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# Reduction of metallic ions by molten gallium under ultrasonic irradiation and interactions between the formed metals and the gallium

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ABSTRACT

Metallic gallium can reduce ions of silver, copper or gold in a slow spontaneous reaction to form the free metals. However, when the reduction is performed with molten gallium under ultrasonic irradiation, the gallium is dispersed into micrometric spheres and the reduction rate is enhanced dramatically. This is due to the large surface area of unoxidized gallium that is formed, on which the heterogeneous reduction occurs. Each of these metals formed also a certain amount of an intermetallic compound with the gallium: $Ag_2Ga$, $CuGa_2$ and $AuGa_2$. Zinc has a more negative reduction potential than gallium and therefore no reduction of zinc ions was expected. Nevertheless we conducted an experiment using a solution of zinc ions to check whether the extremely high temperature that develops near the surface of the particles during cavitation can overcome the energetic barrier for such reduction.



## 1. Introduction

Sonication of molten metals is used mainly to obtain alloys with improved properties, as well as achieving homogeneous dispersion of additives or grain refinement. For example, Yang et al. [1] performed ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy to form lightweight metal matrix nano-composites (MMMC). Eskin et al. [2] treated molten and solidifying metals by sonication to disperse intermetallic particles in Al ingots. Grain refinement in various alloys by ultrasonic treatment was reported recently by several groups [3–5] A different use of ultrasonic energy in connection with molten metals was reported by Han et al. [6] They irradiated molten indium and molten Field's metal (Bi–In–Sn alloy) in silicone oil containing a surfactant to form stable nanoparticles of these metals.

Recently we reported on the reactions and interactions between some low melting-point metals in the molten state under ultrasonic irradiation [7,8]. The procedure included melting a granule of the metal in a quartz test tube containing silicone oil at ca. 400 °C, thus forming two separate liquids. Dipping an ultrasonic horn in the oil and irradiation for 2–3 min dispersed the metals into particles, forming a suspension in the oil. After cooling to ambient temperature, the solid particles were separated by centrifugation, rinsed with hexane and dried in a glove box under $N_2$ atmosphere. This procedure was tested with several pure metals (Zn, In, Sn. Pb, Bi, Ga) and two eutectic alloys (Au–Si and Ag–Ge) and in all cases micron-size spheres were obtained. In the cases of the gallium and mercury this procedure could be performed in water, due to their very low melting temperatures. The formations of gallium spheres in water and organic solvents [9] and in aqueous solutions of organic compounds [10] were reported. In the latter study it was found that organic compounds could be entrapped within the gallium spheres and then leach out when the spheres were immersed in pure water.

Ultrasonic irradiation caused dispersion of the molten metals into particles, but different interactions were found to occur between the various pairs of metals: Bi–Sn and Bi–Zn formed metal matrix composites, where the spheres were composed of the two metals, each bearing its crystalline structure. Bi–In formed the intermetallic compounds BiIn and $BiIn_2$, where the quantitative ratio between them was a function of the initial ratio between the metals. The Bi–Ga pair formed an alloy in which the Bi was crystalline and the gallium was amorphous.

Performing our procedure with metals of higher melting points (>400 °C) is a challenge, because of the limitation in heating liquids above these temperatures. However, it is known that in the nanometric scale the physical properties of materials change

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dramatically, including a prominent decrease in their melting points [11]. Thus, starting from nanometric particles of such metals could perhaps enable their melting together with other metals such as gallium or bismuth. A possible way of doing that was to form nanoparticles of metals having high reduction potentials (such as gold and silver) via heterogeneous reduction of their ions by metallic gallium. If gallium is present in stoichiometric excess, some of it would be left after the reduction and the two metals could be melted together and irradiated with ultrasonic energy. In practice, it was found that the heterogeneous reduction by metallic gallium was very slow, whereas melting the gallium followed by ultrasonic irradiation enhanced dramatically the reduction rate. This paper describes the results of sonication of molten gallium in aqueous solutions of four metals. According to the standard reduction potentials, three of them (Ag, Cu, Au) should be spontaneously reduced by gallium whereas one (zinc) should not. The overall standard potentials of these reactions are given here:

$$Ga_{(s)} + 3Ag^{+}_{(aq)} \rightarrow Ga^{3+}_{(aq)} + 3Ag_{(s)} \quad E^0 = 1.360\ V \tag{1}$$

$$2Ga_{(s)} + 3Cu^{2+}_{(aq)} \rightarrow 2Ga^{3+}_{(aq)} + 3Cu_{(s)} \quad E^0 = 0.902\ V \tag{2}$$

$$Ga_{(s)} + Au^{3+}_{(aq)} \rightarrow Ga^{3+}_{(aq)} + Au_{(s)} \quad E^0 = 2.252\ V \tag{3}$$

$$2Ga_{(s)} + 3Zn^{2+}_{(aq)} \rightarrow Ga^{3+}_{(aq)} + 3Zn_{(s)} \quad E^0 = -0.202\ V \tag{4}$$

The products of the various reactions were analyzed by X-ray diffraction and by electron-microscopy techniques and are described herein.

## 2. Experimental

### 2.1. Chemicals

Gallium (99.99%), silver nitrate (99.99%), copper acetate monohydrate (99.98%), copper sulfate (99.93%), gold (III) chloride trihydrate (99.95%), nickel sulfate (99.98%), nickel nitrate (99.98%) and zinc acetate (99.8%) were purchased from Sigma–Aldrich. Solutions of all the salts were prepared with double distilled water.

### 2.2. Experimental setup and procedure

The Ultrasonic transducer (model VCX 750, frequency 20 kHz, and amplitude 40%, 230 V AC, the horn was made of Titanium alloy Ti–6Al–4V horn). The sonicator was manufactured by Sonics and Materials Inc., USA. The sonication experiments of molten gallium in solutions of the various metals were performed in a glass test tube with a spherical bottom, which was dipped in a water bath that was usually kept at 55 °C for melting the gallium. The tip of the ultrasonic transducer was suspended in the solution, ca. 2 cm above the gallium. Ultrasonic irradiation was applied for 3 min, causing dispersion of the gallium and formation of a grey suspension of particles. These were separated by centrifugation at 6000 rpm for 10 min, followed by washing with pure water and drying in the anti-chamber of the glove box under Ar atmosphere.

### 2.3. Analysis

X-ray diffraction (XRD) measurements were performed with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation operating at 40 kV/30 mA with a 0.02 step size and a 1 s step. High resolution scanning electron microscope (HRSEM) images were obtained with a FEI Megallon 400L microscope, operated at 20 kV. Samples were applied on a sample holder covered with carbon tape, and dried at ambient atmosphere. No gold coating of the sample was needed due to the conductivity of the samples. Elemental analysis and elemental mapping were performed using HRSEM Energy Dispersive X-ray Spectroscopy (EDS). The Transmission Electron Microscope (TEM) was a Tecnai G2, FEI High Contrast/Cryo TEM, Oregon USA, equipped with a Bottom CCD camera 1 K × 1 K. Samples for TEM were prepared by making a suspension of the particles in isopropanol, using an ultrasonic cleaning bath. Two small droplets were applied on a C-coated TEM copper grid and dried in a covered Petri dish. For the Cu–Ga system a Ni grid was used. High Resolution TEM (HRTEM) was done with a JEOL 2100 microscope, at 200 keV. Inductively coupled plasma-optical emission spectroscopy (ICP–OES) analysis was done with the Horiba instrument model Ultima 2.

### 2.4. Data processing

Rietveld's method [12–14] was applied, using the public domain programs FullProf [15]. The FullProf performs refinement of the crystal data (atomic positions, cell parameters and phase amounts).

## 3. Results

### 3.1. Silver–gallium

The spontaneous reduction of silver ions by gallium was examined first without stirring or applying ultrasonic energy, at room temperature. A granule of gallium (0.5 g, 7.2 mmol) was immersed in 14 mL of 1 M $AgNO_3$ solution (14 mmol) and after several hours formation of some silver coating was observed. A SEM image of a sample that was immersed for 72 h is shown in Fig. 1, in two magnifications. Fine coral-like deposits of silver were formed on the surface of the solid gallium, and the EDS analysis showed major signals for silver and gallium.

Experiments with molten gallium under ultrasonic irradiation were conducted in 0.1–1.0 M $AgNO_3$ solutions, in the temperatures range 25–55 °C (Table 1). In each experiment, a granule of gallium (ca. 0.5 g) was inserted into a test tube containing 14 mL of the silver nitrate aqueous solution, which was heated in a water bath for 40 min (except in one case) for melting the gallium. Ultrasonic irradiation for 3 min caused dispersion of the molten gallium into suspensions of small particles, which were separated by centrifugation, rinsed with pure water and dried in a glove box under Ar atmosphere. The resulting powders were examined by SEM, and were found to have a porous microstructure that seemed to be formed by aggregation of smaller particles (Fig. S1, see the Supporting information). Essentially there were no structural differences between the products formed at different

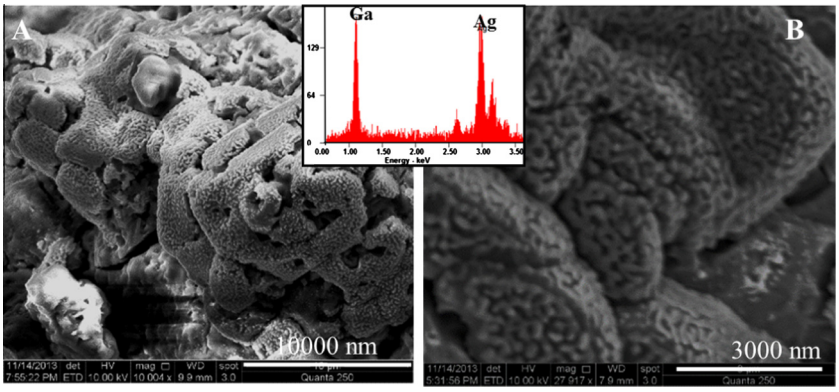


**Fig. 1.** SEM images of spontaneous deposition of silver from 1 M $AgNO_3$ on metallic gallium. Inset: EDS elemental analysis of the surface.