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A Top-Down Approach of Making Sn-3.5Ag Nanosolder Alloy by Swirl Method

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ABSTRACT

The nanoparticles of tin-silver solder, Sn-3.5Ag, of necklace geometry were made in a swirl batch. It was found that the addition of the element, Ag, did not vary the microstructure of the solder matrix, but Ag simply diluted into the Sn matrix randomly. The swirl flow facilitated the formation of particles with different sizes. It was found that the size distribution of the nanoparticles was strongly related to the height in the swirl batch. In addition, the aggregation of the nanoparticles was explored and the dispersion of the nanoparticles was achieved by adjusting the pH value of the solution near the neutral value.

Keywords*: *Swirl Flow, Particle Size Distribution, Nanoparticle Aggregation

1. Introduction

Due to the advances in semiconductor manufacturing technology, the feature size of the complementary metal-oxide semiconductor (CMOS) structure could approache nano-scale length. Metal tin is always a major component of the solder matrix which serves as an interconnection between the device and substrate. However, it cannot withstand the mechanical requirements at elevated temperatures. Traditional lead alloys are being phased out [1]. Many researchers have been looking for alternatives to replace lead [2-4]. Eutectic tin-silver, Sn-3.5Ag, is a popular replacement since the soldering temperature and surface tension near to that of Sn-37Pb solder [5]. Metal nanoparticles have recently received great attention. The nano-metal is not only employed in photonics, but it also has potential applications in optoelectronics [6]. Moreover, tin particles also follow Barbier-type allyation reactions and also serve as an abrasive to antiwear under loading, resulting in reduction of the particle size to the nanometer scale [7]. Based on these specific advantages, the size of the Sn-3.5Ag alloy is scaled down to nanometer scale using the swirl method; a technique to sieve solid particle size in fluidic bed facilities [8].

2. Experimental Procedure

Metals Sn (99.8%), Ag (99.9%) and paraffin oil (99.8%) were commercial chemicals. 9.65 grams of Sn powder was blended with 0.35 grams of Ag powder in a sealed vacuum glass tube. The tube was heated to 260˚C in an oven for 2 hours with intermittent shaking. This alloy was then checked for uniformity and then immersed in the heating solvent swirl batch of paraffin oil, at 320˚C for 10 hours. Aliquots were removed and quenched into liquid nitrogen to prevent aggregation. The viscous solution, composed of nanoparticles and paraffin, was blended with chloroform to dilute the paraffin. The solution was centrifuged and then was diluted in turn three times. The nanoparticles formed as black sediments at the bottom of the tube. The nanoparticles were washed with water and acetone several times until pH = 7 then vacuum dried at 40˚C for 12hrs. The upper zone, chloroform, was dried out and then the black sediment was sampled to identify its phase with X-ray diffraction (Rikagu). To prevent the nanoparticles from aggregation, the rest of the sediment was dissolved in ammonium hydroxide (NH_4OH) and dispersed using an ultrasonic shaker. The alkaline, NH_4OH solution was dispensed onto a glass substrate. After drying, the morphology of the particle was investigated by a scanning electron mi-

croscope (SEM 2500, Hitachi) and the diffraction pattern was obtained by a high resolution TEM (JEOL 2100).

3. Results and Discussion

3.1. Morphology Investigation and Phase Identification

Uniform Sn-3.5Ag nanoparticles were prepared and dispersed successfully by the swirl method. However, the nanoparticles did not disperse individually but joined together with necklace morphology. The nanoparticles thus formed showed active surfaces [9].

The trace element, Ag, was resolved in the tin matrix homogeneously. **Figure 1** shows the HRTEM diffraction pattern of Sn-3.5Ag nanoparticles. This pattern was identified to be a space group of $I4_1/amd$ with lattice parameters, a, 5.819 Å, and b, 3.175 Å, respectively. This pattern is consistent with the tetragonal system [10], as that of the synthesized tin. Thus, the addition of the silver did not vary the microstructure of the tin matrix.

3.2. Kinetics of the Formation of Sn-3.5Ag Nanoparticles

The size of the nanoparticles was determined by Oswald ripening and the rotational speed of the swirl. **Figure 2** showed the particle size variation for subsequent sampling time with a constant sampling height. It is noted that the particle size decreased initially, then reached the minimum value and finally recoiled appreciably. This indicated a specific formation procedure as proposed in the following section.

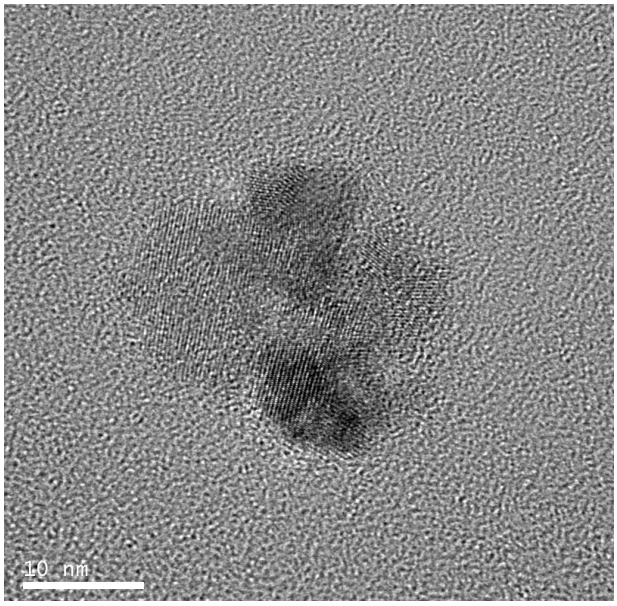

Figure 1. HRTEM diffraction pattern of Sn-3.5Ag nanosolder.

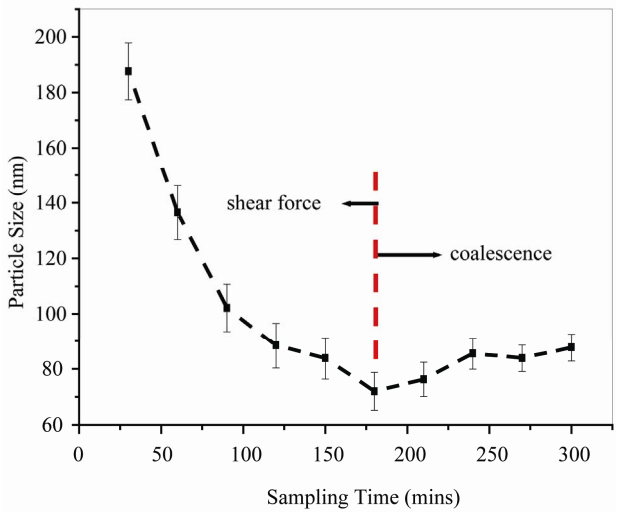

Figure 2. Particle size variation with respect to sampling time.

Initially, the swirl flow quickly reached steady state. The bulk homogeneous Sn-Ag alloy was heated and showed a viscous fluid with a coherence force to maintain its spherical-like shape. Because the Sn-Ag alloy did not resolve in the paraffin solvent, the coherence force prevailed. When the viscous Sn-Ag alloy was deposited on the floor of the rotational bath, the immiscible phase, paraffin and also the Sn-3.5Ag were subjected to fluid shear stresses. Because the shear force was larger than the coherence force, the bulk viscous fluid in the bottom layer was dissevered. This dissevered debris climbed peripherally up and was dissevered again. Meanwhile the quantum effect emerged due to the small size of the Sn-Ag alloy while approaching the nano-scale [11]. Finally, the shear force could not eclipse the incoherent force and the alloy volume was maintained. The shape of the nanoparticles could not maintain its spherical features when the quantum effect balanced the incoherent force [12]. The swirl flow facilitated a particle size distribution with respect to different sampling heights of the swirl batch as shown in **Figure 3**. The size of the nanoparticles decreased with increasing sampling height. A force balance model was constructed to analyze the particles in the swirl batch. In the swirl flow, the nanoparticles were balanced by the flow force and rotated with the same velocity as that of the fluid. The velocity was a function of both the radical distance and height of the batch. Except at the center of the batch, the nanoparticles experienced a net force perpendicular to the surface of the swirl flow layer.

3.3. Dispersion of the Aggregated Nanoparticles

The aggregated nanoparticles were dispersed freely by

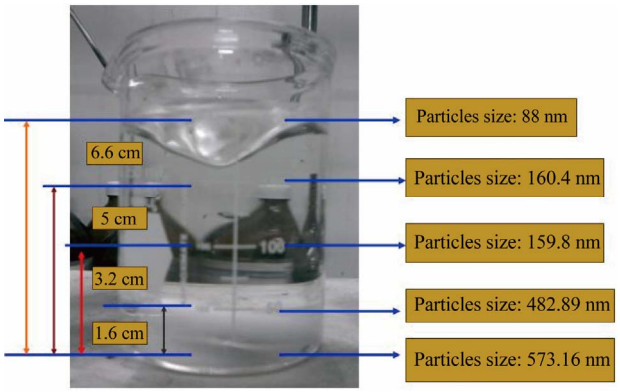

Figure 3. The average particle size dipped at different heights.

adjusting the pH value of the solution. Particle size decreased with increasing pH values (**Figure 4**) up to 8.54, but then increased appreciably up to pH value of 11.2. However, the nanoparticles aggregated again, as the solution changed from neutral to alkaline. It has been reported that the metallic nanoparticles possess negative electrical carriers [13]. In acidic solutions the hydrogen ions, neutralizes the nanoparticle's surface. The zeta potential of the nanoaparticles thus approaches zero. An increase in pH changed the charge of the nanoparticles from positive to negative. The repulsive force also increased to counteract the attractive force. However, the nanoparticles became unstable as the negative surface charge became immoderate. The systematic energy thus had to be reduced due to the flocculation of the particles [14]. The particle size was no more spherical but tetragonal. The non-spherical shape of the particle indicated that some force dominated the lattice assembly. The shape hence showed a distinct morphology; namely polyhedral rather than the traditional spherical shape.

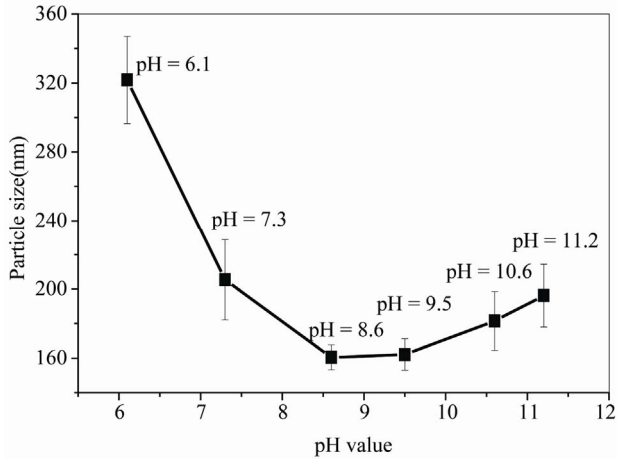

Figure 4. Particle size distribution v.s pH values in the dispersive solution.

4. Conclusions

Tin-silver nanoparticles were prepared successfully by a swirl method with the trace element, Ag, resolved in the tin matrix homogeneously. Because the particle size could approach a steady state value, the kinetics was investigated in this study. The size of the nanoparticles was determined by the rotational velocity of the swirl and height off the bottom. To avoid the aggregation of the nanoparticles, the pH value of the solution was adjusted and the aggregated particles were dispersed successfully.

5. Acknowledgements

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REFERENCES

[1] Y. Li and C. P. Wong, "Recent Advances of Conductive Adhesives as a Lead-Free Alternative in Electronic Packaging: Materials, Processing, Reliability and Applications," *Materials Science and Engineering, R: Reports*, Vol. 51, No. 1-3, 2006, pp. 1-35. doi:10.1016/j.mser.2006.01.001

[2] M. Abtew and G. Selvaduray, "Lead-Free Solders in Microelectronics," *Material Science Engineering, R: Reports*, Vol. 27, No. 5-6, 2000, pp. 95-141.

[3] M. McCormack, S. Jin, G. W. Kammlott and H. S. Chen, "New Lead-Free, Sn-Ag-Zn-Cu Solder Alloy with Improved Mechanical Properties," *Applied Physics Letters*, Vol. 63, No. 1, 1993, pp. 15-17.

[4] I.E. Anderson, J. C. Foley, B.A. Cook, J. Harringa, R.L. Terpstra and O. Unal, "Alloying Effects in Near-Eutectic Sn-Ag-Cu Solder Alloys for Improved Microstructural Stability," *Journal of Electronic Materials*, Vol. 30, No. 9, 2001, pp. 1050-1059. doi:10.1007/s11664-001-0129-5

[5] P.T. Vianco and A.C. Claghorn, "Effect of Substrate Preheating on Solderability Performance as a Guideline for Assembly Process Development Part 1: Baseline Analysis," *Soldering & Surface Mount Technology*, Vol. 8, No. 3, 1996, pp. 12-18. doi:10.1108/09540919610777708

[6] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requicha and H. A. Atwater, "Plasmonics a Route to Nanoscale Optical Devices," *Advanced Materials*, Vol. 13, No. 19, 2001, pp. 1501-1505. doi:10.1002/1521-4095(200110)13:19<1501::AID-ADMA1501>3.0.CO;2-Z

[7] Z. Zha, S. Qiao, J. Jiang, Y. Wang, Q. Miao and Z. Wang, "Barbier-Type Reaction Mediated with Tin Nano-Particles in Water," *Tetrahedron*, Vol. 61, No. 9, 2005, pp. 2521-2527. doi:10.1016/j.tet.2004.12.063

[8] M. Athar, U. C. Kothyari and R. J. Garde, "Distribution of Sediment Concentration in the Vortex Chamber Type Sediment Extractor," *International Journal of Hydraulic Research*, Vol. 41, No. 4, 2003, pp. 427-438.

doi:10.1080/00221680309499987

[9] K. S. Le Corre, E. Valsami-Jones, P. Hobbs, B. Jefferson and S. A. Parsons, "Agglomeration of struvite crystals," *Water Research*, Vol. 41, No. 2, 2007, pp. 419-425. doi:10.1016/j.watres.2006.10.025

[10] Y. Zhao, Z. Zhang and H. Dang, "Preparation of Tin Nanoparticles by Solution Dispersion," *Material Science and Engineering A*, Vol. 359, No. 1-2, 2003, pp. 405-407. doi:10.1016/S0921-5093(03)00395-2

[11] A. Bhardwaj, P. Srivastava and H. K. Sehgal, "Chemically Deposited PbSe Nanoparticle Films Variation in Shape and Size," *Journal of Electrochemical Society*, Vol. 154, No. 10, 2007, pp. 83-86. doi:10.1149/1.2763963

[12] E. Pan, Y. Zhang, P. W. Chung and M. Denda, "Strain Energy on the Surface of an Anisotropic Half-Space Substrate: Effect of Quantum-Dot Shape and Depth," *CMES—Computer Modeling in Engineering & Sciences*, Vol. 24, No. 2-3, 2008, pp. 157-167.

[13] J. Duan and J. Gregory, "Coagulation by Hydrolysing Metal Salts," *Advances in Colloid Interface Science and Technology*, Vol. 10, 2003, pp. 100-102.

[14] J. Gregory, "Particles in Water: Properties and Processes," IWA Publishing, London, 2006.

