Metallurgical mechanisms in direct laser sintering of Cu–CuSn–CuP mixed powder

Dongdong Gu*, Yifu Shen, Shangqing Fang, Jun Xiao

College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics,
29 Yudao Street, 210016 Nanjing, PR China

Received 7 July 2006; received in revised form 13 August 2006; accepted 15 August 2006
Available online 12 September 2006

Abstract

This work presents a detailed investigation into the metallurgical mechanisms in direct laser sintering of a multi-component Cu-based metal powder consisting of a mixture of Cu, Cu–10Sn, and Cu–8.4P. The phases, compositions, and microstructures of the laser sintered sample were characterized by XRD, EDX, and SEM. It is found that laser sintering of this powder system is based on the mechanism of liquid phase sintering with the complete melting of the binder Cu–10Sn and the non-melting of the structural metal Cu. The phosphorus element can act as a deoxidizer to prevent both the sintering mixture and the sintered layer from oxidation by formation of P2O5 and CuPO3, thereby improving the liquid–solid wettability and the resultant interlayer bonding coherence. The phosphorus element shows a high concentration along grain boundaries in the sintered structure, due to a low mutual solubility of P in Cu and an extremely short thermal cycle of laser sintering.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Laser processing; Microstructure; Rapid prototyping (RP); Direct metal laser sintering (DMLS); Cu-based metal powder

1. Introduction

Direct metal laser sintering (DMLS) is a newly developed rapid prototyping (RP) technique that generates metallic components in a layer-by-layer fashion using the loose powder and the computer controlled laser [1–4]. DMLS implies layer-wise shaping and consolidation of metal powder to complex shaped three-dimensional (3D) parts with full or near full density in a single process, while minimal or no post-processing steps such as furnace densification or secondary infiltration are required [5–7]. The recent major advance of DMLS research is in the net-shape fabrication of prototypes and the small-volume tooling for injection molding and dies casting [8–10].

Although DMLS holds a great potential in fabricating high performance metallic components with controlled microstructures and mechanical properties, it is still in its early stage of development [3,11]. Common problems associated with this process such as balling phenomenon, curling deformation, low sintered density, weak strength, and high surface roughness are still difficult to completely overcome [9,12,13]. In fact, DMLS is a complex metallurgical process exhibiting multiple modes of heat and mass transfer, and in some instances, chemical reactions [2,6,14]. However, not much previous work has been focused on the basic principles of DMLS in terms of microstructural evolutions, sintering mechanisms, and processing conditions. Further research and understanding of the metallurgical fundamentals of DMLS, therefore, is regarded particularly necessary.

In this study, a multi-component Cu-based metal powder was chosen for direct laser sintering. The suitable processing conditions of this powder system have been well determined in our previous work [15], so as to obtain a sound sinterability with minor or no balling effect. This paper presents the sintering behavior, phase transformation, and microstructural evolution of the powder during laser sintering, with an overall aim to conclude generic metallurgical mechanisms in DMLS process.

2. Experimental

2.1. Materials

Electrolytic 99% purity Cu powder with an irregular shape and a mean equivalent spherical diameter of 54 μm, water-atomized CuSn (10 wt.% Sn) powder with an ellipsoidal shape and an average particle size of 28 μm, and gas-atomized...
CuP (8.4 wt.% P) powder with a spherical morphology and a mean particle size of 16 μm were used in this study. Phosphorus element, taking as a fluxing agent, was added in the form of pre-alloyed Cu–8.4P to improve the wetting characteristics in the powder system. The three components were homogeneously dispersed according to the Cu:CuSn:CuP weight ratio of 60:30:10 in a cylindrical vessel with a vacuum pumping system at a rotation velocity of 100 rpm for 90 min. The characteristic morphology of the as-prepared powder mixture is shown in Fig. 1.

2.2. Processing

The used DMLS apparatus mainly consisted of a continuous wave CO₂ (λ = 10.6 μm) laser with a maximum output power of 2000 W, an automatic powder delivery system, and a computer system for process control. Prior to the laser sintering process, a steel substrate was placed on the building platform and leveled. Then, a thin layer of loose powder with the thickness of 0.20 mm was spread on the substrate by the roller. Subsequently, the laser beam scanned the powder bed surface to form a layer-wise profile according to the CAD data of the part. The similar process was repeated until the specimen was finished. The laser sintering process was performed in ambient atmosphere at room temperature. The following laser processing parameters were used: spot size of 0.30 mm, laser power of 375 W, scan speed of 0.04 m/s, and scan line spacing of 0.15 mm. A rectangular sample with dimensions of 50 mm × 50 mm × 6 mm, as shown in Fig. 2, was successfully fabricated.

2.3. Characterization

The density of the laser sintered sample was calculated based on the Archimedes principle. A HBE-3000 Brinell hardness tester was used to determine the hardness of the sample. The tensile strength test was carried out at room temperature in a digitally controlled CMT-5105 testing machine at a loading rate of 1.0 mm/min. The tensile direction, X-direction in Fig. 2, was parallel to the sintered layers. Samples for metallographic examinations were prepared using standard procedures and etched with a mixture of FeCl₃ (5 g), HCl (10 ml), and distilled water (100 ml) for 30 s. Microstructures were characterized using a QUANTA 200 scanning electron microscopy (SEM). Chemical compositions were examined by an EDAX energy dispersive X-ray (EDX) spectroscopy. Phase identification was performed with a BRUKER D8 ADVANCE X-ray diffraction (XRD) analyzer.

3. Results and discussion

3.1. Phase

Fig. 3 shows the typical XRD spectrum of the laser sintered sample. It is clear that a new Cu-based phase α-CuSn, which is known as a solid solution of Sn in Cu, was presented after sintering, and, meanwhile, the starting Cu phase was retained in the sintered structure (Fig. 3). In the powder system as investigated, the pre-alloyed Cu–10Sn powder melts incongruently and has a relatively lower solidus temperature (~840 °C) and a liquidus one (~1020 °C) than the melting point of the Cu (~1083 °C) (Fig. 4a). Generally, the direct laser sintering of this powder system is based on the mechanism of liquid phase sintering involving the complete melting of the CuSn powder (so-called the binder) and the non-melting of the Cu powder (so-called the structural metal). The Cu–10Sn powder melts and, subsequently, precipitates again in the form of α-CuSn, leading to an efficient consolidation of liquid–solid mixture on cooling. Furthermore, Fig. 3 reveals that the P element was presented...
in the form of CuPO₃ after sintering, but without the existence of CuO or Cu₂O. Above the solidus temperature of Cu–10Sn (∼840 °C), the pre-alloyed Cu–8.4P powder is expected to be fully molten, because of a lower eutectic temperature of ∼714 °C (Fig. 4b). The dissociative phosphorus element will act as an in situ deoxidizer to have a preferential reaction with CuO:

\[
5\text{CuO} + 2\text{P} \rightarrow \text{P}_2\text{O}_5 + 5\text{Cu}
\]  

According to Table 1, the change in the Gibbs free energies (ΔG) of reaction (1) is −714.23 kJ/mol. Since ΔG is negative, the above reaction can proceed spontaneously. The reducing product (P₂O₅) will have a further reaction with Cu₂O, leading to the formation of copper phosphate (CuPO₃):

\[
\text{Cu}_2\text{O} + \text{P}_2\text{O}_5 \rightarrow 2\text{CuPO}_3
\]  

Generally, the surfaces of the commercial metal powder consist of many impurities, especially the oxide film on the particle surfaces [18]. Consequently, the wetting characteristic of a solid–liquid mixture during laser sintering is similar to the ceramic/metal system. The occurrence of the above two reactions can eliminate the oxide film and prevent the clean metal powder surfaces from reoxidation, leading to clean metal/metal interfaces in the sintering system. The presence of such oxide-free interfaces can improve the wetting properties between liquid phase and solid phase, thereby facilitating a more efficient densification without the balling effect.

### 3.2 Microstructure and composition

Fig. 5a shows the characteristic microstructure of the polished but non-etched sample. A pretty dense sintered...
structure surrounded with dark networks (grain boundaries) can be observed. Fig. 5b shows the EDX line scan results concerning the distributions of various elements along line AB in Fig. 5a. It is clear that the distributions of Cu and Sn elements show a relatively slight change. The distribution of P element, interestingly, shows a significant fluctuation at grain boundaries. During laser sintering, the binder Cu–10Sn and the additive Cu–8.4P, generally, melt completely to form the liquid phase. The Cu powder, due to the relatively higher melting temperature, dissolves slightly in the wetting liquid. As the laser beam moves away, the solid–liquid mixture undergoes a rapid solidification process. The high temperature phase α–Cu firstly starts to solidify. Due to a relatively high mutual solubility of Sn and Cu (∼11 wt.% at 350°C) (Fig. 4a), a relatively homogenous distribution of the Sn element in the Cu matrix in the form of α–CuSn solid solution is obtained after solidification (Figs. 3 and 5b). However, because of a low solubility of P in Cu (less than 1 wt.% at 350°C) (Fig. 4b), the P element tends to be pushed away from the Cu phase and, subsequently, segregates along the solidified phase, resulting in a high concentration along grain boundaries. On the other hand, since the thermal cycle in DMLS process is extremely short, the time for the homogenizing of the P in the Cu matrix is too short, thereby causing the non-uniform distribution of the P element in the sintered structure (Fig. 5b).

Fig. 6. SEM image showing the characteristic microstructure of the etched sample.

Fig. 7. EDX analyses showing chemical compositions in Zone A (a), Zone B (b), and Zone C (c) in Fig. 6.
Fig. 6 shows the characteristic microstructure of the etched sample. Fig. 7 depicts the chemical compositions measured in the various zones in Fig. 6. It is clear that a continuous network of dendrites was formed after sintering. Combined with XRD and EDX results (Figs. 3 and 7b), it is reasonable to conclude that such dendrites (Zone B in Fig. 6) were \( \alpha \)-CuSn solid solution. The structure surrounded by the dendrites (Zone A in Fig. 6) was consisted of a unique element Cu (Fig. 7a). Thus, the laser sintering mechanism of this multi-component powder system can be well explained as follows. In DMLS process, the binder CuSn melts and penetrates into the voids between the structural metal Cu, thereby surrounding and wetting the Cu particles. The solid particles undergo a rapid arrangement under the action of capillary forces exerted on them by the wetting liquid. As the liquid phase precipitates again in the dendrite morphology, the solids are bonded together to realize a densification of the sintering system. Furthermore, Fig. 7c shows that the P element was presented at grain boundaries (Zone C in Fig. 6), which is in accordance with the experimental results shown in Fig. 5. Also, Fig. 7c reveals the segregation of the oxygen towards the P-rich areas. This is because the phosphorus acts as an in situ sink for the oxygen during sintering, as indicated by reactions (1) and (2) in Section 3.1.

Table 2
Mechanical properties of the laser sintered sample

<table>
<thead>
<tr>
<th>Property</th>
<th>Measured value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative density (%)</td>
<td>94.6</td>
</tr>
<tr>
<td>Fracture strength (MPa)</td>
<td>169.2</td>
</tr>
<tr>
<td>Hardness (HB)</td>
<td>101.7</td>
</tr>
</tbody>
</table>

Fig. 8. SEM images showing the typical fracture surface of the laser sintered sample (a); local magnifications of Zones A and B (b and c).
Table 2 lists the mechanical properties of the laser sintered sample. It is reasonable to conclude that the DMLS process demonstrates a great promise to manufacture metal components with basic properties equivalent to conventionally processed Cu-based materials [19]. Fig. 8 shows the characteristic microstructure of the fracture surface of the laser sintered sample. Metallographic study at a relatively low magnification reveals the presence of diverse types of fracture (Fig. 8a). The fracture surface was mainly characterized by a ductile type of fracture, since a number of dimples were generally observed in a majority of areas (similar to Zone A in Fig. 8a) (Fig. 8b). Furthermore, a small fraction of areas (similar to Zone B in Fig. 8a) clearly exhibited the debonding along phase (or particle) boundaries, showing a typical intercrystalline fracture (Fig. 8c). Since DMLS is a layer-by-layer additive process, oxidation of the laser-processed powder is a severe impediment to liquid–solid wettability and, accordingly, causes delamination induced by poor interlayer bonding [6,20]. In the present study, the chemical reactions between phosphorus and oxygen, as mentioned above, allow the formation of phosphorus-based phases. Since these substances are generally lighter than the liquid metal, they tend to float on the top of the melt under the action of localized mass transfer within the molten pool [18,21]. After solidification, the phosphorous-based substances cover the surface of the sintered layer, thereby forming a protective film between the laser-processed materials and the ambient atmosphere. The effective protection of such film prevents the sintered layer from oxidation and, thus, ensures good wetting and coherent interlayer consolidation during laser sintering of the subsequent layer, leading to the presence of the strong ductile and intercrystalline types of fracture (Fig. 8b and c). However, Fig. 8b also reveals the formation of a small amount of pores on the fracture surface. In DMLS process, the laser beam scans over the powder bed in a line-by-line fashion and the duration of the laser irradiation at any powder particles is extremely short (typically less than 4 ms) [22]. The rapid and localized nature of DMLS prevents the sufficient removal and diffusion of the liquid phase in certain laser-irradiated areas, hence weakening the bonding cohesion of the structural metal by the liquid and, accordingly, leaving some pores in the sintered structure (Fig. 8b).

4. Conclusions

We have performed a detailed investigation into the metallurgical mechanisms in direct laser sintering of a multi-component Cu-based metal powder consisting of a mixture of Cu, Cu–10Sn, and Cu–8.4P. The liquid phase sintering with the complete melting of the binder CuSn and the non-melting of the structural metal Cu acts as a feasible mechanism of laser sintering. The additive phosphorus element can act as an in situ deoxidizer to prevent the sintering system from oxidation by formation of P₂O₅ and CuPO₃, thereby improving the liquid–solid wetting characteristics and the resultant sintered densification. The phosphorus element shows a high concentration along grain boundaries, due to a low mutual solubility of P and Cu as well as the short thermal cycle during laser sintering. The fracture surface of the laser sintered sample is primarily characterized by a strong ductile type of fracture, which is attributed to the efficient protection of phosphorous element against the interlayer oxidation.

Acknowledgements

The authors would like to thank the financial support from the Joint Fund of National Natural Science Foundation of China and China Academy of Engineering Physics (10276017), the Aeronautical Science Foundation of China (04H52061), and the Scientific Research Innovations Foundation of Nanjing University of Aeronautics and Astronautics (S0403-061). One of the authors (Dongdong Gu) gratefully acknowledges the support from the Graduate School, Nanjing University of Aeronautics and Astronautics.

References