SYNTHESIS OF TiC-Al_2O_3 NANOCOMPOSITE FROM IMPURE TiO_2 BY MECHANICAL ACTIVATED SINTERING

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Abstract In this research, the production possibility of TiC-Al_2O_3 nanocomposite, as a useful ceramic from commercially pure TiO_2, aluminum powder and carbon black has been investigated. Routile (TiO_2) with carbon black and aluminum were placed in a high energy ball mill and sampled during different milling times. Then, the activated powders were synthesized at different temperatures in an atmosphere control tube furnace. Our results show that using this method has decreased the synthesizing temperature to 1000-1250˚C by increasing the milling time. Also the width of X-ray patterns peaks, had made it apparent that, the size of produced TiC crystals was in order of nanometer. Furthermore it was detected that the lattice parameter deviated slightly from the standard size.

Keywords Nanocrystal, Mechanical Activated, Titanium Carbide, Routile

چکیده در این پژوهش، امکان تهیه نانوکامپوزیت TiC-Al_2O_3 به عنوان یک سرامیک مفید از TiO_2 ناخالص، دوده و پودر آلومینیم با استفاده از فعال سازی مکانیکی بررسی گردید. روتایل همراه با دوده و آلومینیم در یک آسیای پرانرژی قرار داده شد و در زمان های مختلف از آن نمونه برداری شد. پودر های اکتیو شده در یک کوره تیوپی دارای اتمسفر کنترل شده در دماهای مختلف سنتز شد. مطالعات نشان داد دمای سنتز با افزایش زمان آسیا به مقدار قابل توجهی کاهش یافته و به دمایی بین ۱۰۰۰˚C تا ۱۲۵۰˚C رسیده است. همچنین از روی پهنای پیک های الگوی پراش اشعه ایکس، دیده شد که اندازه کریستال های TiC تولید شده در حد نانو می‌باشد در حالی که میزان پارامتر شبکه از حالت استاندارد انحراف اندکی نشان می‌دهد.

1. INTRODUCTION

Titanium carbide (TiC) is an interesting commercial material because of its vast range of desirable properties. It is one of the hardest known metal carbides with low density and relatively high thermal and electrical conductivity. TiC also is very stable along with a high melting point of (3100˚C) which does not go through any phase transformations. Also it has a high thermal shock and high abrasion resistance [1,2]. This material has the sodium-chloride (NaCl) structure, with face-centered-cubic Ti with carbon atoms in the octahedral interstices [3]. TiC is used to manufacture cutting tools, grinding wheels, polishing paste or can even be combined with other ceramics such as Al_2O_3 and Si_3N_4 for the production of components used in high temperatures, erosive and/or corrosive applications [3,4].

Recently, mechanically activated sintering (MSA) process, including a combination of mechanical alloying (MA) to a superfine structure followed by sintering has attracted much interest. It is due to the fact that the mechanically prepared alloyed powder

consists of many fine particles with large grain boundary areas, and the buildup of defects and also the formation of internal strains, which improve the sinter ability; therefore the sintering temperature decreases in the second step [5,6].

In this work the feasibility of producing TiC-Al_2O_3 composite from cheaper materials, via mechanically activated sintering and also the effect of parameters on the formation of this material, will be studied and discussed.

2. EXPERIMENTAL

The TiO_2 used in this work was commercially pure with particle size of < 200 mesh (< 75 μm). X-ray fluorescence (XRF) showed that the TiO_2 has 0.53 wt % Si, 0.41 wt % Fe and 0.08 wt % of other elements as impurities, but X-ray diffraction (XRD) showed that the only existing phase was routile (TiO_2).

Carbon black with particle size of < 250 mesh (< 65 μm) was used as the source of carbon. XRD analysis expressed that the carbon black has an amorphous structure. Also aluminum with purity of 99.9 wt % and particle size less than 100μm was used in this experiment.

The applied ball mill was of planetary type. This type is classified as high-energy ball mills. The ball to the powder weight ratio during experiments was 10:1 and three similar balls with the diameter of 20 mm were utilized. In order to protect the materials from oxidation, argon with the purity of 99.9999 % and pressure of 2.5bar was charged in the cylindrical container of raw materials. Materials with stoichiometry ratio were mixed (according to following reaction) with 10 wt % Al. Then they were milled for 5, 10, 20 and 50 hours.

$$TiO_2 + 3C = TiC + 2CO \quad (1)$$

After the evaluation of milled powders, for completion of reactions and desired phases, also investigating the milling effect on the activated materials and TiC synthesizing temperature, heat treatment was performed. Two samples, one without milling and the other with the longest milling time were selected and heat treated. Heat treatment was performed in an atmosphere control tube furnace. Dick samples with 20 mm diameter and 5 mm thickness were produced in a steel die using load of 1000 Kgf to prevent the specimens from oxidation and undesired reactions, argon with the flow of 1.9 - 2.2 lit/min was used. To decrease the oxygen impurity in argon gas, argon was passed through copper wire and titanium components which had a temperature of about 200˚C before entering the furnace. Heating rate was constant and equal to 10˚C/min. The samples were held in furnace at 1000, 1250 and 1500˚C and then cooled in the furnace to room temperature. The holding time was one hour for the maximum temperature.

In order to detect the type of synthesized phases and components, XRD analysis with the voltage and current of 30 kV and 25 mA respectively and CuKα radiation (λ = 1. 54Å) was carried out. The crystallite size and strain of the system were calculated from the width of XRD pattern peaks through Williamson-Hall, et al [7] method. Also, for investigation the influence of milling on lattice parameter could be considered using Nelson-Riley, et al [8] method. The lattice parameter of TiC is 0.4327 nm in accordance to file no, 73-0472 of the international center for diffraction date (JCPDS-ICDD 2000).

3. RESULTS AND DISCUSSION

The results of XRD analysis of the samples containing TiO_2, Al and C which have been milled for 5, 10, 15, 20 and 50 hours are shown in Figure 1. It can be seen that milling did not have any influence on the type of exciting and detectable phases, which were TiO_2 and Al. Therefore, TiO_2 can not be reduced by Al even with long milling time. The only significant changes which took place during the milling time were a small broadening of the peaks and reduction of their intensity which could mean that TiC had become finer.

X-ray diffraction of the heat treated samples in two conditions of non-milling and after 50 hours milling are shown in Figure 2a. In the non-milling specimen, TiO_2 and Al_2O_3 were the only phases that were detected, and TiC was not formed even at 1500˚C. Hence these temperatures were not high enough for synthesizing TiC.

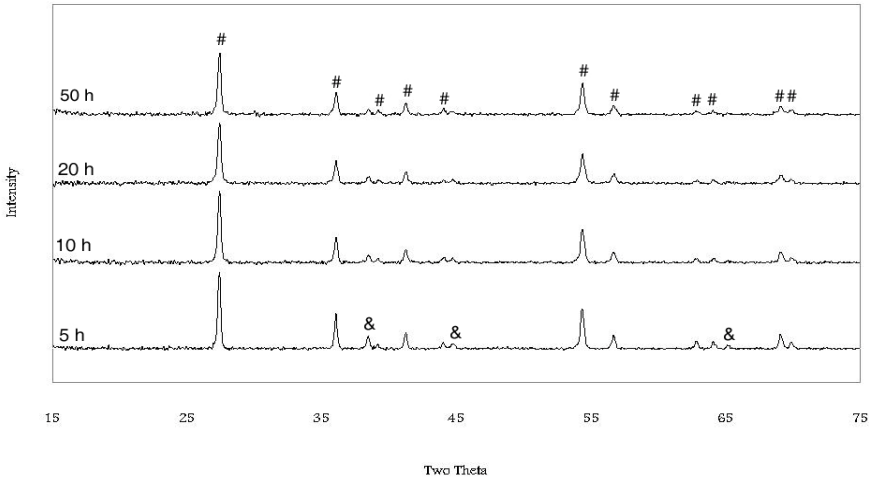


Figure 1. XRD pattern of milled specimens containing TiO_2-C-Al (#) TiO_2, Al (&).

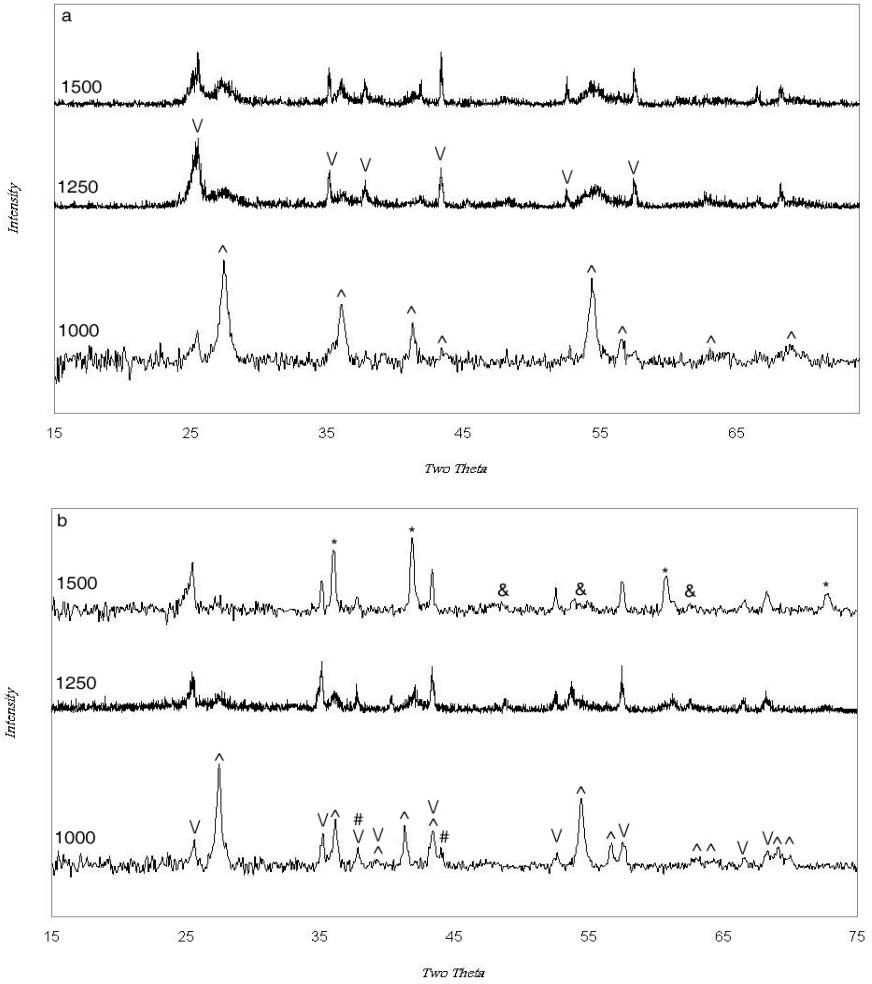


Figure 2. XRD pattern of TiO_2-C-Al containing heat treated specimens (a) not milled condition (b) after 50 hours milling Tic (*), Al (#), Ti_2O_3 (&), Al_2O_3 (\/),TiO_2 (^).

But in milled samples which have been heat treated at 1000˚C, the sharp peaks corresponded to TiO_2 and Al_2O_3, although certainly the existence of weak peaks of TiC and Al were not discredited (Figure 2b). Increasing the temperature of the heat treatment to 1250˚C led the formation of TiC with Al_2O_3. Strong TiC peaks can be observed by increasing the temperature to 1500˚C with Al_2O_3 peaks and weak peaks of Ti_2O_3. Additional milling caused the TiO_2-C-Al powder to be activated, hence synthesizing temperature reduced (1000˚C-1250˚C). In this system, the reaction which is supposed for the formation of TiC and Al_2O_3 from TiO_2, Al and carbon is:

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

The equilibrium formation temperature of TiC from TiO_2 and Al can be calculated theoretically. According to this calculation the temperature range of the reactive free energy during our experiment was negative. Thus synthesis of TiC-Al_2O_3 from TiO_2, C and Al at these temperatures is feasible.

The mean grain size of produced TiC powder and amount of stress in the system were determined. The plot resulted from Williamson-Hall method is shown in Figure 3. The results are presented in Table 1. It can be seen that the size of TiC crystals is about nanometer and increasing the temperature during heat treatment leads the crystals to grow and reduce in strain.

In Figure 4, the SEM images of the powders milled for 5 and 50 h are beheld. It was observed that while the milling time increases, the inhomogeneity and the particle size decrease. Figure 5 shows the bright-field TEM image of the sample after milling for 50h.There are much smaller grains in a particle. The grain size from this image is almost equal to the measurement by the Williamson-Hall method.

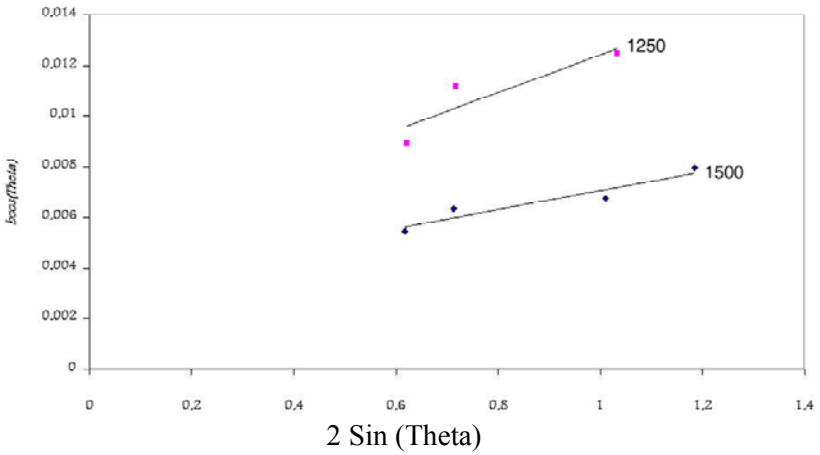
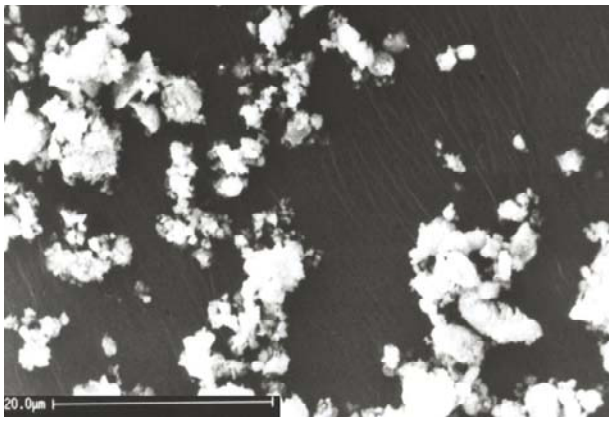


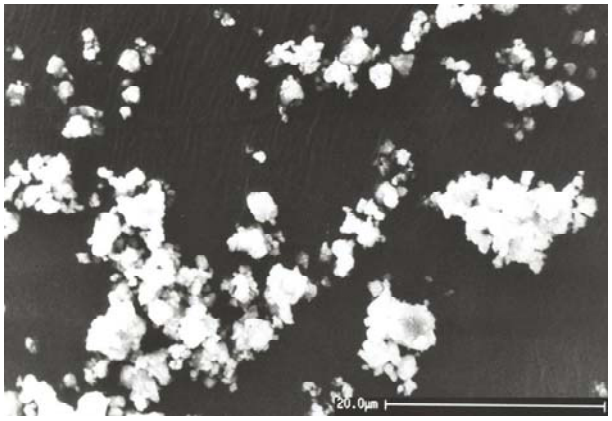
Figure 3. Calculation of grain size for specimen milled 50 hours and heat treated at 1250˚C and 1500˚C using williamson-hal equation in TiO_2-C-Alcontaining mixture.

TABLE 1. Mean Grain Size and Stress Amount of Tio_2-C-Al Mixture Milled for 50 Hours and Heat Treated at 1250˚C and 1500˚C Based on Williamson-Hal Equation.

Heat Treatment Temperature (˚C)	y = ax + b		d_{TiC} (nm)	η_{TiC} (%)	R^2
	a	b			
1250	0.0075	0.0049	28.29	0.75	0.8078
1500	0.0038	0.0033	42.01	0.38	0.9028



(a)



(b)

Figure 4. SEM images of milled samples in (a)5 h and (b) 50 h.

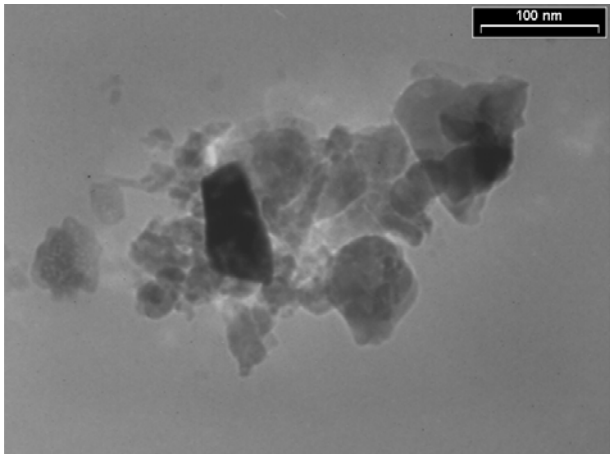


Figure 5. BFI of a mechanically alloyed sample after milling for 50 hr.

The lattice parameter is calculated using Nelson-Riley equation in Figure 6. The quantity that can be calculated is 0.4290 nm and 0.4306 nm for temperature of 1250˚C and 1500˚C respectively. The amount of deviation from standard state of TiC is 0.0037 nm and 0.0021 nm.

Generally, the lattice parameter deviation of TiC from the standard state can be attributed to three facts:

- Existence of defects and strain in the system caused by the increase of temperature (Table 1);
- None calibrated instruments and deviation from standard state;
- None observance of exact stoichiometric ratio of the produced TiC.

Figure7 shows the equilibrium phase diagram of Ti-C [10]. In accordance to this figure, the ratio of C: Ti is 0.55-0.95 at ambient temperature. Thus, the deviation of the lattice parameter can be caused by non-stoichiometric ratio of the synthesized carbide.

4. CONCLUSION

- Milling without subsequent heat treatment could not reduce the mixture containing TiO_2, Al and C.
- Heat treatment of TiO_2, Al and C containing mixture did not result in formation of TiC. But in the specimen milled for 50 hours, TiC-Al_2O_3 nano powder was formed at 1000˚C-1250˚C.
- Despite performing heat treatment on milled samples, TiC crystallite size was in nanometer order.
- Milling the mixture of powders resulted in deviation of TiC lattice parameter from standard state. This deviation can be related to increment in the amount of strain, formation of TiC with non-stoichiometric ratio and lack of instrument calibration.

5. REFERENCES

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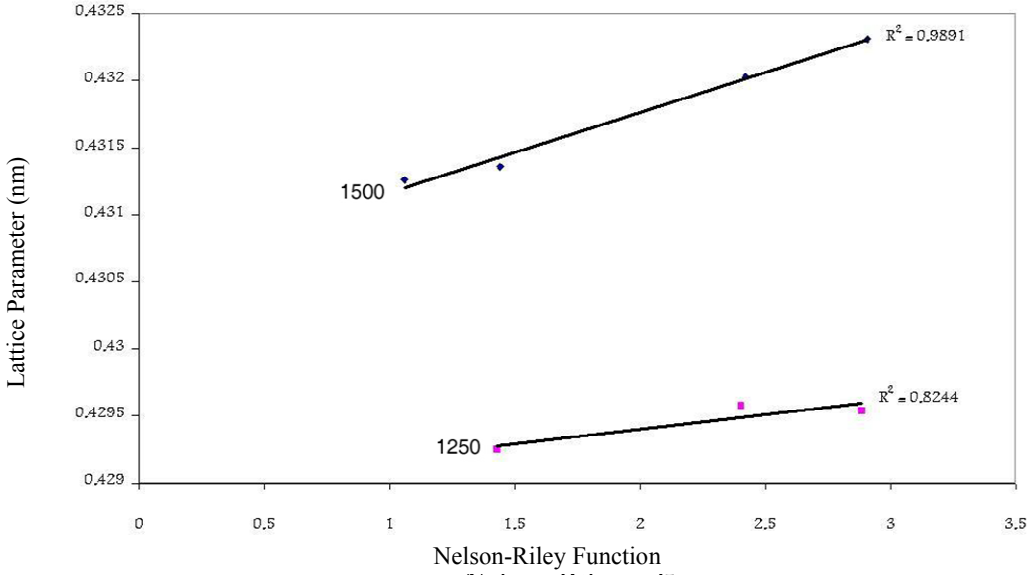

Figure 6. Determination of TiC lattice parameter in TiO_2-C-Al system after 50 hours milling and heat treating at 1250˚C and 1500˚C using Nelson-Riley equation.

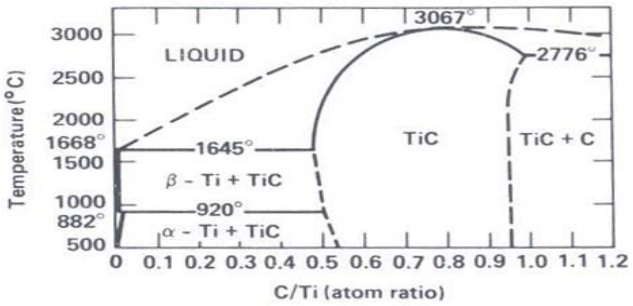

Figure 7. Ti-C equilibrium diagram [10].

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