



# Preparation of metal–ceramic composites by sonochemical synthesis of metallic nano-particles and in-situ decoration on ceramic powders



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## ABSTRACT

Copper and nickel nanoparticles were synthesized using reducing agents in the presence of direct high energy ultra-sonication. The metallic nanoparticles were decorated on various ceramic substrates (e.g.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>) leading to metal reinforced ceramics with up to 45% metallic content. Different parameters, such as the amount of precursor material or the substrate, as well as the intensity of ultrasound were examined, in order to evaluate the percentage of final metallic decoration on the composite materials. All products were characterized by means of Inductively Coupled Plasma Spectroscopy in order to investigate the loading with metallic particles. X-ray Diffraction and Scanning Electron Microscopy were also used for further sample characterization. Selected samples were examined using Transmission Electron Microscopy, while finally, some of the powders synthesized, were densified by means of Spark Plasma Sintering, followed by a SEM/EDX examination and an estimation of their porosity.

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## 1. Introduction

Nowadays, in most engineering and high-tech branches there is an urgent need for development of novel products with better properties and innovative functionalities. Ceramic Matrix Composites (CMC), incorporating metallic inclusions present improved properties, necessary in innovating applications. In the past two decades, considerable efforts were put on the synthesis and decoration of metallic particles on various ceramic substrates. The final composites have gained great interest due to their unusual properties and potential applications in catalytic, electronic and magnetic material field [1,2].

Recent advances in nanostructured composites have been led by the development of new synthetic methods such as photolytic reduction [3], sonochemical method [4], micro emulsion technique [5] and alcohol reduction [6] that provide control over size, morphology and nano or microstructure. Among these techniques, sonochemical processing has been proven to be a useful tool for generating novel materials with unusual properties [7].

The application of ultrasound covers different fields such as electro-plating, electro-organic synthesis, electro-polymerization, electro-analytical chemistry and the sonochemical synthesis of nanoparticles [8–11]. In this work we will focus on sonochemistry as a new, cost-effective and green method for the synthesis and decoration of metallic particles on various ceramic substrates.

Sonochemistry is the research area in which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz). The chemical effects of ultrasound arise from a physical phenomenon known as acoustic cavitation. This phenomenon consists of the formation, growth, and implosive collapse of bubbles in the liquid, which invoke unusual chemical environments. The collapse of these bubbles, described as an adiabatic implosion in the hot-spot theory, is the origin of extreme local conditions, such as high temperature (more than 5000 K) and high pressure (up to 2000 bar). The cooling rates obtained following the collapse, are also greater than 10<sup>10</sup> K s<sup>-1</sup> [12,13], while the mean life time of the bubble does not exceed 300–400  $\mu$ s. These extreme conditions attained during bubble collapse, allow the synthesis of nanoscale metals, metal oxides, and nanocomposites [14–16].

The first report on the use of ultrasound for the fabrication of noble metals was in 1987 by the work of Gutierrez et al. [17] followed by the work of Nagata et al. [18] in 1992 who studied the reduction of silver ions. Nanostructured metals were

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sonochemically first prepared in non-aqueous solutions. For example, Suslick et al. developed a novel route to prepare amorphous iron metal and colloidal iron nanoparticles [12,13,19].

The effect of surfactants and their use during sonication also seemed to be a big concern for the research community. Okitsu et al. [20] studied the role of surfactants on the size of Pd nanoparticles and the sonochemical reduction mechanisms of Pd(II). Mizukoshi et al. [21] also investigated the effect of different surfactants on the sonochemical reduction of Pt(IV) ions.

In general, sonochemical synthesis produces spherical metal nanoparticles, and thus the process had been limited in preparing other metal nanostructures (e.g. nanorods, nanowires etc.). Recently, Han et al. [22] reported an intriguing result on shape control. In their synthetic approach, ultrasonic irradiation of an aqueous HAuCl<sub>4</sub> solution containing  $\alpha$ -D-glucose produced gold nanobelts having a width of 30–50 nm and a length of several micrometers. Another shape control method using ultrasound was reported by Liz-Marzán et al. [23,24] who synthesized monodispersed gold nanodecahedra via ultrasound-induced reduction of HAuCl<sub>4</sub> in DMF solution. A similar synthetic strategy was also followed by Zhu et al. [25] in the synthesis of silver nanoplates.

Finally, the effect of different experimental parameters such as time, concentration and ultrasonic frequency on the particle size and shape is covered by a big part of the corresponding literature [7,26–32].

## 2. Experimental

### 2.1. Sonochemical synthesis of copper particles and decoration on ceramic substrates

The experimental procedure was based on the work of Tao et al. [33] followed by some variations in order to ensure the decoration of copper particles on the ceramic substrates. The basic steps of the sonochemical synthesis were the following: 2 g of L-ascorbic acid (reducing agent), 3.4 g of CTAB (dispersant), 1 g of the ceramic substrate (e.g.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub>) and 75 ml of distilled water were added into a round bottom flask to form Solution 1 (S<sub>1</sub>). Then, 1 g of the metal precursor CuCl<sub>2</sub>·2H<sub>2</sub>O, 6 ml of NH<sub>3</sub> (pH regulator) and 15 ml of deionized water were used to form Solution 2 (S<sub>2</sub>). An ultrasonic horn (20 kHz, 100 W/cm<sup>2</sup>) was introduced in the flask containing S<sub>1</sub>, thermo stated at 62 °C and irradiated for 30 min, generating a colorless and transparent fluid. S<sub>2</sub> was then added to S<sub>1</sub> in one single addition and the resultant mixed solutions, with a total volume of 100 ml, were additionally irradiated for 2 h. Finally, the precipitates were collected from the reaction system by centrifugation (3000 rpm) in glass tubes, washed thoroughly with deionized water and dried at 100 °C overnight.

Different amount ratios of the precursor and substrates (commercial  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 1–5 micron powder supplied by Strem Chemicals, laboratory synthesized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (annealed at 1200 °C) and commercial TiO<sub>2</sub> 1077 supplied by Kronos with a specific area of 12 m<sup>2</sup>/g), as well as changes in the intensity of ultrasound (100 and 30 W/cm<sup>2</sup>) were examined as summarized in Table 1.

### 2.2. Sonochemical synthesis of nickel particles and decoration on ceramic substrates

Based on the work of Wu and Chen [34] the typical procedure in the case of nickel synthesis is briefed as follows: a certain amount of NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in ethylene glycol and then hydrazine was added. An appropriate amount of NaOH was then added in order to adjust the solution pH and act as a catalyst. An ultrasonic horn (20 kHz, 100 W/cm<sup>2</sup>) was introduced for 2 h in the flask containing the final solution, while the temperature was kept at 62 °C

**Table 1**  
Conditions for the sonochemically synthesized samples of Cu.

Sample code name	Precursor CuCl <sub>2</sub> ·2H <sub>2</sub> O (g)	Ceramic substrate	Ultrasound intensity (W/cm <sup>2</sup> )
C1	1.5	0.25 g lab/ry $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (1200 °C)	100
C2	1.5	1.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	100
C3	1.5	2.0 g commercial TiO <sub>2</sub>	100
C4	1.5	–	100
C5	0.5	1.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	100
C6	1.0	1.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	100
C7	2.0	1.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	100
C8	1.0	1.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	30
C9	1.5	1.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	30
C10	0.5	2.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	100
C11	2.0	2.0 g commercial $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	100

throughout the reaction, as it was found that the reaction was completed only at elevated temperature. The powder obtained was isolated by centrifugation (3000 rpm) in glass tubes, washed thoroughly with deionized water and dried at 100 °C overnight. The decoration of nickel particles on ceramic substrates, as well as its progress with time was further examined.

All samples were characterized by means of Inductively Coupled Plasma Spectroscopy (ICP-AES) and powder X-ray Diffraction techniques. Their microstructure was studied by Scanning Electron Microscopy (SEM) followed by EDX analysis. Selected samples were examined using Transmission Electron Microscopy (TEM), while some of the Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders became dense by means of Spark Plasma Sintering (SPS) for their further characterization.

### 2.3. Spark Plasma Sintering

SPS experiments were carried out in a Dr. Sinter 515S Syntex apparatus. The powders were poured into a carbon die of 8 mm diameter, the internal face of which was covered with a thin graphite foil (papayex<sup>®</sup>) to avoid direct contact between the powder and the graphite die. The die was closed by carbon punches at both sides that are used as current contacts, as well as to apply uniaxial pressure. DC pulses were delivered to the die by the punches allowing the temperature of the die to rise rapidly. Graphite felt around the die was also used to reduce the heat loss by radiation. Sintering temperature was measured by an optical pyrometer focused on a small hole in the graphite die. For maximum reproducibility, the sintering temperature and pressure were controlled by automatic controller units. The samples were heated by applying pulsed direct current which passes through punch and die system. The pulse time duration was set at 3.3 ms, a pulse pattern consisted of 12 pulses each followed by a period of 6.6 ms during which no current was used. All experiments were conducted in vacuum of about 30 mbar.

To produce fully densified samples with a fine grain size, a two-steps sintering process was used. In all cases, the temperature was automatically raised to 600 °C within 1 min and kept constant for 6 min prior to the start of the experiment, during which it was monitored and regulated using a pyrometer. Afterwards samples were heated to the first step temperature  $T_1 = 1000$  °C with a heating rate of 100 °C/min. As soon as the temperature  $T_1$  was reached, a constant uniaxial pressure of 5 kN was applied on the die. The sample was maintained at this temperature for a first step sintering time of 20 min. The temperature was then increased, with the same heating rate, to the second sintering temperature  $T_2 = 1200$  °C and hold there for 20 min. A rapid cooling, during which the pressure was linearly decreased, ended the sintering cycle. After sintering, the samples were cut, mounted and polished according to a specific preparation process for their further characterization.

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