but the silicon content of the starting composition was crucial point on the formation of MAX phase. TiSi, SiC, TiC and Ti_3SiC_2 phases were detected in the sintered samples.

Key words: Titanium, silicon, carbon, ceramic,

1. Introduction

MAX phase was discovered by Nowontny and co-workers[1,2], but these new discovered phases did not receive much attention until Ti_3SiC_2 phase purely produced by Barsoum and El Ragby[3]. MAX phase, M is early group of 2 elements, A is transition elements and X is C or N in the system. MAX phases can be classified into two groups are MAX phase system and stoichiometric structure. According to the material system, there are more than ten discovered MAX systems, the second classification is based on the stoichiometric structure of MAX phases which are 211, 312, 431, 523 and 735[1-5].

MAX phase materials combine metal and ceramic material properties[5,6]. The materials are very stable and desired at high temperature applications[6-8]. They have unique mechanical, thermal and chemical properties which are used wide range of applications from cutting tools[9, 10] to as a radiation shielding material in nuclear reactants[11]. These materials are new generation materials which replaced with the advanced ceramics in the near future. The decomposition temperatures of the materials change between 850-2300°C, depending upon the type and number of impurities present[12-14]. Among the MAX phase ceramics, Ti_3SiC_2 is one of the most attraction material which is half of the published on the MAX phase material papers were about it[6, 15] because it combines metals and ceramic properties, such as excellent thermal conductivity and thermal shock resistance and high temperature oxidation resistance. Many methods, such as solid state reaction[16], hot izostatik pressing[17], self-propagating high-temperature process[18], acr-melting[19], hot pressing[20] have been used to produce pure Ti_3SiC_2 . It is usually processed from pure Ti, Si, SiC and TiC powders or metallic salt forms of C (CCl_4), Ti ($TiCl_4$) and Si ($SiCl_4$) in presence of H_2 are used to obtain Ti_3SiC_2 . The aim of the work presented here is to investigate the processing and formation of 312 $TiSiC$ MAX phase from the elemental form of Ti, Si and graphite and to determine the optimum condition for synthesis a MAX phase.

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2. Materials and Method

In the present study, high purity Ti, Si and graphite powders were used as starting materials to synthesis Ti_3SiC_2 phase. The characteristic of the powders are given in Table 1. Titanium and silicon powders were provided from the Alfa Aesar company and graphite as a carbon source was obtained from SKC firm.

Table 1. Some properties of the starting powders.

	Mp °C	D (g/cm ³)	Par. size	Purity (%)
Ti	1668	4.506	5-7 um	99.99
Si	1412	2.33	2-5 um	99.5
Graphite	1000 (sb)	0.95	2m	93

2.1. Theory

The solid-state reaction method was chosen to produce Ti_3SiC_2 by given reaction.



To prepare homogeneous mixture corresponding to the desired stoichiometric, the powders were ball milled with SiC balls for 6 h. After the mixing stage, green compacts were obtained from the cold compaction of mixture with a uniaxial pressure of 300 MPa. After words the green compacts were placed in a graphite crucible and sintered at temperatures between 1300-1500 °C under argon atmosphere for various holding times.

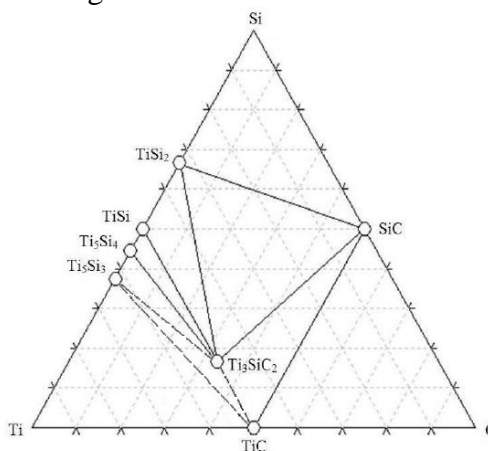


Figure 1. Isotherm a cross-section of Ti-Si-C phase diagram at 1300 °C [21].

2.2. Characterizations

The density of the green and the sintered samples were measured by Archimedes method. For the determination of mineral in the starting mixtures and the obtained phases in the products, X-ray diffraction method (D/max Rigaku, Japan) was used at the condition of Cu K α radiation ($\lambda=0.15418$ nm) with a step size of 0.02° (2θ) and a scanning rate of 2° min^{-1} . Energy dispersive analytical X-ray (EDAX) was also used for basic chemical analysis. Thermal analysis of the

mixture was performed on a simultaneous thermal analyser (Netzsch STA 400, Germany). TG/DTA was performed in an alumina crucible, under nitrogen atmosphere in the temperature range of 20-1450 °C and heating rate of 10 °C/min. For microstructure and morphology of the starting and the reduced samples were investigated by scanning electron microscopy (SEM) coupled energy dispersive X-ray spectroscopy (EDX).

3. Results

According to the overall reaction 1, the based on the mass balance requirement the starting composition is would be in the dashed line region given in Fig.1. Before any sintering processes, the X-ray diffraction pattern of the mixture was given in Fig. 2. It shows strong peaks of metallic Ti, Si and C powders that were identified on it.

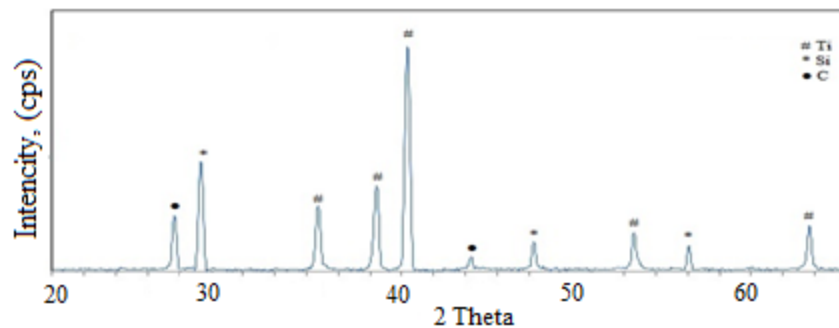


Figure 2. XRD pattern of the starting mixture of Ti, Si, C powders with stoichiometric ratio.

3.1. Phase Identification and microstructure

The phase analysis of the sintered samples were carried by XRD method and were presented in Figures 3- 6. It is clear that, 312 MAX phase was dominant and major phase at reaction temperature of 1300 and 1350 °C for 2 and 4 h. holding times.

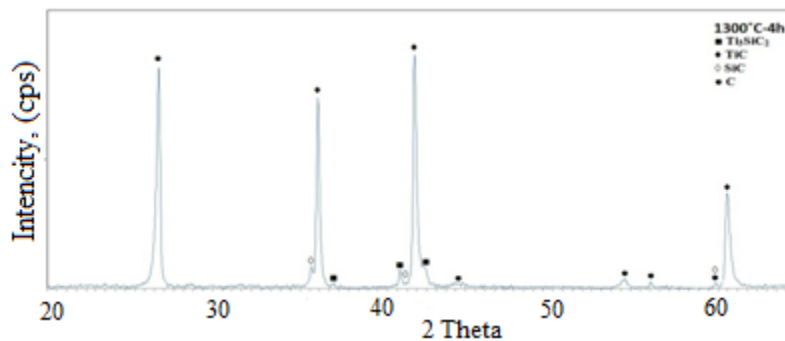


Figure 3. XRD pattern of the sintered powders at 1300 °C for 4h. with stoichiometric ratio.

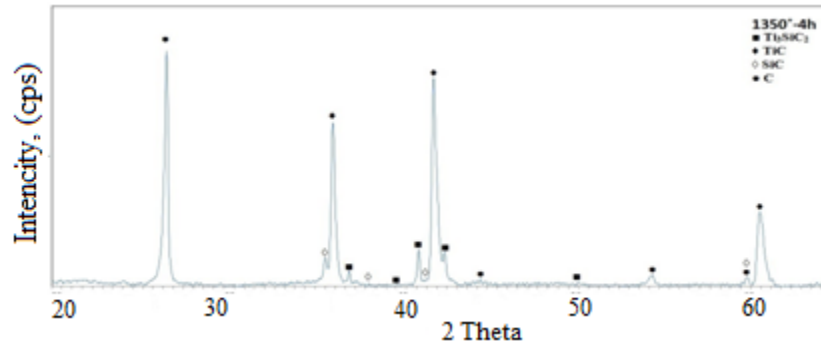


Figure 4. XRD pattern of the sintered powders at 1350 °C for 4h. with stoichiometric ratio.

At higher reaction temperature than 1450 °C, the major phases were identified as carbide phases of Ti and Si. The formed titanosilicocarbide was decomposed to Ti and Si carbides.

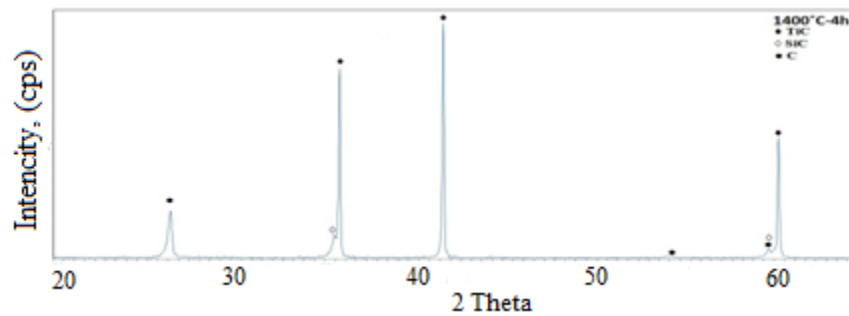


Figure 5. XRD pattern of the sintered powders at 1400 °C for 4h. with stoichiometric ratio.

As seen in Fig. 5 Ti_3SiC_2 was disappeared and the major phases were the carbide phases of Si and Ti. The formed MAX phase at lower temperature was decomposed to carbides since the starting composition consisted of 4 times carbon than stoichiometric requirement.

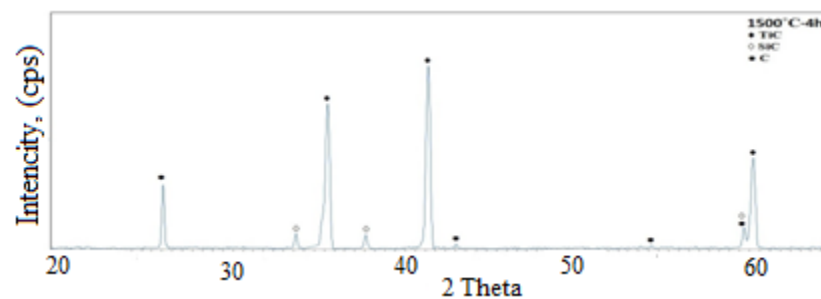


Figure 6. XRD pattern of the sintered powders at 1500 °C for 4h. with stoichiometric ratio.

3.2. Reaction mechanism of Ti_3SiC_2

Figure 6 shows thermogravimetric (TG), differential thermal analysis (DTA) and differential thermal gravimetric analyses of the starting composition. From the DTA curve of the mixture, it can be seen that an endothermic peak appears below 300 °C. The main reason should be

attributed to the mixture absorb heat for drying.

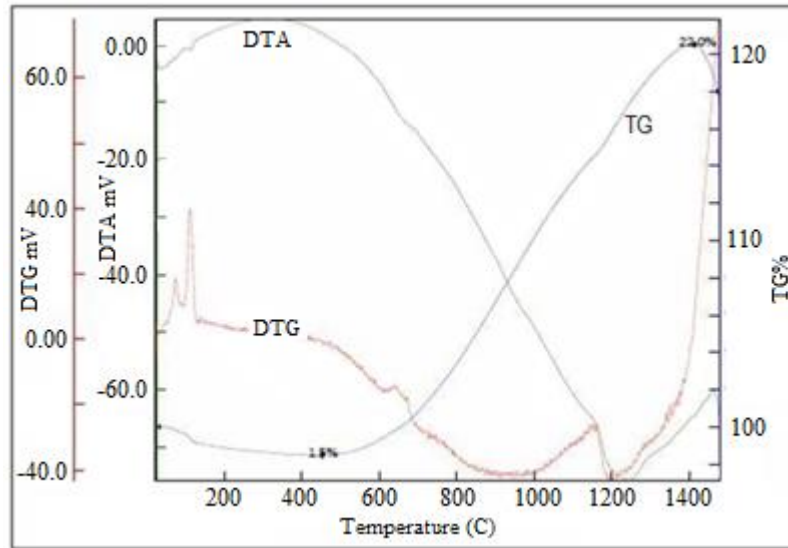


Figure 6. TG/DTA curves of mixture powders of Ti, Si and C.

A sharp exothermic peak appearing at about 1340 °C indicated that the reaction between Si and Ti starts at that temperature. In the case of study, the reaction mechanism is occurred in three stages that ;

- i-the formation of carbide phase,
- ii-the formation of inter metallic Ti and Si phase,
- iii-finally the formation of MAX phase.

From the TG curve, the weight increased from 1200 °C and 4% weight gain attained at 1450 °C. If Si reacted with Ti completely to form titaniosilicocarbide (Ti_3SiC_2) and SiC, the weight of the starting mixture would not be changed before and after reaction. The weight gain in the experiment may be resulted from the oxidation of powders.

Thermal conductivity of Si is much better than Ti. According to the phase diagram of Ti-Si-C system given in Figure 1, silicides such as TiSi, TiSi₂, Ti₅Si₃ are stable phases. Under the experimental conditions, following reactions may took place;

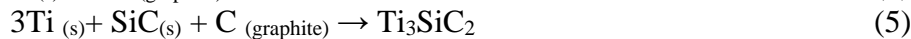


Table 2. The formed phases at different sintering temperatures and holding times.

Temp. (°C)	Sintering time	Identified phases
1300	2 h.	C, TiC, SiC, Ti ₃ SiC ₂
	4 h.	C, TiC, SiC, Ti ₃ SiC ₂
1350	4 h.	C, TiC, SiC, Ti ₃ SiC ₂
	4 h.	C, TiC, SiC, Ti ₃ SiC ₂
1400	2 h.	C, TiC, SiC
	4 h.	C, TiC, SiC

1450	4 h.	C, TiC, SiC
1500	2 h.	C, TiC, SiC
	4 h.	C, TiC, SiC

Figures 7 and 8 show scanning electron microscope of the obtained reaction particles at 1300-1350 °C. The particle size of Ti_3SiC_2 is elongated grains with layered structure. The smaller particles belong to SiC and TiC in the samples.

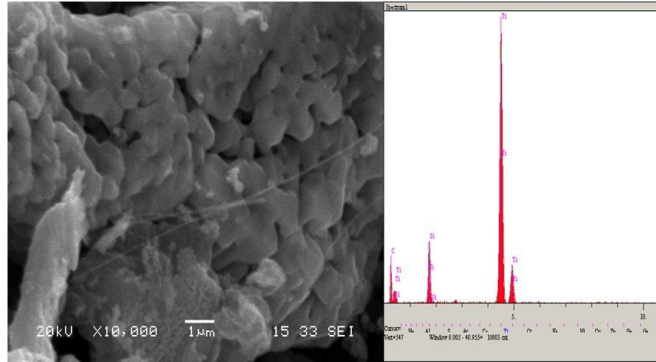


Figure 7. Scanning electron micrograph of the sintered sample at 1350 °C for 4h.

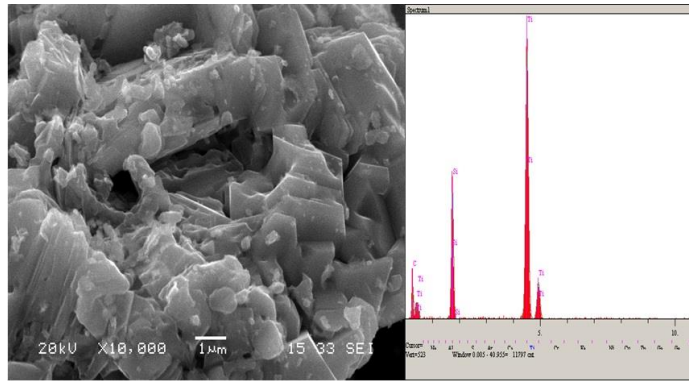


Figure 8. Scanning electron micrograph of the sintered sample at 1400 °C for 4h.

4. Discussion

As indicated in the first section of the study, there are many investigations on the processing, thermal behaviour, microstructure or other properties of Ti-Si-C system using different starting materials from pure elements, carbides or combination of element-carbide. The starting powders used in this study are different from the literature, but the reaction model for the formation of the 312 MAX phase would be applied to the study.

From the Ti-Si-C system, silicides such as TiSi, TiSi₂ and Ti₅Si₃ are stable phases. The overall reaction of the work was given in the reaction 1, but there are more reactions during the formation of the desired phase. In this work, more detailed investigation on the thermodynamic formation and kinetics were not performed.

Conclusions

One of MAX phase ceramic, Ti_3SiC_2 , has been synthesized by sintering of high purity Ti, Si and graphite powders at a time temperature schedule of 1300-1500 °C for 2 and 4 h. SiC, TiC and Ti_3SiC_2 phases were obtained as a major phases in the processed samples. The formation of the MAX phase is more favorable at lower temperature than higher one under the experimental conditions. Fine particle SiC and TiC restrained the growth of Ti_3SiC_2 and resulted in forming a fine-grained matrix with a particle size around 10 μm . When temperature increased to 1400 °C, the major phases of the samples are TiC and SiC. It was suggested that, at higher temperatures, the MAX phase decomposes to the carbides of Ti and Si which depends on the carbon content of the starting mixture.

Acknowledgements

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