Support-free sintering of 3D printed binder jet copper and stainless steel parts

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Abstract

Binder jet additive manufacturing involves selectively applying a binder, layer-by-layer, to produce green parts, followed by a high temperature sintering treatment. During sintering, green parts are inherently prone to undesired part distortion/sag in the unsupported regions. Traditional methods use 3D printed supports or machined ceramic setters to avoid the part distortion/sag during sintering. We introduce a shape-retaining-stimulus coating that will mitigate/eliminate the need of additional supports during sintering. Simply supported coper and stainless steel green parts of various thickness were evaluated for part distortion. Our experimental results demonstrate that a selective application of the shape-retaining-stimulus coating on 3D printed copper parts with a spanning up to 50 mm, and stainless steel parts spanning up to 33 mm can be sintered without auxiliary supports. Our shape-retaining-stimulus coating produces exceptional results, and the ease of removal makes it an attractive candidate.

Introduction

According to ASTM F2792 − 12a, additive manufacturing, is defined as a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies [1]. In metal additive manufacturing the raw material can be metal powder, filament, or wire depending on the type of process used. In laser powder bed fusion and electron beam melting, a layer of powder is spread, and a localized heat source melts a precise volume of metal, typically on the order of a few hundred microns. The heat source rasters across the powder bed based on the slice dimensions defined by the CAD model to melt and solidify the powder. The process is repeated layer-by-layer until the part is fully built [2]. In wire arc additive manufacturing, a track of material is weld-deposited by melting of the feed wire and the process is continued to deposit layers of weld beads to build a 3D part [3]. In direct energy deposition, a stream of metal powder is jetted into a small molten pool of metal, and material is deposited track- by-track and layer-by-layer to build a 3D part [2]. In all the above processes where melting and solidification is involved, a part with overhanging features is provided with support structures which are built under the part. Support structures are well defined thin structures that provide necessary support to avoid part distortion/sag. Finally, these printed support structures are machined off the part surfaces. For example, consider a part with a simply supported configuration (figure 1a) to be built using laser powder bed process, the overhang span region will require support structures underneath (figure 1b).

Binder jetting of metal is an additive manufacturing process in which a liquid binding agent is selectively deposited to bind metal powder together in a layer-by-layer fashion to create 3D objects, named green parts [4]. After binder jetting, the green parts are subjected to a de-bind treatment, followed by a high-temperature densification process called sintering. As the temperature is increased during debind/sintering, the binder decomposes and leaves the green part.

Simultaneously, metal particle-to-particle necking initiates, and bonding cross-sectional area increases as sintering progresses. An increase in the bond area leads to an increase in the part strength. On the other hand, due to the prevailing high temperatures, the overall tensile strength is compromised. Therefore, the balance between the high temperature tensile strength and bonding area dictates the extent of part sag [5]. During sintering, as the temperature is increased, parts with overhanging or spanned features tend to distort/sag under gravitational forces. Support structures or systems are essential on parts with spanned or cantilevered features to counteract sag or other geometric distortions in the final part. The current solutions used in the industry are (i) to print a live-setter along with the part and apply an inter layer of ceramic coating before assembling them for sintering, figure 2a; (ii) provide machined ceramic setters to support the parts during sintering, figure 2b. These solutions were derived from traditional MIM sintering industry experience and are widely accepted and have proven successful. In metal fused filament fabrication (FFF) metal powder and the binder is extruded into thin tracks make a layer, and the process is repeated to produce a 3D green part [6]. To counteract sintering distortion in FFF parts, methods similar to the binder jet part sintering are employed. Up to this point in time there have been no solutions available in the open literature to sinter binder jet printed green parts without support structures.

In the current work, we present a new innovative method to sinter binder jet printed green parts in simply supported configuration without support structures. Proprietery shape-retaining-stimulus coatings developed at HP Labs were used in the study. Shape-retaining-stimulus coatings were selectively applied to the green part to counter distortion/sag during sintering. We demonstrate support-free sintering of 3D printed green parts made of copper and stainless steel.

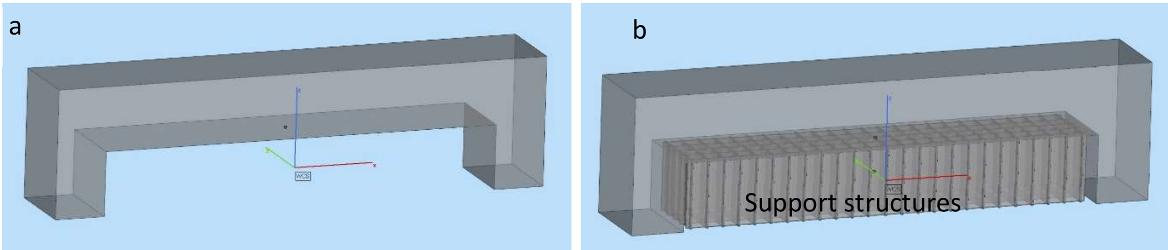

Figure 1. (a) CAD design of a part in simply supported beam configuration (b) CAD design of a simple supported beam part with support structures.

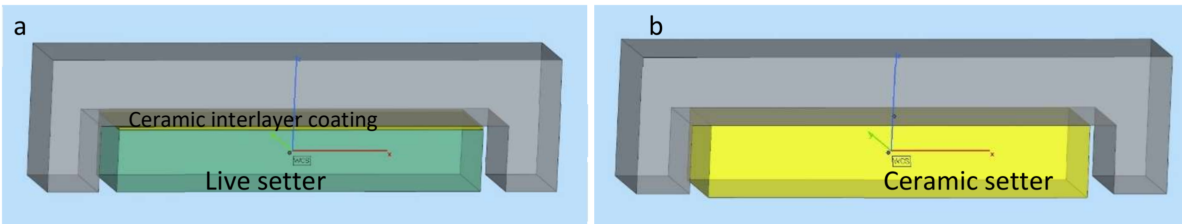

Figure 2. (a) CAD design of a simple supported part with a live-setter with ceramic interlayer coating (b) CAD design of a simple supported part with ceramic setter.

Experimental work

Binder jet green parts of copper and stainless steel were produced using HP Metal Jet technology. Binding agents used in the study were aqueous solutions. A pre-defined amount of binder was jetted on to metal powder in a layer-by-layer fashion. Simply supported parts were produced to study deformation during sintering. A sample CAD geometry of the part is presented in figure 1a. Copper green parts with an overhanging span of 28 mm and 50 mm; and stainless steel green parts with an overhang span of 33 mm were considered in the study. After the part is 3D printed, with the parts in the build bed are subjected to a drying and curing process in a curing station. In the curing station, binder solvents evaporates and, decompose forming a strong bond between the powder particles to produce strong green parts. The green parts are then subjected to de-bind and sintering treatment. The de-binding process fully decomposes the binder; simultaneously necking initiates at the particle contact points. To estimate copper part distortion in the overhang region the green parts were subjected to sintering at different temperatures from 500°C to 1040°C. Final sintering of copper parts and were carried out at 1040°C for 4 h and stainless steel parts at 1370°C for 2 h in forming gas. Part distortion was characterized by the angle of deflection at the edge of the simply supported beam. To mitigate the part distortion several different proprietary shape-retaining-stimulus coatings were developed. The coatings used in this study are referred to as coating SRSC-Cu and coating SRSC-Steel, for copper and stainless steel, respectively. The coatings were applied on the green part surfaces in a slurry form and dried before subjecting to sintering. After sintering, the coating on the part surfaces were brushed off and part surfaces are sand blasted for final cleaning.

Results and discussion

Support-free sintering of copper green parts:

Copper powder from Goodfellow Cambridge Ltd., with a particle size up to 50 µm was used in the study. An SEM micrograph and the particle size distribution (PSD) plot of the powder is presented in figure 3. The SEM micrograph shows the powder has spherical morphology, which is an important powder characteristic for good flowability. The PSD analysis showed $D_{90} \approx 50$ µm, $D_{10} \approx 14$ µm, and $D_{50} \approx 30$ µm in diameter. The average particle size was ≈33 µm in diameter.

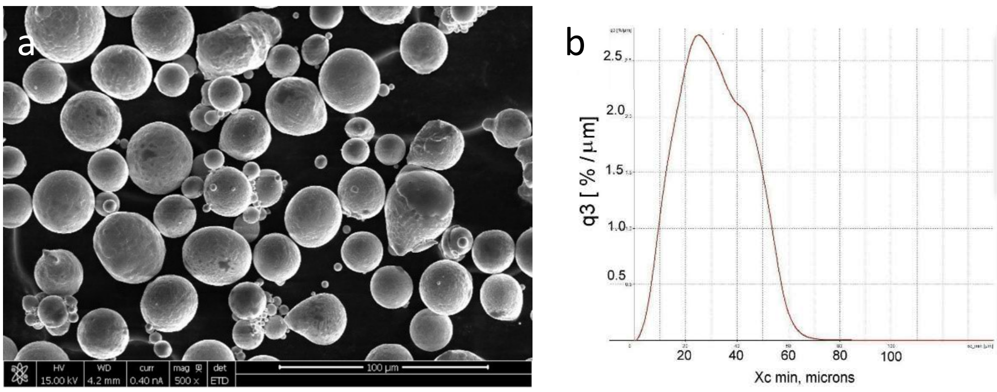

Figure 3 (a) SEM micrograph and (b) PSD plot of copper powder used in the study.

The copper powder is heated to nearly 100°C on the bed before printing and the build bed temperature is maintained throughout the print process. During the print process, the binder jet on the metal powder particles undergoes multiple thermal cycles, where it undergoes solvent evaporation→ dehydration → partial decomposition and bind the powder particle together. After curing the full green strength was realized. Typical green part strengths were on the order of 5 to 8 MPa. Figure 4 shows a photograph of green parts on the powder bed, and an SEM cross-section of the fracture surface of a green part showing particles bound together with the binder.

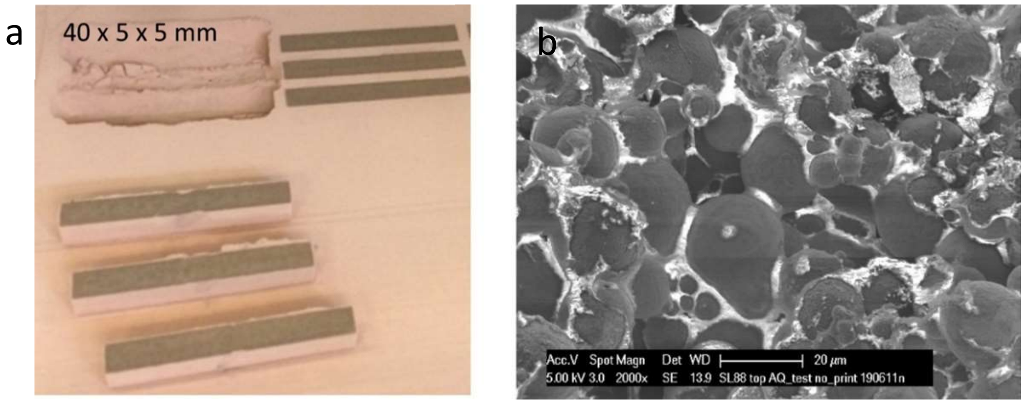

Figure 4 (a) Sample green parts after cure, and (b) SEM micrograph showing fracture surface of a green part.

A green part in a simply supported beam configuration was sintered at 1040°C for 4 h. The green part and as-sintered part are presented in figure 5 a & b, respectively. The sintered part shows severe distortion/sag in the span region. To estimate the progress of sag with respect to temperature, green parts with 28 mm span were sintered at different temperatures and the angle of distortion was measured. By measuring the angle of deflection, the amount of distortion was evaluated. The results present in Table 1 show an increase in distortion angle with an increase in sintering temperature. The part sag is attributed to the reduction in tensile strength as the temperature is increased, and the tensile strength is defined by the necking bonding area in the part. Thereofore, the part is not able to withstand its weight and it slowly sags under gravity [5].

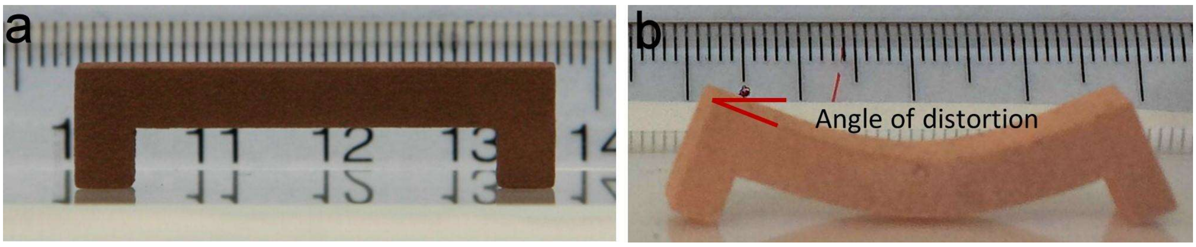

Figure 5 (a) Green part in simply supported configuration and (b) sintered part showing severe sag. (Note: 1 div = 1 mm on the ruler)

Table 1. Effect of sintering temperatures on the angle of distortion.

Sintering treatment	Angle of distortion
500°C-30 min	< 1°
800°C-30 min	5°
1000°C-30 min	12°
1040°C-4 h	20°

In order to minimize the amount of part sag, multi-step sintering experiments were carried out. The following multi-step sintering profiles were used:

i. 300°C -1 h + 500°C -2 h +650°C-1 h+1000°C-30 min
ii. 600°C -1 h + 1000°C-30 min

Figure 6 shows the part sintered using profile (i) listed above. During multi-step sintering the part is held at lower temperatures before reaching the final sintering temperature, this allows the bonding area between the powder particles to increase, thereby increasing the load bearing ability of the part. In both the multi-step sintering experiments the parts showed a 33% decrease in the angle of distortion, from 12° to 8°. Although these results showed an improvement with a reduced distrotion, the mutli-step sintering approach does not fully eliminate part distortion.

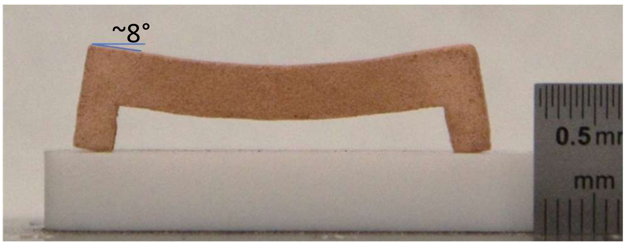

Figure 6 Sintered part showing reduction in the angle of distortion after multi-step sintering. (Note: 1 div = 1 mm on the ruler)

HP Labs has developed shape-retaining-stimulus coatings to mitigate part sag during sintering [7,8,9]. The proprietary coatings material was mixed with the aqueous binding agent to form a slurry and then applied to the green part surfaces as shown in figure 7. The coated green part was cured for sufficient time for the binder to hold the coating in place. For initial experiments, a green part measuring 40 x 5 x 2.4 mm was placed over green parts at either end to form a unsupported span of 28 mm. The assembly was subjected to the following sintering cycle: 300°C-1h + 500°C-2h + 650°C-1h + 1000°C-30 min. The sintered assembly of parts is presented in figure 8 a & b. After sintering the part without coating has sagged significantly, whereas the part with coating stayed intact without any distortion/sag.

The coating was then applied to the simply supported bars with a span of 28 mm and 50 mm as shown in figure 9 and 10. The green parts with coating were cured and sintered at high temperature. After sintering, parts with spans of 28 mm and 50 mm, the parts did not sag and retained their shape during sintering process. The SRSC coating undergoes a chemical reaction during sintering resulting in a porous network product, and it’s weakly adhered to the part. With slight application of force, the coating can be peeled and brushed off from the final part surfaces, which makes it convenient and easy to remove. After sintering, the parts after were cleaned by simply brushing off and sand blasting. A sintered part after final cleaning is shown in figure 9c, with no evidence of coating application. The coating was applied to green part with overhanging structures inclined at 30°, 45° and 60° angles (figure 11) prior sintering. The part was sintered with the overhang’s bottom surface facing downwards. The sintered part with and without coating presented in figure 12 showing that the coating was able to successfully retain the structure and avoid part sag. Our results demonstrate that fundamentally challenging, inherent part distortion during sintering can be addressed by application of HP Labs’ propriety coatings on 3D printed part surfaces.

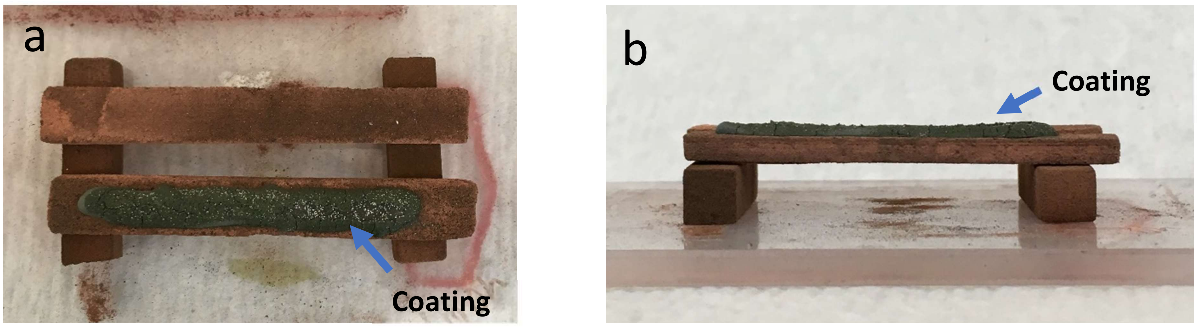

Figure 7 Green parts of dimensions 40x5x2.4 mm were arranged in simply supported configuration. Green parts with and without coating (a) top view, and (b) side view.

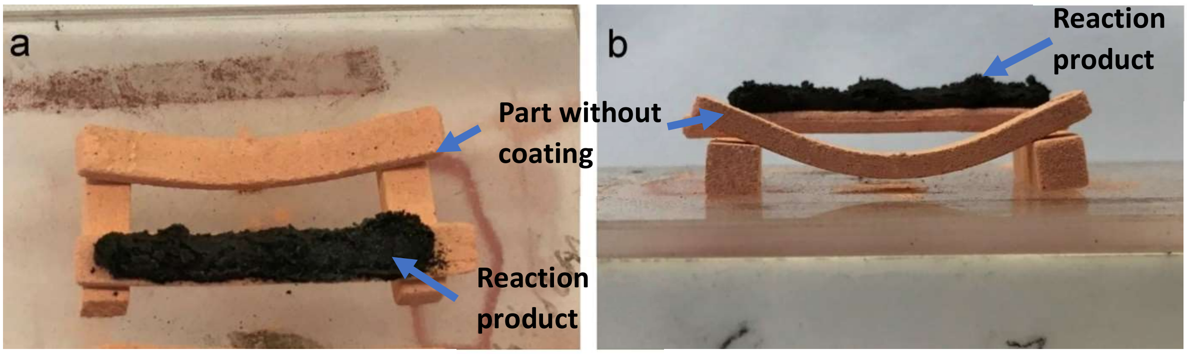

Figure 8 A sintered part with coating showed no part sag, whereas the part without coating sagged significantly, (a) top and (b) side view (photo was taken from opposite end of Figure 7b for clear representation).

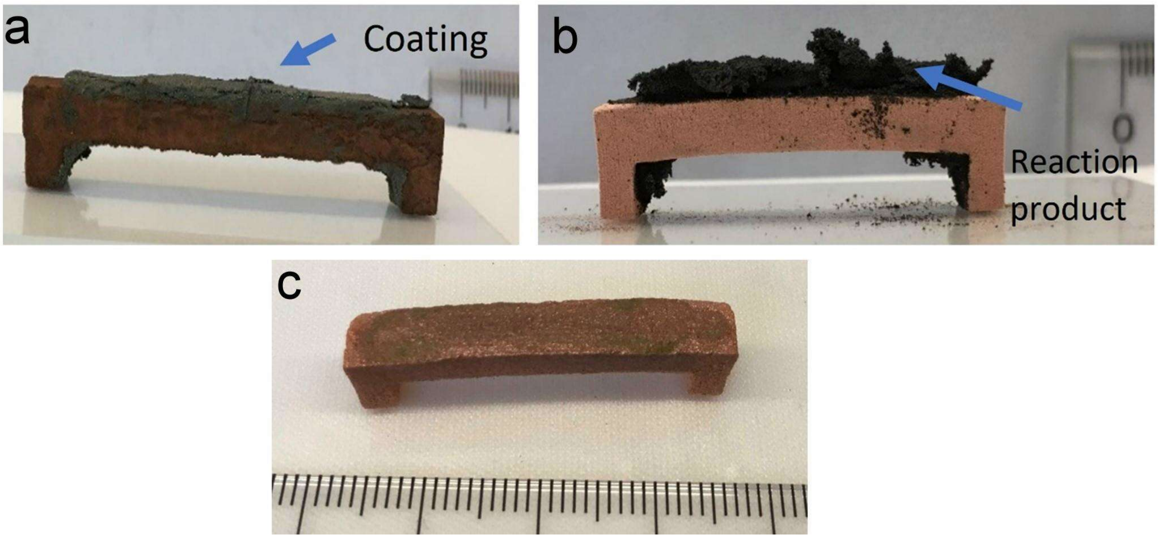

Figure 9 Part in simply supported beam configuration (28 mm span) (a) green part with applied coating, (b) part after sintering retained its shape without sag, (c) part after cleaning. (Note: 1 div = 1 mm on the ruler)

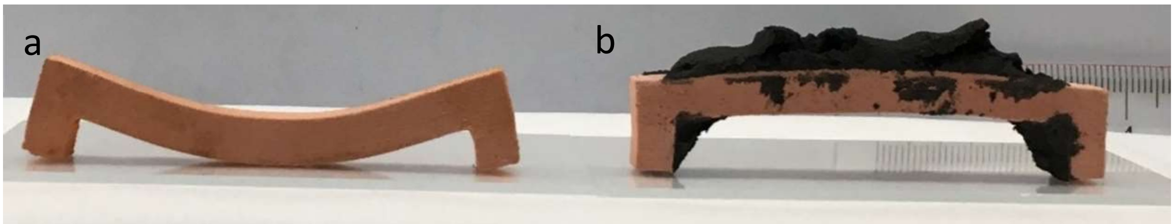

Figure 10 Sintered part in simply supported beam configuration part with 50 mm span (a) without coating and (b) with coating retained its shape without sag. (Note: 1 div = 1 mm on the ruler)

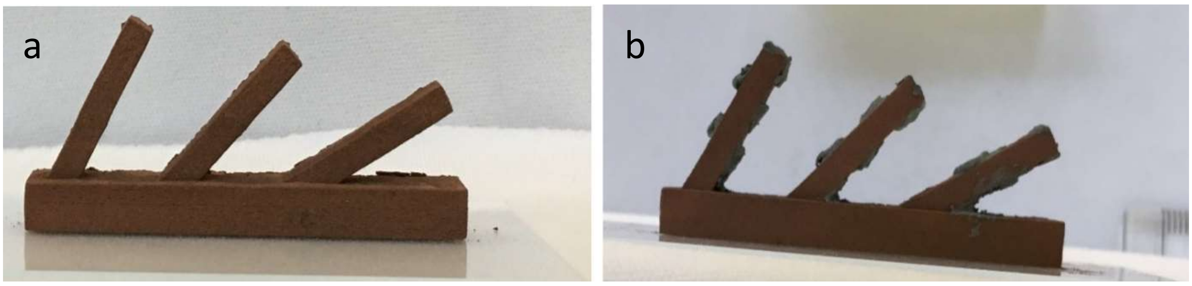

Figure 11 Green part with overhangs of 30°, 45° and 60°, (a) without SRSC coating and (b) with selective application of SRSC coating. (Note: 1 div = 1 mm on the ruler)

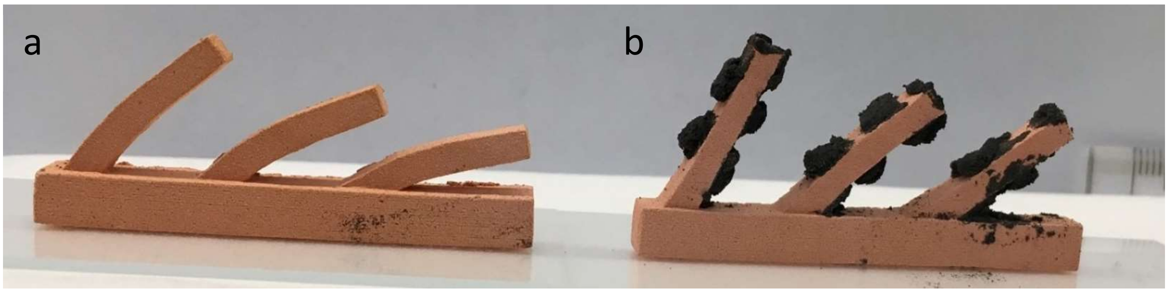

Figure 12 Sintered part with overhangs of 30°, 45° and 60°, (a) sections without coating show sag and (b) with selective application of coating retained its shape. (Note: 1 div = 1 mm on the ruler)

To understand the mechanism of support-free sintering using the SRSC coating, two different sintering studies were carried out, (i) 300C-1h+500°C-2h and (ii) 300C-1h+ 500C-2h+600°C-30 min. Figure 13a shows a part with coating sintered at 500°C and figure 13b shows cross-section stereomicrograph of the broken part. The coating showed strong bonding with the part surface and provided the necessary support to avoid sag. During the high temperature hold, neck-bonds between the particles increase in volume, and the part would be able to support itself thereon. The green part with the coating sintered at 600°C is presented in figure 14a, show that the coating underwent a chemical reaction and result in a porous network adhered to the part. The coating can be cleaved off easily by the application of some force, figure 14b.

The coating application methodology and coating composition was optimized during the study. A few examples of minimal and patterned coating were presented in figure 15. A thin layer of 150 to 200 μm was applied to the part surfaces (a) as a thin layer and (b) selective application of coating and (c) patterning of coating.

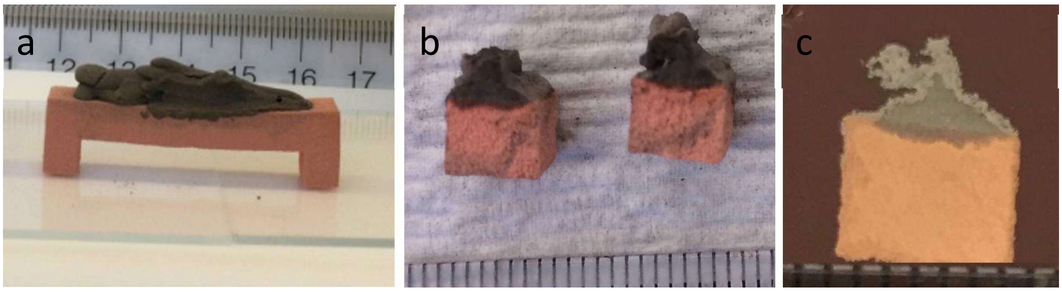

Figure 13 (a) A part with coating treated at 500°C, (b & c) sintered part broken surfaces showing strong bonding between the part and the coating. (Note: 1 div = 1 mm on the ruler)

Figure 14 (a) A part with coating treated at 600°C, (b) peeled off coating by application of force, and (c) part after cleaning. (Note: 1 div = 1 mm on the ruler)

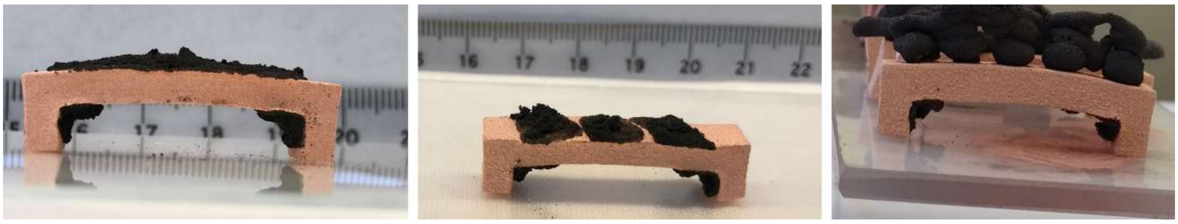

Figure 15 Sintered parts with reduced coating amount, and patterning of coating showed no part sag during sintering. (Note: 1 div = 1 mm on the ruler)

Further, a dotted pattern with reduced amount of SRSC-Cu coating (slightly modified composition) was applied on the green part before sintering at 1040C- 4 h. The dotted pattern SRSC-Cu coating covered 20 -25% of the part top surface area. Figure 16 shows the sintered part could resist sag to some degree. The dotted pattering provides a plausible means to automate the slurry application on the part surfaces. The above mentioned studies involved manual application of the coating. However, further studies are necessary to precisely control the amount and method of application of the coating.

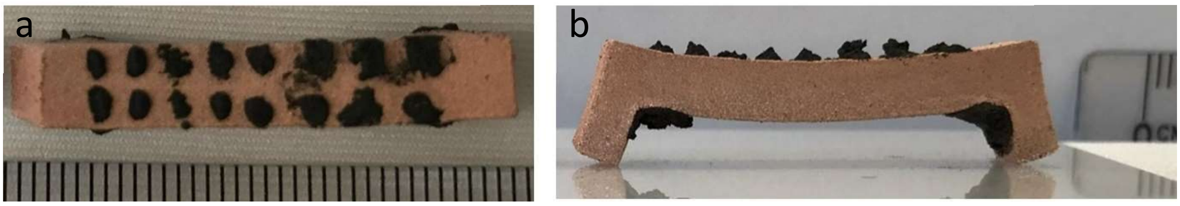

Figure 16 A dotted patterned coating with SRSC-Cu coating show to overcome part sag during sintering (a) top view (b) side view. (Note: 1 div = 1 mm on the ruler)

Support-free sintering studies on stainless steel parts:

Stainless steel AISI316 (-22 microns, Sandvik Inc.) was used to print green parts in a simply supported configuration using an aqueous binder on HP's Metal Jet Printer. To assess the stainless steel part distortion during sintering of a simply-supported beam, a part with dimensions: span of 33 mm, width of 7 mm, span area thickness t=5.7 mm and t=2.8 mm, overall length of 42 mm, and height of 11 mm (figure 17) was considered. By measuring the angle of deflection, the amount of distortion was evaluated. A stainless steel part with an overhanging span of 33 mm showed a distortion of about 13° for a 5.7 mm thickness and 16° for a 2.8 mm thickness during sintering. The current work uses an applcation of SRSC-Steel coatings on top of the green part surfaces to avoid distortion during high-temperature sintering. During intital stages of sintering/debind, these coatings metallurgically bond with the green part and provide the necessary strength to avoid distortion. As the temperature exceeds 900°C, stainless steel particle-to-particle necking starts and increases in width with temperature. The increased necking of the particles imparts strength to the sintering part.

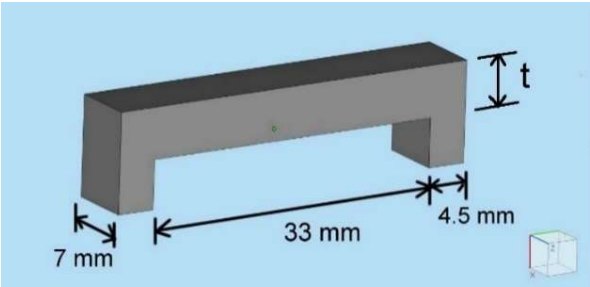

Figure 17 CAD model of the simply supported beam configuration.

Sintering of the part was carried out at 1370°C for 2h in the ArH2 atmosphere. Figure 18a shows a stainless steel green part 5.7 mm thick and a distorted part after sintering and the distortion angle was measured ~13°. The Archimedes density of the sintered part was measured to be 7.2 to 7.4 g/cc (92-94%).

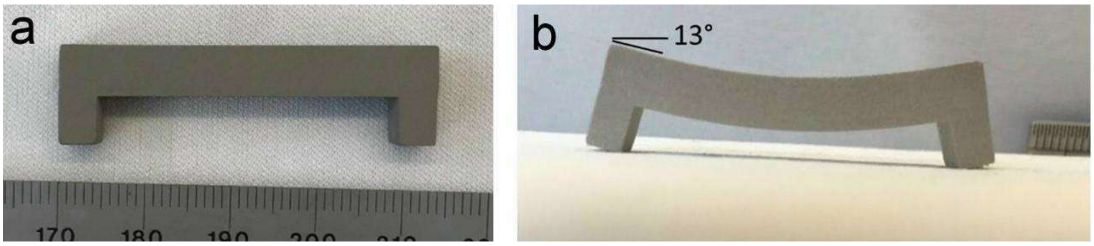

Figure 18 (a) Photograph of a green part in simply supported beam configuration (b) part after sintering at 1370°C-2h showing sag. (Note: 1 div = 1 mm on the ruler)

The SRSC-Steel coating developed for stainless steel was applied as a slurry to the green part surfaces and subjected to sintering treatment. Figure 19 shows the green part with coating before sintering. The photograph of the part after sintering is shown in figure 20 demonstrate no part distortion/sag. The SRSC-steel coating underwent a chemical reaction during sintering, and the product is weaky adhered to the part. The part after cleaning and sandblasting is shown in figure

20 c & d. The part surface after cleaning shows no traces of prior coating application, which was highly encouraging. Figure 21 shows a sintered part with a 2.8 mm thick section underwent severe distortion compared to the part with coating.

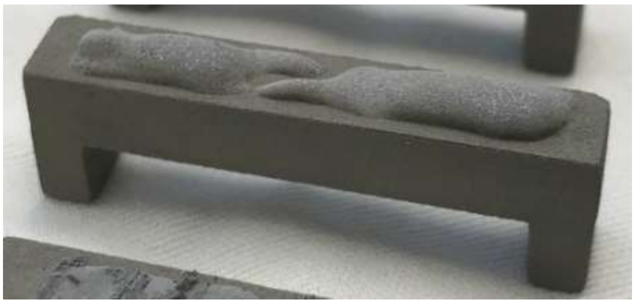

Figure 19 Stainless steel green part with shape-retaining-stimulus coating (SRSC-Steel).

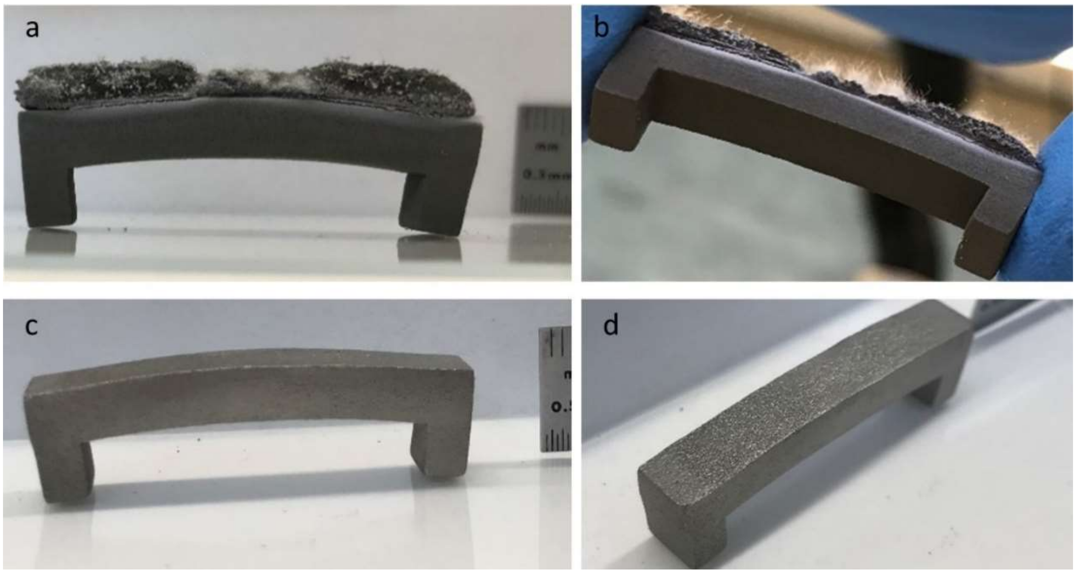

Figure 20 (a, b) Sintered stainless steel part of 5.7 mm thick with SRSC-Steel coating show no distortion (b, c) After cleaning and sand blasting the part surface show no traces of coating application. (Note: 1 div = 1 mm on the ruler)

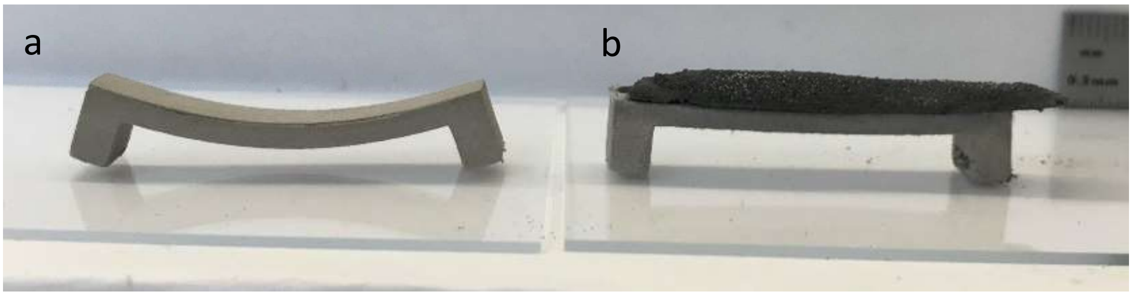

Figure 21 (a) Stainless steel part of 2.8 mm thick without SRSC-steel coating after sintering showed severe distortion compared to the part (b) with coating. (Note: 1 div = 1 mm on the ruler)

Shape-inducing-stimulus coating application to copper parts

During the development of the shape-retaining-stimulus coating, some combinations of coating mixture were shown to induce shape deformation during sintering of copper parts. A part with shape-inducing composition coating showed positive deformation against gravity. Figure 22 shows a rectangular bar sintered in simply supported assembly. The shape-inducing-stimulus coating caused the part to curl up, defying gravity and countering the natural phenomenon of part sag. Further, the coating was optimized and formulated to induce a shape in the 3D printed green parts during sintering and we were able demonstrate controlled amount of deformation induced into the part. Figure 23 shows the parts with shape-inducing-stimulus coating on the surfaces were able to add new dimension to the 3D printed green part during sintering (US patent #US2021362234) [8, 10]. The use of shape stimulus coating can be further extended to produce self-assembly metal structures, details can be found in US patent #US20220226892A1 [11]. The phenomenon of adding a new dimension to the existing 3D printed green part can be referred to as "***4D Metal Printing***".

Figure 22 A rectangular copper bar with shape-inducing-stimulus coating showing positive deformation defying gravity. (Note: 1 div = 1 mm on the ruler)

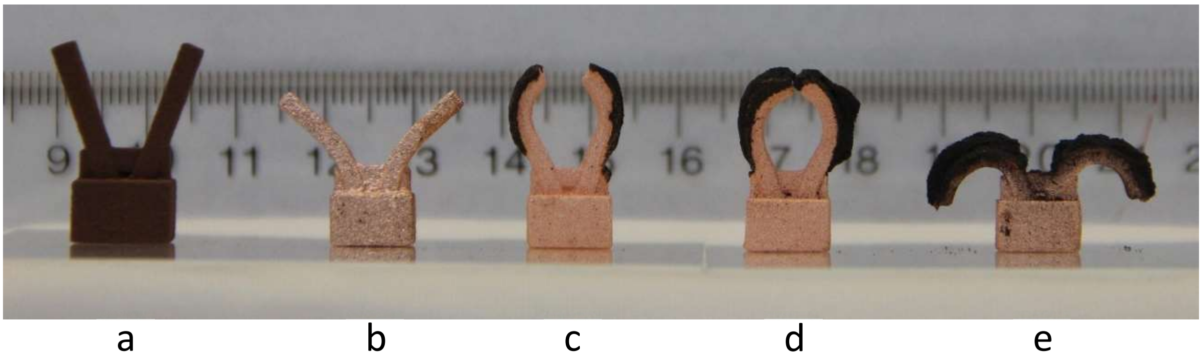

Figure 23 Copper parts with shape-inducing-stimulus coating showing a possibility of controlled amount of positive deformation can be induced in a 3D printed part during sintering. (a) green part (b) sintered part (c) sintered part with coating (less amount) (d) optimum amount of coating on the part to allow closing the loop and (e) coating applied on top surface of overhang areas. (Note: 1 div = 1 mm on the ruler)

Summary

Spans and overhanging features of binder jet 3D printed (BJ3DP) parts inevitably suffer from part distortion and sag during high temperature sintering. Today, distortion is mitigated by placing printed supports, live setters, and/or ceramic setters underneath the part during sintering. By introducing a shape-retaining-stimulus coating (SRSC) on green parts printed in copper and stainless steel, distortion and sag is counteracted thereby enabling shape retention through sinter. Our results demonstrate that copper parts with spans of 28 mm to 50 mm can be successfully sintered without distortion by the application of the SRSC-Cu coating. In the case of stainless steel, a span of 33 mm was successfully sintered by the application of the SRSC-steel coating. The proposed method on support-free sintering allows manufacturing of 3D parts where placement of supports is challenging, or support removal is difficult, thereby expanding the design space while providing cost savings. The introduction of shape-inducing-stimulus coatings can potentially open new arenas of research on binder jet metal additive manufacturing, such as "4D Metal printing" and "self-assembling metal structures".

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