Hybrid atomization method suitable for production of fine spherical lead-free solder powder

Kazumi Minagawa, Hideki Kakisawa, Susumu Takamori, Yoshiaki Osawa, Kohmei Halada

Abstract In response to the problem of environmental protection, the electronic industry is studying the lead-free alloys as substitutes for lead-containing solder alloys. At the same time, with progress in electronic devices in recent years, smaller size and higher precision are strongly demanded in electronic board connections. Therefore, it is necessary to prepare fine powders of solder paste for these connections. To produce such lead-free solder balls, a novel powder-making process, "hybrid atomization" that combines gas atomization and centrifugal atomization, was used. This technique produces very fine and spherical tin alloy powders with a mean diameter of about ten micrometers and very narrow size distribution with few satellites at low production cost. Taking a Sn-9mass%Zn alloy as an example, process experiments were carried out, and the effect of temperature, spray distance and disk rotating speed on the resultant powder properties were examined. The optimal processing conditions were determined from the results; the influences of the processing parameters on the properties of the obtained powders were quite different from those in the conventional atomization processes. The spherical powder with a mean diameter of 10.6 μ m and a standard deviation of 1.3 ~ 1.7 was obtained in the determined optimum condition.

Key words lead-free solder • fine spherical powder • hybrid atomization

K. Minagawa[⊠], H. Kakisawa, S. Takamori, Y. Osawa, K. Halada Ecocirculation Processing Group, Ecomaterials Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba City, Ibaraki 305-0047, Japan, Tel.: +81 29 859 2642, Fax: +81 29 859 2601, E-mail: Minagawa.Kazumi@nims.go.jp

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Introduction

Soldering technique is a method of joining metals and tin-lead alloys have been applied as the dominant soldering materials. With the progress of advanced electronic technology, soldering technique is finding more applications in small electronic devices such as cell phones, digital cameras, and notebook-type personal computers. However, it has been indicated that lead contained in electronic devices by soldering in the landfills may possibly leach out, and then pollute the groundwater and rivers, and consequently affect the central nervous system of human bodies by beverages. From the viewpoint of protecting the global environment, legal regulations on solder which contains lead have been studied and implemented in many nations [1, 2]. Based on this background, lead-free solder alloys have been the object of considerable research and development, and a changeover from the conventional lead-containing solder to lead-free solders is underway.

Research and development has been carried out on a variety of alloy systems for lead-free solders [7, 15], and the mechanical strength, joining properties, wet ability, and other properties of alloys have well been studied [3, 5, 9, 11]. Meanwhile, with improvement in the performance of electronic devices, smaller and more precise connections in electronic boards are required. Thus, reforming the organic substances in lead-free



Fig. 1. A photograph of production by the centrifugal atomization.

solder paste and development of fine spherical powders [12] are strongly desired. This paper introduces a new powder production technology that enables an efficient production of high quality fine spherical powder with a size of 20 μ m or less, much finer than those made with the conventional solder production.

Conventional solder powder production process

Conventional solder powder is mainly produced using the centrifugal atomization. A photograph of production by the centrifugal atomization is shown in Fig. 1. Molten solder alloy is fed under free fall to the center of a rotating disk (material: metal, graphite, ceramics) installed at the bottom of the device, and forms a liquid film on the disk. Powder is produced by allowing molten droplets to scatter, in the form of droplet, from the edge of the disk as it rotates at a high speed. As an advantage of this method, the powders with low-content oxygen can be easily produced because the powder is produced in an inert gas atmosphere. Furthermore, because the liquid film scatters in the form of droplet, void-free powders with preferable properties, such as fluidity and arrangement, can be obtained. However, with the centrifugal atomization, if the melt is not poured onto the center of the rotating disk, the high-speed disk will

become unbalanced, making it difficult to form a stable liquid film, and then the preparation of powders will become impossible. Therefore, there are restrictions on the metal melt feed rate, and the liquid film on the rotating disk must be thick. This means the particle size of powders produced by this method is large, of several $100 \,\mu\text{m}$. Moreover, due to the properties of the metal melt, namely, its high density and low viscosity, the atomization modes of melts under centrifugal force [13, 14] are limited to film formation or columnar formation mode, as shown in Figs. 2c and 2d. Thus, under the current conditions, it is difficult to form fine particles of solder alloys. To solve these problems, it has been tried to dramatically increase the rotational parameters, such as the rotational speed or the radius of the rotating disk, or to reduce the melt feed rate [4]. Even though, the average particle size is limited to approximately $30-50 \ \mu m$ under the optimum production conditions. Commercial solder pastes are composed of particles of several µm size level, but with the present technology, these powders must be obtained by screening powders produced by the conventional method. In light of future requirements for miniaturization and higher functionality in electronic devices, fine spherical solder powder with a size of 20 µm is demanded, considering high density packaging in board connections.

Development of new powder production method

In previous documents, it has been reported that the atomization modes of droplets due to centrifugal force in the centrifugal atomization comprise the four atomization modes shown in Fig. 2. Among these, film formation and columnar formation in the previous section are the conventional atomization modes of metal droplets. However, according to the previous experiments and discussions about the aqueous solutions and organic solutions, etc. [6, 10], direct drop formation and ligament formation shown in Figs. 2a and 2b have been reported. This suggests that, if it were possible to shift a molten metal to the powder formation mode displayed by organic solutions, dramatic refinement in particle size in comparison with the conventio-



Fig. 2. Powder formation mode in the centrifugal atomization.



Fig. 3. A schematic diagram of hybrid atomization procedure.

nal method and control of the size distribution would become possible.

The authors [8], therefore, conceived a novel powder production method, termed the hybrid atomization, which realizes an atomization mode that had been impossible with the conventional method from the various viewpoints mentioned above. The hybrid atomization is a method which incorporates the advantages of the two methods of atomization based a fluid jet (gas atomization) and atomization utilizing the inherent instability of the molten material (centrifugal atomization). Concretely, as shown in Fig. 3 (schematic diagram and photograph of production process), this is a method in which the molten metal is atomized to a size of several 10 to several 100 µm by the gas atomization and sprayed uniformly with over the entire surface of the rotating disk. The disk is rotated at high speed, while forming a uniform liquid film with a thickness of $10 \,\mu m$ or less, and powder is produced by causing fine droplets to scatter from the edge of the disk. As can be observed in the photograph, when the fine droplets are scattered from the edge of the rotating disk, the produced powder displays a smoke-like consistency. From this, it can be inferred that the powder is extremely fine.

Moreover, with this method, (as with the centrifugal atomization), a fine spherical powder with a size of $10 \,\mu\text{m}$ or less can be produced efficiently by controlling the physical properties (density, surface tension, viscosity) of the metal melt and the speed of the rotating disk, and simultaneously, production of powders within a narrow size distribution is also possible.

Production of fine spherical lead-free solder powder with both

Centrifugal atomization and hybrid atomization

This section will describe the production of a fine spherical powder by the hybrid atomization using a Sn-9mass%Zn lead-free solder, whose melting point

is close to that of the conventional tin-lead eutectic solder. The present technique is economical in terms of material cost, and enables soldering without changing the packaging temperature conditions in electronic device manufacture.

Figure 4 shows the particle size distribution of the Sn-9mass%Zn powder produced by the centrifugal atomization and the hybrid atomization. The production conditions with the respective powders in this case were uniform, with a metal melt temperature of 573 K and a rotating disk diameter of 50 mm. Powders were produced using a rotating disk speed of 50,000 rpm with the centrifugal atomization and 5000 rpm with the hybrid atomization. The gas atomization pressure used with the hybrid atomization was 1/10 that in ordinary gas atomization.

The width of the particle size distribution of the powders produced by the two atomization methods is controlled by the balance of centrifugal force and physical properties of the melt. However, the peak position value shifts to the finer side with the powder size produced by hybrid atomization. Furthermore, the mean particle size of the powder produced by the centrifugal atomization was 28.6 μ m, but in contrast, this was refined to 17.8 μ m with the hybrid atomization,



Fig. 4. Comparison of results between hybrid atomization and centrifugal atomization.

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Weight [%]

even though the speed of the rotating disk was only 1/10as fast as with the conventional method.

This fact relates to the thickness of the liquid film of the molten metal on the rotating disk. With the centrifugal atomization, the melt must be supplied to the center of the rotating disk due to limitations on the molten metal feed rate. Then, the molten metal forms a thick film in the center of the disk. This is pulled by centrifugal force to the disk edge, where it forms droplets which are scattered from the edge, producing powder. Accordingly, a thick film of the liquid naturally forms at the edge of the rotating disk, and the atomization mode of droplets is limited to film formation or columnar formation mode, even under high speed rotation at 50,000 rpm, thus limiting refinement of the powder size.

On the other hand, with the hybrid atomization, it is conjectured that fine powder can be produced from the droplets scattered from the edge of the rotating disk at 1/10 the rotational speed used with the centrifugal atomization, even with the same melt feed rate, because the melt is broken up once into fine droplets by the gas atomization and sprayed uniformly over the entire surface of the rotating disk, where it forms a thin (10 µm or less) and uniform liquid film.

Refinement of powder size by hybrid atomization

With the hybrid atomization, similar to the centrifugal atomization, refinement of the powder size can be promoted by controlling the physical properties of the metal and the speed of the rotating disk. This section will discuss refinement in a case where the physical properties of the metal are changed. Figure 5 shows the size distribution of powders produced when the speed of the rotating disk was held constant at 5000 rpm and the melt temperature was varied to 573 K, 673 K, and 823 K. As the melt temperature increases, the mean particle size of the produced powder becomes smaller, and is extremely fine, at 12.5 µm, at a temperature of 673 K. In the particle size distribution, the 1st peak, which can be seen at around $15 \,\mu\text{m}$, had decreased, while the second peak, at $10 \,\mu\text{m}$ and less, had increased. However, the powder produced at 823 K was coarser than the other powders. It was

Fig. 5. Particle size distributions of powders under different superheating.

Table 1. The values of all the physical properties of the Sn-9 mass%Zn alloy

	573 K	673 K
Surface tension [N/m]	0.563	0.555
Viscosity [Pa·s]	0.00205	0.00162
Density [kg/m ³]	6896	6830

inferred that this occurred because the melt temperature was 10 K higher than the vaporization temperature of Zn, which is 813 K. As a result, the Zn content decreased, causing a deviation in the alloy composition, and the melting point of the alloy shifted to the high temperature side, resulting in coarsening of the produced powder. Nevertheless, these results clearly show that refinement of the powder size displays temperature dependency. In other words, as shown in Table 1, the values of all the physical properties of the Sn-9mass%Zn alloy, including surface tension, viscosity, and density, decreased as the temperature increased, and the powder produced when the physical property values of the metal melt were reduced clearly showed a finer particle size.

Next, with regard to the relationship with the rotational speed of the disk, which is another factor in particle size refinement. Figure 6 shows the size distribution of the powders produced when the rotational speed was changed from 5000 rpm to 20,000 rpm. The melt temperature was held constant at 673 K, because this is the temperature which gives the optimum particle size refinement, as mentioned above.

Scanning electron microscope images of the produced powders are shown in Fig. 7. As the rotational speed of the disk was increased, a large amount of powder with a size of under 5 µm was observed, and the powder displayed a spherical shape. In these particle size distributions, the mean particle size decreased as the rotational speed increased, and became extremely fine, at 10.6 µm, at a speed of 20,000 rpm. The yield of under $26 \,\mu\text{m}$ showed a high value of 90%. The powder showed a size distribution with two peaks in which the 1st peak, at around 15 µm, decreased, while the 2nd peak, at around 5 µm, increased with rotational speed. This particle size distribution corresponds to direct drop formation mode as the atomization mode of droplets due to centrifugal

Fig. 6. Particle size distribution of powders under different disk rotation speeds and diameters.









force, as shown in Fig. 2. In direct drop formation mode, droplets grow at the end of the disk under the balance of surface tension and centrifugal force. Then a droplet removes from the disk by the centrifugal force when the surface tension cannot support it. This mode results in main droplets with nearly the same diameter and subdroplet which are formed at the tail of main drops. Therefore, the size distribution has a double peak. In the hybrid atomization, a uniform liquid film with a thickness of 10 µm or less forms over the entire surface of the rotating disk. In this case, the supply rate of droplets which scatter from the edge of the rotating disk is extremely small in comparison with that in the conventional method. It was, therefore, conjectured that the atomization mode was direct drop formation, as shown in Fig. 2a, because the relative effect of the physical properties of the molten metal and centrifugal force was larger than the droplet supply rate, and as a result, a two-peak particle size distribution was obtained. Thus, although separation in the form of droplets had not been possible with molten metals using the conventional powder production method, these results suggest that it is possible to realize the droplet atomization mode observed with organic liquid and other substances in metal melts for the first time by using the hybrid atomization.

Conclusion

This paper has described a production method for fine spherical lead-free solder powder for realizing high density packaging in advanced electronic devices. This technique, called the hybrid atomization, enables efficient production of fine spherical powders with sizes of 20 µm and less, which could not be obtained with the conventional powder production method, and also allows easy control of the particle size distribution of the spherical powder being produced by controlling the physical properties of the metal melt and the speed of the rotating disk. As a more efficient production method for fine spherical powders, which will be indispensable in the extremely small and complex connections required in electronic boards accompanying miniaturization, higher density, and higher performance in future electronic devices, the hybrid atomization is

a new powder production process which offers an alternative to the existing processes. In the future, application to the production of various lead-free solder powders, which are now under development, is also expected.

References

- 1. European Commission (1997) End of life electrical and electronic equipment working paper. Directive General IV, Document E 3, 9, October 1997
- 2. European Commission (1998) End of life electrical and electronic equipment working paper, second draft. Directive General IV, 27 July 1998
- Fuji T, Hirose A, Kobayashi K (2000) Microstructure and mechanical properties of microjoints with Sn-Ag lead free solders. In: Proc of the 7th Symp on Microjoining and Assembly Technology in Electronics, Yokohama, Japan, pp 211–216
- Halada K, Suga H (1990) Theoretical investigation on parameters of centrifugal atomization of metal powder. Journal of the Japan of Powder and Powder Metallurgy 37;4:492–499
- Kariya Y (2003) The influence of Ag concentration on shear fafigue properties of the Sn-Ag-Cu solder vamp for flip chip junction. Metal 73;7:635–639
- Matsumoto S, Takashima Y (1983) Recent progress of liquid atomization technology. The Society of Chemical Engineers, Japan 47;9:540–543
- McCormack M, Jin S, Kammlott GW, Chen HS (1993) New Pb-free solder alloy with superior mechanical properties. Appl Phys Lett 63;1:15–17
- Minagawa K, Halada K (2005) Production of metal fine powder. Patent No. 3511082, Japan
- Nakahara Y, Ninomiya R, Matsunaga J, Takemoto T (1999) Mechanical properties and oint strength of Sn-3.5Ag-3In-xBi solders. In: 6th Symp on Microjoining and Assembly Technology in Electronics, Yokohama, Japan, pp 341–346
- 10. Shiya T (1972) Fine particle refinement by rotation disk. The Society of Chemical Engineers, Japan 36;1:10–16
- 11. Suga T (1999) Lead-free solder technique. The Nikkankogto Shmbun Ltd
- 12. Suganuma K (2003) Restriction in Europe and current state of technology for lead free solder. Metal 73;7:648-659
- Tanazawa Y, Miyasaka Y, Umehara M (1959) On the filamentation of liquid by means of rotating discs (1st Report, Mode of filamentation of viscous liquid). Mechanical Engineers 25;156:879–888

- Tanazawa Y, Miyasaka Y, Umehara M (1959) On the filamentation of liquid by means of rotating discs (2nd Report, Mode of filamentation of viscous liquid). Mechanical Engineers 25;156:888–897
- Vianco PT, Frear DD (1993) Issues in the emplacement of lead-bearing solders. Jon – Journal of the Minerals Metals and Materials Society 45;7:14–19