Electronic Supporting Information (ESI)

Continuous Flow Photochemical Synthesis of Metal-Ceramic Composite Microparticles

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Overview

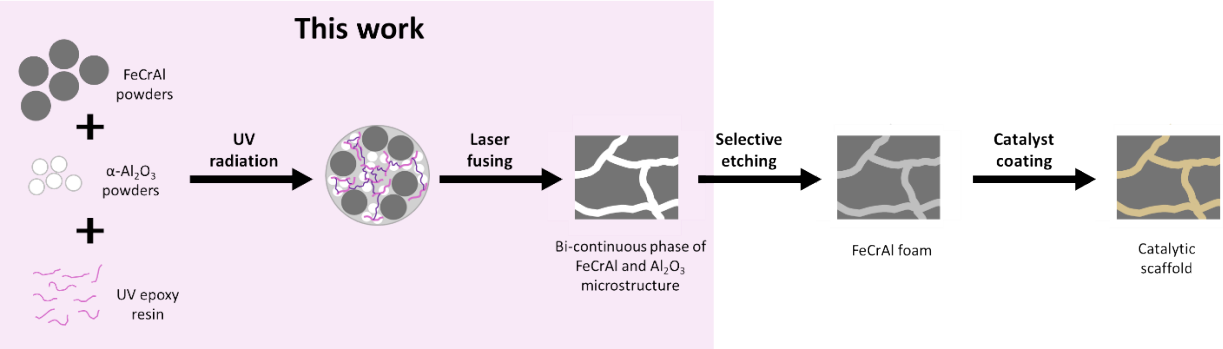

Fig. S1. Schematics showing potential catalytic scaffold application fabricating from composite microparticles.

Experimental section

Materials:

Fecralloy, FeCrAl powder (45 µm, Oerlikon), alpha-alumina, α-Al_2O_3 powder (10 µm, spherical, Inframat Advanced Materials), UV epoxy resin (clear hard type, Let's Resin UV Resin, Shenzhen Yi You Life Technology Co., Ltd) was used to formulate the inks without further modification. The mixture of silicone oil (Viscosity 2000 cps, Thermo Scientific Chemicals) was used as a continuous oil phase.

The UV epoxy resin used is a commercially available resin (Let's Resin UV Resin, Shenzhen Yi You Life Technology Co., Ltd), which consists of urethane acrylate oligomers (42 wt%), 2-hydroxyethyl methacrylate monomer (40 wt%), and 2-hydroxy-2-methylpropiophenone photoinitiator (18 wt%). The

photoinitiator is a Type I alpha-hydroxy ketone compound that absorbs UV-A light within the 365–405 nm wavelength range, enabling rapid free-radical photopolymerization.

Experimental Methods:

Precursor Ink Preparation

The UV curable ink was formulated by mixing 15 wt% of UV epoxy resin, 64 wt% of FeCrAl powder, and 21 wt% of α-Al_2O_3 powder. Prior to microfluidic droplet generation, the FeCrAl and α-Al_2O_3 powders were first pre-mixed using a vortex mixer to promote initial blending of the two powders. The pre-mixed powder blend was then gradually added into the UV epoxy resin while stirring with a stirring rod for 10 minutes to ensure uniform dispersion of both powder components within the resin matrix. This two-step mixing process produced well-dispersed precursor inks, as confirmed by the elemental mapping shown in Figure 3c, where the distributions of C, Al, Cr, and Fe demonstrate homogenous mixing of the composite constituents within the fabricated microparticles.

Microfluidic setup

The microfluidic system was constructed by connecting a dispensing tip (200 μm, 27G) to a mixer to generate precursor droplets. PVC tubing (clear, 1/16" ID), serve as transport tubing was used to transport the oil phase and dispensed droplets. The syringe was filled with UV-curable precursor ink, containing FeCrAl powder, α- Al_2O_3 powder, and UV epoxy resin, was continuously dispensed into the oil-phase using a high-precision fluid dispenser (Nordson EFD, Ultimus V). Shear forces within the flowing oil phase enabled stable droplet formation. The continuous oil phase enables the formation of droplets in a dispersed manner. These droplets travel through the curing zone equipped with a UV light LED strip (60W, 395-405 nm, YGS-Tech), and the droplets will be polymerized and form microparticles.

UV Curing Process

The curing system consisted of a 395–405 nm LED strip (60 W total power) mounted along a PVC transparent tubing section of 50 cm in length. Based on the applied flow rates (0.5–3 mL/min) and tubing dimensions, the estimated droplet residence time within the curing zone ranged from 20 to 120 seconds, providing sufficient UV exposure to achieve complete polymerization of the resin during continuous operation. The combination of small droplet size (~100–300 μm) and high photoinitiator content ensured efficient polymerization throughout the droplets, despite the high solid loading. The reproducibility of the curing process was confirmed by consistent droplet size control (Fig. 3), and uniform elemental mapping (Fig. 3c).

Characterization of Composite Powder

A FEI Quanta 600 SEM equipped with an energy-dispersive spectroscopy (EDS) detector was used to examine the surface morphology and elemental composition of FeCrAl-Al_2O_3 composite samples. The microscopy images were subsequently analyzed by the Image process software (Image Pro and Image J) to quantify the microparticle size in diameter, size distribution, and circularity. The circularity of the resulting beads was measured using the aspect ratio function in ImagePro, as sphericity impacts the flowability of the powders.

Emulation of Powder-based Metal 3D Printing using Laser Welder

The laser welding process was carried out using a Xing Laser system (1070 nm, fiber laser, pulse mode) with parameters set at 400 W, 500 W, and 600 W, combined with pulse durations of 180 ms, 200 ms, and 250 ms (forming a 3×3 matrix). Two base layers were initially printed using FeCrAl powder under 500 W and 200 ms conditions. Subsequently, a composite powder layer was applied and welded using varying laser parameters. The process was repeated layer by layer, stacking melted pools to build up the composite structure.

Results and Discussion

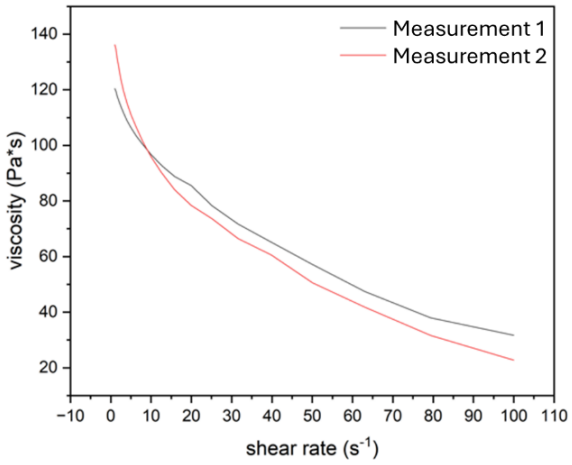

Fig. S2. Viscosity vs. shear rate for UV-curable precursor ink. Two repeated measurements were performed on the same sample to confirm the reproducibility of the viscosity data. The shear-thinning behavior observed in Fig. S2 reflects the stable dispersion of the FeCrAl and Al_2O_3 particles within the UV resin matrix. At low shear rates, loosely interacting particles can form transient clusters or networks, resulting in a higher apparent viscosity. As the shear rate increases, these structures are disrupted, and the suspended particles align with the flow direction, reducing resistance and resulting in lower viscosity. This shear-thinning profile indicates that the composite ink maintains stable dispersion without significant agglomeration. Such rheological behavior is favorable for generating stable droplets during microfluidic processing.

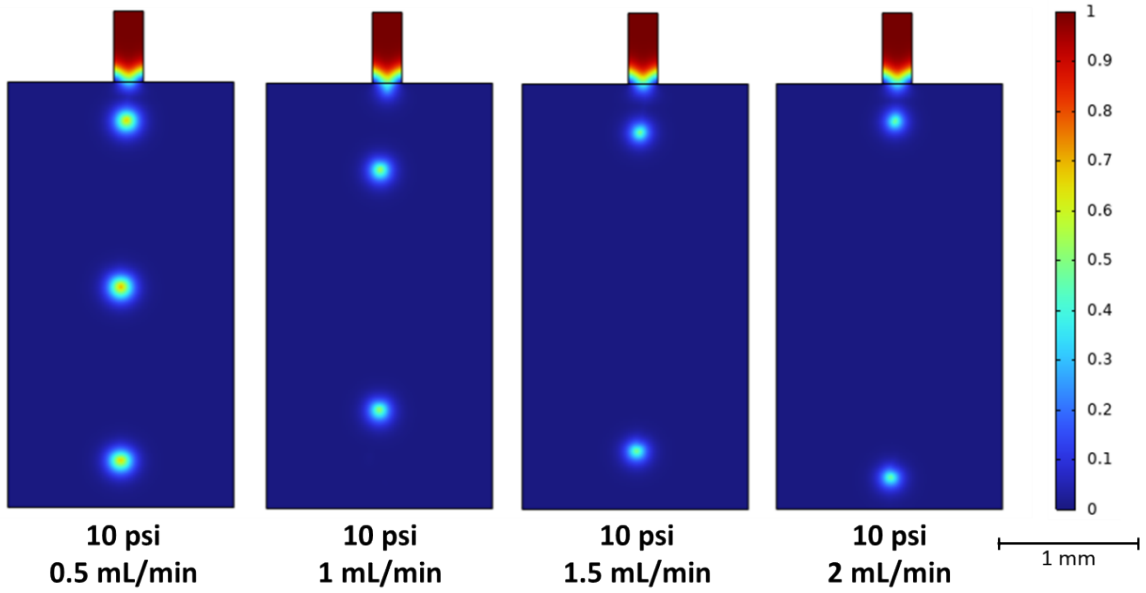

Fig. S3. Simulation results of droplet formation in COMSOL at dispense pressure of 10 psi and flow rates of 0.5, 1.0, 1.5, and 2.0 mL/min.

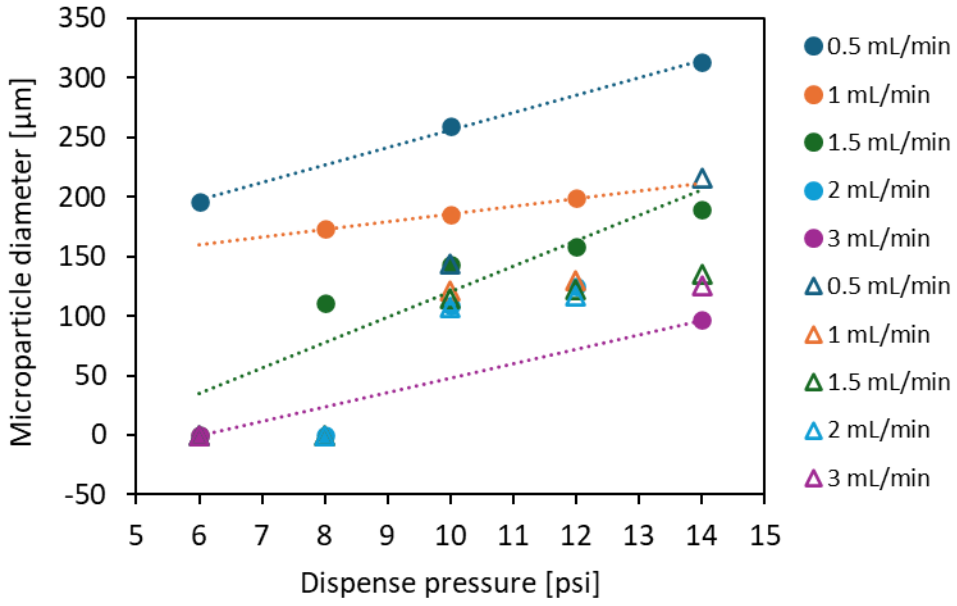

Fig. S4. Microparticle diameters from experiments and COMSOL simulations are shown. Circles represent experimental data, while triangles indicate COMSOL results for the same conditions. The plot reveals a similar trend: the diameter increases as dispensing pressure increases at a constant flow rate. Conversely, the diameter decreases when the flow rate increases at constant pressure.

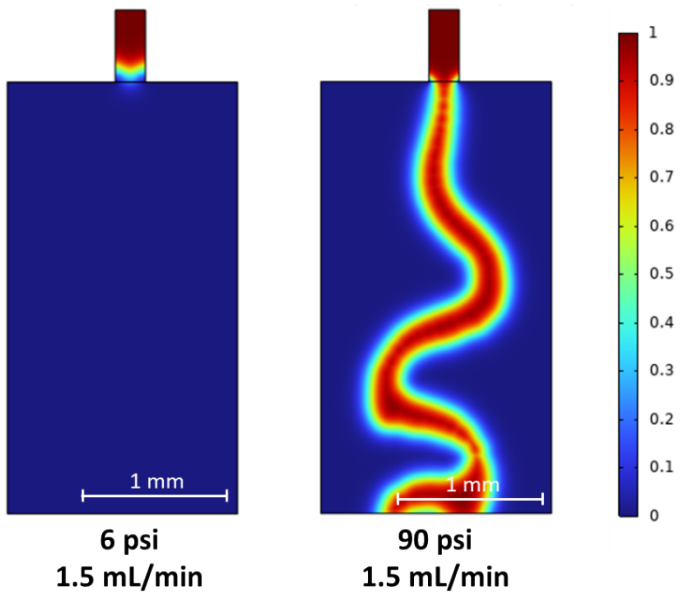

Fig. S5. COMSOL simulations showing volume fraction of the dispersed fluid under extreme flow conditions. At low pressure (6 psi, 1.5 mL/min), droplet formation is suppressed, and no distinct droplet is generated. At high pressure (90 psi, 1.5 mL/min), a continuous, unstable jet forms, indicating a transition toward the jetting regime without discrete droplet breakup. These additional simulations qualitatively reflect the boundaries of stable droplet formation and demonstrate that, despite its simplifications, the current model is capable of capturing flow behavior at the extremes, such as jetting and suppressed droplet formation, beyond the dripping regime.

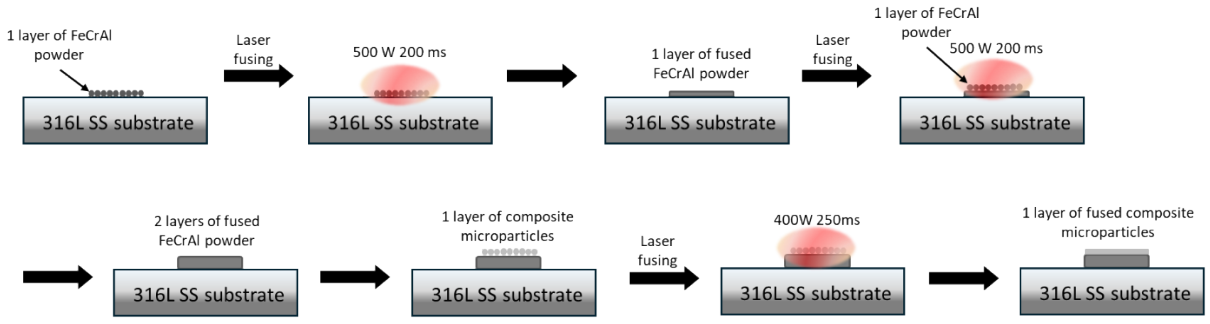

Fig. S6. Schematic diagram illustrates the laser fusing process for composite microparticles. Initially, two layers of FeCrAl powders were fused using a 500 W laser with a 200 ms pulse. A layer of composite microparticles was then applied over the fused FeCrAl and fused under selected laser conditions. This process of layering composite microparticles and laser fusing was repeated to create a 10-layer structure.

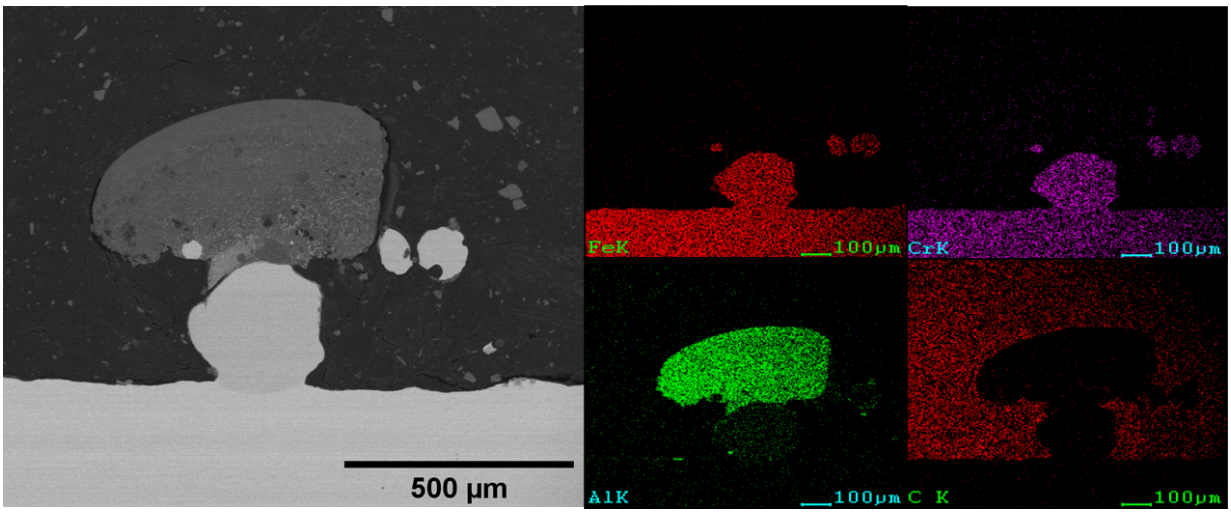

Fig. S7. BSE and EDS images of composite microparticles under laser conditions of 400 W and 250 ms. The BSE image highlights the Al_2O_3 phase as white-gray regions and the FeCrAl matrix as dark-gray regions. The C intensities are from the carbon powder used for mounting samples.