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Synthesis of Tantalum Carbide/Boride Nanocomposite Powders by Mechanochemical Method

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ABSTRACT

In this study, mechanochemcical process (MCP) is applied to synthesize ultrafine TaC powders. In this research, nanopowder composite TaC-TaB_2 was produced using mixtures of tantalum carbide and boron carbide as raw materials, via mechanochemical process. The phase formation characterization during the process was utilized by X-ray diffractometry (XRD). The morphology of synthesized powder was studied using scanning electron microscopy (SEM).

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1. INTRODUCTION

Development of the ceramic matrix composites (CMCs) that combine the advantageous properties of the individual components for high performance applications is of special interest to the ceramic industry [1]. With the rapid development of aerospace technology, it is urgent to study the new materials used in high temperature structural components [2].Tantalum Carbide (TaC) is an ultra high-temperature ceramic (UHTCs) for high performance applications with a melting point in excess of 3900˚C [1-3]. Unique combination of good chemical stability, good corrosion resistance, high modulus (537GPa), high hardness(15–19GPa) and other good mechanical properties make it a candidate material for rocket propulsion components [4, 5] and many applications as high speed cutting tools, wear resistant parts, hard coating on hard metals and high temperature structural materials [1]. Performance of this material at high temperature needs good oxidation resistance [5]. Researchers have found that TaB_2 is a suitable additive [4]. Tantalum borides have not been studied as extensively as other borides, like TiB_2 [6], ZrB_2 [7], and HfB_2 [8]. According to the Ta–B phase diagram [9], there are five boride phases including Ta_2B, Ta_3B_2, TaB, Ta_3B_4, and TaB_2. Besides these, a new phase, Ta_5B_6, and its crystal structure was later identified by Bolmgren et al. [10]. On the formation of tantalum borides, a variety of processing routes have been utilized. For example, Hideaki et al. [11] produced TaB_2, TaB, and Ta_3B_4 by solid state reactions of mixed Ta and amorphous boron powders under corresponding compositions at 800, 900, and 1800˚C, respectively. Peshev [12] obtained TaB_2 through borothermic reduction of Ta_2O_5 at 1650˚C for 1 h. The tantalum diboride (TaB_2) with comparable mechanical properties to ZrB_2 and HfB_2 was also fabricated by reducing Ta_2O_5 with B_4C and graphite at 1600˚C.The ternary phase diagram (Figure 1) has been known since 1963 [13]. It is well known that the properties of composite TaC-TaB_2 are strongly dependent on the relative amounts and types of the various phases formed. It has to be noted that B_4C, which is also a component of the Ta–C–B ternary system, is not chemically compatible with Ta or TaC. It reacts with Ta and TaC forming TaB_2 and free carbon that has been used for the synthesis and processing of diboride-containing ceramics [14]. Recently, mechanical activation and mechanical milling have been extensively used for synthesis of advanced materials.

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The technological advantages of the mechanochemical synthesis are obvious. High-temperature processes and furnaces for synthesis of this composite are avoided.
The product is finely dispersed and has a defect structure which increases the sinterability of TaC-TaB_2 powder. This article demonstrates the formation of TaC-TaB_2 by ball milling a mixture of TaC and B_4C with the stoichiometry of the reaction (1):

$$TaC + B_4C = TaB_2 + 3C \qquad \Delta H^{\circ}_{298} = -59.67 \text{ kJ/mol} \tag{1}$$

The negative value of ΔH°_{298} suggests that this reaction is exothermic and should be self-sustaining.

2. EXPERIMENTAL

2. 1. Raw Materials The characteristics of the raw material are listed in Table 1. The TaC content in the TaC powder was higher than 99%. The main impurities were 0.3 wt% Nb, 0.1 wt% Fe, 0.20 wt% O,0.15 wt% free carbon, 0.05 wt% N, and Al, Ca, K, Na, Ti with a total amount <0.05 wt%. The B_4C was >95 wt% pure with major impurities being free carbon.

2. 2. Powder Preparation 25g TaC and 2.0%wt. B_4C were mixed in a 250ml WC cylinder using 150gr WC balls as mixing media. Ball milling of the powder mixture was carried out in a planetary ball mill at room temperature in n-hexane and under argon atmosphere. The ball-to-powder weight ratio and the rotational speed of vial were 20:1 and 250 rpm, respectively for 3, 6 and 12hours. The milling was interrupted at selected times and a small amount of powder was removed for further characterization.

2. 3. XRD Analysis Phase transformations during milling were determined by X-ray diffraction (XRD) in a Philips X'PERT MPD diffractometer using filtered Co Kα radiation (λ = 0.178 nm). The lattice parameter of a cubic substance is directly proportional to the spacing 'd' of any particular set of lattice planes (Equation (2)) [15].

$$a = \frac{d}{\sqrt{h^2 + k^2 + l^2}} \tag{2}$$

where *h, k, l are* Miller indices. the Nelson–Riley method was used to minimize errors caused by aberration of 2θ variation and the lattice parameter 'a' of TaC was calculated for at least three peaks, using Equation (3) [16].

$$F(\theta) = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \tag{3}$$

Silicon standard sample with large grains and free from defect broadening was used as a standard to increase the precision of the instrumental broadening.

TABLE 1. Raw material characteristics.

Material	Purity	Particle size	supplier
TaC	99%	1.25 µm	Ningxia Orient
B_4C	>95 wt%	300 nm	Jingangzuan

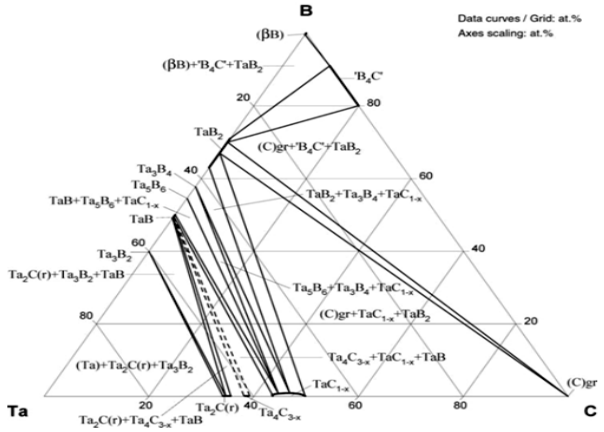

Figure 1.ternary diagram B-Ta-C[13].

Then, the error of diffractometer was eliminated by Equation (4) [16].

$$b = b_{size} + b_{strain} = \sqrt{b_0^2 - b_s^2} \tag{4}$$

where 'b_s' is the FWHM of the main peak of Si standard sample (2theta=28.5°) used for calibration and 'b_0' is the FWHM of TaC's peaks. Both 'b_s' and 'b_0' were calculated by X-Pert High Score software. Crystallite size and internal strain of specimens (μ) were calculated from broadening of XRD peaks using the Williamson-Hall method [17].

$$\beta\text{Cos}\theta = K\lambda / d + \mu\text{Sin}\theta \tag{5}$$

where θ is the Bragg diffraction angle, d the average crystallite size, k a constant (with a value of 0.9), λ the wavelength of the radiation used, and β the diffraction peak width at half maximum intensity. The morphology and microstructure of the milled powder particles were examined by SEM images in a Philips XL30 at an accelerating voltage of 30 kV.

2. 4. Morphology of Powders The morphology of selected mechanically alloyed powders was examined by a Scanning Electron Microscope (SEM-Philips XL30) operating at 30 kV.

3. RESULTS AND SIDCUSSION

3. 1. X-Ray Diffraction Analysis A commercial software program (HSC Chemistry) was used to identify the probable reaction using thermodynamic data. Figure

2 shows X-ray diffraction patterns of the TaC and TaC-TaB_2 powder after various milling times. Figure (2-a) shows XRD pattern of raw tantalum carbide powder without milling. Figure (2-b) shows XRD pattern of powder after 3 hours of milling were identified as a mixture of starting

The results show that no new phase is formed in the powder milled for 3 hours. B_4C phase in the XRD spectra was studied in some detail because of its small amount, only 2% by weight. Figure (2-c) shows the XRD results of the powders milled for 6 hours, TaB_2 phase reverted and there were still some B_4C in the composition. The XRD analysis indicated that only TaB and TaB_2, as presented in Figure (2-d), were produced from the samples of their equivalent stoichiometries. Figure (2-d) shows that the final products obtained from mechanochemical synthesis was free from three Ta-rich samples of Ta_2B= 2:1, Ta_3B_2=3:2 and Ta_3B_4=3:4 and contained a large amount of residual Ta. After 12h milling very small amount of TaB has been observed (Figure (2-d)). No XRD peaks were observed for B_4C, suggesting that a reaction had occurred in the system.

Since both cup and balls of the ball mill were made from WC, so the X-ray results show that increasing milling time up to 12 hours has caused a spike of tungsten carbide (Figure (2-d). The lattice parameter of TaC powder obtained from 3, 6 and 12 h milling is calculated by Nelson–Riley method from the XRD analysis (Figure 3). In this method, the accurate lattice parameter is obtained by extending the lattice parameter function and its connection to zero content of Nelson–Riley parameter. Figure 3 shows that the lattice parameter increases by increasing milling time. The change of lattice parameter of milled samples for 3, 6 and 12 h is presented in Table 2.

TABLE 2. The lattice parameter of TaC powder after 3, 6 and 12 h milling times.

Milling time (h)	Lattice parameter (Å), Nelson–Riley method
3	4.4446
6	4.4571
12	4.4712

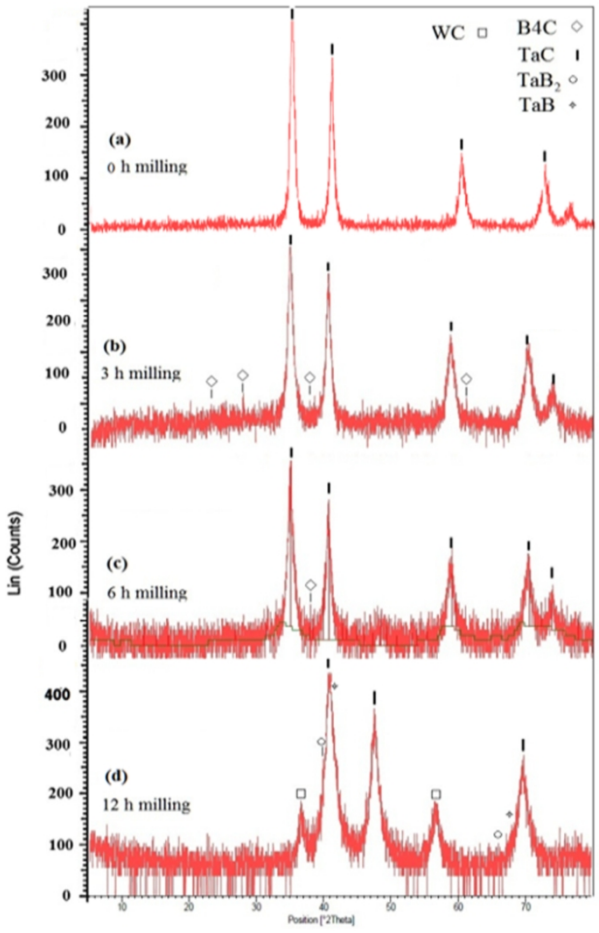

Figure 2. XRD patterns of TaC-B4C powder after various milling times:(a) 0, (b) 3, (c) 6, and (d) 12 h.

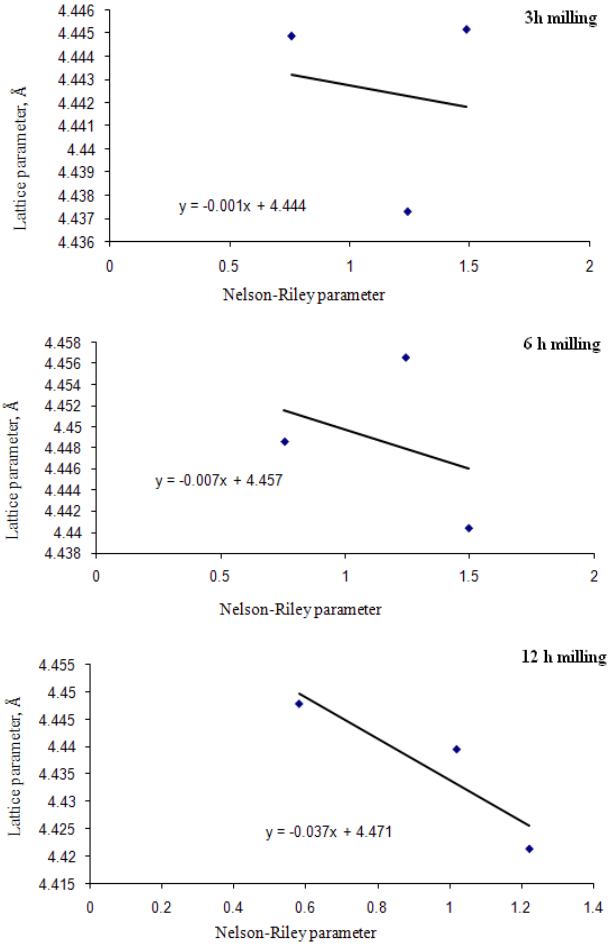

Figure 3. Nelson–Riley parameter for obtaining the lattice parameter of TaC phase after 3, 6 and 12 milling times.

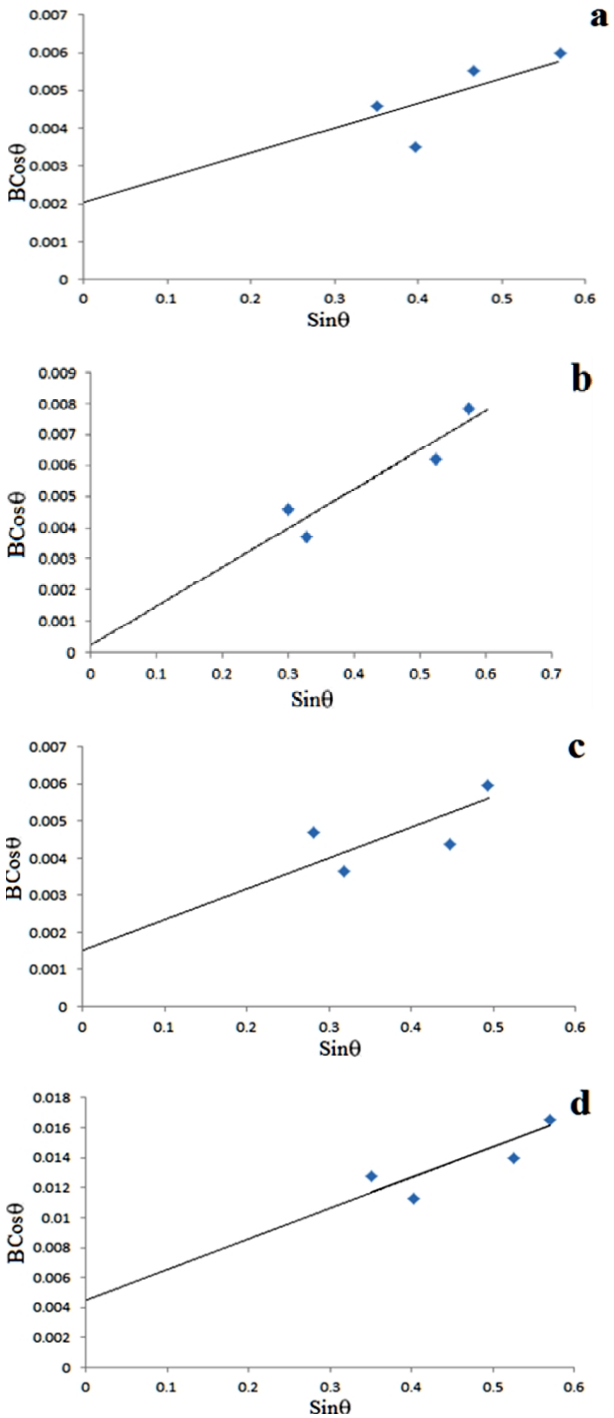

Figure 4. Plot of Bcosθ versus sinθ for TaC-B_4C milled powders: (a) 0, (b) 3, (c) 6, and (d) 12 h.

From Table 1, it is concluded that there is little increase in the lattice parameter by increasing milling time, suggesting the formation of a solid solution between TaC and B_4C. This observation is consistent with the Ta–B–C phase diagram, which indicates that B is partially soluble in TaC[13]. The addition of B_4C led to an increase in the lattice of TaC [18]. The TaC composition (C/Ta ratio) was related to the lattice parameter (a0) using the equation (C/Ta=-25.641+5.9757a0) given by Storms [19].

As this equation was established based on pure TaC, it is not accurate to use it to calculate the C/Ta ratio for the compositions that also contain B. However, the measured lattice parameter increased for specimens with additives, indicating that B and/or C from the additives probably entered into the TaC lattice. The grain size 'd' and strain 'μ' of TaC products during milling were measured using the Williamson–Hall method (Figure 4). The FWHM of the diffraction peak is wider with milling time due to the strain and the refinement of the powder. A plot of B cosθ versus sinθ [20] is shown in Figure 4. The average grain sizes of the TaC calculated from the XRD data were about 801, 267, 94 and 34 nm for the samples with milling times of 0, 3, 6, and 12 h. Using Equation (5) and the Williamson-Hall calculation method, internal strain and crystallite size of milled powder are as shown in Figure 5. Internal strain of powders has increased with increasing milling time, and crystallite size is reduced.

3. 2. Microscopic Examination SEM images of TaC powder with milling time are shown in Figure 6. This figure shows morphology of powder particles after different milling times. SEM images of TaC powder with milling time are shown in Figure 6. The unmilled TaC powder is angular in shape. Figure (6-b) shows that particle size reduction after 3 h of milling. At the beginning of the milling process, the brittle particles (TaC) fragmented and comminuted, and TaC powder became rounder, and some refinement occurred with milling time. Figure (6-c) shows that after 6 h milling the powder particles became nearly equiaxed in shape with a wide size distribution of 0.3-1μm. By increasing the milling time to 12 h the rate of fracturing increased, and as a result the size of powder particles decreased.

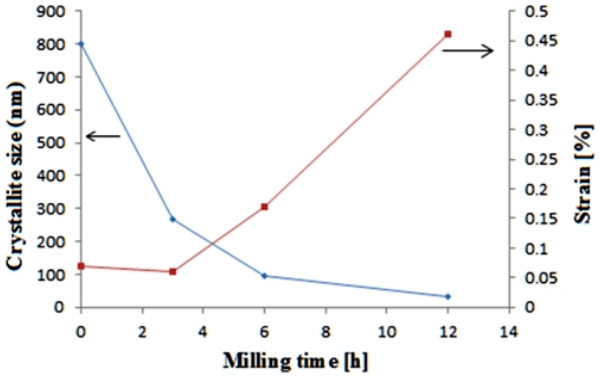

Figure 5. Effect of milling time on the crystallite size and internal strain of powders

At this stage, the morphology of powder particles was almost equiaxed (Figure (6-d)). The powder particles after 12 h of milling time are large agglomerates of ultrafine particles ranging from 0.1 μm to 2 μm.

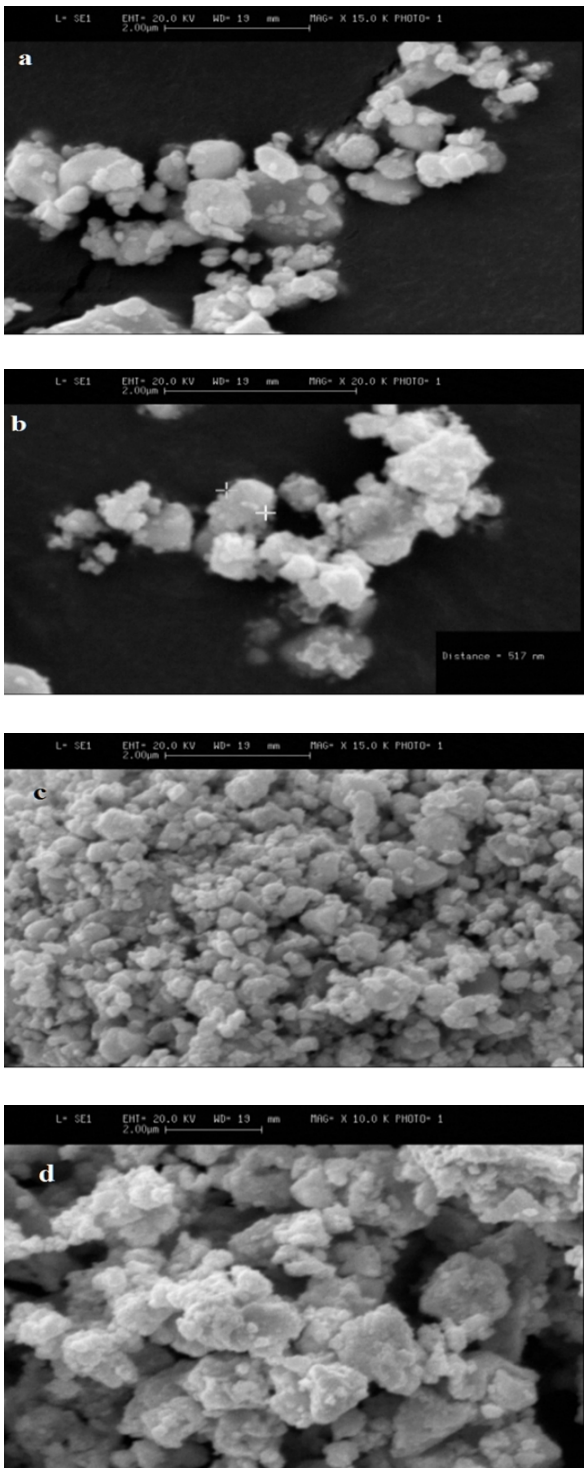

Figure 6. SEM micrographs of starting powders' particles (a) TaC powder, (b) after 3 h, (c) 6 h and (d) 12 h of milling times

4. CONCLUSION

$TaC-TaB_2$ composite powder has been synthesised by a low temperature solid-state reaction between tantalum carbide and boron carbide. Studies show that by milling TaC and B_4C powders, TaB_2 phase and the resulting composite $TaC-TaB_2$ is composed. Prolonging the milling time up to 12 h resulted in a decrease of grain size to nano scale along with increasing strain and a slight increase in lattice parameter of TaC phase. Crystallite size of milled powder decreased with increasing milling time up to 3, 6 and 12 h. the powder particle size reached to 267 were 94 and 34 nm. TaB_2 phase in the powder milled for 12h was observed, indicating that some mechanochemical synthesis process is carried out. Increasing milling time increased internal strain of crystallits.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. Squire, T. H. and Marschall, J., "Material property requirements for analysis and design of UHTC components in hypersonic applications", ***Journal of the European Ceramic Society***, Vol. 30, No. 11, (2010), 2239-2251.
2. Monteverde, F., Bellosi, A. and Scatteia, L., "Processing and properties of ultra-high temperature ceramics for space applications", ***Materials Science and Engineering: A***, Vol. 485, No. 1, (2008), 415-421.
3. Kwon, D.-H., Hong, S.-H. and Kim, B.-K., "Fabrication of ultrafine TaC powders by mechano-chemical process", ***Materials Letters***, Vol. 58, No. 30, (2004), 3863-3867.
4. Zhang, X., Hilmas, G. E. and Fahrenholtz, W. G., "Densification and mechanical properties of TaC-based ceramics", ***Materials Science and Engineering: A***, Vol. 501, No. 1, (2009), 37-43.
5. Hagemann, G., Immich, H., Nguyen, T. V. and Dumnov, G. E., "Advanced rocket nozzles", ***Journal of Propulsion and Power***, Vol. 14, No. 5, (1998), 620-634.
6. Munro, R. G., "Material properties of titanium diboride", ***Journal of Research of the National Institute of Standards and Technology***, Vol. 105, No. 5, (2000), 709-720.
7. Fahrenholtz, W. G., Hilmas, G. E., Talmy, I. G. and Zaykoski, J. A., "Refractory diborides of zirconium and hafnium", ***Journal of the American Ceramic Society***, Vol. 90, No. 5, (2007), 1347-1364.
8. Licheri, R., Orrù, R., Musa, C., Locci, A. M. and Cao, G., "Consolidation via spark plasma sintering of HfB2/SiC and HfB2HfC/SiC composite powders obtained by self-propagating high-temperature synthesis", ***Journal of Alloys and Compounds***, Vol. 478, No. 1, (2009), 572-578.

9. Massalski, T. B., Murray, J. L., Bennett, L. H. and Baker, H., "Binary alloy phase diagrams, American Society for Metals Metals Park, OH, Vol. 1, (1986).
10. Bolmgren, H., Lundstrom, T., Tergenius, L. E., Okada, S. and Higashi, I., "The crystal structure of Ta5B6", ***Journal of Less Comm. Met***, Vol. 161, (1990), 341-345.
11. Itoh, H., Satoh, Y., Kodama, S. and Naka, S., "Synthesis of tantalum boride powder by solid state reaction and its sintering", ***Journal of the Ceramic Society of Japan***, Vol. 98, No. 3, (1990), 264-268.
12. Peshev, P., Leyarovska, L. and Bliznakov, G., "On the borothermic preparation of some vanadium, niobium and tantalum borides", ***Journal of the Less Common Metals***, Vol. 15, No. 3, (1968), 259-267.
13. McHale, A. E., "System B-Ta-C. Isothermal Section at 1750°C. Phase Equilibria Diagrams, Phase Diagrams for Ceramists, Westerville, OH, The American Ceramic Society, Vol. X Borides, Carbides, and Nitrides, (1994).
14. Talmy, I., Zaykoski, J. and Opeka, M., "Synthesis, processing and properties of TaC–TaB2–C ceramics", ***Journal of the European Ceramic Society***, Vol. 30, No. 11, (2010), 2253-2263.
15. Cullity, B. D., "Elements of X-ray Diffraction", ***American Journal of Physics***, Vol. 25, (1957), 394-395.
16. Nelson, J. B. and Riley, D., "An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals", ***Proceedings of the Physical Society***, Vol. 57, No. 3, (1945), 160.
17. Williamson, G. and Hall, W., "X-ray line broadening from filed aluminium and wolfram", ***Acta Metallurgica***, Vol. 1, No. 1, (1953), 22-31.
18. Zhang, X., Hilmas, G. E., Fahrenholtz, W. G. and Deason, D. M., "Hot pressing of tantalum carbide with and without sintering additives", ***Journal of the American Ceramic Society***, Vol. 90, No. 2, (2007), 393-401.
19. Storms, E. K., "The refractory carbides, Academic Press New York, Vol. 2, (1967).
20. Suryanarayana, C. and Norton, M. G., "X-ray diffraction: a practical approach", ***New York and London***, (1998).

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چکیده

در این تحقیق روش مکانوشیمیایی برای سنتز پودر زیر میکرونی TaC مورد بررسی قرار گرفته است. در این روش، کامپوزیت نانو پودر TaC-TaB_2 با استفاده از مواد اولیه پودری کاربید تانتالم و کاربید بور و آسیاب کردن آن‌ها سنتز شد. فازهای تشکیل شده در حین سنتز با استفاده از طیف سنج پراش اشعه ایکس (XRD) تعیین شدند. مورفولوژی پودر سنتز شده نیز با استفاده از میکروسکوپ الکترونی (SEM) مورد بررسی قرار کرفت.

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