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Research Article

Effect of Rapid Solidification Rates on Preparation of Ni-Pb Alloy Hollow Particles with Low Pb Content

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Using Ni-5 wt.% Pb alloys with low Pb content as master alloys, the Ni-5 wt.% Pb alloy hollow particles were prepared by rapid solidification. Moreover, the alloy particles' microstructure and formation mechanism were investigated. The results show that the particles' microstructure consisted of Ni-rich and Pb phases. The Ni-rich phase was formed in the dendrite, and the Pb phase was distributed in the grain boundary or interdendrites. With the roller speeds increasing, the sizes of hollow particles and holes were decreased which were deviated from the particle center, while the hollow ratio, shear stress, and turbulence intensity of the hollow particles were increased. The formation of alloy hollow particles is attributed to interaction between the high-speed fluid and environment gas on the liquid/gas interface. The increase in roller speeds was conducive to the formation of Ni-Pb alloy hollow particles with low Pb content.

1. Introduction

Alloy hollow particle [1] is a kind of fine particle, which is formed by the suspension of micropowder in the high-temperature airflow or the atomization of melt in the high-pressure air stream. It has the common characteristics of the hollow particle material, such as not only low density, high surface area, well thermal stability, and good fluidity, but also specially photoelectric and magnetic properties. Currently, the alloy hollow particles are used in chemical industry, machinery manufacturing, and automobile industry and will be used as the cryptomorphic coating materials in the military field and the microwave absorbing material in the production life field in the future. For example, Zhu et al. [2] had prepared the electromagnetic functional materials coated with Ni hollow particles. They found that their permeability and magnetic loss tangent were higher and dielectric constant was lower, which would be an excellent microwave-absorbing material. Various research results showed that alloy hollow particles had the above advantages and wide applications. How to prepare metal alloy hollow particles has become a research hotspot. Therefore, the preparing methods of hollow particles have attracted much more attention in the materials science and condensed state physics field [3]. At present, the prepared methods of alloy hollow particles are surface chemical plating [4], microemulsion method [5], template interface reaction [6], and layer-by-layer self-assembly method [7]. The surface chemical plating method is easy to be operated with simple equipment to obtain good coating effect, but its microstructure has more complex phase composition, which makes phase-growth controlling not easy. This method is based on the redox reaction principle, and metal ions in solution are reduced into the metal deposited on the surface of various materials to form dense coating with strong reducing agents. Therefore, this method is bound to bring new "complex phase composition" applicable to any alloy system, which is caused by strong reducing agents and chemical reactions. While the microemulsion method and template interface reaction method have complex process with the reaction template, these two methods are not easy to operate. Although the layer-by-layer self-assembly method process is simple and easy to operate, it also has the complex phase composition and higher production cost. Therefore, it also has not to be selected as the optimal method for preparing alloy hollow particles. In summary, it can be found that most of these methods for preparing alloy particles belong to the chemical synthesis method. The process of these methods is not easy to control, and the preparing products are complex. Moreover, the experimental cost of these methods is too high to prepare a large number of alloy hollow particles.

While different from the above methods, the hollow particle structure could also be formed by rapid solidification belonging to solidification casting technology, which has a simple production process and lower production cost. At the same time, according to the phase diagram, in the rapid solidification process, the Ni-Pb alloy can be only precipitated as two "simple phases composition" including Ni phase and Pb phase, and no other phases are brought in relative to the surface chemical plating method. Thus, the alloy hollow particles prepared by rapid solidification were not only prepared with simple phase composition, less mesoporous rate, and sealing structure, but also with the uniform hollow structure microstructure and less segregation. Therefore, the rapid solidification technology can be considered as the first choice for alloy hollow particles preparation.

Based on the above analyses, compared with all methods for preparing alloy hollow particles, Ni-5 wt.% Pb hollow particles were prepared by rapid solidification with the single-roller method in this work, and microstructure and formation mechanism of Ni-Pb alloy hollow particles were investigated to provide theoretical and experimental bases on alloy hollow particles preparation.

2. Experimental Procedures

2.1. Materials. In this study, Ni-5 wt.% Pb alloy was used as the master alloy to perform rapid solidification of Ni-Pb alloy hollow particles. The high-purity Ni and Pb (99.99%) were fused by high-frequency induction heating. The master alloy sample was button ingot, and the sample quality was about 1.0~1.2 g.

Rapid solidification experiments in this work were carried out using the single-roller method. The master alloy sample was packed in a quartz tube with diameter 16 mm and length 150 mm (the quartz tube bottom has a nozzle with a diameter of 0.5~1.0 mm), which was placed in the top roller equipped with a vacuum cover. In the rapid solidification process, the sample was heated by high-frequency induction heating equipment at 1600°C and then kept isothermal for 3–5 minutes so as to homogenize the original ingot composition. Then, the motor was started and the single-roller speed was adjusted to stable the situation. Subsequently, the sample was rapidly injected into the roller surface and solidified to form alloy hollow particles.

In rapid solidification technique, the alloy melt cooling rate could be controlled by single-roller speed changes. Therefore, the rapid solidification rate could simplify replace the roller speed. The single-roller speeds in this work were selected as 30 m/s and 50 m/s.

2.2. Characterization. Then, alloy particles were collected and embedded, grinded and polished, and finally etched by the "5 g $FeCl_3$ + 100 mL HCl + 100 mL H_2O" solution. The microstructure and morphology of alloy hollow particles were observed and analyzed by using a XJG-05 optical microscope and JSM-5800 scanning electron microscope (SEM). The chemical analysis of particles was characterized by energy-dispersive spectroscopy (EDS) with SEM. The phase analysis was investigated by means of the X-ray powder diffraction (XRD, D/max-3).

3. Results and Discussion

3.1. Microstructure and Phase Analysis of Ni-5 wt.% Pb Alloy Hollow Particles at 30 m/s. Figure 1 shows the microstructure and EDS spectrum of Ni-5 wt% Pb alloy hollow particles at a rapid solidification rate of 30 m/s. Figure 1(a) shows the overall microstructure morphology of the hollow particle. It could be found that alloy particles' surface with less mesoporosity was closed, and their microstructure with homogenous fine equiaxed grains did not show obviously macro segregation. There was a hole in the center of the particles. The main reason is that there existed lower temperature gradient on the inner surface and higher on the outer surface during alloy liquid droplet solidification. Under the action of the Marangoni [8] migration, the hole was transferred to the internal liquid droplet, finally located at the center of the particles, and solidified into alloy hollow particles.

Through the further analysis by EDS and XRD, there appeared the single-phase Ni phase and Pb phase in Ni-5 wt % Pb alloy hollow particles in Figures 1(c), 1(d), and 2. Figure 1(b) shows the solidification microstructure enlarged view of the particles inner face. The EDS results indicated that particles' microstructure consisted of Ni-rich and Pb phases. The Ni-rich phase was formed in the equiaxed grain dendrite, and the Pb phase was distributed in grain boundary and interdendrites [9].

3.2. Microstructure of Ni-5 wt.% Pb Alloy Hollow Particles at 50 m/s. With the solidification rate rapid increasing, the size of alloy hollow particles was decreased and the solidification microstructure of the inner face were also changed as shown in Figure 3. Figure 3 shows the microstructure and EDS spectrum of Ni-5 wt.% Pb alloy hollow particles at a rapid solidification rate of 50 m/s. It can be seen that the contour shape of hollow particles was rounding. The inner surface and external surface solidification microstructure of particles were mainly dendrites with equiaxed grains, but the inner surface microstructure was more coarse. It is because that the inner surface of particles was away from the Cu roller face and the temperature gradient was lower than that in the external surface. In addition, compared with Figure 1(a), the hole size in the Ni-5 wt.% Pb alloy hollow particles was decreased and the hole was moved to the hollow particles edge. The solidification microstructure of hollow particles was uniform as clearly seen from the figure. Through chemical analysis by EDS, there appeared the

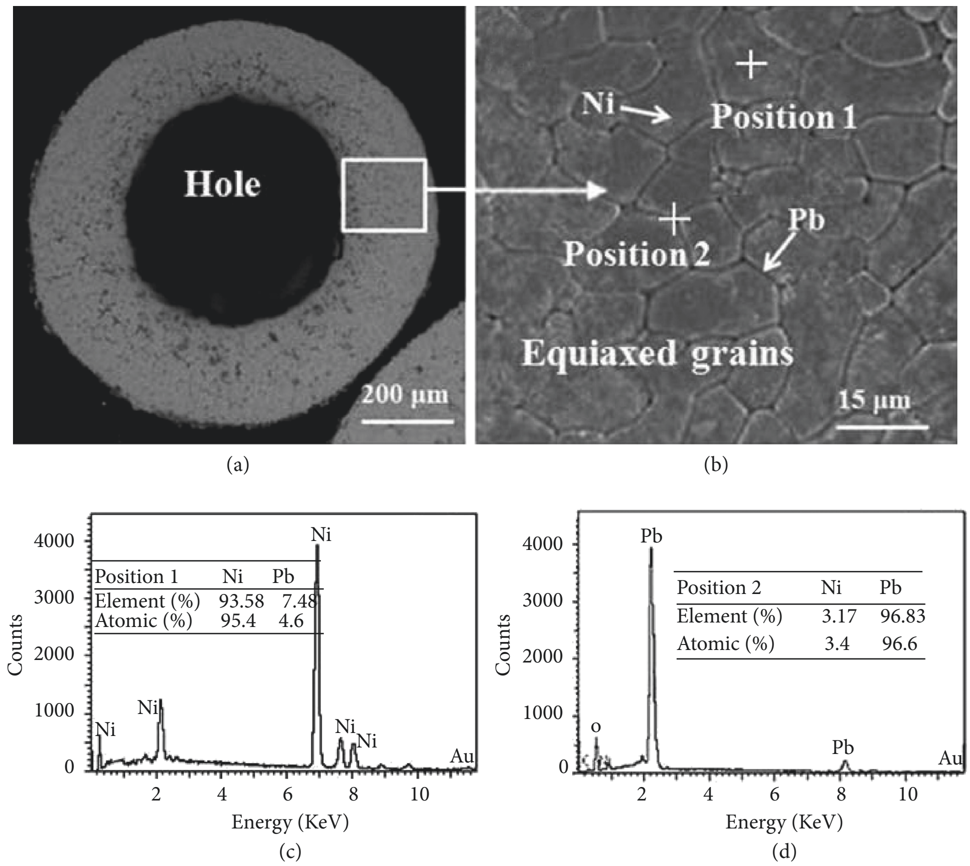

Figure 1: Microstructure and EDS spectrum of Ni-5% Pb alloy hollow particles at 30 m/s: (a) the overall microstructure; (b) the microstructure enlarged view; (c) the EDS spectrum of position 1; (d) the EDS spectrum of position 2.

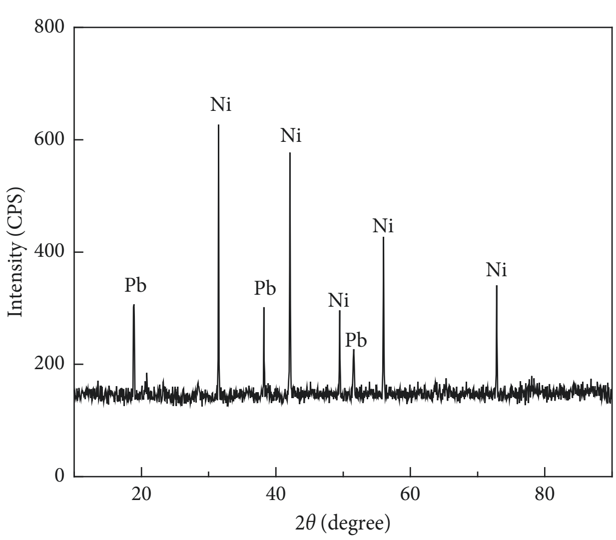

Figure 2: The XRD diffraction of Ni-5% Pb alloy hollow particles at 30 m/s.

single-phase, Ni-rich phase, and Pb phase as shown in Figures 3(b) and 3(c). The Ni-rich phase was grown as dendrites, and the Pb phase was uniformly distributed in the grain boundary of Ni dendrite, which formed fine bulk equiaxed grains with symplastic growth [9]. From the above results, it could be inferred that because of increase in the solidification rate, the shear stress and turbulence intensity of the Ni-5% Pb alloy hollow particles were greatly improved. Moreover, through particle size and hole size measured at 30 and 50 m/s, these changes as function of the roller speed were quantified as shown in Figure 4. The sizes of particle and hole measured were decreased with solidification rates increasing. By the fitting analysis, the function on particle size and hole size changes with the roller speed were linear relationship. It can be predicted that smaller size hollow particles could be obtained by increasing the roller speed.

3.3. Formation Mechanism of Alloy Hollow Particle. Through the above analysis, the hollow structure could be finally formed in alloy particles under the single-roller rapid solidification process only when the external gas invaded into alloy droplets. So, the formation mechanism of Ni-5 wt.% Pb alloy hollow structure is mainly decided by invading ways of gas in the process of rapid quenching. In this work, it is considered that there are several ways for the gas entering alloy liquid droplets. Firstly, under condition of melt superheating, the atomic distance in melt metal was increased, the hole density was raised, and its volume was expanded by 3~5%. The higher superheating and hole density caused the atoms in the melt metal to be more activated and the solubility of gas atoms to be increased.

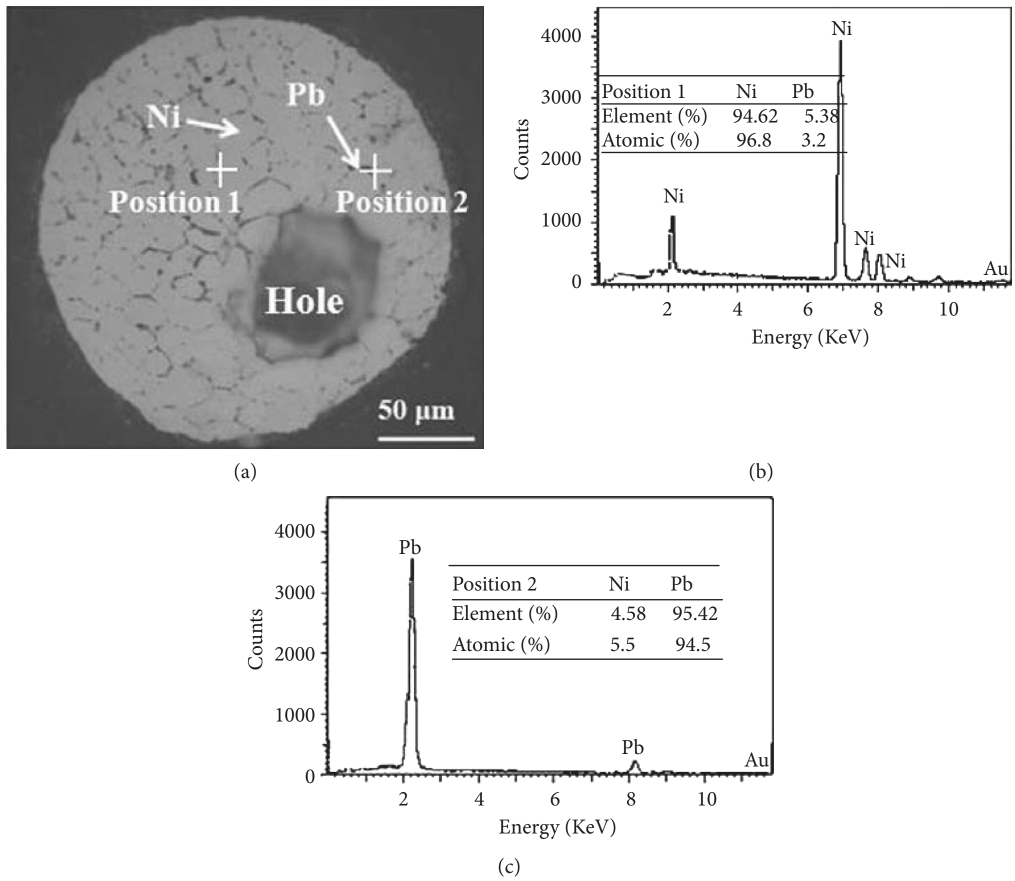

Figure 3: Microstructure and EDS spectrum of Ni-5% Pb alloy hollow particles at 50 m/s: (a) the microstructure; (b) the EDS spectrum of position 1; (c) the EDS spectrum of position 2.

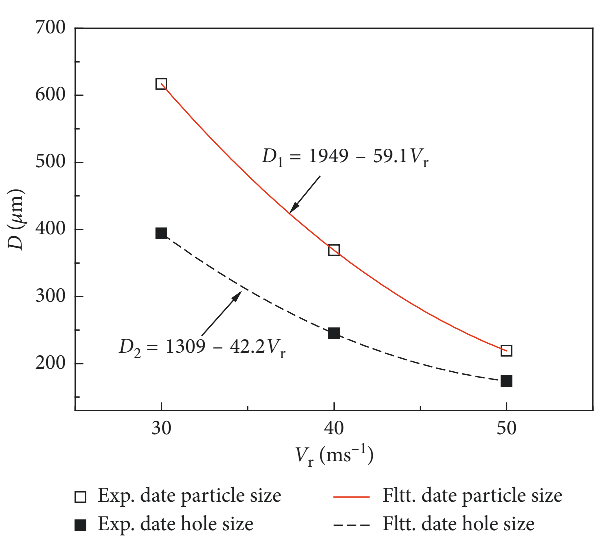

Figure 4: Particle size and hole size of Ni-5% Pb alloy hollow particles versus rate.

Under high-velocity flow, the melt surface was broken. The gas atoms rapidly immersed into the melt and occupied the hole position. Then, microgas cores were formed by the collision and coalescence, which resulted in the natural aeration [10]. Secondly, the alloy melt was jetted out from the nozzle and contacted to the Cu roller surface with high-speed rotation. Because the superheat melt flowed at high velocity, turbulent flow appeared, which could further cover and involve the ambient gas to result in the forced aeration. Thirdly, Ni is a high melting point component, while Pb is a low melting point component. Under higher superheating, the low melting point component underwent gasification and formed a gas nucleus, resulting in self-aeration. The above three invading ways may cause the gas to enter into the alloy liquid droplets and stay inside, thus solidifying into alloy hollow particle structure during rapid solidification.

In this work, the formation process of Ni-5 wt.% Pb alloy hollow structure is shown in Figure 5. At time t_0, the continuous melt was broken to form small Ni-Pb alloy droplets under the gas pressure. Because of higher rotating speed of the Cu roller, the effect of shear stress by Cu roller surface was great. At the moment Ni-Pb droplet was blown out, the surrounding gas began to overcome the surface tension in droplets considering increased turbulence and reduced pressure. Then, the droplet surface was depressed from outside to inside at the moment t_1 shown in Figure 5. With the roller rotating speed increasing, the turbulence was further increased and the depth of droplet surface was deepened as shown at t_2 moment. When roller speed was increased to the maximum, the outer ambient gas and the Pb vapor gas in the solidification process began to overcome the

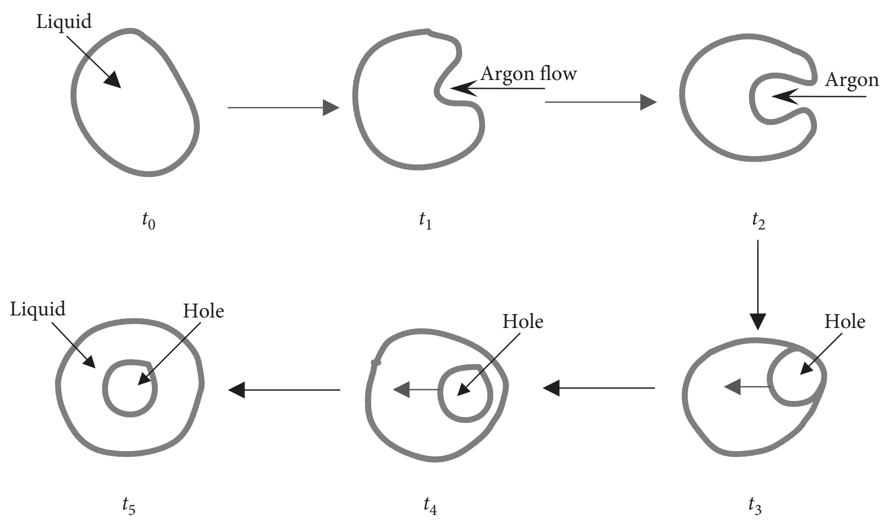

FIGURE 5: Schematic diagram of the formation of hollow particles. t_0: melt rapidly quenched into small droplets; t_0~t_1: liquid interface dropped; t_1~t_2: droplet surface deepened further; t_2~t_3: gas entered into liquid under pressure; t_3~t_4: the hole closed inside the droplet; t_4~t_5: the hole migrated to the interior of droplet.

melt surface tension into the droplets, such as the t_3 moment shown. At time t_4, due to the high solidification rate and smaller Ni-Pb alloy droplet, the droplet surface could be solidified rapidly; then, these gases in droplets could not escape and were trapped in alloy droplets with the formation of holes [11]. While the hole in particle was forced to move toward the high-temperature area (the central part of hollow particles) under the positive temperature gradient, the hole was migrated to the center of droplet at t_5 time [12, 13]. Therefore, the holes were all in the interior of alloy particles in this experiment as shown in Figures 1 and 3. The reason of the hole in alloy particles deviated into particles center is that the hole did not migrate to the center when the solidification completed.

Actually, in our work, we have done a lot of experiments at the same rapid solidification rate, and a large number of particles were obtained and collected from the experiment. The different results of some individual single particles had been prepared and achieved during the whole solidification process as shown in Figure 6. These results showed that, under same conditions, the hollow structure of particles are not quite the same, including all the results at each time in Figure 5. The liquid droplet surface was depressed from outside to inside in Figure 6(a), which agrees with the analysis at moment t_1 in Figure 5. The morphology in Figure 6(b) shows the outer ambient gas and the Pb vapor gas in the solidification process began to overcome the melt surface tension into the droplets while the hole in the particle moved toward the central part of the hollow particles as shown in Figures 6(c) and 6(d). Although Figure 6 shows the results of a single particle through the whole solidification process, the individual results have been contacted to the continuous solidification process, which could also help us to analyze and infer the dynamic formation process shown in Figure 5.

Through further analysis in this work, it was found that, with the roller speeds increasing, hollow ratio of hollow particles were increased as shown in Figure 7, and the

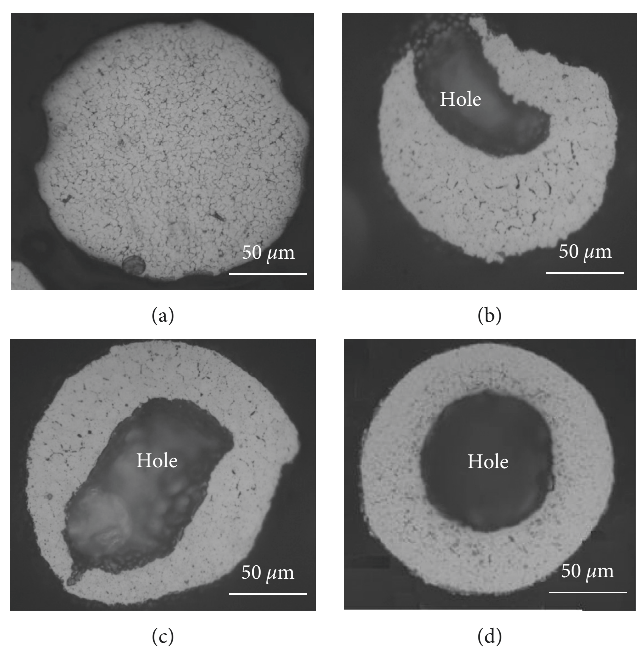

FIGURE 6: Several different morphologies of Ni-Pb alloy hollow particles at 50 m/s.

turbulence was further increased. Although the Pb content of Ni-5 wt.% Pb alloy hollow particles was too lower to form more Pb vapor gas, the outer ambient gas and the Pb vapor gas in the solidification process more easily overcame the melt surface tension in the droplets, then formed the hollow particles. The increase in roller speeds was conducive to Ni-5 wt.% Pb alloy hollow particles formed with low Pb content.

4. Conclusion

(1) Ni-5 wt.% Pb alloy hollow particles with low Pb content were prepared by the single-roller method

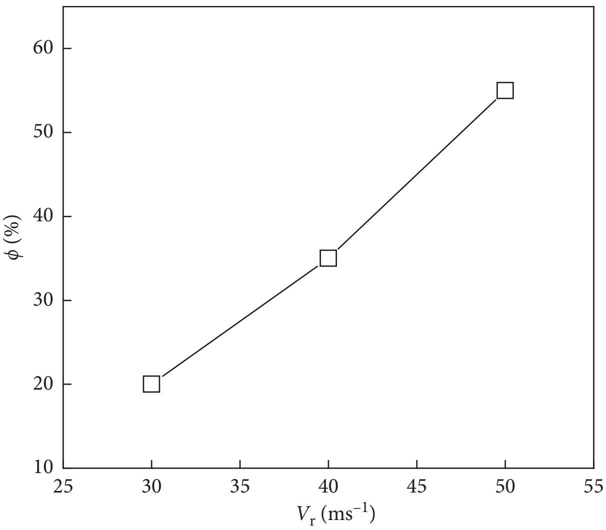

Figure 7: Relationship between the hollow ratio of Ni-5% Pb alloys with low Pb content and the roller speed.

rapid solidification technology at different solidification rates. The hollow particle shape was regular, rounded, and closed, in which its microstructure consisted of the Ni-rich phase with equiaxed grain and rich Pb phase distributed in Ni dendrites boundaries. With increase of the solidification rate, the size of alloy hollow particles and their volume of holes were decreased. Moreover, the hole was deviated from the center of particles.

(2) The formation of rapid solidification of Ni-5 wt.% Pb alloy hollow particles is mainly the interaction between the high-velocity fluid and the ambient gas at the liquid/gas interface. Under the condition of rapid solidification, the melt turbulence is enhanced by the larger shearing effect of Cu roller surface. The surrounding gas and Pb vapor could easily overcome the surface tension and enter into the liquid drops to become the hollow structure particles. The increase in roller speeds was conducive to Ni-Pb alloy hollow particles formed with low Pb content.

Data Availability

The XRD and SEM expression data are available from the manuscript, and other data generated or analyzed during this study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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