

# Investigation on Quick Surface Metallization of Nano Titania Powder<sup>\*</sup>

Xu Lina<sup>1,2\*\*</sup> Zhou Kaichang<sup>1</sup> Liu Chunping<sup>2</sup> Ou Danlin<sup>2</sup> Gu Ning<sup>1</sup> Liu Juzheng<sup>2</sup> Chen Kunji<sup>3</sup>

(<sup>1</sup>National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096, China)

(<sup>2</sup>Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China)

(<sup>3</sup>Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210008, China)

**Abstract:** Quick surface metallization of titania powder was carried out by electroless chemical deposition of nickel. The fabricated product was characterized by XRD, SEM, FTIR and cross-section metallography. The analysis results show that titania particles are completely coated by a thin nickel shell about 600 nm thick, composed of nano-sized crystalline nickel particles. Mechanism of nickel chemical deposition on nano powder is proposed.

**Key words:** electroless chemical deposition, nickel metallization, nano titania

Metal-ceramic composites can improve application properties of the materials such as hardness tensile, compressive strength, wear and abrasion resistance. How to fabricate the composites has been highly focused on. Many techniques have come forth, such as liquid metallurgy techniques including casting or infiltration processes, liquid phase sintering, and etc. The most promising fabrication method might be the electroless plating technique which permits ceramic dispersed homogeneously with metal in an aqueous solution and improves the properties of composites in wettability and conductivity. These kinds of products have been widely used as strengthened<sup>[1,2]</sup>, electric contact materials<sup>[3,4]</sup>. Up to now, almost all of the core ceramic particles for the metal electroless plating were micro-sized powders<sup>[5,6]</sup>, except that nano powder were practised by Wang, et al. recently<sup>[7]</sup>.

It is well known that nano titania possesses especial physical and chemical properties and has a wide range of applications such as catalysis, dope, solar energy cell, electronic information, UV absorbing materials, bactericide. Considering that pure black nickel has good conductivity and high light-absorbing rate, we expect that the Ni-TiO<sub>2</sub> composite may be novel materials with light-weighted and special electro-magnetic effect.

The present study has been concerned with ultrasonic-assisted electroless plating of pure nickel on nano titania powder, using palladium as the catalyst and hydrazine as the reducing agent.

## 1 Experimental Sections

A given amount of nano titania powder were dispersed and directly catalyzed by immersing into palladium chloride solution for ten minutes, followed by reduction pretreatment using hydrazine aqueous solution of low concentration. Then the catalyzed nano titania particles were introduced into the electroless plating bath which is consisted of NiSO<sub>4</sub> · 6H<sub>2</sub>O, 7.5 g/L; N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O, 2.5 mL/L; K<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · 1/2H<sub>2</sub>O, 8 g/L and a very little amount of composite stabilizer. The pH of the plating solution was firstly adjusted to 11 using ammonia and then adjusted to 12 - 13 using sodium hydroxide. The mixture was placed into water bath keeping temperature at 85 °C, homogenized continuously using an ultrasonic stirrer. Twenty minutes later, the suspension was cooled quickly to room temperature and separated by magnetic force. The obtained black product was rinsed with water followed by magnetic centrifugal separation over three times, and dried at 80 °C in a vacuum oven.

SEM analysis of the product was carried out on a JSM-6300 type scanning electronic microscope. Cross-section metallography was obtained with MEF-3 type optical microscopy. XRD patterns were recorded using a D/max RA X-ray diffractometer. FTIR analysis was performed on a Nicolet-750 type apparatus.

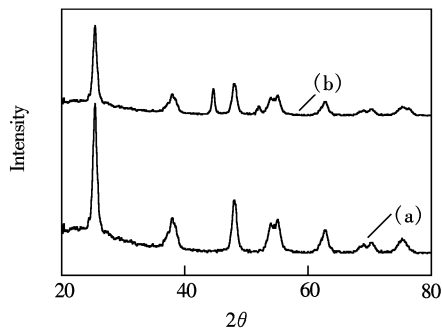
## 2 Results and Discussions

Fig.1 shows the XRD patterns of nano titania pow-

Received 2001 - 12 - 07.

\* The project supported by the National Natural Science Foundation of China (69890220) and Open Project Foundation of Laboratory of Solid State Microstructures of Nanjing University.

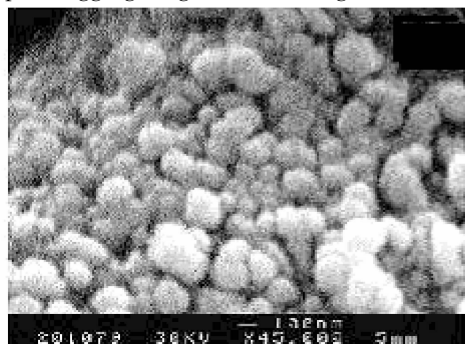
\*\* Born in 1969, female, graduate.



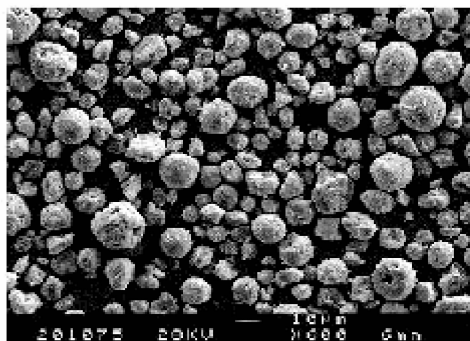
**Fig.1** XRD patterns. (a) pure titania powder; (b) the product

der (a) and the product (b), respectively. Compared Fig.1 (a) with (b), it can be clearly seen that there is an obvious peak at the  $2\theta$  angle about  $44.5^\circ$  in Fig. 1(b), which is the characteristic of Ni(111) crystal face diffraction. It can be confirmed that the product is of Ni-TiO<sub>2</sub> composite. Based on Scherrer formula  $C' = \frac{0.9\lambda}{W' \cos\theta}$ , the size of the nickel particles is calculated to be 10.8 nm according to the Ni(111) main peak.

Fig.2 shows the SEM micrographs of titania and the product. It is obvious in Fig.2(a) that nano titania were apt to aggregating due to its high surface energy.



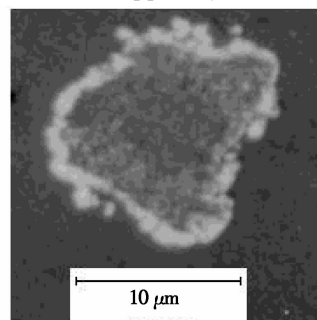
(a)



(b)

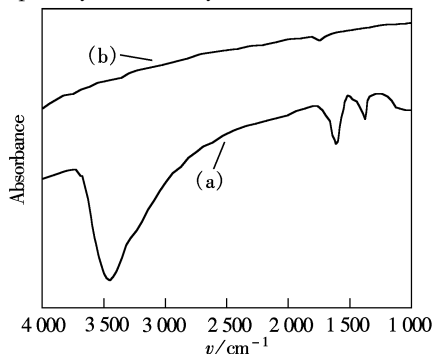
**Fig.2** SEM images. (a) pure titania powder; (b) the product. The nickel coated product, semispheres with narrow dimensional distribution approximately arranged from 5  $\mu\text{m}$  to 20  $\mu\text{m}$ , shows good dispersity. The cross-section image of the product is shown in Fig.3. As can be seen, the product has a uniform and bright shell of

metallic nickel about 600 nm thick. Besides, the dimension and micrograph of the core layer suggest that multi-particles are enwrapped by the nickel shell.



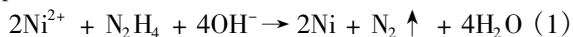
**Fig.3** Cross-section image of the product

The nickel coatings can be confirmed by the FTIR analysis. Fig.4 shows TiO<sub>2</sub> has three distinct absorbance peaks at 3 451  $\text{cm}^{-1}$ , 1 637  $\text{cm}^{-1}$ , 1 384  $\text{cm}^{-1}$ , respectively, and there are hardly any peaks observed in the product spectrum. This indicates that the product hasn't any naked TiO<sub>2</sub>, TiO<sub>2</sub> particles must become the cores completely covered by nickel films.



**Fig.4** FTIR spectra. (a) titania; (b) the product

The phenomena may be interpreted by the following mechanism. Reaction (1) was quickly initiated by palladium catalyst absorbed on the surfaces of nano titania powder at 85  $^\circ\text{C}$ , nickel ions were reduced to black nickel metal by hydrazine in the alkaline solution, and then deposited on titania with the palladium as the nucleator.



The original formed ultrafine Ni coated TiO<sub>2</sub> particles, auto-catalytically active, induced the redox reaction and fast deposition of later produced nickel on them with the earlier-produced nickel as the nucleator. However, the ultrafine particles have strong self-aggregation tendency due to the high surface energy. Earlier formed Ni-TiO<sub>2</sub> congregated simultaneously under the continuous strong collision and assembled into stabilized semispheres. And then the freshly formed nickel was deposited on those congeries and

formed a metallic shell steadily and continuously. Finally, bright nickel shell coated semispheres were fabricated. Nano titania powder was completely covered by metal. It may be inferred that it is very difficult to fabricate single dispersed metal composite only cored with a single nano particle by this method due to its uncontrollable, fast auto-catalytic deposition.

3 Conclusion

Electroless chemical deposition of nickel on nano TiO<sub>2</sub> powder had been successfully performed, using palladium as the catalyst and hydrazine as the reducing agent. Ni-TiO<sub>2</sub> composites were fabricated and characterized by XRD, SEM, FTIR and cross-section metallography. Analysis results show that multi-titania particles are completely enwrapped by a thin nickel shell, which is about 600 nm thick and composed of nano-sized crystalline nickel particles. The metallized semispheres possess good dispersibility. Thereout, mechanism of nickel chemical deposition on nano powder is proposed.

References

[1] Leon C A, Drew R A L. Preparation of nickel-coated powders

Al<sub>2</sub>O<sub>3</sub> and SiC as precursors to reinforce MMCs[J]. *J Mater Sci*, 2000,**35**:4763 – 4768.

[2] Lin L, Xue Q J, Zhao J Z. Microstructure and tribological behaviour of electroless Ni-P plating reinforced by fine TiN powders[J]. *Tribology*, 1995,**15**(2): 104 – 104.

[3] Chang S Y, Lin J H, Lin S J, et al. Processing copper and silver matrix composites by electroless plating and hot pressing [J]. *Metallur & Mater Trans A*, 1999,**30**(4): 1119 – 1136.

[4] Joshi P B, Murti N S S, Gadgil V L, et al. Preparation and characterization of Ag-ZnO powders for applications in electrical contact materials[J]. *J Mater Sci Lett*, 1995,**14**:1099 – 1101.

[5] Harizanov O A, Stefchev P L, Iossifova A. Metal coated alumina powder for metaloceramics [J]. *Mater Lett*, 1998,**33**(5 – 6):297 – 299.

[6] Wen G W, Guo Z X, Davies C. Electroless plating for the enhancement of material performance[J]. *Mater Tech*, 1999,**14**: 210 – 217.

[7] Wang C Y, Zhou Y, Zhu Y R, et al. Synthesis and characterization of NiP-TiO<sub>2</sub> ultrafine composite particles[J]. *Mater Sci & Eng*, 2000,**B77**(1):135 – 137.

[8] Li Y D, Li C W, Wang H R, et al. Preparation of nickel ultrafine powder and crystalline film by chemical control reduction[J]. *Mater Chem & Phys*, 1999,**59**:88 – 90.

纳米二氧化钛表面快速金属化的研究

徐丽娜<sup>1,2</sup> 周凯常<sup>1</sup> 刘春平<sup>2</sup> 欧丹林<sup>2</sup> 顾 宁<sup>1</sup> 刘举正<sup>2</sup> 陈坤基<sup>3</sup>

(<sup>1</sup> 东南大学分子与生物分子电子学教育部重点实验室, 南京 210096)

(<sup>2</sup> 东南大学化学化工系, 南京, 210096)

(<sup>3</sup> 南京大学固体微结构开放实验室, 南京 210008)

**摘 要** 采用镍的无电子化学沉积方法研究了纳米二氧化钛粉末表面的快速金属化. 所得产物经 XRD、SEM、FTIR 及剖面金相显微术进行了表征. 分析结果表明二氧化钛粒子完全被金属镍包覆, 金属壳层 600 nm 厚, 由镍的纳米晶粒组成. 由此提出了镍在纳米粉末上的化学沉积机理.

**关键词** 无电子化学沉积, 镍金属化, 纳米二氧化钛

**中图分类号** O647.11