

## Hollow Metal Spheres Created with Polymer Core Results in Strong, Porous, Lightweight Structures

The Fraunhofer Institute for Manufacturing and Advanced Materials in Dresden, Germany, has introduced a powder metallurgy (P/M) approach for the production of lightweight, hollow metal spheres. In this process, a polymer core is coated with a powdered metal slurry to create the desired wall thickness, then conventional P/M binder-removal and sintering operations are used to produce hollow spheres with fully dense shells. Individual green (unfired) or sintered spheres can be sinter-bonded, brazed, or sintered and then adhesively bonded together to fabricate porous structures with low bulk densities and very high specific strengths. A schematic representation of the production process for sintered components is shown in Figure 1.

Sphere outside diameters from 0.5 mm to 10 mm with wall thicknesses of 20–1000  $\mu\text{m}$  have been produced in a wide range of compositions including Fe, stainless steels, Ti alloys, Ni, and Ni-based superalloys. Since the process represents only a minor variation in traditional powdered metal and ceramic processing, the list of possible compositions is almost limitless. Compared to commercially available porous composite and polymer structures, the use of hollow spheres addresses applications where elevated operating temperatures, corrosive environments, or other factors must be considered. The fabrication of lightweight components using hollow spheres also provides more predictable macroscopic properties than do other cellular materials, due to the high degree of uniformity achievable in size, wall thickness, and porosity level. Furthermore, by combining multiple sphere sizes, structures with very specific mechanical, thermal, and microstructural

properties can be developed.

The mechanical properties of hollow sphere structures have been evaluated using cylindrical samples fabricated from different sphere compositions. The

results in Figure 2 show a compressive stress-strain curve and associated deformation behavior during compaction of 316L stainless-steel spheres. Compaction begins at about 60–70% strain with a rela-

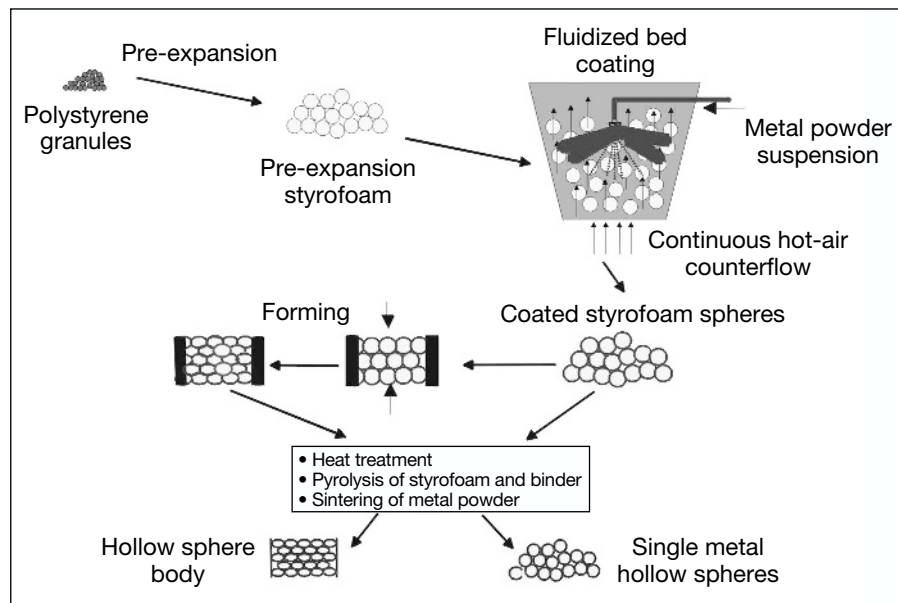


Figure 1. Process schematic for the production of hollow metal spheres and components.

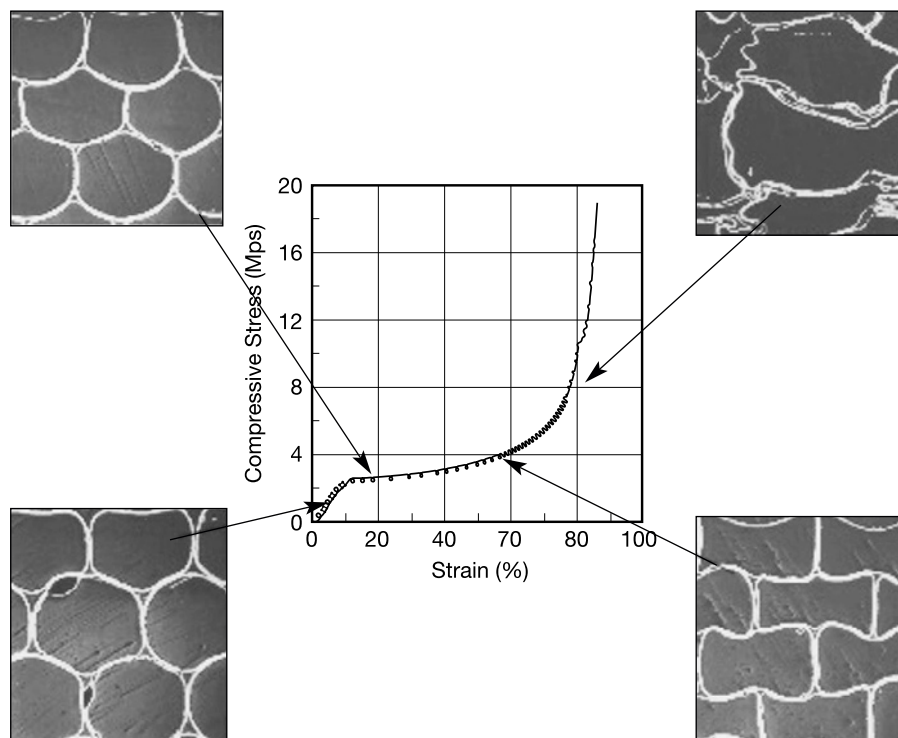


Figure 2. Compressive stress-strain curves and related deformation behavior for 316L stainless-steel hollow-sphere structures.

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tively linear response, followed by a long region of plastic deformation. Ductile behavior has been shown not only for individual spheres under compressive loads, but also for structures fabricated from sphere arrays.

Another promising property is the energy-attenuation ability of hollow-sphere arrays. Porous structures are known to have sound-absorption properties. While fibrous materials (e.g., fiberglass "wool") or cellular polymers are used routinely as acoustic isolation materials, hollow spheres provide alternative solutions for harsh conditions such as high temperatures and corrosive environ-

ments, and also provide tunable acoustic-absorption characteristics by varying pore size and distribution.

Hollow spheres and structures present a new class of lightweight materials within the family of cellular materials. Since hollow spheres can be fabricated from a wide range of P/M materials, the potential application fields are wide-ranging. Some of the applications that are expected to be addressed with the hollow-sphere technology include thermal insulation, lightweight structural members, catalytic substrates, bioimplants, jewelry, crashworthy components, acoustic and mechanical isolators, and seals and valves.

**Opportunities**

Fraunhofer has developed strategic partnerships with raw-materials suppliers and sphere manufacturers, and welcomes inquiries about joint development and licensing of the technology for new industrial applications and materials systems.

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**Zirconia Sensor Detects CO<sub>2</sub> Emission in 60 s**

With increasing demands to limit CO<sub>2</sub> emissions, a gas sensor for CO<sub>2</sub> monitoring is needed in order to assess the measures aimed at its reduction. Electrochemical sensors can be used to determine the concentration of CO<sub>2</sub> in the atmosphere. This type of sensor for CO<sub>2</sub> monitoring is being developed at the University of New South Wales (UNSW) in Australia. It has a response time of 60 s and is based on cubic zirconia (ZrO<sub>2</sub>) as the solid electrolyte and a mixture of carbonates as a CO<sub>2</sub>-sensitive electrode.

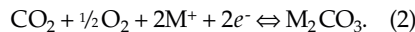
Electrochemical gas sensors are solid galvanic cells in which the electromotive force (EMF) can be related to the concentration of selected gases. The electrochemical chain of the galvanic cell for CO<sub>2</sub> sensing, which consists of connected phases that use mobile ionic defects to transfer charges, includes (1) an electronic conductor made of gold; (2) a sensing material, consisting of both lithium and barium carbonates, that is reactive to the CO<sub>2</sub> in the gas phase; (3) an ionic bridge formed as a reaction between the sensing phase and the solid electrolyte; (4) a solid electrolyte made of cubic zirconia; and (5) an electronic conductor made of platinum, shown in Figure 1. The relation between the EMF of the cell and the partial pressure of the CO<sub>2</sub>,  $p(\text{CO}_2)$ , is given by the Nernst relation, which expresses the electromotive force of a cell:

$$E = E^0 + (RT/nF) \ln p(\text{CO}_2), \quad (1)$$

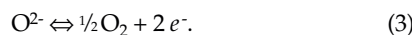
where  $E$  is the EMF,  $E^0$  is the cell's standard EMF,  $n$  is the number of electrons involved in the cell reaction,  $R$  is the gas constant (8.314 J/K mol),  $T$  is the absolute temperature (in degrees kelvin), and  $F$  is the Faraday constant ( $9.648 \times 10^4$  C/mol). Calibration of the cell consists of the deter-

mination of  $E$  as a function of  $p(\text{CO}_2)$ .

The sensing signal is generated according to the reaction:



This signal is the electrical potential that is generated at the triple-phase boundary formed between the electron conductor, the sensing material, and the analyzed gas as a consequence of the chemical reaction at the electrode. Similarly, for the reference signal, the reference gas replaces the gas being analyzed. (The electrode is a triple-phase system consisting of the metal conductor, the sensing material, and the gas phase involved in the electrode reaction.)



The EMF of the cell is generated only after the third phase required to establish the cell's electrochemical chain is formed, specifically the ionic bridge that is

formed as a reaction between the sensing phase and the solid electrolyte.

The criteria used by the developers in selecting the materials for the sensing phase include (1) high reactivity with CO<sub>2</sub>, (2) ionic conductivity, (3) low reactivity with the solid electrolyte, (4) a short response time for the electrical signal, (5) a high melting point, (6) chemical and mechanical properties compatible with the solid electrolyte, and (7) low reactivity with other gases and water vapor. The results of their investigation show that composites of two or three carbonates exhibit better properties than individual compounds. Additions to alkaline metal carbonates of BaCO<sub>3</sub> (barium carbonate), CaCO<sub>3</sub> (calcium carbonate), and SrCO<sub>3</sub> (strontium carbonate), as well as metal oxides, have a beneficial effect on the sensor's performance. This suggests that interfaces formed between the alkaline metal carbonates and the metal oxide

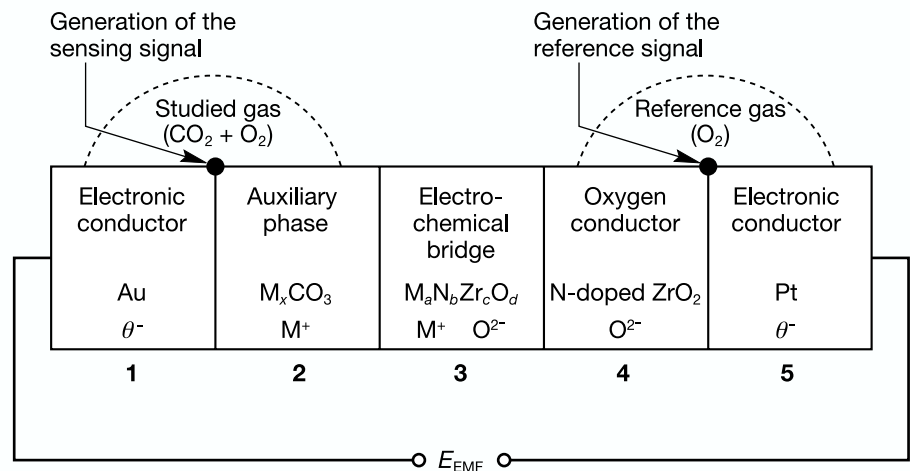


Figure 1. The electrochemical chain of the CO<sub>2</sub> chemical sensor.

additions play a significant role in the generation of the sensing signal.

Several materials were investigated for the solid electrolyte: zirconia, NASICON ( $\text{Na}_2\text{Zr}_2\text{Si}_4\text{P}_3\text{O}_{12}$ ),  $\beta$ - and  $\beta''$ - alumina ( $\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$ ), and solid carbonates. Both NASICON and  $\beta$ -alumina react with water. Therefore, the

performance characteristics of sensors based on these electrolytes are not stable in humid atmospheres. The carbonates are gas-permeable, and their ionic conduction is too low. Zirconia, which exhibits low reactivity with water and can form high-density ceramic structures (a requirement for blocking gas-permeability) was select-

ed as the optimal candidate for electrochemical sensors. To date, only Mg-doped zirconia has been investigated.

Figure 2 shows the performance characteristics of a zirconia-based (fully stabilized cubic zirconia) electrochemical sensor for  $\text{CO}_2$  monitoring during two subsequent experimental runs, involving a decrease and increase of  $\text{CO}_2$  concentration between 18.45 ppm and 12.3 ppm. As can be seen, the sensor exhibits good EMF versus time reproducibility (reaching the same EMF value at the end as it had in the beginning), with response time (the time required to reach a new EMF value) of about 60 s. It does not exhibit cross-sensitivity with respect to  $\text{SO}_x$  or  $\text{NO}_x$ , or CO below 1000 ppm.

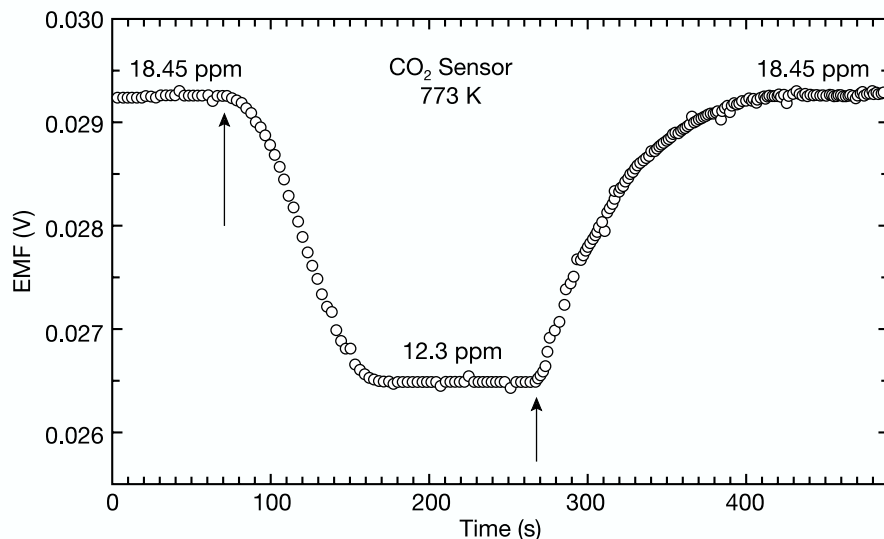


Figure 2. The electromotive force versus time characteristics of the  $\text{CO}_2$  sensor.

### Opportunities

The UNSW researchers (J. Nowotny, T. Bak, M. Rekas, and C.C. Sorrell) welcome inquiries from those interested in joint research and development to commercialize these sensors.

Source: Dr. Janusz Nowotny, Center for Materials Research in Energy Conversion, School of Materials Science and Engineering, The University of New South Wales, UNSW Sydney, NSW 2052, Australia; fax 61-2-9385-6467 and e-mail J.Nowotny@unsw.edu.au.

### Clay Platelets Modified with Organic Molecules Result in Transparent and Colored Nanocomposite Coatings

The incorporation of silicate layers in organic and organic-inorganic hybrid coatings by modifying clay platelets with organic molecules that contain two or more charged functional groups results in the formation of clay platelets "coated" with charges that are mutually repelling. These platelets can be readily dispersed in coating systems since they offer potential applications as (multi)functional fillers in the coatings providing corrosion resistance, barrier properties, and color. This is the basis of the Planomer<sup>®</sup> concept developed at TNO in The Netherlands.

The layered silicates are typically organically modified by replacing the charge-balancing interlayer cations with, for example, ammonium ions, in order to render the silicate layers organophilic. Depending on the interaction between the layered silicates, different types of nanocomposites can be produced, ranging from intercalated to exfoliated nanocomposites. Recent methods to incorporate

separated layered silicates in polymers (nanocomposites) involve the addition of the modified silicates to a solvent-swollen polymer or to the polymer melt during processing and also during the polymerization process. Because of the high aspect ratios of layered silicates, materials are obtained that show improved mechanical, thermal, and barrier properties without a significant loss of optical transparency, toughness, or impact strength compared to the original, nonmodified material. Currently the work at TNO focuses on a method (patent pending) for the exfoliation of layered silicates in coatings.

The incorporation of single clay sheets into coatings is more difficult than in bulk materials because the two-component system, polymer/clay, is replaced by a three-component system, (pre)polymer/solvent/clay. The coating systems need to stay homogeneous during all processing and curing steps. This can be achieved, in the ion-exchange step, by the use of organic modifiers with two or more functional groups. The cations located between the clay platelets are exchanged with one of the functional groups of these organic molecules, such as an ammonium group,

leaving another functional group (which can be positively or negatively charged) present on the clay platelets. The platelets are "coated" with charged molecules, which results in their becoming mutually strongly repellent and, therefore, homogeneously dispersed in polymeric matrices.

The coating matrices used to date are acrylic polymer dispersions in water and

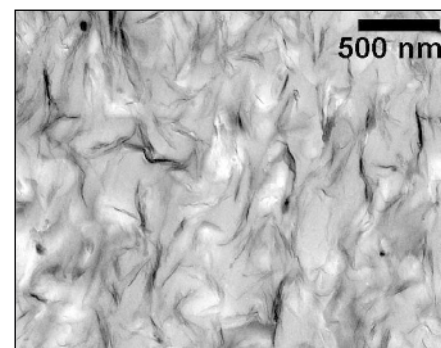


Figure 1. Transmission electron micrograph of an organic-inorganic hybrid nanocomposite coating with 5.0 wt% clay content, modified with methylene blue dye.

polyurethane dispersions in water, as well as organic-inorganic hybrid coating systems. Coatings with various amounts of modified clays (0–20 wt% based on solid coating material) have been obtained. Agglomeration of the clay in the organic-inorganic hybrid coatings does not occur up to 20 wt% clay, based on solid coating material, and the nanocomposite coatings of both organic and organic-inorganic hybrids remain transparent up to 15 wt% clay. The dispersion of the clay platelets in the organic-inorganic hybrid coating is very homogeneous, as shown in Figure 1. These nanocomposite coatings are highly transparent at a layer thickness ranging from 10  $\mu\text{m}$  to 40  $\mu\text{m}$ , and have improved barrier properties, such as a decreased permeability to oxygen and water, improved corrosion resistance, and increased thermal stability compared to the original, nonmodified material. The wet coating systems can be applied and thermally or photochemically cured onto a variety of substrates such as glass, steel, aluminum, and plastics.

The use of colored modifiers for the clays, such as methylene blue, results in colored nanocomposite coatings (Plano-



Figure 2: Photograph of transparent, colored nanocomposite Planomer® coatings (showing yellow, blue, and orange) with 5 wt% clay homogeneously dispersed in the solid coating material. The layer thickness is 10–15  $\mu\text{m}$ .

colors) with improved UV stability and resistance to solvents compared to the original, nonmodified material. Colored nanocomposite coatings do not discolor when exposed to UV irradiation for one week, while coatings colored with methylene blue without the clay additive discolor after 1 h. Furthermore, immersion

of the nanocomposite coatings (5 wt% clay based on solids) in water, acetone, or ethanol for 4 h does not result in the release of the dye, indicating a strong bonding of the dye with the clay platelets. Coatings with a corresponding amount of dye but without added clay release the methylene blue dye.

Figure 2, a photograph of various nanocomposite Planomer coatings in which clay particles are homogeneously dispersed, shows their transparency. Potential applications of this technology are barrier and anti-corrosive coatings, decorative transparent coatings, coatings with increased UV stability, and environmentally friendly colored coatings.

#### Opportunities

TNO welcomes inquiries to discuss/establish possibilities for a partnership in further development of the planomer technology.

Source: Dr. Hartmut Fischer, Head of the Nanocomposite Program, Materials division, TNO-TPD, P.O. Box 595, 5600 AN Eindhoven, The Netherlands; tel. 31-40-2650-151, fax 31-40-244-9350, and e-mail hfischer@tpd.tno.nl; www.tpd.tno.nl/TPD/smartsite40.html. □

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