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Study on Preparation and Forming of TiC Steel-Bonded Cemented Carbide Paste for Direct Writing Printing

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Abstract: TiC steel-bound cemented carbide body was prepared by direct writing printing. The effects of powder content (89.28, 89.49, 89.69, 89.88, and 90.07 wt%) and dispersant content (0.017, 0.034, 0.051, and 0.068 wt%) on the slurry and printing body were studied. The experimental results show that with the increase of powder content, the viscosity of the slurry gradually increases, the settlement rate gradually decreases, and the size and linewidth of the blank body gradually decreases. When the powder content is 89.69 wt%, the sedimentation stability and extrusion stability of the slurry are the best, and the density of the blank body is the highest, which is 3.8275 g/cm^3, which is suitable for direct writing printing. The addition of dispersant reduced the viscosity of the slurry; With the increase of dispersant content, the surface line width and size of the printed body gradually increased. When the dispersant content is 0.034 wt%, the extrusion stability of the slurry is the best, and the density of the body is the highest, which is 3.8901 g/cm^3.

Keywords: Direct writing printing; Steel-bonded cemented carbide; Powder content; Dispersant

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1. Introduction

TiC base steel-bonded cemented carbide is a kind of metal matrix composite material with TiC as the main ceramic phase and Fe as the binder, which combines the excellent properties of metal and ceramics, with high hardness, high melting point, good wear resistance, chemical inertness, and thermal stability [1]. Widely used in mold, tool, oil drilling, and other fields [2].

At present, the preparation process of steel-bonded cemented carbide materials is still based on the traditional powder metallurgy process are pressing and sintering, and the high hardness and high wear resistance lead to the mechanical processing of steel-bonded cemented carbide materials is very difficult. This process makes the preparation process complex, difficult to prepare special shape parts, and also the loss of raw materials, increasing the production cost of parts. The preparation of some parts will also be limited by processing technology and tools. Therefore, the steel-cemented carbide product development process is simple and cost-effective. As a result, low-cost near-net forming technology has become the focus of the field of steel-cemented carbide research content.

3D printing is based on the "discrete-stacking" principle of a forming technology, also known as additive manufacturing, which is a non-traditional advanced processing and manufacturing method, no mold, free interface, in principle can achieve the forming of any complex structure [3]. The near-net forming characteristics of 3D printing also reduce the waste [4] of materials in the subsequent processing process. At present, the most widely used types of 3D printing are light curing (SLA) [5], melt deposition molding (FDM) [6,7], direct writing printing (DIW) [8,9], and laser selection sintering molding (SLS) [10-12]. Among them, direct writing printing is a kind of non-die-forming technology that extrudes the rheological paste through a specific extrusion device. It has the advantages of simple equipment, low investment, and fine and complex three-dimensional structures that can be prepared at room temperature [13]. At present, there is research on the preparation of TiC steel-bonded cemented carbide by direct writing printing. Therefore, this paper takes the direct writing 3D printer as the extrusion tool to study the influence of powder and dispersant content on slurry viscosity, settlement stability, extrusion stability, and printing billet and clarify its mechanism, aiming to provide a theoretical basis for the preparation of TiC steel-bonded cemented carbide and related materials.

2. Experiment

2.1. Experimental materials

High-purity titanium carbide powder with an average particle size of 5 μm (Hebei Yanyu Metal Materials Co., LTD.), spherical iron powder with an average particle size of 1 μm (Shanghai Xiangtian Nanomaterials Co., LTD.), alloy powder with a particle size of 300 mesh (Hebei Yanyu Metal Materials Co., LTD.), carbon black with a particle size of 500 nm and 5 μm Mo powder are used as raw materials. Oleic acid is used as a dispersant.

2.2. Preparation of slurry

The raw materials were weighed according to the mixture ratio of powder as shown in **Table 1**, and then put into the roller ball mill for ball grinding. The ball mill speed was 240 rpm/min and the ball milling time was four hours to obtain the steel-bonded cemented carbide mixture powder.

Table 1. Ratio of mixed powder (wt%)

Ingredients	High-purity TiC powder	Mo	C	Alloy powder	Spherical iron powder
Content	35.00	2.10	0.5	17.1	45.3

Mix the solvent and binder in a certain proportion to get the premix, then weight X (89.28, 89.49, 89.69, 89.88, 90.07 wt%, X = the mass of the mixed powder)/(the mass of the mixed liquid + the mass of the mixed powder), add the mixed powder in batches to the premix and stir well with a mixer. The oleic acid of different content Y (0.017, 0.034, 0.051, 0.068, 0.085 wt%, Y = the mass of oleic acid/the mass of the mixed powder) is added to the slurry, and the slurry can be printed by stirring evenly with the blender.

2.3. Direct write print molding

At room temperature, select a needle with an inner diameter of 0.33 mm, pressure is 0.05 MPa, printing speed is 20 mm/s, layer thickness is 0.475 mm, line width is 0.5 mm, and after stacking layers, the blank body of direct writing is obtained, and the size of the blank body is set to 30 mm × 10 mm × 2.85 mm.

2.4. Characterization method

The viscosity of the slurry was characterized by NDJ-8S digital display viscometer. The parameters of the viscometer were rotor 4 and speed 6 rpm. A 3D printer was used to record the extrusion quality of the slurry every 10 seconds and calculate the extrusion deviation of the slurry, the formula is: where is the average mass of the slurry extrusion per unit time, is the quality of the slurry extrusion per unit time, the greater the extrusion deviation, the worse the extrusion stability of the slurry as shown below:

$$\sqrt{\frac{1}{n-i}\sum_{i=1}^{n}(x_i-\bar{x})^2} \tag{1}$$

Static settling experiment is used to measure the settling stability of the slurry, the settling rate is, where H_0 is the height of decline over time, and H is the initial height. The shape of the blank was characterized by SEM. The density of the billet was characterized by the Archimedean drainage method.

$$(H_0\ /\ H) \times 100\% \tag{2}$$

3. Results and discussion

3.1. Rheological properties of slurry

3.1.1. Influence of powder content on rheological properties of slurry

(1) The viscosity of the slurry with different powder content, the viscosity of the slurry with powder content of 89.28, 89.49, 89.69, 89.88, and 90.07 wt% is 17382.2, 19614.7, 20275.23, 22522.37 and 24764.26 mPa·s, respectively. That is, with the increase of powder content, the viscosity of the slurry gradually increases. When the powder content increases, the number of powder particles in the slurry increases, resulting in an increase in the number of collisions between powder particles, and the distance between particles decreases. When the slurry flows, the resistance it receives will increase with the increase in the powder content. The larger the powder content, the larger the specific surface area of the powder, the larger the contact area between the powder and the premix, the greater the friction resistance generated by the movement between the powder and the premix, resulting in the larger shear viscosity of the slurry [14].

(2) The sedimentation rate of the slurry with different powder content, and the sedimentation rate of the slurry with different powder content gradually increases with the increase of time, which is caused by the gravity of the slurry itself (**Figure 1**). With the increase of powder content, the settlement rate is reduced, because the powder content increases, the Van der Waals force between particles gradually increases, resulting in a lower settlement rate of the slurry with high powder content, that is, the greater the viscosity of the slurry, the lower the settlement rate [15].

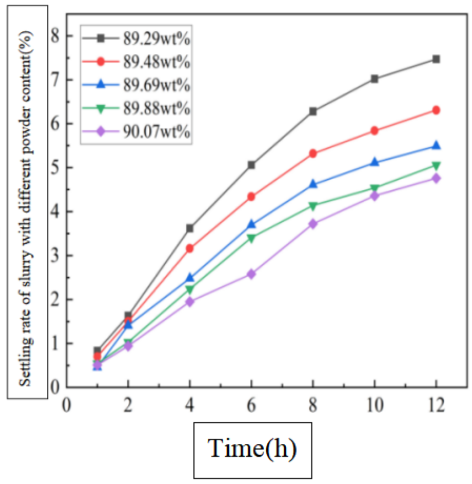

Figure 1. The sedimentation rate of the slurry with different powder content against time

(3) Extrusion standard deviation of slurry with different powder content is shown in **Figure 2**. From the figure, with the increase of powder content, the extrusion standard deviation decreases first and then increases. When the powder content is 89.69 wt%, the extrusion standard deviation is the smallest, and the extrusion standard deviation is 6.29%. When the powder content is lower than 89.69 wt%, the excess premix exists in the slurry, the settlement rate increases and the premix may be unevenly distributed during the extrusion process, resulting in a high extrusion standard deviation. When the powder content is 89.69 wt%, the powder dispersion is more uniform, so the extrusion deviation of the slurry is minimal when the powder content is 89.69 wt%. When the powder content is higher than 89.69 wt%, the powder is present in the slurry, and the powder may flocculate or agglomerate, resulting in a larger extrusion standard deviation. In short, when the powder content is too high or too low, the powder or premix distribution is not uniform, and the extrusion stability of the slurry is poor.

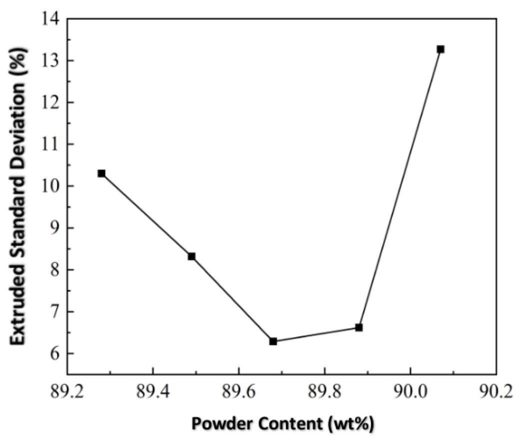

Figure 2. Extrusion standard deviation of slurry with different powder content

3.1.2. Influence of dispersant on rheology of slurry

(1) To obtain a uniform slurry, it is necessary to have a good dispersion of the mixed powder in the slurry. However, when a variety of powders are mixed, due to the interaction between the particles, there is

inevitably a tendency of agglomeration between the particles. A common way to reduce the viscosity of the slurry is to add a dispersant to the slurry because the raw material used in this paper does not have an electric charge, therefore, this paper uses a non-ionic dispersant oleic acid as an additive. Add different amounts of oleic acid to the viscosity of the slurry. The addition of oleic acid reduced the viscosity of the slurry, and the viscosity of the slurry gradually decreased with the increase of oleic acid content, and the viscosity was 20179.45, 20054.39, 19284.50, 18952.17 and 18212.33 mPa·s, respectively shown as **Figure 3**. This is due to the hydrophilic carboxyl (COOH) and lipophilic groups in its molecular structure. The hydrophilic end of oleic acid molecules will be attached to the surface of powder particles, resulting in repulsion between particles and separation from each other. The particles are gradually wetted and become lipophilic, which can be well suspended in organic solvents.

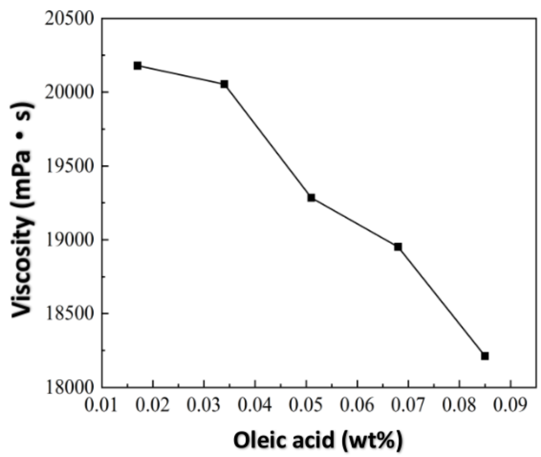

Figure 3. Viscosity of the slurry against oleic acid content

(2) Add different content of oleic acid slurry sedimentation rate. With the increase of time, the sedimentation rate of the slurry with different oleic acid content gradually increases, which is due to the gravitational action of the slurry itself. With the increase of oleic acid content, the sedimentation rate of the slurry decreases first and then increases. When 0.034 wt% oleic acid is added, the sedimentation rate of the slurry is the lowest, which is 4.69%. When oleic acid is not added or the oleic acid content is lower than 0.034 wt% (0.017 wt%), the surface of the particles is not completely wet, and the particles cannot be effectively modified, resulting in the increased sedimentation rate. When the oleic acid content is properly increased, it is conducive to improving the coverage rate of the particle surface, easy to form a network structure inside the slurry, and forms an organic protective film on the particle surface to prevent particles from colliding with each other, and the adsorption of the particle surface reaches saturation. The concentration of oleic acid is too high, the free dispersant molecules will exist in the skeleton between the particles, the resistance between the particles of the powder is reduced, and the interaction force is reduced, resulting in an increase in the settlement rate.

(3) When the powder content is 89.69 wt%, the standard deviation of extrusion of oleic acid slurry with different content is obtained. With the increase of oleic acid content, the extrusion standard deviation of the slurry first decreased and then increased, while the extrusion standard deviation of the slurry without oleic acid was 6.29%. The standard deviation of 0.034 wt% oleic acid is the smallest, which

is 5.82%, and the extrusion stability of the slurry is the best. When 0.017 wt% oleic acid was added, the extrusion standard deviation of the slurry increased, which may be because the addition of a small amount of oleic acid made the slurry incomplete dispersion, and the interaction between particles led to the instability of the slurry extrusion. When oleic acid is added greater than 0.034 wt%, the fluidity of the slurry becomes larger, and excessive and free dispersant molecules will exist between the particles, resulting in uneven dispersion of the slurry at the top and bottom, and poor extrusion stability during the extrusion process.

3.2. Influence of powder content on printing billet

3.2.1. The influence of powder content on the surface morphology of the printed billet

The surface morphology of the slurry-forming billet with different powder content is shown in **Figure 4**. As can be seen from the figure, the linewidths of the body corresponding to different powder contents (89.28, 89.49, 89.69, 89.88, 90.07 wt%) are 0.525, 0.515, 0.505, 0.49 and 0.48 mm, respectively. With the increase of powder content, the linewidths of the body surface gradually decrease, and the surface lines of the body become clearer. This is due to increase of powder content, the viscosity of the slurry increases, and the extrusion amount of the slurry decreases. When the printing speed is the same, the slurry stroke is the same, and the line width of the billet decreases gradually. With the increase of powder content, the fluidity of the slurry is poor, the "groove" formed in the printing process is difficult to fill, and the lines on the surface of the billet are clearer. When the powder content is 89.69 wt%, the line width is 0.505 mm, the error between the line width and the set value is minimal, and the filling property of the blank body is better at this time.

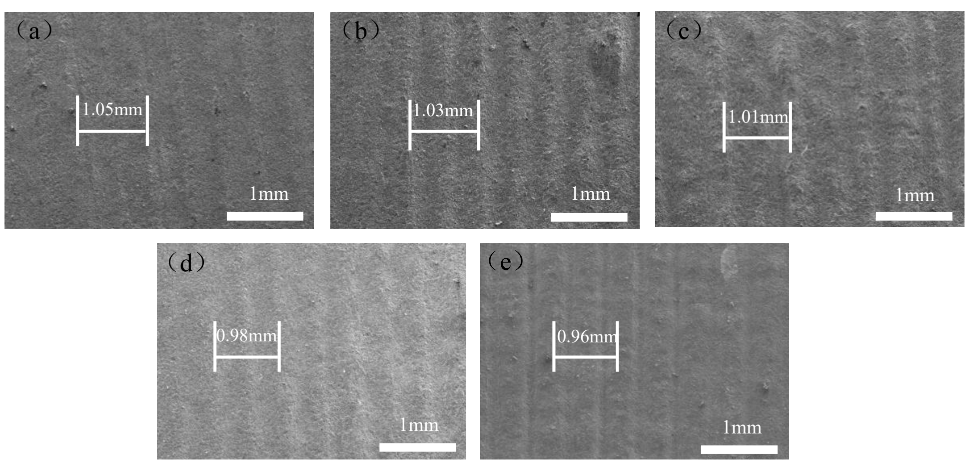

Figure 4. The apparent morphology of the paste printing body with different powder content. (a) 89.28 wt%; (b) 89.49 wt%; (c) 89.69 wt%; (d) 89.88 wt%; (e) 90.07 wt%

According to the figure, the side topography of the paste printing body with different powder content. It can be seen from the figure that with the increase in powder content, the side morphology of the blank body changes from uneven to flat to convex (concave). This is because the slurry with low powder content (89.28, 89.49 wt%) has low viscosity, large fluidity, and poor extrusion stability of the slurry. When the slurry is extruded for a long time, the slurry flows more to the side of the billet, which looks "high," and conversely, it is "low," resulting in uneven side morphology of the billet. And high powder content (89.88, 90.07 wt%) of the slurry viscosity is larger, when the extrusion amount is more, the slurry fluidity is poor, forming a pile-like convex, and vice versa to form a depression.

3.2.2. Influence of powder content on the fracture morphology and density of print billet

Figures 5 and **6** show the section morphology and density of the printed billet under different powder content. As can be seen from the figure, when the powder content is low (89.28 wt% and 89.49 wt%), the blank body has large pores (**Figure 5a, 5b**). This is because on the one hand, when the powder content is low, the spacing between particles is large, and more pores are formed after the liquid phase in the premix evaporates. On the other hand, when the powder content is low, the slurry viscosity is low, the fluidity is large, the layer spacing is the same, the filling between layers is poor, and the billet has large pores. When the powder content is high (89.88 wt% and 90.07 wt%), there are more pores in the blank body (**Figure 5d, 5e**). It may be because the spacing between particles decreases when the powder content is high, the slurry may tend to agglomerate or flocculate, and the slurry is not evenly dispersed, so there are more pores. The body with a powder content of 89.69 wt% had fewer pores (**Figure 5c**). As can be seen from **Figure 6**, the density of the body is the highest when the powder content is 89.69 wt%, and the density is 3.8275 g/cm^3, which corresponds to **Figure 5**.

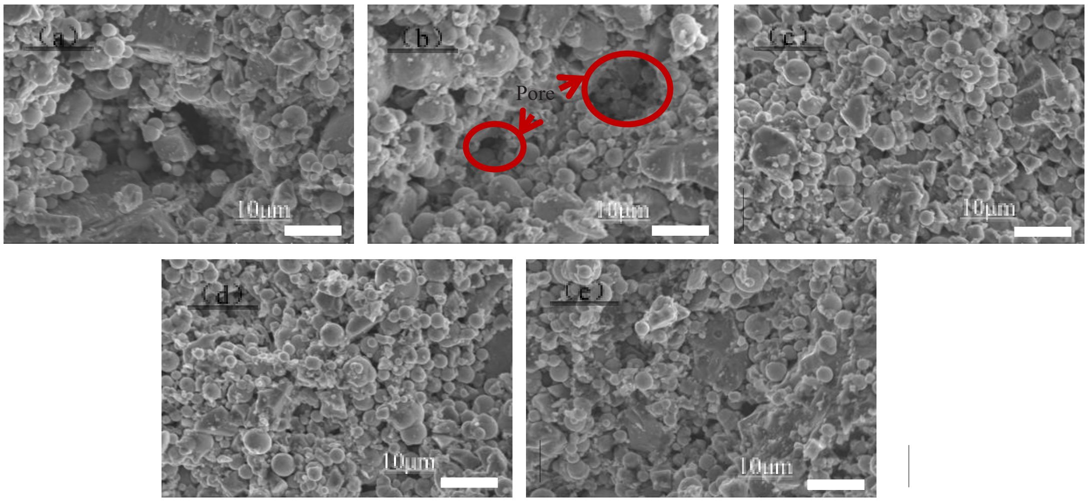

Figure 5. Section morphology of printed billet under different powder content. (a) 89.28 wt%; (b) 89.49 wt%; (c) 89.69 wt%; (d) 89.88 wt%; (e) 90.07 wt%

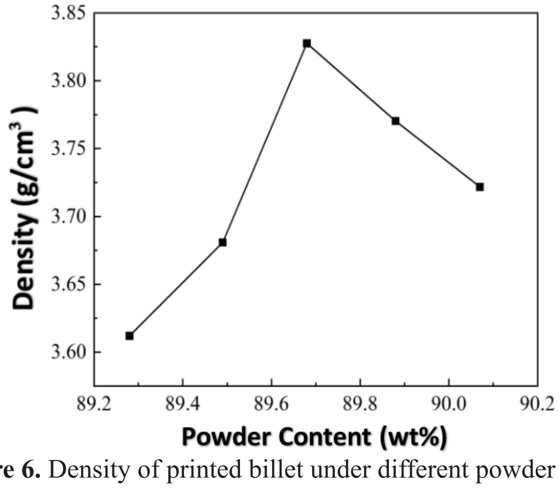

Figure 6. Density of printed billet under different powder content

3.2.3. Influence of oleic acid content on the surface morphology of printed billet

With the increase of oleic acid content, the body length, width, and height of the blank gradually increase, and the change of the size of the paste with different oleic acid content corresponds to the viscosity of the slurry with the same oleic acid content. The lower the viscosity of the slurry, the more slurry will be extruder per unit time. When the printing speed is the same and the stroke is the same, the body size will gradually increase. **Figure 2** shows the side topography of the paste printing billet with different oleic acid content. As can be seen from the figure, with the increase of oleic acid content, the profile of the sideline first changes from uneven to flat and then becomes convex. This is because when the oleic acid content is low (0.017 wt%) or high (0.051, 0.068, 0.085 wt%), the extrusion deviation of the slurry is large and the fluidity is high, resulting in the uneven profile of the printing billet. When the oleic acid content is 0.034 wt%, the slurry printing molding effect is the best.

3.2.4. Influence of oleic acid content on the fracture morphology and density of printing blank

Section morphology and density of different content oleic acid printing billet. With the increase of oleic acid content, the porosity of the body decreases first and then increases, and the porosity is the least when the oleic acid content is 0.034 wt%. With the increase of oleic acid content, the body density first increased and then decreased. When the oleic acid content is 0.034 wt%, the density is the highest, and the density is 3.8901 g/cm^3. This is because the addition of oleic acid overcomes the van der Waals force between particles, making the slurry disperse more evenly and have a higher density. When the oleic acid content is low (0 wt%, 0.017 wt%), oleic acid cannot disperse the powder sufficiently, resulting in its low density. When the oleic acid content is high (0.051 wt%, 0.068 wt%, 0.085 wt%), due to the larger fluidity of the slurry, the poor filling between layers, excessive dispersant will exist between particles, and the spacing between particles of the powder will be large, resulting in its low density shown in **Figure 7.**

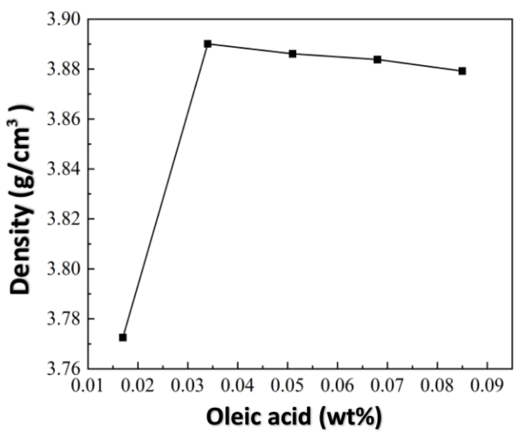

Figure 7. The density of printed billets with different oleic acid content

4. Conclusion

In this paper, the pulp with different powder content and oleic acid content was prepared and its rheological property was tested. The shape, size, and density of the blank printed with different slurries were studied, and the following conclusions were drawn:

(1) With the increase of powder content, the viscosity of the slurry increases and the sedimentation rate decreases. When the powder content is 89.69 wt%, the sedimentation rate and standard extrusion deviation are 5.49% and 6.29% respectively, and the rheological property of the slurry is the best. The line width and size of the printed billet gradually decrease the side topography from uneven to flat to convex (concave), and the density of the billet is the highest, 3.8275 g/cm^3.

(2) With the increase of oleic acid content, the viscosity of the slurry showed a decreasing trend. When 0.034 wt% oleic acid was added, the sedimentation rate and standard extrusion deviation were 4.69% and 5.82%, respectively. The rheological property of the slurry was the best. The line width and size of the printing body gradually increased, from uneven to flat and then convex, the density of the body is the highest, the density is 3.8901 g/cm^3, and the forming effect of the body is the best.

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Disclosure statement

The authors declare no conflict of interest.

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