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Direct ink writing of WC-Co composite with flexible green bodies

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Direct ink writing of 3D WC-Co with conformable green bodies was achieved benefiting from the highly flexible WC-Co paste with high solid loading. Rheology properties of the paste, microstructure of the 3D structure was investigated. Organic-based paste of WC-8Co with a high solid content of 91 wt% were prepared, which exhibited shear thinning behavior and had a high storage modulus, two key parameters for ensuring the smooth printing. After secondary molding, 3D WC-Co green bodies with overhanging structure and no cracks were confirmed through secondary treatment of twisting or bending. Sound 3D structures with uniform and dense microstructure were obtained after debinding and sintering in vacuum. This work showed a facile route for the fabrication of 3D bone cemented carbides by direct ink writing with flexible green bodies.

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Keywords: Cemented carbide, Direct ink writing, Secondary molding, Flexible green bodies

1. Introduction

Cemented carbides show excellent wear resistance, high hardness and toughness, and high temperature mechanical properties, which are widely used as medical orthopedic materials, metal-extrusion dies, wear-resistance pipes and plates, etc [1-3]. These materials with high quality are commonly fabricated via conventional molding routes, like Powder Injection Molding (PIM) [4], extrusion molding for rods with high aspect ratios, and Powder Metallurgy (PM) with cold pressing and sintering [5]. Although complex and fine components of WC-Co could be achieved via advanced subtractive manufacturing, i.e. numerical control machining by diamond grinding wheel or tools, and electrical discharge machining, additive manufacturing (AM) attracts much attentions due to its high efficiency for customized structure and low costs [6]. Cutting tools with internal helical cooling channels could be used for high speed cutting with improved life.

Various AM methods have been reported for the preparation of WC-Co, like Selective laser melting (SLM) [7], Laser engineering net shaping (LENS) [8], Binder jet printing (BJP) [9],

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Fused filament fabrication (FFF)[10] and 3D gel-printing (3DGP) [11]. Owing to the high melting point, decomposition of the carbides, and small carbon interval of WC-Co, it is rather difficult to obtain qualified samples with controlled morphology using laser powder bed fusion [7]. Based on this, indirect 3D printing (3D structures built via the binding strength of organic binders) has been gradually attracting attention, benefiting from the subsequently debinding and sintering like conventional PM route. Enneti [12] prepared WC-12Co with nearly full density and satisfactory mechanical properties by BJP. Cramer [13] prepared 3D WC-Co by BJP combined with Co infiltration, and dense parts were achieved with some residue carbon-deficient phases. Lengauer[10] showed an example for preparing WC-10Co and Ti(C,N)-based cermets by FFF, using filaments of the composites. 3DGP for WC-20Co was reported by Zhang [11], which was a method combined gel casting and direct ink writing (also called Robocasting). The WC-Co ink, with catalyst and initiator were simultaneously extruded via the nozzle. Owing to the in-situ formation of WC-Co gel after extrusion, an impressive bevel milling cutter with dense and uniform microstructure was successfully fabricated by 3DGP [11].

Compared with other AM technologies, direct ink writing exhibits the advantage for fabricating various composites with porous lattice structure, large-scale production and low costs [14]. Based on the CAD mode, the ink was extruded from the nozzle and gradually formed 3D structure via depositing on the plate layer by layer. In order to obtain smooth printing and good shape retention, the inks should be easily extruded from a small nozzle with stable flow; after extruded, the inks should have certain strength to hold its shape, especially for the spanning structure [15]. Therefore, in order to realize the direct ink writing of WC-Co, preparation of the suitable WC-Co inks is the key step. Nowadays, direct ink writing has been widely used for fabricating of ceramics [14], metals [16] and cermets [17]. Few literatures concerning direct ink writing of WC-Co are available, except the 3DGP route [11]. Recently, direct ink writing of ceramics with flexible green bodies were proven [18,19], taking the inspiration from suspensions of tape casting. It is noteworthy that the post-printing shaping was a solution for overcome the limitation of direct ink writing for overhanging features.

In this work, we proposed a new type of WC-8Co ink with modified rheology properties. 3D green structure with highly flexible was confirmed, and the microstructure after debinding and sintering was investigated.

2. Materials and methods

WC (Grade: GWC007) and Co (Grade: GCo012D) powders with the grain size of 0.71 μm and 1.18 μm were purchased from Xiamen Golden Egret Special Alloy Co., Ltd (Xiamen, China). Polyvinyl butyral (PVB) was used as the binder, which was provided by Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Triethyl phosphate (TEP) was adopted as the dispersion of WC-Co powders, which was purchased from Sigma Aldrich (Shanghai) Trading Co., Ltd (Shanghai, China). Polyethylene glycol 2000 (PEG) was used as the plasticizer, which was purchased from Sinorpharm Chemical Reagent Co., Ltd (Shanghai, China). Solvents of ethanol and xylene were purchased from Sinorpharm Chemical Reagent Co., Ltd (Shanghai, China).

Figure 1 shows the flow-chart diagram for fabricating of 3D WC-Co by direct ink writing, which includes ink preparation, direct ink writing, secondary molding, drying, and debinding and

sintering. Firstly, the WC-Co ink (also named paste) was prepared as follows. Table 1 shows the nominal composition for the designing of WC-Co ink. PVB, PEG and TEP were firstly dissolved in the mixture of ethanol and xylene. The solvent mixture were chosen to balance the evaporation rate for fabricating the paste, and also showed better dispersion of WC-Co powders. Then, the powders were added in the solvent and put into a teflon bottle for milling. The milling time was kept for 12 h and the ZrO_2 ball to powder ratio was 3:1. After that, the milled suspension was heated at 60℃ by magnetic stirring to remove partial solvent, in order to adjust the solid content. Black WC-Co paste was gradually formed, with the solid content of 91 wt%. Before printing, the WC-Co ink was transferred into a 10 ml syringe. In order to remove the residue air in the ink, the syringe was treated by centrifugal force with a speed of 2000 r/min for 2 min.

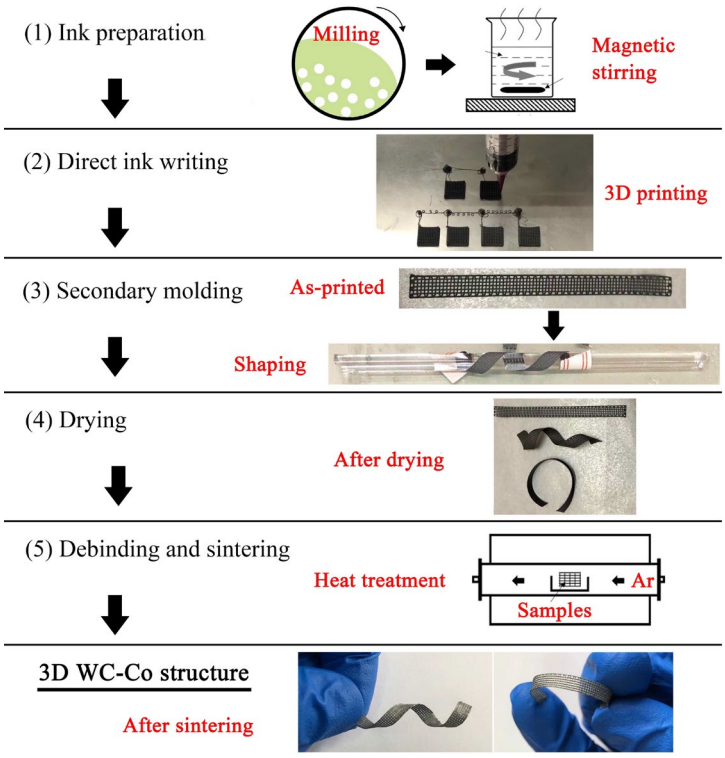

Fig. 1. The fabrication process of 3D WC-Co with conformable green bodies via direct ink writing. Five steps are included, which are ink preparation, direct ink writing, secondary molding, drying, and debinding and sintering. Twisted and bending WC-Co based lattices are successfully prepared.

Table 1. Nominal composition of the milled suspension and as-prepared WC-8Co paste (wt%).

Composition	Weighted for milling	WC-Co paste after evaporation	Purpose
WC powders	63.65	83.72	-
Co powders	5.53	7.27	-
TEP	0.46	0.60	Dispersion
PVB	2.33	3.06	Binder
PEG	0.46	0.60	Plasticizer
Ethanol	12.25	-	Easy evaporation for forming paste
Xylene	15.32	4.73	Low evaporation rate to avoid cracks

The printing machine (JDX02) was purchased from Changsha Nano Instrument Technology Co., Ltd (Changsha, China). The syringe was hold in a screw pump, with the maximum force of 2000 N. The paste was extruded from a nozzle with the diameter of 250 μm, and deposited on a stainless plat, which was controlled by the pump at a flowing speed of 6~8 ml/h. Based on the CAD mode, WC-Co lattices were printed. After printing, the as-printed structure was treated by bending, or twisting around a glass rod, with both ends stuck by stickers. In order to evaluate the capability of flexible of extruded filaments, a extremely twisted WC-Co rope by weaving was also prepared. The as-printed lattices, and green bodies via secondary molding was placed in air over night. Then, the green bodies were dried in a drier at 50 ℃ for 24h before the debinding and sintering. The debinding and sintering process was carried out in a tube furnace. The debinding process was firstly held at 500 ℃ for 2h, with a heating rate of 1℃/min. And then, the samples were presintered at 800℃ for 1h with partial strength for the investigation of the morphology after debinding. Finally, the samples were sintered in vacuum at 1420℃ for 1h, and dense 3D WC-Co was obtained.

The rheology properties of WC-Co pastes was measured at ambient temperature using a rotational rheometer (AR2000EX, TA instruments, USA). The optical views of the as-printed structure were taken using a 3D microscope (3E-H20053D, Shenzhen San Hui Industrial Co., Ltd, China). SEM images of the samples were detected by a scanning electron microscope (Mira3, Tescan, Czech), equipped with an EDS detector.

3. Results and discussion

Figure 2(a) shows the viscosity of WC-Co paste with solid content of 91 wt% under different shear rate. With the shear rate increased from 0.01 1/s to 63.10 1/s, the viscosity greatly decreased from 10650 Pa to 1.95 Pa. Shear shining behavior was confirmed, which played a key role in keeping stable state during the extrusion process [15]. The decreased viscosity reduced friction at the nozzle wall, ensuring the smooth printing. For shear thinning behavior, the shear thinning coefficient (n) of the suspension is in the range of 0~1, which can be expressed by the following equation [20].

$$\tau = \tau_{\mathrm{y}} + K\gamma^{\mathrm{n}} \tag{1}$$

where τ is the shear stress for the suspension, τ_y is the yield stress, K is a constant of viscosity, and γ is the related shear rate. As shown in Figure 2(b), the crossover point of storage modulus and loss modulus represented for the yield point, and τ_y was 501.2 Pa. Therefore, according to Equation (1), the shear thinning behavior (n) of WC-Co ink was calculated to be 0.4, which was suitable for a typical shear-thining paste [18].

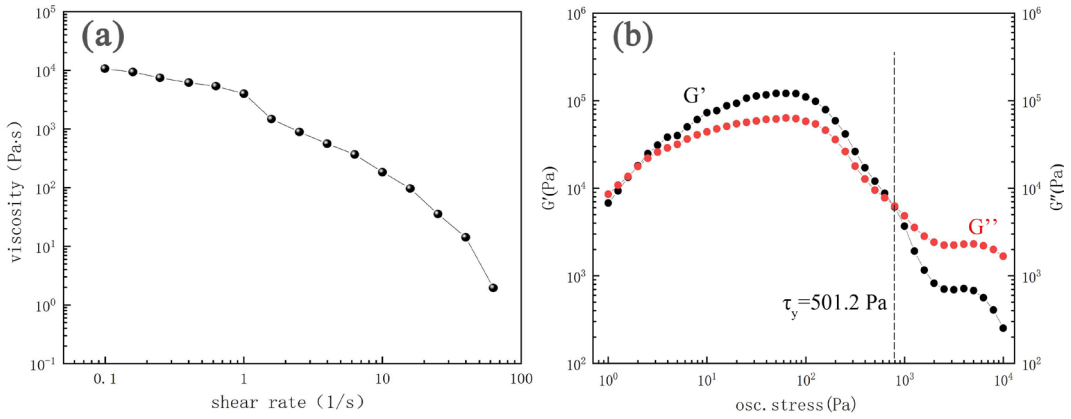

Fig. 2. (a) Viscosity vs shear rate for concentrated WC-8Co suspension with solid loading of 91 wt%. (b) Log-log plot of the storage modulus (G') and loss modulus (G") as a function of increased shear stress.

The yield stress of WC-Co ink was relatively higher than the water-based inks of ceramics [14,18], indicating that higher pressure was needed for the ongoing of extrusion. Compared to commonly applied inks with mono polymer, the storage modulus of WC-Co with a shear stress lower than τ_y, was not stable. When increasing the shear stress in Figure 2(b), both the modulus was firstly gradually increased, and then quickly went down. Insufficient shear stress could not break down the aggregation of polymer molecules [18,21], otherwise, increase the modulus due to the twinning behavior of molecules between the dissolved binder (PVB) and plasticizer (PEG). Without external force, the storage modulus was around 10^4 Pa, which was enough to achieve a satisfactory shape retention. Overall, according to the viscosity and storage modulus properties, the WC-Co ink was suitable for direct ink writing, with the capability of stable extrusion and shape preserving.

Fig. 3 displays the morphology of as-printed WC-Co lattices, with the capability of shaping like bending and twisting. The diameter of the filament is around 260 μm, slight larger than the nozzle size. The extruded filaments from the nozzle tended to expand without the high pressure. 3D WC-Co structures with good retention were obtained, benefiting from the shear-thinning paste with satisfactory modulus. Lattice with regular size indicated a good printability, and uniformly dispersed ink. With the addition of PVB and PEG, the 3D structure exhibited high flexibility, and a twisted rope (see Figure 3(b)) was achieved using the extruded filaments. The as-printed 3D structure showed good strength, and various types of shapes could be realized in molds [19]. It is noteworthy that no cracks were formed on the surface of filaments during the subsequently drying and handling, owing to the low evaporation rate of xylene.

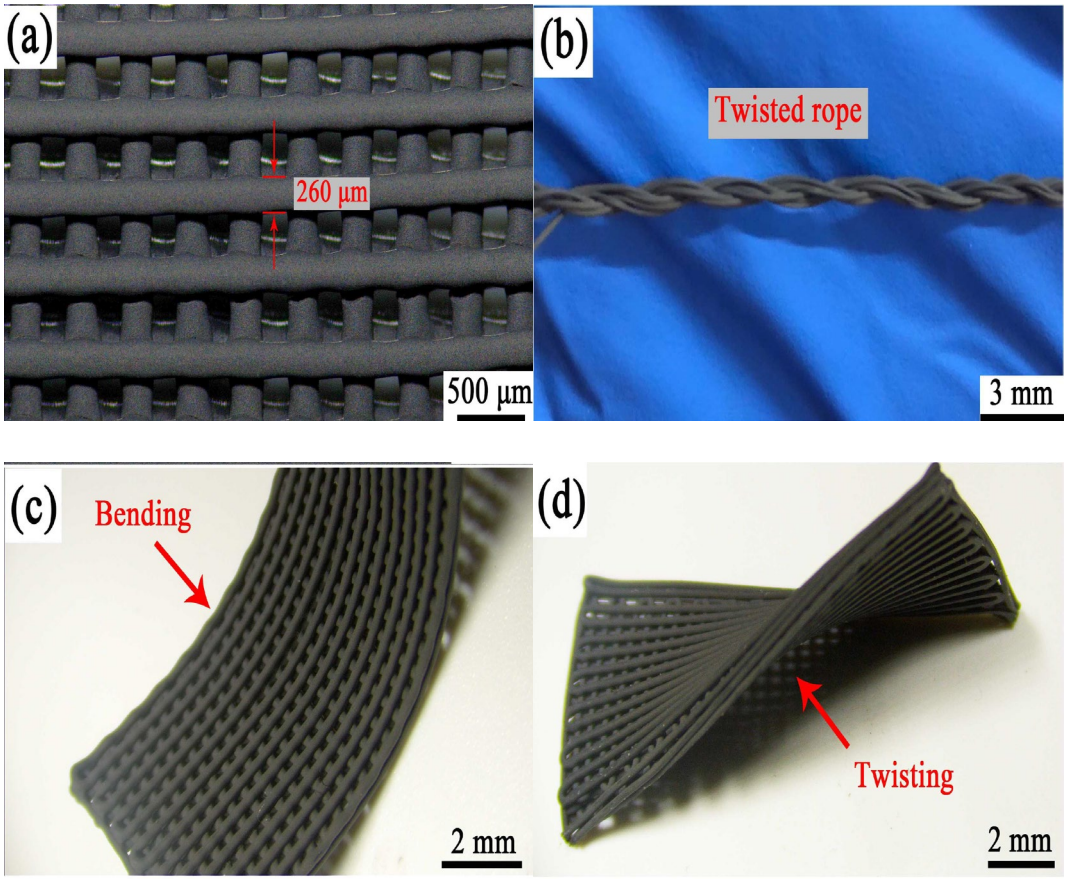

Fig. 3. Optical images of the as-printed lattices or weaved rope-like WC-Co. (a) As-printed WC-Co lattices, (b) A twisted rope using extruded filaments, (c) Lattice after bending, (d) Lattice after twisting.

In order to investigate the morphology evolution of as-printed WC-Co lattices during the heat treatment, the surface and fracture microstructure of the lattices after debinding and sintering were provided, as shown in Figure 4. Compared to the WC-Co powders, around 4.6 wt% organic polymers were left in the green bodies. Therefore, appropriate firing schedule should be used to remove the binders and also avoid the deformation of lattices. As shown in Figures 4a, smooth surface of the filament was confirmed, indicating the evenly removed polymers without affecting the macroscopic structure. The fracture views (see Figures 4b and c) showed that no residue bubbles existed, and submicron WC particles, Co metals were uniformly dispersed in the green bodies. For sintered WC-Co structure, regular lattice and dense surface, fracture morphology was obtained. Several gray points were found on the surface of filaments, which were Co-rich binders, formed during the solidification process [5]. Typical triangle grains of WC could be observed, formed via the liquid sintering of WC-Co. Inset (f1) in Figure 4(f) displays the EDS results on the fracture surface of sintered WC-Co. Common WC-Co phases were formed. Although the final mechanical properties of the 3D WC-Co remain to be evaluated and have certain space to be improved, a feasible and simple route is proved, at least, for the direct ink writing of 3D WC-Co composites with attracting comformable green structure.

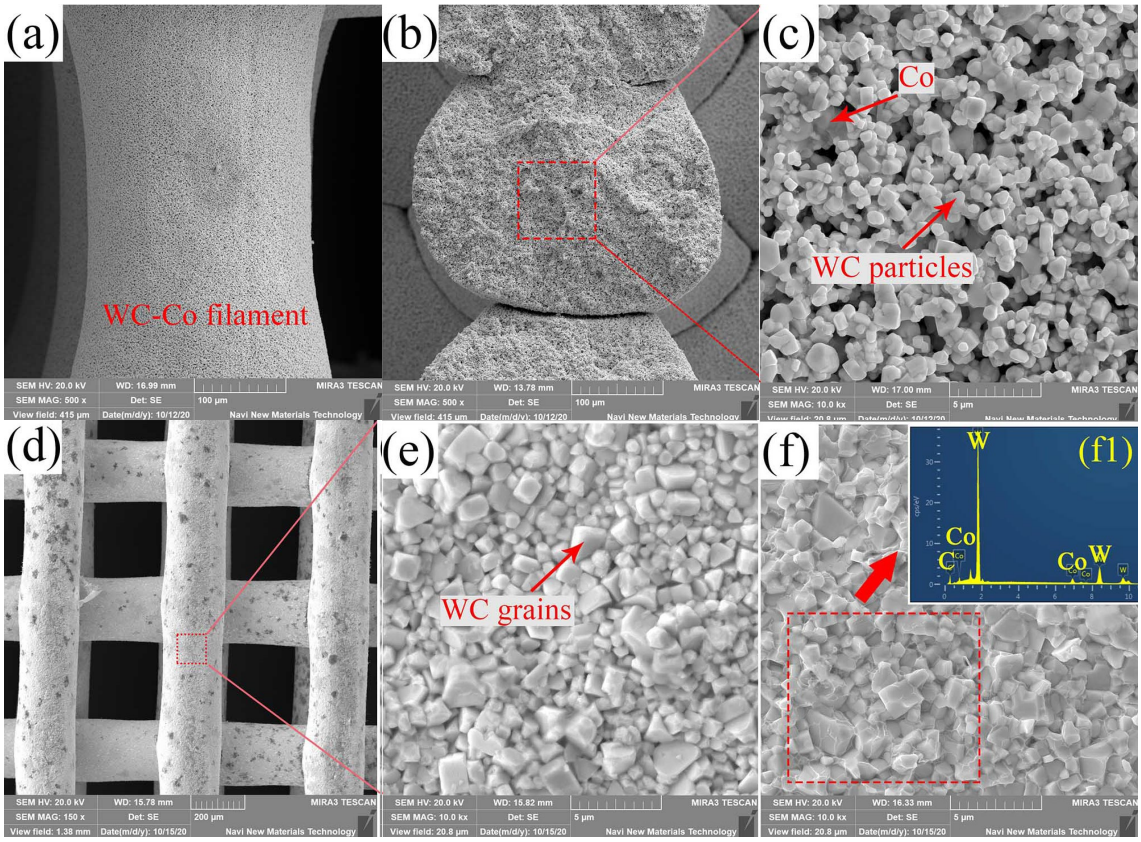

Fig. 4. SEM images of 3D WC-Co structure after debinding and sintering. (a-c) Surface and fracture morphology of WC-Co samples after debinding at 800℃for 1h. (d-f) Microstructure of samples after sintering at 1420℃for 1h. Inset of f1 is the EDS result of the red square in (f).

4. Conclusion

3D WC-Co structure was prepared via direct ink writing of flexible paste, with the capability of secondary molding (i. e. bending and twisting) for fabricating 3D overhanging models without the need of supports during printing. Rheology properties of the ink, and microstructure of the 3D WC-Co were investigated. Main conclusions were drawn as follows.

(1) WC-Co based paste with a mass content of 91 wt% showed shear thinning behavior, and relatively high shear stress (yield shear stress τ_y was 501.2 Pa) was essential for the extrusion process. Shear thinning behavior and satisfactory storage modulus of the paste ensured the success of direct ink writing.

(2) Good shape retention of filaments after extrusion was achieved. Sound morphology of the printed lattices without cracks was confirmed after bending and twisting, due to the high binding strength of the binders, and the low evaporation of the solvent.

(3) 3D WC-Co with uniform microstructure was obtained after sintering. Direct ink writing of WC-Co with conformable green body was proven to be a facile method.

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