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Colloidal processing of highly concentrated aqueous copper suspensions

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ABSTRACT

This work deals with the preparation of copper dense compacts using an aqueous colloidal route. Concentrated suspensions of Cu powders were prepared in water with a polyelectrolyte and tetramethylammonium hydroxide at alkaline pH as dispersing agents. Suspensions were optimized by measuring the rheological behavior as a function of pH and volume fraction of solids. The slurries showed a pseudoplastic behavior with thixotropy due to the additives added. The suspensions were slip cast in plaster molds leading to high green densities (~61% TD), as a consequence of the particles' shape and size distribution packing characteristics. Sintering studies were performed at 900 °C in flowing Ar/5% H_2 atmosphere. The green and dense compacts shaped by this route were characterized by SEM and Archimedes' density.

1. Introduction

The difficulty in dispersing submicron sized metal particles in water is due to their strong tendency towards agglomeration and their high density that facilitates sedimentation. The former investigations regarding the feasibility of colloidal processing of metal powders in water were done using nickel powders in the earlier 2000s. The main focus was the development of new shaping routes to produce anodes for fuel cells, coatings, and metal–ceramic composites [1–5]. Recently, Lussoli et al. [6] conducted a study with the aim to disperse Fe particles in an aqueous media, producing bulk compacts which acted as carriers of ceramic nanoparticles applied to the nucleation of graphite in gray cast irons.

When a metal is exposed to air, an oxide layer of a few nanometers is readily formed that quickly stabilizes. However, upon contact with water important changes of the surface charge occur under specific conditions of pH. It has been shown [1] that the surface of Ni particles reached the isoelectric point at pH between 3.5 and 4.0. At acidic pH, partial dissolution at the surface occurs liberating Ni^{+2} ions, which readily degrades the metal particles. However, at basic pH (to pH 9), a passivation layer of $NiO(OH)_2$ is formed. Thus, for the preparation of aqueous suspensions of metal particles it is desirable to work at alkaline conditions to minimize the hydroxylation of the particle surfaces. Although the formation of a thin oxidation layer is unavoidable, its thickness is small at these conditions and can be easily removed on sintering under reducing atmospheres.

Copper is one of the most important non-ferrous metals used in large scale in industry. Its main property is the electrical conductivity, which is just below that of silver. Copper is generally used as bronze alloys with additions of Ni, Sn, Pb and C (graphite bronze). Thus, copper alloys are used in conditions requiring high corrosion resistance, ductility and thermal and electrical conductivities [7]. Enhanced mechanical properties and longer lifetime of copper materials can be obtained by introducing a ceramic phase homogeneously dispersed into the copper matrix, such as Al_2O_3 [7,8], SiC [9–11], TiB_2 [12], carbon nanotubes [13], diamond [14] or complex carbides like Ti_2SnC [15] and $TiAlC_2$ [16].

Currently, there is an interest to reduce the operating temperatures of solid oxide fuel cells (SOFC) below 800 °C without too much loss in efficiency. The configuration using Ni/YSZ as the anode, however, presents some drawbacks. When hydrocarbons are used as fuel, carbon deposition can occur as whisker decreasing their performance [17]. To overcome this problem, the production of copper anodes has been tested. Copper does not present the inconvenience of carbon deposition, it is reasonably tolerant to the presence of sulfur and is cheaper than nickel. Copper based composites like Cu/YSZ and Cu/CeO_2 have been proposed as anodes to work at intermediate temperatures [18–20].

The main objective of this work was to study the viability of the colloidal approach for the manufacture of copper compacts using ceramic processing techniques enabling the future production of components with enhanced mechanical and electrical behavior.

2. Experimental

As a starting material a commercial copper powder (602, ACu Powder, USA) with an average particle size of 4.5 μm, a specific surface area of 0.3 $m^2.g^{-1}$, and a density of 8.7 $g.cm^{-3}$ was used. Characterization of the as-received powder was performed by measuring the particle size

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distribution by laser diffraction (Mastersizer S, Malvern, UK), the specific surface area using the single-point BET method (Monosorb™ Surface Area Analyzer MS-13, Quantachrome Corporation, USA) after degassing at 150 ºC, the density by He-pycnometry (Multipycnometer, Quantachrome Corporation, USA), and the morphology by field emission scanning electron microscopy (FE-SEM Hitachi S-4700, Japan). Fig. 1 shows the particle size distribution of the as-received copper powder. It has a broad size distribution, with average diameters ranging from 1 to more than 10 μm and d_{50} of 4.5 μm.

Zeta potential measurements of copper powder were determined by laser Doppler velocimetry (Zetasizer NanoZS, Malvern, UK). For this purpose, suspensions with solid concentration of 0.1 $g.l^{-1}$ were prepared in a 10^{-3} M KCl aqueous solution by ultrasonic mixing, using a 400 W sonication probe (dr. Hielscher GmbH, UP400S, Germany) for 1 min. The pH control was done using 10^{-1} M HCl and KOH solutions. Specific samples were prepared at each pH value and when pH reached an equilibrium value the suspensions were centrifuged and the liquid-phase was analyzed by inductively coupled plasma-emission atomic spectrometry (ICP-OES, Iris Advantage, Thermo Jarrel-Ash, USA) in order to determine the concentration of soluble species. An average of three measurements is always given and the error of the ICP-OES measurements was below 1% of measured value.

Based on zeta potential optimized pH conditions, concentrated suspensions of Cu were prepared to final solid contents of 50, 55 and 58 vol.% (i.e., 89.7, 91.4, and 92.3 wt.%, respectively). These suspensions were stabilized with a commercial polyacrylic acid based polyelectrolyte (Duramax D-3005, Rohm & Haas, USA) accomplished to the addition of tetramethyl ammonium hydroxide (TMAH) up to pH 10 in order to maintain a pH high enough as to prevent dissolution and excessive surface oxidation of the Cu powder, as expected from the zeta potential and chemical analysis measurements. The synergistic effect of the co-dispersion with polyacrylates and TMAH has been described for complex oxides and non-oxides [21]. Suspensions were prepared by mixing for 2 min with an ultrasound probe (Dr. Hielscher UP400S, Germany).

Rheological characterization was carried out using a rheometer RS50 (Thermo Haake, Germany) with a double-cone/plate sensor configuration (DC60/2°, Haake, Germany) that requires a sample volume of 5 ml and a testing temperature of 25 °C. The flow behavior was measured by controlled rate (CR) tests. To obtain the high shear flow behavior CR experiments were carried out employing a measuring program in three stages: first a linear increase of shear rate from 0 to 1000 s^{-1} in 3 min; a plateau at the maximum shear rate (1000 s^{-1}) for 30 s; and a decrease to zero shear rate in 3 min. All slurries were slip cast on a plaster flat mold using a polymeric cylindrical drain mold with 15 mm in diameter to assure uniaxial filtration. After casting, the samples were removed from the mold and left in air for drying for 24 h. Cast green densities were determined by Archimedes' method in mercury. Dynamic sintering studies were performed, under Ar/5% H_2 flowing atmosphere, with a differential dilatometer (Netzsch 402 EP, Germany) at 10 $°C.min^{-1}$ up to 900 °C. The dry green casts were heated to burn out the polymeric additive at 500 °C for 60 min and further sintered at 900 °C for 1 h, under Ar/5% H_2 reducing atmosphere. Sintered densities were measured by immersion in water.

The final microstructure of the green (fractured) and sintered bodies was observed by scanning electron microscopy (TM 1000, Hitachi, Japan). Sintered samples were observed on polished surfaces after chemical etching (5 g $FeCl_3$ + 50 ml HCl + 100 ml H_2O). Grain size was measured by image analysis.

3. Results and discussion

The equilibrium diagram of Cu–H_2O [22] plotted in Fig. 2 predicts that the metallic copper in strongly acidic medium suffers dissolution and degradation forming Cu^{+2} ions, which migrate to the liquid whereas at pHs above 6 the precipitation of the hydroxide $Cu(OH)_2$ occurs, which readily coats the metal as a passivated layer, preventing its further oxidation. According to that equilibrium diagram, at alkaline pH the copper precipitates in the form of hydroxide, and the predominant species in the solution is a soluble form of the hydroxide, but in a concentration of four orders of magnitude lower. However, traces of Cu^{2+} and even $CuOH^{+}$ are also present up to pH 9. Although the concentrations of these species are very low they can have some effect on the colloidal stability, greatly dependent on the concentration of multivalent ions. At pH > 9 the alkaline species become predominant (CuO_2H^{-}). This information can help to explain the various phenomena that may occur during the acid–base reactions necessary to describe the results of zeta potential as a function of pH for this material.

Fig. 3 shows the results obtained from zeta potential measurements of the copper suspensions as a function of pH. The results of the solubility measured by ICP after centrifugation of suspensions prepared at various pHs are shown as an inlet in the figure. As can be seen, there are basically three distinct regions. Firstly, between pH 3 and 6, where the zeta potential changes from positive to negative, the isoelectric point occurring at an intermediate pH about 4.2. It is well recognized in the literature on colloid science that the presence of counterions has a great effect in the reduction of the double layer thickness, and this effect multiplies by a factor of c^6, c being the valence of the ion. This makes that a concentration of <0.1 $mmol.l^{-1}$ of Cu^{2+} can lead to coagulation [23,24].

There is a second region comprising the pH interval ranging from 6 to 9, with nearly constant values and, finally, a clear decrease to larger negative values of zeta potential at pHs above 9. The largest absolute value of zeta potential of about −30 mV was reached at pH 10. Up to this pH, the zeta potential values are low primarily due to the corrosion

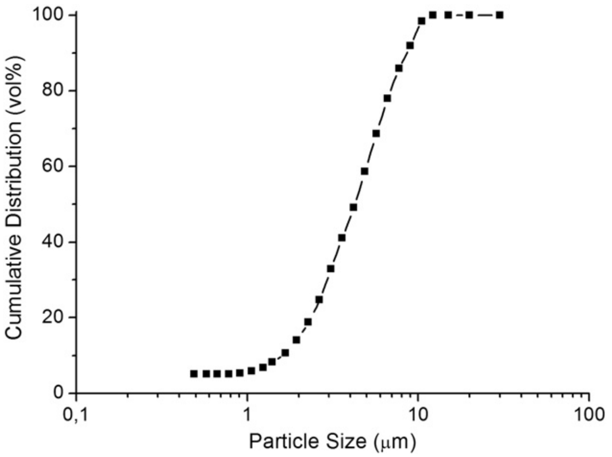

Fig. 1. Cumulative particle size distribution of copper powder.

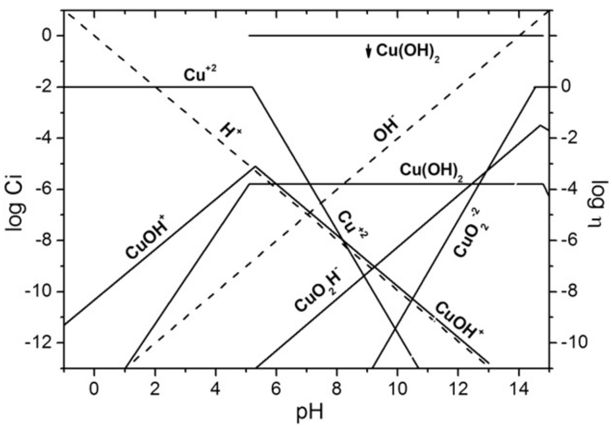

Fig. 2. Cu–H_2O equilibrium phase diagram [22].