RESEARCH ARTICLE OPEN ACCESS

Direct gelcast3D Printing of Multi-material AlN Interposer and Mo

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ABSTRACT:
In this paper, we investigate the use of direct gelcast 3D printing method to produce near net shape multi-material component using the natural-occurring gelcasting monomer, ovalbumin for both AlN ceramics and Mo metals. The simplified process will able to directly produce parts from CAD design into functional multi-material parts. The multi-material 3D structure was printed using a thick paste extruder, followed by sintering to 1600^{o}C to form the final functional part, a high-performance circuit. The result shows that the high-performance circuit functions well with the light emitting diode (LED) having a good electrical conductivity of 4.1 x $10^{-4}\Omega$.cm and high thermal conductivity of 17 W/mK.
Keywords: AlN, Gelcast Printing, 3D Printing, ceramic, gelcasting

Date Of Submission:13-09-2018 Date Of Acceptance: 28-09-2018

I. INTRODUCTION:

The revolution of additive manufacturing (AM) or commonly known as 3D printing is one of the driving forces for the realization of the fourth technology revolution that shift from mass production to mass customization. This supersedes the previous revolution that shifts from using animal to mechanical machinery for production, then to mass production and into using digital control [1].

The International Organization for Standardization (ISO)/ American Society for Testing and Materials (ASTM) 52900:2015 standard has to define AM as the “process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing and formative manufacturing methodologies” [2, 3] and the typical application is in rapid prototyping to produce physical products from a digital generated model [4, 5]. Some of the key characteristics of AM technologies are i) capable to produce parts with highly complex design, ii) fewer assembly parts requirement, iii) less time required, iv) less requirement for fabrication skills know-how, v) low cost for small volume size, vi) less waste produced, vii) able to produce exact replica and viii) less constraints of creativity [5, 6].

There are mainly seven process categories in AM; i) binder jetting, ii) directed energy deposition, iii) material extrusion, iv) material jetting, v) powder bed fusion, vi) sheet lamination and vii) vat photopolymerisation[7]. The 3D printing technology has been improving dramatically in the last decade with continual improvement in quality, build size, the range of materials and applications. Currently, the most common material used for 3D printing, plastic, and metal has been widely used in the industry to increase the speed for time-to-market and to lower production costs in industries such as automotive, aerospace and electronics. The technology has evolved from rapid prototyping into manufacturing of functional parts that improve products in terms of less weight, less production time, less tooling cost with highly complex geometries.

However, the use of ceramics in 3D printing is still lagging but there it is on the rise due to several promising applications [1]. The growth of ceramics in 3D printing has seen impressive demand, indicated by the compound annual growth rate (CAGR) of 21.4 percent from 2015 to 2017 with 3D printing of technical ceramics is expected to rise from US$ 174 million in 2017 to US$ 544 million by 2022 [8], and US$ 3.1 billion by 2027 globally [9].

Technical ceramics, sometimes known as industrial, engineering or advanced ceramics has some exceptional properties including resistance to high temperature, toughness in strength, chemical resistance and abrasion resistance. In certain applications, technical ceramics can be better than metals and the demand in industries are growing rapidly. Also, 3D printing of technical ceramics has great potential with the ability to replace some traditional manufacturing processes including ceramic injection molding (CIM), hot isostatic pressing (HIP) and castings technology for manufacturing complex parts with short lead time and reduced cost [1]. Aluminum nitride (AlN) is an important technical ceramic with properties such as high thermal conductivity,good electrical resistivity, low dielectric constant, high dielectric strength, high melting temperature with good mechanical strength and corrosion resistance [10-13].

Environmental-friendly industrial process technologies is high in demand and give rise to aqueous-based additives, water-based injection moulding[14], tape-casting[15] and gelcasting[16]. Gelcasting, first introduced by Omatateet. al. [16] to solve the problem with traditional casting method is known to have advantage in near net-shape process that produces high green capacity, relatively short in time of forming, high yields and relatively lower cost of machining. This technology has shown to be better in many categories as compared to slip casting, injection molding and pressure casting [17].

The production of AlN ceramics by gelcastinghas been reported previously using aqueous [18] and non-aqueous [19, 20] processes. Koket. al[21, 22]has recently reported using ovalbumin monomer for the gelcasting of AlN. The advantage of using ovalbumin as gelcasting monomer is because the process does not require any initiator because gelation occurs by heating to a temperature of 80^{o}C, where individual ovalbumin protein molecules start to denature and form a covalent bonded thermos-irreversible gel [23]. In addition, ovalbumin is a natural protein and therefore is nontoxic and can be obtained from a sustainable source [24].

There has not been any report of using gelcast binder system for direct 3D printing and ovalbumin are selected as the binder of choice to due to the simplicity of processing. Also, the previous study on 3D multi-materials printing using polymers such as material jetting systems, inkjet-based 3D printers with drop-on-demand (DOD) printing method [7, 25-27]. In this study, direct gelcast 3D printing of multilayers of ceramics and metal were being investigated.

II. EXPERIMENTAL:

2.1 Preparation of Ceramic Slurry

Figure 1 shows the preparation of the AlN ceramic slurry using ovalbumin as the gelcasting monomer. Ovalbumin natural protein was obtained by separating fresh egg-yolk and the then 1 wt% silicon oil (Unichem) was added to the mixture to reduce froth formation. The mixture was stirred for 2 hours using a magnetic stirrer and removes the froth that was remained to be used to prepare the slurry.

The previous study by W.H.Kok et al [22] has shown that bimodal AlN has better performance and therefore, a bimodal AlNwith the particle size of 3μm and 5μm (Hongwu) was used in this study. The AlN powder was first treated with 0.5 wt% of Stearic Acid (Arachem) in ethanol and the dried mixture was then added with 2 wt% of sintering aid, Y_2O_3 (Acros, 99.99%),10 wt% of dispersant, polyethylene glycol 4000 (Fluka) and 50 wt% of ovalbumin premix. The mixture was mixed thoroughly using mortar and pestle for 15 min or ball mill at 150rpm for 2 hours to form the gelcast slurry.

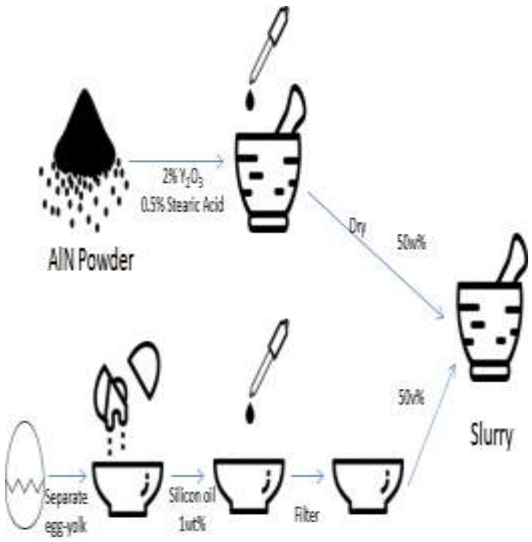


Figure 1 Preparation of AlN slurry.

2.2 Preparation of Molybdenum Slurry

Figure 2 shows the preparation of the Molybdenum slurry. Ovalbumin natural protein was prepared similar to section 2.1.Molybdenum (Mo) powder used in this study is from SAT Nano (China) with an average particle size of 1μm. The Mo powders were added with 0.5 wt% of Stearic Acid (Arachem) in ethanol as the dispersant agent and to protect the Mo powder from hydrolysis. The mixture was mixed thoroughly grounded using mortar and pestle and the sample was dried. 10 wt% of the dispersant, polyethylene glycol 4000 (Fluka) was added and mixed using mortar and pestle, followed by the 50 wt% of ovalbumin protein that forms the gelcast slurry for printing.

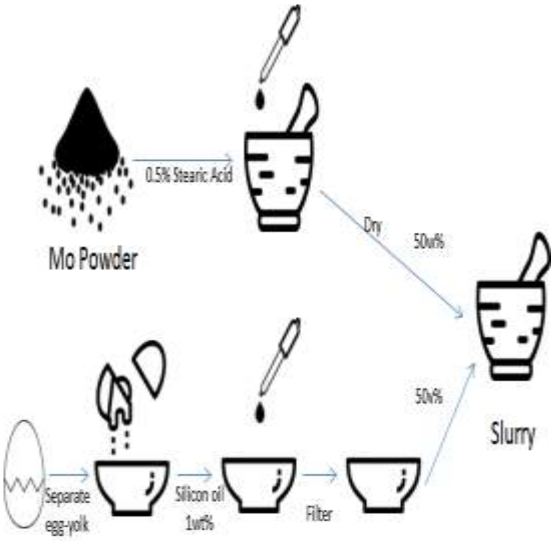


Figure 2 Preparation of Molybdenum slurry.

2.3 3D Printing Process and Sintering

The gelcast slurry was poured into the syringe and the printing plate was preheated to 80°C before the printing begin using a thick paste extruder, ZMorph 2.0 (Figure 3). After printing, the articles were then dried in air for 6 hours before demolding it from the surface. The dried samples were then debindedand sintered using PT1700 Atmosphere Furnace from Zhengzhou Protechin a nitrogen atmosphere (0.08 MPa) to form the final part.

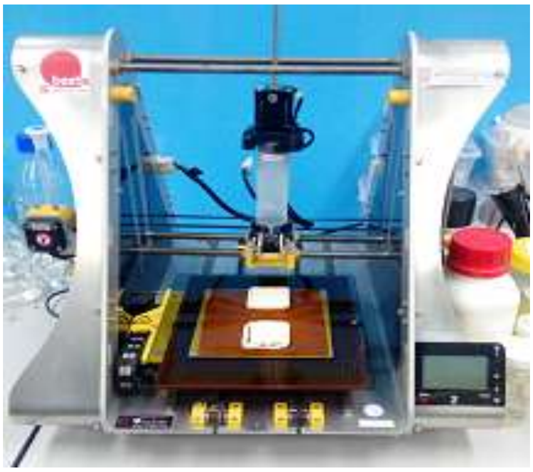


Figure3 Thick paste extruder (ZMorph 2.0).

2.4 Characterization

The viscosity of the slurry was measured using a digital rotating viscometer, NDJ-5S/8S (Shanghai Pingxuan Instrument Co., Ltd) using rotor 4 with a rotating speed of 60 rpm. Flashline TM 2000 was used for measuring the thermal conductivity of the sample using heat capacity and thermal diffusivity. The technique is an absolute method that uses Pyroceram as the calibration sample for drift correction. The density of the samples was measured using density balance that uses the Arrhenius principle (JA203M, Changzhou Xingyun Electronic Equipment Co., Ltd). Thickness of the sample was measured using a digital vernier caliper (Absolute Digimatic, Mitutoyo).

Flexural measurement by measuring the load x displacement curved obtained using Instron 5565 on printed bars of 25 x 10 x 3mm that was subjected to three-point bending with 0.5 mm/min crosshead speed. The shrinkage of the sintered samples was determined by measuring the reduction in sample thickness using a digital vernier caliper (Absolute Digimatic, Mitutoyo).). The electrical measurement of the conducting line was measured using a 4-point probe with Agilent 43388 Milliohmmeter.

III. RESULTS AND DISCUSSION:

3.1 AlN ceramics

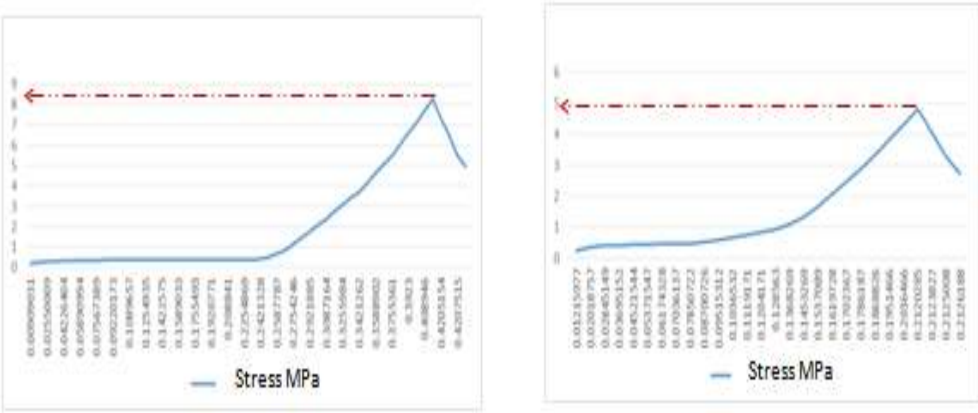
The viscometer of the slurry at 25°C is 800 mPa.s. Table 1 shows the physical characterization of sintered AlN parts prepared using slurry prepared by ball milling and mortar and pestle. It is clearly shown that samples prepared with ball mill slurry have a much lower density (52% vs 91%) and flexural strength (5 MPa vs 8.25 MPa) compared to mortar and pestle slurry.

Type of particle mixing	Density after sintering (g/cm^3)	Relative Density (%)	Flexural Strength (MPa)	Thermal Conductivity (W/mK)
Mortar & Pestle	2.960	91	8.27	17
Ball mill (150 rpm)	1.970	52	5.00	10

Table 1 Physical parameters of AlN sintered samples.

Figure 3 shows flexural measurement cure for samples prepared using ball mill slurry and mortar and pestle slurry. The reason for the inferior physical properties for samples prepared with ball mill slurry is because the ball milling process rigorously mixes the slurry and causes more air bubbles being trapped. This is different from the more gentle mixing of mortar and pestle that has fewer air bubbles trapped in the slurry. The trapped bubbles cause weakness in the sintered structure and therefore, lower flexural strength. Figure 4 shows optical images of the parts after drying and it can be clearly seen that samples using ball mill has significant pores observed and this is directly related to reducing flexural strength by about 40% and lower density. Ball milling under vacuum condition causes enhanced drying of the slurry that will affect the viscosity and therefore, printing quality.

The 3D printed AlN parts have good heat dissipation with a good thermal conductivity of 17 W/mK, which is higher than the conventional interposer material, epoxy mold compound of 0.2 W/mK. Shrinkage is around 20% for all samples.



(a) (b)

Figure 3 Flexural strength measurement of (a) slurry prepared using a mortar and pestle (20 min) and (b) slurry prepared using a ball mill (150 rpm for 1 hour).

(a) (b)

Figure 4 Optical image of AlN sintered sample with the slurry prepared using (a) mortar and pestle for 20 minutes and (b) ball mill at 150rpm for 1 hour.

3.2 3D Printing

The flowing fluid of the thick paste extruder, described by a velocity field, $\vec{v}$. The vector-valued function of space and time will vary in magnitude and direction within the fluid:

$$\vec{v}(x,y,z,t) = u(x,y,z,t)\hat{x} + v(x,y,z,t)\hat{y} + w(x,y,z,t)\hat{z} \quad (1)$$

The volumetric flow rate Q through an area is

$$Q = \int \vec{v} \cdot \hat{n}\, dA \quad (2)$$

If U_{ave} , the average velocity normal to a planar area A, $Q = U_{ave} \cdot A$ (m^3s^{-1}) and therefore, mass flow rate is

$$\dot{m} = \rho U_{ave} A \quad (3)$$

Where ρ is the fluid density.$\dot{M}$, the momentum flow rate obtained by multiplying $\dot{m}$with fluid velocity [28].

$$\dot{M} = \rho U_{ave}^2 A \quad (4)$$

Table 2 shows the printing parameter for gelcast printing. The temperature of the printing plate must be heated to 80^{o}C in order for fast gelling upon slurry dropping to the plate to ensure the integrity of the parts. Ovalbumin molecules will denaturethat forms the thermo-irreversible gel when heated to 80^{o}C and are held together by covalent bond [23].

Table 2 Optimum printing parameters:

Parameters	Optimal Value
Layer height	2mm/layer
Infill ratio	25%
Infill type	Rectlinear (to ensure jetting slurry in straight lines)
Temperature	80-100°C
E-speed	5mm/s
XY-speed	200mm/s
Z-speed	20mm/s

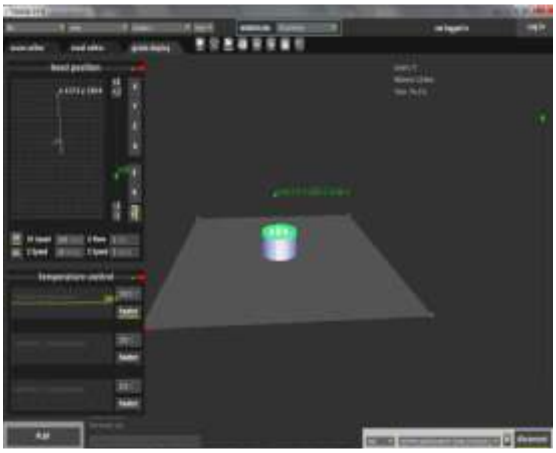


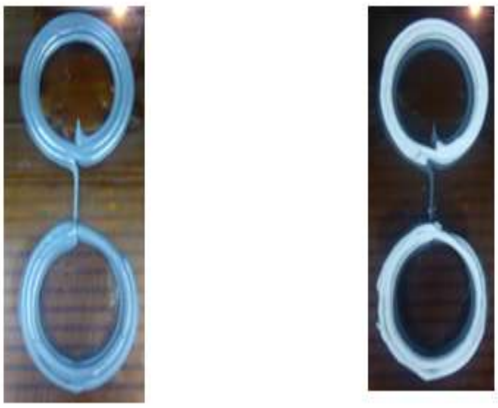
Figure 5 Voxelizer software for printing.

Figure 6 shows the 3D structures of AlN ceramics that was successfully printed using the thick paste extruder.

Figure 6 3D structures of AlN.

3.3 Directgelcast 3D Printing of Multilayer of AlN and Mo

Figure 7 shows the direct gelcast printing of multi-materials. Initially, Mo was printed in a cylinder form and the printer was able to accurately print AlN on top of Mo. The structure was then debinded and sintered to form the final part. No cracks were observed showing the good integrity of the structure showing multilayer printing of multi-materials could be printed.



(a) (b)

Figure 7 Direct gelcast printing of multi-material a) Mo, b) AlN on Mo.

Figure 8 shows the step-by-step fabrication of high-performance circuitry by a direct gelcast 3D printing of multi-layer AlN interposer with Mo. Figure 9 shows the functional circuitry after sintering that is able to power-up the LED. Mo conducting line has a good electrical conductivity of 4.10 x 10^{-4} Ohm.cm

(a) (b) (c)

Figure 8 Directgelcast printing of multi-layer materials in the following sequence (a) AlN interposer, (b) Mo conducting line, (c) AlN interposer on top of Mo line.

(a) (B)

Figure 9 Functional interposer with AlN with embedded Molybdenum conducting line (a) before applying current (b) LED turn on when applying DC current.

As both the AlN and Mo uses ovalbumin as the natural binder, the same sintering profile can be used for both materials and therefore, the functionalization of the product could be achieved using single step sintering. In addition, the coefficient of thermal expansion (CTE) of AlN (4.5 x $10^{-6}/^{o}C$) is close to the CTE for Mo (4.8 x $10^{-6}/^{o}C$) that reduces strain caused during shrinkage as both materials having similar shrinkage profile. No interface crack between AlN and Mo was observed indicating that the structure was intact after co-sintering to form the final interposer.

IV. CONCLUSION:

Direct gelcast 3D printing to produce high-performance circuitry that consists of high thermal conductivity AlN interposer and Mo conducting line was proven successfully using environmentally sustainable ovalbumin monomer system. The process is simple and fast that will contribute significantly to the development of the industry of mass customization of high-performance multi-materials.

ACKNOWLEDGEMENTS:

The author would offer deep gratitude to Hong Kong Polytechnic University (studentaccount code RUV-3), the Hong Kong Research Grant Council (Hong Kong PhDFellowship Scheme, Ref No. PF14-11496), the PolyU Micro Fund, and the ElectroPrecision Technology SdnBhd for support and budget support that make the research work in this paper realizable.

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W.H.Kok "Direct gelcast3D Printing of Multi-material AlN Interposer and Mo "International Journal of Engineering Research and Applications (IJERA) , vol. 8, no.9, 2018, pp 25-31