THE EFFECT OF MILLING CONDITIONS ON THE MECHANICAL ALLOYING AND COMBUSTION SYNTHESIS OF TiO_2-Al-C POWDER MIXTURE

S. H. R. Fatemi Nayeri, M. R. Aboutalebi and J. Vahdati Khaki
fatemih@metaleng.iust.ac.ir

Advanced Materials Research Center, Department of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran

Abstract: *A mixture of TiO_2+Al+C powders was mechanically activated using a planetary ball mill under different milling conditions wherein the milled powders were further subjected to combustion synthesis to produce TiC+Al_2O_3 composite. The mechanically alloyed powders were characterized by X-Ray diffraction analysis and TEM investigations. XRD analysis of milled powder mixture showed no significant reaction between TiO_2, Al and C while a significant amorphization of powder mixtures was observed. TEM analysis indicated the formation of a composite structure of powder particles after milling. The subsequent thermal treatment of the milled powder mix showed that the milling of initial powder mixture under dry environment using mixed large and small balls had a great effect on reaction efficiency and yielded to the highest TiC + Al_2O_3 ratio in the synthesized products.*

Keywords: *Milling condition; TiC + Al_2O_3, Combustion synthesis*

1. INTRODUCTION

Mechanical alloying (MA) as an effective powder metallurgy method has been successfully used to produce highly metastable as well as reactive metal powders [1]. This method can help in modifying the conditions for chemical reactions, either by changing the reactivity of as-milled solids or by inducing chemical reactions during milling [2]. In addition, amorphization as a result of ball milling is one of the most frequently reported phenomena in mechanically alloyed powder mixtures [3, 4, 5]. During MA, repeated fracturing and rewelding of powder particles occurs due to ball-powder and ball-powder-container collisions [6]. It is suggested that the amorphous phase forms instantaneously at the powders interlayer during mechanical milling, because of the compressive stresses on the impacted powder [7]. However, there are some influencing factors such as milling time, size of grinding medium, and milling environment that affect the final structure and composition of the powders [3, 8].

Various researches were carried out to evaluate the effects of mechanical activation in TiO_2- Al and TiO_2- Al-C systems on the combustion synthesis of Ti-Al intermetallics and TiC [9, 10]. Welham [9] and Ying et al. [10] reported on the formation of a powder composed of alumina and titanium trialuminide $TiAl_3$ via combustion synthesis of milled TiO_2 -Al powder mixture. Arik [11, 4] reported on the formation of Al_4C_3 during sintering of pre-milled aluminum powders and carbon black. Koc [12] investigated the kinetics of TiC formation in the carbothermal reduction process of ultrafine TiO_2 and carbon mixture. Pallone et al. [13] have studied the microstructural evolution during synthesis of TiC+Al_2O_3 composite by reactive milling of the powder mixtures of TiO_2+Al+C. They performed high-energy ball milling in a SPEX 8000 shaker/mill apparatus under air environment, and the reaction was being monitored by a thermocouple fixed in the external surface of the vial, which allowed the recording of the temperature peak associated with the beginning of the reaction. They showed that the formation of TiC+Al_2O_3 could be triggered by milling of TiO_2+Al+C powder mixture.

In spite of intensive studies on the combustion synthesis in TiO_2-Al-C system [14-23], no clear information; however, are available on the influence of pre-milling on the combustion

synthesis in this system. Thus, this research work has been undertaken to investigate the influence of milling conditions on the mechanical alloying and subsequent thermal treatment in TiO_2-Al-C system. Based on X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) observations, the as milled structure and phases produced via combustion synthesis process were investigated.

2. EXPERIMENTAL PROCEDURE

The materials used in this study were 99% pure rutile (TiO_2) powder with the particle size of less than 1 μm supplied by Kronos , pure Al powder (> 98% in purity) with the particle size of <100 μm supplied by KPM, and graphite powder containing 99%C with a maximum particle size of 40 μm supplied by Razi. Powder mixture of rutile, Al, and graphite, were prepared according to stoichiometric reaction given in Eq. 1:

$$3TiO_2+4Al+3C=3TiC+2Al_2O_3 \quad (1)$$

The milling experiments were carried out under air atmosphere in a planetary ball mill with an alumina vial of 750 cm^3 inner volume charged with alumina balls of 20 and 10 mm diameters, with the constant ball to powder ratio of 4:1. The rotation speed of vials was 1000 rpm. The milling of powder mixture was carried out under different milling conditions as described in Table 1. The milling was made under dry and wet environments in which the wet environment was made by addition of ethanol solution to the powder mixture at the amount of 5 wt%. The samples were milled for up to 72 hrs and were further subjected to thermal treatment. A 24-hour milled powder was found to be an appropriate sample for subsequent thermal treatment as previously described by the authors [24]. Thus, a 24-hr milled sample weighing 70 mg was synthesized by heating up to 1450 ˚C in an alumina crucible under argon atmosphere at a heating rate of 10˚C/min. using a Netzch STA 409 differential thermal analyzer. The unmilled and milled powders were examined by a JEOL JDX-8030 X-Ray diffractometer at 30 kV / 20 mA with Cu Kα radiation for phase identification. To investigate the morphology of as-milled powder particles, a LEO 912AB TEM with a tungsten gun at an accelerating voltage of 120 kv was used. In order to prepare the TEM samples, the as-milled powder particles were ultra sounded to have the agglomerated particles separated and then were put on carbon grids for observation. The phases of TiO_2, Al and graphite in the unmilled powder mixture were first identified by TEM separately and then the phases in the as-milled powder mixtures were determined by comparison with the images of individual phase.

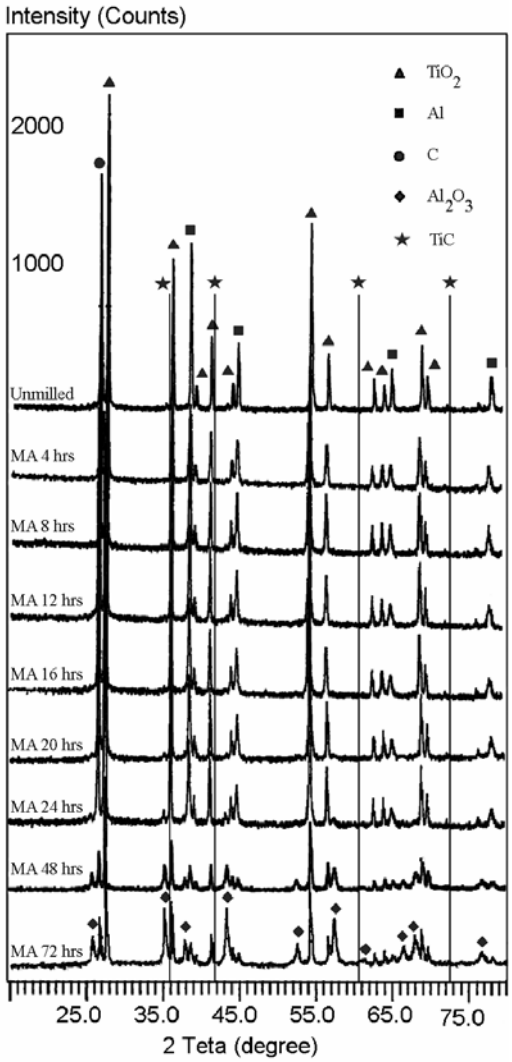

Fig. 1. XRD patterns of TiO_2+Al+C powder mixture before and after milling for different times under K1 conditions.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Mechanically Activated Powders

3.1.1. X-ray diffraction (XRD) analysis

The XRD patterns of as-milled powders as a function of milling times for K1, K2, and K3 series of experiments are shown in Figs. 1 to 3,

respectively. As can be seen from these figures, the main phases shown in these patterns were TiO_2, Al, and C suggesting that no significant reactions occurred between the constituents of the powders during milling. Comparing these patterns, one can see that by increasing the milling times all the peaks were broadened due to the refinement of particles and the residual strain caused by plastic deformation. However, the broadening is more severe in K3 series of experiments rather than in K2, and K1 series.

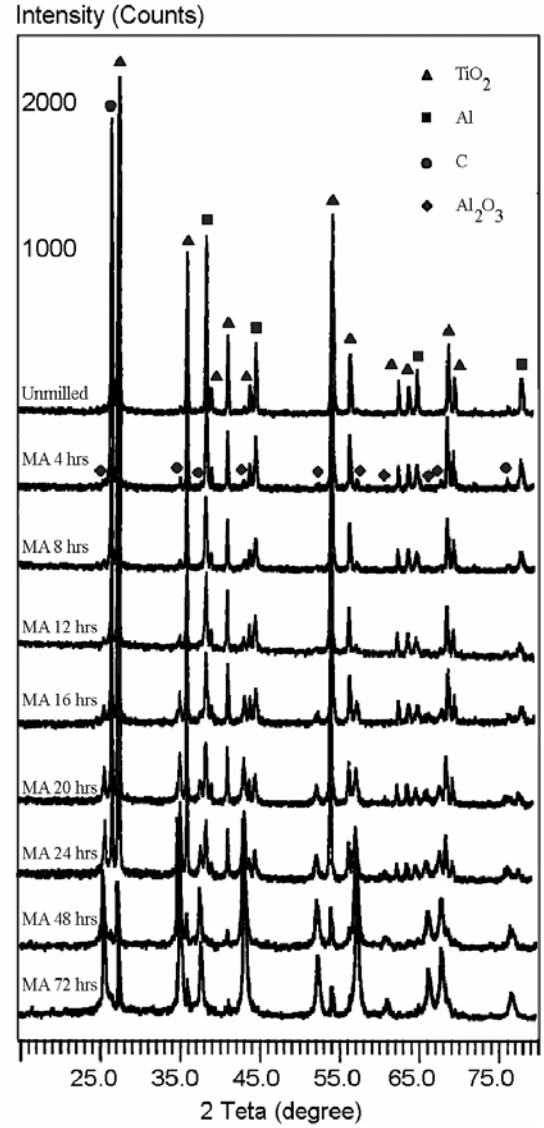

Fig. 2. XRD patterns of TiO_2+Al+C powder mixture before and after milling for different times under K2 conditions.

After milling for 72 hrs in K2 and 24 hrs in K3 series, Bragg peaks of graphite have disappeared. This phenomenon occurred for aluminum after 48 hrs in K2 and 72 hrs in K3 series, suggesting the formation of amorphous phases coexisting with rutile crystals. Therefore, the highest rate of amorphization taken place for graphite in K3 conditions and the lowest rate of amorphization happened in K1 conditions.

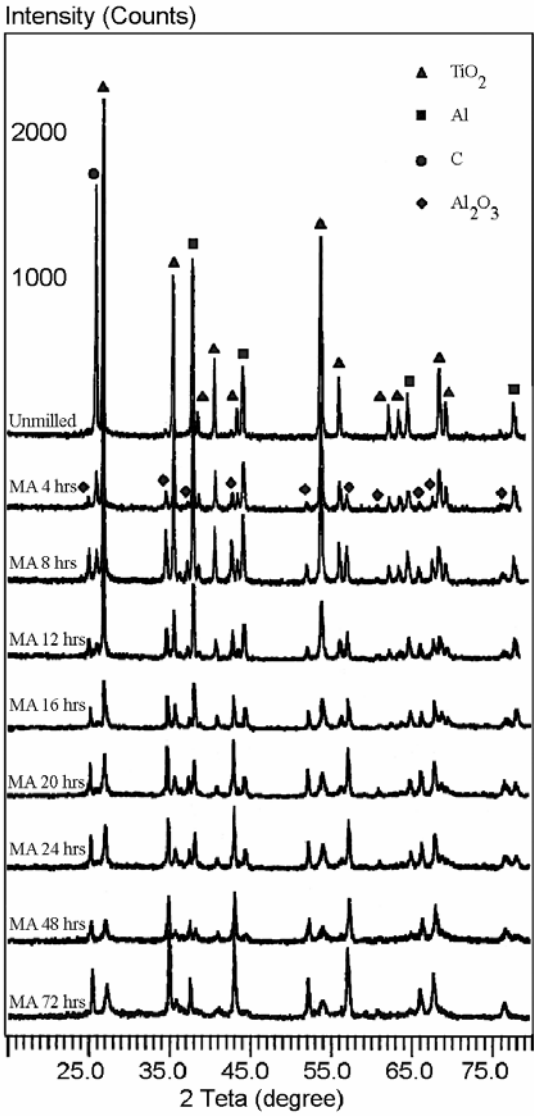

Fig. 3. XRD patterns of TiO_2+Al+C powder mixture before and after milling for different times under K3 conditions.

This behavior can be attributed to the milling environment as well as using a mixed large and small size balls which make the mechanical milling be more efficient due to the increase of collision surfaces and frequencies between the powder particles and the balls. Although the reaction given in Eq. 1 is thermodynamically favorable [25], it is clear from the relevant XRD patterns that even after milling the powder mixture for 72 hrs there is no evidence of

reaction between the constituents of the powders.

The absence of any reaction during milling in these conditions could be due to the kinetic barriers which could not be overcome under these milling conditions. Nevertheless, Pallone et al. [13] showed that milling of this powder mixture in a SPEX 8000 mill could trigger the reaction, which could be due to the higher energy of SPEX 8000 milling machine in comparison with the planetary milling machine used in this work.

3.1.2. Transmission electron microscope (TEM) analysis

TEM analysis of powder mixtures being milled for 24 hrs along with the XRD profile line analysis, allow a precise definition of the particular structure formed during mechanical alloying under different conditions. The XRD analysis of mechanically milled powders represents more severe broadening phenomena in K3 series of milling experiments than that of K1 series suggesting higher rate of energy induced in the powders, during milling at K3 condition than that in K2 and specially K1 condition. In order to investigate the structure of the milled powder under these two milling conditions, two samples of 24hr –milled powders under K3 and K1 milling condition*s* were analyzed by TEM examination.

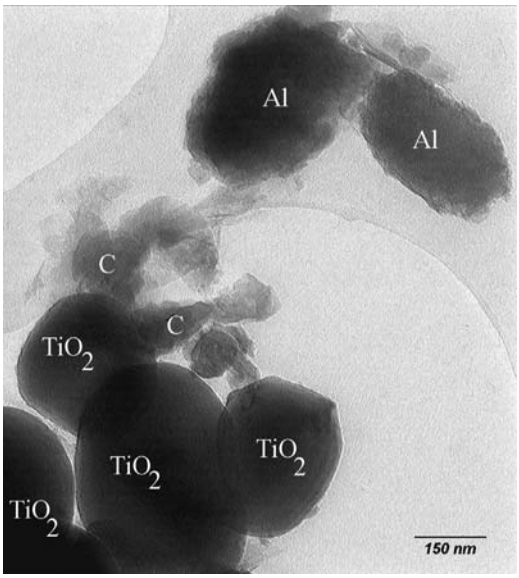

Fig. 4. TEM micrograph of 24 hr-milled powder particles under K1 conditions.

Figs 4 and 5 show typical TEM micrographs of the powder mixture samples milled for 24 hrs at K1 and K3 conditions respectively. As seen from Fig. 4, in K1 series of experiments the milled powder is composed of nanostructured aggregates of primary constituents which individual phases can be simply detected while at K3 condition there are homogenized composite particles in which the primary constituents can hardly be identified (Fig. 5).

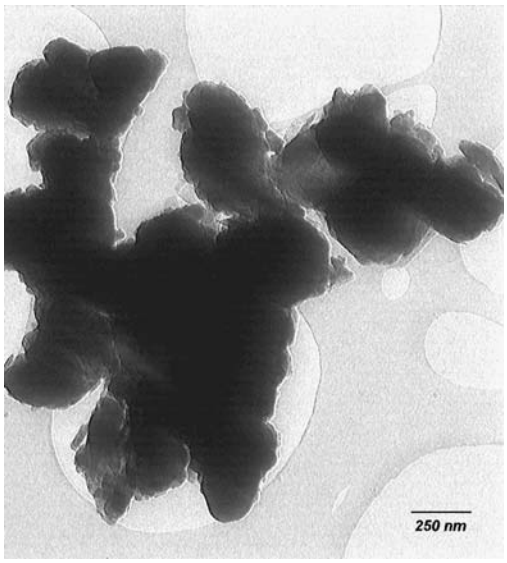

Fig. 5. TEM micrograph of 24 hr-milled powder particles under K3 conditions.

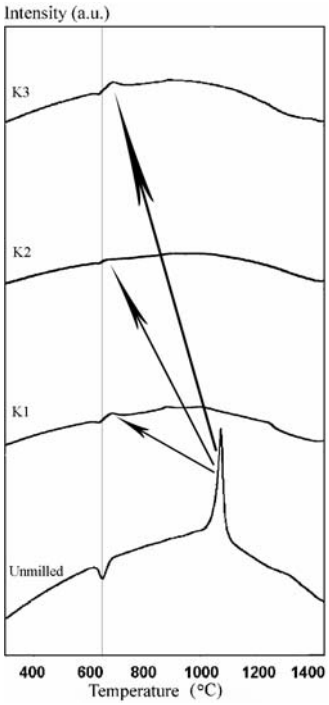

Fig. 6. DTA curves of powder mixture pre-milled for 24 hrs in different conditions.

Table 1. Milling conditions for different series of experiments (ball to powder ratio: 4:1).

Experimental series	Milling environment	Ball diameter	Milling time
K1	Wet (Wetting agent: ethanol solution amounted to 5wt %)	20 mm	4, 8, 12, 16, 20, 24, 48, and 72 hrs
K2	"	66%wt (20 mm) + 34%wt (10 mm)	"
K3	Dry	"	"

1. Synthesis of Powder Mixtures

Fig. 6 shows the DTA curves of unmilled and 24 hr-milled powders under different mechanical alloying conditions given in Table 1. The DTA trace for unmilled powder shows an endothermic peak during heating at about 648 ˚C, and a sharp exothermic peak at about 1079 ˚C. The position of endothermic peak suggests that it was due to the melting of aluminum. The exothermic peak appeared at about 1079 ˚C could be due to the exothermic reaction occurred between rutile (TiO_2) particles and molten aluminum.

Comparing the DTA traces in Fig. 6 shows that the position of exothermic peak has been shifted to lower temperatures as the milling conditions vary according to Table 1. As can be seen, the temperature of the exothermic peak decreases about 381-402 ˚C for different milling conditions. This behavior can be mainly attributed to the decrease in particle size and increase of the surface area of the reactants as Pallone et al. [13] explained in their research work. On the other hand, an increase of internal energy level of the milled powders facilitates the reaction between the constituents of the powder mixture [1]. The mechanism of combustion synthesis of TiC- Al_2O_3 in Al-TiO_2-C system was studied by Choi et al. [26] and Cho et.al. [27] in which they showed that the combustion reaction is a combined process in which the aluminothermic reduction of TiO_2, and TiC formation reactions occur sequentially. Based on the above mechanism, it can be suggested that the mechanical alloying of TiO_2-Al-C mixture must have enhanced the reaction between TiO_2 and Al by increasing the contact area and decreasing the diffusion distance between reactants. This may lower the difference between the energy of reactants and products which can be resulted in the severe decrease of the exothermic peak intensity in the DTA curve [9].

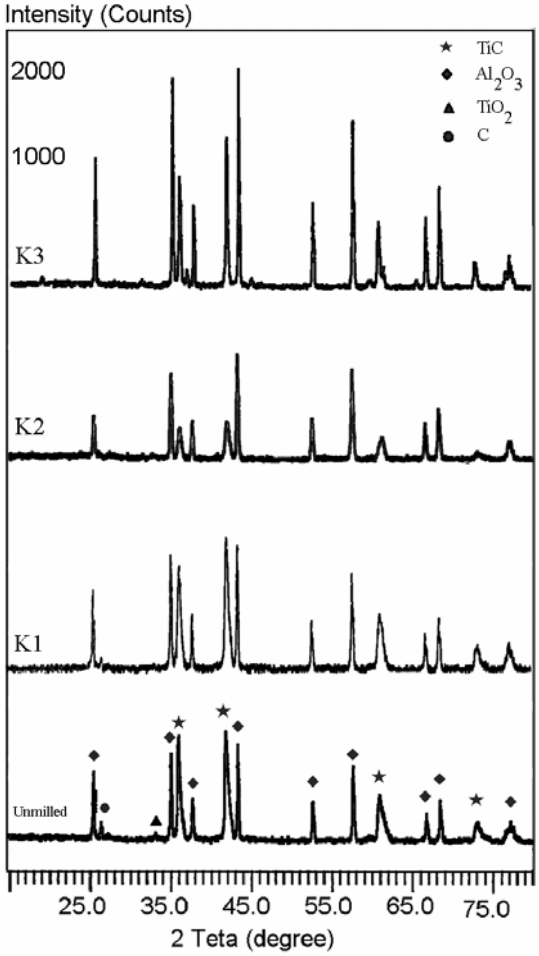

Fig. 7. DTA curves of powder mixture pre-milled for 24 hrs in different conditions.

XRD patterns of synthesized unmilled and milled powders under different conditions are shown in Fig. 7. As can be seen the phases existing in the synthesized product are mainly titanium carbide and aluminum oxide. This means that the reaction between Al, TiO_2, and C leads to the formation of TiC and Al_2O_3, even though some TiO_2 and C are still left. From comparison of the patterns shown in Fig. 7, it can be deduced that the highest ratio of desired mixture (TiC +

Al_2O_3) is achieved for the powder mixture milled in dry environment (K3 series of experiment).

4. CONCLUSIONS

Analysis of the milled powder mixture of TiO_2+Al+C for different times showed no significant chemical reaction between the constituents of powder mixture while an amorphous structure was obtained for graphite and aluminum after milling for certain times.

Milling in dry environment with mixed large and small size balls has the highest effect on the homogenization of the phases and the enhancement of the amorphization process.

Milling has a great effect on the mechanism of TiC+Al_2O_3 synthesis in TiO_2-Al-C system. It makes the reaction temperature and DTA peak intensity of reaction decrease. The energy required for the reaction is decreased significantly by mechanical activation of the reactants.

Milling of the reactants powder mixture for 24 hrs in dry environment yields to the highest TiC+Al_2O_3 (desired phases) ratio in the synthesized products, in comparison with other milling conditions, tested.

REFERENCES

1. J. Lagerbom, T. Tiainen, M.Lehtonen, and P. Lintula, Effect of partial alloying on self-propagating high-temperature synthesis of Ni_3Si, J. Mater. Sci. 34 (1999) 1477-1482.
2. E. Gaffet, F. Bernard, J. C. Niepee, F. Charlot, C. Gras, G. Caer, J.L. Guichard, P. Deleroix, A. Mocellin and O. Tillement, Some recent developments in mechanical activation and mechanosynthesis, J Mater. Chem. 9 (1999) 305-314.
3. C. Suryanarayana, Mechanical alloying and milling, Prog. Materials Science, 46 (2001) 1-184.
4. M. Sherif El-Eskandary, Mechanical alloying for fabrication of advanced engineering materials, Noyes, New York, 2001.
5. E. Ivanov, C. Suryanarayana, Materials and process design through mechanochemical routes, J. Materials Synthesis and Processing 8 (2000), 235-244.
6. P. B. Joshi, G.R. Marathe, N.S.S. Murti, V.K. Kaushik , and P. Ramakrishnan, Reactive synthesis of titanium matrix composite powders, Mater. Letters 56 (2002) 322-328.
7. G. Cocco, F. Delogu, and L. Schiffini, Toward a quantitative understanding of the mechanical alloying process, J. Mater. Synth. Proc. 8 (2000) 167-180.
8. H. Arik, Production and characterization of in situ Al_4C_3 reinforced aluminum based composite produced by mechanical alloying technique, Mater. Design 25 (2004) 31-40.
9. N. J. Welham, Mechanical activation of the formation of an Alumina-Titanium trialuminide composite, Intermetallics 6 (1998) 363-368.
10. D. Y. Ying, D. L. Zhang, and M. Newby, Solid-state reactions during heating mechanically milled Al/TiO_2 composite powders, Metal. and Mater. Trans. A 35A (2004) 2115-2125.
11. H. Arik, Investigation of Influences of pressing pressure and sintering temperature on the mechanical properties of Al-Al_4C_3 composite materials, Turkish J. of Eng. and Environment Sci. 27 (2003) 53-58.
12. R. Koc, Kinetics and phase evolution during carbothermal synthesis of titanium carbide from ultrafine titania/carbon mixture, J. Mater. Sci. 33 (1998) 1049-1055.
13. E. M. J. A. Pallone, R. Tomasi, F. Botta, and J. Walter, Microstructural evolution during high-energy ball milling of TiO_2-Al-C mixtures, Acta Microscópica 8 A (1999) 19-20.
14. W. Zhou, W. B. Hu, and D. Zhang, Combustion synthesis of highly porous ceramics: The TiC-Al_2O_3 system, J. Mater. Sci. 34 (1999) 4469 – 4473.
15. C. R. Bowen, and D. Derby, The formation of TiC/ Al_2O_3 microstructures by a self-propagating high-temperature synthesis reaction, J. Materials Science, 31 (1996) 3791– 3803.
16. J. H. Lee, S. K. Ko, and C. W. Won, Sintering behavior of Al_2O_3-TiC composite powder prepared by SHS process, Mater. Res. Bul. 36 (2001) 989–996.
17. T. D. Xia, T. Z. Liu, W. J. Zhao, B. Y. Ma, and T. M. Wang, Self-propagating high-temperature, synthesis of Al_2O_3-TiC-Al composites by aluminothermic reactions, J.

Materials Science, 36 (2001) 5581 – 5584.
18. H. J. Fenk, J. J. Moore, and D. G. Wirth, Combustion synthesis of ceramic-metal composite materials: the TiC-Al_2O_3-Al system, Metal. Trans. A 32A (1992) 2373-2379.
19. U. Tamburini, F. Maglia, G. Spinolo, S. Doppiu, M. Monagheddu, and G. Cocco, Self-propagating reactions in the Ti–Si system: A SHS-MASHS comparative study, J. Mater. Synth. Proc. 8 (2000) 377-388.
20. Ch. Gras, D. Vrel, E. Gaffet, and F. Bernard, Mechanical activation effect on the self-sustaining combustion reaction in the Mo–Si system, J. Alloys and compounds 314 (2001) 240–250.
21. R. Abramovici, Composite ceramics in powder or sintered form obtained by aluminothermal reactions, Mater. Sci. Eng. 71 (1985) 313-320.
22. D. Atong, and D. E. Clark, Ignition behavior and characteristics of microwave-combustion synthesized Al_2O_3–TiC powders, Ceram. Int. 30 (2004) 1909–1912.
23. S. Adachi, T. Wada, T. Mihara, Y. Miyamoto, and M. Koizumi, High-pressure self-combustion sintering of alumina-titanium carbide ceramic composite, J. Amer. Ceram. Soc. 73 (1990) 1451-1452.
24. S. H. R. Fatemi Nayeri, J. Vahdati Khaki, and M. R. Aboutalebi, To study the TiC+Al_2O_3 combustion synthesis in mechanically activated TiO_2-Al-C system, Proceeding of the10th annual congress of Iranian metallurgical engineers society, Ferdowsi university of Mashad, Nov. 2006. (In press)
25. N. J. Welham, Mechanical activation of the solid-state reaction between Al and TiO_2, Mater. Sci. Eng. A255 (1998) 81–89.
26. Y. Choi, and S.W. Rhee, Reaction of TiO_2-Al-C in the combustion synthesis of TiC-Al_2O_3 composite, J. Amer. Ceram. Soc. 78 (1995) 986-992.
27. C. H. Cho, D. K. Kim, Microstructure evolution and isothermal compaction in TiO_2-Al-C combustion reaction, J. Mater. Synth. Proc. 10 (2002) 127-134.