Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Title: Solvent-cast based Metal 3D Printing and Secondary Metallic Infiltration

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Keywords: 3D printing, solvent-cast, metal, sintering, metallic infiltration

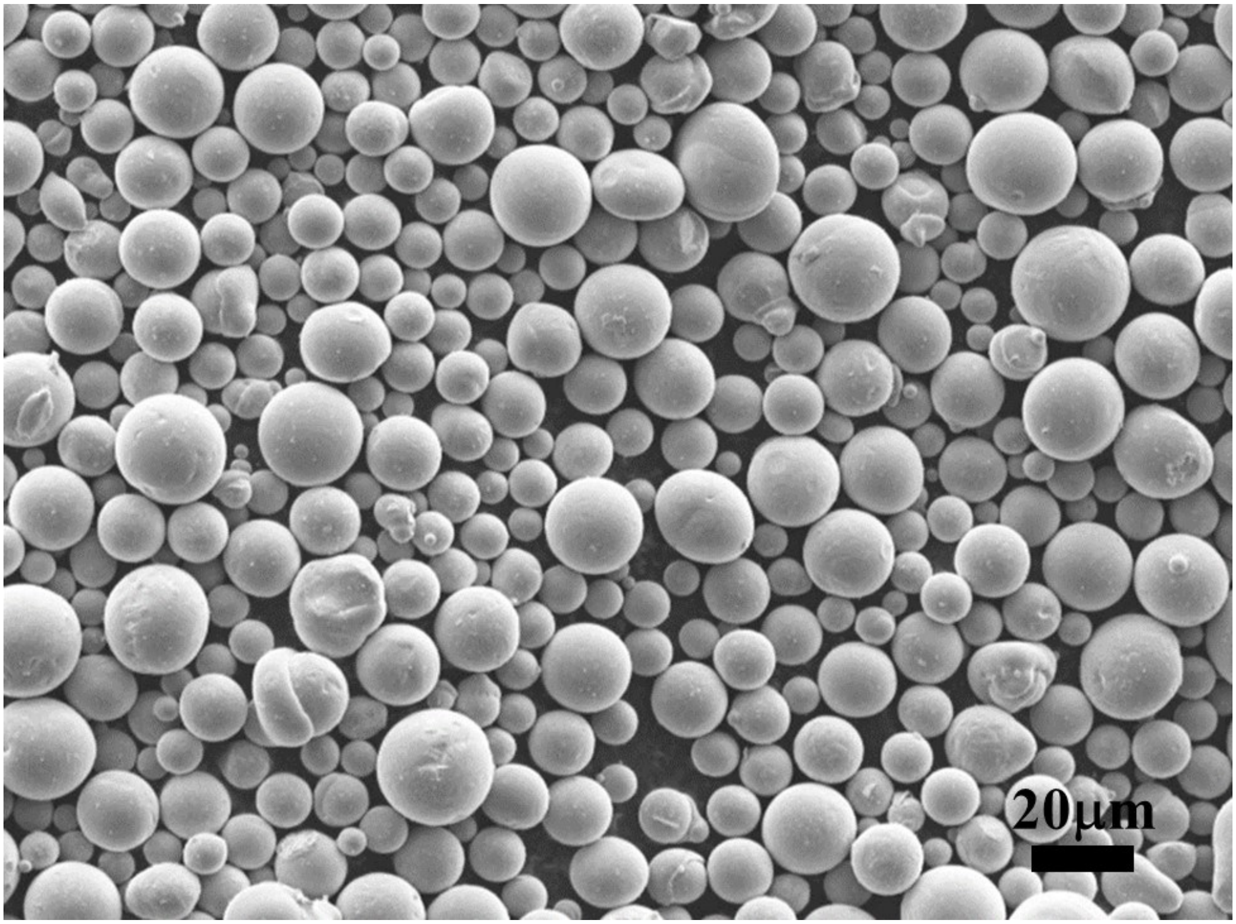

Figure S1. Secondary electron micrograph of HAS powder particles (≤ 20 μm).

Table S1. Ink formulations created for 3D printing

Ink constituent	85 wt.% (47 vol.%) HAS/PLA ink [g]	90 wt.% (59 vol.%) HAS/PLA ink [g]	95 wt.% (75 vol.%) HAS/PLA ink [g]	98 wt.% (90 vol.%) HAS/PLA ink [g]
PLA	15	10	5	2
DCM	60	40	20	18
HAS microparticles	85	90	95	98

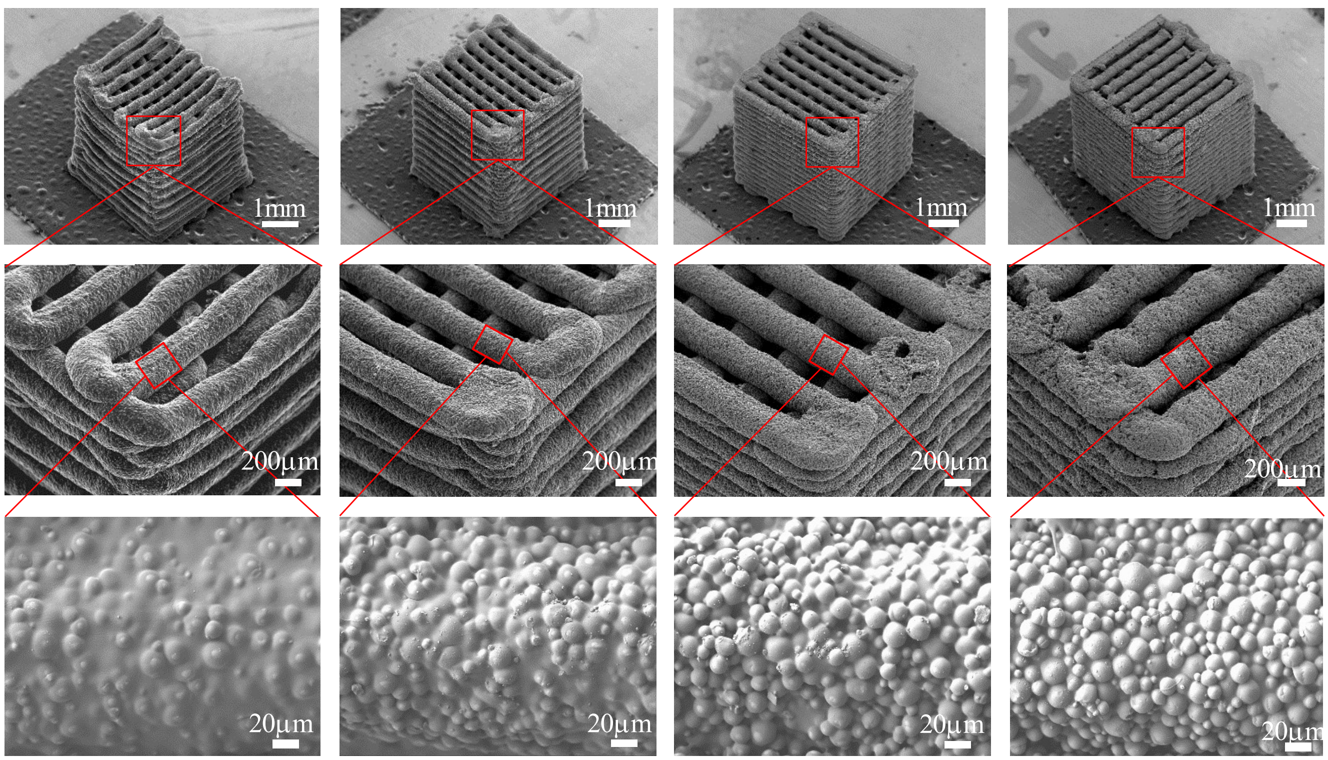

Figure S2. SEM images of as-printed 20-layers scaffolds of different concentrated inks (85, 90, 95, 98 wt.%) (first row from left to right) and their close-up view images (middle and bottom rows). The HAS microparticles are covered and bonded by the polymer. The filaments of all four scaffolds align well. However, the 85 wt.% scaffold distorts and the surface of the 98 wt.% scaffold is rough.

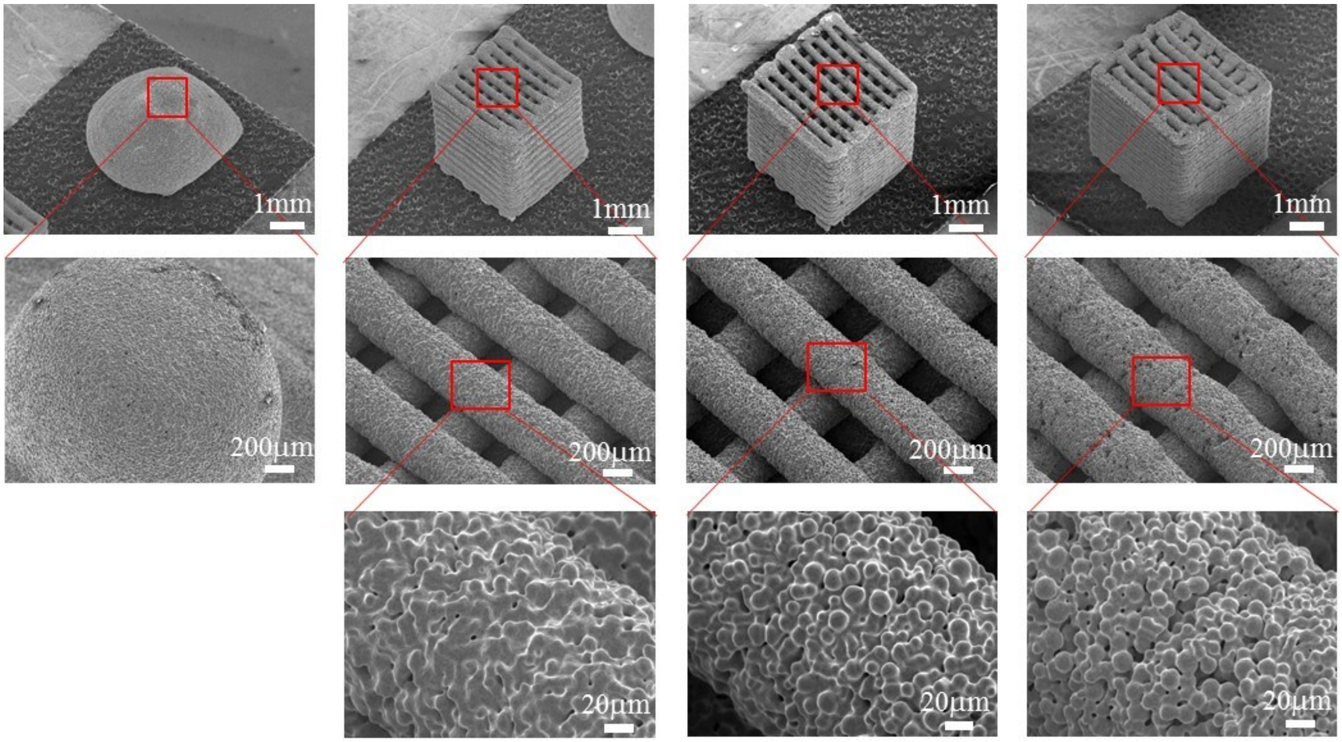

Figure S3. SEM images of sintered 20-layers scaffolds of different concentrated inks (85, 90, 95, 98 wt.%) (first row from left to right) and their close-up view images (middle and bottom rows). After sintering, the polymer is burned away and the HAS microparticles are sintered together. The filaments of 90, 95 and 98 wt.% scaffold keep their shapes and align well, while the 85 wt.% ink printed scaffold collapses during sintering and the surface of 98 wt.% scaffold is rough.

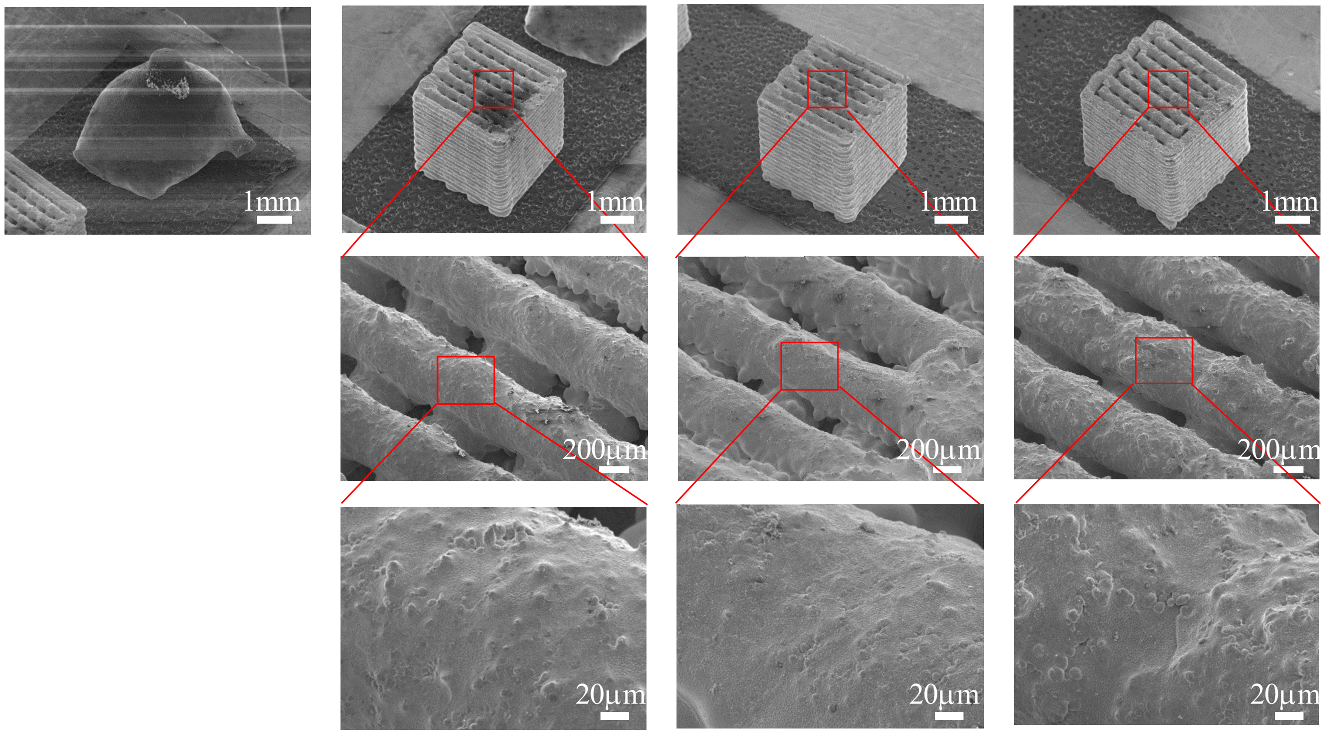

Figure S4. SEM images of copper infiltrated 20-layers scaffolds of different concentrated inks (90, 95, 98 wt.%) (first row from left to right) and their close-up view images (middle and bottom rows). Melted copper infiltrated into the sintered filaments. Some excessed copper is left on the top of the scaffold.

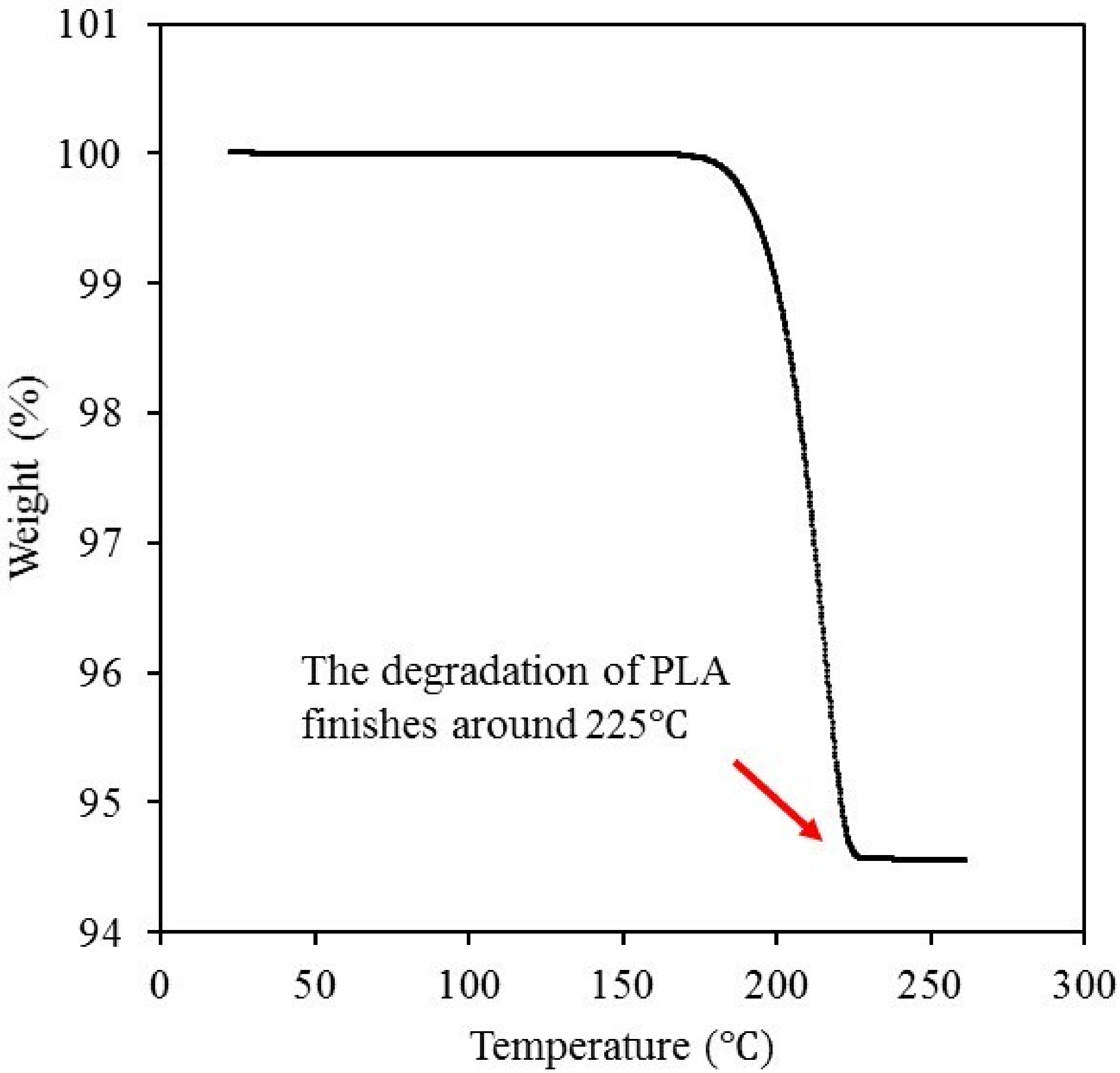

Figure S5. TGA results of 95 wt.% HAS/PLA scaffold. The temperature is raised from 20 ℃ to 500 ℃ at a rate of 1 ℃/min (the same heating rate as the sintering process). The degradation of PLA finishes before 225 ℃.

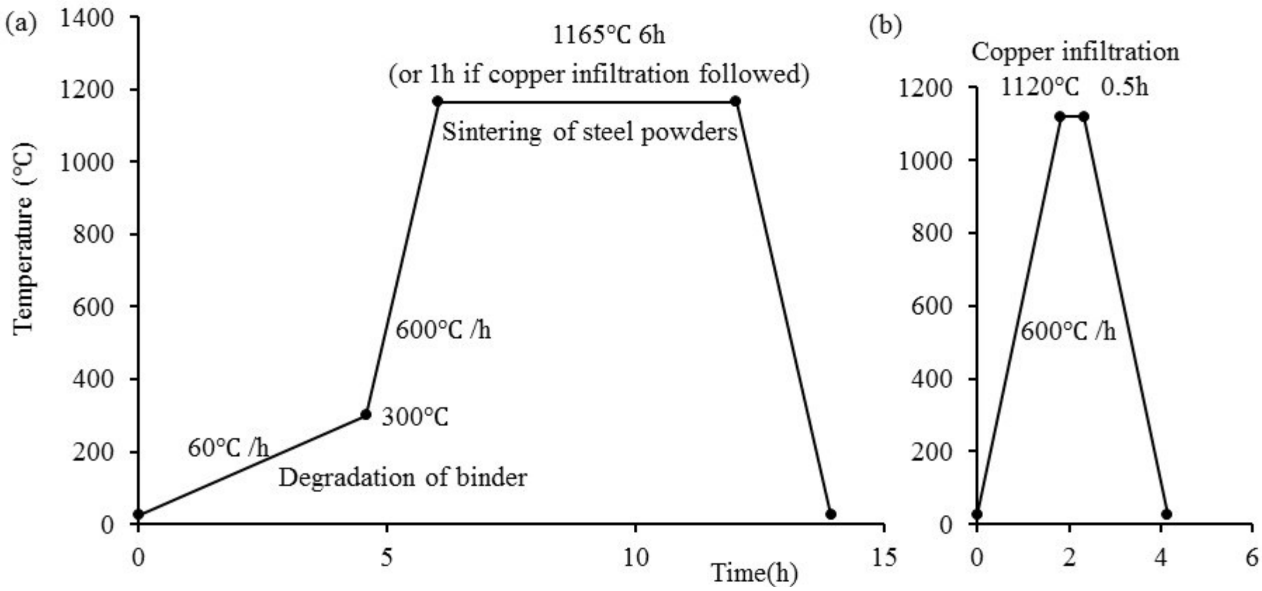

Figure S6. Temperature profiles using during sintering and copper infiltration. Debinding starts from 25 °C to 300 °C with a heating rate of 60 °C/h. Then the temperature is raised up to 1165 °C with a heating rate of 600 °C/h and held at 1165 °C for 6h for sintering. For copper infiltration, the temperature is raised up to 1120 °C and held for 0.5 h, then cooled down to the room temperature.

Table S2. Preliminary shrinkage analysis results of 85, 90, 95 and 98 wt.% as-printed, sintered (6h) and copper infiltrated 20-layer scaffolds. The values shown are the heights of the scaffolds compared to the as-programmed height value.

	85 wt.% (47 vol.%) HAS/PLA ink	**90 wt.% (59 vol.%) HAS/PLA ink**	**95 wt.% (75 vol.%) HAS/PLA ink**	**98 wt.% (90 vol.%) HAS/PLA ink**
As-programmed	100%	100%	100%	100%
As-printed	101.4%*	101.1%*	101.2% ± 0.7%	100.7%*
Sintered	N/A**	81.3%*	85.9% ± 0.6%	89.1%*
Copper infiltrated	N/A**	85.7%*	89.7% ± 0.8%	92.2%*

*The value is measured on a single sample.
**The value is not available since the 85 wt.% scaffold collapsed during sintering.

Table S3. Porosity analysis results of 90, 95 and 98 wt.% sintered (6h) and copper infiltrated 20-layer scaffolds.

Porosity	**90 wt.%**	**95 wt.%**	**98 wt.%**
Sintered	10.4 % ± 4.4 %	12.1 % ± 5.3 %	12.4 % ± 2.0 %
Copper infiltrated	0.3 % ± 0.3 %	0.2 % ± 0.1 %	0.2 % ± 0.2 %

Table S4. Tensile test results of 95 wt.% as-printed, sintered and copper infiltrated tensile bars compared with: (1) Wrought stainless steel[42], (2) Nitrogen alloyed, high strength, medium elongation, sintered at 1290 °C (2350 °F) in dissociated ammonia[43], (3) PM steel containing 0.8% carbon and 2% copper[43], and (4) Copper infiltrated steel containing 0.8% carbon[43].

	E [GPa]	**UTS [MPa]**	**Elongation [%]**
As-printed sample	3.1 ± 0.3	28.0 ± 3.0	1.45 ± 0.10
Sintered sample	196 ± 16	485 ± 70	0.47 ± 0.06
Copper infiltrated sample	195 ± 16	511 ± 57	0.77 ± 0.07
Wrought stainless steel: SS-316 (1)	193	515	30
PM steel stainless steel: SS-316N2-38 (2)	140	480	13
PM steel FC-0208-60 (3)	155	520	< 1
Cu infiltrated PM steel: FX-2008-60 (4)	145	550	1

Movie S1. 3D printing of an 8-layers tensile bars with 95 wt.% ink and 250 μm tapered nozzle at a speed of 10 mm/s.