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Preparation of metal alloy powder by semi-solid processing

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Abstract A laboratory study was carried out, using Pb–15 wt.% Sn alloy on self-made apparatus, to determine the solidification behavior of the semi-solid slurry with the solid fraction beyond 0.6. It is found that the solid–liquid separation is obvious in the samples with the solid fraction beyond 0.6. According to this character of semi-solid processing, a kind of single-crystal powder coated with Pb–Sn eutectic was made during continuous stirring and cooling processes. The analysis and discussion indicated that this approach can reduce the content of oxide and impurity in the powder.

Introduction

In recent years, semi-solid metal (SSM) processing has become a competitive manufacturing routes for military, aerospace and most notably automotive components gradually [1–3]. In Europe, suspension parts, engine brackets and fuel rails for automotives are being produced through SSM processing. In the USA, examples made by SSM processing also include mechanical parts for mountain bikes and snowmobiles [4], while in Asia, more concentration is on the production of electronic components such as laptop cases and electrical housing components, specially in magnesium alloys via thixomolding e.g. [3]. In these processes a molten metal is cooled with the stirring. Through stirring, they will show a globular growth instead of a dendritic growth for the primary phase, and these spherical particles disperse in the melt. From the point of view of most current researcher, the most important advantage of this process is the non-turbulent filling of the die, which results in forming the unique rheological properties in alloy slurries with a solid fraction less than 0.6 sheared between their liquidus and solidus temperatures [5]. All of the present SSM processing techniques, e.g. predominantly thixo- and rheo-casting/moulding routes, rely upon these properties. Now it has been clearly known that the unique rheological properties are originally from the non-dendritic microstructure in the semi-solid slurries during SSM processing. Therefore, the microstructural evolution with the solid fraction less than 0.6 in the semi-solid slurry under shear has been extensively investigated in the last three decades [3–7].

However, one thing need to be mentioned is that apart from the solidification behavior with the solid fraction of 0–0.6 under shearing, the morphological selection with the solid fraction beyond 0.6 under stirring is also an interesting research field. It should be indicated that, under this condition, through stirring and simultaneous cooling, the solid phase can be separated easily from the two phases' mixture, because of the weak inter-granular bonding force. This solidification character can be utilized to prepare metal powder. Unfortunately, few attentions have been paid

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on it so far. Hence, in this paper, a new method was proposed to investigate the microstructure evolution with the solid fraction beyond 0.6 under stirring. The objective of this work was to make powders through SSM processing by using Sn–15 wt.% Pb alloy.

Experiment procedure

Material preparation

The Sn–15 wt.% Pb alloys, whose phase diagram is given in Fig. 1, were prepared from 99.8wt% Sn and 99.8wt% Pb by electric resistance furnace melting process in an plumbago crucible under high purity argon atmosphere. Then, the rod specimens with 14 mm of diameter and 14 mm of length were fabricated by casting. The associated liquidus temperature T_l is 215 °C and the freezing range ΔT_0 is 32 °C. The experimental temperature range was set from 215 °C to 183 °C. The specimens were placed into the crucible in self-made apparatus as shown in Fig. 2.

Powder-making processing

The samples were heated up to 255 °C which is 40 °C above the temperature of liquidus with the heating rate $K = 50$ °C/min and kept in this temperature for 5 min in order to obtain chemical homogeneity, then the temperature was decreased. When the temperature decreased to 235 °C, the melt is kept for 5 min with mechanical stirring under this environment, after that, the temperature was cooled down to 200 °C with cooling rate of 2 °C/min and shear rate of 280 s^{-1}.

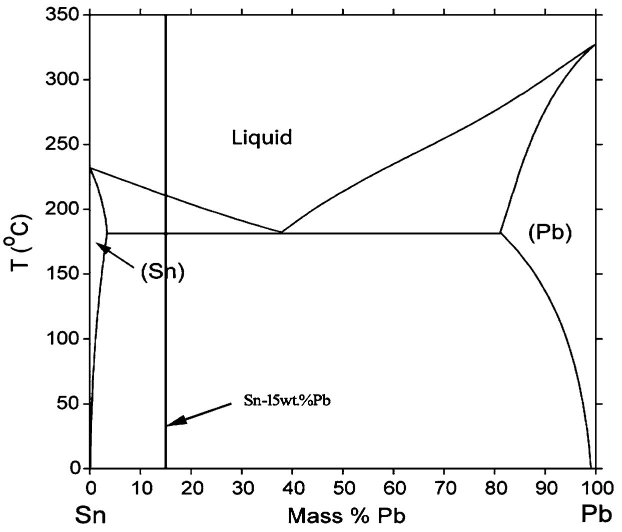


Fig. 1 Sn–Pb alloy phase diagram

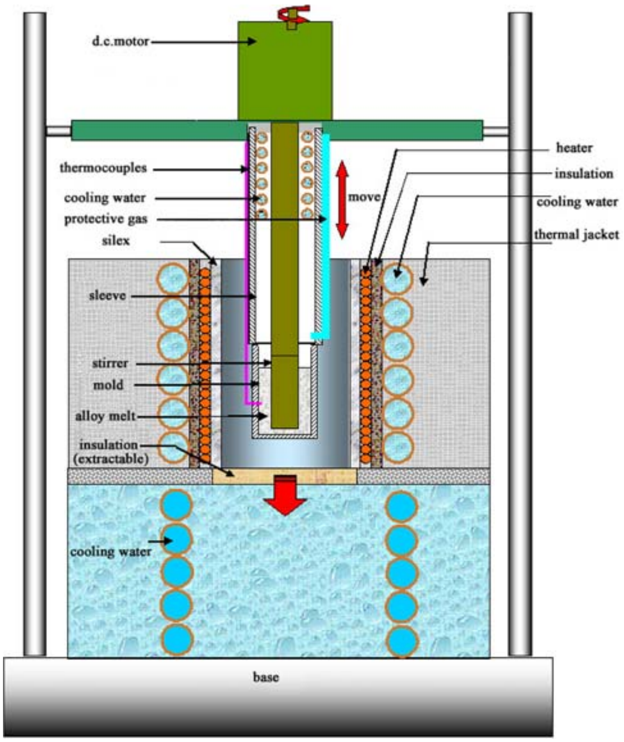


Fig. 2 Schematic of semi-solid mechanical stirring process system

At this moment, the solid fraction of the semi-solid slurry could be beyond 0.45 according to the Scheil equation, which can be expressed as follows [8]:

$$f_s = 1 - \left(\frac{T_M - T_L}{T_M - T}\right)^{\frac{1}{1-k}} \quad (1)$$

where f_s is the solid fraction of semi-solid slurry and T_M is the melting point of the pure solvent. Then the shear rate was decreased to 30 s^{-1} for the sake of safety. When the temperature was lower than the solidus temperature, the stirring was stopped and the specimens with crucible were quenched. It was interesting to note that the final production in specimens mainly consisted of the powders. The powder formation processing and the temperature variation during this process are respectively illustrated in Fig. 3 and Fig. 4.

Characterization

The microstructures of the samples were characterized using optical microscopy with Leica Cambridge Quantimet 500 Image Processing and Analysis System. Electron micrographs of the powder particles were recorded using a Scanning Electron Microscope (AMARY-1000B). The analysis of elemental compo-

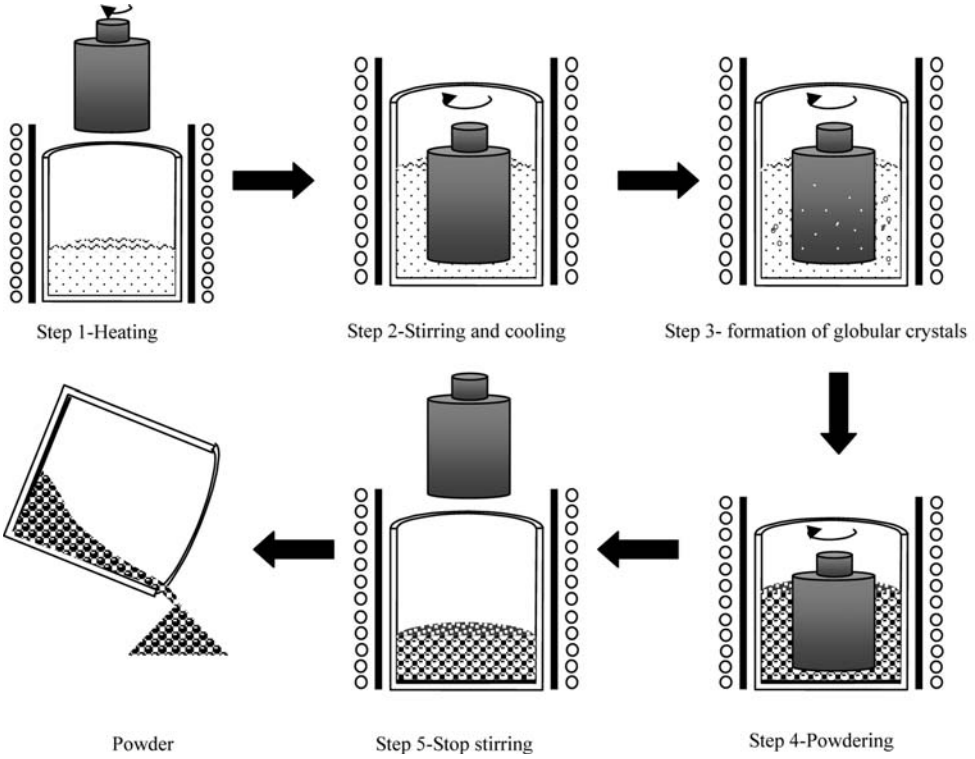


Fig. 3 Schematic illustration of powder preparation by semi-solid processing

sition was carried out by energy-dispersive X-ray spectroscopy (Finder-1000).

Results and analyses

Microstructure

Microstructure of the Sn–15 wt.% Pb alloy samples under continuous cooling and shearing are shown in Fig. 5. After the step-1 heating (step-1 to step-5 refer to Fig. 3) in 255 °C and step-2cooling with 2°C/min and shearing with 280 s^{-1}, the liquid alloy was gradually solidified to mushy (semi-solid) state. During this process, nucleation happened in the liquid and the spherical particle was first observed around the rotator in step-3 as shown in Fig. 5a. Furthermore, the particles grew to a certain size under the stirring and cooling, the amount of the primary globular crystals increased rapidly instead of the further growth of the already existing nuclei as shown in Fig. 5b. After the change of the stirring rate, lots of new particles appeared as shown in Fig. 5c. When the temperature went on falling to the solidius temperature, it was found that the solid–liquid separation was obvious in the samples for the solid fraction beyond 0.6. There were more solid particles in the upper part of the sample and more particles aggregating at the same time. The solid fractions at the bottom were relatively smaller than that in the upper of sample. Consequently, when the temperature was further decreased to 182 °C, which is just below the solidus temperature, the solid–liquid separation became more and more obvious, and lots of powders were observed in the sample as shown in Fig. 5d. It was found that the obtained powder was spherical or near-spherical particles and lots of them stuck together to form a bigger powder. No pore and impurity were found in the powders. In addition, every particle was a single crystal grown from the melt.

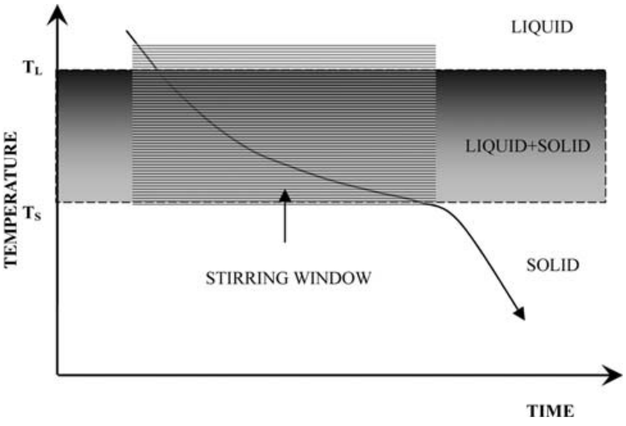
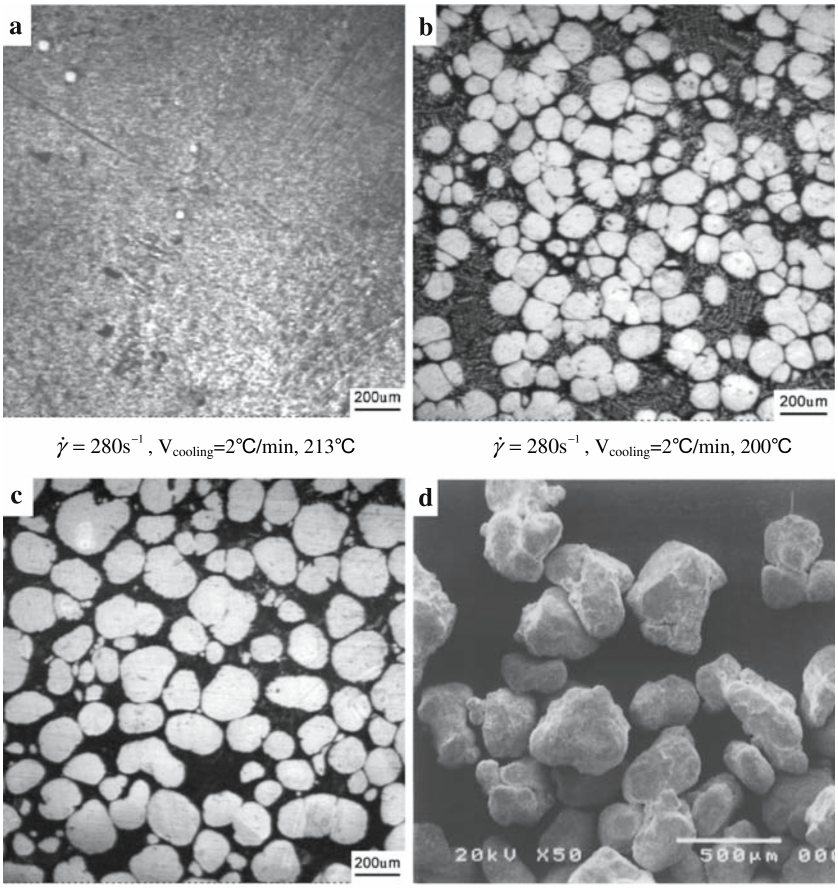


Fig. 4 Schematic representation of the temperature control in powder preparation by semi-solid processing

Fig. 5 Microstructure evolution of Sn–15 wt.% Pb alloy under semi-solid processing



a: $\dot{\gamma} = 280\mathrm{s}^{-1}$, $V_{cooling}$=2°C/min, 213°C

b: $\dot{\gamma} = 280\mathrm{s}^{-1}$, $V_{cooling}$=2°C/min, 200°C

c: $\dot{\gamma} = 30\mathrm{s}^{-1}$, $V_{cooling}$=2°C/min, 190°C

d: $\dot{\gamma} = 30\mathrm{s}^{-1}$, $V_{cooling}$=2°C/min, 182°C

These experiments suggested that the single-crystal powders can be directly obtained by semi-solid processing.

Composition

When the temperature decreased to the solidius line, the fraction of remained liquid was below 0.33 according to Eq. 1. Due to the composition segregation, the composition of remained liquid would be near or reach the eutectic composition (61.9 wt.% Sn, 38.1 wt.% Pb) as shown in Sn–Pb alloy phase diagram Fig. 1. The experimental results showed that a part of the remained liquid sank at the bottom of the crucible and others were wrapped on the solid particle surface, which making the particles sticking together as shown in Fig. 5d. The presence of a homogeneous coating layer can be proven indirectly by indicating the characteristic surface morphology of the particles using the EDX technique as well as by qualitative and semi-quantitative investigations of cross-sections of the powders. Table 1 shows the composition at the surface of the particles by surface scanning of EDX spectra. It can be found that the surface composition does approach to the eutectic composition of this alloy. The composition along the cross section of a powder was also recorded from the surface to the centre of the powder by EDX spectra. The spectral distribution of Pb and Sn in Fig. 6 shows a clear enrichment of Sn on the surface of the powder, the more it closes to the powder centre, the more Pb it enriches, and however Sn shows the opposite pattern. The enrichment of Sn on the surface of the powder can be regarded as a proof of the eutectic coating. It can be found from

Table 1 The surface chemical composition of Sn–Pb alloy powder

Wt.%	Eutectic composition	Sample 1	Sample 2	Sample 3	Average composition
Pb	38.1	39.03	33.55	21.06	31.21
Sn	61.9	60.97	66.45	78.94	68.79

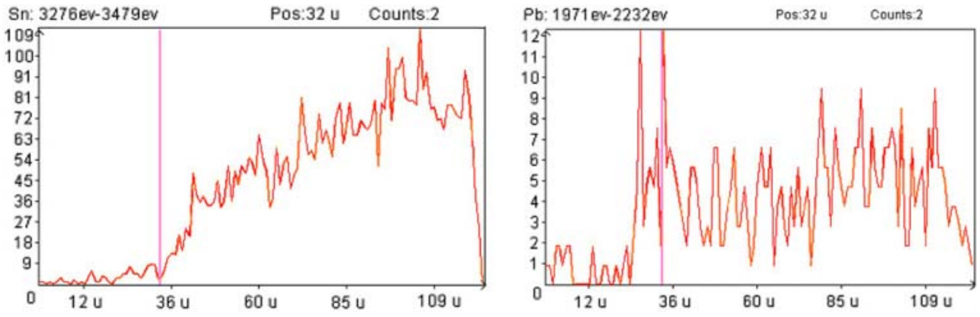


Fig. 6 The composition distribution of Sn–Pb alloy powders prepared by the SSM technology

Fig. 6 that the compositional distribution is relatively uniform in the inner of the powder, which means that the metal powder obtained by this way has obvious benefits in avoiding the powder impurity and solute segregation.

Discussion

It can be seen that the homogeneous single-crystal powders can be obtained if the semi-solid stirring process was controlled properly, as shown in Fig. 3. The primary structure which nucleates and grows up in the low under cooling melt under stirring is different from the dendrite structure obtained in conventional solidification processing, and the primary structure during semi-solid stirring can keep spherical growth to form the spherical particle. With the liquid fraction decreasing gradually, more and more spherical particles appear and grow in the melt. After the solid fraction is beyond 0.6, these spherical particles can be separated from the melt and then the single-crystal metal powder is obtained.

Solute segregation is a general phenomenon during dendritic growth, which results in the impurities being rich in the inter-dendrite due to the complex side-branches, and spherical interface has not complex side-branches, and the smooth liquid–solid interface pushes the impurities into the front liquid, when this process reaches the steady state, it will make the composition in the inner of spherical structure more homogeneous than that in the dendrite. In fact, many previous investigations have been carried out on the compositional distribution on the spherical microstructures under stirring, Young, Rick, Flemings etc. [9] on the stainless steel 304, Lehuy, Masounave, Blain etc. [10]. on the Zn–27 wt.% Al, Molennar and Kool [11] on the Al–6 wt.% Cu, Zhang Shijiang [12] on the Zn–22 wt.% Al, all have observed the inner composition of primary spherical particles distributing uniformly and the solute segregation is small in them. This is an important advantage compared with the conventional solidified microstructures obtained under non-stirring.

It should be pointed out that the existence of the complicate defects are the primary problem to impede the development of powder metallurgy, particularly, among the main three defects (original grain boundary, thermal induced cavity and non-metallic impurity) of the high-performance alloy powders, the most critical one is the non-metallic inclusion, whose size and amount are the main influencing factors of fracture toughness and fatigue life of powder alloy. The non-metallic inclusion is primarily decided by the solidification process. Up to now, the manufacturing method for preparation of powders can be mainly grouped under two categories, ‘‘crushing’’ and ‘‘atomisation’’. Crushing methods include crushing, rolling, milling and grinding, and atomisation methods include Rotating Electrode, Vibrating Electrode (arc), Centrifugal (from a melt) and Rapid Solidification. The most commonly used methods are water or gas atomization. In addition, normally, most of the powders made by these methods are poly-crystals, and the structure mainly consists of the fine dendrites in these processes. So it’s difficult to avoid shrinkage cavity and impurity for general dendritic growth, meanwhile, the solute segregation is serious relatively. In contrast, the obtained spherical powder by semi-solid process forms in the melt, and its surface contacts little with the oxygen, air etc., therefore it can reduce the forming of oxide and non-metallic impurity in the powder.

One more thing need to be indicated is that the present method can realize the in situ autogenic forming of the low-melting alloy coating layer on the particle surface as shown in Table 1. This kind of coating layer is of great benefit to powder metallurgy processing. For example, when the alloy powders are sintered and forming, it can avoid the formation of impurity and heterogeneous microstructure by using chemical agglutinant. So, it will show a beneficial direction to prepare single-crystal alloy powders if these particles can be well separated from the melts.

Summary

This paper presents a new method for manufacturing metal powder by using semi-solid process. It is shown that this method can produce homogeneous single-crystal metal powder with low-melting alloy coating layer. The process mainly consist of using the semi-solid processing to form spherical crystals and separating them from the remaining melt under stirring and simultaneous cooling, which is simple and flexible. It is applicable to almost all kinds of metal alloys. Compared with the conventional powder preparing technology, it is an effective process in improving the uniform of powder composition and avoiding impurity and oxide, which contributes to a big improvement of the mechanical property of materials. Also, it should be noted that this investigation is just a preliminary study and lots of further research should be done theoretically and experimentally to establish the relationships between the desired powder microstructure and the semi-solid processing conditions.

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