

Synthesis of Ti₂N Powders by Vacuum Slowly Vapor Deposition Using Urea as Nitrogen Source

Sun Jinfeng, Yan Shuai, Yu Hui

Key Lab of Material Near Net Forming Technology of
Hebei Province
Hebei University of Science and Technology
Shijiazhuang, China
e-mail: sjf301@126.com, 2903651890@qq.com,
1924173913@qq.com

Quan Kun

Polytechnic College of Hebei University of Science and
Technology
Shijiazhuang, China
e-mail: xiangwang120@126.com

Abstract—Hydrochloric acid solution of TiCl₃ was synthesized by reacting of Ti powders and hydrochloric acid in high-pressure reactor at 145°C. After vacuum drying TiCl₃·6H₂O crystalline were obtained. TiCl₃·6H₂O crystalline and urea, being as nitrogen source, were put into the vacuum slowly vapor deposition reactor. The heating temperature and holding time were 600°C and 10 min separately. The deposited powders at different temperature were analyzed by X-ray diffraction (XRD). The results show: Ti₂N powders can be synthesized at the range of 450°C to 600°C. The powders deposited at low temperature (< 80°C) were NH₄Cl and the organics decomposed from urea.

Keywords—urea; TiCl₃; vacuum slow deposition; TiN

I. INTRODUCTION

Titanium nitride, which structure is face-centered cubic, possesses high melting point, high hardness, low friction coefficient, high electrical and thermal conductivity and good chemical stability [1-3]. So TiN is widely used, such as the protective layer of mechanical parts, wear-resistant coating of cutting tools, corrosion-resisting coating of metals and diffusion barrier in semiconductor industry [4-7]. The conventional methods of synthesizing TiN include direct nitridation, carbothermal reduction nitridation of TiO₂, self-propagating high temperature synthesis, plasma method, reactive ball milling and chemical vapor deposition (CVD) method [8-13]. All of above methods expect reactive ball milling and CVD, need high temperature (≥1200°C), which will consume much energy and lead to poor sinterability of the TiN powders because of the coarse grain and big particle size. In reactive ball milling, impurities will often be introduced into the powders from the milling medium, therefore, the ideal low energy cost method for synthesizing pure TiN is CVD. The raw materials for synthesizing TiN by CVD are usually TiCl₄, N₂ and H₂, and the synthesis temperature is in the range of 750°C to 1000°C [14-16]. N. Ramanuja et al synthesized TiN coating by low-pressure chemical vapor deposition (LPCVD) using TiCl₄ and NH₃ as raw materials. They found the synthesis temperature can be reduced by using NH₃ replace N₂ and H₂ as raw materials that the TiN coating can be synthesized in the range of 450°C to 850°C [17]. The disadvantages of CVD are the costly

equipment and low efficiency. Therefore, in order to synthesizing TiN at low temperature and using simple equipment, solid state nitrogen source of urea and TiCl₃ were used as raw materials to synthesize TiN by vacuum slow deposition.

II. EXPERIMENTS

Titanium powders (~200 mesh, 99.0 wt%) and hydrochloric acid (34vol%) were put into the polytetrafluoroethylene high-pressure reactor (φ30mm×60mm) which was heating in a electric blastdrying oven (DHG-9420A, Shanghai Yiheng Instruments Co., Ltd.) at 145°C. The raw material ratio and holding time are listed in Table I.

The reaction products were then dried in vacuum, the purple crystalline obtained were then analyzed by X-ray diffraction (XRD, D/MAX-2500, Rigaku, Japanese). Five gram purple crystalline powders and 50 g (excess) urea were then filled into two stainless steel jars separately (φ50mm×150mm) which were put into the vacuum slow deposition reactor (CMD-800, Yanshan University, China). Schematic diagram of the vacuum slow deposition reactor is shown as Figure 1.

In Figure 1, all the substrates are iron sheet, the low temperature substrate is close to the cooling water zone (150°C), the temperature at the middle temperature substrate is 450°C, the high temperature substrate is near the center of the reactor (600°C). Two butterfly valves with 30 mm diameter are set on the pipe between the reactor and the vacuum pump. There is a hole with 1 mm diameter on the

TABLE I. EXPERIMENTAL SCHEME OF REACTION OF TI AND HYDROCHLORIC ACID

Projec t	Ti/ g	Temperature /°C	Hydrochloric acid /ml	Hoding time/h
1	1	145	6	3
2	1	145	6	5
3	1	145	10	3

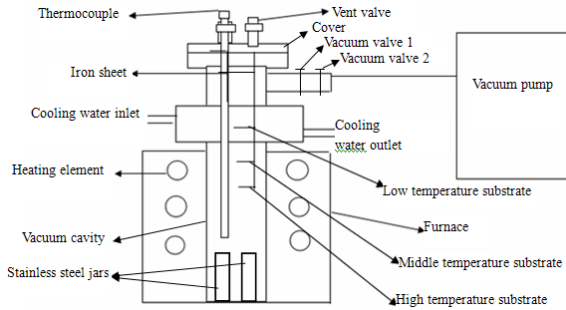


Figure 1. Schematic diagram of the vacuum slow deposition reactor for synthesizing TiN

valve 1, so the reactor can be pumped slowly when valve 2 is open and valve 1 is closed. The vacuum slow deposition process is that, firstly, pump the reactor to 5 pa by opening valve 1 and valve 2; then close both valve 1 and valve 2 meanwhile heat the reactor to 400°C with the heating rate is 10°C/min; open valve 2 ten seconds interval 5 minutes closed for slow pumping until heating to 600°C, stop heating after holding 10 min. All the substrates with the deposited powders were analyzed by XRD.

III. RESULTS AND DISCUSSION

The XRD patterns of the powders which were obtained by reacting between Ti powders and hydrochloric acid and then vacuum drying are shown in Figure 2.

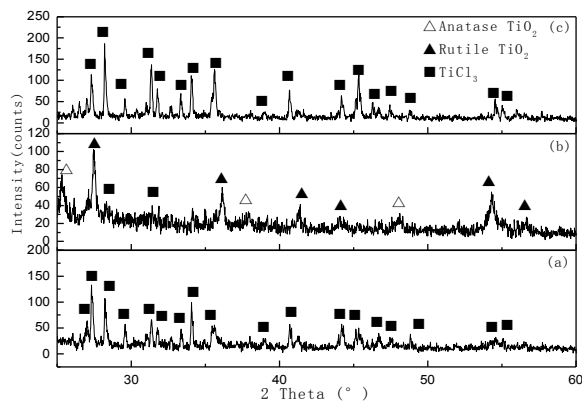


Figure 2. XRD patterns of the purple crystalline powders obtained by reacting between 1 g Ti powders and different volume hydrochloric acid (HCl) at 145°C for different holding time
(a) HCl 6ml, 3h (b) HCl 6ml, 5h (c) HCl 10ml, 3h

The reaction product is $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ for 6 ml hydrochloric acid and 3 h holding time, as shown in Figure 2(a). For the same volume of hydrochloric acid, increase the holding time from 3 h to 5 h, the main products are TiO_2 with small fraction of TiCl_3 , as shown in Figure 2(b). The reason may be that increasing the holding time, more hydrochloric acid was react with Ti and small amount of residual hydrochloric acid was volatilized when open the high-pressure reactor,

supersaturated TiCl_3 in the hydrochloric acid was precipitated and react with air to form TiO_2 . For the same holding time, increasing the volume of hydrochloric acid from 6 ml to 10 ml, the product is not changed, $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$, as shown in Figure 2(c). The difference is that the intensity of diffraction peak is higher which means high crystallinity. The product in the high-pressure reactor is purple solution, which is hydrochloric acid solution of TiCl_3 . Hu et al found that Ti can be react with HCl at above 800°C to form TiCl_3 by thermodynamic calculation [18]. The temperature can be decreased to 145°C in high-pressure reactor in this paper.

The XRD patterns of different substrates with deposited powders are shown in Figure 3. There is only Fe diffraction peak of iron sheet for low temperature substrate. A thin white layer, formed on the low temperature substrate, can be seen by visual, which may be the organic decomposed from the urea. For the middle temperature (450°C) and high temperature (600°C) substrates, Ti_2N and $\text{C}_4\text{H}_{12}\text{N}_2\text{O}_6$ diffraction peaks can be found, except Fe diffraction peaks. On the cover and cooling water wall (< 60°C), a lot of white crystalline powders were deposited, which were NH_4Cl and $\text{CH}_4\text{N}_2\text{O}$ analyzed by XRD as shown in Figure 4.

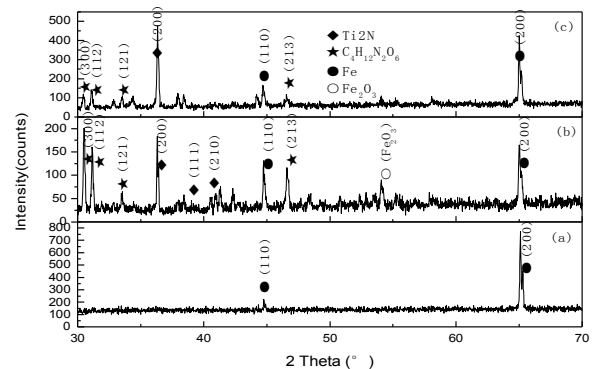


Figure 3. XRD patterns of different powders deposited on different temperature substrates
(a) 150°C (b) 450°C (c) 600°C

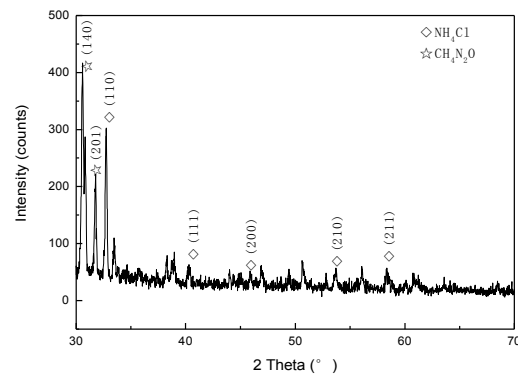


Figure 4. The XRD patterns of the powders deposited on the cover and cooling water wall (<60°C) of the vacuum slow deposition reactor

It can be found by comprehensive analyzing different powders deposited on different temperature zone that Ti_2N can be synthesized in vacuum slow deposition reactor at $600^{\circ}C$ with the substrate temperature above $450^{\circ}C$ using urea and $TiCl_3 \cdot 6H_2O$ as raw materials. NH_4Cl and organic decomposed can be deposited in low temperature zone. References about CVD suggested that it was easier to form TiN for higher substrate temperature and the synthesis temperature and substrate temperature were often above $1000^{\circ}C$ and $700^{\circ}C$ separately [14-16]. Hu et al considered that $TiCl_3$ could react with the decompose gases of NH_3 at $570^{\circ}C$ to form TiN by thermodynamic calculation [18]. Tan et al also suggested that $TiCl_4$ could react with the mixture of N_2 and H_2 at $900^{\circ}C$ - $1000^{\circ}C$ in CVD process, but replacing the mixture of N_2 and H_2 by NH_3 , the reactive temperature can be reduced to $500^{\circ}C$ - $700^{\circ}C$ [19]. The results of this paper are consistent with Hu and Tan that Ti_2N can be synthesized at $600^{\circ}C$. Ti_2N deposited at middle temperature substrate ($450^{\circ}C$) may be the products synthesized at high temperature brought by the flow of the gas of HCl and NH_3 decomposed from urea. NH_4Cl deposited on the top of the vacuum slow deposition reactor was the production of reaction between of NH_3 and HCl. There was no NH_4Cl deposited at high temperature zone because it would be decomposed at $337.8^{\circ}C$.

IV. CONCLUSION

Titanium can react with hydrochloric acid to form hydrochloric acid solution of $TiCl_3$ in high-pressure reactor at $145^{\circ}C$ for 3 hours. The amount of the $TiCl_3$ increased with the volume of hydrochloric acid increasing. After vacuum drying, $TiCl_3 \cdot 6H_2O$ purple crystalline can be obtained.

Ti_2N can be synthesized by vacuum slow deposition at $600^{\circ}C$ using $TiCl_3 \cdot 6H_2O$ and urea as raw materials.

ACKNOWLEDGMENT

The authors would like to thank the foundation of college students' innovation and entrepreneurship training program of Hebei province.

REFERENCES

- [1] F. Noli, P. Misaelides, A. Hatzidimitriou, E. Pavlidou, and A.D. Pogrebnjak, "Investigation of the characteristics and corrosion resistance of Al_2O_3/TiN coatings," *Appl. Surf. Sci.*, vol.252, 2006, pp. 8043-8049.
- [2] A. Krella, "Cavitation erosion of TiN and CrN coatings deposited on different substrates," *Wear*297, 2013, pp. 992-997.
- [3] N.D. Nam, D. S. Jo, J.G. Kim, and D. H. Yoon, "Corrosion protection of CrN/TiN multi-coating for bipolar plate of polym electrolyte membrane fuel cell," *Thin Solid Films* 519, 2011, pp. 6787-6791.
- [4] A. Öztürk, K.V. Ezirmik, K. Kazmanlı, M. Ürgen, O.L. Eryılmaz, and A. Erdemir, "Comparative tribological behaviors of TiN-, CrN- and MoN-Cu nanocomposite coatings," *Tribol. Int.* 41, 2008, pp. 49-59.
- [5] A. Shenhar, I. Gotman, S. Radin, and P. Ducheyne, "Microstructure and fretting behavior of hard TiN-based coatings on surgical titanium alloys," *Ceram. Int.* 26, 2000, pp. 709-713.
- [6] J. Zhang, Q. Xue, and S.X. Li, "Microstructure and corrosion behavior of TiC/Ti(CN)/TiN multilayer CVD coatings on high strength steels," *Applied Surface Science*, 280, 2013, pp. 626-631.
- [7] J.S. Huang, A.S. Oates, and J. Zhao, "Effect of cracks in TiN anti-reflection coating layers on early via electromigration failure," *Thin Solid Films* 365, 2000, pp. 110-115.
- [8] L.P. Zhu, M.S. Ohashi, and S.J. Yamanaka, "Novel Synthesis of TiN Fine Powders by Nitridation with Ammonium Chloride," *Materials Research Bulletin*, 2002, 37, pp. 475-483.
- [9] T. Jiang, X.X. Xue, P.N. Duan, X. Liu, S.H. Zhang, and R. Liu, "Carbothermal Reduction-nitridation of Titania-bearing Blast Furnace Slag," *Ceramics International*, 2008, 34, pp. 1643-1651.
- [10] D. Carole, N. Fréty, S. Paris, D. Vrel, F. Bernard, and R.M. Marin-Ayral, "Investigation of the SHS Mechanisms of Titanium Nitride by in situ Time-resolved Diffraction and Infrared Thermography," *Journal of Alloys and Compounds*, 2007, 436, pp. 181-186.
- [11] J.L.H. Chau, C.C. Kao, "Microwave Plasma Synthesis of TiN and ZrN Nanopowders," *Materials Letters*, 2007, 61, pp. 1583-1587.
- [12] J.F. Sun, M.Z. Wang, Y.C. Zhao, X.P. Li, and B.Y. Liang, "Synthesis of titanium nitride powders by reactive ball milling of titanium and urea," *Journal of Alloys and Compounds* 482, 2009, pp. L29-L31.
- [13] A. Gomathi, and C.N.R. Rao, Nanostructures of the Binary Nitrides, BN, TiN, and NbN, Prepared by the Urea-route. *Materials Research Bulletin*, 2006, 41, pp. 941-947.
- [14] S.Y. Tang, S. Gao, S.X. Wang, J.L. Wang, Q. Zhu, Y.Q. Chen, and X.Y. Li, "Characterization of CVD TiN coating at different deposition temperatures and its application in hydrocarbon pyrolysis," *Surface & Coatings Technology* 258, 2014, pp. 1060-1067.
- [15] J. Wagner, C. Mitterer, M. Penoy, C. Michotte, W. Wallgram, and M. Kathrein, "The effect of deposition temperature on microstructure and properties of thermal CVD TiN coatings," *International Journal of Refractory Metals & Hard Materials* 26, 2008, pp. 120-126.
- [16] S.Y. Tang, J.L. Wang, Q. Zhu, Y.Q. Chen, and X.Y. Li, "Oxidation behavior of CVD star-shaped TiN coating in ambient air," *Ceramics International*41, 2015, pp. 9549-9554
- [17] N. Ramanuja, R.A. Levy, S.N. Dharmadhikari, E. Ramos, C.W. Pearce, S.C. Menasian, P.C. Schamberger, and C.C. Collins, "Synthesis and Characterization of Low Pressure Chemically Vapor Deposited Titanium Nitride Films Using $TiCl_4$ and NH_3 ," *Materials Letters*, 2002, 57, pp. 261-269
- [18] C.S. Hu, Z.X. Yuan, "THE THERMO DYN AM ICS O F CV D T I N CO AT I N GS W I T H T I T A N I U M HALIDES," *Journal of Wuhan Yejin University of Science and Technology*, 1996, 19(4), pp. 418-423.
- [19] K. Tan, M.H. Lin, N.Q. Wang, and Q.E. Zhang, "Quantum chemical study on synthesis of nano TiN by CVD," *Nineth national quantum chemistry academic conference of Chinese Chemical Society*, 2005-10