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Ultrasonic cavitation of molten gallium: Formation of micro- and nano-spheres

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ABSTRACT

Pure gallium has a low melting point (29.8 °C) and can be melted in warm water or organic liquids, thus forming two immiscible liquid phases. Irradiation of this system with ultrasonic energy causes cavitation and dispersion of the molten gallium as microscopic spheres. The resultant spheres were found to have radii range of 0.2–5 μm and they do not coalesce upon cessation of irradiation, although the ambient temperature is well above the m.p. of gallium. It was found that the spheres formed in water are covered with crystallites of GaO(OH), whereas those formed in organic liquids (hexane and n-dodecane) are smooth, lacking such crystallites. However, Raman spectroscopy revealed that the spheres formed in organic liquids are coated with a carbon film. The latter may be the factor preventing their coalescence at temperatures above the m.p. of gallium.

1. Introduction

Recently we reported on the formation of micro- and nano-spheres of low-melting-point metals by ultrasonic cavitation in silicone oil [1,2]. The method includes the heating of a granule of such metal in a quartz test tube containing silicone oil till it melts, and then irradiating the system with ultrasonic energy. This induces a cavitation process which involves the growth and collapse of gas bubbles in the oil, and causes the dispersion of the molten metals into microscopic spheres. This method was applied to seven pristine metals (Ga, In, Sn, Bi, Pb, Zn, Hg) and to two alloys (Au–Ge and Au–Si). In all cases suspensions in silicone oil were obtained and the particles were separated and studied.

Furthermore, nanoparticles of pure metals, of alloys and of metallic compounds (such as oxides, sulfides, selenides, etc.) were produced by reaction of dissolved metallic precursors (salts or complexes) under ultrasonic irradiation [3]. For example, gold nanoparticles were produced by reduction of $KAu(CN)_2$ with ascorbic acid under sonication [4]. Bimetallic nanoparticles of Au/Pd were obtained by the sonochemical reduction of an aqueous solution containing $Pd(NO_3)_2$ and $HAuCl_4$ [5]. Sonoelectro-reduction was utilized for metals with large negative reduction potentials, such as Mg [6] and Al [7], which cannot be reduced chemically. Alternatively, metals and alloys were formed by the decomposition of metal–carbonyl compounds under the extreme local conditions of temperature and pressure attained during the bubble collapse in the cavitation process. Thus, iron powder was formed by ultrasonic irradiation of $Fe(CO)_5$ [8], and a Fe/Co alloy was obtained by irradiation of a mixture of $Fe(CO)_5$ and $Co(NO)(CO)_3$ [9]. Raabe and Hessling [10] utilized ultrasonic radiation to prepare metallic nano- and micro-particles in an emulsion of molten Field's Alloy (In–Bi–Sn, m.p. 62 °C) in hot water. SEM images revealed that the particles were mostly spherical and some of them appeared to be hollow.

In the present work we focus on the formation of gallium microspheres. Due to the low melting point (m.p.) of gallium (29.8 °C), it can be melted in warm water (ca. 50 °C) or in organic liquids which are not too volatile, and thus produce two immiscible liquid phases. Irradiation of such a liquid system with ultrasonic energy induces cavitation in the liquid, which results in dispersion of the molten gallium as microspheres. The influence of several experimental parameters, such as removal of oxygen, the duration of sonication, the amount of gallium and the nature of the medium on the resultant spheres were studied.

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2. Experimental

2.1. Chemicals

Metallic gallium (>99.8%), n-hexane (99.1%), decane (99.3%), and dodecane (99.8%) were purchased from Aldrich and used as received. Ar (99.999%) was used for purging the water of oxygen. Distilled water was obtained from a TREION™ purification system.

2.2. Equipment

The Ultrasonic transducer (model 51-05-290) was purchased from Ultrasonic Power Corporation, Freeport, Illinois. The ultrasonic power during the experiments was 80 W. Scanning electron microscopy (SEM) was performed using an Inspect FEI microscope and high resolution SEM (HRSEM) was done with a FEI Megallon 400 L microscope. The samples were prepared by applying a small portion of the particles, which have been dried in a glove box, on a sample holder coated with a carbon tape. No gold coating was needed, due to the good conductivity of the Ga micro/nanospheres. Transmission electron microscopy (TEM) was done with a Tecnai G2, FEI is a High Contrast/Cryo TEM, Oregon USA, equipped with Bottom CCD camera 1 K × 1 K. Samples for TEM were prepared by making a suspension of the particles in isopropanol, using water-bath sonication. Two small droplets were then applied on a TEM copper grid, coated with a carbon film, and dried in a covered Petri dish. High resolution TEM (HRTEM) was done with a JEOL 2100 microscope, at 200 keV. X-ray diffraction (XRD) was performed with a Bruker D8 Advance or with Philips PW1050 X-ray diffractometer using Cu Kα radiation operating at 40 kV/30 mA with a 0.02 step size and a 1 s step. Dynamic light scattering (DLS) measurements of the particles' size-distribution was performed on ZetaSizer Nano-ZS (Malvern Instruments Ltd., Worcestershire, UK). The specific surface area of the particles was measured by the BET method at 77 k under liquid nitrogen on a Micromeritics instrument (Gemini 2375) after the samples had been evacuated at 25 °C for 12 h with a evacuator (Micromeritics, Flow Prep 060).

2.3. Preparation of gallium spheres

Gallium micro- and nanospheres were prepared in water in the following manner: A weighted granule of gallium (0.3–0.5 g) was inserted into a conical test tube, which contained 15–25 mL of pure water. It was heated in a water bath at 55 °C for ca. 40 min to assure full melting of the gallium which formed a separate liquid phase at the bottom of the test tube. The tip of an ultrasonic transducer was dipped into the test tube with its end suspended in the water 2 cm above the liquid gallium. Irradiation of the water–gallium system for a certain period of time (3–20 min.) caused dispersion of the molten gallium and formation of a grey suspension of microscopic particles. The temperature within the test tube was measured during the sonication by a thermocouple, which showed only a moderate increase up to 64 °C. The fabrication yield of the Ga spheres was >90%, *i.e.* in most cases the whole molten granule was converted into particles. The particles formed by sonication did not re-coalesce after sonication was stopped, although the ambient temperature was above the melting point of gallium. The particles were separated by centrifugation at 8000 rpm, followed by decantation of the water and washing the precipitate with a portion of pure water. This procedure was repeated twice and then the precipitate was dried in a vacuum chamber. A similar procedure was applied to form gallium microspheres in the non-aqueous liquids, n-hexane and dodecane. The amount of the organic liquids was also 15–25 mL.

3. Results

3.1. Formation of Ga micro/nanospheres in pure water

Several sets of experiments were performed, in which gallium particles were formed by ultrasonic irradiation of molten gallium in pure warm water. First we examined whether dissolved oxygen in the water has any influence on the resultant spheres, *i.e.* their shapes, composition or tendency to aggregate or re-coalesce, via

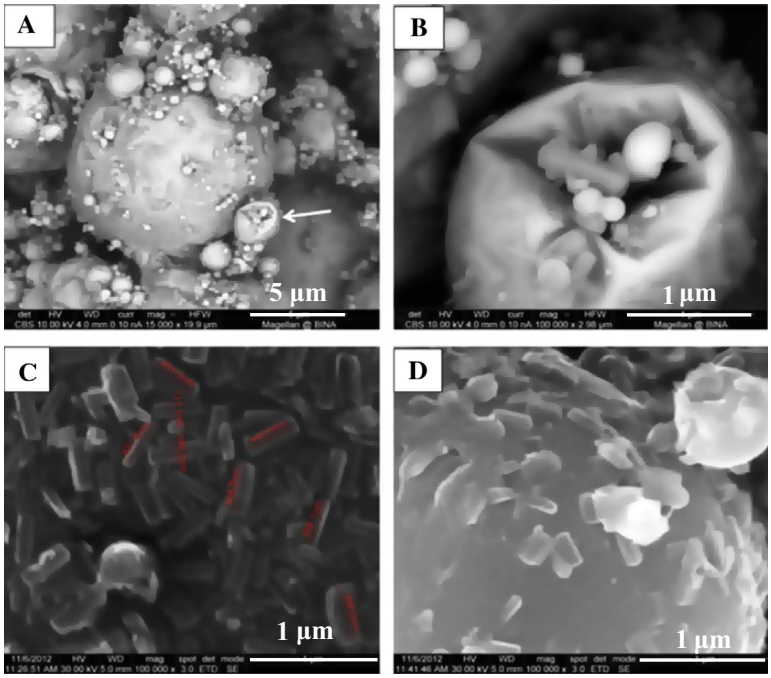

Fig. 1. SEM images of particles formed by ultrasonic cavitation of molten gallium in water. (A) A cluster of spherical particles in a wide range of diameters. (B) A close-up view of the squashed particle marked on A. (C) The crystallites that appear on the surface of many of the particles. The particles shown in A–C were obtained in water without Ar purging. (D) Two spheres which were formed under the same conditions but with Ar purging prior to sonication.