

AgNi15 composite particles prepared by ultrasonic arc spray atomization method

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Abstract: Ultrasonic arc spray atomization (UASA) method was used to prepare high-melting-point, immiscible AgNi15 (mass fraction, %) composite particles. Sieving was used to determine the size distribution of the AgNi15 particles. The morphology, rapidly solidified structure and metastable solution expansion of the AgNi15 particles were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS), respectively. The results show that the AgNi15 composite particles are spherical and well-dispersed, and the mass fractions of the particles with diameters <74 μm and <55 μm are 99.5% and 98%, respectively. The rapidly solidified structure of the AgNi15 particles consists of spherical nickel-rich $\beta(\text{Ni})$ -phase particles dispersed throughout a silver-rich $\alpha(\text{Ag})$ -phase matrix and $\alpha(\text{Ag})$ -phase nanoparticles dispersed throughout larger $\beta(\text{Ni})$ -phase particles. The silver and nickel in the AgNi15 particles form a reciprocally extended metastable solution, and the solid solubility of nickel in the silver matrix at room temperature is in the range of 0.16%–0.36% (mole fraction).

Key words: AgNi15 composite particle; ultrasonic arc spray atomization; rapidly solidified structure; metastable solution extension

1 Introduction

Ag–Ni composite materials as electrical contact materials were developed in the last century and have been researched ever since. They are widely used throughout the electrical appliance industry [1–6]. However, only the two traditional powder metallurgy methods, namely, chemical coprecipitation and mechanical mixing, which have high production costs and require complex preparation procedures, are currently used to manufacture Ag–Ni composites because solid Ag–Ni is immiscible and the mutual solubility of liquid Ag–Ni is very low [7]. Furthermore, Ag–Ni composite materials produced using the traditional methods contain monodispersed silver and nickel particles, which significantly degrade the electrical contact performance of the composites. Many methods of preparing Ag–Ni composites have been developed to solve this problem. Conventional gas and water atomization have been used to manufacture Ag–Ni composites in order to shorten the production period and improve the electrical contact performance of the

composites [3–5]. However, these methods cannot be used in industrial applications because they have many disadvantages. For example, they can only be used for low-melting-temperature metals, crucibles and nozzle of the apparatus can contaminate the powder and cause damage, the content of nickel in the Ag–Ni composites is less than 5% (mass fraction), and the resulting powder particles are coarse. Mechanical alloying method [8–10] has also been used to prepare highly dispersed $\alpha(\text{Ag})$ and $\beta(\text{Ni})$ composite particles whose metastable solid solubility and electrical contact performance are superior to those of composite particles prepared using conventional gas and water atomization. However, mechanical alloying is unsuitable for the large-scale production of Ag–Ni composites because it requires a long production period and it is inefficient and expensive. Based on the principle of arc spraying [11,12], ultrasonic arc spray atomization (UASA) was recently used to produce immiscible silver-matrix composite particles [13–15]. Ag–Ni composite wires of silver-coated nickel were used as the positive and negative arc consumable electrodes in UASA. The wires, which were located at the tips of the arc consumable electrodes and uniformly

fed into the UASA apparatus, were melted by the electric arc. The molten metals were subsequently atomized into tiny particles by ultrasonic airflow that were accelerated by de Laval nozzles, and the resulting particles were collected in a cooling medium. UASA method has many advantages. For example, it can be used with high-melting-temperature metals, a very small volume of the metals is continuously melted, the powder particles are not contaminated because of elimination of crucible and nozzle, and the metals droplets are well atomized. Therefore, it is an effective method of preparing high-purity, high-melting-point and immiscible metallic particles.

In this work, UASA was used to prepare high-melting-point and immiscible AgNi15 composite particles, and the morphology, rapidly solidified structure and metastable solution expansion of the particles were studied. This work has important values for producing high performance silver-nickel composite materials.

2 Experimental

2.1 Preparation of AgNi15 particles

Two AgNi15 (purity of 99.95%) composite wires of silver-coated nickel with 1.98 mm in diameter were used as the positive and negative arc consumable electrodes to prepare the AgNi15 particles. An automatic wire feeder was simultaneously fed the wires at a uniform velocity into the de Laval nozzles of the UASA atomization equipment. The electric arc was then ignited at 30 V and 220 A to melt the wires. Nitrogen was then ultrasonically flowed at a static 0.9 MPa through the de Laval nozzles, which accelerated the melt of AgNi15 droplets and subsequently sprayed them into water containers. The AgNi15 composite particles were then gathered into a desiccator, and were dried below 100 °C.

2.2 Measurement of particle-diameter distribution

Vibrating-screen sieving was used to measure the diameter distribution of the AgNi15 particles prepared by UASA. 40 g of the particles and vibration sieves with the size of 25 μm–74 μm were used, and the vibration time was set as 10 min during screening. The residual sieved particles in the vibration screens were weighed and the mass fraction of the particles whose diameters were in various ranges determined by the meshes of the sieves was calculated. The diameter distribution of the AgNi15 particles from these data was subsequently determined. Scanning electron microscopy (SEM) was used to study the diameter distribution of the AgNi15 particles.

2.3 Characterization of microstructure

Samples of the AgNi15 composite particles were consecutively inlaid, polished and surface-sprayed with

carbon. SEM (QUANTA200) equipped with energy dispersive spectroscopy (EDS) was used to study the organized structures and analyze the elements in the AgNi15 composite particles, and X-ray diffractometer (XRD, D/max-3b diffractometer) with Cu K_α radiation ($\lambda=1.54056 \text{ \AA}$, 30 kV) was used to analyze the crystallinity of the phases and determine the lattice constants of the AgNi15 composite particles.

3 Results and discussion

3.1 Morphology of AgNi15 composite particles

Figure 1 shows the SEM image of the AgNi15 particles. The AgNi15 composite particles prepared by UASA clearly show a fine spherical morphology, uniform dispersion, and narrow particle-diameter distribution.

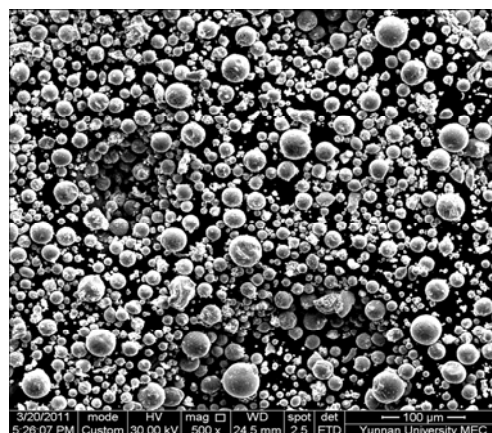


Fig. 1 SEM image of AgNi15 particles prepared by UASA

The shapes of the particles are related to the spheroidizing and solidification time of molten alloy droplets. The spheroidizing time of the molten alloy droplet, τ_{sph} , can be expressed as follows [16]:

$$\tau_{\text{sph}} = 0.88 \frac{\eta d}{\sigma} \quad (1)$$

where τ_{sph} is the spheroidizing time of the atomized droplet from the molten alloy; d is the diameter of the atomized droplet; η is the viscosity of the molten droplet; σ is the surface tension of the molten droplet.

The spheroidizing time of the molten AgNi15 droplets with the diameter in the range of 10–80 μm can be obtained as 10^{-7} – 10^{-8} s from Eq. (1) when the viscosity and surface tension of the molten AgNi15 droplet are approximately the same as those of the molten silver droplet, which are 3.53 Pa·s/mol and 966 N/(m⁻¹·mol), respectively. The superheat of molten silver alloy droplets is more than 1000 °C since molten silver alloy droplets prepared by UASA were cooled at 10^5 – 10^7 °C/s [17], and the solidification time of molten silver

alloy droplets is in the range of 10^{-2} – 10^{-3} s, which is longer than the spheroidizing time of molten silver alloy droplets. Thus, all the AgNi15 particles prepared by UASA should be theoretically spherical.

3.2 Diameter distribution of AgNi15 composite particles

Table 1 lists the diameter distribution and mass fractions of the AgNi15 particles prepared by UASA. The total mass of the particles was 40 g. The AgNi15 particles with the diameter in the range of 25–55 μm comprise 94% of the total mass of the particles, and the AgNi15 particles with diameter less than 55 μm comprise more than 97% of the total mass of the particles. The particles with diameter more than 74 μm comprise 0.43% of the total mass of the particles. The average diameter (d_{50}) of the atomized particles is about 30 μm .

Table 1 Diameter distribution and mass fraction of AgNi15 particles

Particle diameter/ μm	Mass fraction/%
>74	0.43
55–74	1.90
38–54	13.45
30–37	18.55
25–29	62.30
<25	3.37

The effects of atomization on the molten-AgNi15 droplets prepared by UASA can be evaluated by measuring the average diameter (d_{50}) of the atomized particles. When the atomization pressure is less than 1 MPa, which corresponds to atomization pressure of 0.5–1 MPa in UASA. MILLER et al [18] proposed the semiempirical formula for the relationship between the average diameter of the atomized particles and the atomization parameters as follows:

$$d_{50} = \left(\frac{K \eta^2 \sigma^3 D}{u_g^2 \rho_g^3 \rho^3} \right)^{\frac{1}{6}} \left(\frac{J}{J_g} \right)^{\frac{1}{2}} \quad (2)$$

where d_{50} is the average diameter of the atomized particles; K is the proportional constant; σ is the surface tension; η is the viscosity of the atomized molten metal droplets; D is the diameter of the catheter; u_g is the gas velocity; ρ_g and ρ are the densities of the gas and the molten metal droplets, respectively; J_g and J are the flow rate of the gas and the molten metal droplets, respectively.

Equation (2) shows that finely atomized particles are produced when the velocity and flow rate of the gas increase, or when the diameter of catheter or the surface

tension and viscosity of the molten droplets decrease. Although a catheter is not required in order to atomize molten metal droplets during UASA process, a gas velocity of about 600 m/s is required. The diameter of the wire electrode is less than that of the catheter, the temperature of the molten metal droplets is above 2500 $^{\circ}\text{C}$, and the surface tension and viscosity of the molten droplets remarkably decrease. Therefore, UASA-induced atomization is superior to conventional atomization, and UASA is especially suitable for preparing high-melting-point, immiscible composite particles such as Ag–Ni composite particles.

3.3 Metastable microstructure of AgNi15 composite particles

Figure 2(a) shows the SEM image of the metastable microstructure of AgNi15 composite particle. The light grey represents a silver-rich $\alpha(\text{Ag})$ -phase matrix, and the dark grey represents spherical nickel-rich $\beta(\text{Ni})$ -phase particles dispersed throughout the silver-rich matrix. Larger $\beta(\text{Ni})$ particles have clearly formed inside larger AgNi15 particles, indicating that nickel-rich particles have accumulated inside the AgNi15 particles when the atomized molten AgNi15 droplets solidify and the heat conduction of the atomized droplets is spherically symmetric. The smaller-diameter particles solidify faster

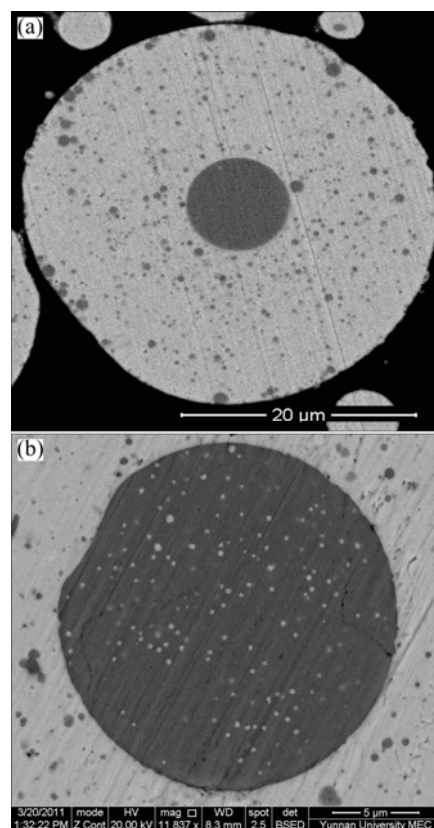


Fig. 2 SEM images of AgNi15 particles prepared by UASA: (a) $\beta(\text{Ni})$ dispersed throughout $\alpha(\text{Ag})$ matrix; (b) $\alpha(\text{Ag})$ dispersed throughout $\beta(\text{Ni})$ phase

than the larger-diameter ones, so the $\beta(\text{Ni})$ particles will be smaller in the smaller $\alpha(\text{Ag})$ matrix. Figure 2(b) shows that spherical $\alpha(\text{Ag})$ nanoparticles (i.e., the light grey particles) can be dispersed inside larger $\beta(\text{Ni})$ particles, indicating that a large number of silver-rich droplets can be precipitated inside larger-diameter nickel-rich droplets when molten Ag–Ni alloy droplets solidify. Further, it is difficult for the silver-rich phase to accumulate and form a precipitate of $\alpha(\text{Ag})$ nanoparticles dispersed throughout the $\beta(\text{Ni})$ phase because the nickel-rich liquid phase has solidified first.

Figure 3 shows the results of the EDS analysis for the particles in Fig. 2. The content of Ni in the $\alpha(\text{Ag})$ -phase matrix (Fig. 2(a)) is about 11% (mole fraction), and the content of Ag in the $\beta(\text{Ni})$ -phase large particles (Fig. 3(b)) is about 2.8%, as shown in Figs. 3(c) and (d), respectively. The results of the EDS analysis from the X-ray diffraction spectra show that solidifying atomized molten-metal droplets appear to extend the mutual solubility of Ag and Ni. The characteristics of the solidified structure show that atomized AgNi15 droplets rapidly solidify and a metastable organized structure forms during supersonic arc jet atomization. The AgNi15 particles prepared by UASA which show mutually dispersed solid-solution structures are significantly

different from Ag–Ni particles prepared using conventional powder metallurgy methods which are merely mixed particles of Ag and Ni metal.

The solidified structure of AgNi15 composite particles is closely related to the solidification velocity of molten AgNi15 droplets prepared by UASA. The Ag–Ni phase diagram [9,19] shows a liquid-phase miscibility gap and a monotectic reaction region for almost all compositions. The temperature of the liquid-phase miscibility and solidification regions are close to 500 °C. The microstructure of Ag–Ni consists of an immiscible, nonuniformly dispersed layer during equilibrium solidification at room temperature. Therefore, Ag–Ni composite materials cannot be prepared using conventional methods of casting except for microalloying. In UASA, however, Ag/Ni electrode wires are instantly melted into Ag–Ni solid solution as the electric arc reaches 2500 °C and simultaneously atomized into tiny molten alloy droplets by supersonically flowing nitrogen. The droplets then form mutually dispersed $\alpha(\text{Ag})$ and $\beta(\text{Ni})$ liquid particles at the liquid-phase immiscible region and solidify near the monotectic reaction temperature. The solute migration of liquid and solid phases is suppressed, hence, the rapidly solidified metastable structure forms.

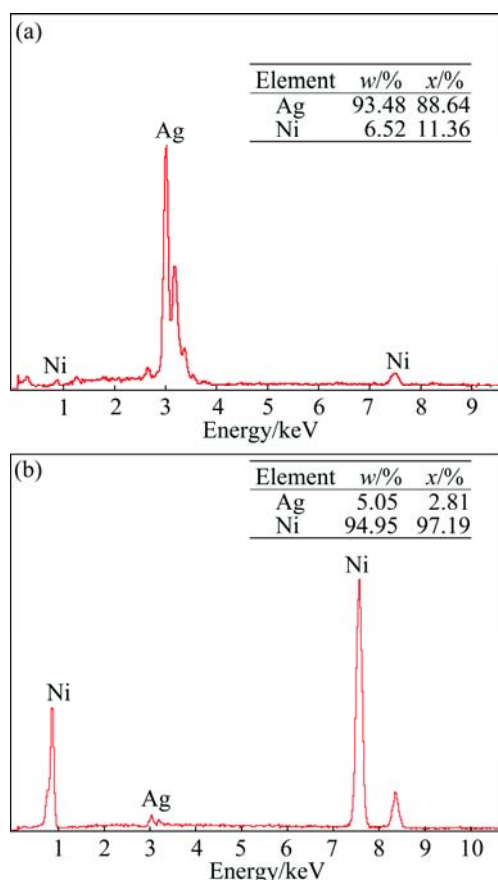


Fig. 3 EDS spectra of AgNi15 particles prepared by UASA: (a) $\alpha(\text{Ag})$ matrix in area shown in Fig. 2(a); (b) Larger $\beta(\text{Ni})$ particles in area shown in Fig. 2(b)

3.4 Metastable solution expansion of AgNi15 composite particles

Figure 4 shows the XRD patterns for the AgNi15 particles with the diameters of 38–55, 30–38, 25–30, and <25 μm . The diffraction peaks of Ni are at $2\theta=51.899^\circ$ and 93.001° , and those of Ag and Ni are at 2θ in the range of 76° – 78° . Table 2 lists the angles of the diffraction peaks of Ag and Ni and the corresponding full widths at half-maximum (FWHMs) for the diffraction peaks shown in Fig. 4. Table 2 shows that the angles of the diffraction peaks of the silver-rich $\alpha(\text{Ag})$ matrix in the AgNi15 particles of various diameters are higher than those of the diffraction peaks of annealed silver, and the FWHM of the diffraction peak of the silver-rich $\alpha(\text{Ag})$ matrix in the various-sized AgNi15 particles is larger than that of the diffraction peak of the annealed silver. The diffraction peaks of the Ag in the AgNi15 particles have all shifted to angles higher than those of the diffraction peaks of annealed pure Ag. Further, the diffraction peaks of the Ni in the AgNi15 particles have all shifted to angles lower than those of the diffraction peaks of annealed pure Ni. The width of the diffraction peaks increases with decreasing the particle size. The shifts in the diffraction peaks of Ag and Ni show that Ag and Ni form an extension of mutual solid solubility and grain refinement broadens the diffraction peaks.

Table 2 Diffraction angles and corresponding FWHMs of diffraction peaks of $\alpha(\text{Ag})$ in AgNi15 particles with various diameters

Peak	AgNi15 particle						Annealed Ag	
	38–55 μm		30–38 μm		<25 μm		$2\theta/(\circ)$	FWHM
	$2\theta/(\circ)$	FWHM	$2\theta/(\circ)$	FWHM	$2\theta/(\circ)$	FWHM		
1	338.098	0.175	38.118	0.165	38.121	0.206	38.061	0.147
2	444.421	0.260	44.301	0.241	44.34	0.262	44.242	0.150
3	464.462	0.218	64.481	0.205	64.483	0.205	64.40	0.156
4	677.441	0.266	77.442	0.259	77.480	0.264	77.36	0.167
5	881.581	0.268	81.601	0.194	81.638	0.329	81.501	0.162
6	997.941	0.422	97.961	0.337	97.963	0.372	97.861	0.210
7	1110.562	0.378	110.601	0.273	110.602	0.403	110.481	0.196
8	1115.002	0.435	115.022	0.373	115.062	0.446	114.901	0.212

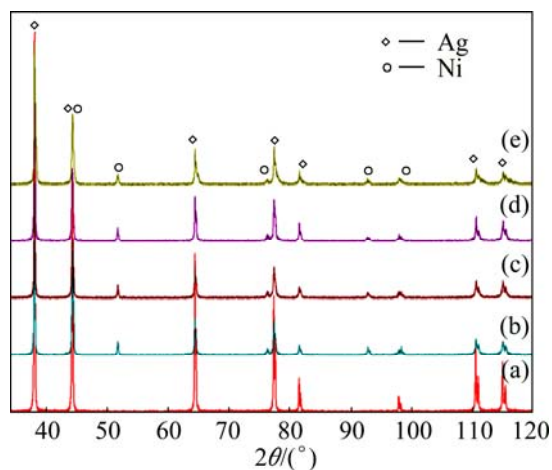
**Fig. 4** XRD patterns of annealed silver (a) and AgNi₁₅ particles prepared by UASA with different diameters of 38–55 μm (b), 30–38 μm (c), 25–30 μm (d) and <25 μm (e)

Table 3 lists the lattice parameters for the Ag matrix and the solid solubility of Ni in the AgNi15 particles prepared by UASA. The solid solubility of Ni in the Ag matrix at room temperature is in the range of 0.16%–0.36% and increases with decreasing particle diameter. During UASA process, the molten alloy is atomized into liquid droplets with different diameters and different solidification rates by high-pressure gas. The smaller droplets solidify faster than the larger ones, hence, the smaller particles show greater extensions of solid solubility than the larger particles.

Table 3 Lattice constants of $\alpha(\text{Ag})$ and solid solubility of Ni in AgNi15 particles with various diameters

Particle diameter/ μm	Lattice constant/nm	Solid solubility/%
38–55	0.40855	0.1601
30–38	0.40849	0.2312
25–30	0.40844	0.3202
<25	0.40842	0.3557

4 Conclusions

1) The UASA-prepared AgNi15 composite particles show uniformly spherical morphology. The particles with diameters less than 55 μm comprise more than 97% of the total mass of the particles, and the particles with diameters more than 74 μm comprise only 0.43% of the total mass of the particles. The average diameter (d_{50}) of the atomized particles is about 30 μm .

2) The AgNi15 composite particles show a rapidly solidified metastable microstructure consisting of spherical nickel-rich $\beta(\text{Ni})$ -phase particles dispersed throughout a silver-rich $\alpha(\text{Ag})$ -phase matrix and $\alpha(\text{Ag})$ nanoparticles dispersed throughout the $\beta(\text{Ni})$ -phase particles. The Ag and Ni form a mutual extension of solid solubility, and the solid solubility of Ni in the Ag matrix at room temperature is in the range of 0.16%–0.36% and increases with decreasing particle diameter.

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超音速电弧喷射雾化制备 AgNi15 复合颗粒

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摘 要: 采用超音速电弧喷射雾化法(UASA)制备高熔点、难互溶的 AgNi15 复合颗粒, 采用筛分法测量复合颗粒粒度分布, 使用 SEM、EDS 和 XRD 分析颗粒形貌、凝固组织结构和亚稳固溶扩展。结果表明: 采用 UASA 制备的 AgNi15 复合颗粒具有球形度高和分散性好的特点, 直径小于 74 和 55 μm 颗粒的质量分数分别为 99.5%和 98%。复合颗粒凝固组织结构为富镍相 $\beta(\text{Ni})$ 球形颗粒弥散分布在富银相 $\alpha(\text{Ag})$ 基体中, 而较大的 $\beta(\text{Ni})$ 颗粒中又弥散分布着 $\alpha(\text{Ag})$ 颗粒。Ag 和 Ni 相互实现了亚稳固溶扩展, 在室温条件 Ni 在 Ag 中的固溶度在 0.16%~0.3%之间(摩尔分数)。

关键词: AgNi15 复合颗粒; 超音速电弧喷射雾化; 快速凝固结构; 亚稳固溶扩展

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