

Preparation of metallic cobalt and cobalt-barium titanate spheres as high temperature media for magnetically stabilized fluidized bed reactors

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Fluidized bed reactors are extremely efficient when mass transfer limitations dominate global reaction rates, such as in combustion or incineration [1, 2]. Because fluidized beds operate using a balance between direct fluid dynamic forces and the gravitational restoring force, the maximum mass transfer rates for a given reactor configuration are limited by gravity. This limitation has been overcome using magnetic fields acting upon magnetically susceptible fluidization media to augment the force of gravity [3–7]. However, the use of magnetically stabilized fluidized beds in high temperature reactions has been limited by the lack of suitable media. Three magnetic properties are required to obtain suitable media: high magnetic susceptibility, high Curie temperature, and low coercivity. Cobalt, with a Curie temperature of 1121 °C, meets these requirements. We have investigated the preparation of two forms of cobalt containing spherical fluidization media: metallic cobalt, and cobalt impregnated barium titanate.

Novel ferromagnetic media including cobalt impregnated barium titanate and metallic cobalt spheres have been prepared for high temperature application in magnetically stabilized fluidized beds. Spherical polymeric beads were initially formed by gelation of an alginate-precursor oxide suspension. Water was then eliminated from the hydrous gel at low temperature and the organic polymer was removed by oxidation in air. The temperature was then raised and the firing atmosphere changed to a reducing mixture containing hydrogen. Under these conditions, cobalt oxide was first reduced to the metallic form, and at a sufficiently high temperature, densification occurred via sintering.

Cobalt impregnated barium titanate was prepared by intimately mixing BaCO₃, TiO₂, MgSO₄, SiO₂, and Co₃O₄ in a ball mill using zirconium oxide milling media, with molar ratios corresponding to one mole of Ba_{0.95}Mg_{0.05}TiO₃, 0.064 moles of TiO₂, 0.311 moles of Co, and 0.0207 moles of SiO₂. The excess TiO₂ and SiO₂ form a low melting eutectic, predominately BaTiSi₂O₇, which melts at 1245 °C and acts as a sintering aide. The cobalt content corresponds to 10% (w/w) of the resulting BaTiO₃. The oxides, carbonates, and sulfates were initially added to 1.4 times their weight

of water containing 0.5% (w/w) tannic acid, as a dispersion aide and the pH was raised to 10 with ammonium hydroxide. Following milling, the slurry was dried and calcined at 1100 °C, forming a cobalt oxide-barium titanate solid solution. The calcined material was then remilled for 4 h and dried.

Spheres containing the solid solution were formed by gelation as calcium alginate. The oxide mixture was dispersed in 1.2–1.4 times its weight of water containing 0.25% (w/w) tannic acid at pH 10. Then a 3% (w/w) solution of high viscosity sodium alginate binder was slowly added until a homogeneous mixture was obtained. After mixing, the viscosity was adjusted by addition of water and by heating. Spherical particles between 1.5 and 4 mm in diameter were formed by gelation of droplets issuing from a syringe into a 5% (w/w) CaCl₂ solution. The beads were dried at room temperature for 24 h followed by 12 h at 80 °C. The beads were heated to 500 °C at 1 °C/min in air to remove the alginate binder, and then heated at a 5 °C/min rate to 1100 °C under a reducing atmosphere consisting of 5% H₂ in nitrogen and saturated with water vapor at 25 °C to reduce cobalt oxide to the metallic state. To ensure complete conversion of cobalt oxide, the maximum temperature was maintained for 10 h. Due to insufficient densification, the beads were subsequently placed in a high temperature furnace and fired at 1325 °C for 2 h using the same reducing atmosphere.

The resulting cobalt impregnated barium titanate beads were ~1–2 mm in diameter. A scanning electron microscopic (SEM) photomicrograph of the surface of one of these beads is shown in Fig. 1. The bead is composed of interconnected barium titanate/cobalt grains, between 0.75 and 3 μm in diameter. This composite structure, with thin necking regions between individual grains, represents the initial stages of sintering. The porosity in this bead is clearly interconnected. Based on a linear point count methodology applied to polished sections, porosity for this sample was 21.7% ± 2.5%. For application in gas phase fluidization processes this type of morphology can serve as an excellent catalyst support by providing high surface areas with rapid gas exchange to interior surfaces.

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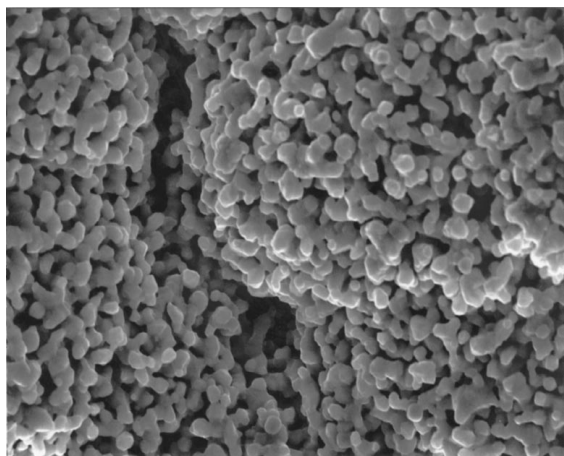


Figure 1 Surface SEM photomicrograph of a cobalt impregnated BaTiO₃ bead (3300×).

Metallic cobalt beads were prepared from Co₃O₄ using two variations of the alginate gelation method. First, cobalt oxide was dispersed in aqueous 0.25% (w/w) tannic acid at pH 10–11. The suspension was heated to 50 °C and 5% (w/w) of medium viscosity sodium alginate was slowly added until a homogeneous slurry was obtained. Droplets of this slurry were then gelled by addition to a 5% (w/w) calcium chloride solution using the methods described above. Spherical cobalt oxide impregnated calcium alginate particles between 3–4 mm in diameter were formed. Removal of the organic binder and the initial reduction were conducted as described above. The beads were then fired at 1200 °C for an additional 5 h under the reducing atmosphere to achieve further densification. The resulting cobalt beads were ~1–2 mm in diameter with a porosity of 8.8% ± 2.7%, the majority of which was not interconnected. As shown in the SEM photomicrograph of Fig. 2, the surface exhibited an undulating granular morphology containing many porous cavities. The average cobalt grain size varied between 5–10 μm.

A second batch was prepared using a dispersion of Co₃O₄ in 1% (w/w) citric acid and 0.25% (w/w) tannic acid, with pH > 10. Medium viscosity sodium alginate (6%) was slowly added with vigorous stirring until a homogeneous suspension was obtained. Droplets of this slurry were then gelled by addition to a 15% cobalt

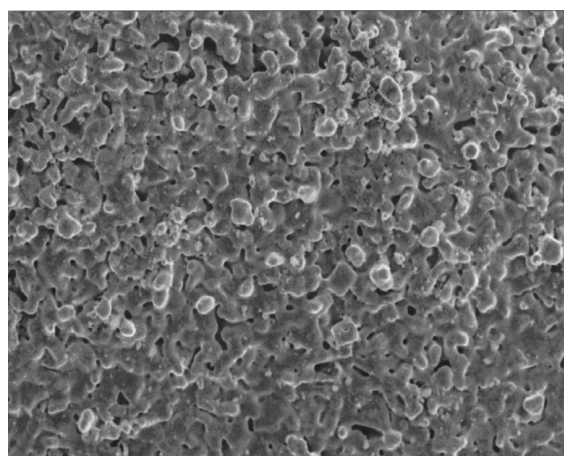


Figure 2 Surface SEM photomicrograph of cobalt bead gelled in CaCl₂ and reduced at 1200 °C (550×).

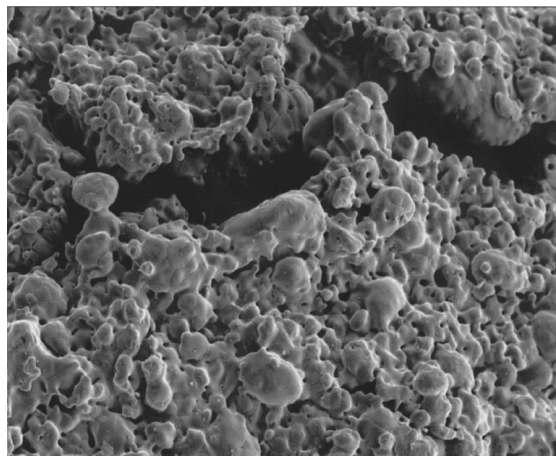


Figure 3 Surface SEM photomicrograph of cobalt bead gelled in CoCl₂ and reduced at 1100 °C (350×).

chloride solution. The rate at which these droplets gelled was slower than when using calcium chloride. The resulting alginate beads were processed similarly, but with the omission of the final thermal treatment at 1200 °C. As before, the cobalt beads were ~1–2 mm in diameter. An SEM image is shown in Fig. 3. Porosity of the resulting beads was estimated as 17.6% ± 2.8%. The pores in these cobalt chloride gelled beads were isolated and larger than those in the calcium chloride gelled beads. The observed differences in relative densities achieved by the two methods at the same firing temperature indicates that calcium residue left from the gelation process inhibits densification. The grain size distribution increased from 5–10 μm in the calcium gelled batch to 20–50 μm in the cobalt chloride gelled batch. These differences can be explained by an increase in grain boundary mobility for the cobalt chloride gelled samples. This also produced larger pores, due to rapid grain growth during sintering.

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