Large undercooling, rapid solidification and nucleation mechanism in multi-stage atomization

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Abstract

The large undercooling and rapid quenching during multi-stage atomization were studied both theoretically and experimentally. Results show that these two processes are related closely to, and promoted by, each other. The extent of the undercooling of droplets is dependent on the alloy composition and powder size. Experiments on Sn–Pb alloys reveal that the extent of undercooling has a linear relationship with the logarithm of the mean powder size. Based on the present results, a mechanism of the preferred nucleation on the surface oxide is proposed, to give a quantitative interpretation of the experimental observations. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

In rapid solidification, the undercooled nucleation behavior of metallic melts influences the solid structure profoundly [1], but it is difficult to measure on-line and study the nucleation and solidification laws during the rapid solidification process. Since multi-stage atomization is a new technology for powder metallurgy and rapid solidification, the present understanding of the solidification laws and nucleation behavior during multi-stage atomization is in its embryonic state. Yet, further study and development in this field will be very helpful in developing multi-stage atomization technology, designing new methods for powder-making and producing advanced materials for powder metallurgy. Therefore it is very important to study the principle of solidification during multi-stage atomization although it is extremely difficult or impossible to measure the temperature changes and nucleation behavior of the atomized droplets on-line.

2. Experimental

The typical multi-stage atomization device used in the present work is illustrated schematically in Fig. 1. Sn–Pb alloys with 14 different compositions were molten in the electric furnace under a nitrogen atmosphere where the superheat was 250 K. The molten alloy was first atomized by means of a high-pressure nitrogen gas jet, which exited from a nozzle. Immediately, the droplets were pulverized again by a high-speed rotating disk. Enforced cooling was conducted by a fluid coolant such as water sprayed upon the smaller droplets that were flying away from the disk. The parameters of the atomization process were the following: melt stream diameter 2 mm; gas pressure 0.8 MPa; spraying height 85 mm. Fine powders with an average particle size of 10–20 \( \mu \text{m} \) were obtained.

2 g of the alloy powder for each composition was mixed with 15 ml organic dispersion agent (polyphenylether) and put into a Rigaku/DTA-10A sample cup. They were then heated and cooled under an argon atmosphere to carry out the DTA experiments with the heating and cooling rate being 20 K/min. The undercooling and nucleation behavior of the metallic droplets was measured by DTA.

3. Experimental results

3.1 Large undercooling phenomenon during multi-stage atomization

The experimental results showed that the large undercooling phenomenon existed indeed for multi-stage
atomized powders of Sn–Pb alloy even under slow cooling rates as in DTA. The droplets nucleated far below their melting points and the maximum undercooling was above 100 K. Since the cooling rates of droplets during typical multi-stage atomization reached $10^5$–$10^6$ K/s and additional dynamic undercooling would be produced under rapid quenching, the actual undercooling during multi-stage atomization would be larger. Fig. 2 showed the typical DTA results of multi-stage atomized Sn–Pb powders with different compositions. For pure tin, the undercooling was $\Delta T = 94$ K; whilst for pure lead, $\Delta T = 54$ K. These were about 26 K lower than the emulsion results obtained by Rasmussen and Loper [2]. This showed that multi-stage atomization belongs to heterogeneous nucleation solidification although there exists large undercooling during the atomization.

3.2. The relation between undercooling and the composition of multi-stage atomized Sn–Pb alloy powders

Fig. 2 also reflects the effect of composition on the nucleation temperature and undercooling of Sn–Pb powders, whilst Fig. 3 shows the relation between nucleation temperatures and phase diagram.

As shown in Fig. 3, for compositions of less than 20 wt% Pb, the nucleation temperatures $T_n$ decline with increasing lead content and are almost parallel to the liquidus line, while for higher compositions, $T_n$ are nearly independent of composition, although $T_n^\prime$ increases with increasing lead content within the range of 25–80 wt% Pb. The phases forming at $T_n^\prime$ and $T_n$ for different compositions were deduced by interrupted cycles in DTA [3]. The results indicate that at $T_n^\prime$ the primary lead-rich phase nucleates while at $T_n$ the tin-rich phase nucleates.

3.3. The relation between the undercooling and particle size of multi-stage atomized Sn–Pb alloy powders

As shown in Fig. 4, the smaller is the average particle size dm (mass median size), the larger is the undercooling $\Delta T$. The undercooling decreases with increasing particle size, but after the average particle size reduces to a certain degree, the increasing trends of undercooling slow down. In addition, the undercooling has a linear relationship with the logarithm of the mass median size during undercooled solidification for the multi-stage atomization of Sn–Pb alloy.

4. Analysis and discussion

4.1. Analysis of multi-stage atomization process

The multi-stage atomization process possesses the characteristics as follows.

(1) Rapid quenching effect. After several times of pulverization, the droplets become very fine, and the rapid quenching effect is very obvious.
According to the Newtonian cooling model [4], \( T \propto K(T - T_s)/(\rho Cr) \). Therefore, the smaller is the droplet radius \( r \), the higher is the cooling rate. Many of the present experimental results showed that the cooling rates of typical multi-stage atomized powders were \( 10^5 - 10^6 \) K/s [5,6].

(2) Large undercooling effect. During multi-stage atomization, water or another inert liquid medium is sprayed onto the rotating disk and this becomes very fine droplets. These droplets separate effectively the metallic droplets produced centrifugally by the rotating disk, act as emulsion media, restrict the nucleation in a small fraction of the droplets and prevent the metallic droplets from rebonding. As a consequence, nearly homogeneous nucleation and a large undercooling effect are realized. During the multi-stage pulverization process, the metallic droplets become increasingly finer, which results in very obvious large undercooling effects.

The above analyses indicate that both, a large undercooling effect and rapid quenching effect coexist in multi-stage atomization because of the multi-stage repeat pulverization process. These two effects act jointly to enhance the rapid solidification effect of metallic melt.

4.2. Theoretical analysis

Based on the nucleation dynamics and the characteristics of the multi-stage atomization process, the following equation is deduced [3]:

\[
\frac{dT_r}{dr} = \frac{1}{r} \frac{C}{\sigma^3 f(\theta)} (1 - T_r) T_r^2 \left( \frac{3T_r}{3T_r - 1} \right)
\]

where \( dT_r/dr \) is the reduced cooling rate; \( T_r \) is the reduced nucleation temperature; and \( C \) is a positive constant which relates to the thermophysical properties, where

\[
C = \frac{3k(\Delta H_v)T_m^2}{16\pi}
\]

From the above equation, discussion can be made as follows.

(a) \( T_r \) decreases with increasing undercooling \( \Delta T \). Since \( T_r \gg 1/3, ((1 - T_r) T_r^2)/(3T_r - 1) \) increases with decreasing \( T_r \), then \( dT_r/dr \) also increases, i.e. the cooling rate of droplets increases with increasing undercooling \( \Delta T \). Contrarily, the undercooling of the droplets also increases with increasing cooling rate. Therefore, both the large undercooling effect and the rapid quenching effect are closely related to, and promoted by, each other.

(b) When the droplet size becomes increasing smaller, nucleation catalysts such as impurities and oxide are trapped within a small fraction of the droplets. In general, the interface energy \( \sigma \) decreases to approach the conditions of homogeneous nucleation. Then \( \Delta T \) increases and \( T_r \) reduces, so that \( dT_r/dr \) and \( \Delta T \) increase jointly.

4.3. Discussion of the experimental results on undercooling

Since some oxidation on the surface of the metallic

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Fig. 4. Effect of mean size on the undercooling of: (a) Sn–20 wt% Pb alloy powders; (b) Sn–38 wt% Pb alloy powders; (c) Sn–60 wt% Pb alloy powders.
droplets certainly occurs during multi-stage atomization, a mechanism of preferred nucleation on surface oxide is proposed to explain the present results:

The main nucleation mechanism during multi-stage atomization is the preferred catalytic nucleation on the surface oxide of droplets for Sn–Pb alloy melts, the tin-rich phase nucleating on SnO₂ particles while the lead-rich phase nucleates on PbO particles. The change of the nucleation temperature laws is caused by the variation of the nucleation mechanism.

When the lead content is lower than 20 wt%, the main composition of the surface oxide of the droplets is SnO₂ and only the tin-rich phase nucleates on it. The particle number and purity of SnO₂ decrease with increasing lead content. The ability of catalytic nucleation reduces and the nucleation temperatures decline. Thus the nucleation temperature line \( T_n \) descends with increasing lead content.

After the composition of droplets increases to some extent (>20 wt% Pb), the lead-rich phase will first nucleate on PbO particles while most of the tin-rich phase nucleates on the primary lead-rich phase. When the lead content increases, the particle number and purity of PbO also increase and its ability of catalytic nucleation is enhanced to promote nucleation. Thus the nucleation temperature line \( T_n \) increases. Because the primary lead-rich phase has grown, the effect of initial composition on its number and ability of catalytic nucleation is very slight. Therefore the nucleation temperatures of the tin-rich phase \( T_n \) remains constant.

When the lead content is very high (>81 wt%) to enter the region of lead solution, only the lead-rich phase can nucleate on PbO particles. Its nucleation mechanism and laws resemble those in the two-phase region (>20 wt% Pb). Thus the nucleation temperature \( T_n \) increases with increasing lead content and forms a continuous and smooth curve up to pure lead.

The above mechanism can explain quantitatively the experimental results and laws. However, it is very difficult to make a dynamic observation and surface analysis of droplets during multi-stage atomization solidification. The above discussion needs further experimental verification.

5. Conclusions

1. Both large undercooling and rapid quenching were first found to coexist in multi-stage atomization. The two effects are closely related to, and enhanced by, each other.

2. The effects of composition and particle size on the undercooling of droplets are remarkable. Experimental results show that the undercooling of Sn–Pb droplets has a linear relationship with the logarithm of the mean powder size.

3. A new nucleation mechanism has been presented to explain the experimental results and laws, although it needs further direct verification.

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