

## Effect of hydrogen peroxide on TiB<sub>2</sub>-based materials

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**Abstract.** TiO<sub>2</sub>/TiB<sub>2</sub> heterostructures were successfully synthesized by a facile hydrothermal approach in an aqueous solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The influence of H<sub>2</sub>O<sub>2</sub> on TiB<sub>2</sub>-based materials was systematically investigated using X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results show that TiB<sub>2</sub> is prone to oxidize in the presence of H<sub>2</sub>O<sub>2</sub>. TiO<sub>2</sub>/TiB<sub>2</sub> heterostructure which high-density anatase-TiO<sub>2</sub> stand on the surface can be gained in the presence of H<sub>2</sub>O<sub>2</sub> solvent and the final composition can be controlled by the temperature and time. The investigation may provide a path to further understand the chemical property of TiB<sub>2</sub>-based materials and synthesis method of heterostructure.

### Introduction

Titanium diboride (TiB<sub>2</sub>) with C32 structure and P6/mmm space group symmetry possesses mixed bonding nature, such as strong covalent bonding between boron, metallic and covalent bonding between titanium, ionic and weak covalent bonding between boron and titanium [1, 2]. Such special electronic properties and structure make it being an increasing important boride in modern engineering ceramic due to its excellent wearing resistance, good chemical stability and extremely high hardness with high thermal and electronic conductivities [3-5]. Therefore, TiB<sub>2</sub>-based materials have attracted a significant attention as high-temperature electrode, armor, cutting tools and structural materials [6-9].

However, it is hard to get superfine TiB<sub>2</sub> powders and dense TiB<sub>2</sub> ceramics because of its strong covalent bond, low self-diffusion coefficient and slow mass transportation [10, 11]. Therefore, current studies for TiB<sub>2</sub> materials appear to be limited to its strong covalent property, namely, mechanical property. To the best of our knowledge, there are few references to be involved in other properties of TiB<sub>2</sub> materials in the last several decades, especially, in chemical property. After all, investigation in depth of chemical properties may lead to a potentially wet-chemical synthesis method for TiB<sub>2</sub> materials and a discernable trend of its' wider application, such as catalyst carrier in PEMFC, electrode materials, microelectronic device, etc [12]. Therefore, it is all the more important to insight the potential properties of TiB<sub>2</sub> with the progress in science and technology.

Here we demonstrated a facile hydrothermal synthesis of TiO<sub>2</sub>/TiB<sub>2</sub> heterostructure using TiB<sub>2</sub> as raw material. Our purpose is mainly involved in the chemical properties of TiB<sub>2</sub>-based materials, preparation of TiO<sub>2</sub>/TiB<sub>2</sub> heterostructure and its rational characterization.

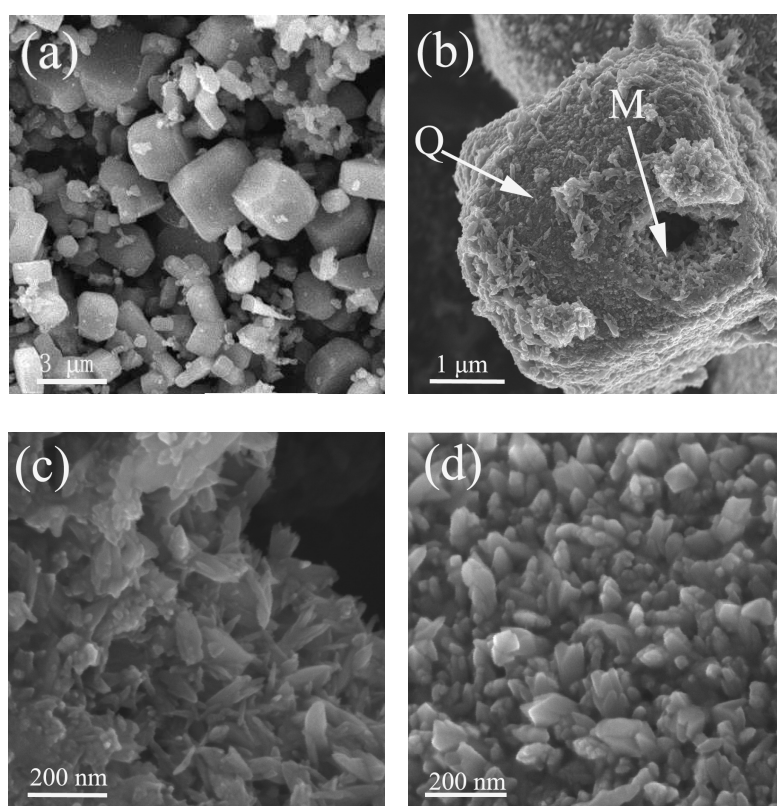
### Experimental

**Materials.** Titanium diboride (TiB<sub>2</sub>, 99.6%) were purchased from Alfa Aesar Inc. (USA). hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) were purchased from Sinopharm Chemical Reagent Co., Ltds (China). All the chemicals were of analytic grade and used without further purification.

**Synthesis of  $\text{TiO}_2/\text{TiB}_2$ .** In a typical procedure,  $\text{TiB}_2$  (0.746g) and  $\text{H}_2\text{O}_2$  (30%, 3.04g) was added into an aqueous deionized water, respectively. Then the mixed solution was transferred to a 50 mL teflon-lined autoclave. Subsequently, the autoclave was sealed and maintained at 80 °C, 120 °C, 160 °C and 180 °C for 24h, respectively, followed by natural cooling to room temperature. Afterwards, the products were centrifugated and washed with deionized water and absolute ethanol for several times, respectively. The final products were dried under vacuum at 80 °C for 12h.

**Characterization.** The morphologies of  $\text{TiO}_2/\text{TiB}_2$  heterostructure were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan). The composition of the products was analyzed by an energy dispersive X-ray detector (EDX, Thermo Noran VANTAG-ESI, 120 kV), X-ray diffraction (XRD, Rigaku D/MAX-rB, Japan) with Cu  $K\alpha$  irradiation,  $\lambda = 0.154056$  nm) and VG Multilab 2000 X-ray photoelectron spectroscopy (XPS, ThermoFisher Corporation, USA).

## Results and Discussion



**Fig. 1.** Typical FESEM images of  $\text{TiB}_2$  powders and the products synthesized at 160 °C for 24h: a) FESEM image of  $\text{TiB}_2$  powders; b) low-magnification FESEM image; c) high-magnification FESEM image in the M area; d) high-magnification FESEM image in the Q area

Fig. 1 presents a set of typical SEM images of  $\text{TiB}_2$  raw materials and the samples synthesized at 160 °C for 24 h. It is clearly observed that the  $\text{H}_2\text{O}_2$  plays a positive role in controlling the morphology of final products. Without  $\text{H}_2\text{O}_2$ , that is,  $\text{TiB}_2$  raw powders are composed of numerous smooth hexagonal structures with the mean particle size of about 7  $\mu\text{m}$  (Fig. 1a). However, when  $\text{TiB}_2$  was treated in the solution of  $\text{H}_2\text{O}_2$  under a certain hydrothermal condition, the surface was evolved to protruding and unsmooth structure, which was composed of numerous nanoparticles on the surface of the products (Fig. 2c). That is, the products form a pineapple structure. Further amplificatory FESEM images indicate that this complex architecture is composed of high-density nanoparticle-built networks, which are about tens of nanometers in diameter (Fig. 1c and 1d). Interestingly, the products are hollow. The results may be because  $\text{H}_2\text{O}_2$  rapidly decompose at high temperature and a certain pressure (to see Eq. 1). Then the oxygen can react with  $\text{TiB}_2$  and get  $\text{TiO}_2$  according to Eq. 2. The

reacted products accumulate rapidly through attaching each other and form hollow structure. Further work is in progress to explore the formation mechanism.

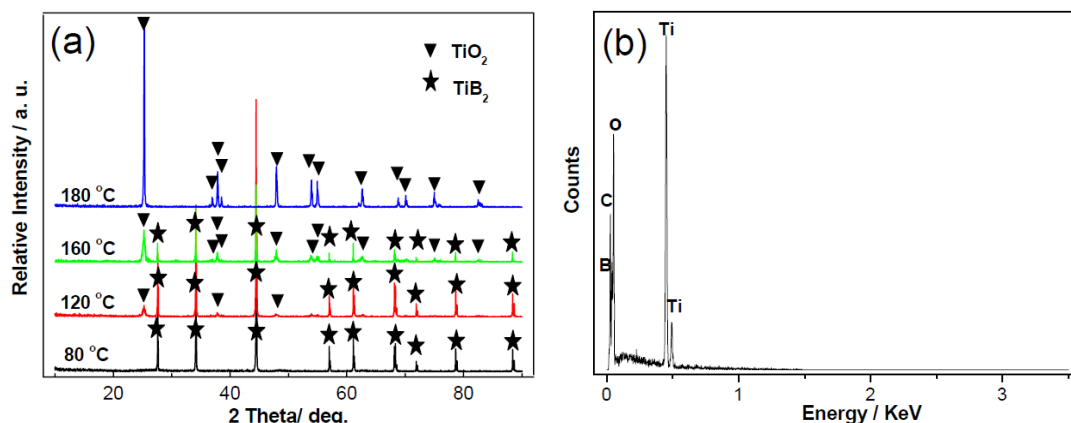
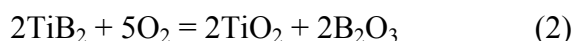
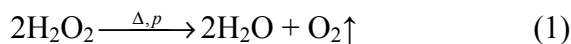


Fig.2 XRD and EDX patterns of the samples: a) XRD pattern of the samples synthesized at different temperatures, b) EDX pattern of the sample synthesized at 160 °C for 24h

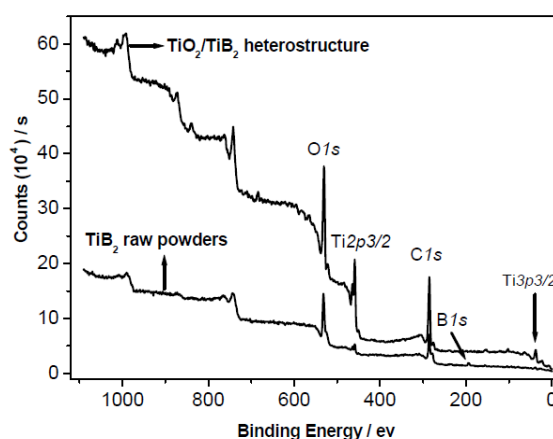


Fig.3 XPS spectrum of  $\text{TiB}_2$  raw powders and the sample synthesized at 160 °C

To verify above-mentioned results, XRD measurements for all the samples were carried out. As shown in Fig.2, it can be seen that the final product is still retained the same phase as raw materials at 80 °C and all the diffraction peaks can be indexed as standard patterns of two-dimensional hexagonal  $\text{TiB}_2$  (JCPDS 75-1045). When the hydrothermal temperature increased to 120 °C, the products consisted of two kinds of phase, namely,  $\text{TiB}_2$  and A- $\text{TiO}_2$  (JCPDS 84-1286), and the main peaks can still be indexed as  $\text{TiB}_2$ , only six weak peaks can be indexed as A- $\text{TiO}_2$ , indicating that the sample was partly converted to the crystalline form of A- $\text{TiO}_2$ . With further increasing the hydrothermal temperature to 160 °C for 24h, the main phase was A- $\text{TiO}_2$ , and a few peaks can be indexed as  $\text{TiB}_2$ . However, Pure A- $\text{TiO}_2$  was obtained at 180 °C, and no other characteristic peaks were detected. That is, the  $\text{TiB}_2/\text{TiO}_2$  hybrid material can be gained when the hydrothermal temperature is 160 °C. EDX patterns further verify the results, which only Ti, B, O elements are present in the Fig. 2b.

Fig. 3 shows the XPS spectrum. According to the American National Institute of Standards and Technology (NIST), when Mg is used as the excitation source, the binding energy of  $\text{TiB}_2$  is as follows:  $\text{Ti}2p_{3/2}$  at 454.4 eV;  $\text{B}1s$  at 187.5 eV; the binding energy of anatase  $\text{TiO}_2$  is as following:  $\text{Ti}2p_{3/2}$  at 458.1 eV;  $\text{O}1s$  at 532.1 eV,  $\text{Ti}3p_{3/2}$  at 37.4 eV; and the binding energy of  $\text{B}_2\text{O}_3$  is as follows:  $\text{B}1s$  at 193.1 eV. From the wide-scan XPS spectrum, the peak of  $\text{TiB}_2$  raw powder appears at 532.004 eV, 458.004 eV and 193.004 eV, which is in agreement with  $\text{O}1s$  in  $\text{TiO}_2$ ,  $\text{Ti}2p_{3/2}$  in  $\text{TiO}_2$  and

B1s in B<sub>2</sub>O<sub>3</sub>. The results indicate that TiB<sub>2</sub> raw powder has been oxidized on the surface. In fact, the phenomenon is normal for non-oxide ceramic. However, the peak of TiB<sub>2</sub>/TiO<sub>2</sub> hydrid material is present at 532.004 eV, 458.004 eV, 37.004 eV, which is in well agreement with O1s in TiO<sub>2</sub>, Ti2p<sub>3/2</sub> in TiO<sub>2</sub> and Ti3p<sub>3/2</sub> in TiO<sub>2</sub>. It should be noted that the peak of B1s wasn't present in TiB<sub>2</sub>/TiO<sub>2</sub> hydrid material, instead of the strong peak of Ti3p<sub>3/2</sub>. The difference between TiB<sub>2</sub> raw material and TiB<sub>2</sub>/TiO<sub>2</sub> hydrid material may be because B<sub>2</sub>O<sub>3</sub> was dissolved in the hot water during the hydrothermal reaction and removed after succedent centrifugation. That is, TiB<sub>2</sub> may be wrapped completely by anatase TiO<sub>2</sub>, not by TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>. Therefore, TiB<sub>2</sub>/TiO<sub>2</sub> hydrid material is a heterostructural material in fact.

### Summary

To sum up, we have systemically discussed the effect of H<sub>2</sub>O<sub>2</sub> on the TiB<sub>2</sub>-based materials. Obviously, H<sub>2</sub>O<sub>2</sub> has important influence on TiB<sub>2</sub>-based materials. Through controlling the process, such as temperature and time, TiO<sub>2</sub>/TiB<sub>2</sub> heterostructure can be successfully synthesized, which high-density anatase-TiO<sub>2</sub> nanoparticles stand on the surface and cover unreacted TiB<sub>2</sub>.

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### References

- [1] H. Schmidt, G. Borchardt, C. Schmalzried, R. Telle, S. Weber and H. Scherrer: J. Appl. Phys. Vol. 93 (2003), p. 907
- [2] X. Y. Ma, C. G. Li, Z. M. Du, W. J. Zhan: J. Alloy. Comp. Vol. 370 (2004), p. 149
- [3] N. Panich, Y. Sun: Surface Coatings Technol. Vol. 198 (2005), p. 14
- [4] H. Y. Zhai, H. M. Christen, and C. Cantoni: Appl. Phys. Lett. Vol. 80 (2002), p. 1963
- [5] R. K. Williams, R. S. Graves, and F. J. Weaver: J. Appl. Phys. Vol. 59 (1986), p. 1986
- [6] G. Will: J. Solid State Chem. Vol. 177 (2004), p. 628
- [7] P. Vajeeston, P. Ravindran, C. Ravi, and R. Asokamani: Phys. Rev. B Vol. 63 (2001), p. 045115
- [8] R. G. Munro: J. Res. Inst. Stand. Technol. Vol. 105 (2000), p. 709
- [9] R. K. Williams, P. F. Becher and C. B. Finch: J. Appl. Phys. Vol. 56 (1984), p. 2295
- [10] M. Shibuya and M. Ohyanagi: J. Eur. Ceram. Soc. Vol. 27 (2007), p. 301
- [11] N. Kumar, Y. Yang, W. Noh, G. S. Girolami and J. R. Abelson: Chem. Mater. Vol. 19 (2007), p. 3802
- [12] C. S. Choi, G. C. Xing, G. A. Ruggles and C. M. Osburn; J. Appl. Phys. Vol. 69 (1991), p. 7853

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10.4028/www.scientific.net/AMR.66

## **Effect of Hydrogen Peroxide on TiB<sub>2</sub>-Based Materials**

10.4028/www.scientific.net/AMR.66.222

### **DOI References**

- [1] H. Schmidt, G. Borchardt, C. Schmalzried, R. Telle, S. Weber and H. Scherrer: J. Appl. Phys. Vol. 93 (2003), p. 907  
doi:10.1063/1.1530715
- [11] N. Kumar, Y. Yang, W. Noh, G. S. Girolami and J. R. Abelson: Chem. Mater. Vol. 19 (2007), p. 3802  
doi:10.1021/cm070277z
- [1] H. Schmidt, G. Borchardt, C. Schmalzried, R. Telle, S. Weber and H. Scherrer: J. Appl. Phys. Vol. 3 (2003), p. 907  
doi:10.1063/1.1530715
- [3] N. Panich, Y. Sun: Surface Coatings Technol. Vol. 198 (2005), p. 14  
doi:10.1016/j.surfcoat.2004.10.096
- [5] R. K. Williams, R. S. Graves, and F. J. Weaver: J. Appl. Phys. Vol. 59 (1986), p. 1986  
doi:10.1118/1.595798
- [7] P. Vajeeston, P. Ravindran, C. Ravi, and R. Asokamani: Phys. Rev. B Vol. 63 (2001), p. 045115  
doi:10.1103/PhysRevB.63.045115
- [10] M. Shibuya and M. Ohyanagi: J. Eur. Ceram. Soc. Vol. 27 (2007), p. 301  
doi:10.1016/j.jeurceramsoc.2006.05.081
- [11] N. Kumar, Y. Yang, W. Noh, G. S. Girolami and J. R. Abelson: Chem. Mater. Vol. 19 (2007), p. 802  
doi:10.1021/cm070277z