Development a Cu-based Metal Powder for Selective Laser Micro Sintering

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Abstract. A Cu-based metal powder which consists of Cu and Cu-P alloy for selective micro laser sintering has been developed based on the theoretical analysis of the characteristics of the laser micro sintering metal powder. The characteristics of the wetting, capillary force and viscosity have been considered. The preliminary experimental investigation on the selective laser micro sintering Cu-based metal powder has been performed. A 50W CW Nd:YAG laser was employed to sinter the developed metal powder mixture. The sintering mechanism and the effect of the process parameters on the characteristics of the sintering samples have been preliminary investigated. The results show that the mechanism of laser micro sintering this developed metal powder is liquid-phase sintering and Cu-P alloy powder plays an effectively binder in the sintering process. The process parameter has significant effects on the characteristics of the sintering parts. From the SEM image, two different microstructures of samples with different scan spacing parameters were compared and a better binding effect was obtained at a parameter of 0.05mm scan spacing.

1. Introduction

As the mechanical engineering industry confront a growing demand of components with um-sized resolution for an increasing range of applications, miniaturization of components and moulds get more and more attractive in mechanical fabrication. Selective laser micro sintering (μ-SLS) can meet these requirements, which is the development from a modified selective laser sintering. Same as SLS process, μ-SLS can fabricate micro mould directly from CAD data. Comparing to SLS process, μ-SLS has the advantages of higher resolution [1].

As the μ-SLS developed, the process attractive more and more attentions, there are more and more researches in recent years. Y.P. Kathuria used a pulsed Nd:YAG laser to achieve a line width of about 221μm with one metal component and a line width of about 470μm with two different metal component in1999[2]. Horst Exner et. employed a Q-switched Nd:YAG laser with mixtures of copper and tungsten successfully obtain a micro part with a spacing resolution of 30μm in ambient atmosphere in 2003[3-4]. Since the beginning of 2005 oxide and non-oxide ceramics were investigated but the characteristics such as aggregation, dissociation, recombination and further reactions of this type material make it difficult to sinter than metals [5]. Although the μ-SLS has been introduced for...
several years, the technology of producing 3-D micro metal parts using μ-SLS process is still in its early stage. The investigation of workable materials is crucial for this technology which decides the feasibility and sinter ability of the process. Balling is a severe problem in laser sintering metallic powder. The previous research shows that the two-phase method is an effective method to overcome the balling effect. In this process, the material system consists of at least two phases with different melting points, which are called binder and structural metal powders. During the process, the binder melts, fills the pores and binds the solid particles together. The liquid flows and the structural particles rearrange under the influence of capillary force, leading to densification of the layered powder material. This paper focused on the development of a Cu-based metal powder for the μ-SLS.

2. Material development

For a superior performance in μ-SLS via liquid phase sintering binding mechanism, there are three significant physical aspects of the materials need to be considered such as wetting, capillary force and viscosity. So find a material system with outstanding characters on these physical aspects will be proper for μ-SLS.

2.1 Wetting

Wetting is the first requirement in laser sintering process, which determines the sinter ability, densification and microstructure. Wetting is expressed by the contact angle and dihedral angle depending on the phases in the system. Contact angle expresses the equilibrium of the interfacial energies in the system including liquid, solid and vapor. Assuming the solid surface is ideal and the curvature of L/V surface can be negligible, the contact angle $\theta$ can be expressed as the following classical Young equation [6]:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$  \hspace{1cm} (1.1)

where $\gamma_{SV}$, $\gamma_{LV}$ and $\gamma_{SL}$ are the surface tensions of the solid-vapor, liquid-vapor and solid-liquid, respectively. The range of the contact angle can be from 0° to 180°. A low contact angle (<90°) means good wetting (Figure 1(a)) and a high contact angle (>90°) means poor wetting (Figure 1(b)). Zero contact angle indicates a perfect wetting.

In systems B/A with negligible mutual solubility, the contact angle $\theta$ can be found from: [7]:

$$\cos \theta = 1 - 0.28\left(\frac{T_{m1}}{T_{m2}} - 1\right)$$  \hspace{1cm} (1.2)

where $T_{m1}$ and $T_{m2}$ are the melting points of solid metal A and liquid metal B, respectively. From Eq. (1.2), it can be seen that same metal $T_{m1}=T_{m2}$, can wet perfectly since $\theta=0°$; if $T_{m1}/T_{m2}<3$, for instance Fe/Ag, it also has good wetting; if $T_{m1}/T_{m2}>4.2$, the insoluble system will not be wetting. Therefore, in liquid phase sintering, the difference of metal melting points must be suitable.
2.2 Capillary Force

Capillary force is the driving force for densification in laser sintering process. Using the two spheres model shown in Figure 2,[6], the capillary force \( F_c \) on one of the particles depends on the meniscus size \( G \) and surface energy of the liquid \( \gamma_{LV} \) as shown in the following equation:

\[
F_c = \pi G^2 \Delta P + 2 \pi G \gamma_{LV} \cos \theta \tag{1.3}
\]

Where \( \Delta P \) is proportional to the surface energy \( \gamma_{LV} \) and is inversely dependent on the radii of curvature, and can be obtained from Eq. (1.4):

\[
\Delta P = \gamma_{LV} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = 2 \gamma_{LV} \cos \theta / d \tag{1.4}
\]

![Figure 2. The two spherical particles model for calculation of capillary force.](image)

The capillary force is attractive for good wetting, leading to the densification of the system, while the force is repulsive for poor wetting, leading to the swelling of the system. From the Eqs. (1.3) and (1.4), it can be found that the wetting force increases with the decrease of the contact angle and of particle separate distance. Thus using smaller binder particle size can lead to a higher capillary force and the pores caused by the melting binder can be easily filled.

2.3 Viscosity

In laser sintering, viscosity acts as a resistant force for the liquid spreading. The reciprocal of viscosity is known as fluidity. Therefore, low viscosity of the molten liquid is another requirement for the successful direct laser sintering processing. The viscosities of liquid metals are in the range of 0.5–8 mPas and decrease quickly with the increase of the temperature. Eq. (1.5) is a typical equation for calculating the viscosity of simple (monoatomic) liquids near the melting point [8]:

\[
\mu_m = 1.6 \times 10^{-4} \left( \frac{MT_m}{V_m} \right)^{1/2} \tag{1.5}
\]

where \( V_m \) is the atomic volume at the melting point and \( M \) is the atomic weight. From Eq. (1.5), it can be found that the viscosities of metals decrease with the increase of the temperature. For most liquid metals the variation of viscosity \( \mu \) with the temperature \( T \) may be written as Eq. (1.6):

\[
\mu = \mu_1 \exp \left( \frac{E}{RT} \right) \tag{1.6}
\]

Where \( \mu_1 \) and \( E \) are constants, and \( R \) is the gas constant. Eq. (1.6) shows that the viscosity of a liquid metal decreases with the increase of the temperature. Therefore, increasing the sintering temperature can lower the viscosity, and hence promote densification.

In the mixture of solid/liquid system, the viscosity of the system is modified because the solid particles act as obstacles. Thus, the solid particles impede the spreading of the liquid. The viscosity of a solid-liquid mixture \( \mu \) is related to the viscosity of the pure liquid phase \( \mu_2 \), and the volume fraction of solid in liquid \( \Phi \) as in:

\[
\mu = \mu_2 \left( 1 - \Phi / \Phi_m \right)^{-2} \tag{1.7}
\]
where $\Phi_{\text{c}}$ is the critical volume fraction above which the mixture has essentially infinite viscosity. Particle bonding is driven by the liquid viscosity $\mu$ if the materials are suitably chosen for the occurrence of the inter-particle wetting. In laser sintering of metal powders, the volume fraction of solid particles is generally in the range of 30~70%. From Eq. (1.7), the viscosity of the solid/liquid mixture in direct laser sintering can be calculated to be about 2~11 times that of the corresponding pure liquid metal, resulting in slow liquid flow. However, the viscosity can be decreased by the use of a low melting point binder, the right solid-liquid ratio, addition of alloy elements and the control of the degree of superheating of the liquid phase. On the other hand, the viscosity cannot be too low because the tendency for balling increases with the decrease of the viscosity[9].

2.4 Design of Cu-based Metal Powder
A Cu-based metal powder has been developed according to the above requirements in this paper. It mainly comprises of two powders: Cu powder and pre-alloyed Cu-P powder. The melting point of the “binary” eutectics Cu-P is 710°C. The ratio of melting point of Cu (1083°C) to melting point Cu-P (710°C) is approximately 1.52, which is lower than 3. Therefore the metal powder system has good wetting. The contact angle $\theta$ calculated according to Eq. (1.2) is approximately 31.46°. Except for the formation of eutectic, another role of phosphorus is as a fluxing agent to improve the wetting characteristics in the system. It decreases the surface tension of the Cu powder, reacts with the copper oxides from the powder surfaces during the laser sintering and protects the metal surfaces from re-oxidation during heating, which permits good wetting and formation of a sound bond. Firstly, the metal powder system consists of two metal powders with dispersive melting points. The melting point of Cu-P at 710°C is rather low, which hence does not require a high laser power to melt it. Secondly, the melting point difference is more than 300°C, which is beneficial to the liquid flow ability. Thirdly, the material system has good wetting and suitable mutual solubility. Lastly, Cu powder is easy to obtain in the market and the Cu-P is easy to produce.

3. Experimental

3.1 Powder preparation
Gas atomic 99% purity Cu_1 powder with spherical shape and a mean particle size of 150um and another Cu_2 powder with also spherical shape and a mean particle size of 75um were firstly mixed with mass ratio Cu_1: Cu_2 of 1: 0.2. Then the mixed Cu powder is mixed with Cu-P alloy (phosphor 7.25wt%, copper 92.75wt %) powder according to mass ratio of 60: 40. The shape of the Cu-P alloy powder is also spherical, and its mean particle size is about 45um. The mixed powders was loaded into the processing cylinder and levered by the blade for obtaining a flat processing surface.

3.2 Laser processing
In the experiments, a 50W CW Nd:YAG laser controlled by a galvanometer scanner was employed for sintering, powders processed in the ambient atmosphere at room temperature, the scan speed was fixed on 10mm/s. The figure3 shows the schematic set-up for laser micro-sintering. The experiment was divided to 3 groups and different scan spacing was conducted in every group to see varied surface morphology of the single layer sample. A 20mm×20mm single layer square CAD profile was created by the controlling computer for sintering blends powders. Every different process parameter were conducted to make a 20mm×20mm square sample for subsequent assessments.

3.3 Characterization
The microstructure and surface morphology analysis of the individual layer samples were characterized using an FEI Sirion 200 Scanning Electron Microscope, the composition of the sintered sample was analysed by an Energy Dispersive X-ray analysis (EDX).
4. Result and discussion

4.1 Sintering Mechanism

Figure 4 shows the SEM image of surface morphology of laser-sintered sample at a scan spacing of 0.05mm and laser power of 10W. From Figure 4, it can clearly find many spherical powders with size around 100um, and some bridges connect the spherical powders. It can also find that many holes in the microstructure, suggesting non-density of the sample.

From the image, it can see that the particles with size of about 100um keep their shapes as sphere very well, which suggest that some powders are not molten during the process. The “bridges” have different shapes, which are significantly differently from the spherical powder. This means that the “bridge” is solidified from a molten powder. The melting point of Cu-P is 710°C and the melting point of Cu is 1083°C. Therefore, melting Cu-P is much easier than that of Cu for same laser energy absorption.
Figure 5. EDX analyses showing chemical compositions of the non-melting powder (a) and binder (b).

The EDX results approve such conclusion. Figure 5 shows the typical EDX analysis results of a spherical powder and the “bridge”. Figure 5(b) shows the components of the bridge. From Figure (b), it can be found that the components of the “bridge” are mainly P and Cu, and the content of P is more than 3 wt%, which is much higher than that of the spherical powder, approving that the “bridge” is solidified by liquid Cu-P pre-alloy powder. Figure 5(a) is the EDX analysis of the spherical powder. The EDX analysis shows that there are two elements in the surface of the powder: P and Cu, but the content of P element is only about 1 wt% and the content of Cu is about 99%, suggesting that Cu powder is not molten during the process. From Figure 5(a), it can also see that it is relatively rough at the surface of the spherical powder, this is because the wetting between the liquid Cu-P and Cu is very good. During laser sintering, the liquid Cu-P coats the Cu powder, after laser removing, the liquid Cu-P solidifies and brings a rough surface of the Cu powder and a minority phosphorous content. From the above analysis, it can found that this kind of sintering is base on the mechanism of liquid phase sintering. During the process, the structure powder with higher melting point is not molten and
another powder with lower melting point is complete molten [10]. In this metal powder system, Cu-P alloy component is melted and plays an effect of binder in the sintering processing and Cu powder has been connected by binder and rearranged to a network, so this Cu-based powder system can sintering by laser irradiation. Amount of Cu powders has been coated by the binder confirm that the Cu-P alloy has an excellent fluidity in this processing temperature.

In the mixed powders, Cu-P alloy as the binder due to it lower melting point (710°C)and higher absorption than Cu (1083°C) component. So when during the laser irradiation, Cu-P alloy can easily be melted and plays like a binder, which connects two adjacent Cu spherical powders. Cu-P alloy materials have a unique characteristic called the Flow Point, the Flow Point is defined as the temperature at which the filler metal is fluid enough to capillary through a joint even though not completely liquid. Another effect phosphorus component can provide in the processing is that the element phosphorus can act as flux to prevent Cu oxidization[11-12].

4.2 Effect of the scan spacing

![Figure 6](image1.jpg)

**Figure 6.** The surface morphology of the sample using different scan spacing.

![Figure 7](image2.jpg)

**Figure 7.** (a) (b) showing the microstructure of Cu ball with a neck of Cu-P respectively at scan spacing 0.05mm (a) and 0.1mm (b).

In the experiments, the laser power was fixed on 10W and the scan speed was kept on 10mm/s, scan spacing changes at the range from 0.1mm to 0.05 mm. Figure6 (a) is the surface morphology of the sample was obtained using scan spacing of 0.05mm and figure6 (b) is the surface morphology of the sample was obtained using scan spacing of 0.1mm. It clear see from figure 6(b) that many Cu-P alloy powders are not melted under 0.1mm scan spacing and
the neck between two Cu powders are not strength enough. It seems that the liquid Cu-P alloy powder cannot flow and coat on Cu powders enough before re-solidify. But Cu-P alloy powders are melted absolutely and coat the Cu powders under 0.05mm scan spacing (figure6(a) and form a denser microstructure than that of using 0.1mm scan spacing. This may because it can have a higher energy injection lead to a higher temperature and capillary force.

Figure7 is the magnification of Figure 6. In the figure7, the microstructure of two Cu spherical powders with a neck under 0.05mm scan spacing (a) and 0.1mm scan spacing (b) are showing. From the (b), in clear see a boundary between the Cu ball and the neck, Cu powders are only a part of spherical surface coated by the binder, but in the (a), the spherical surface of Cu powder are absolutely coated by the binder, so it can not found the boundary between the Cu ball and the neck.

5. Conclusion
A Cu-based metal powder for selective micro laser sintering has been development, the physical character of this material system accord with the theoretical calculation and base on the experiment and analysis above, following conclusion can be given:
- The developed metal powder system is suitable for laser sintering, the mechanism of this laser sintering is liquid-phase sintering.
- Cu-P alloy material plays binder in u-SLS process, while Cu powder plays the structure, the wetting between them is very well.
- Small scan spacing leads to a dense and pretty connection microstructure.

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