

Increase the Synthesis Efficiency of Graphite Encapsulated Cobalt Nanoparticles by Annealing

Mao-Hua Teng and Chun-Chang Lin

Department of Geosciences, National Taiwan University, Taipei, Taiwan,
mhteng@ccsm.ntu.edu.tw

ABSTRACT

Graphite encapsulated cobalt nanocrystal is a composite material with a very special core-and-shell spherical structure (5~50 nm in diameter.) Where the core is fcc cobalt nanocrystals and the shell consists of several to over ten layers of graphitic sheets. As a result, the nanoparticles can be stable against strong acid, and stable at high temperature in an oxygen-free environment. Arc discharge has been proven an effective method to produce the material. However, the yield of successfully encapsulated product had never exceeded 10 wt% before this study. We annealed the raw powder above 400°C in vacuum (vacuum thermal treatment), and significantly raised the yield to over 25%. In addition, we found the best annealing temperature is 500°C, which is 100°C lower than the best graphitization temperature of cobalt.

Keywords: nanoparticles, graphite, encapsulated, annealing.

1 INTRODUCTION

Graphite/carbon encapsulated metal (GEM) nanoparticles (Fig.1) not only provides an opportunity to study dimensionally confined systems, but also could be used in many nanotechnology applications, e.g. recording media, nano-sized wheel bearings, etc. Unlike other metal nanoparticles, the material has a great advantage that it is protected by graphitic outer shells and therefore can survive in severe environments, such as in a strong acid.

Although lots of work had been done on GEM nanoparticles produced by arc-discharged method, yet few on their synthesis efficiency [1-8]. Despite some claimed that only encapsulated nanoparticles were observed in their as-made powder [7], the exact amounts of well-encapsulated particles had never been accurately measured. Furthermore, it is almost impossible to determine the amounts just by SEM or TEM analysis. The method we used to determine the efficiency is a destructive acid-washed method; all the metal particles that encapsulated by defected graphitic shells will dissolve in the acid, and only the well-protected particles and some carbon debris will remain.

In order to explore many potential applications, it is necessary to synthesize GEM effectively and in greater amount. In this study, we used a simple annealing method to facilitate the encapsulation process of graphite, and

greatly increased the percentage of well-encapsulated nanoparticles.

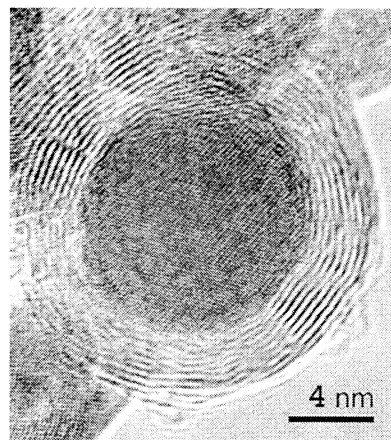


Figure 1: A TEM micrograph of graphite/carbon encapsulated nickel nanoparticle.

2 EXPERIMENTAL

Contrast to the popular carbon arc-discharge method, we used a custom tungsten arc-discharge device (Fig.2) to produce Co-GEM nanoparticles.[8] The setup can routinely produce as-made GEM powder at a rate of 3 g/hr.

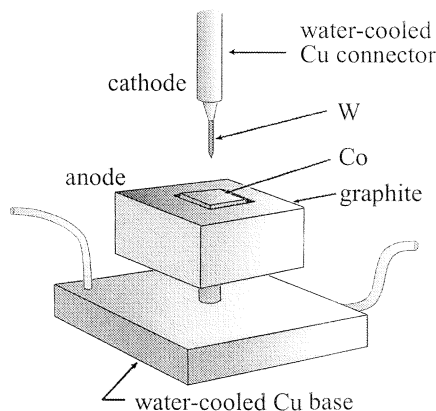


Figure 2: The arc-discharge setup (schematic).

2.1 Arc Discharge Setup

As shown in Fig.2, the cobalt metal block is placed in the graphite crucible as anode, and a tungsten rod as cathode. When cobalt melts in the arc, some graphite will dissolve into the metal liquid pool and evaporate simultaneously with the metal. Then the vapor condenses into the desired nanoparticles. The arc current is 100~300 A, voltage is 20~30 V, and in a 100~400 Torr helium atmosphere. The tungsten arc method increases the metal evaporation while decreases excess carbon debris in the raw product.

2.2 Acid-wash

To separate well-encapsulated Co-GEM from defected ones, we used a destructive acid-wash method. All the raw as-made powder will be put into a strong acid solution. After ultrasound for twenty minutes, all the defected (not well protected) Co particles dissolved. By measuring the weight ratio of residual powder, we derive a relatively reliable yield of the method. This process will be the basic method to determine the yield of Co-GEM in this study.

2.3 Vacuum Annealing

The collected raw powder can be annealed in a vacuum furnace at various temperatures. The vacuum inside the quartz tube is 10^{-5} Torr, and the annealing time is two hours.

2.4 Formation Mechanism

Although several models tried to explain the formation mechanism of GEM, but in author's opinions only the two-step encapsulation model is capable of explaining most experimental results.[4,5] The model describes how the small graphitic flakes condense first inside a liquid metal droplet and "float" to the outer surface of the spherical metal. This is the first step "phase separation," which explains why the turbostratic graphitic shells enclosed a spherical metal nanoparticle. Second step involves the catalytic behaviors of several elements, such as iron, nickel, and cobalt. The model predicts these metals will help amorphous carbon crystallizing into graphite when at a high enough temperature. For more details, please refer to Host *et al.*[4] and Elliott *et al.*[5].

3 RESULTS AND DISCUSSIONS

As shown in figure 3, without annealing we can derive only 5.6% of the as-made powder after acid-washed. After two-hour annealing at 400°C, 500°C, 600°C and 700°C in vacuum, however, the yields increased to 18.4%, 25.1%, 21.6%, and 16.9% respectively. It is obvious that the best annealing temperature for Co-GEM is 500°C, not the best graphitization temperature reported earlier at 600°C.[9] This means that graphitization does not necessary lead to

good encapsulation. In fact, the shells will deteriorate with the proceeding of graphitization process.

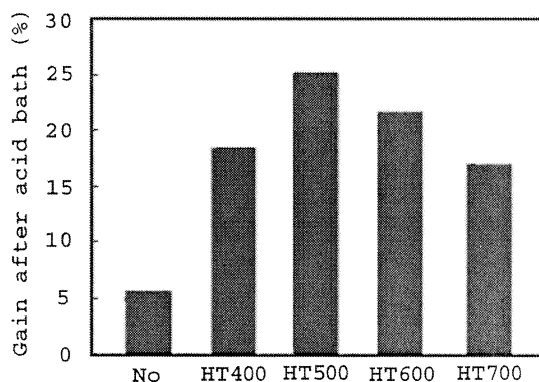


Figure 3: The gain percentage after acid-washed for samples of different annealing temperatures for two hours. Where "No" means as-made powder, and "HT400" represents 400°C, and so on.

From TEM micrographs (Fig.4), the graphitization of the shells after 500°C annealing can be clearly observed. Note that the carbon content in the powder will also influence the results of the annealing process. The higher carbon concentration powder showed better encapsulation during annealing.

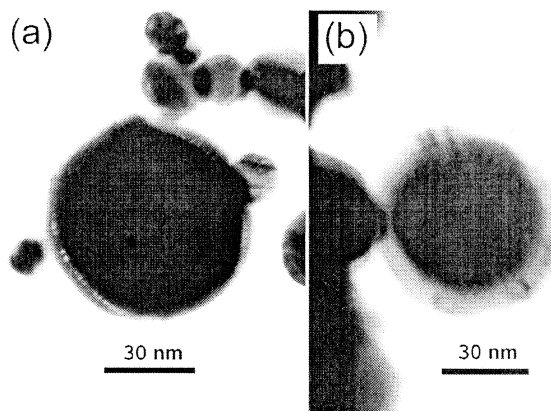


Figure 4: The TEM micrographs of graphite/carbon encapsulated cobalt nanoparticles: (a) before annealing, and (b) after annealing.

Annealing at higher temperature may actually destroy some of the graphite shells, or create more empty graphite balls/cages. This is why there exists an optimal annealing temperature around 500°C. If the annealing temperature is too low, the graphitization process will be too slow to fix the structural defects in the encapsulated shells. On the other hand, if the temperature is too high, the process will accelerate the graphitization and make larger and flatter graphitic sheets. Thus leads to more cavities between the

shell and core. High temperature may also increase the diffusivities of metal atoms so that the metal core may completely diffuse out of the shells and leave an empty cage behind.

The same annealing process may be extended to other GEM materials but with different optimal temperatures. However, the preliminary results of the vacuum annealing of Ni-GEM didn't show a similar increase in yields. Since it could be due to some experimental problems or to our new annealing setup, we cannot confirm the discrepancy at this time.

Based on the effectiveness of the annealing process, we suggest there are at least two extra possible carbon sources during the annealing: the carbon previously dissolved in the metals, and the surrounding carbon debris. They could all contribute to the graphitization process, and make the graphitic shells stronger and tighter around the metal core.

4 CONCLUSIONS

We have demonstrated that a simple vacuum annealing process can increase the percentage of the well-encapsulated cobalt nanoparticles of the as-made powder dramatically, from less than 10% to more than 25%. We also found the best annealing temperature is 500°C, about 100°C lower than the best Co graphitization temperature suggested in previous work.

ACKNOWLEDGMENTS

This work was supported in part by National Science Council, Taiwan, Grant NSC91-2116-M-002-023.

REFERENCES

- [1] V.P. Dravid, J.J. Host, M.H. Teng, B.R. Elliott, J.-H. Hwang, D.L. Johnson, T.O. Mason and J.R. Weertman (1995) *Nature*, 374, 602.
- [2] M.H. Teng, J.J. Host, J.-H. Hwang, B.R. Elliott, J.R. Weertman, T.O. Mason, V.P. Dravid and D.L. Johnson (1995) *J. Mater. Res.*, **10**, 233-236.
- [3] J.-H. Hwang, V.P. Dravid, M. H. Teng, J.J. Host, B.R. Elliott, D.L. Johnson, and T.O. Mason (1997) *J. Mater. Res.*, **12**, 1076-1082.
- [4] J.J. Host, M.H. Teng, B.R. Elliott, J.-H. Hwang, T.O. Mason, J.R. Weertman, D.L. Johnson and V.P. Dravid (1997) *J. Mater. Res.*, **12**, 1268-1273.
- [5] B.R. Elliott, J.J. Host, V.P. Dravid, M.H. Teng and J.-H. Hwang (1997) *J. Mater. Res.*, **12**, 3328-3344.
- [6] J.J. Host, M.H. Teng and V.P. Dravid (1998) *J. Mater. Res.*, **13**, 2547-2555.
- [7] J. Jiao and S. Seraphin (1998) *J. Appl. Phys.*, **83**, 2442-2448.

[8] L.C. Chang, P.Y. Li, J.J. Host and M.H. Teng (1999) *Engineering Chemistry & Metallurgy (China)*, 20, 405-410. (in Chinese)

[9] M. Yudasaka and R. Kikuchi (1996) *Supercarbon*, 99-105.