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Host-guest composites containing ultrasonically arranged particles

M. SAITO, Y. IMANISHI
Department of Electronics and Informatics, Ryukoku University, Seta, Otsu 520-2194, Japan
E-mail: msaito@rins.ryukoku.ac.jp

Ultrasonic particle arrangement method was used for the fabrication of composite materials with layer or lattice structures. Guest particles were periodically arranged in a host solution by using ultrasonic standing waves, and then the solution was solidified to obtain a solid composite material. The sample cell was rotated during the solidification process to prevent particle sedimentation. Polymer, glass, or metal particles with various shapes were ultrasonically arranged in a polysiloxane resin, which was useful as a host material due to its simple solidification process and suitability for forming fine structures. Composite materials with periodic structures were successfully fabricated by this method.

1. Introduction

Composite materials with layer or lattice structures exhibit anisotropies in thermal, mechanical, electrical, or optical properties. In a composite material consisting of metal and dielectric layers, for example, electric and thermal conductivities depend on the direction of conduction. Periodic structures also induce optical or acoustical functions due to the interference of transmitting waves. These functions can be utilized for the fabrication of diffraction gratings or frequency filters. To develop novel materials with these useful functions, fabrication techniques of periodic structures have been intensively studied of late. The interesting prospects for photonic band gap crystals are currently promoting the research in this field [1, 2]. The microprocessing techniques for semiconductor devices, e.g., vapor deposition and photolithography, are usually used for the construction of microstructures. It is difficult, however, to fabricate large bulk materials by using these thin-film techniques.

A bulk material with periodic structure may be obtained by extending the fabrication techniques of host-guest composites. It has been demonstrated recently that a three-dimensional lattice structure is formed in a colloidal suspension of polystyrene spheres due to a repulsive electric force and an attractive van der Waals force between particles [3]. To adopt this self-organizing method, however, the component materials must be in the form of particles and liquids and are consequently limited, and the lattice structure and the lattice constant are difficult to control. A laser trapping technique was also utilized to form a two-dimensional lattice of polystyrene particles in water, and it was reported that a composite material with a lattice structure would have been obtained if the suspending water had been frozen [4]. The laser trapping method, however, cannot be used for opaque materials, and the trapping region is limited to the area around the focal point of the laser beam. A laser beam even induces thermal damage in materials.

We have recently proposed an ultrasonic arrangement method for the fabrication of a periodic structure in composite materials [5]. As described in Sec. 2, particles in liquid aggregate at the nodes of an ultrasonic standing wave [6–10]. Being compared with an optical force in laser trapping, ultrasonic waves exert a large trapping force on particles regardless of their shapes and chemical constitution. In addition, an ultrasonic standing wave can also trap many particles simultaneously and arrange them in a wide region over the entire solution. A composite material with a periodic structure is obtained, if ultrasonic oscillation is continued during the solidification process of the solution. In a previous work, we fabricated polymer composites with acrylic and polysiloxane resins [5, 11]. In this work, we synthesized composite materials with glass or metal particles, which used to be difficult to arrange because of gravitational segregation.

2. Principle

Let us consider a particle suspension that fills the space between two ultrasonic transducers. If ultrasonic waves of an appropriate frequency are transmitted from the two transducers, a standing wave is excited in the liquid, as shown in Fig. 1. The standing wave creates nodal planes at which no ultrasonic oscillation takes place. Then particles in the liquid tend to aggregate at the nodal planes, where they can stay without disturbance [5–13]. As a consequence, particles are arranged in planes of a regular spacing, i.e., half of the ultrasonic wavelength $\Lambda/2$. One can obtain a composite material with layered structure by solidifying this suspension. Further, if two or three ultrasonic standing waves are

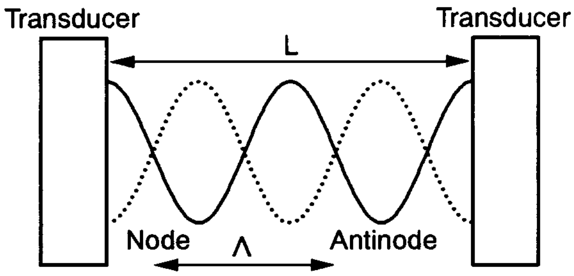

Figure 1 Ultrasonic standing wave between two transducers.

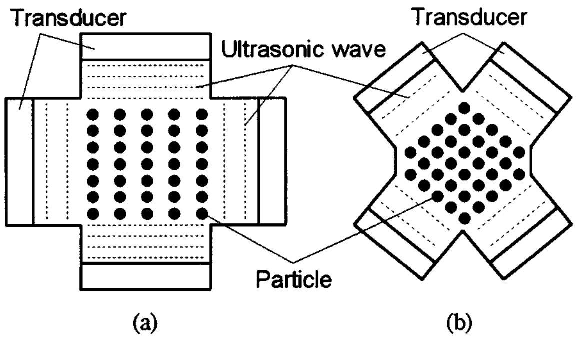

Figure 2 Fabrication method of lattice structures. Particles are trapped at intersecting points of ultrasonic standing wave nodes. (a) Lattice constants (spacing of particles) can be adjusted by tuning the ultrasonic frequencies. (b) Lattice structure can be modified by changing the directions of standing waves.

generated, as shown in Fig. 2, one can fabricate two- or three-dimensional lattice structures in a composite material.

Now let us discuss the problem quantitatively. When an ultrasonic wave of frequency f propagates in a liquid with a sound velocity v, the ultrasonic wavelength Λ is

$$\Lambda = \frac{v}{f} \tag{1}$$

If the spacing between the opposing ultrasonic transducers is L (Fig. 1), the condition of the standing wave excitation (resonance) is

$$L = \frac{m\Lambda}{2} = \frac{mv}{2f} \tag{2}$$

where m is a positive integer. In case of $L = 19$ mm and $v = 980$ m/s, which are the values corresponding to the current experiment (Sec. 3), the resonance frequencies are, for example, $f = 7.995$ MHz ($m = 310$) and 8.021 MHz ($m = 311$) from Equation 2. It follows from this evaluation that one can excite a standing wave by tuning the oscillation frequency between ∼7.99 and ∼8.03 MHz.

The spacing s of arranged particles, i.e., the spacing of the nodes, is

$$s = \frac{\Lambda}{2} = \frac{v}{2f} \tag{3}$$

Equation 3 indicates that a finer structure is obtained by increasing the ultrasonic frequency. If the sound velocity is 980 m/s, for example, the spacing is calculated to be 60 μm for 8 MHz, and 5 μm for 100 MHz. It also follows from Equation 3 that a material with a low sound velocity is preferred to fabricate a fine structure.

The acoustic force that is exerted on a particle has been studied theoretically by many researchers [12–18]. If a spheric particle of volume V is located at a distance x from a node, it suffers an acoustic force

$$F = -\frac{2\pi AVPf}{v^2} \sin \frac{4\pi f x}{v} \tag{4}$$

where P is the ultrasonic power density and A is a constant that is determined by the densities and compressibilities of the particle and the liquid [9, 13]. Equation 4 indicates that the acoustic force is directed toward the node, i.e., $F > 0$ for $x < 0$ and $F < 0$ for $x > 0$, and hence particles are trapped at the node. The theoretical expressions for the trapping force, however, depend strongly on the particle shape [15–18]. Unfortunately there is no simple expression for a general shape. Further the constant A is difficult to evaluate for some particles, since the material constants of particles are occasionally different from those of the corresponding bulk materials. Therefore one can use Equation 4 only for semiquantitative evaluation. Nevertheless Equation 4 provides some useful knowledge concerning particle arrangement; e.g., a high frequency and a low sound velocity is desired not only for attaining a fine structure but also for inducing a large trapping force.

3. Experiments and results

As mentioned in Sec. 2, a material with a low sound velocity is preferred as a host material or a suspending liquid. The liquid also needs to solidify by a simple process. We employed a polysiloxane resin (Shin-Etsu Chemical, KE103) as a host material in this work. This resin can be synthesized easily from a mixed solution of principal and curing agents. The curing time is 8 h at room temperature. The volume shrinkage during solidification is negligible. Synthesized resin is very clear and contains no bubbles. The sound velocity of the polysiloxane resin is 980 m/s, which is lower than that of any other solid material (2000–8000 m/s) or water (1500 m/s) [5].

Guest materials used were polymer, glass, and metal particles. Specifications of the particles are as follows. Acrylic spheres (Hayakawa Rubber, L-11R) are 10 μm in diameter and their density is 1300 kg/m^3. Glass rods (Nippon Electric Glass, PF-90) are 9 μm in diameter and 20–100 μm in length, and their density is 2600 kg/m^3. Silver particles (Tanaka Kikinzoku, AY-6010) have a sphere-like indeterminate shape of 6–13 μm size and their density is 10^4 kg/m^3. Gold leaves (Fukuda Metal Foil & Powder, PH-870) are 0.15 μm in thickness and 1–10 μm in size, and their density is 1.9×10^4 kg/m^3.

Fig. 3 shows a sample cell used for the fabrication of layered composite materials. The sample cell consists of four glass plates. Two ultrasonic transducers are inserted from the opposite sides of the cell to a distance of 6–20 mm from each other. The transducer (Nippon Denpa Kogyo, custom-made) is made of a lead titanate zirconate (PZT) plate with 4×15 mm^2 surface area. The thickness of the PZT plate is adjusted so that the resonance frequency may be in the 8 MHz range. The

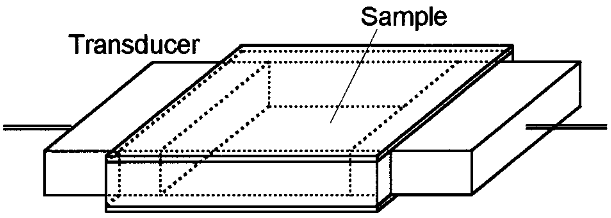

Figure 3 Sample cell for the fabrication of composite materials with layered particle arrangement.

transducer is packed in a plastic case, 6×19 mm^2 in transmission surface area and 15 mm in length, together with an electric circuit for impedance matching. A high-frequency power of ~1 W from an electric source is divided equally and supplied to the two transducers. The oscillation frequency is tuned in the 7.9–8.1 MHz range so as to excite an ultrasonic standing wave in the sample cell. The standing wave excitation can be confirmed either by microscopic observation of particle distribution or by monitoring the rise in signal voltage due to the resonance between the transducers [19].

Fabrication of a layered composite was first attempted by using acrylic particles. Acrylic particles were dispersed in a polysiloxane solution at ~3 vol%. The suspension was poured into the sample cell, and then an ultrasonic standing wave was generated in the suspension. Ultrasonic oscillation was continued for 8 h until the solution solidified. Fig. 4 shows a photomicrograph of the fabricated composite. Acrylic particles are arranged at a spacing of 60 μm, as predicted by Equation 3.

Experiments for the other particles were also conducted in a similar manner. It was difficult, however, to disperse glass and metal particles uniformly over the entire sample, since their densities were too large to suspend in the polysiloxane solution whose density is as low as 970 kg/m^3. Although the starting mixture of particles and polysiloxane was stirred continuously until it became viscoidal midway through the solidification process, most particles sedimented at the bottom before the solution completely solidified. Fig. 5 shows the photomicrographs that were taken at the upper and lower parts of the fabricated composites. Particles are seen to have sedimented at the bottoms of the samples, forming large colonies. Particles sedimenting on the bottom were difficult to arrange ultrasonically because of frictional or adsorptive forces at the glass surface.

To prevent particle sedimentation, we prepared a rotation apparatus shown in Fig. 6. An aluminum plate, on which a sample cell is mounted, rotates at 10 rounds per minute being driven by a motor. High-frequency electric power is supplied to the transducers through a rotary connector to prevent a twist in the electric cable.

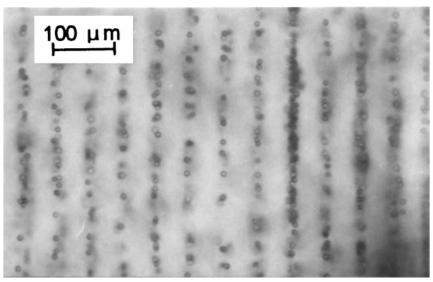

Figure 4 Polysiloxane composite with acrylic particle layers.

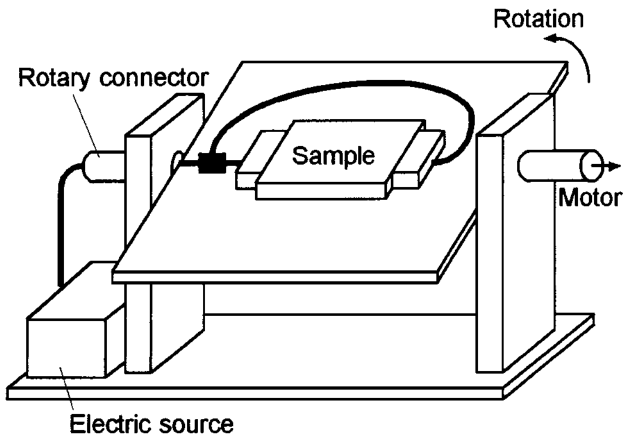

Figure 6 Rotation apparatus for preventing particle sedimentation.

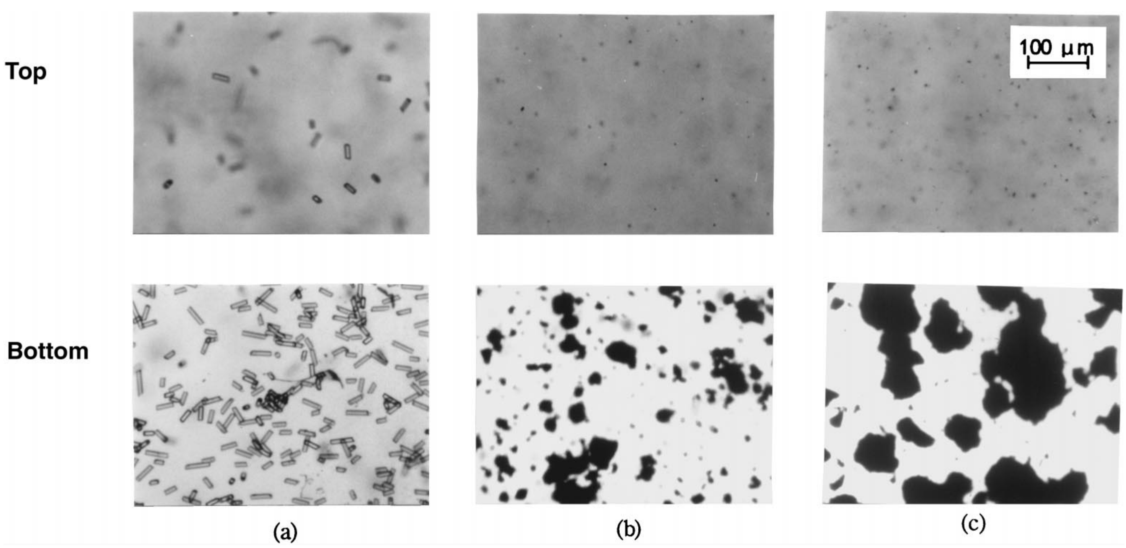

Figure 5 Particle distributions at the top and the bottom of the polysiloxane resins. (a) Glass rods, (b) silver particles, and (c) gold leaves are dispersed in the resin.

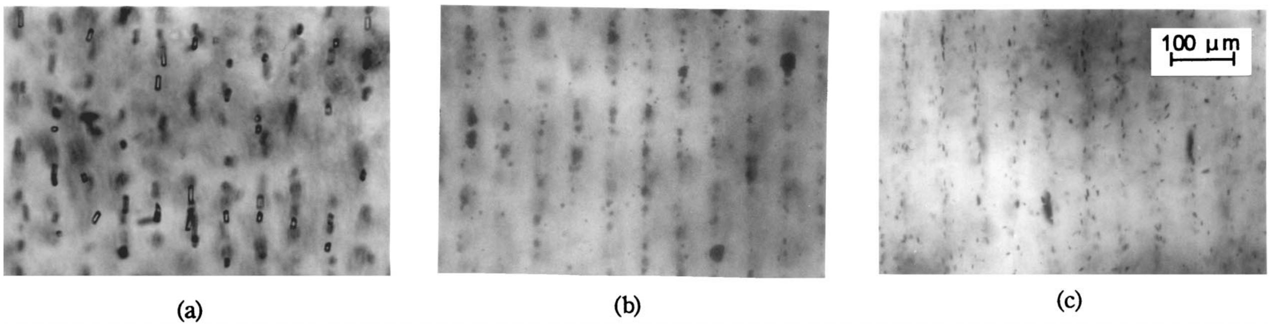

Figure 7 Polysiloxane composites with periodic arrangement of (a) glass rods, (b) silver particles, or (c) gold leaves.

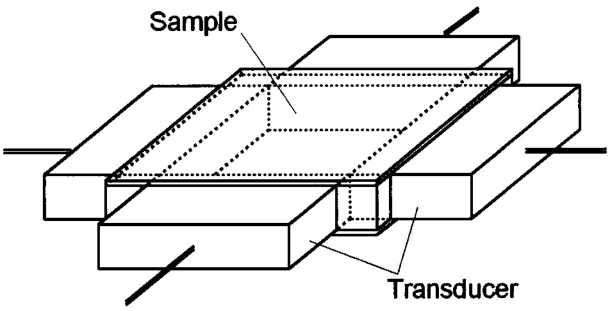

Figure 8 Sample cell for the fabrication of lattice structure.

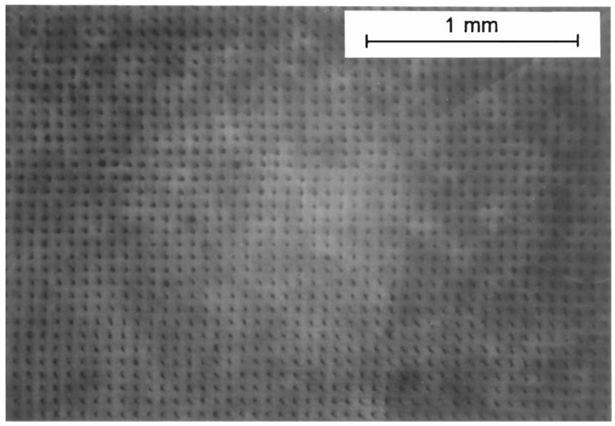

Figure 9 Polysiloxane/acrylate polymer composite with lattice structure. The spacing of acrylic particles is $\sim$60 μm.

Composite materials with glass rods ($\sim$0.1 vol%), silver particles ($\sim$0.02 vol%), or gold leaves ($\sim$0.02 vol%) were fabricated by using this apparatus. Rotation and ultrasonic oscillation were continued throughout the solidification process. Fig. 7 shows the photomicrographs of the fabricated composites. Particle layers of $\sim$60 μm spacing are observed in the composites.

Finally, two-dimensional lattice structures were fabricated by using a sample cell shown in Fig. 8. The top and bottom of the sample cell are made of glass plates, and the sides are enclosed with four PZT transducers. The cross section of the transducers is 6×19 mm^2, and accordingly the inner size of the sample cell is $6 \times 19 \times 19$ mm^3. A pair of opposing transducers are driven by an electric source ($\sim$1 W), and the other pair by another electric source ($\sim$1 W). The oscillation frequency of both electric sources are adjusted around 8 MHz so as to excite two ultrasonic standing waves simultaneously in orthogonal directions. An experiment was conducted by dispersing $\sim$0.3 vol% acrylic particles in a polysiloxane solution. As Fig. 9 shows, a lattice structure was successfully constructed in a composite material.

4. Discussion

It has been demonstrated in the current experiment that ultrasonic arrangement method is adoptable for various particles regardless of their material and shape. Therefore this method seems more versatile than the laser trapping method, which restricts the adoptable refractive index and transmissivity of composing materials. If other materials, e.g., ultraviolet curing resin or sol-gel glass, can be employed as host materials, the ultrasonic arrangement technique will find more application fields.

In this work, we fabricated composite materials with one- or two-dimensional particle arrangement. This technique can be extended to the fabrication of three-dimensional lattice structure. As mentioned in Sec. 1, fabrication methods of three-dimensional lattice structures are being studied intensively in the field of optics to realize photonic band gap crystals. Currently it is not certain whether the ultrasonic arrangement technique is applicable to the fabrication of photonic band gap crystals, since ultrasonic waves of submicrometer wavelength are required for the construction of a fine structure. One problem is the attenuation of ultrasonic waves; i.e., the attenuation constant of ultrasonic waves increases in proportion to the square of the frequency, and hence excitation of a standing wave becomes more difficult for high-frequency ultrasonic waves. There are some other difficulties including the machining precision of a sample cell and the thermal expansion due to ultrasonic oscillation. We are currently making efforts to overcome these difficulties. Even if such a fine structure cannot be realized, however, periodic structures still exhibit useful functions based on anisotropy and interference. We have already demonstrated some of these functions [5, 11], and will further look for novel functions through the characterization of fabricated composites.

5. Conclusion

Ultrasonic waves are useful for arranging small particles, since it simultaneously exerts a sufficient trapping force on many particles that are dispersed in a wide region. By using a polysiloxane resin as a host material, small-periodicity structures can be constructed, and the structures are not disturbed during the solidification process. Sedimentation of heavy particles can be prevented by continuing the rotation of the sample cell until the suspension solidifies completely. Polymer, glass, and metal particles were successfully arranged in a polysiloxane resin, forming composite materials with layer or lattice structures.

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References

1. E. YABLONOVITCH, *Phys. Rev. Lett.* **58** (1987) 2059.
2. C. T. WHIPPLE, *Photonics Spectra* (1999) 110.
3. I. I. TARHAN and G. H. WATSON, *Phys. Rev. Lett.* **76** (1996) 315.
4. M. M. BURNS, J.-M. FOURNIER and J. A. GOLOVCHENKO, *Science* **249** (1990) 749.
5. M. SAITO, T. DAIAN, K. HAYASHI and S. IZUMIDA, *J. Appl. Phys.* **83** (1998) 3490.
6. J. WU, *J. Acoust. Soc. Am.* **89** (1991) 2140.
7. T. TOLT and D. J. FEKE, *ibid.* **91** (1992) 3152.
8. M. TAKEUCHI and K. YAMANOUCHI, *Jpn. J. Appl. Phys.* **33** (1994) 3045.
9. K. YASUDA, S. UMEMURA and K. TAKEDA, *ibid.* **34** (1995) 2715.
10. M. SAITO, S. IZUMIDA and J. HIROTA, *Appl. Phys. Lett.* **71** (1997) 1909.
11. M. SAITO, K. ITAGAKI, K. HAYASHI and K. TSUBATA, *Jpn. J. Appl. Phys.* **38** (1999) 3028.
12. L. V. KING, *Proc. Roy. Soc. (London)* **A147** (1934) 212.
13. K. YOSIOKA and Y. KAWASHIMA, *Acustica* **5** (1955) 167.
14. W. L. NYBORG, *J. Acoust. Soc. Am.* **42** (1967) 947.
15. L. V. KING, *Proc. Roy. Soc. (London)* **A153** (1936) 1.
16. A. S. AHUJA and W. R. HENDEE, *J. Acoust. Soc. Am.* **63** (1978) 1074.
17. M. A. H. WEISER and R. E. APFEL, *ibid.* **71** (1982) 1261.
18. T. HASEGAWA, K. SAKA, N. INOUE and K. MATSUZAWA, *ibid.* **83** (1988) 1770.
19. M. SAITO, S. IZUMIDA, K. ONISHI and J. AKAZAWA, *J. Appl. Phys.* **85** (1999) 6353.

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