RAPID QUENCHING AND LARGE UNDERCOOLING IN MULTISTAGE RAPID SOLIDIFICATION POWDER-MAKING PROCESS[①]

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ABSTRACT

The rapid quenching and large undercooling phenomena and device working principle in the rapid solidification process are analyzed, and the working characteristics are presented in detail. The results show that these multistage device are ideal for making amorphous, quasicrystalline, microcrystalline and fine metallic powders.
Key words: rapid quenching large undercooling multistage rapid salidification powder-making

1 INTRODUCTION

Generally, the so-called rapid solidfication process includes two aspects, one is the rapid quenching process, the another is large undercooling process. Technically, the rapid quenching process means enhancing the heat transfer between metallic melt and circumstance, so as to increase the cooling rate of the melt during the solidification process. In this process, the nuclei can not timely form near the equilibrious melting point, so the solidification occurs at the temperature far below the melting point. Therefore, large undercooling and rapid solidification can be realized. As a contrast, large undercooling process means depressing the heterogeneous nucleation in the melt, and then, at the situation of homogeneous nucleation, at relatively slow cooling rate, the maximum undercooling level could be large and this results in the rapid solidification of the melt. Obviously, both rapid quenching and large undercooling processes can cause large undercooling in the melt and rapid solidification. For the sake of contrast, in the present paper, the rapid solidification effect proceed from rapid quenching process and large undercooling process are defined as rapid quenching effect and large undercooling effect respectively.

So far, the rapid quenching technology has been widely used, but large undercooling process has only been studied theoretically in laboratory. The authors think that in the rapid quenching technology, there coexists the large undercooling process, and these two processes could be ultilized intently in the rapid solidification process of the melt, and result in both rapid quenching and can large undercooling effects. According to this thought, a series of multistage rapid solidification powder-making devices have been developed, whose working principle and characteristics are presented in the previous publication[1]. In this paper the highlights are the rapid quenching process and large undercool-

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ing process in the powder-making process.

2 THE ORINGIN OF THE PROBLEM

Usually, in the powder- making process, the attention is paid only to the rapid quenching effect, and the large undercooling effect is neglected. In fact, in various RS powder-making devices, the melt dispersion by means of gas or centrifugal atomization results in two effects: (1) melt dispersion and pulverization increase the specific area of the melt and enhance the heat transfer between the melt and the heat sink, promote the rapid quenching process; (2) melt dispersion isolates the nucleating sites. Therefore, in most droplets, heterogeneous nucleation is eliminated or depressed, undercooling level increased and large uudercooling rapid solidification is realized.

Technically, repeating melt droplets dispersion and pulverization process (we call this multistage process) will make the droplets finer, and then result in higher cooling rate, larger undercooling and better homogeneous nucleating situation. Rapid quenching effect and large undercooling effect joint together to enhance the rapid solidification of the melt.

If the rapid quenching effect and large undercooling effect coexist in a powder-making process, then, the process and device will be very useful for making amorphous, quasicystalline, microcrystalline powders and fine metallic powders.

3 MULTISTAGE RS POWDER-MAKING DEVICES WORKING PRINCIPLE AND PROCESS

Guided by the above hypothesis, a series of novel RS multistage powder- making devices were developed[2-4]. As illustrated in Fig. 1, the metallic liquid is firstly superheated to a high temperature. Secondly, the melt is atomized with an ordinary gas atomizer or USGA nozzle into fine droplets. Then the droplets are sprayed onto the high-speed rotating disc or rollers and further pulverized for one time or several times by the rotators. Coolant is sprayed onto the rotators and centrifugally pulverized into fine liquid droplets. These droplets are mixed with the metallic droplets and seperate these metallic droplets. The devices are carefully controlled so that most of the droplets do not solidify on the medium pulverizing stages. but be solidified during their flight. Water, liquid nitrogen or organic oil and other inert liquid media are used as cooling agent. The process can run continuously.

The multistage RS powder- making process possess 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 formula describing the Newtonian cooling[5] $\dot{T} \propto K(T_0 - T)/(\rho c r)$. where $\dot{T}$ is the cooling rate; T_0 the metallic droplet temperature; T environmental temperature; ρ the density of the material; c the average specific heat of the material in the solidfication process; K the heat transfer coefficient; r the droplet radius, we know, the smaller the droplet radius r , the higher the cooling rate; the higher the environmental temperature, the lower the cooling rate.

(2) Large undercooling effect

Usually, the methods of obtaining large undercooling effects are in two categories. One is metallic melt dispersion, the other is the method used for bulk melt such as drop tube method. In the first category, emulsion method invented by David Turnbull is very famous and useful[6]. The often- used emulsion media are eutectic chloride salts etc.

In the multistage RS powder- making

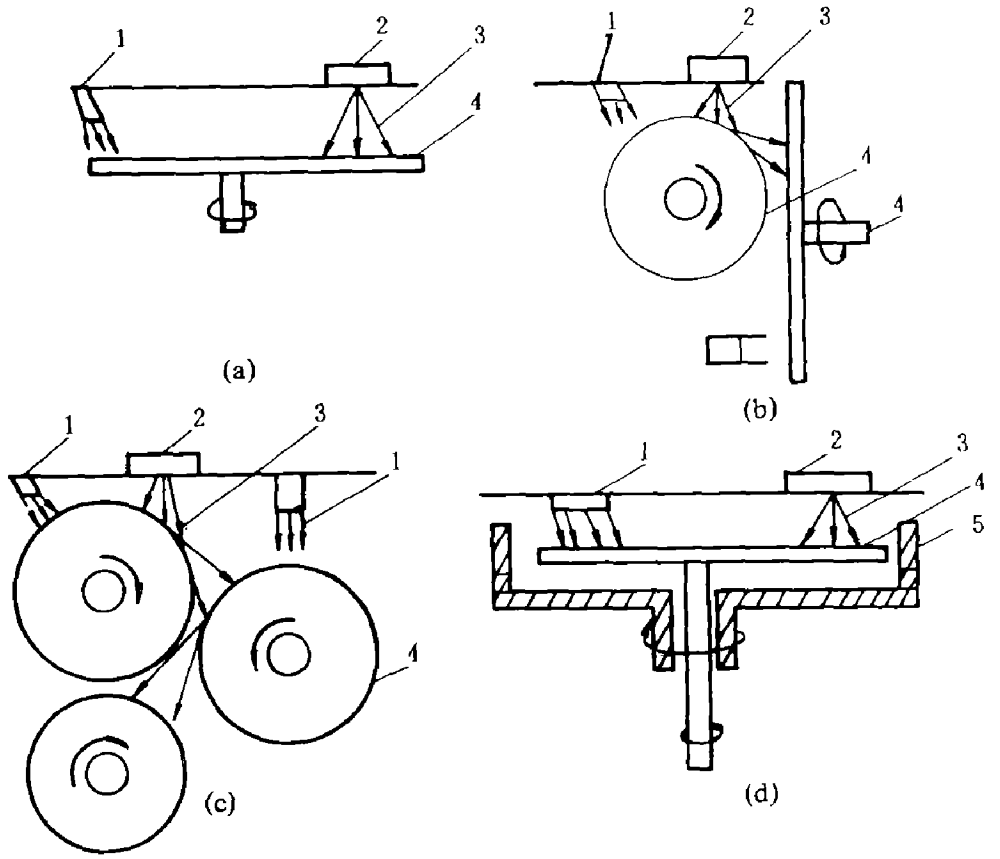

Fig. 1 A schematic diagram of multistage atomization-rapid solidfication powder-making devices
1—cooling agent; 2—nozzle; 3—droplets; 4—rotating disc; 5—rotating cup

process, water, oil, and liquid N_2 or other inert liquid media are sprayed onto the rotating disks or rollers, and become very fine droplets. These droplets seperate effectively these metallic droplets centrifugally produced with the rotating device, restrict the nucleation in a small fraction of the droplets and prevent the metallic droplets from rebonding, as a consequence, realize homogeneous nucleation and large undercooling effect. During the multistage pulverization process, the metallic droplets become finer and finer, this results in more obvious large undercooling effects. It is necessary to mention that, applying water as melt dispersion medium the large undercooling effect is remarkable also. According to the work of other researchers[7] and ours, despite some oxidation in the surface of the metallic droplets may occur when some special liquid is used, because the multistage process is a very short one, the effect of tiny oxidation on large undercooling is negligible.

(3) Multistage RS powder-making

The so-called multistage process means the repeated metallic droplets dispersion and pulverization process in the RS powder-making device. Technically, it is adjusted that most of the melt droplets can be repeatedly pulverized through the process and do not solidify in the middle stage and this is based on the reasons as follows: (a) The melt is overheated to a higher temperature before it is atomized. (b) Very fine droplets possess large undercooling level, therefore at the temperature far more below the melting point, most droplets are in an undercooling state, they still can be pulverized. (c) Calculation[1] indicated that because of the very short process, the droplets do not solidify in spite that the fine metallic droplets are surrounded by coolant.

The above analyses demonstrate that in the multistage RS process, there exist indeed rapid quenching process and large undercooling process. They act jointly to enhance the rapid solidfication effect of metallic melt.

4 CHARACTERISTICS OF THE MULTISTAGE RS POWDER- MAKING DEVICES

4.1 *Fine Powder Making*

For the device shown in Fig. 1 (a), if only employing the gas atomizer on the top (N_2 0.6～1.0 MPa), the obtained Al powder possesses an average particle size of 100～150 μm, cooling rate is 10^2～10^3 K/s. In case of operating the whole device, the average particle size can decrease to 12～15 μm, and the corresponding cooling rate reaches 10^5～10^6K/s.

For the device illustrated in Fig. 1 (b), if turning off the last rotating disc, the produced Al powder has average particle size of 30～35 μm, if the whole device works, the average particte size could decrease to 10～15 μm.

For the device demonstrated in Fig. 1 (c), turning off the last roller will produce an Al powder with average particle size of 15～20 μm; however the average size will be 10～13 μm when the whole device are operated.

For the device 1 (d), if the outer rotating cup do not work, then the device is similar to device 1 (a). When operating the rotating cap reversely, the Al powder obtained will have an average particle size of 7～11 μm.

4.2 *Particle Size and Shape of Powders*

Table 1 Average particle size and size distribution of powders produced with the devices

sample	average particle size /μm	size distribution/%						
		0～5 μm	5～10 μm	10～15 μm	15～20 μm	20～25 μm	25～30 μm	>30 μm
Al	12.0	11.1	24.4	36.0	17.2	2.41	2.91	bal.
Al	10.6	15.3	36.2	30.3	10.2	1.82	1.75	bal.
Sn	14.5	8.57	16.7	26.9	23.4	1.40	4.22	bal.
Al-Si_{12}	9.4	18.4	39.7	25.5	9.8	1.05	1.01	bal.
Cu	12.3	14.5	25.5	21.3	20.0	9.0	3.2	bal.
Bi	3.68	60.6	20.8	10.1	bal.			
Sb	4.93	52.5	36.9	7.6	3.0	9.0	3.2	bal.
Zn	14.0	9.05	18.3	29.8	25.0	11.2	4.35	bal.
$Sn_{55}B_{45}$	11.7	12.4	30.4	19.8	13.6	9.3	4.99	bal.
$Pb_{55}Bi_{45}$	13.5	12.4	24.9	16.0	13.9	9.78	6.89	bal.

Table 1 lists the particle size distribution of several powders produced in our lab (detected with a SKC—2000 Micron Photo Sizer made by SEISHIN Company of Japan), it shows that by using this multistage device, very fine powders can be obtained. As shown in Fig. 2, the powder particles have spherical shape or sphere-like, tear shape. This is because the contacting time of the droplets on the disks is very short. most of the droplets solidified during the flight by the coolant, some particles have the shape of dumb-bells

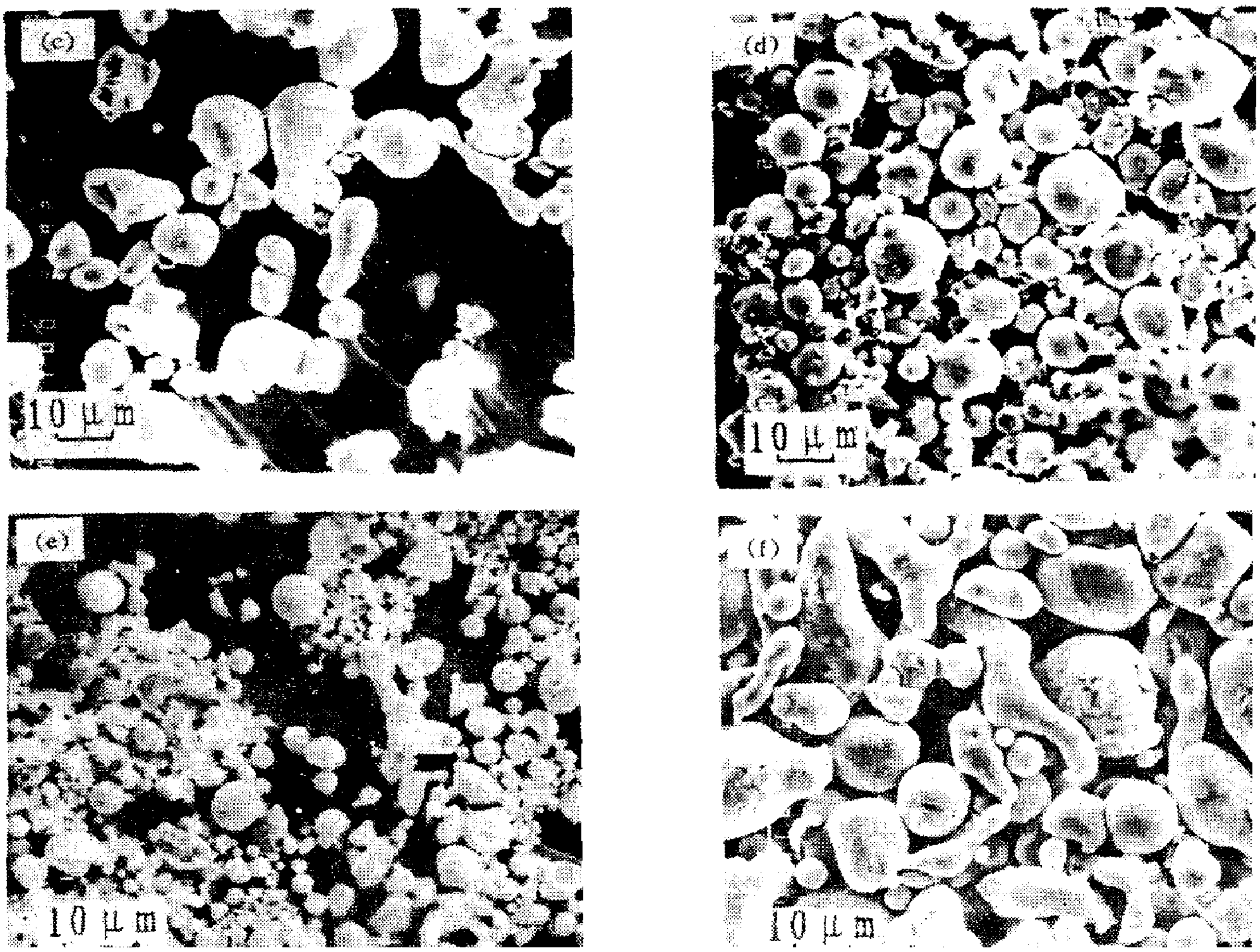

Fig. 2 Morphology of powders produced with the multistage atomization-rapid solidification device

or granule. They reflect some pulverizing characteristics of the device.

4.3 *Cooling Rate of the Melt Droplets*

with the multistage RS devices, near 100 amorphous, quasicrystalline and microcrystalline fine powders have been prepared. In Table 2 some of them are listed. X-Ray diffraction and electron diffraction reveal that the phase purity of the amorphous and quasicrystalline phase is quite high as demonstrated in Fig. 3. For the microcrystalline particle, the Second Dendritic Arm Spacing (SDAS) in its microstructure is 0.4～1 μm, for some alloy powders such as Al-Si, Al-Fe-V-Si, Al-Mn, optical featureless zone in their metallographic structure is observed (Fig. 4 (b)).

According to the relationship between SADS and cooling rate suggested by Matyia *et al* [8], it is concluded that the cooling rate is $10^5 \sim 10^6$ K/s. But, as the above analysis indicated, in the multistage RS process, there exist both rapid quenching and large underloooing effects, therefore, it is correct to say that the equivalent cooling rate is $10^5 \sim 10^6$ K/s.

4.4 *Parameters and Characteristics of Multistage RS Powder-making Process*

The cooling rate, powder particle size and particle shape mainly depends on the process factors. These factors are: what metal or alloy being used, melt temperature, atomization nozzle parameters, the distance between the nozzle and the rotating disc or roller, the arrangment of the disc and rollers and the distance between them, the pressure and flowrate of the cooling agent, rotating speed and material of the discs and rollers.

Generlly 0.6～1.5 MPa N_2, Ar air were used as atomizing media. The metallic

Table 2 Amorphous, quasicrystalline and microcrystalline powders produced with the multistage atomization rapid solidfication device

Amorphous	Fe80P20, Fe80B20, Fe80P13C7, Fe80P13B7, Al80Ni10Y10, Al85Ni5Y10, Fe87P13
Quasicrystalline	Al77.5Mn22.5, Al85Cr15, Al65Cu20Fe15, Al65Cu20Cr15, Al65Cu20Mn15, Al78Mn18Cr4, Al70Pd20Mn10
Microcrystalline	Al55Si45, Al70Si30, Al80Si20, Al82Fe14Y2Si2, Al86Fe10V2Si2, Ni70Mn25Co5, Cu90Al10, Cu85Zn15, Ni3Al, Al88Fe8Ce4, Al88Fe8Mo4, Al87Cu2Mg1Zn10, Al88Fe8Mo4

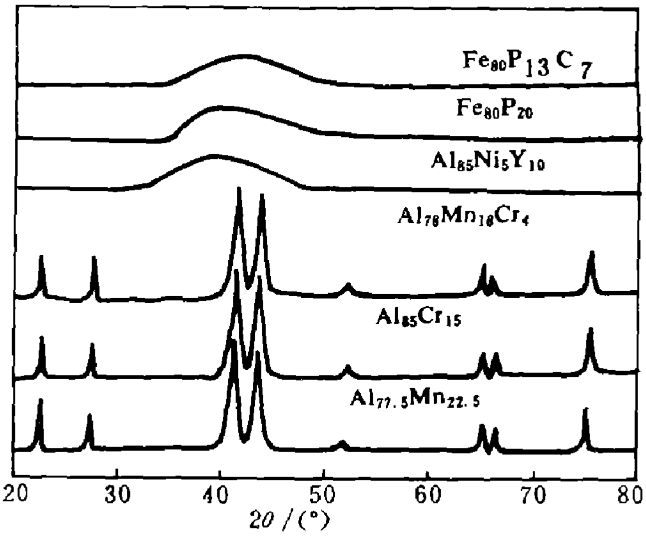

Fig. 3 XRP Patterns of amorphous and quasicryatalline powders

melts were superheated to 200 ～ 300 ℃ above the melting points. Ordinary circular nozzle was employed, disks and rollers linear velocity is 150～200 m/s, and production rate is 2～5 kg/min.

Compared with other process, this process possess some characteristics as follows.

(1) These devices can continuously run at the production rate of 2～5 kg/min. The production cost (including device expense) is

low, the process is very simple. The devices are easy to operate. This is a "wet" process so the pollution of powder dust is very slight. Therefore, the process is a clean, safe one.

Fig. 4 Microstructure of microcrystalline powders

(a) —the second dendritic arm spacing of Al-Cu-Mg-Zn alloy, ×2 000; (b) —the opticalfeatureless zone of Al-Fe-V-Si ally, ×2 000

These devices can meet with the need of powder production in industry scale. Two pilot plants have been established with annual production capacity of 1 000 t of Al, Cu, Sn alloy powders.

(2) Fine powders (10～40 μm) can be directly produced with these devices, needless to employ the gas classfication process. Desired average particle size can be obtained by adjusting the process paramter. The repeatablility of particle size and particle size distribution is satisfactory. Various medium or coarse powders can also be made using this technique.

(3) The oxygen content of the powders is very low. After dehydrating with vacuum filter and the following low temperature, vacuum evaporation process, the obatined dry powders have good flowability, their oxygen content is 0. 05～0. 1 wt. -% and it does not increase when the powders are in storage for a long time in air.

5 SUMMARY

Based on the hypothesis of multistage metallic melt atomization- rapid solidfication, the authors developed a series of RS powder-making devices. These devices possesses an equivalent cooling ability of 10^5～10^6 K/s, production rate of 2～5 kg/min. The obtained finest powders have average particle size of 5～10 μm. These devices can run continously. Near 100 kinds of amorphous quasicryatalline and microcystalline fine powders have been produced with these devices. These devices are very ideal for the making of amorphous, quasicystalline, microcrystalline powders and fine powders.

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