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Simulation study of influence of Al, Si and B on the growth of TiC

Haimin Ding*, Kaiyu Chu, Jinfeng Wang

Department of Mechanical Engineering, North China Electric Power University, Baoding 071003, PR China

*Corresponding author. Tel: (86) 312 7525041; Fax: (86) 312-7525045; E-mail: dinghaimin@yahoo.cn

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ABSTRACT

The influence of Al, Si and B on the growth of TiC is studied in this article. It is found that the adsorption of Al is more favorable on TiC {111} than that on {001}. Therefore, under the influence of it, the growth rate of {111} will be accelerated and result in the decreasing of the relative growth rate between {001} and {111}. Therefore, TiC will grow into truncated-octahedron. But when TiC is formed under the influence of Si and B, they will grow into hexagonal platelets due to the preferential adsorption of Si and B on {011} and {001}. Copyright©2011 VBRI press.

Keywords: Ceramics; simulation and modeling; crystal growth.

Haimin Ding is a Lecture of North China Electric Power University, baoding, China. He received his Ph.D degree from School of Material Science and Engineering, Shandong University. His current field of interest is the preparation of ceramic materials and has published about 20 research articles in international journals.

Kaiyu Chu is an Assist. Professor of North China Electric Power University, baoding, China. He is involved in research on mechanical engineering manufacture.

Jinfeng Wang is a Lecture of North China Electric Power University, baoding, China. He is received his master degree from Department of Mechanical Engineering, North China Electric Power University. He is involved in research on mechanical engineering manufacture and automatization and has published about 10 research articles.

Introduction

TiC has been paid much attention due to its high melting point, high modulus, great hardness, high chemical stability, as well as excellent resistances to corrosion, oxidation and wear [**1, 2**]. It is widely used as refractory materials for cutting tools, wear resistant components and a reinforcing phase in composites [**3, 4**].

It is known that TiC is a typical faceted crystal with a NaCl-type structure and should be grown into octahedral shape when it is freely formed under equilibrium conditions. But some factors such as growth kinetics and environmental condition will influence its morphologies. For example, TiC with dendrite [**5**], rod [**6**], whisker [**7**], nanowires [**8**] and hollow sphere shapes [**9**] have been reported. It is inevitable that the properties of TiC particles will be affected by the shapes. Therefore, researching the influence factors on the growth of TiC is important for its application.

A lot of works revealed that when there is Al, Si or B during the synthesis, the shapes of TiC will be obviously changed. Therefore, in this article, the simulation method was used to study the influence of them on the growth of TiC.

Experimental

The adsorption energy of Al, Si and B on different TiC crystal planes is calculated using CASTEP with the Perdew-Wang 1991 version of the generalized gradient approximation (GGA-PW91) [**10**]. The calculations are

conducted on 1×1 TiC {001}, {111}, {011} surfaces with six layers and 15 Å vacuum. 1ML M (Al, Si, and B) atoms are placed on the top of the first layer of different surfaces. And M atoms and the two top layers of the slab are set free to move, while the other layers are constrained to simulate a bulk-like environment. The plane-wave cut off energy of 350ev is employed, which assured a total energy convergence of 5.0×10^{-6}ev atom^{-1} or better. And the k-point set mesh parameter was (8, 8, and 1). In addition, molecular dynamics approach is also used to further examine the adsorption of Al, Si and B atoms on TiC surfaces. The FORCITE module of Material Studio is used to perform geometry optimization of a model with 1059 atoms which contains a sphere TiC cluster. And the Universal (UFF) [**11**] force field was adopted.

Results and discussion

The adsorption energy (E_{ad}) which is designated as the energy needed to adsorb 1ML M (Al, Si or B) atoms on the surfaces is the key to assess the interaction of the M atoms and the TiC surfaces. It is calculated by:

$$E_{ad} = E_{M+S} - (E_S + NE_M) \quad (1)$$

Where E_S is the energy of TiC{001},{111} and {011} planes, respectively; E_M is the energy of single Al, Si or B atom; N is the number of the M atoms; E_{M+S} is the total energy of the TiC{001},{011} and {111} with the adsorption of M.

The E_{ad} values based on formula (1) are shown in **Table 1** and **Fig.1**. It can be found from **Table 1** that the adsorptions of Al, Si and B on TiC are exothermal. For different crystal planes, the TiC {011} is the most preferential adsorption site. The difference is that the {111} is the second favorable adsorption plane and the {011} is the last in the adsorption of Al; but in the adsorption of Si and B, the second favorable adsorption plane is TiC{001} and the last one is {111}. The E_{ad} of B on {011} is the biggest among all of them and the E_{ad} of Al is the smallest as shown in **Fig. 1**.

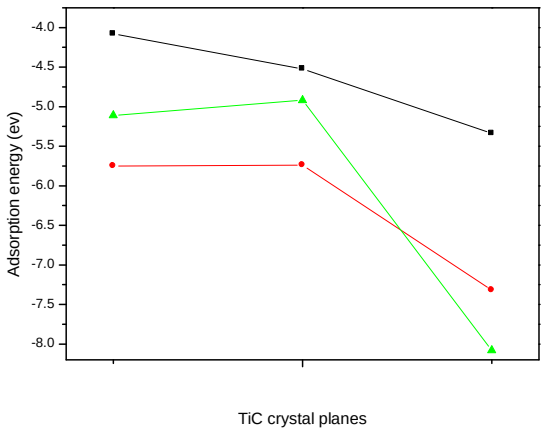

Fig. 1. Scheme of adsorption energy of Al, Si and B on different crystal planes of TiC.

Table 1 Adsorption energy of Al, Si and B on different crystal planes of TiC

Atom types	Adsorption energy (ev)		
	{001}	{111}	{011}
Al	-4.08	-4.52	-5.34
Si	-5.75	-5.74	-7.32
B	-5.11	-4.92	-8.08

Fig. 2 presents the results of the molecular dynamics simulation. In the simulation model, a spheroidal TiC cluster is surrounded by Al, Si and B atoms. The configuration of TiC with Al atoms after geometry optimization is shown in **Fig. 2b**. It is found that the stacking of Al atoms on TiC [001] direction is more significant than that on [011] direction. But this difference is decreased with the stacking of Si on TiC [001] and [011] as shown in **Fig. 2c**. When the surround atoms are B, it is found the configuration is sphere after the geometry optimization as shown in **Fig. 2d**. The results indicate that the influence of Si and B on TiC {001} plane is stronger than that of Al, which is in accordance with the results in **Table 1**.

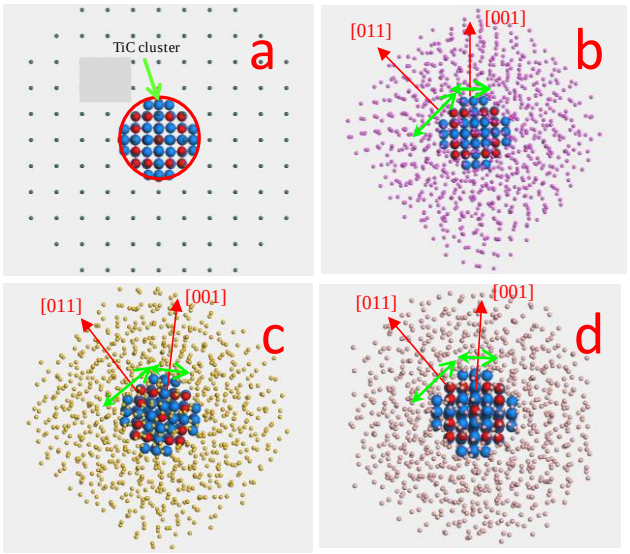

Fig. 2. Configurations of TiC cluster with different atoms (a) the original model, (b-d) TiC cluster surrounded by Al, Si, and B atoms, respectively.

It is well known that the crystalline shape is determined by the relative growth rate on the different planes. If TiC freely grows in liquid under equilibrium solidification, an ideal morphology of TiC particles with octahedral shape would be formed [**12**]. In this condition, the $R_{[001)/(111)]}$ which is designated as the relative growth rate between {001} and {111} is 1.73, and the $R_{[011)/(111)]}$ is 1.22 as shown in **Fig. 3a**. It has been reported that the presence of impurities in TiC, such as Al, Si and B, induced high density of planar defects within the TiC grains [**13- 15**]. And the high density of defects can promote the growth of the related plane and then influences the shapes of TiC. So the more Al, Si or B is adsorbed on the TiC, the faster the

related crystal plane grows. According to the results mentioned above, Al atoms are more favorable to adsorb on TiC{011} and {111} than on {001} plane. This indicates that the growth rate of {011} and {111} will be accelerated with the influence of Al. As a result, the relative growth rate between {001} and {111} will be decreased. And It should be noticed that when the $R_{[001)/(111)]} < 1.73$, the TiC will grow into truncated-octahedron as shown in **Fig. 3b**. But when TiC is formed in the melts containing Si and B, the growth of {011} and {001} planes will be promoted due to their preferential adsorption on these planes. So the relative growth rate $R_{[001)/(111)]}$ will increase to be greater than 1.73 and the $R_{[011)/(111)]}$ will be greater than 1.22. In addition, the $R_{[011)/(111)]}$ will also be decreased due to more favorable adsorption of Si and B on TiC{011}.And when $R_{[011)/(111)]}$ is decreased to 1.15, the TiC will grow into hexagonal platelets as shown in **Fig. 3c**.

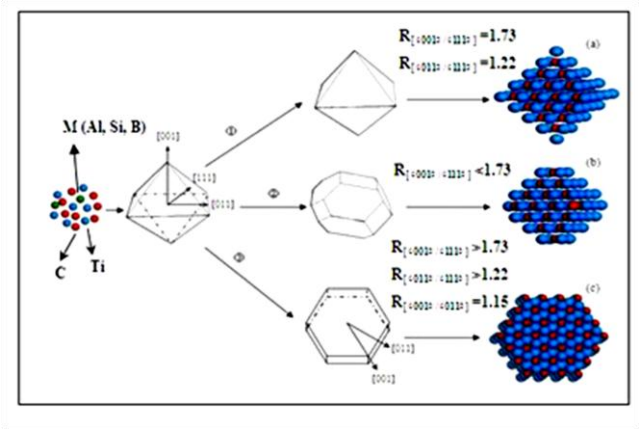

Fig. 3. Growth of TiC (a) free growth, (b) under the influence of Al, and (c) under the influence of Si or B.

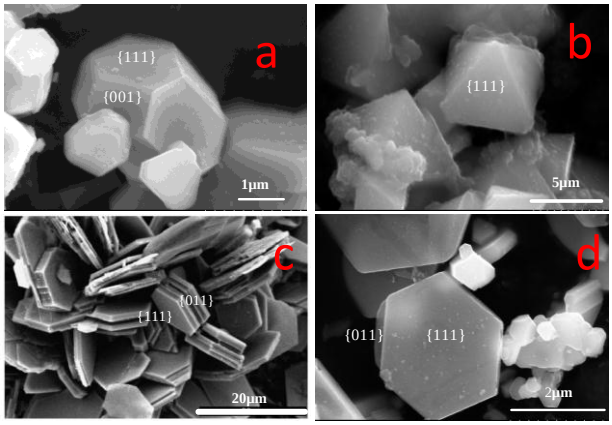

Fig. 4. Shapes of TiC prepared in different conditions (a) TiC prepared in Al melts with lower temperature, (b) prepared in Al melts with the temperature above 1600°C, (c) prepared in Al melts containing Si [**16**], and (d) prepared in Al melts containing B [**17**].

The simulation data are in very good agreement with the experimental results. It has been found that when TiC is prepared in Al-Ti-C system, it usually grows into truncated-octahedron which is due to the influence of Al as shown in **Fig. 4a**, but if the temperature of the melts is above 1600°C, the shape of TiC will be octahedron as shown in **Fig. 4b**. It is deduced that the influence of Al will be faded with the increasing of the temperature. And when the temperature of the melts is above 1600°C, Al atoms cannot adsorb on TiC planes, so it can freely grow into octahedral shape. If Si or B exists in the melts, the influence of them will be dominant. Li SB.etal [**16**] has found that TiC particles will be hexagonal platelets with the influence of Si, as shown in **Fig. 4c**. And Nie JF.etal [**17**] found that TiC will also grow into hexagonal platelets when B is doped during the formation of TiC, as shown in **Fig. 4d.**

Conclusion

The influence of Al, Si and B on the growth of TiC is studied by the simulation method. It is found that the adsorption of Al is more favorable on TiC {111} than that on {001} planes and TiC will grow into truncated-octahedron under its influence. But when TiC is formed under the influence of Si and B, the growth of {011} and {001} planes will be promoted due to their preferential adsorption on them. As a result, TiC will grow into hexagonal platelets. It is found that the simulation results are in very good agreement with the experiments.

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Reference

1. Wen, G.; Li, S.B.; Zhang, B.S.; Guo, Z.X. *Acta Mater.* **2001**, *49(8)*, 1463. **DOI:** 10.1016/S1359-6454(01)00034-9
2. Vallauri, D.; Atias Adrian, I.C.; Chrysanthou, A. *J Eur Ceram Soc.* **2008**, *28*, 1697. **DOI:**10.1016/j.jeurceramsoc.2007.11.011
3. Li, B.H.; Liu, Y.; Cao, H.; He, L.; Li, J. *Mater Lett.* **2009**, *63*, 2010. **DOI:**10.1016/j.matlet.2009.06.037
4. Razavia, M.; Yaghmaeea, M. S.; Rahimipour, M. R.; Salmana, S.; Tousia, R. *Inter J Miner Proceess.* **2010**, *94*, 97. **DOI:**10.1016/j.minpro.2010.01.002
5. Chen, Y.; Wang, H.M. *J Alloys Compd.* **2003**, *351*, 304. **DOI:** 10.1016/S0925-8388(02)01077-0
6. Liang, C.H.; Meng, G.W.; Chen, W.; Wang, Y.W.; Zhang, L.D. *J Cryst Growth.* **2000**, *220*, 296. **DOI:** 10.1016/S0022-0248(00)00849-6
7. Yuan, Y.; Pan, J. *J Cryst Growth.* **1998**, *193*, 585. **DOI:** 10.1016/S0022-0248(98)00484-9
8. Liu, B.Q.; Huan, C.Z.; Lu, X.Y.; Gu, M.L.; Liu, H. L. *Ceram Inter.* **2007**, *33*, 1475. **DOI:**10.1016/j.ceramint.2006.05.015
9. Gu, Y.L.; Chen, L.Y.; Li, Z.F.; Qian, Y.T.; Zhang, W.Q. *Carbon.* **2004**, *42*, 235. **DOI:**10.1016/j.carbon.2003.10.019
10. Tsetseris, L.; Pantelides, S.T. *Acta Mater.* **2008**, *56*, 2864. **DOI:**10.1016/j.actamat.2008.02.020
11. Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard III, W. A.; Skiff, W. M. *J Am Chem Soc.* **1992**, *114(25)*, 10024. **DOI:**10.1021/ja00051a040
12. Song, M.S.; Huang, B.; Huo, Y.Q.; Zhang, S.G.; Zhang, M.X.; Hu, Q.D.; Li, J.G. *J Cryst Growth.* **2009**, *311*, 378. **DOI:**10.1016/j.jcrysgro.2008.10.065
13. Yu, R.; He, L.L.; Ye, H.Q. *Acta Mater.* **2003**, *51*, 2477. **DOI:**10.1016/S1359-6454(03)00032-6
14. Kooi, B.J.; Kabel, M.; Kloosterman, A.B.; DeHosson, J.Th.M. *Acta Mater.* **1999**, *47*, 3105. **DOI:** 10.1016/S1359-6454(99)00151-2
15. Chien, F.R.; Nutt, S.R.; Cummings, D. *Phil Mag A.* **1993**, *68*, 325.

DOI: 10.1080/01418619308221208
16. Li, S.B.; Xiang, W.H.; Zhai, H.X.; Zhou, Y. *Powder Technol.* **2008**, *185*, 49.
DOI:10.1016/j.jcrysgro.2008.10.065
17. Nie, J.F.; Liu, X.F.; Ma, X.G. *J Alloys Compd.* **2010**, *491*, 113.
DOI:10.1016/j.jallcom.2009.10.148