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Ti_3SiC_2 MAX Phase from TiC-Si-Ti Mixture

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Abstract: There are more than ten MAX phase systems and more than fifty MAX phases. This work is focused to produce Ti3SiC2 MAX phase using Si, C, TiC powders. On the DTA curve of the mixture showed two exothermic peaks at temperature 970 and 1250 ˚C which were related with the formation of the MAX structure on the carbide layer. TiSi, SiC, TiC and Ti3SiC2 phases were detected in the sintered samples at temperature above 1300 ˚C for 3 h sintering time. At higher temperature and longer reaction time, SiC decomposes depending on the holding and reaction temperature. The silicon to titanium carbide and carbon ratios should be in stoichiometric but the silicon content of the starting composition requires more than 20% excess.

Keywords: TiC, Silicon, Carbide, Machinable Ceramic

1. Introduction

Max phase was discovered by Nowontny and co-workers(Noontny 1970, 1982), but these new discovered phases did not receive much attention until pure Ti_3SiC_2 phase purely produced(Barsoum 1996). MAX phase, M is early group of 2 elements, A is transition elements and X is C or N in the system. There are more than ten discovered MAX phase systems can be classified according to the stoichiometric structure of the phases which are 211, 312, 431, 523 and 735(Hu 2013). There are growing interests on the MAX materials family at the last two decades because of the MAX phase materials combine metal and ceramic material properties (Rodovic 2013; Barsoum 2001). The materials are very stable and desired at high temperature applications (Chen 2001; Sunberg 2004). They have unique mechanical, thermal and chemical properties which are used wide range of applications from cutting tools (Gilbert 2000), to as a radiation shielding material in nuclear reactants(Hoffman 2012). 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 (Li 2003; Bao 2004; Zhen 2005). Preparation and processing methods of MAX phase include solid state synthesis, mechanical alloying (Raoult 1994; Orthner 2002), arc melting (Gupta 2004), hot pressing (Zhou 2000a), chemical vapour deposition(Zhou 2000b), spark plasma sintering (Zhou 2000c), pulse discharge sintering, pressure less sintering(Sun 2002) and self-propagation (Merzhanov 2004; Mishra 2011). Among the MAX phase ceramics, Ti3SiC2 is one of the most attraction material which is half of the published papers were about it (Barsoum 2001; Raoult 1994). It is usually processed from pure Ti, Si, SiC and TiC powders or combinations at high temperature (Barsoum 2000; Etzkorn 2007; Sun 2004; Pampunch 1989; El Saeed 2012). In our previous studies, high purity and composite powders were synthesized successfully using a number of different starting materials and compositions by pressure less and thermic processes. Depending on the starting composition, the desired MAX phase was obtained by the aluminothermic reduction and carburizing of TiO_2/SiO_2/C/Al powders at 1400 ˚C for 2h. (Atasoy, 2016). A series of experimental studies have been carried using high purity Ti, Si and graphite powders at a time temperature schedule of 1350 ˚C for 2 and 4 h. Addition of the Ti_3SiC_2, SiC and TiC phases were formed. The formation of the MAX phase is more favourable at lower temperature. It was found that, the carbon content has significant effect on the formed MAX phase in which it decomposes

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to the carbides of Ti and Si at higher temperatures (Atasoy 2017). Based on our experimental studies, the aim of the work presented here is to investigate the processing and formation of 312 TiSiC MAX phase from the mixture of TiC, Ti and Si.

2.Materials and Method

In the present study, high purity TiC, Ti and Si powders were used as starting materials to synthesis Ti_3SiC_2 phase. The characteristic of the powders are given in Table 1.Titanim and silicon powders were provided from the Alfa Aesar company. TiC powder was provided from.

Table 1. Some properties of the starting powders.

	Mp ˚C	D ($g.cm^{-3}$)	Par. size	Purity (%)
TiC	3200	4.93	5-20µm	99.99
Ti	1668	4.506	5-7 µm	99.99
Si	1412	2.33	2-5 µm	99.5

To prepare homogeneous mixture corresponding to the desired stoichiometric, the powders were ball milled with silicon carbide balls for 6 h. After the mixing operation, 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 Ar atmosphere for various holding times. 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 Kα radiation (λ=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).

For the preparing of ternary compound Ti3SiC2in a single stage, the solid-state reaction method was chosen. Overall reaction to produce Ti3SiC2 by given reactions.

$$2TiC\,(s) + Ti + Si(s) + \rightarrow Ti_3SiC_2 \tag{1}$$

To prepare homogeneous mixture corresponding to the desired stoichiometric, to minimize any contaminations, 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.

For the determination of crystalline of 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 Kα radiation (λ=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

For the preparing of ternary compound Ti_3SiC_2in a single stage, the solid-state reaction method was chosen. The first step is the preparation of TiC, Ti and Si powder according to the reaction 1 in a stoichiometric ratio. A green compact is prepared with this homogeneous mixture and put in an graphite crucible. They were sintered at temperatures between 1300-1500 ˚C for various holding times under Ar.

In Figure 1 shows the X-ray diffraction pattern of the starting composition (at the bottom line). As expected it consisted TiC, Si and Ti. This figure also presents the X-ray diffraction patterns of the sintered samples at 1300 ˚C for various holding times. depending on the sintering time, it was clear that the figure displays different patterns and different newly formed phases such as SiC, TiSi inter metallic and Ti_3SiC_2. At this sintering temperature, the sintering time has key role on the formation of the desired structure which needs more than 2 h. At the experimental condition, the high percentage of the MAX phase was formed in 4 h. holding time.

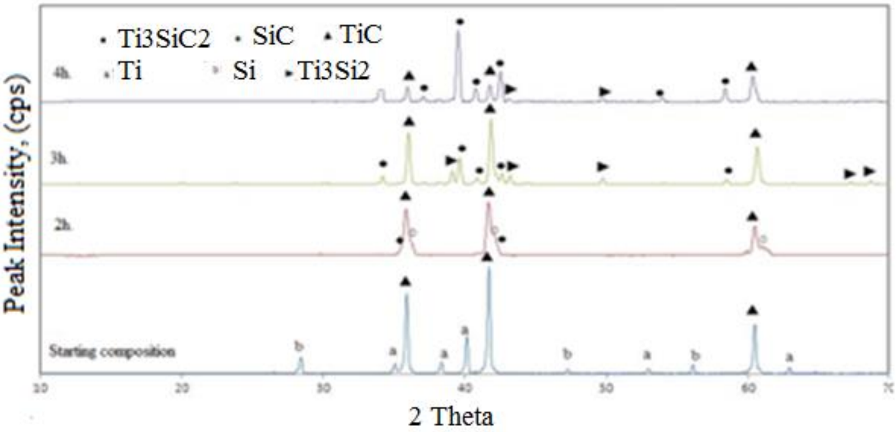

Figure 1.XRD pattern of the sintered sample at 1300 ˚C for various times.

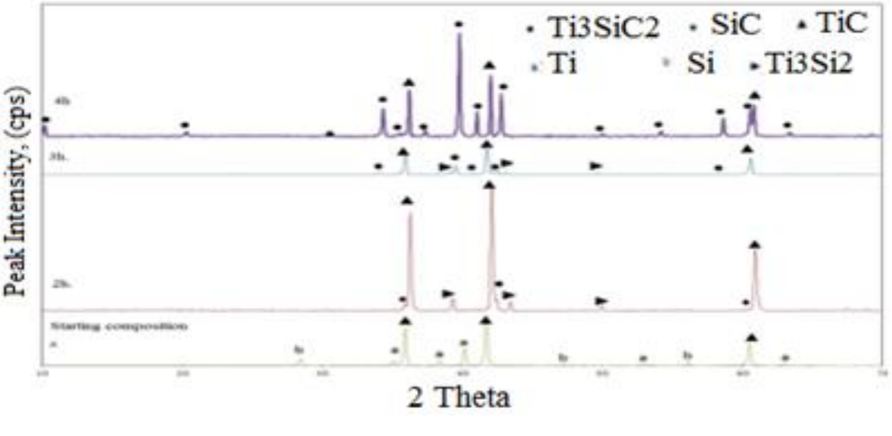

Figure 2. XRD pattern of the sintered sample at 1400 ˚C for various times.

Figure 2 shows the sintered samples at 1400 ˚C which displays different patterns and the new formed phases. At this temperature, the first reaction products were inter metallic phases of Ti-Si system where were TiSi, $TiSi_2$ and Ti_5Si_3. When the sintering time increases they were converted into the carbides and Ti_3SiC_2phases. This observation and the results suggests that the formation of the phase starts with inter metallic and carbide phases both depending on the sintering temperature and holding time.

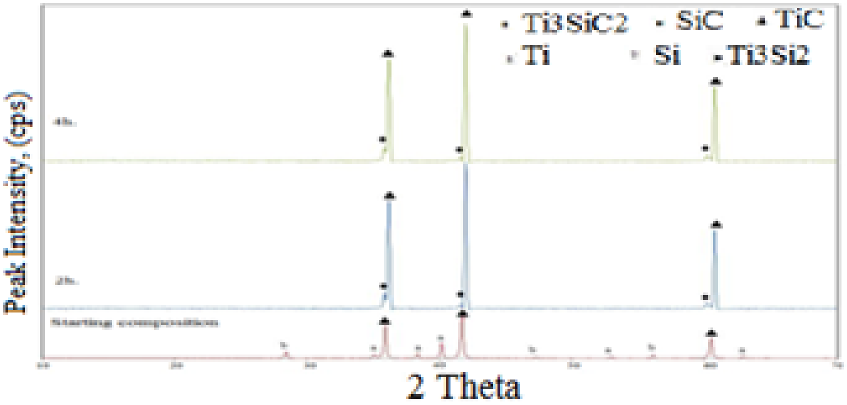

Figure 3. XRD pattern of the sintered sample at 1500 ˚C for various times.

Final X-ray diffraction patterns of the sintered samples at 1500 ˚C for various holding times were presented in Figure3. As seen from it, TiC phase was increased and SiC was formed. It was very amazing results that at his temperature, the formed MAX phase was disappeared. Our experiments showed that, the formed Ti_3SiC_2 phase was decomposed to TiC and SiC at both holding time. It was also assumed that the type of the used crucible was important that when graphite crucible was used the formation of carbide phases was accelerated as well as it decomposes the formed Ti_3SiC_2 phase to carbides at higher temperatures. Our results showed that, the stability of Ti_3SiC_2 phase was related with the carbon content of the initial composition and the type of crucible used.

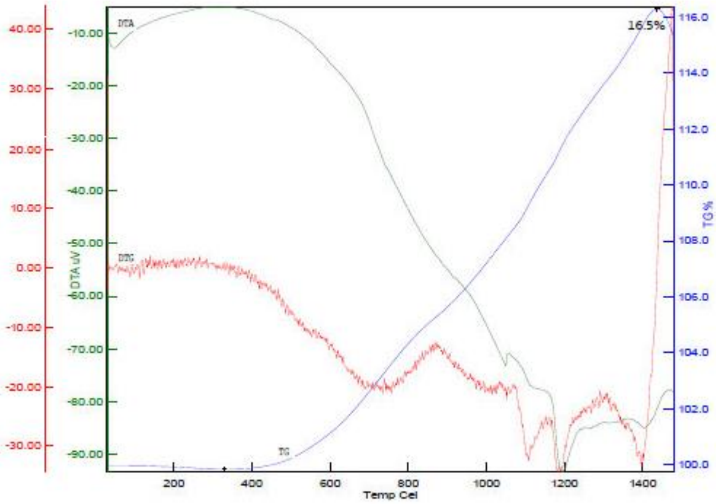

Figure 4. TG/DTA curves of mixture powders of Ti, TiC, Si and C powders.

Thermal analysis of the mixture of TiC, Ti and Si powder was presented in Figure 4. As seen from the TG curve of the mixture, there is weight gain during the experiment. It can be seen that the weight gaining starts at temperature above 400 ˚C and continuous with sintering temperature. Under the experimental conditions, both of the starting powders were stable and the experiment was carried out in argon flow. This kind of weight gaining can be explained by the oxidation of carbide or metallic portion of the starting composition. More investigations are necessary to clarify the weight gaining of the mixture. On the other, three endothermic and one exothermic peaks are observed on the DTA curve of the mixture. When compared them, they were resulted in conflicting conclusions. Again, in presence of Ar flow, any oxidation reaction should not take place in the mixture. However, some oxide content may come from the ball which was used for milling stage. This kind of contamination may resulted weight gain in the sintered samples.

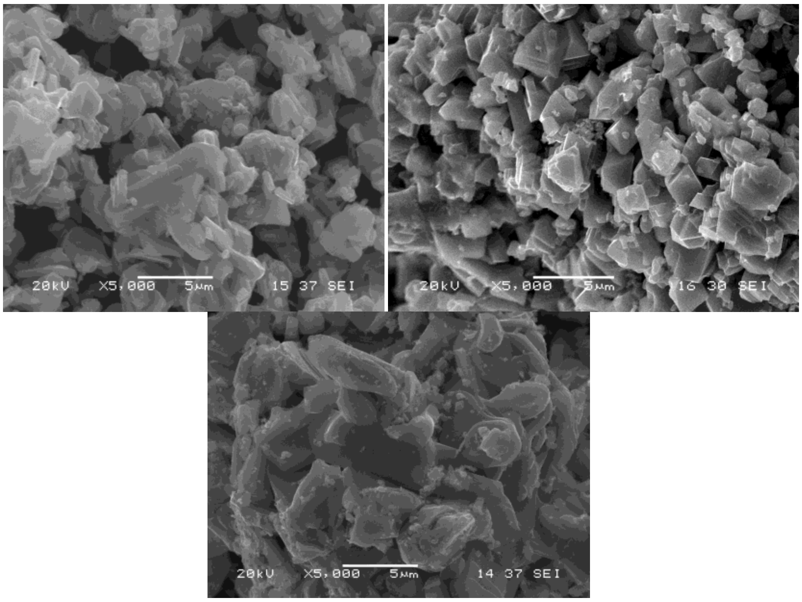

Figure 5.SEM micrograph of the sintered samples at 1300, 1400 and 1500 ˚C for 2h holding times.

Figure 5 shows the selected SEM micrograph after heat treating at different sintering temperatures for 2h. The particles were composed of TiC, SiC and Ti_3SiC_2. At 1400 ˚C, the structure seems to be layered and has more Ti_3SiC_2 particles than the right and left side pictures. As confirmed by the X-ray diffraction patterns (Figure 3) the particles on the right side of the Figure 5 belongs to TiC and SiC.

The reaction mechanism of the Ti_3SiC_2 phase depends on the used powders. When thermo chemically stable powders were used the reaction mechanism controls by diffusion model with solid state reaction between the reactants. In the case of TiC-Ti and Si powders, the formation of Ti_3SiC_2 phase rate controlling by the overall reaction. The first nucleation of the Ti_3SiC_2 starts on the surface of TiC and grows epitaxial.

4. Discussion and Conclusions

Many attempts have been reported the formation of the 312 phase. It was reported the phase composition and the reaction mechanism of the MAX phase depends on the starting powders, the sintering conditions and parameters and even depends on used crucible. When TiC and Si were used as starting powders, the Ti3SiC2 forms on the TiC phase. The wet ability of Si is more feasible and covers all around TiC particles during the sintering stage. The growth mechanism of theTi3SiC2 is epitaxial.

It was very interesting results that there was no MAX phase at sintering temperature of 1500 ˚C for the shorter or the longer holding times. The phase was decomposed into the carbides of Si and Ti. The tendency of decomposition reaction may be related with the used crucible which was graphite where creates carbon source that plays critical point in the system. The DTA curve showed a big exothermic peak nearly the same temperature as those determined by the XRD analysis.

The results of X-Ray diffraction analysis were presented in Fig 1-3 showing the relative intensity of the newly formed phases of the sintered samples. As the sintering time was increased, the formation of the desired phase increased linearly except the highest sintering temperature of the mixture.

The results of TG/DTA experiments were reported in Fig 4 showing the relative mass variations and its derivative as a function of temperature with a heating rate of 10 ˚Cmin-1. A significant mass gaining was observed at temperature between 400-1500˚C.

Ti_3SiC_2 is a bridge material between ceramics and metals. It is also new generation ceramics. TiC, Ti and Si powders used for synthesis of Ti_3SiC_2MAX phase by solid state method at a time-temperature schedule of 1300-1500 ˚C in Ar atmosphere condition. Depending on the reaction temperatures and the sintering time, TiSi, SiC and Ti_3SiC_2 phases were formed. TiC and SiC with elongated or equiaxed shape distributed in Ti3SiC2 matrix. The formation of Ti3SiC2 depends on Ti-Si binary phases. Silicon content plays an important role in the wetting of TiC particle and the formation of Ti_3SiC_2phase.Ti_3SiC_2 phase was successfully obtained at 1300 ˚C for 3 h sintering time, and it was decomposed into TiC and SiC at higher temperature.

The further work should be performed to optimize the sintering process parameters and to investigate the mechanical properties of the sintered samples.

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