Study on the process of TC4 powders prepared by electrode induction melting gas atomization for laser 3D printing

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Abstract. This study employed TC4 rod as raw material to fabricate TC4 powders for laser 3D printing via electrode induction melting gas atomization (EIGA). The morphologies, phase compositions, particle size distributions, apparent densities and flowabilities of the powders were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), laser particle size analyzer (LPS) and Hall flowmeter, respectively. Moreover, the effects of gas atomization pressure and melting temperature on the yield of TC4 powders for laser 3D printing were studied. The results showed that TC4 powders morphology was nearly regular spherical. The particle size of TC4 powders showed a single peak normal distribution, mainly distributed in the range of 15–180 μm. The powder was α’−Ti of a single phase solid solution. The optimum parameters were gas atomization pressure of 5MPa, melting temperature of 1750℃. Under the optimized condition, the average particle size D50 was 60.2 μm, the yield of printable TC4 powders was 35.6%, the flowability was 41.2 s/50g, the apparent density was 2.76 g/cm³ and oxygen content was 800 ppm, which was in line with the ASTM test standard and was conformed to the requirement for laser 3D printing.

1. Introduction

3D printing technology is a kind of rapid prototyping technology. It has become research hotspot all over the world, because of high precision, high efficiency, materials saving and being suitable for manufacturing complex parts [1,2]. For metal laser 3D printing technology, the morphology, oxygen content, fluidity, apparent density and particle size of the powders directly determine the performance of the final product [3].

Ti-6Al-4V has drawn increasing attention for 3D printing applications in aerospace, automobile and biomedical fields due to low density, high specific strength, good corrosion resistance, high heat resistance and good biocompatibility. Such as, engine fans, diffuser, cockpit window frames, aircraft structural beams, bone and joint, dental restoration materials, etc. [4-6]. TC4 powders produced in China has the defects of low sphericity, high oxygen and large particle size, the high-quality spherical TC4 powders still need to be imported, which seriously restricts the development of local 3D printing industry. Therefore, mastering the preparation technology of high-performance spherical TC4 powders is the key to the autonomy of 3D printing powders in China.

The preparation methods of spherical TC4 powders for laser 3D printing mainly include electrode induction melting gas atomization (EIGA) [7], induction plasma spheroidization (PS) [8], plasma rotating electrode process (PREP) [9] and plasma atomization (PA) [10]. Nevertheless, the particle size and composition of PS powders are affected by the original powders, and the powders have high
oxygen content, which are not suitable for 3D printing in aerospace and biomedical fields [11]. The powders prepared by PREP have excellent sphericity and high purity. However, due to the limitation of rotating speed, it is difficult to prepare the powders between 15 and 45 μm [12]. The powders prepared by the PA have good spherical shape and good particle size, but the domestic technology has not yet been refined. The powders prepared by EIGA have the advantages of high purity, high sphericity, narrow particle size distribution, fast cooling rate and small environmental pollution [7]. Therefore, EIGA has become a major method for preparing TC4 powders. The particle size distribution primarily depends on the argon pressure, over-heat temperature and nozzle structure [13].

Laser 3D printing requires powder with a particle size of 15-45 μm which is defined as the yield of printable TC4 powders in the paper. At present, there is a problem that the yield of printable TC4 powders is low by EIGA, which results in a high price of printable TC4 powders. Therefore, the study focused on improving the yield of printable TC4 powders by studying argon pressure and melting temperature in the process of EIGA, in order to provide reference for the industrial production of laser 3D printing TC4 powders.

2. Experiment methods

The raw material in this study was TC4 rod with diameters of 45mm produced by Baoji Hi-Tech Zone Xinglong Titanium Industry Co., Ltd. The chemical composition of Ti-6Al-4V rod is shown in table 1. The end of the titanium rod was machined to an angle of 45°. The surface was cleaned with alcohol to remove grease. The atomizing gas was high purity argon (purity≥99.999%) supplied by Sichuan Pangang Messer Gas Products Co., Ltd.

Table 1. Chemical composition of Ti-6Al-4V rod (wt.%).

| C  | H  | O  | N  | Fe  | Al | V | Ti |
|----|----|----|----|-----|----|---|----|
| 0.041 | 0.011 | 0.048 | 0.003 | 0.026 | 6.21 | 3.87 | bal |

During the experiment, the TC4 rod rotated at low speed into the water-cooled copper induction coil for heating. The molten metal droplets were continuously dripped and atomized by the high-speed argon gas sprayed from the nozzle. Then, spray droplets were spheroidized and solidified into spherical particles. At last, TC4 powders were collected in the powder storage tank through the cyclone. Schematic of the atomizing processes was illustrated in figure 1.

![Figure 1. Schematic of TC4 powders prepared by EIGA.](image)

The morphology and microstructure of TC4 powders were investigated using scanning electron microscopy (SEM, MLA650F, FEI, USA). The particle size distributions of TC4 powders were observed using a laser micron sizer (LMS, ZS90, Malver, UK). The phase constituents of TC4 powders were analyzed by X-ray powder diffraction (XRD, Empyrean, PANalytical B.V., The
Netherlands). The oxygen contents in the powders were recorded by using an oxygen and nitrogen analyzer (TC600, LECO, USA). The concentrations of metallic elements were determined by using an inductively coupled plasma atomic emission spectrometer (ICAP6300, Thermo, USA). The flowability and apparent density of TC4 powders were measured by using a Hall flowmeter (HY-102, Dandong Haoyu Technology Co., Ltd., China). All measurements were taken three times, and the average results were reported.

3. Results and discussion

3.1. Effect of atomizing gas pressure on yield of printable TC4 powders

The EIGA method used argon gas to break molten metal stream into droplets and solidify into powders. The breakup process was mainly divided into three stages [14]: (1) The metal stream was torn into thin sheet by high-speed argon gas and left the atomizing gas center. (2) Thin sheets were torn into thin rod droplets under the action of the airflow field. (3) The thin rod droplets were torn into a large number of fine droplets due to surface tension and airflow field.

During the cooling process, the morphology of the powder was related to the spheroidization time and solidification time of the droplet. When the spheroidization time was less than the solidification time, the droplet had sufficient time to be spheroidized before being solidified, and finally the powder was spherical. When the spheroidization time was longer than the solidification time, and there was not enough time for the droplet to be spheroidized before being solidified. At last, irregular shape powder was obtained.

The atomizing gas pressure determines the gas flow rate Q and the flow velocity v. Generally, the larger the kinetic energy of the atomizing gas is, the better the breakup effect is. According to the principle of fluid dynamics, the kinetic energy of the atomizing gas can be calculated using equation (1) [15].

\[
e = \frac{1}{2} m v_g^2 = \frac{1}{2} \rho_g d V \left( \frac{Q}{S} \right)^2 = \frac{1}{2} \rho_g d V \times \frac{4Q^2}{\pi d^4} = \frac{8 \rho_g Q^3}{\pi^2 d^4}
\]

Where \( m \) is the mass flow rate of the gas, \( v_g \) is the speed at which the gas stream contacts the solution, \( Q \) is the gas flow rate, \( \rho_g \) is the density of the gas, \( d \) is the internal diameter of tuyere. From the equation (1), it was clearly that with a fixed gas nozzle design and metal composition, the particle size was dominated by atomizing gas pressure. In other words, a higher atomizing gas pressure could result in a higher yield of printable TC4 powders.

![Figure 2](image1.png) **Figure 2.** Yield of printable TC4 powders under different atomization gas pressure.

![Figure 3](image2.png) **Figure 3.** Yield of printable TC4 powders under different melting temperature.

It can be seen from figure 2 that the pressure of the atomizing gas increased, the yield of printable
TC4 powders increased. When the pressure of the atomizing gas was 5 MPa and 6 MPa, the yield of printable TC4 powders was 35.6% and 36.8% respectively. When the pressure of the atomizing gas exceeded 5 MPa, the atomizing gas flow rate was greater than the design speed of the atomizing nozzle, the yield of printable TC4 powders didn't increase significantly.

3.2. Effects of melting temperature on yield of printable TC4 powders

The relationship between the surface tension of metal melt and the temperature can be expressed by the Ramsay-Sheilds formula [16].

\[ \sigma = K(T_c - T - 6)V_m^{-2/3} \]

(2)

Where \( \sigma \) is the surface tension of metal melt, \( K \) is the empirical constant, \( T_c \) is the critical temperature when the surface tension is zero, \( T \) is the actual temperature of the alloy liquid, and \( V_m \) is the molar volume of the alloy liquid. The relationship between viscosity of metal melt and temperature is explained in equation (3) [17].

\[ \eta = Ae^{E/(kT)} \]

(3)

Where \( \eta \) is the viscosity of metal melt, \( A \) is a constant, \( E \) is the activation energy, \( k \) is the Boltzmann constant, and \( T \) is the actual temperature of the alloy liquid.

It could be seen from equations (2) and (3) that as melting temperature increased, the surface tension and viscosity of the alloy liquid decreased. Therefore, molten metal stream was easy to break into small droplets in the breakup stage. The yield of printable powders increased with increasing melting temperature up to 35.6%. After that, the yield began to reduce gradually as shown in figure 3. This was attributed to the powders adhered to each other and agglomerated during the slow solidification causing by higher temperature. The powders could be easily oxidized under high temperature conditions. When the temperature was below 1750°C, the solidification time of the particles was less than spheroidization time, and the particles were solidified before being spheroidized, the TC4 powders were irregular in shape as shown in figure 4(b).

![Figure 4. SEM morphology of TC4 powders under different melting temperature. (a) 1750°C and (b) 1700°C.](image)

3.3. The optimum process parameters

Considering the yield of printable TC4 powders and cost of argon, the optimum process parameters were found to be melting temperature of 1750°C and atomizing gas pressure of 5 MPa. The yield of printable TC4 powders was 35.6%.

Figure 4(a) shows the micrograph of TC4 powders. It was apparent that most of the TC4 powders had good sphericity and smooth surface, indicating that the TC4 droplet had been fully spheroidized.
before solidification. Some small satellite balls adhered to the surface of the spherical particles. This was mainly attributed to the much higher cooling rate for small particles as compared to the large particles. The small particles which first solidified adhered to the surface of the unsolidified large particles by the air current to form satellite balls. The satellite particles had a negative influence on the free-flowing of the powders, which were thus not desired for 3D printing.

Figure 5 shows the XRD diffraction pattern of the TC4 powders. According to the standard titanium card, the TC4 alloy powders prepared by the EIGA method was a close-packed hexagonal phase. After being crushed by high-speed argon gas, the TC4 droplets were spheroidized and solidified. During rapid cooling, the β-phase of the body-centered cubic was transformed into a close-packed cell through a non-diffusion phase transition process. The alpha phase of the hexagonal structure finally produced a metastable state HCP-α' phase.

![Figure 5. XRD pattern of TC4 powders.](image)

![Figure 6. The particle size distributions of TC4 powders.](image)

It can be seen from figure 6 that TC4 powders mainly distributed in the range of 15−180 μm. The particle size differential distribution curve of TC4 powders was a single peak and was approximately normal distribution, the average particle size D50 was 60.2 μm.

![Table 2. Properties of TC4 powders prepared by EIGA.](image)

Properties of TC4 powders were shown in table 2, the contents of oxygen and nitrogen were 800 ppm and 70 ppm respectively. The combination of high sphericity and non-satellite particles contributed to improve its flowability. The flowability was 41.2 s/50g, the apparent density was 2.76 g/cm³, which was in line with the ASTM test standard and was conformed to the requirement for laser 3D printing.

4. Conclusion

- As the pressure of the atomizing gas increased, the yield of the printable TC4 powders increased. The yield of printable TC4 powders first increased and then decreased with increasing melting temperature. The optimum parameters were gas atomization pressure of 5 MPa, melting temperature of 1750°C.
- Under the optimized condition, TC4 powders morphology was nearly regular spherical, which surface adhered a small amount of satellite balls. The powder was α′−Ti of a single phase solid solution, the average particle size D50 was 60.2 μm, the yield of printable TC4 powders was
35.6%.

- The flowability was 41.2 s/50g, the apparent density was 2.76 g/cm$^3$ and oxygen content was 800 ppm, which was in line with the ASTM test standard and was conformed to the requirement for laser 3D printing.

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