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Role of reactant concentration in size control of SnAgCu nanoparticles

Wei-peng ZHANG[1,2], Bing-ge ZHAO[1,2], Chang-dong ZOU[2], Qi-jie ZHAI[2], Yu-lai GAO[1,2]

1. Laboratory for Microstructures, Shanghai University, Shanghai 200436, China;
2. School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

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Abstract: Attributing to the melting temperature depressing resulted from the size effect of nanoparticles, the SnAgCu alloy system can be a promising candidate to replace the traditional toxic SnPb solder in the field of electronic packaging. Chemical reduction method was used to fabricate the Sn3.0Ag0.5Cu (SAC) (mass fraction, %) alloy nanoparticles. Sodium borohydride and 1,10-phenanthroline were chosen as the reducing agent and surfactant respectively. In addition, the morphology of the synthesized nanoparticles was investigated by field emission scanning electron microscopy (FE-SEM), and the size distribution of the as-prepared particles was obtained from the image analysis. It was found that the particle size increased with increasing the reactant concentration. Finally, theoretical analysis was employed to illustrate the influence of reactant concentration on the particle size.
Key words: chemical reduction method; lead-free solder; SnAgCu alloy; nanoparticle; size control; reactant concentration

1 Introduction

The traditional Sn−Pb solders have been phased out in the electronic industry due to the toxicity nature of lead. Much attention has been paid to the development of new lead-free solders. Among them, the Sn−Ag−Cu (SAC) alloy system is the most promising candidate that can replace the Sn−Pb solder. The eutectic Sn3.0Ag0.5Cu is widely used in the field of electronic packaging in particularly [1]. The mechanical properties of this newly developed lead-free solder are affected by the solidification structures. Three main phases, β-Sn, Ag_3Sn and Cu_6Sn_5 are formed during the solidification process [2,3]. The latter two intermetallics dispersed in the β-Sn matrix lead to the generally superior mechanical properties [4,5]. Even so, there are still some defects in this system. One of them is the higher melting temperature compared to Sn−Pb solder, as high as 217.8 °C [6]. The melting temperature of solder plays an important role in the packaging performance and the product reliability. Though the use of lead-free solder is an irresistible general trend, the high melting point of Sn3.0Ag0.5Cu solder will still cause some unexpected disadvantages. For example, the weak combination with the substrate will increase the possibility of substrate damage.

In order to decrease the melting temperature of Sn3.0Ag0.5Cu eutectic solder, nanotechnology is employed. The size-dependent melting temperature of alloy has been studied by JESSER et al [7]. Various methods have been developed to manufacture nanoparticles [8−13]. Among them, the chemical reduction method, which is considered the most suitable technique for industrial manufacture, is always used in the fabrication process of lead-free solder. It has been found to be a comparatively inexpensive and flexible way to produce nanoparticles with controllable size and morphology. LIN et al [14] used a chemical reduction method to synthesize Sn−3.5Ag−xZn (x=0.5−3.5; mass fraction, %) alloy nanoparticles. The morphology and size of the isolated nanoparticles were well controlled. Due to the strong aggregation, the major particle sizes in the scanning electron microscopy (SEM) images were in the range of 60−80 nm. In the Sn−Ag based alloy system, Sn−3.5Ag and Sn−3.0Ag−0.5Cu were studied by JIANG et al [15,16]. In their experiment, however, nanoparticles were fabricated through chemical reduction method at −20 °C in inert gas atmosphere. The relatively harsh reaction conditions would limit the industrial applications of this method. HSIAO and DUH [17] also prepared successfully Sn−3.5Ag−xCu (x=0.2, 0.5, 1.0%)

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Corresponding author: Yu-lai GAO; Tel: +86-21-56332144; E-mail: ylgao@shu.edu.cn
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through the chemical reduction method with $NaBH_4$ as the reduction agent.

In the aspect of practical production, the size and morphology control of the synthesized nanoparticles are very important. However, little information about this control process could be found in literatures. In the present work, the role of reactant concentration in the size control of Sn3.0Ag0.5Cu nanoparticles was discussed in the case of dilute solution of reducing agent and surfactant.

2 Experimental

In the precursor solution, the reactants used to synthesize Sn3.0Ag0.5Cu (mass fraction) nanoparticles were tin (II) 2-ethylhexanoate ($C_{16}H_{30}O_4Sn$), silver nitrate ($AgNO_3$) and copper (II) ethoxide monohydrate ($Cu(OC_2H_5)_2{\cdot}H_2O$). Sodium borohydride ($NaBH_4$), 1,10-phenanthroline ($C_{12}H_8N_2{\cdot}H_2O$) and anhydrous ethanol (CH_3CH_2OH) were selected as the reducing agent, the surfactant and the solvent, respectively.

Due to the fact that the mass ratio of metallic ions used to synthesize SnAgCu nanoparticles was a constant, namely, the proportion of Sn:Ag:Cu was 96.5:3.0:0.5, the reactant concentration could be expressed by concentration of tin (II) 2-ethylhexanoate. In different cases, different amounts of tin (II) 2-ethylhexanoate were mixed into 60 mL anhydrous ethanol and the concentrations for SAC1, SAC2, SAC3, SAC4 were 0.0068, 0.0101, 0.0202 and 0.0271 mol/L, respectively. In a typical synthesis process, for example SAC1, 0.222 g surfactant was added into the solution and intensively stirred for about 2 h in atmospheric environment. Afterwards 0.0946 g reducing agent was added into the homogeneous precursor solution and stirred for another 1 h till the end of the reaction.

The synthesis parameters are listed in Table 1.

The synthesized nanoparticles were precipitated by a centrifugal separator at 4000 r/min for 20 min and washed with anhydrous ethanol three times. Then the particles were dried in a vacuum drying chamber at 40 °C for 12 h.

The morphologies of the synthesized particles were observed with a field emission scanning electron microscope (FE-SEM, model JSM−6700F).

3 Results and discussion

The SEM images of the synthesized SAC nanoparticle are shown in Fig. 1. The reactant concentrations were 0.0068, 0.0101, 0.0202 and 0.0271 mol/L, respectively. It was found from the SEM images that the particles grew with the increase of reactant concentration. However, the morphology of the synthesized nanoparticles, which were mostly spherical, was basically unchanged.

The size distribution of the synthesized nanoparticles could be estimated from the SEM images by image analysis, and the average diameters could be obtained from the results of the Gauss fit of the size distribution [18]. The statistical results of particle size are illustrated in Fig. 2.

As can be seen from Fig. 2, both the size distribution and average diameter of the synthesized nanoparticles became larger with the increase of reactant concentration. The particle sizes of SAC1 and SAC2, whose solution concentrations were at relatively low level, were smaller than 50 nm and mainly concentrated in the range of 15−40 nm. In the case of higher reactant concentration, namely SAC3 and SAC4, the proportion of particles less than 50 nm was rapidly reduced to about 65%. Despite the average diameters for SAC3 and SAC4 were almost the same, the size distribution of the latter was much larger due to the thicker reactant. It should be noticed that there were even particles of about 200 nm in the SAC4 sample. In addition, the particle sizes of SAC1 and SAC2 were well controlled considering the lower level of surfactant concentration. That is to say, the particle size was mainly influenced by the reactant concentration.

The proportion of particles in different size ranges was studied, which is shown in Fig. 3. Those particles with size between 15 nm to 40 nm diminished rapidly with the increase of reactant concentration. The same trend could be found in the particles less than 50 nm. As for the larger ones, i.e. particles larger than 50 nm, the

Table 1 Synthesis parameters of Sn3.0Ag0.5Cu nanoparticles

Sample	Concentration/ ($mol{\cdot}L^{-1}$)	$m(C_{16}H_{30}O_4Sn)$/ g	$m(AgNO_3)$/ g	$m(Cu(OC_2H_5)_2{\cdot}H_2O)$/ g	$V(CH_3CH_2OH)$/ mL	$m(C_{12}H_8N_2{\cdot}H_2O)$/ g	$m(NaBH_4)$/ g
SAC1	0.0068	0.1647	0.0024	0.0009	60	0.2220	0.0946
SAC2	0.0101	0.2470	0.0035	0.0013	60	0.3330	0.1419
SAC3	0.0202	0.4940	0.0047	0.0026	60	0.6660	0.2838
SAC4	0.0271	0.6586	0.0094	0.0034	60	0.8880	0.3784

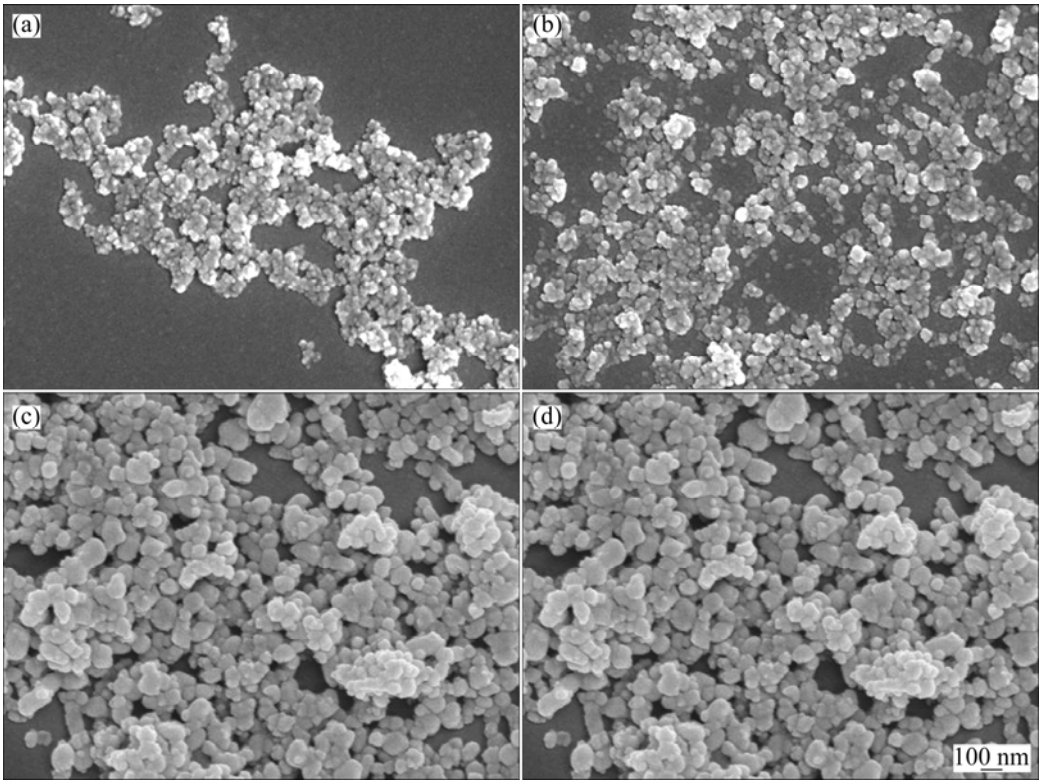

Fig. 1 SEM images of synthesized Sn3.0Ag0.5Cu nanoparticles with different reactant concentrations: (a) SAC1; (b) SAC2; (c) SAC3; (d) SAC4

trend was the opposite. It could also be found that the average diameter of the synthesized nanoparticles increased rapidly with increasing the reactant concentration as shown in Fig. 4. Hence, Sn3.0Ag0.5Cu nanoparticles with small average diameter and narrow size distribution could be obtained by controlling the reactant concentration.

In fact, the influence of reactant concentration on the particle size can be investigated through the nucleation rate and the growth rate of nucleus. The nucleation rate in the chemical reduction process can be described by the following formula [19]:

$$R_{\mathrm{N}} = A\exp\left(\frac{-16\pi\sigma^3 v^2}{3k^3T^3(\ln S)^2}\right) \tag{1}$$

where R_{N} is the nucleation rate; A is the pre-exponential factor in the a range of (10^{25}−10^{56}) $\mathrm{s^{-1}\cdot m^{-3}}$; σ is the surface tension of the liquid−solid interface; v is the atomic volume of solute; k is the Boltzmann constant; T is the reaction temperature; S is the supersaturation of the solute. Among them, the parameter S can be expressed as

$$S = c/c_{\mathrm{eq}} \tag{2}$$

where c and c_{eq} is the solute concentrations of saturation state and equilibrium state, respectively. The nucleation rate cannot be neglected when the supersaturation of the solute exceeds a critical value.

The growth rate of the nuclei G can be described by the following power law equation [19]:

$$G = k_{\mathrm{G}}S^g \tag{3}$$

where k_{G} and g is the constant of growth rate and growth series, respectively.

Ostwald-Ripening mechanism always takes place during the growth process of nuclei. That is to say, particles with small size will be absorbed by the relatively large ones. Ostwald-Ripening process, which has an important impact on the size, morphology and performance of the synthesized nanoparticles, can be described by the theory proposed by LIFSHITZ et al [20] and WANER [21]. The main aspect of this theory is shown as follows [19,22].

1) In a diffusion-controlled growth process, the mean diameter of the synthesized particles is a function of time,

$$\overline{R}(t) = \sqrt[3]{Kt} \tag{4}$$

where K is the growth rate of crystalline grain and can be expressed by $K=4aD_i/9$, with D_i being the diffusion current of solute at the grain boundary.

2) In a diffusion-controlled Ostwald-Ripening process, the number density N of the nuclei decays with time.

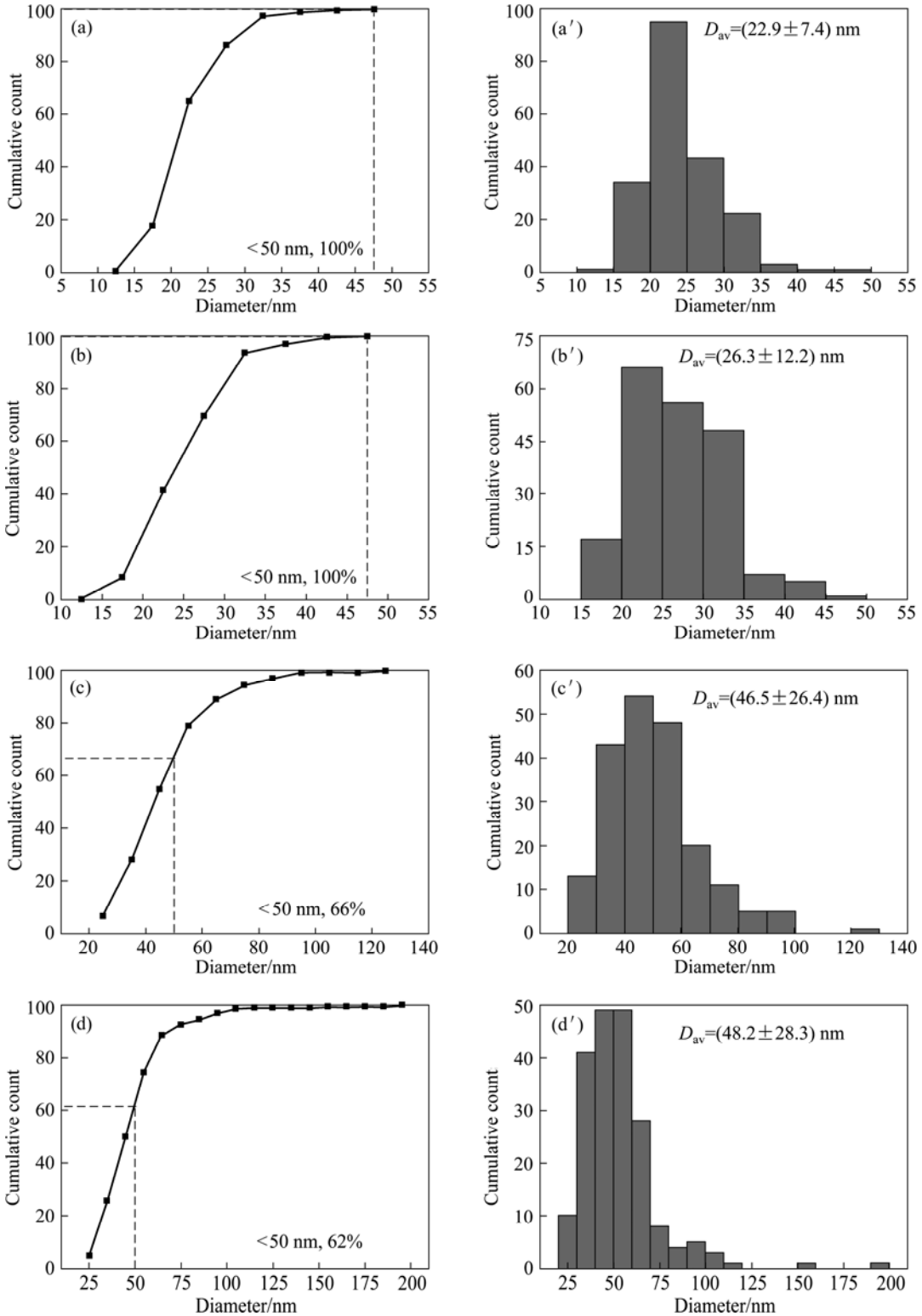

Fig. 2 Size distribution of synthesized Sn3.0Ag0.5Cu nanoparticles: (a, a′) SAC1; (b, b′) SAC2; (c, c′) SAC3; (d, d′) SAC4

$$N(t)=\frac{0.22Q_0}{\overline{R}(t)} \tag{5}$$

where Q_0 is the initial super-saturation concentration of the solute.

3) The final size distribution function of the product can be expressed as

$$f(R,t)=\left[\frac{N(t)}{\overline{R}(t)}\right]P_0(\rho(t))=\left[\frac{0.22Q_0}{[\overline{R}(t)]^2}\right]P_0(\rho(t)) \tag{6}$$

where $\rho(t)=R/\overline{R}(t)$ is the absolute size of particles and $P_0(\rho(t))$ is a function that does not change with time.

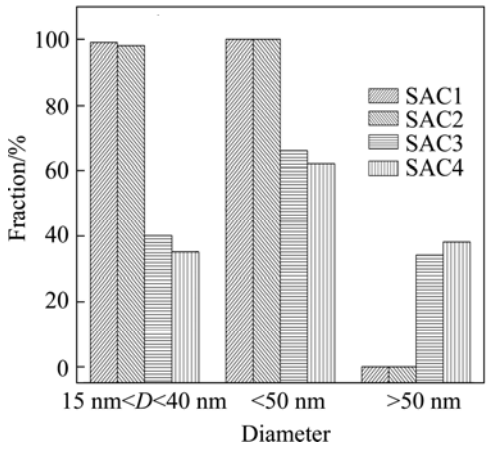

Fig. 3 Proportion of Sn3.0Ag0.5Cu nanoparticles in different size ranges

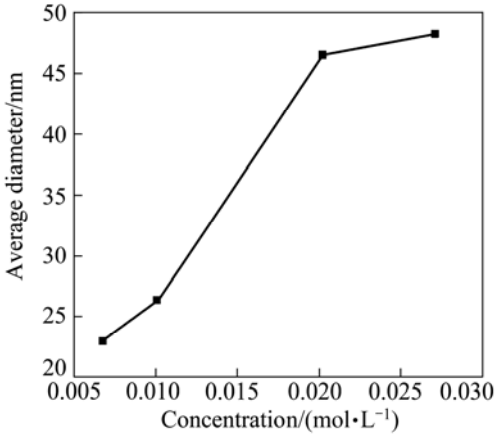

Fig. 4 Relationship between average diameter and reactant concentration

It can be found from Eqs. (1)−(6) that the nucleation rate of the nuclei and the growth rate of the particle are greatly affected by the concentration of solute in the solution. These two factors will finally determine the particle size and size distribution. From the viewpoint of nucleation rate, a higher nucleation rate can be obtained when the solute concentration is larger. Thus, much more nuclei will form in the solution. The high nucleation rate will lead to two possible results: in the first case, the solution system is stable and the growth or aggregation of nuclei is controlled by other methods; then nanoparticles with small size and narrow size distribution can be obtained. However, this synthesis process is hard to be controlled. In the other case, the large number of nuclei formed during the reaction can greatly increase their collision probability. The growth of nuclei and the aggregation of particles will be promoted. Therefore, coarsened particles will be obtained finally.

In the current study, the ideal product of the first case was hard to fabricate. The actual reaction belonged to the second case. That is to say, the increase of the precursor concentration in the reaction system would result in the number of nuclei increasing, and then the increase of nuclei collision probability. Therefore, the rates of growth and aggregation of Sn3.0Ag0.5Cu nanoparticles were enhanced, which was shown as the increase of particle size with increasing the reactant concentration.

4 Conclusions

1) Nanoparticles of SnAgCu lead-free solder could be successfully fabricated by means of chemical reduction method. The particle size increased with increasing the reactant concentration.

2) The ideal nanoparticles with small average diameter and narrow size distribution could be obtained when the reactant concentration was well controlled. Based on the theoretical analysis, it was deemed that a large number of collisions of nuclei could greatly enhance the growth and aggregation rate of nanoparticles during the reaction.

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反应物浓度在 SnAgCu 纳米颗粒尺寸控制中的作用

张卫鹏[1,2]，赵炳戈[1,2]，邹长东[2]，翟启杰[2]，高玉来[1,2]

1. 上海大学 微结构实验室，上海 200436；
2. 上海大学 材料科学与工程学院，上海 200072

摘 要：在电子封装领域，通过利用纳米颗粒尺寸效应带来的熔点降低，SnAgCu 合金体系有希望替代传统的但有毒的 SnPb 焊料体系。分别选用硼氢化钠和邻啡罗琳作为还原剂和表面活性剂，采用化学还原法制备出 Sn3.0Ag0.5Cu (质量分数)合金纳米粒子。对合成的纳米颗粒形貌采用场发射扫描电镜(FE-SEM)进行表征。通过对扫描电镜数据的分析，可统计出纳米颗粒的尺寸分布。研究表明，所合成的纳米颗粒尺寸随着反应物浓度的增加而增大。通过理论分析，对反应物浓度在纳米颗粒尺寸控制中的作用进行了阐述。

关键词：化学还原法；无铅焊料；SnAgCu 合金；纳米颗粒；尺寸控制；反应物浓度

(Edited by Hua YANG)