Carbon coating of magnesium particles

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A B S T R A C T

Magnesium when hydrided has low thermal and electrical conductivity and carbon coating would be useful to remedy this for a variety of purposes. In this study, carbon coating was achieved by co-feeding magnesium and methane into a thermal plasma reactor. This yielded carbonaceous material with magnesium particles 5–10 nm in size embedded in graphitic matrix. A further reduction down to 2–3 nm was possible but required reductions in the precursor feed rate. 2 wt% carbon was sufficient to fully protect magnesium particles of approx. 260 nm in size. Light milling, however, disrupts the continuity of graphitic envelop and the particles then react both with oxygen and hydrogen.

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1. Introduction

Metallic nanopowders, especially below a size of 100 nm, are highly reactive and, therefore, it is necessary to protect them, not only to prevent their reaction with air but also to prevent their agglomeration. Thus metallic nanopowders are often passivated by a number of methods [1]. This include controlled exposure to air, i.e. forming a thin oxide layer outside, or applying a thin polymeric coatings, etc. (e.g. [2,3]). Among these carbon coating is perhaps the most effective. Thus magnetic nanoparticles such as Fe, Ni, Co can be encapsulated with carbon [4,5], some via processing in thermal plasma, so as to maintain their small size.

Magnesium as a metal is already quite reactive. Magnesium is capable of storing 7.6 wt% hydrogen which is highest among metals and therefore suitable as a hydrogen storage medium both for solid-gas [6–8] and for electrochemical storage [9]. MgH2, however, has insufficient thermal [10] and electrical conductivity [11] and it is necessary to remedy this by suitable measures. Thus, in solid-gas storage, nano structured magnesium powders are often mixed with expanded graphite [12–14]. This, not only improves the thermal conductivity of powders, but also separating the particles

apart, prevents the sintering of particles which could be exposed to elevated temperatures during their use [12–15]. Similarly, carbon black (or other similar additives) are often added to the anode in electrochemical hydrogen storage so as to improve their electrical conductivity [16]. However, the use of Mg or Mg rich active materials is hampered not only by their insufficient conductivity but also because they suffer a severe corrosion in alkaline environment [17].

In above studies, the nanostructured Mg materials are physically mixed with carbon so as to counteract their deficiencies. The current study was undertaken to examine whether or not magnesium could be carbon coated directly without the need for physical mixture. Direct coating of particles could reduce the carbon content and would thus allow a more efficient packing. The method of coating is based on co-processing of magnesium and methane in r.f. thermal plasma.

2. Experimental

Mg used in this study was 99.8% pure with −300 mesh size (Alfa Aesar). Methane, used as a source of carbon, was of %99.995(Linde Gas). Encapsulation experiments were conducted in a 30 kW RF thermal plasma system (Tekna). A schematic representation of the reactor is given in Fig. 1. Here Mg powder was fed to the reactor using a vibratory feeder with argon as carrier gas (5 sl/min). Methane was fed to the carrier gas at the selected rate. Thus, both methane and Mg were fed to injection probe placed centrally in the

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torch from above. Central gas, fed through the inner quartz tube, was Ar (99.995%) with a flow rate of 15 sl/min. Sheath gas, fed through the annular interspace between the inner tube and the outer confinement tube, was a mixture of Ar and H2 (99.995%) with flow rates of 60 and 6 sl/min, respectively. Quenching gas was nitrogen (99.99%) used at a flow rate of 150 sl/min injected through channels into the reactor radially at an angle.

The reactor was operated at a power of 25 kW. The pressure was at 0.97 bar in all experiments (i.e. slightly below atmospheric pressure). The experiments were run typically for a duration of 15 min. The resulting powders are collected from the powder collector, though small fraction which cannot follow the gas stream did accumulate in the bottom collector and in the cyclone collector. Particles collected in the powder collector were subjected to a back pressure at intervals. As a result, powders fall into an air-tight removable canister.

Powders were taken from the canister in the controlled manner. Having ascertained that they were not reactive, powders were characterized structurally by X-ray diffraction using CuK$_\alpha$ radiation. Powders were also examined using field emission scanning electron microscope (SEM) for morphological observations as well as for the energy dispersive spectroscopy (EDS) analysis. So as to examine the success of this experiment, i.e. whether or not Mg particles were encapsulated with carbon, a sample was examined with transmission electron microscope (TEM). For this purpose, a small amount of sample was sonicated for 5 min in methanol. Then, following 10 min of rest, 1–2 drops of the liquid were applied to carbon grid (200 mesh).

3. Results and discussion

The initial encapsulation experiments were carried out by co-feeding Mg powders 0.25 g/min with methane 1 sl/min mixed to the carrier gas (argon 5 sl/min), see Table 1. This has yielded carbonaceous material black in color. SEM observations verified that a greater portion of this material was indeed carbon. XRD pattern of the resulting material is given in Fig. 2. The pattern shows that the product do contain graphite as well as Mg, MgO and Mg(OH)2. The main diffraction peak of graphite was at $2\theta = 25.9°$. This angle is less than that would be expected from (002) of graphite ($2\theta = 26.6°$) implying that graphite is of turbostratic type [18].

TEM observations made on the sample were compatible with X-ray diffraction results in that a greater fraction was of carbonaceous material. In fact, it was so rich in carbon that it was difficult to locate a metallic particle within the sample. The particles that were encountered were embedded in graphitic matrix and not in the form of stand-alone particles encapsulated with carbon. Fig. 3 is a rare example in which a small Mg particle is seen to be wrapped by graphic layer, all embedded in a graphitic matrix.

The graphitic layers had a spacing of 0.334 nm in conformity with d(002) = 0.3347 nm of graphite and similarly, measurements on FFT image of metallic particle yielded a value of 0.190 nm. This value is compatible with the spacing of (102) in Mg.

As the metallic content was rather low in the above experiment, a new experiment was designed in which the flow rate of methane was reduced to one tenth of the original value, i.e. 0.1 sl/min instead of 1 sl/min. No encapsulated particles was observed in these experiments. Instead, Mg was formed as small particles embedded in carbonaceous matrix. The particles, however, were extremely small 3–5 nm in size, Fig. 4. Due to their small size, the lattice imaging did not yield reliable results, but values measured were close to the spacing values of Mg.

Whether or not the carbonaceous matrix provides a protection for embedded Mg particles, the mixture obtained from the reactor
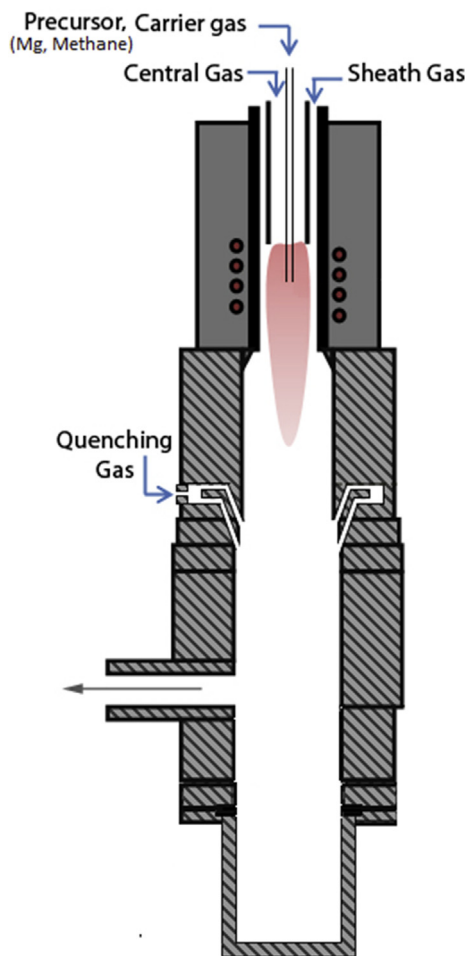

Fig. 1. Schematic representation of nano-powder reactor used in carbon coating of magnesium. Note that the precursors Mg and methane are fed to induction plasma via an injector placed at the top of the reactor.

was directly exposed to air without passivation. No reaction was observed. Obviously, this was due to the fact that the nanosize particles were protected by the carbonaceous material into which they were embedded. Since the protection of such nanosize particles would be useful for a variety of purposes, a special experiment was designed in which the feed rate of methane was kept constant, but the feed rate of Mg was increased progressively so as to obtain the protected mixture richer in Mg content.

Table 1
Carbon coating experiments in relation to their C content.

	C wt %											
	2	.	6	8	9	.	12	14	17	22	…	67
Base Experiment												
Mg g/m												1
CH4 sl/m												1
Reduced Methane												
Mg g/min								1				
CH4 sl/m								0.1				
Constant Methane												
Mg g/min			8	6.5	5.2		3.9	3.2	2.6	1.9		
CH4 sl/m			1	1	1		1	1	1	1		
Constant Mg												
Mg g/m	2.6			2.6			2.6		2.6			
CH4 sl/m	0.1			0.4			0.7		1			