Selective Laser Sintering of Binary Metallic Powder

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Abstract

A selective laser sintering technique has been used to process metal powders and powder blends. Precursor powders include copper, tin, a 70Pb-30Sn solder and their blends. Excessive balling due to surface free energy effects occurred in single layer tests when the laser fluence was sufficient to cause melting of monolithic tin or solder. Improvements in single layer quality were obtained using copper-solder powder blends in a reducing atmosphere. The binary powder layers were characterized metallographically and the effect of processing parameters such as laser fluence and scan speed were assessed. Post-process annealing improved interparticle wetting and part strength. The influence of $ZnCl_2$ flux was investigated when present as a coating in copper-solder blends. Multiple layer tests were performed on the most promising powder blends and the results are presented.

Introduction

Laser processing of metals has been widely reported with special emphasis on areas such as cutting, microalloying and cladding[1-3]. Recently, a novel technique called selective laser sintering has been developed to produce three-dimensional objects directly from a CAD database without part-specific tooling or human intervention[4]. This technique has been utilized to study the feasibility of producing metal parts from metallic powders. The goal is to use this process to create metallic parts which can compete in strength with those already being made by powder compaction, casting, machining or other conventional manufacturing processes. Four important areas of interest in laser-metal processing are laser parameters, material properties, environmental conditions and laser-material interactions. The first group comprises parameters such as laser output power and power density, laser wavelength and beam size. The second group includes parameters such as particle size/shape, thermal conductivity, thermal diffusivity, melting point and optical reflectivity. The third group consists of factors such as the type and conditions of the processing atmosphere. And finally, the fourth group comprises all the effects that could enhance or reduce the otherwise steady coupling between the material and the laser.

In the present work, the first three groups have been studied relative to the production of metal parts using the selective laser technique on metallic powder precursors. The analysis of laser-material interactions in these material systems has not been initiated.

Experimental

A computer controlled, low-power, Q-switched, TEM_{00} Nd:YAG laser (λ= 1.06μm, nominal power capacity = 100 W, beam size = 0.5 mm) was used to selectively sinter metal powders under two different conditions. Starting powders include 99.0% copper (-100 mesh), 99.5% tin (-100 mesh) and a 70 Pb-30 Sn solder mixture (-100 mesh). The maximum particle size was 150 μm. When a flux was applied, crystals of $ZnCl_2$ were dissolved in alcohol and a 50Cu-50 solder powder (by weight) blend was added to this alcohol solution. The solution was dried in vacuum at a temperature of 60-90 C and finally sieved to produce a $ZnCl_2$ coated metal powder mixture. The fraction of $ZnCl_2$ in the mixture was 5 percent by weight.

The work station providing selective laser sintering has been described elsewhere[4]. Either air or a localized flow of nonflammable, reducing Forming Gas ($96N_2$-$4H_2$) was used in the experiments to compare their effects on the surface quality of single layer tests and later on interlayer bonding of multiple layer tests. The computer program controlling the laser allowed some variation in the processing parameters so their influence on part quality could be analyzed. Output power of the laser was in the range of 8 to 26 watt and the scanning speed was in the range 3.4 to 6.8 cm/sec. This yielded incident power densities ranging between approximately 4 x10^3 to 1 x10^4 W/cm^2. Scanning Electron Microscopy (SEM) was used to determine the extent of sintering in the samples. X-ray analysis and energy dispersive spectroscopy (EDS) were performed to determine the effect of the $ZnCl_2$ coating on the samples as processed and after a post-process anneal of 1 hour at 400 C in a hydrogen atmosphere.

Results

Monolithic Tin

Despite being a low melting point element the laser sintering of tin powder is not straightforward. Surface free energy effects as well as optical properties (reflectivity) dominate in this process. The latter factor has been widely recognized and described in earlier work on surface melting of copper using high-power (1.5 kw) lasers[5-7]. Here, surface free energy effects are thought to be dominant. In Figure 1 are shown the effects of laser power and scanning speed on the degree of sintering (single layers) of tin powders under a localized reducing gas flow. At lowest power densities tin powders do not melt or sinter. Once melting occurs, a ball-type pattern results independent of the scanning rate and the power density. The effect of increasing the laser power and/or decreasing the scanning speed is then to increase the size of the balls.

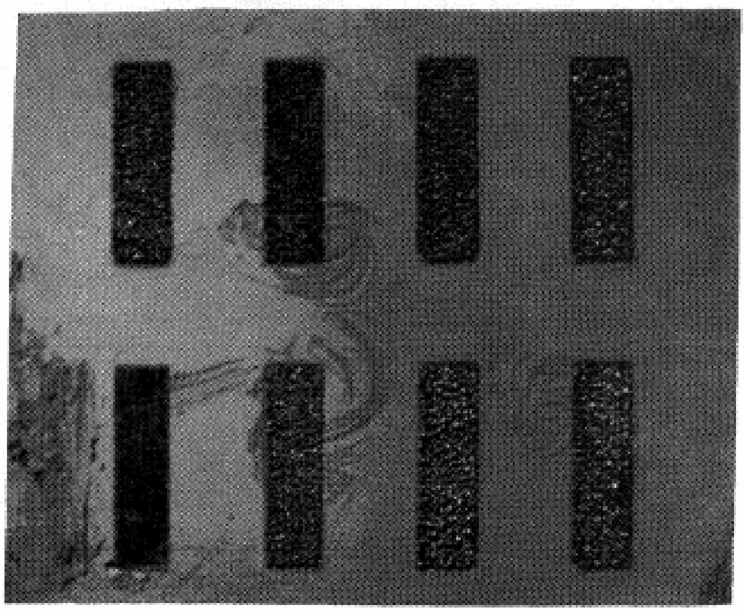

Figure 1 - Influence of laser output power and scanning speed on the surface melting characteristics of powdered tin under a localized Forming Gas flow and at room temperature. The top row shows samples with the same sintering power (P= 24 W) but different scanning speeds (6.8, 4.5, 3.4, 2.7 cm/sec from left to right). The bottom row shows samples with the same scanning speed (3.4 cm/sec) but different sintering powers (8, 18, 22, 26 W from left to right). The actual dimensions of each rectangle are 6 mm by 25 mm.

Copper-Solder powder blends

A 50Cu-50 solder powder blend was used to produce single layers under localized Forming Gas flow. The results are shown in Figure 2 for P= 24 W and a scanning speed of 3.4 cm/sec. The solder melted under laser irradiation and solidified in a ball pattern similar to the monolithic tin powder. Poor wetting over the copper particles was achieved. The effect of laser power and scanning speed was approximately identical to the monolithic tin case as well.

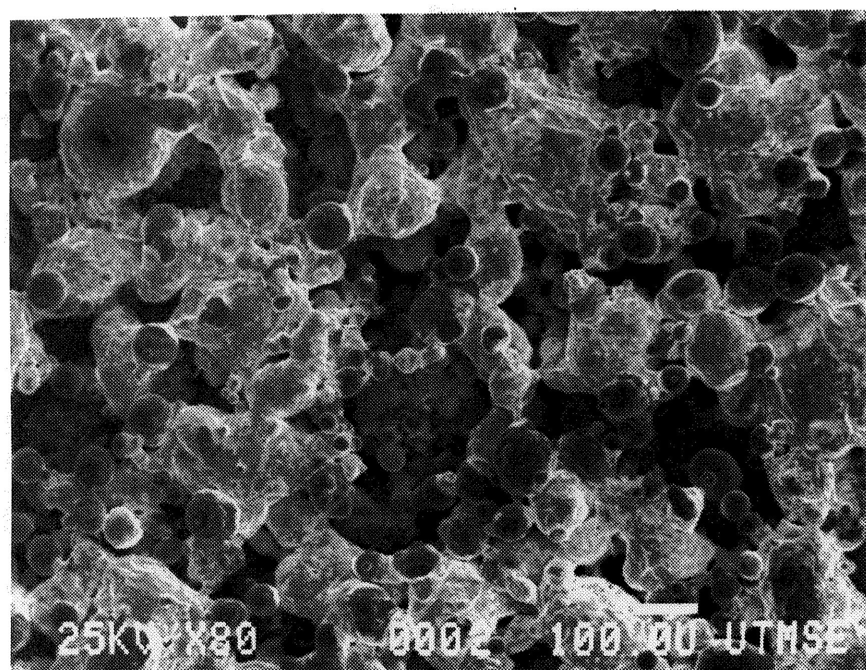

Figure 2 - Micrograph showing the surface sintering characteristics on the final surface of a four layer part. The initial powder mixture was 50Cu-50 solder (150 μm). Test parameters are P= 24 W, Scanning Speed = 3.4 cm/sec, room temperature under a localized Forming Gas flow. When the solder melts it tends to agglomerate and does not adequately wet the copper particles. The white bar represents 100 μm.

Multiple layer tests were performed on this material system to determine the extent of interlayer bonding. Figure 3 shows a cross section of a four layer part after fracturing. The four layers are visible, and an accumulation of loose powder is present (upper right hand side). This accumulation is powder which was under the first sintered layer at the start of the process. Significant bonding between layers does not occur, and this sample separated along layer interfaces with minimum effort. Part density was not measured, but from the SEM micrograph appears to be very low, possibly about 60 percent.

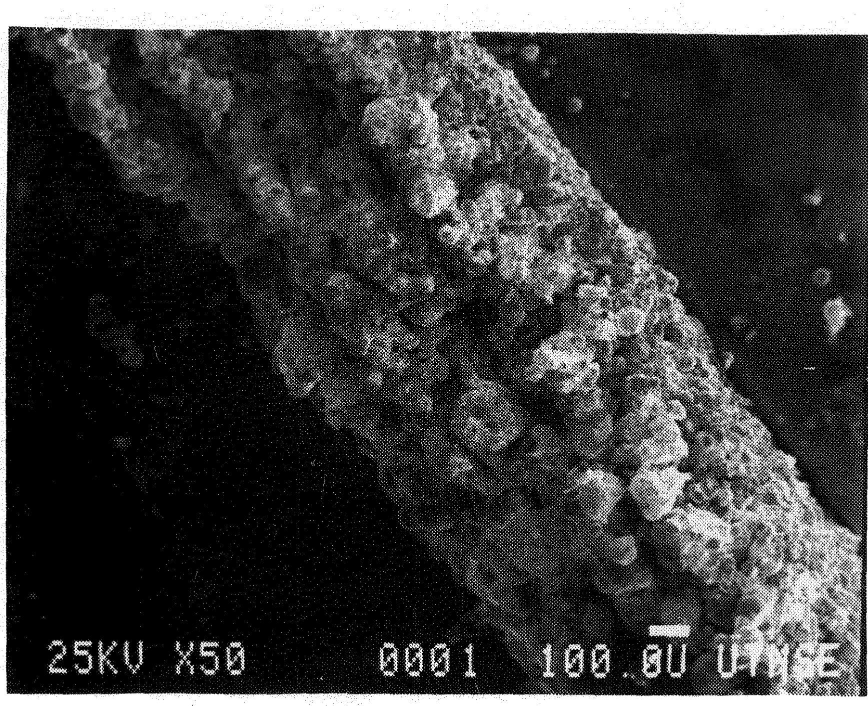

Figure 3 - This is a micrograph of a cross section of the same part shown in Figure 2. Note that the four layers can be easily distinguished. The bonding between layers is generally poor. The top layer of fine powder is loose powder that was not cleaned from the bottom of the as-processed part before analysis. The white bar represents 100 μm.

Copper-Solder/$ZnCl_2$ powder blends

Since $ZnCl_2$ is a main component in standard solder fluxes, the addition of $ZnCl_2$ to the starting powder was expected to improve the wetting of the molten solder on the copper particles during laser processing. Figure 4 shows the top surface of a six layer part processed at 26 W and a scanning speed of 3.4 cm/sec. The appearance of this surface indicates that better wetting was achieved although the surface still appears to be very porous (cf., Figure 2). An overview of a part made of 72 layers is shown in Figure 5. Figure 6 shows a cross section of the same part shown in Figure 4 after fracturing. It indicates that a better bonding between layers was achieved than in the Forming Gas experiments, as the cross section looks homogeneous even though it consists of six layers (i.e., individual layers are not easily distinguished). Post processing of this piece was performed and part integrity was increased. However, a much improved structural state of the as-processed parts is desirable if post processing is to produce optimum properties in the final parts.

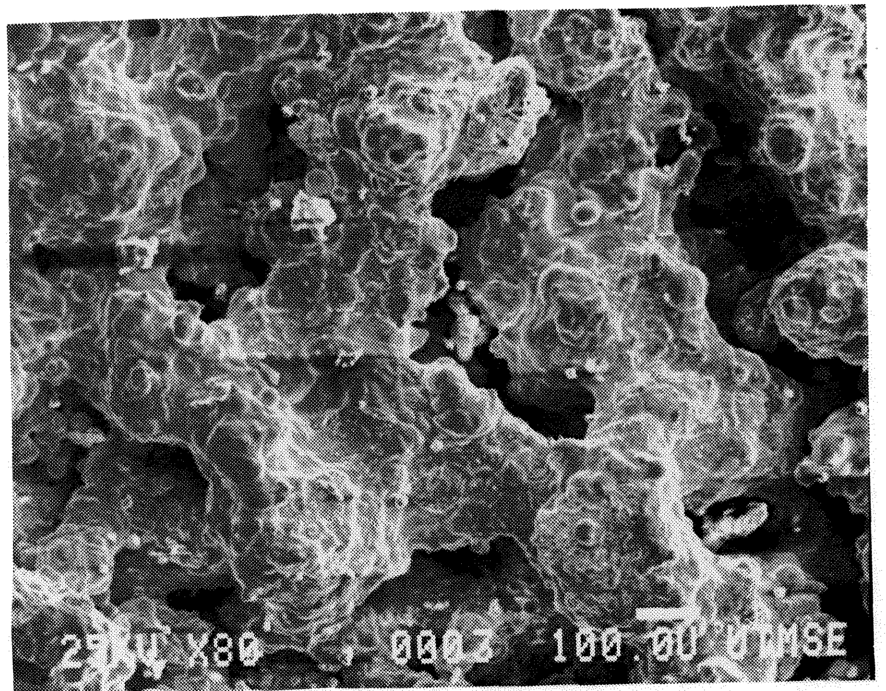

Figure 4 - Micrograph showing the surface sintering characteristics on the top surface of a six layer part. The initial powder mixture was 95 percent 50Cu/50 solder with 5 percent $ZnCl_2$ added. Test parameters are P = 26 W, scanning speed = 3.4 cm/sec, room temperature, under a localized Forming Gas flow. This specimen exhibited better wetting characteristics than the samples processed without a flux. The white bar represents 100 µm.

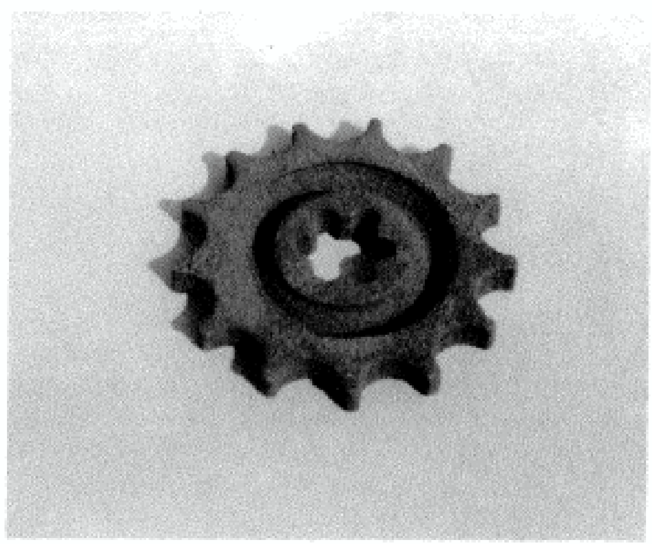

Figure 5 - An overview of a part made of 72 layers. The maximum particle size was 150 µm. The initial powder mixture was 95 percent 50Cu/50 solder with 5 prcent $ZnCl_2$ added. Test parameters are P = 26W, scanning speed = 4.5 cm/sec in air and initial powder temperature above 90 degrees C.

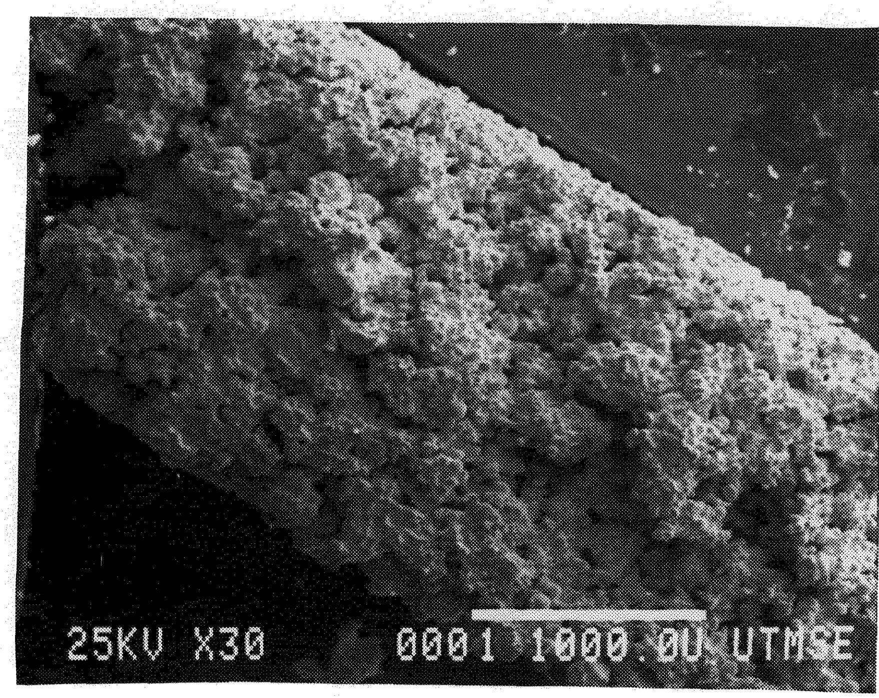

Figure 6 - Micrograph showing a cross section of the part shown in Figure 4. A more homogeneous cross section surface, evidenced by lack of a distinguishable layer structure, indicates better bonding among layers. The white bar represents 1 mm.

X-ray and EDS measurements indicate that when $ZnCl_2$ (5% by weight) was added to the copper-solder powder mixture it effectively coated the particles of the mixture even after lasing. This can be deduced from the high content of $ZnCl_2$ evenly detected when the surface of an as-lased copper-solder/$ZnCl_2$ powder sample was analyzed using EDS. After the powder was selectively laser sintered a significant amount of $ZnCl_2$ still remained on the surface. However, after post processing, the content of $ZnCl_2$ on the surface was significantly reduced.

Atmosphere effects

Initial experiments on tin and copper-solder blends were carried out using an atmosphere of air or a localized flow of Forming Gas, with the latter being more effective with respect to improved interparticle bonding. This is thought to be due to a decrease in melt surface oxidation which improves wettability of the lower melting point phase[8]. It is not currently possible to monitor the quality of the atmosphere in the current experimental apparatus, although modifications are underway to alleviate this problem. It is therefore unclear at present whether atmosphere alone will be able to provide adequate shielding during selective laser sintering.

Discussion

In metallic systems, surface free energy is expected to be dominant in the precise control of the melting reaction on the surface of the samples. This in turn controls the results of interparticle bonding in the first stage of the selective laser sintering technique. As indicated in Figures 1 and 2, the density and, by implication, the strength of tin- and copper-solder laser sintered parts was extremely low due to poor wetting achieved on these samples. Both a localized flow of reducing gas and the addition of $ZnCl_2$ were intended to improve the wetting characteristics of the molten zone on the unmelted particles of copper before resolidification occurs. This was partially achieved as seen in Figure 4, where random bridges or ligaments formed between resolidified zones. This has also been achieved in single layer tests when Forming Gas blanketed the powder surface during lasing[8].

It is believed that the dissolved $ZnCl_2$ effectively coated the copper and solder particulates after the whole solution was precipitated and dried. Thus, during laser sintering the $ZnCl_2$ reduced the effect of the impurities/oxides and improved wetting could be achieved. The high content of $ZnCl_2$ on the surface after laser sintering could be due to the fact that resolidification occurs in a very short time after the lasing of the solder and $ZnCl_2$ particles. However, during the post-process annealing of the sample both the solder and $ZnCl_2$ melt. From EDS of the post-processed specimen, the chlorine content is much reduced. This is most likely due to volatilization of the flux at least on the specimen surface.

Viewing the selective laser sintering process from an overall perspective, it is clear that one of the major issues to be addressed is the low apparent density of all parts produced, with and without subsequent post processing. While conventional powder processing techniques such as hot isostatic pressing would undoubtedly improve part density without destroying the part geometry, it tends to defeat the purpose of selective laser sintering, namely, to produce structural parts quickly.

Conclusions

Metal parts have been produced using a technique known as selective laser sintering. Elemental particulates upon melting tended to ball up due to surface free energy effects. This was eliminated by using a powder blend of a high melting point powder and a low melting point powder. The intention was that the latter would melt under the beam during processing and would wet the non-melted, high melting point powder. It was found that the use of a localized reducing atmosphere and addition of a $ZnCl_2$ flux in the starting powder mixture led to better bonding among metal particles after the laser sintering process. Samples showed sufficient strength to be handled but still lacked the strength required for service applications. SEM and EDS analysis indicated that even though low density pieces are being produced in the experiments so far, the wetting of Cu particles by molten solder and $ZnCl_2$ was improved.

For the future, better control of the atmosphere, the thermal gradient across the sample and the study of new compositions and blends are of essential importance in this stage of the novel manufacturing process development. Also, an understanding of heat transfer and laser-material interactions in the powder assemblage are needed to support new experiments.

Acknowledgments

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