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Magnetic packing of graphite encapsulated nickel nanoparticles

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ABSTRACT

Graphite encapsulated metal nanoparticles (GEM) have a very special core-and-shell spherical structure (5–100 nm in diameter). The core is metal nanoparticle and the shell consists of several to over ten layers of graphitic sheets. Because the outer shell protects the inner metal nanoparticles, the materials remain stable in strong acid as well as at high temperature in an oxygen-free environment. Nanoparticles are usually very difficult to compress; with the ferromagnetic metal core of Ni-GEM, one would expect its compaction to be even more difficult. In this work, however, a new and simple magnetic packing method was developed, by which >90% dense Ni-GEM bulk can be produced without going through any of the conventional compaction procedures. The as-made GEM powder will first be purified via an acid-bath to remove any poorly encapsulated Ni particles. Then the GEM is dispersed in methanol, and subjected to a strong magnetic field. After the entire amount of methanol has been evaporated, many small pieces of high-density bulk GEM material can be obtained. Preliminary results show there are several important factors which affect the final packing density of bulk Ni-GEM: the type of dispersant, the dispersant's evaporation rate and the magnetic field intensity.

1. Introduction

Graphite encapsulated metal nanoparticles (GEM) (see Fig. 1) are spherical core-and-shell structured material with a diameter ranging between 5 and 100 nm [1–7]. With their graphitic shells to protect the inner metallic core from oxidation and acid erosion, GEM can survive in harsh environments. GEM is also a potentially useful material in regard to many applications, e.g., in fuel cells, some GEM materials have shown very promising hydrogen storage ability. Although there are several other methods which can be used to synthesize GEM, e.g., CVD and laser ablation methods, only the tungsten arc-discharge method delivers both a higher production rate and good efficiency [1]. (For more details, please refer to Host et al. [8] and Elliott et al. [9].)

Nano-material is very difficult to compress. Nanoparticles tend to agglomerate together; thus, under normal condition it is almost impossible to derive high-density packed nanoparticle compaction. One may need to apply high temperature and pressure (up to several GPa) to nanoparticles to produce high-density compaction, albeit at the cost of creating grain growth and losing their nanocrystalline properties. As a result, the purpose of this paper is to introduce a new and simple magnetic packing method by which the Ni-GEM becomes high-density bulk material without going through any of the conventional compaction procedures.

2. Experimental

The Ni-GEM nanoparticles used in this work were produced by a customized tungsten arc-discharge device. The tungsten arc-discharge method uses tungsten rod as cathode, and the graphite crucible as anode, running at 200 Torr helium pressure, 25–15 V, and 100–150 A. Nickel pieces and synthetic diamond powder (as carbon source) were set in the graphite crucible anode. During the arcing process, nickel and carbon evaporated and condensed into the core–shell Ni-GEM material [6,7]. Although the tungsten arc-discharge method can produce much more GEM powder than the popular carbon arc-discharge method (i.e., Krätschmer–Huffman method) does, its production efficiency is still relatively poor in terms of meeting the required amount for all of our experiments. Therefore, several dozen synthesizing experiments had to be done beforehand, so that a sufficient quantity of Ni-GEM could be accumulated to carry out the selected packing experiments.

However, the as-made GEM powder cannot be used directly because it is mixed with a high percentage of poorly encapsulated Ni nanoparticles which will have to be removed by an acid-bath procedure. The purified high percentage Ni-GEM nanoparticles will then be dispersed in several solutions (e.g. methanol), and subjected to the field of a strong magnet (0.19 T). Consequently, the strong magnetic force will immediately attract all of the ferromagnetic Ni-GEM nanoparticles attached to the smooth wall of the glass beaker. After all of the methanol has been evaporated from the beaker, many small pieces of 5–10 mm in diameter, 2–3 mm thick high-density bulk GEM material can be obtained (see Fig. 2). In the following sections, we refer to the above procedures as the "standard" procedure for convenience sake. Fig. 3 shows the surface SEM image of the bulk material, where all of the nanoparticles are closely packed, and the estimated porosity is less than 10%.

The Ni-GEM nanoparticles are reasonably pure. XRD analysis shows only the diffraction peaks of fcc nickel, and EDX results show that there are only two elements, nickel and carbon, in the Ni-GEM samples. Several other analyses using

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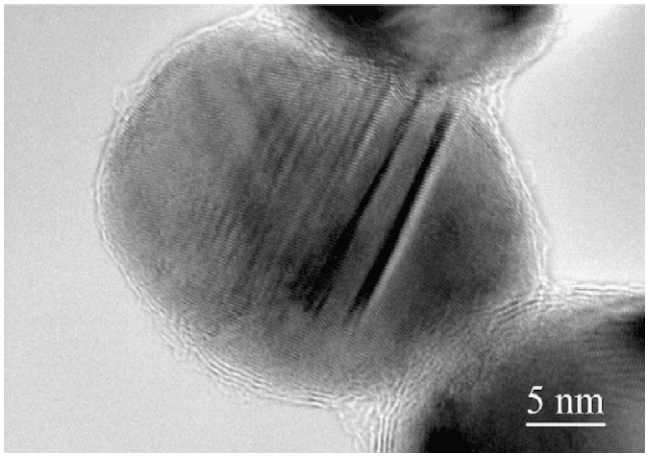

Fig. 1. TEM micrograph of Ni-GEM nanoparticles before being packed.

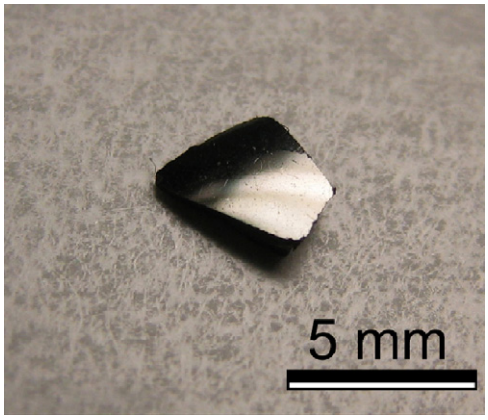

Fig. 2. One of the magnetic packed Ni-GEM bulk pieces collected from the wall of a glass beaker. The smooth and gently curved glossy surface shows the shape of the beaker.

TGA, Mercury Intrusion Porosimetry (MIP) and Archimedes techniques were also employed in this research.

3. Results and discussions

Evidence shows that the Ni-GEM bulk pieces collected from the wall of the beaker are very dense. In addition to the SEM micrographs (see Fig. 3), where all of the nanoparticles are closely packed without any visible pores, Archimedes measurements of the densities of these bulk pieces also attest to the high-density results. With a TGA analysis, we knew that the weight ratio of Ni to carbon is about 9:1, giving us an estimated overall average density of 6.87 g/cm^3 for the Ni-GEM. Because the Archimedes method routinely determined that the densities of the bulk pieces were greater than 5.5 g/cm^3, with a few even larger than 6.5 g/cm^3, we verified that these are indeed very high-density bulk pieces.

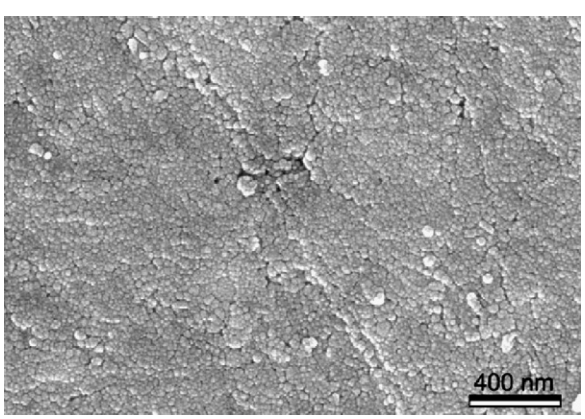

Fig. 3. SEM micrograph of the magnetic packed Ni-GEM bulk. The particle sizes vary from 10 to 50 nm. Note that there are hardly any pores larger than the size of a single particle.

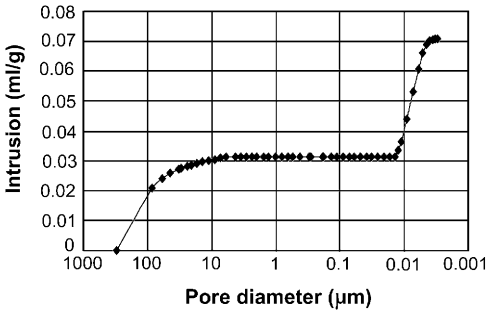

Fig. 4. Results of a mercury intrusion porosimetry (MIP) analysis. There are only two groups of pores, one is larger than 10 μm, and another one small than 20 nm; almost no pores are sized between 10 μm and 20 nm. The large pores (>10 μm) are probably surface fractures. The smaller pores (<20 nm), however, may represent the pores between individual Ni-GEM nanoparticles, and the total volume of these pores is about 10%.

Mercury intrusion porosimetry (MIP) can also determine the density of a material by determining its pore size distribution. But MIP is a destructive analytical method, and it requires a large sample to derive an accurate result. Therefore, after all of the non-destructive analyses had been done, all the remaining bulk pieces produced by the "standard" procedure, i.e., except for those derived from other modified methods, were put together to conduct one MIP measurement. In Fig. 4, there are almost no pore sizes ranging from 10 μm to 20 nm. Although there are a few large pores (>10 μm), they are probably just surface fractures. The pore sizes smaller than 20 nm, however, may represent the pores between individual Ni-GEM nanoparticles; the total volume of these pores is about 10%. The result confirms that our Ni-GEM bulk pieces reached a very high average density (about 90%), well over the theoretical closest pack density of 73%.

According to the BET specific area measurements, the specific area of Ni-GEM loose powder (12.8 m^2/g) is about 20% larger than that of the high-density bulk pieces (9.8 m^2/g). This means that during the magnetic compaction process, the surface areas have decreased by 20%, which may indicate a lot of particle movement, such as rotation or translation, so that the open surface area decreased dramatically.

Although we could not directly observe the compaction processes, a number of possible mechanisms (or important factors) can be reasonably postulated qualitatively. The first factor is the dispersant methanol, which could attach to the surface of the outer graphitic shell of a Ni-GEM and effectively reduce the van der Waals and magnetic forces between the nanoparticles. Three other dispersants: acetone, de-ionized water and ethanol, were tested in the same magnetic compaction procedures and unsurprisingly, ethanol yielded a very similar result to that of methanol, while the other two utterly failed.

The second factor is the strong magnetic field. A strong NdFeB magnet (0.19 T) was used in this work to apply the required magnetic field. Although a very strong magnetic force may force the Ni-GEM nanoparticles to rotate and move closer, a relatively weak one may fail to do so. Indeed, when replacing the NdFeB magnet with an ordinary ferrite magnet (0.09 T), the final density dropped to 60–70%; when there was no magnet present, the Ni-GEM powder simply would not be packed.

Table 1
The results of various magnetic packing procedures. The first row is the "standard" procedure without any variations, and the next eight rows are the results when one of the processes has been removed or modified. In comparison, the final two rows are the results of uniaxial compactions in a die.

Changed process	Variables	Glossy surface	Block sizes	Relative density (%)	Appearance
None	None	Yes	1–20 mm^2, 1 mm thick	>80	Irregular sheet
Dispersant	Acetone	Yes	1 mm^2	N.D.	Sheet
	De-ionized water	Yes	1 mm^2	N.D.	Sheet
	Ethanol	Yes	1–20 mm^2, 1 mm thick	80	Irregular sheet
Magnetic field	Magnet (0.09 T)	Yes	1–20 mm^2, 1 mm thick	60–70	Irregular sheet
	None	No	Powder	N.D.	No shape
Evaporation	In oven	Yes	1–5 mm^2, 1 mm thick	70	Irregular sheet
Acid bath	No	No	5–10 mm	25–30	Strip shape
Ultrasound	No	Yes	1–20 mm^2, 1 mm thick	50–60	Irregular sheet
Uniaxial compaction at 200 MPa in a 5 mm die	Dry powder	Yes	0.5 mm thick	38	Circular flat
	Wet with methanol	Yes	0.5 mm thick	42	Circular flat

The third factor is the evaporation of the dispersant. During the evaporation process, capillarity forces gradually push all of the nanoparticles tightly together. Therefore, if we speed up the evaporation process, some of the dispersant may evaporate too quickly, rendering the capillarity forces less effective. In the experiment, when the methanol was dried in an oven at 80 °C, not only did the density of the Ni-GEM bulk decrease to about 70%, but the sizes of the bulk pieces also decreased to 1–5 mm^2 due to uneven shrinkage.

Table 1 summarizes the results on the above-mentioned three important factors. From Table 1, it is clear that the acid-bath and ultrasound procedures are also very important, in particular the acid-bath procedure, by which the poorly encapsulated Ni-GEM was dissolved and the nanoparticle chains broken up. Without this procedure, it would be impossible to compact a high-density bulk out of the as-made Ni-GEM powder. In comparison, the final two rows of the table are the results of two uniaxial compactions of the Ni-GEM powder at 200 MPa in a die, and the packing densities were only about 40%.

The graphitic shell of the Ni-GEM plays an important role in the success of this new magnetic compaction method. The graphitic shells work as a lubricant in the methanol solution. Therefore, the Ni-GEM nanoparticles could slide, rotate and move against each other readily in a strong magnetic field. Note that pure nickel nanoparticles [10] (without the outer graphitic shells), when using the same "standard" magnetic packing procedure, will not pack nearly as well as Ni-GEM does. This means that the graphitic shell is the key to the success of this new method; therefore, other nanomaterials may not be applicable.

The major difficulty in this research was to produce enough well-encapsulated Ni-GEM for our experiments. If the production efficiency could be improved, then many future experiments could answer questions related to: the influence of the sizes and size distribution of Ni-GEM to packing density; the relationship between magnetic forces and packing density; whether this method could be used to produce high-density bulk in complex shapes; and whether this method could also be applied to other ferromagnetic Co-GEM and Fe-GEM.

4. Conclusions

A simple magnetic packing method was developed to produce high-density Ni-GEM bulk pieces. Experimental results from SEM micrographs, Archimedes measurements and MIP analyses all show the packing density of Ni-GEM nanoparticles to be over 80%. Although the exact mechanism of the process is still not clear, preliminary results show that several possible factors, including the type of dispersant, the dispersant's evaporation rate and magnetic field intensity, could all affect the packing density of bulk Ni-GEM. This work also provides valuable information on the behaviors of GEM nanoparticles in a dispersant and under a magnetic field.

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