Synthesis of Ti$_2$N Powders by Vacuum Slowly Vapor Deposition Using Urea as Nitrogen Source

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Abstract—Hydrochloric acid solution of TiCl$_3$ was synthesized by reacting of Ti powders and hydrochloric acid in high-pressure reactor at 145°C. After vacuum drying TiCl$_3$-6H$_2$O crystalline were obtained. TiCl$_3$-6H$_2$O crystalline and urea, as being 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: Ti$_2$N powders can be synthesized at the range of 450°C to 600°C. The powders deposited at low temperature (<80°C) were NH$_4$Cl and the organics decomposed from urea.

Keywords—urea; TiCl$_3$; vacuum slow deposition; Ti$_2$N

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 TiO$_2$, 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 TiCl$_4$, N$_2$ and H$_2$, 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 TiCl$_4$ and NH$_3$ as raw materials. They found the synthesis temperature can be reduced by using NH$_3$ replace N$_2$ and H$_2$ 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 TiCl$_3$ 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 heated in a electrical blasting drying 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 grams 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 | Ti / g | Temperature / °C | Hydrochloric acid / ml | Holding time / h |
| 1 | 1 | 145 | 6 | 3 |
| 2 | 1 | 145 | 6 | 5 |
| 3 | 1 | 145 | 10 | 3 |
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℃ by opening 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℃ with the heating rate is 10℃/min; open valve 2 ten seconds and interval 5 minutes closed for slow pumping until heating to 600℃ 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 1. Schematic diagram of the vacuum slow deposition reactor for synthesizing TiN](image)

The reaction product is TiCl$_3$·6H$_2$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$_4$, 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, TiCl$_3$·6H$_2$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℃ to form TiCl$_4$ by thermodynamic calculation [18]. The temperature can be decreased to 145℃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℃) and high temperature (600℃) substrates, Ti$_2$N and C$_6$H$_{12}$N$_2$O$_4$ diffraction peaks can be found, except Fe diffraction peaks. On the cover and cooling water wall of the vacuum slow deposition reactor (< 60℃), a lot of white crystalline powders were deposited, which were NH$_4$Cl and CH$_3$N$_2$O analyzed by XRD as shown in Figure 4.

![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℃for different holding time](image)

(a) HCl 6ml, 3h  (b) HCl 6ml, 5h  (c) HCl 10ml, 3h

![Figure 3. XRD patterns of different powders deposited on different temperature substrates](image)

(a) 150℃  (b) 450℃  (c) 600℃

![Figure 4. The XRD patterns of the powders deposited on the cover and cooling water wall (<60℃) of the vacuum slow deposition reactor](image)
It can be found by comprehensive analyzing different powders deposited on different temperature zone that Ti$_3$N can be synthesize in vacuum slow deposition reactor at 600°C with the substrate temperature above 450°C using urea and TiCl$_4$·6H$_2$O as raw materials. NH$_3$Cl 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°C and 700°C separately [14-16]. Hu et al considered that TiCl$_4$ could react with the decompose gases of NH$_3$ at 570°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°C-1000°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°C-700°C [19]. The results of this paper are consistent with Hu and Tan that Ti$_3$N can be synthesized at 600°C Ti$_3$N deposited at middle temperature substrate (450°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$_4$Cl 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$_4$Cl deposited at high temperature zone because it would be decomposed at 337.8°C.

IV. CONCLUSION

Titanium can react with hydrochloric acid to form hydrochloric acid solution of TiCl$_4$ in high-pressure reactor at 145°C for 3 hours. The amount of the TiCl$_4$ increased with the volume of hydrochloric acid increasing. After vacuum drying, TiCl$_4$·6H$_2$O purple crystalline can be obtained.

Ti$_3$N can be synthesized by vacuum slow deposition at 600°C using TiCl$_4$·6H$_2$O and urea as raw materials.

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REFERENCES


