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ZERO VALENT METAL PARTICLES FROM OXIDE
PRECURSORS

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Intended for: IMECE2010



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IMECE2010-39075

**AEROSOL SYNTHESIS OF NANO AND MICRO-SCALE ZERO VALENT METAL
PARTICLES FROM OXIDE PRECURSORS**

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ABSTRACT

In this work a novel aerosol method, derived from the batch Reduction/Expansion Synthesis (RES) method, for production of nano / micro-scale metal particles from oxides and hydroxides is presented. In the Aerosol-RES (A-RES) method, an aerosol, consisting of a physical mixture of urea and metal oxide or hydroxides, is passed through a heated oven (1000 °C) with a residence time of the order of 1 second, producing pure (zero valent) metal particles. It appears that the process is flexible regarding metal or alloy identity, allows control of particle size and can be readily scaled to very large throughput. Current work is focused on creating nanoparticles of metal and metal alloy using this method. Although this is primarily a report on observations, some key elements of the chemistry are clear. In particular, the reducing species produced by urea decomposition are the primary agents responsible for reduction of oxides and hydroxides to metal. It is also likely that the rapid expansion that takes place when solid/liquid urea decomposes to form gas species influences the final morphology of the particles.

INTRODUCTION

Synthesis of metallic nanoparticles has been the focus of many research articles lately due to their unique properties such as optical gain^[1], water purification^[2], and in biological applications^[3]. Moreover, magnetic nanoparticles have been of particular interest specifically, the synthesis of nanometer nickel due to the significant interest in its applications^[4] as a catalyst and in pigments^[5, 6]. Additionally, such particles were found to have great use in the magnetic data storage media industry^[7], as elements of chemical and biological sensors^[8], as well as in biomedical applications^[9-13].

Due to these exciting applications and discoveries a significant amount of effort and funding has been given to study synthesis of such ultrafine particles. A number of techniques have been introduced and used as a means of production of such metallic nanoparticles such as sono-chemistry^[14-15], wet chemistry methods^[16-20], co-precipitation^[21, 22], micro-emulsion methods^[6], laser-driven thermal methods^[23-26] and plasma methods (REPS). Virtually all prior reported work in this field conveyed obstacles of contamination, expensive processes, low yields, and difficulty of mass productions and industrial up scaling.

Herein we describe an aerosol method (A-RES) by which we produce micro and nano zero valent nickel (ZVN) particles from Nickel(II) hydroxide and Ni(II) Oxide. Characterization of the particles clearly identifies them as being pure (zero valent) Ni with varying sizes. The particles are micro and nano in size with micron particles forming from nanoparticles, which have sintered, into microparticles. Observation with the scanning electron microscope (SEM) shows that the particles are porous. The A-RES method lends itself to continuous synthesis of particles for industrial scale-up.

EXPERIMENTAL SETUP

Materials

Solid urea was purchased from EMD Chemicals and ground into a fine powder that was passed through a 400 mesh. The urea was then added to a flask of either Nickel(II) Hydroxide or Nickel(II) Oxide. Both nickel compounds were purchased from Sigma-Aldrich and used without any modifications.

A 1:7 ratio between the nickel in the Nickel(II) Hydroxide and the amine functional group in the urea (-NH₂) in this work. Specifically for this work, this was obtained by adding 3 g of Ni(OH)₂ to 16.17 g of ground urea powder in the flask. Similarly, to achieve a 1:7 ratio between Nickel in the Nickel(II) Oxide and the amine function group in urea, a sample was prepared by adding 4 g of NiO to 26.75 g of ground urea powder in the flask.

In order to obtain a more uniform heterogeneous mixture of the urea and nickel compounds, flasks of the compounds were shaken lightly. An acceptable mixture was obtained when the color of the mixture was uniform. Flasks were sealed with a two-hole rubber stopper.

Apparatus and procedure

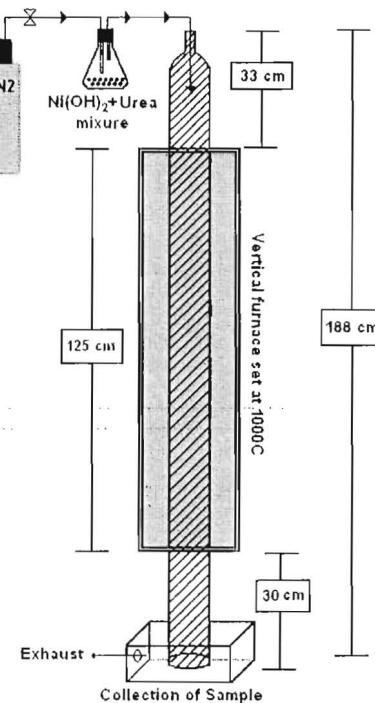


Fig. 0 Furnace used in synthesis of micro and nanoparticles of nickel from Nickel(II) Hydroxide and Nickel(II)Oxide

Fig. 1 shows a diagram of the A-RES reactor used in synthesis of ZVN. It consists of a 188 cm quartz tube with an outer diameter of 38 mm and 35 mm inner diameter. On the top end, this tube has a 5 cm gas port with a 10.5 mm ID and 12.75 mm

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J. Phillips, C. C. Luhrs, M. Richard, 'Engineering Particles Using the Aerosol-Through-Plasma Method', *IEEE Transactions on Plasmas* 37, 726-739 (2009).
Luhrs, C.C., C. Peng, P. Fanson and J. Phillips, 'Engineering Aerosol-Through-Plasma Torch Ceramic Particulate Structures: Influence of Precursor Composition', *J. Mat Res.* 23, 1870 (2008).

OD, a 125 cm long vertical furnace. The tube was inserted in the furnace such that approximately 33 cm from each side of the tube was located outside the furnace.]

The experiments commenced by purging the system with 900 sccm of ultra high purity Nitrogen (99.9999%) while heating the single-zone furnace to the desired temperature (1000 °C). Flow of the gas was controlled by a rotameter. When the furnace reached the desired temperature, the nitrogen feed was switched to the flask containing the mixtures at a rate of 900 sccm through one of the two holes of its stopper and another feed was connected from the flask to the quartz tube, see Figure 1. The flask was gently vibrated to create the aerosol.

This fine powder traveled through the hoses in to the quartz tube depositing green, white, and black materials on the side of the upper part of the quartz tube. A fine, dark and metallic powder was also collected using a weighing paper in an empty beaker beneath the outlet of the quartz tube. The beaker was placed in a plastic box that had an opening on its top with a 38 mm diameter to allow the quartz tube entry into the box via close tolerances. Nitrogen flowing through the tube pressurized the plastic box such that air was prevented from coming into contact with the product.

Characterization

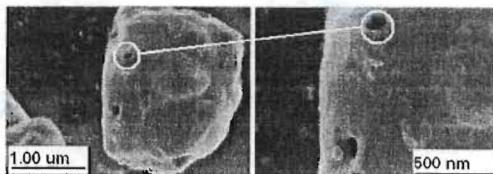
The nickel particles were collected in the bottom of the reactor with minimal exposure to air. Particles from both the Nickel(II) Hydroxide and Nickel(II) Oxide mixed with urea were loosely agglomerated and black in color. They were attracted to permanent magnet as a powder as well as when dispersed in a solvent – a quick verification that we indeed have nickel. Control experiments were conducted by passing Ni(OH)_2 and NiO separately in the furnace at 1000 °C without any urea. There was a slight change of color but neither powder was attracted by permanent magnet. Additional preparation of samples was performed per the method of analysis used. Specifics are outlined in subsequent sections.

The ZVN particles were characterized using a scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction, and FIB. Scanning electron microscopy (SEM) was performed with a Hitachi S5200 Nano SEM to capture images of the metallic powder. High-resolution transmission electron microscopy (HRTEM) was used to determine the nickel's structure with a JEOL 2010 at 200 keV. Samples for TEM analysis were ultrasonically dispersed in ethyl alcohol and transferred dropwise to a 200-mesh holey carbon grid. X-ray diffraction (XRD) was used for crystallographic analysis using a Scintag PAD V X-ray diffractometer with Scintillation detector.

RESULTS AND DISCUSSION

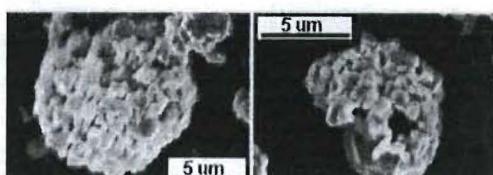
The following subsections describe the results from each of the mentioned characterization techniques. Each subsection contains a brief analysis of the results germane to that technique.

Scanning electron microscopy (SEM)



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Fig. 1 SEM images of Nickel particles obtained after they were produced from Ni(OH)_2 at 1000 °C. Images were taken at 2.0kV x30.0k



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Fig. 2 SEM images of Nickel particles obtained after they were reduced from NiO at 1000 °C. Images were taken at 15.0kV x7.00k and x8.96k

A sample of the particles was investigated using the SEM. The sample was placed on carbon tape and a standard SEM holder was used. Figure 2 shows SEM images of ZVN particles prepared from the reduction of Nickel Hydroxide at 1000 °C. A substantial number of particles were observed to have holes. Some of the particles prepared were large hollow spheres while others were in aggregates of nano and micro particles.

As seen in Fig. 3, particles approximately 1 μm in size are sintered together to form larger particles. Similar results were found for particle made from Nickel Hydroxide. The Fannan temperature of Nickel is 643 °C, at which point the sintering process is believed to occur.^[27] Since the temperature used in our reactor is at 1000 °C, we attribute this phenomenon to sintering.

Using several SEM micrographs a particle size distribution (PSD) was created. A total of 415 particles were measured and their sizes ranged from 0.4 μm to 9.7 μm . The average particle size was 1.9 μm with a standard deviation of 1.5 μm .

High-resolution transmission electron microscopy (HRTEM)

A TEM sample was prepared by dispersing a small amount of solid powder of Nickel produced from Ni(OH)_2 and NiO in ethanol and using an ultrasonic bath to help the powder dispersion. TEM images, e.g. Figure 4, indicated a substantial amount of nanoparticles. It is estimated that as much as 5% of the metal was in the form of nanoparticles, clearly indicating the existence of a bimodal particle distribution. Standard mechanistic models of particle growth (nucleation/growth/agglomeration/ripening) do not predict the formation of bimodal particle distributions. Recently it was suggested that bimodal distributions form via shattering of larger particles.

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Phillips, J., C. C. Luhrs and P. Fanson, 'Production of Complex Cerium-Aluminum Oxides Using an Atmospheric Pressure Plasma Torch', *Langmuir* 23, 7055-7064.(2007)

A study of the particle size distribution of nanoparticles only (576 particles) indicated an average of 15.8 nm with a standard deviation of 12.4 nm.

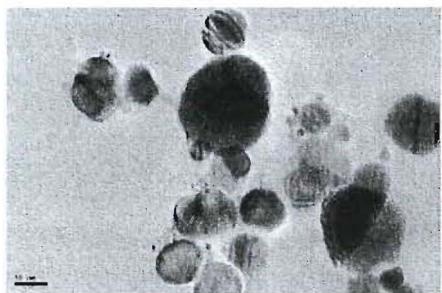


Fig. 4 TEM images (scale bar 50nm) of Nickel obtained from Ni(OH)_2

X-Ray Diffraction

X-ray diffraction (XRD) was also used to characterize the samples yielded from this experiment. The results are shown in Figs. 5 and 6. Dominant peaks in these plots are Ni; secondary peaks are urea and the precursor. Urea and the precursor remain presumably because the two molecules never came into contact in the reactor.

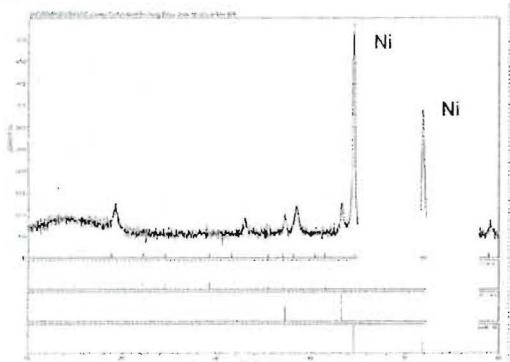


Fig. 5 X-Ray diffraction pattern of Nickel particles obtained from Ni(OH)_2

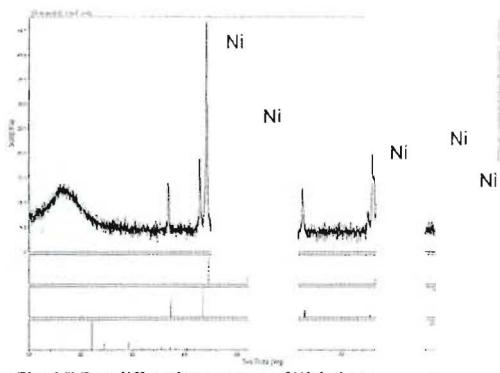


Fig. 6 X-Ray diffraction pattern of Nickel par
from NiO

CONCLUSIONS

Nanometer nickel powders have been successfully prepared from Ni(OH)_2 and NiO each mixed with urea in a 1:7 ratio. The method utilized was the A-RES method at 1000 °C. The morphology, particle size distribution and composition were determined using SEM, HRTEM, and XRD. Results indicate that reduction of Ni(OH)_2 and NiO are possible via the decomposed products of urea. The A-RES method is a continuous method that lends itself to transformation into a mass production method.

ACKNOWLEDGMENTS

This work was completed in part at the University of New Mexico Manufacturing Training and Technology Center.

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