Structure of nano-copper and nano-conductive fibers

ZHANG Zhikun¹, CUI Zuolin¹, CHEN Kezheng¹, WANG Yanni¹ and NING Yingpei²

1. Institute of Nanostructured Materials, Qingdao Institute of Chemical Technology, Qingdao 266042, China; 2. Department of Rubber of Qingdao Institute of Chemical Technology, Qingdao 266042, China

Keywords: polymerization, nano-copper, nano-conductive fibers.

VARIOUS small inorganic solid grain catalysts, alloys and films consisting of various nano-size particles were prepared by chemical methods. The study of catalytic properties of nanostructured materials integrated material physics with chemistry, which promoted the development of materials science.

Chemists have been familiar with the subject of ultrafine metal particles as the catalyst^[1], e.g. the platinum black used in the platinum reforming reactions. But recently many kinds of nano-metal particles have been prepared under a vacuum condition by physical methods and the nano-particles have nanometer scale grain size and large special surface area. There are no pores in the particles and polarized materials on their surfaces. Therefore, it is interesting to study the catalytic properties of the nano-metal particles.

This note reported that a new kind of elastic nano-conductive fibers (nano-f) was produced in a polymerization reaction of acetylene with nano-copper as catalyst. This kind of nano-conductive fibers can be separated in alcohol one by one, which has not been reported before.

1 Preparation and structure characteristics of nano-copper

The bulk copper with high purity (99.99%) was put into the molybdenum boat in a vacuum chamber.

 H_2 + Ar thermal arc plasma was fired by the heat of resistance. The high temperature area was formed around the molybdenum boat. Then bulk copper was melted and evaporated into copper atom vapor from the liquid metal surface. The copper atoms collided with the mixture gas molecules, changed their movement directions and lost their kinetic energy. Finally the copper atoms condensated as nano-copper particles on the vacuum chamber wall were cooled by liquid nitrogen.

The morphology of nano-copper particles were observed by TEM experiment. It was dis-



covered that the morphology of nano-copper particles is polyhedron. The average particle size is 30 nm which was calculated by a statistic method. There are no pores on the surfaces identified by the uniform contrast on TEM of the particles (see figure 1).

DTA experiment shows that the melting point of nano-copper particles is 750° C which is 300° C lower than that of bulk copper. There is a small releasing thermal peak in $100-300^{\circ}$ C which is similar to that of the releasing deformation energy of a deformed bulk copper in low temperature range^[2]. There exist a lot of defects on the surfaces of nanocopper, and the activity of the catalysis is increased. The nano-copper particles are used as catalysts due to their properties^[3].

2 Nano-meter conductive fiber and its characteristics

Fig. 1. The TEM photo of nanocrystalline copper.

Polymerization of acetylene was carried out in a

glass reactor with nano-copper as catalyst. The poly-

mer of acetylene is yellow loose elastic bulk material. The mechanism and the reaction process have been reported^[4].

This note shows the nano-conductive fiber and its characteristics in microstructure. XRD experiment shows that there are sharp peaks of nano-copper and a diffuse peak of the polyacetylene in low angle region in XRD pattern. It was found from DTA experiment under the condition of nitrogen atmosphere and temperature rising at 10° C/min that when the polymer formed was heated to 816° C, there was an obvious peak of absorption heat of a phase transition.

The polyacetylene after phase change became black, still elastic and conductive materials. In addition, there is a small releasing heat peak induced by releasing small atomic clusters, such as CH_3 . When the polyacetylene was heated in vacuum chamber, the change of resistance of the polyacetylene is listed in table 1.

Table 1 The change of resistance of the polyacetylene with temperature								
t/°C	100	200	300	400	500	600	700	800
R/Ω	>10 ⁸	>10 ⁸	>108	>10 ⁸	100M	200K	7K	20

To study the microstructure of the polyacetylene, the polymers before and after phase transitions were observed by JEM-2000EX electron microscopy. The morphology of the poly-acetylene before the phase transition was fiber and both ends of every fiber connected with nano-copper particles (see. fig. 2). The morphology of the polyacetylene after the phase transition is shown in figure 3.

Figure 3 shows that the polyacetylene is still fiber and in elastic state. TEM photos clearly show that nano-copper induces the free-radical polymerization^[4]. The polyacetylene ended on the nano-copper particles. Nano-copper is conductor itself. The average size of nano-copper particles is 40 nm. Although the nano-copper particles still remained in the fibers, no effect on



Fig. 2. The morphology of polyacetylene before phase transition.

Fig. 3. The morphology of polyacetylene after phase transition.

the stability of polyacetylene was observed after the 10^4 -h aging experiment. The aging experiment is being carried out at present. The morphology of polyacetylene after phase transition was still in fiber state, but the fibers possess the shape of a spiral spring. The length and diameter of the fibers are several hundred manometers and some microns to tens of microns respectively. Therefore it can be called nano-f. FIR experiments of the different temperature range show that the small clusters containing H and C were broken from the main chain of the polymer and C—C skeleton was formed which maintained the shape of the fibers and the elasticity. XRD experiment supported the analysis. The XRD peaks of nano-fiber after phase transition were similar to those of the carbon.

By applying the nano-f as a filler, we prepared the nano-f silicon conductive rubber. It was found that nano-f silicon conductive rubber has the following advantages: (|) nano-f can be added by above 50% of silicon rubber, and the silicon rubber still keeps good elasticity. But normal carbon black only can be added by about 10%, and meanwhile the silicon rubber becomes hard; (|) the ability of restoring elasticity of nano-f silicon conductive rubber is 10 times higher than that of carbon-black-filled silicon conductive rubber; (|) nano-f has no effect on the sulphurizing system, but the normal cabin black has the effect^[5]. At the same time the aging experiment for 10⁴ h shows no change in the conductivity of the polymer.

(Received April 17, 1997)

References

- 1 Emmett, P. H., The Physical Basis of Heterogeneous Catalysis, New York: Plenum, 1975.
- 2 Zhang, Z. K., Wang, Y. M., Dislocations in deformed aluminum alloy, Powder Diffraction, 1988, 3(3): 138.
- 3 Hang, J. Y., He, A. Q., Wu, Y, K., Nanocrystalline Cu-Fe solid solutions prepared by mechanical alloying, *Nanostructured Materials*, 1994, 4(1); 1.
- 4 Wang, Y. N., Zhang, Z. K., Cui, Z. L., Catalysis of nanocrystalline metal particles for polymerization of acetylene, Chi-

BULLETIN

nese Journal of Catalysis, 1995, 16(4): 1585.

5 Ning, Y. P., Lu, X. L., Zhang, Z. K. et al., Properties of VQM-110 vulcanizes filled with nanometer conductive fiber, China Synthetic Rubber Industry (in Chinese), 1995, 18(6): 332.

Acknowledgement This work was supported by the State Planning Commission of China and Natural Science Foundation of Shandong Province.