Effect of Ni-Cr-Fe powder formulation on performance of porous materials based on Ink-jet Printing technology

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Abstract. Ni-Cr-Fe porous material has the advantages of high temperature resistance, corrosion resistance and good permeability. It has good application prospect and development value as filtration, sound absorption, energy absorption and biological functional materials. In this paper, Ni-Cr-Fe as the main raw material, and PVP, carbon powder, starch as additives, using In-kjet printing molding process, the proportion of raw materials and additives as different levels of orthogonal experiment, the optimal formula was studied. The optimum combination of parameters was obtained by means of open porosity test, hardness test, compression test and comprehensive factor balance analysis. The results showed that the ratio of Ni-Cr-Fe was 20:50:30, carbon powder was 3%, PVP was 15%, and starch was 0.8%. The technological process of preparing Ni-Cr-Fe porous materials by Ink-jet printing technology is discussed in detail, and the adhesive formula and ink formula suitable for Ni-Cr-Fe powder material are provided, which provides practical proof for the indirect pore forming theory of binder.

Keywords: Ni-Cr-Fe porous material, Ink-jet Printing technology, Powder formula, Preparation process, Performance

1. Introduction
Ni-Cr-Fe porous material as adsorption carrier has an important application prospect in the field of high temperature filtration. At present, a variety of additive manufacturing processes have been applied to metal printing, which can be divided into three categories according to the forming methods. The first type is the processing methods using laser, electron beam and arc with high energy density: Direct metal Laser Sintering (DMLS) [1], Selective Laser Sintering (SLS) [2], Selective Laser Melting (SLM) [3-4], Laser Engineered Net Shaping (LENS) [5] and Electron Beam Melting (EBM) [6]. The second type is Ink-jet Printing (IJP) or Three-dimensional Printing (3DP) [7-8]. The third type is Fused Deposition Modeling (FDM) [9]. Among them, DMLS, SLS, SLM, LENS, EBM technology can be used to prepare porous metal parts, and the porous structure can be made more fine, which is the main research method at present stage. The process is relatively mature, but the printing equipment is expensive and energy consumption is large. The porous structure materials that can be prepared by FDM technology are limited, such as low melting point thermoplastic materials or low melting point alloy materials [10-11]. Ink-jet Printing technology is not only suitable for a wide range of printing materials, can print gypsum,
ceramics, metals and composite materials, but also can play the dual advantages of design pore making and adhesive indirect pore forming, meet the performance requirements of porous materials, and the cost is lower than DMLS, SLS, SLM, LENS, EBM technology. Therefore, it is necessary to study the preparation and performance control of Ni-Cr-Fe porous materials under the background of Ink-jet Printing technology, which has certain research value and practical significance.

As shown in Fig. 1, the green part making process of Ink-jet Printing technology is as follows: Firstly, a certain amount of molding powder is evenly and evenly spread on the surface of part building chamber by powder laying roller. Secondly, under the control of the computer, the special nozzle sprays the matching adhesive according to the section information obtained in advance on the powder surface just laid, and sprays the matching adhesive according to the way of scanning line by line, so as to make the powder in the specific area bond together, thus completing the printing of a layer of cross section. After that, the piston of the powder supply chamber drops one layer of powder height, the powder laying roller lays the powder again, and the nozzle sprays the adhesive again. By repeating the above steps, layer by layer, from bottom to top, until all sections of the required parts are bonded and stacked, the green part is obtained, and the final printing product is obtained through independent debonding, sintering and post-treatment.

![Figure 1. Schematic diagram of Ink-jet Printing technology [12]](image)

2. Experimental equipment and methods

2.1. Experimental equipment
The Ink-jet Printing equipment uses RF1001 scientific research type printer produced by Suzhou Ruifa Technology Co., Ltd., as shown in Fig. 2.

![Figure 2. Three dimensional structure and physical picture of printing equipment (I and III are power supply chamber, II is part building chamber).](image)
2.2. Material

2.2.1. Metal powder raw materials. The raw materials of Ni, Cr and Fe metal powders used in the experiment were purchased from Beijing Xingrongyuan Technology Co., Ltd., and the powder particle size range was 15-53 µm.

2.2.2. Auxiliary powder materials. The auxiliary raw materials used in the experiment include K-90 PVP, activated carbon and starch. Starch and PVP powder can improve the bonding strength. Activated carbon can enhance the fluidity of the mixed powder and is also the main pore forming agent. It plays an indirect role in pore forming during sintering.

2.2.3. Ink. The ink used in this experiment is made up of deionized water, PEG400 and diethylene glycol at the mass ratio of 90:8:2. Among them, deionized water can prevent impurities in water from blocking the nozzle. In addition, deionized water can also be mixed with PVP powder and starch in the powder to form a binder, so as to enhance the bonding strength between the powders. Diethylene glycol can improve the flow quality and viscosity quality of the adhesive. PEG400 is a kind of surfactant, which can change the surface tension of adhesive.

2.3. Test methods

2.3.1. Hardness test. The sintered samples were polished on a polishing machine until the surface was smooth. The hardness of the porous Ni-Cr-Fe materials was measured by D-type shore hardness tester. Five points are selected for each porous material, the highest and lowest hardness points are removed respectively, and the average value of the other three points is taken as the hardness of the nickel based porous material.

2.3.2. Open porosity test. The open porosity is the percentage of the volume of the sintered sample. The method of GB 5164-85 "Permeable sintered metal materials - Determination of open porosity" was used to determine the open porosity of samples [13].

2.3.3. Compressive strength test. The WDW-50 universal testing machine of Jinan Hengruijin testing machine Co., Ltd. is used for compressive strength test, and GB/T7314-2017 "Compression test method for metallic materials at room temperature" is used for the test. The sample was polished with sandpaper to ensure the smoothness of the upper and lower planes of the sample, and avoid the inaccurate fracture peak value caused by the uneven stress during the compression process.

3. Preparation and performance analysis of porous materials

3.1. Orthogonal experimental scheme
The ratio of Ni,Cr and Fe metal powder and the mass ratio of carbon powder, PVP powder and starch were selected as experimental factors. Without considering the interaction among factors, four factors can be observed by using $L_9(3^4)$ orthogonal experiment table, and three levels of each factor are designed, as shown in Tab. 1.
Table 1. Orthogonal experiment design table ($L_9(3^4)$)

| Experimental numbers | A  | B           | C          | D           |
|----------------------|----|-------------|------------|-------------|
|                      | Ratio of Ni, Cr and Fe (wt%) | Proportion of carbon powder (wt%) | Proportion of PVP powder (wt%) | Proportion of starch (wt%) |
| 1                    | 1(52:18:30) | 1(1) | 1(5) | 1(0.6) |
| 2                    | 1 | 2(2) | 2(10) | 2(0.8) |
| 3                    | 1 | 3(3) | 3(15) | 3(1) |
| 4                    | 2(30:40:30) | 1 | 2 | 3 |
| 5                    | 2 | 2 | 3 | 1 |
| 6                    | 2 | 3 | 1 | 2 |
| 7                    | 3(20:50:30) | 1 | 3 | 2 |
| 8                    | 3 | 2 | 1 | 3 |
| 9                    | 3 | 3 | 2 | 1 |

3.2. Preparation of mixed powder
Before preparing the mixed powder, Ni-Cr-Fe powder, PVP powder, carbon powder and starch were dried. Then calculate the mass of each component according to the set experimental scheme, weigh it with electronic scale and pour it into the ball mill pot, and grind it with QW-QX4 omnidirectional planetary ball mill. Finally, after grinding, put it into the electric blast drying oven for drying, and take it out before printing.

3.3. Printing
SolidWorks 2014 is used to carry out 3D modeling, and the parts are $\varphi 30 \times 10$ cylinder, which is converted into .STL file. Import the .STL file into Slic3R and RF1001 Converter software, and set the printing parameters. The printing process and green part are shown in Fig. 3.

3.4. Degreasing and sintering
The printed green part needs degreasing and sintering treatment to make it have better mechanical properties and meet the requirements of use. The degreasing and sintering process curve and sintered part are shown in Fig. 4.


(a) Degreasing and sintering process curve  
(b) Sintered part

**Figure. 4** Debinding and sintering of green part.

### 3.5. Performance analysis of sintered parts

#### 3.5.1. Range analysis.

The effects of different factors and their levels on the hardness, open porosity and compressive strength of the parts were studied by orthogonal experiment. The test results are shown in Tab. 2.

| Experimental numbers | Experimental factors | Hardness (HD) | Open porosity (%) | Ultimate compressive strength (kN) |
|----------------------|----------------------|---------------|-------------------|-----------------------------------|
|                      | A                    | B             | C                 | D                   | E   | F   | G             |
| 1                    | 1(52:18:30)          | 1(1)          | 1(5)              | 1(0.6)              | 84.2 | 15.4 | 32.1          |
| 2                    | 1(2)                 | 2(10)         | 2(0.8)            | 86                  | 17.8 | 33.5 |
| 3                    | 1(3)                 | 3(15)         | 3(1)              | 87.5                | 20.6 | 33.8 |
| 4                    | 2(30:40:30)          | 1(2)          | 2                 | 3                   | 85   | 16.5 | 33.1          |
| 5                    | 2(3)                 | 3             | 1                 | 2                   | 83.5 | 18.8 | 33.5          |
| 6                    | 3(20:50:30)          | 1(3)          | 2                 | 3                   | 86.3 | 19.9 | 31.8          |
| 7                    | 3(20:50:30)          | 1(3)          | 2                 | 3                   | 91.5 | 17.5 | 32.7          |
| 8                    | 3(2)                 | 2             | 1                 | 3                   | 101  | 18.9 | 33.2          |
| 9                    | 3(3)                 | 3             | 2                 | 1                   | 103.5 | 20.1 | 34.5          |

The experimental results are calculated and analyzed, and $K_i$ and $R_j$ values are calculated. $K_i$ represents the average value of the performance index of factor $j$ under the action of level $i$. $R_j$ represents the range of the performance index under the influence of factor $j$.
The trend chart of factors and test indexes is drawn from Tab. 2, as shown in Fig. 5 (a) - (c). The graph can intuitively analyze the fluctuation relationship between different indicators and the levels of various factors.

![Trend chart of factors and test indexes](image)

**Figure 5.** Trend chart of factors and test indexes.

According to the range value in Tab. 2, the influence of each factor on the index is obtained. Combined with the trend chart of Figure 5, the best level value of each factor can be obtained. For hardness, the best combination of factors is $A_3B_3C_2D_3$. For open porosity, the best combination of factors is $A_2B_3C_1D_1$. For compressive strength, the best combination of factors is $A_3B_2C_2D_2$. According to the optimal combination of parameters, the relative error of the specimen is less than 1.1%, and the verification results further prove the influence law of the factors.

### 3.6. Comprehensive balance analysis

![SEM images of different combinations](image)

**Figure 6.** SEM images of different combinations
According to the requirements of each performance, the comprehensive balance analysis is carried out to determine the optimal level of each factor. The open porosity is the first, $A_3B_3C_3D_2$ is selected, the tensile strength is the second, and $D_2$ is taken. Therefore, the final optimal combination is $A_3B_3C_3D_2$.

The other three groups of experimental samples were randomly selected for observation, the results are shown in Fig. 6 (a), (b) and (c), and the optimal combination was observed, as shown in Fig. 6 (d). The material in Fig. 6 (a) has the largest porosity, but its pore distribution and pore size are not uniform. In Fig. 6 (b), the pores are small and the sintering is uneven. In Fig. 6 (c), the distribution of pores is uneven and the pores are small. The pores in Fig. 6 (d) are regular and evenly distributed. The results of electron microscopy are in good agreement with the results of comprehensive equilibrium analysis.

The optimal factor level obtained by comprehensive balance analysis is $A_3B_3C_3D_2$, but this experimental scheme is not included in the orthogonal experiment, and the verification experiment should be added. The post-treatment process adopts the same process as the orthogonal experiment scheme. The performance test of the parts after the post-treatment is carried out. The comparison between the test results and the optimal performance parameters is shown in Tab. 3.

| Performance                          | Hardness (HD) | Open porosity (%) | Ultimate compressive strength (kN) |
|--------------------------------------|---------------|-------------------|-----------------------------------|
| The best performance in orthogonal experiment | 103.5         | 20.6              | 34.5                              |
| Performance of $A_3B_3C_3D_2$ combination | 101.7         | 21.2              | 35.0                              |

It can be seen from Tab. 3 that the deviation between the results of comprehensive balance analysis and the optimal value of various performance tests in the orthogonal experiment is less than 3%. It can be considered that the combination $A_3B_3C_3D_2$ is the optimal group in all combinations, that is, the ratio of Ni-Cr-Fe is 20:50:30, the proportion of carbon powder is 3%, the proportion of PVP is 15%, and the proportion of starch is 0.8%.

4. Conclusion
Based on Ink-jet Printing technology, the effect of Ni-Cr-Fe powder formula on the properties of parts was studied:

(1) Adding PVP, carbon and starch into Ni-Cr-Fe powder can improve the forming quality of the green part. In particular, it plays an indirect role in pore formation.

(2) Through orthogonal experiment, the optimum formula of hardness, open porosity and maximum compressive strength was studied. Combined with the comprehensive balance analysis method, the optimal factor combination $A_3B_3C_3D_2$ was obtained, that is, the ratio of Ni-Cr-Fe was 20:50:30, the proportion of carbon powder was 3%, the proportion of PVP powder was 15%, and the proportion of starch was 0.8%.

(3) Compared with the best performance in orthogonal experiment, the deviation is less than 3%, which verifies the rationality and accuracy of the optimal factor combination.

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