Processing of TiC-Al₂O₃ Powders

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Abstract

In this study, the formation of TiC-Al₂O₃ ceramic composite powders has been investigated using a powder mixture of TiO_2, Al and C by the aluminothermic method. Thermal analysis (TG/DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods were used for the characterisation of the starting and the processed samples. It was found that the two exothermic peaks, as a twin peak, were observed on the DTA curve of the mixture after aluminium melted, which indicated the reduction of TiO_2 by molten aluminium. A further increase in temperature of up to 950˚C in the second exothermic peak was observed and was related to the formation of TiC by the in-situ reaction of Ti with C. X-ray diffraction was confirmed, the processed sample phases were Al₂O₃ and TiC, depending on the reaction temperature and time. The determined phases in the starting composition disappeared in the processed samples. With the increase in temperature, the conversion of TiO_2 to Ti, the formation of TiC and the formation of Al₂O₃ occurred during the process.

Keywords: Titanium carbide, aluminothermic process, thermal analysis, alumina

1. Introduction

Carbides are among the advanced ceramics group and have a wide range of applications in many fields due to their superior properties, such as high melting points, extreme hardness and high resistance to oxidation and corrosion[Hwu and Chen 2005, Liu, et al. 2007, Strzeciwilk, et al. 2003]. TiC is one of them, and is the most important advanced engineering carbide material in technological applications[Zhou, et al. 2012]. The typical synthesis of TiC involves the reduction of titania with carbon[Koc and Folmer, 1997], direct carbonation of the Ti element[Jia, et al. 2009], combustion[Halverson, et al. 1993], spark plasma sintering[Houyem, et al. 2011] and self-propagating high-temperature processes[Lee, et al. 2001]. TiC is used extensively in many high-temperature structural applications or as a reinforcing and hardening component in metals and ceramics, especially cutting tools and wear-resistant coating[Bellosi, et al. 2003].

Interest is growing in ceramic matrix composites with an oxide matrix[Zou, et al. 2014], with Al₂O₃ being dominant[Hu, et al. 2008]. Alumina-based ceramic matrix composites reinforced with carbides have attracted considerable attention due to their excellent properties for structural applications. One of them is Al₂O₃/TiC composites[Gar, et al. 2002]. They are excellent refractory materials[Bhardwaj and Singh 2012]. Commercially, this kind of material is directly produced by the mixing of alumina and titanium carbide powders, followed by pressure-less sintering[Culter, et al. 1988], hot pressing[Yanzhi, et al. 2013] or spark plasma sintering methods[Zhang, et al 2006]. Alternatively, elements of Ti, Al and C powders are used to obtain Al₂O₃-TiC by sintering in an oxygen atmosphere[Razavi and Rahimipour 2008]. It is known that starting powder form, composition, particle size, heating rate, reduction atmosphere and other processing parameters are very important in terms of the final product's properties[Rachedi, 2010, Atasoy, 2009, 2010].

In the present work, TiC-Al₂O₃ were in-situ work, an aluminothermic process was applied for the production of TiC-Al₂O₃ ceramic powders. The effect of the reaction temperature, carbon and holding time on the aluminothermic reduction of titanium dioxide in the presence of solid carbon was investigated. The next part of the work discusses and reports on the reaction mechanism and combustion behavior.

2. Experimental work

The raw materials were used in this study were TiO_2 (99.8% TiO_2, 1-5µm DuPont), petroleum coke (1-5 µm TUPRAS) and metallic aluminum powder (99.5%, d<50 µm, GURAL). The mixture was ball milled with alumina balls in ethanol for 6 h and then it was dried at 120 °C for overnight.

For the determination of mineral in the starting powder and the reaction phases in the produced metallic beads, 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 20-1500 °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).

Table 1. Possible reactions during the process

No	Reactions
1	$3TiO_{2\,(s)} + 4Al_{(s)} + 3C_{(s)} \rightarrow 2Al_2O_{3\,(s)} + 3TiC_{(s)}$
2	$TiO_2 + Al \rightarrow Ti + Al_2O_3$
3	$Ti + C \rightarrow TiC$
4	$Ti + C + Al \rightarrow AlTiC$

According to the reaction 1 was given in Table 1, stoichiometric and non-stoichiometric mixtures were prepared. Each run, 6 g. mixtures were put into a graphite crucible. A horizontal programmable electric furnace was used under inert atmosphere. With a 6 °C/min heating rate was used to heat the mixture to the required temperature which changed from 1300 to 1500 °C. After the aluminothermic process, the reaction product was allowed to cool room temperature. To remove any carbon content of the reduced samples, it was calcinated at 700°C in air for 2 h.

3. Results and Discussions

X-ray diffraction analysis was used to determine the phases in the starting composition and the reduced samples. Figure 1 shows the X-ray diffraction patterns of the stating composition. As seen from the XRD pattern of the starting mixture the major peaks belong to titanium dioxide, other minor peaks represent metallic aluminum content of the mixture. Carbon does not give good peaks, but the carbon content can be seen up to 12° (2Theta) in the figure.
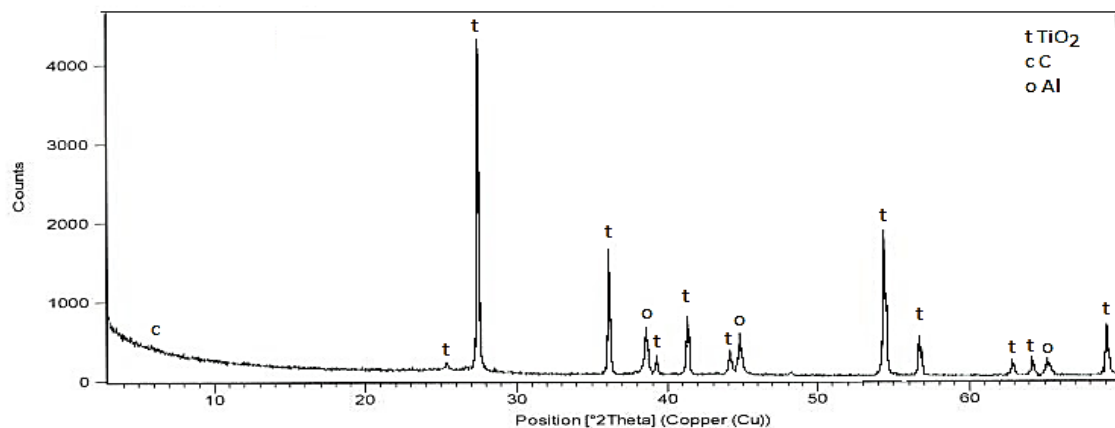

Figure 1. XRD pattern of the starting composition.

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Scanning electron micrograph of the starting composition was shown in Figure 2. As seen from the image, there were dark, gray and lighter tones. Dark particles belongs to carbon, gray is TiO_2 and the lighter particles than these two are metallic aluminum particle. TiO_2 powder is in irregular shape and means particle size is around 10 µm. As seen from it, the powders were irregular shape.
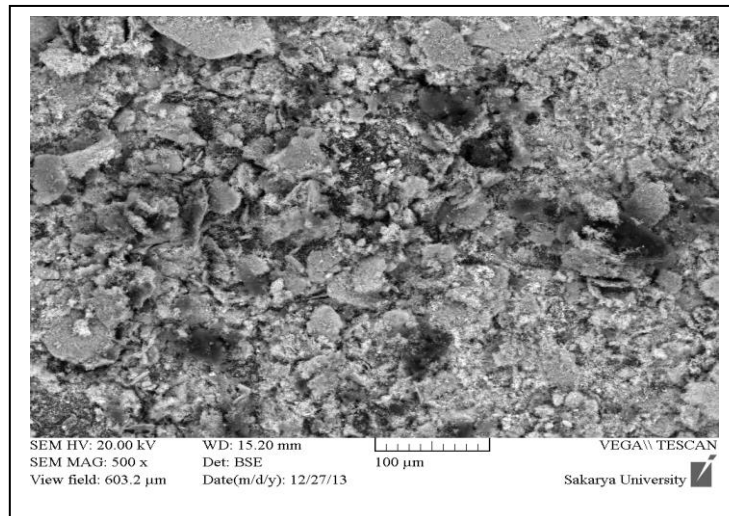

Figure 2. Back scattering image of the mixture.

TG curve of the starting composition at temperature between 25-1500 °C was presented in Figure 3. There is significance change in mass of the mixture, during TG experiment. As seen from the curve, it can be divided into two zones which are the mass lose and the mass gain zones. It is clear from the TG curve that, up to 850 °C the mixture continuous the weight loose equals to 27% in the total. According to the slope of the zone, it can be subdivided into three stages; the first stage starts from room temperature to 300°C, the second stage was between 300°C and 600°C, the third stage is from 600°C up to 850°C.

The mass gain zone starts from 850 °C up to 1500°C. As seen from the curve, the zone also shows some differences on the slope of the curve. There is fast mass gain at temperature between 850°C-1050°C, after this temperature, the process is slow down and continuous to put on weight up to 1500°C with steady speed. As explained above, the mass gain zone can be subdivided into two steps. At the first step of the gaining process, there is fast and sharp increase in the mass of the sample was around 5%. In the second step, the mass gaining was around 2.5%. When comparison of the loosing and the gaining of the mixture, there was around 20% mass lose in the sample. It was assumed that there is linear relationship between the mass loose of the mixture with the reduction of the oxide content and as well as the mass gaining of the sample with the formation of carbide in the processed sample.

The non-isothermal aluminothermic reduction of titanium dioxide was investigated from room temperature to 1500 °C using DTA. Figure gives the weight loss of the mixture between these temperatures. The titanium dioxide was started to react with molten aluminum at temperature higher than 600 °C and a final mass loss of about 20% was obtained at 1500 °C. About 27.5% of the mixture was reduced at temperature close to 850 °C. There are up and down in the mass loss of reaction and at higher temperature the mass loss was slowed down and increased again at temperature above 1050 °C. Possible reactions among TiO_2, Al and C in the initial composition were presented in Table 1. It was suggested that the first reaction starts at 600 °C, according the reaction 2 is a solid-solid reaction mechanism which starts to yield Ti and alumina. After this reaction, the formation of titanium carbide was took place in the mixture with the given reaction 3. There is possibility for the formation of AlTiC compound with the reaction 4.
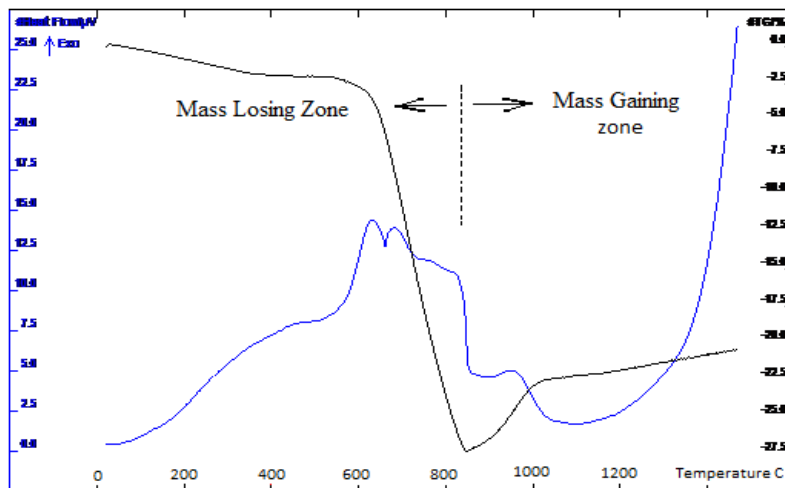
Figure 3. TG/DTA curves of the mixture.

DTA curve of the starting materials was given in Figure 3. As seen from it, the mixture shows endothermic and exothermic peaks. The first peak was endothermic, at 650 °C and it corresponds to the melting point of aluminum. There are five exothermic peaks at temperatures approximately 600, 680, 780, 810 and 950 °C. The first two peaks are major peaks on the DTA curve of the sample. It was suggested that, the reduction of titanium dioxide by Al starts before the melting of Al or at around 600°C, the reaction between TiO_2 with Al is highly exothermic which generates huge amount of heat. The reduction process was completed at around 850°C which stops the mass loss of the sample. Up to 600°C, the heat flow of the sample was increased, after this temperature it uses for the reduction with the aluminothermic process. After the reduction process is completed, the formation of the carbide phase occurs at temperature above 950°C, in the sample.

Depending on the starting composition, mixture and experimental parameters and conditions, TG/DTA curves may change. In the TG experiments was carried out in presence of nitrogen and there is possible thermodynamic conditions for the formation of nitrides phases such as AlN and TiN which are ignored in the present study.

To understand, the formation mechanism of the titanium carbide and alumina, a series of time, temperature dependence experiments were carried out. X-ray diffraction patterns of the reduced samples at different temperatures for 2 h. was presented in Figure 4 and for 4 h. holding time was given in Figure 5. As seen from the XRD pattern of the starting and the reduced samples, there are a lot of differences between peaks, intensity and phases in the figures. In another words, depending on the starting composition, reaction time and temperature the formation of the phases were changed. At temperature 1300 °C, the formation of titanium aluminate was detected in the XRD. The phase was disappeared at higher reaction temperatures. The first peak of the titanium carbide phase was detected at 1400 °C.
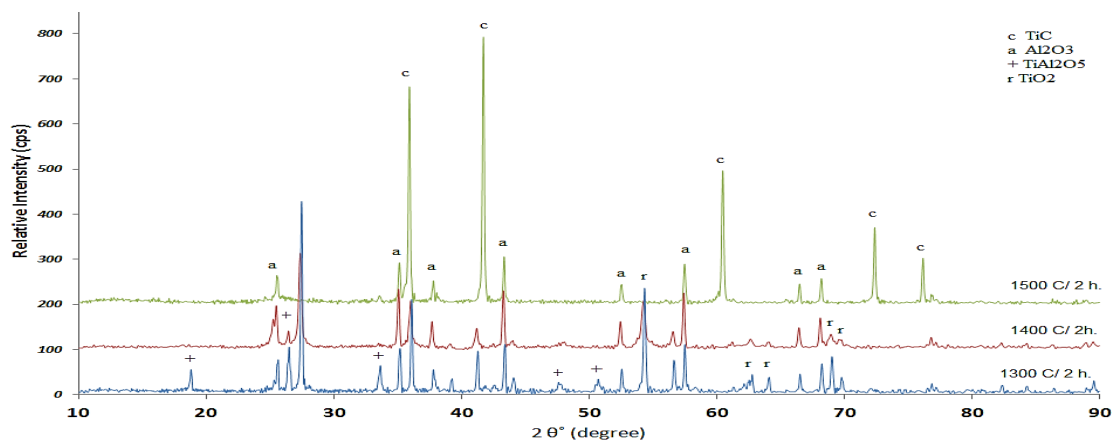

Figure 4. XRD patterns of the reduced samples at various temperatures for 2 h.

In the Al_2O_3-TiC system, it was assumed that the process was involved in three stages where is the melting of aluminum powder takes place at around 660°C, the reduction of titanium dioxide by aluminothermic and finally the formation of TiC. One of the advantages of the process is the changing of reaction state from solid-solid to solid-liquid. Another important feature of the process is the heat requirements for the formation of TiC phase. Since the aluminothermic process generates large amount of heat. The difference between particle sizes of the starting materials may be important in the solid to solid reaction systems. It was suggested that the first reaction takes place at the contact point between titanium oxide and aluminum particles at around 600 °C which was lower than the melting point of the reducing metal in the mixture. But after the melting of the metallic aluminum or at 650 °C, the process changes the reaction mechanism and creates an interface between liquid metal and solid parts and the wettability of each one determines the rate of the reaction in the process. In another words, it was assumed that the particle size of the starting composition less effective on the rate of the reduction. However, the carbon content of the mixture plays important role in the process. It has a key role for the formation of carbide phase but it would create a kind of thin film barrier between molten metal with the oxide particles. As seen from the figure, at 1300 °C for 2 h. there were the formed new phases in the sample such as $TiAlO_5$ phase. At this temperature, the gray powder was obtained under the experimental conditions. When the reaction temperature was increased to 1400 °C for the same holding time, the formed phases were changed as seen from the figure. As seen from these figures, the formation of Al_2O_3 and TiC phases were detected. At 1400 °C for 2 h reaction time, the metallic aluminum peaks in the starting composition was disappeared and resulted a new phase of Al_2O_3 peak in the reduced powder. The peak of TiO_2 also could not determine in the reduced sample. The result indicates that the total titanium dioxide content was converted into TiC or other new phases. Above this temperature, all peaks were the desired phases which were TiC and alumina ceramic composite powder was obtained.
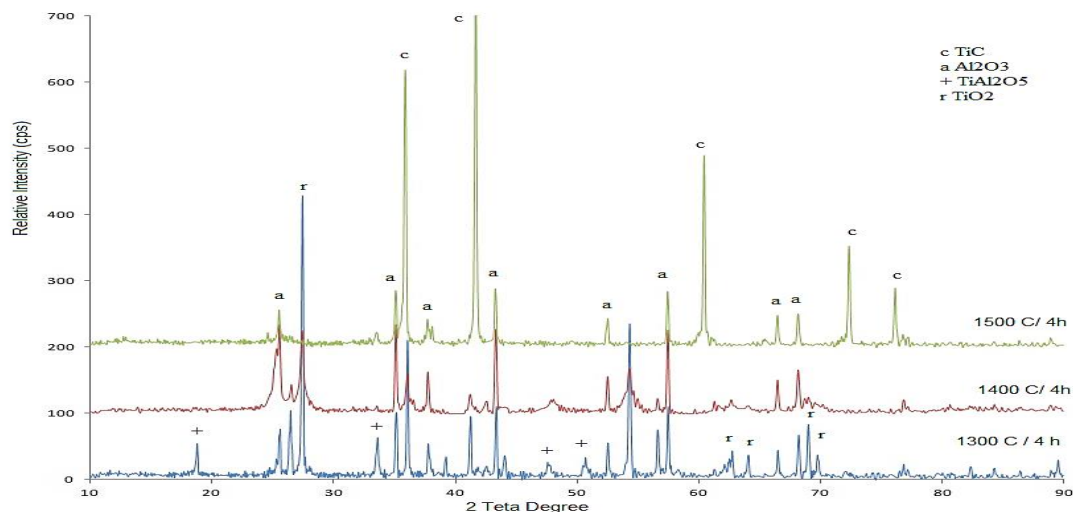

Figure 5. XRD pattern of the reduced sample at various temperature °C for 4 h.

When the reaction time was changed to 4 h, the peak intensity and the formed phase were changed and the results were presented in Figure 5. With the addition of these two phases the peak of TiO_2 in the starting composition could not determine in the reduced sample.

It is possible the reduced Ti may react with liquid Al to form other compounds were likely formed. According to the binary phase diagram of Ti and Al, TiAl, $TiAl_3$, and Ti_3Al can be detected in the reduced samples, but as a result of the Gibbs energy formation of these phases were smaller than TiC phase. Because of that, these phases were not determined in the XRD patterns of the reduced samples. The determined peaks of TiO_2 and Al and C in the starting composition did not detect in the reduced sample. It indicates that the total titanium dioxide content was converted into TiC or other new phases. The intensities of the reduced samples phases were increased with holding time and temperature.

As seen from these figures, there were big differences between the pattern of the samples as well as the obtained phases. The formation of Al_2O_3 was indicated that the process was feasible and the reduction starts at 1300 °C, but TiC phase was detected at 1400 °C and the process was successfully completed at 1500 °C. With the addition of these two phases, other compound phases can be expected in the reduced

samples such as TiAl, Ti_3AlC. Since aluminum content of the process controlled, these phases did not determined in the processed sample. Only TiC and Al_2O_3 phases were determined in the reduced sample which confirms that the total oxide content of the starting materials converted into the desired phase.
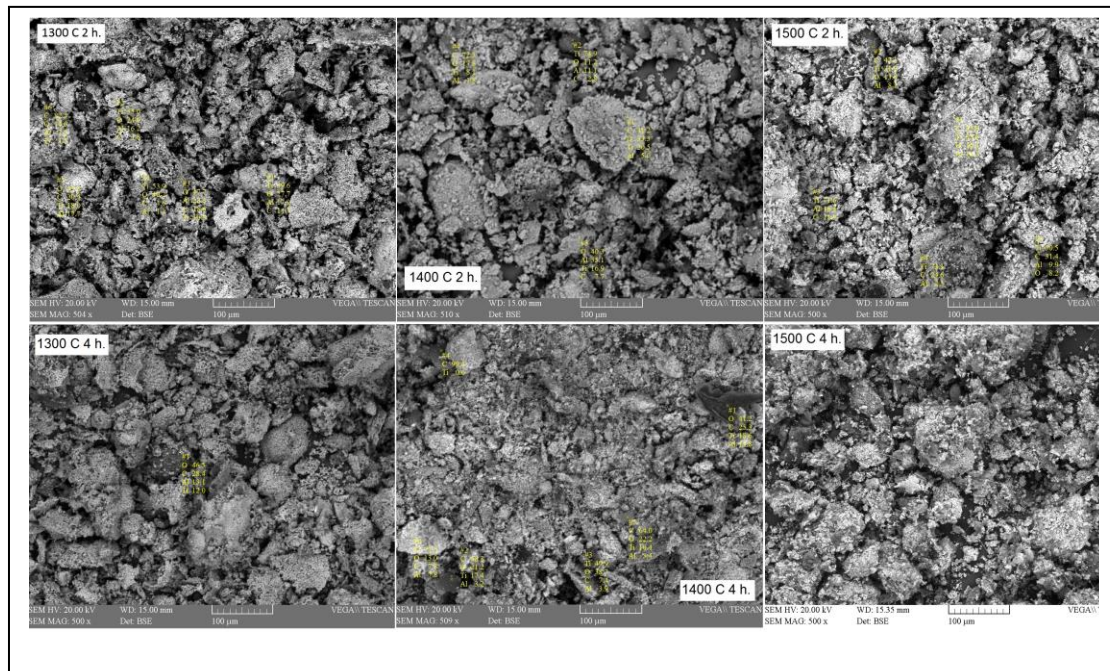

Figure 6. SEM and EDS pattern of the reduced samples at different temperatures and times.

Scanning electron micrograph of the reduced powders was presented in Figure 6. When comparison of the starting mixture with the reduced samples forms, there were big differences between two samples. It was assumed that larger particles and agglomeration were obtained as a result of the liquid phase. As seen from the figures, TiC particles are in spherical and alumina particles were irregular shapes.

EDS analysis of the final product was presented in Table 2. The determined C, O_2, Ti and Al elements belong to the phases determined in the X-ray analysis. In the commercial Al_2O_3-TiC composite powder consists of 53% Al_2O_3 and 47% TiC. If it requires, alumina content of the composite can be easily removed from the carbide phase. By comparison of the chemical compositions, the powder produced in this study was very close to the commercial product. The experimental results were indicated that, the reaction mechanism of the mixture was the liquid-solid.

Table 2. EDS analysis of the reduced samples at different reaction temperatures given in Figure 6.

Elements	1300 ˚C	1500 ˚C
	2 h.	4 h.
O	29.56	8.92
C	24.78	32.96
Al	12.4	9.42
Ti	33.26	48.65
Total	98.5	99.95

The bulk density of the obtained powders was in the range of 2.16- 3.07 g/cm^3. The differences in the density of the samples may be explained with the effect of the combustion temperature and the reaction time. The results were showed that higher reaction temperature and holding time were resulted in higher density of the products. The particle sizes of the powder were in the range of 10-50 μm. The difference in the particle size could be explained with the effect reaction temperature and time which were resulted to agglomeration in the sample. However, there is uniform particle distribution in the product.

4. Conclusions

The use of metal as reducing agent is common in metallurgical applications. TiC-Al$_2$O$_3$ ceramic composite powders were successfully obtained from inexpensive TiO$_2$, Al and C powders by carbo-aluminothermic process. In the case of Al content of the mixture, the Al content was changed the reaction mechanism of the process. The process has some advantages as a result of the low melting point of aluminum and the desired oxide product. The Al content was keep in stoichiometric amount according to the overall reaction but the higher carbon content was yielded more TiC than the stoichiometric requirement. The XRD results showed that the intensity of the obtained TiC and alumina phases increased with reaction temperature. Any titania was not determined in the reduced samples. The kinetics, the mechanical and physical properties of the obtained composite powder will be presented in another study.

References

Atasoy, A. (2010). The aluminothermic reduction of boric acid. Int J Ref Met Hard Mat. 28, 616-612.

Atasoy, A., & Sale, F.R. (2009). An investigation on the solid state reduction of chromite concentrate. Solid State Phenomena. 147, 752-757.

Bellosi, A. et al. (2003). Characterization and application of titanium carbonitride-based cutting tools. J Mater Process Technol. 143, 527-532.

Bhardwaj, P., & Singh, S. (2012). Structural phase stability and elastic properties of refractory carbides. Int J Ref Met Hard Mat. 35, 115-21.

Culter, R.A. et al. (1988). Pressureless sintered Al$_2$O$_3$-TiC composite. Mat Sci. Eng A. 105, 183-192.

Fei, Y. H. et al. (2014). Mechanical properties of Al$_2$O$_3$-TiC-TiN ceramic tool materials. Ceram Inter 40, 10205-10209

Gar, K.F. et al. (2002). Preparation microstructure and properties of TiC-Al$_2$O$_3$ composite. Ceramic International 28, 217-222.

Halverson, D.C. et al. (1993). Influence of reactant characteristics on the microstructure of combustion-synthesis titanium carbide. J Mater Sci., 28, 4583-4594.

Houyem, A.H. et al. (2011). Spark plasma sintering consolidation of nano structured TiC prepared by mechanical alloying. Int J Ref Met Hard Mat. 29, 170-176.

Hu, Q. et al. (2008). Microstructures, densification and mechanical properties of TiC-Al$_2$O$_3$-Al composite by field activated combustion synthesis. Mat Sci Eng. A. 86, 215-221.

Hwu, H.H., & Chen, J.G.G. (2005). Surface chemistry of transition metal carbides. Chem Rev. 105, 185-192.

Jia, H. et al. (2009). Formation of nano crystalline TiC from titanium and different carbon sources by mechanical alloying. J Alloys Compd. 472, 97-103.

Koc, R., & Folmer, J.S. (1997). Carbothermal synthesis of titanium carbide using ultra-fine titania powders. J Mater Sci. 9, 1172-1176.

Lee, J.H. et al. (2001). Combustion characteristics of TiO$_2$/Al/C composite. Mat Research Bull. 36, 157-167.

Liu, B. et al. (2007). Preparation and mechanical properties of in situ growth TiC whiskers toughening Al$_2$O$_3$ ceramic matrix composite. Mat Sci Eng. A. 460, 146-148.

Razavi, M., & Rahimipour, M. R. (2008). Synthetic of TiC-Al$_2$O$_3$ Nano composite from impure TiO$_2$ by mechanical activation sintering. J Alloys Compd. 450, 463-467.

Strzeciwilk, D. et al. (2003). Microstructure of TiC crystals obtained from high temperature nickel solution. J Alloys Compd. 350, 256-261.

Yanzhi, C.Y. et al. (2013). Microstructures and mechanical properties of Ti_3SiC_2/TiC-Al_2O_3 composites synthesized by reactive hot pressing. Mat Sci Eng. A. 571, 137-143.

Zhang, Y. et al. (2006). Microstructure and properties of Nano composites fabricated by spark plasma sintering from high energy ball milled reactants. J Euro Ceram Soc. 26, 3393-3397.

Zou, B. et al. (2014). Effects of super fine refractory carbide additives on microstructure and mechanical properties of TiB_2-TiC-Al_2O_3 composite ceramic cutting tool materials. J Alloy Compd. 585, 192-02.

Zou, B. et al. (2012). Mechanical properties and microstructure of TiB2-TiC composite ceramic cutting tool material. Int J Ref Met Hard Mat. 35, 1-9.