Preparation and properties of titanium alloy with binder based on 3DP method

Yuanyuan Xu1,*, Hai Gu1,2, Bin Li1,2, Jie Zhang1,2, Jie Jiang1,2 and Jianhua Sun1
1School of Mechanical Engineering, Nantong Institute of Technology, Nantong, China
2Jiangsu Key Laboratory of 3D Printing Equipment and Application Technology, Nantong Institute of Technology, Nantong, China
*Corresponding author: xuyy@ntit.edu.cn

Abstract. TC4 material has good comprehensive mechanical properties, but its development is limited due to its complex preparation process and high cost. Three-dimensional printing forming technology has the characteristics of low cost, wide range of materials, fast forming speed, etc. In this paper, the binder and powder formula of 3D printing molding process were studied. According to the viscosity value, surface tension, bonding effect and the service life of nozzle, the optimal formula of binder was selected. Finally, according to the formulation of binder and mixed powder, TC4 blank was prepared by 3d printing machine, TG-DSC curve of PVA and starch was analyzed, degreasing sintering process was designed, degreasing and sintering of TC4 porous material was carried out. Finally, the performance of the parts under different time - aging treatment is studied.

Keywords: TC4 powder, Three-dimensional Printing forming technology, Adhesive, Powder characteristics

1. Introduction
3D Printing technology is also known as Additive Manufacturing (AM) technology, which is an Additive Manufacturing method of solid parts using the method of material accumulation layer by layer through CAD design data. Compared with the traditional material removal processing technology, it is a bottom-up Additive Manufacturing method [1]. There are many technological methods for 3D printing, among which the more common ones are melt deposition modeling (FDM), photocuring three-dimensional modeling (SLA), selective laser sintering (SLS), and three-dimensional printing molding (3DP) [2]. 3DP is belonging to an important branch of rapid prototyping technology, it was based on the digital model as the basis of development, using composite material with adhesive effect, through the nozzle spray liquid adhesives and make the powder binder, for printing of each layer of technology, finally after many repeated print form object type [3-5].

According to the different state of the material, the preparation method of the porous structure is also different, each preparation method has its own characteristics, but mostly because its process is complex
and its cost is high, and difficult to control in the process of preparation of porous characteristics, make the
preparation of porous structure will have some performance issues, and 3DP technology can effectively
solve some problems existing in the traditional process. This technology provides a more convenient method
for the preparation of metal materials, and can improve the work efficiency. The preparation of porous
materials using 3DP process will become a research hotspot in the future [6].

2. Preparation of adhesive
The binder compositions prepared in this study mainly include deionized water, surfactant (PEG400) and
diethylene glycol, and are configured in a certain proportion. The prepared binder should be tested for
viscosity, surface tension and other aspects. The greater the viscosity value, the better the bonding effect,
but easy to plug the nozzle, so that the service life of the nozzle is reduced. The surface tension affects
the smoothness and printing quality of the adhesive during injection. Due to high surface tension, the adhesive
is not easy to moisten the sprinkler head, causing difficulty in spraying, which will lead to nozzle blockage
for a long time. And the surface tension is small, the adhesive is easy to drop directly, unable to form a
stable ink droplets, or the phenomenon of trailing, resulting in the quality of printing [7].

The HAAKE Viscotester E rotary viscometer was used to test the viscosity at room temperature, and the
bZy-1 surface tensiometer was used to test the surface tension of the adhesive, and the effect of the adhesive
was evaluated.

(1) The influence of diethylene glycol content on the viscosity value, surface tension, bonding effect and
nozzle life of the adhesive was studied under the condition that the content of surfactant PEG400 remained
unchanged. The specific formula and test results are shown in Table 1.

| NO. | Formulation (Volume ratio) | Viscosity number (mPa·s) | Surface tension (mN·m⁻¹) | Bond effect | Service life of sprinkler (h) |
|-----|-----------------------------|--------------------------|---------------------------|-------------|-----------------------------|
| No. 1 binder | Plasma water: surfactant: diethylene glycol=90:5:5 | 3.183 | 58.32 | commonly | 11 |
| No. 2 binder | Plasma water: surfactant: diethylene glycol=87:5:8 | 3.505 | 54.72 | Better | 16 |
| No. 3 binder | Plasma water: surfactant: diethylene glycol=84:5:11 | 4.749 | 56.43 | Better | 12 |

As can be seen from Table 1, with the increase of diethylene glycol content, the viscosity value also
increases, and the surface tension changes. The viscosity values of No. 1, No. 2 and No. 3 adhesive are all
within the reference range. The surface tension of No. 2 adhesive is suitable for smooth inking and can
guarantee the printing quality. The results showed that increasing the content of diethylene glycol was
helpful to increase the viscosity of the adhesive, but it would affect the surface tension of the mixed solution,
thus affecting the service life of the nozzle.

(2) The influence of surfactant PEG PEG400 on viscosity value, surface tension, bonding effect and
nozzle life was studied under the condition of constant diethylene glycol content. The specific formula and
test results are shown in Table 2.
Table 2. Preparation test of adhesive.

| NO.   | Formulation                  | Viscosity number (mPa·s) | Surface tension (mN·m^{-1}) | Bond effect | Service life of sprinkler (h) |
|-------|------------------------------|--------------------------|-----------------------------|-------------|------------------------------|
| No. 4 | binder                       |                          |                             |                          |                              |
|       | Plasma water: surfactant: diethylene glycol = 90:2:8 | 3.224                    | 60.88                       | commonly     | 10                           |
| No. 5 | binder                       |                          |                             |                          |                              |
|       | Plasma water: surfactant: diethylene glycol = 87:5:8 | 3.505                    | 54.72                       | Better       | 16                           |
| No. 6 | binder                       |                          |                             |                          |                              |
|       | Plasma water: surfactant: diethylene glycol = 84:8:8 | 3.732                    | 55.35                       | Better       | 13                           |
|       | Reference                    |                          |                             |                          |                              |
|       |                              | 1-15                     | 25-60                       |              |                              |

As can be seen from Table 2, when the content of diethylene glycol remains unchanged, the surface tension of the mixed solution decreases with the increase of the surfactant content, but the decrease is not significant. At the same time, with the increase of viscosity, the bonding effect increases. The test results show that increasing the amount of surfactant can reduce the surface tension of the mixed solution and effectively improve the life of the nozzle, but the more the better. After reaching a certain amount, the surface tension will not always decrease, but will increase slightly. Increasing the content of surfactant also increases the viscosity value slightly, which can improve the printing quality.

In conclusion, according to the viscosity value, surface tension, the service life of the bond effect and the nozzle, NO.2 (5) formula. Namely, plasma water: surfactant PEG 400: diethylene glycol = 87:5:8, its viscosity value (room temperature) 3.505 mPa·s, surface tension 54.72 mN·m^{-1}, good bonding effect, the longest service life of the nozzle. Select this formula to print the following TC4 green part.

3. Preparation of porous titanium samples

3.1. Sample design

The model was drawn by software, and a cylinder with a diameter of 30mm and a height of 8mm was selected in consideration of the requirements of subsequent pressure pump test for porosity experiment. Considering the requirements of subsequent compressive strength experiments, a cylinder with a diameter of 10mm and a height of 10mm was selected for the model.

3.2. Sample preparation

![Printing process](a)  
![Green part](b)

**Figure 1.** The printing process and Green part.

The titanium alloy mixed powder and binder formula were prepared, and the 3d printing equipment was used for printing molding. Set the printing process parameters, spray the nozzle according to the coordinates.
generated by the part model, after the first layer of section printing, the powder supply warehouse rises, and scrape the powder rod to spread the material to the molding warehouse in the middle. This process is then repeated until the printing is complete and the piece is finished. The printing process and green part are shown in Fig.1.

3.3. Degreasing and sintering of porous titanium samples

The printed parts also need post-processing, degreasing and sintering are the most important steps. PVA and starch were first analyzed by DTG to determine sintering temperature [8].

The test conditions were as follows: Al₂O₃ crucible, the sample mass was 4.135 and 3.855 mg respectively, the atmosphere was air, the initial temperature was room temperature, the rate of warming was 10 K/min, and the termination temperature was 800 °C. The TG-DSC curves of the two kinds of binder powder materials were measured. As shown in Fig. 2, TG curve represents the relationship between the mass of the sample to be tested and the temperature change, while DSC curve represents the relationship between the energy difference between the sample to be tested and the reference object with the change of temperature.

![Figure 2. TG-DSC diagram of binder.](image)

According to the TG curve of PVA shown in Fig.2 (b), when the heating temperature reaches 110 °C, the mass of PVA decreases from the initial 100% to about 97%, and the weight loss rate is about 3%. The main reason is similar to starch, a small amount of water volatilization, corresponding to the DSC curve between 50 ~ 120 °C is not very obvious heat absorption peak. When the heating temperature is between 110 °C and 215 °C, the TG curve is relatively smooth and the weight loss rate is very small. At this time, condensation reaction mainly occurs in the side group of PVA. When the heating temperature is between 215 °C and 550 °C, the TG curve drops sharply, and the weight loss rate and weight loss rate increase simultaneously, indicating that the PVA molecular chain begins to break and decompose at this temperature, corresponding to the heat absorption peak around 490 °C in the DSC curve. After the heating temperature was 550 °C, TG curve almost did not decrease, indicating that PVA basically decomposed and volatilified.

Based on the above analysis, starch began to decompose at 260 °C, and volatilization ended at 550 °C. PVA began to decompose at 215 °C, and the decomposition also ended at 550 °C. Considering the effect of PVA and starch decomposition rate and efficiency in the billet, and the preliminary test shows that the part with the sintering temperature of 1100 °C has the best performance, the technical specification of debonding and sintering is formulated. Namely, the temperature was raised from room temperature to 150 °C in 75 min at
2°C/min for 1h, then the temperature was raised to 300°C in 75min at 2°C/min for 1h, then the temperature was raised to 600°C in 100min at 3°C/min, and the debonding was completed for 4h. The sintering process was increased to 1100°C at 1°C/min after 510min, holding temperature for 5h, and degreasing sintering was completed. Wait until the parts are cooled in the furnace to obtain 3DP 3d printing samples. The process curves of debonding and sintering are shown in Fig.3.

Figure 3. Degreasing and sintering curves.

4. Test and analysis of sample performance
The parts after degreasing and sintering are aged. The aging process was carried out with a box-type resistance furnace, the aging temperature was 550°C, and the treatment duration was 2 hours, 3 hours and 4 hours respectively.

4.1. Density and porosity tests
The micrometer is used to measure the diameter and height of the piece, then the volume is calculated. The mass M1 of the workpiece is measured with a balance, and the workpiece is immersed in water for a sufficient time so that the water can fully fill the pores. Take out the piece and measure its mass M2. The difference between the two masses is the mass of water, and we can figure out the volume of water. The density and porosity of the product can then be obtained from the given data. The data in Table 3 were obtained through three experiments for each workpiece with processing time. The data were the mean values obtained from the three measurements, and the relationship between density and porosity with the change of processing time was thus obtained, as shown in Fig.4.

Table 3. Density and porosity.

| Processing time (h) | Diameter (cm) | Height (cm) | Volume (cm³) | Quality M1 (g) | Quality M2 (g) | Density (g·cm⁻³) | Porosity (%) |
|--------------------|---------------|-------------|-------------|---------------|---------------|-----------------|--------------|
| 2h                 | 3.282         | 0.836       | 7.069       | 21.055        | 23.051        | 4.151           | 28.24        |
| 3h                 | 3.282         | 0.840       | 7.103       | 21.11         | 22.958        | 4.017           | 26.02        |
| 4h                 | 3.284         | 0.810       | 6.860       | 20.412        | 22.045        | 3.905           | 23.81        |

It can be seen from Fig. 4 (a) that with the extension of time, the density of the part will decrease. After 2h aging treatment, the density of the part is 4.154g·cm⁻³. At 4h, the density of the part is 3.905g·cm⁻³, and the density of the part decreases by 5.99%. It can be seen from Fig.4 (b) that with the extension of time, the
The porosity of the parts decreases as well. After 2h aging treatment, the porosity of the parts is 28.24%, while after 4h treatment, the porosity is 23.81%, with a decrease rate of 15.69%. Therefore, with the increase of processing time, the density and porosity of the parts decreased. 

![Diagram](image1)

(a) Dealing with the Time-Density relationship  
(b) Deal with the Time-Porosity relationship

**Figure 4.** Density and porosity are related to treatment time.

4.2. **Compressive strength test**

The compression experiment was carried out by Jinan Henruijin Testing Machine Co., LTD. WDW-100 universal testing machine in accordance with GB/T7314-2017 Room temperature Compression Test Method for Metal Materials. Sandpaper is applied to the samples to ensure the flatness of the upper and lower planes of the samples, and to avoid the uneven stress during the compression process of the samples leading to inaccurate fracture peaks. The required data are obtained through experiments with pieces of different lengths. The following data are the average values obtained after three measurements, as shown in Table 4.

| Time/h | Compressive strength $\sigma_{bc}$ (MPa) | Maximum stress (kN) |
|--------|----------------------------------------|---------------------|
| 2      | 735                                    | 57.849              |
| 3      | 700                                    | 55.105              |
| 4      | 690                                    | 54.097              |

According to the test data, the stress-strain curve (Fig.5) and the treatment time-compressive strength curve (Fig.6) are as follows:

![Diagram](image2)

It can be seen from Fig.5 and Fig.6 that the longer the aging treatment time is, the smaller the compressive strength of the parts will be. The compressive strength was 735MPa at 2h and 700MPa at 3h. The compressive strength decreased by 35MPa in one hour. From 3h to 4h, the compressive strength decreased from 700MPa to 690MPa, only 10MPa. Therefore, with the increase of aging treatment time, the compressive strength of the parts becomes smaller and smaller.
5. Conclusion
Based on Three-Dimensional Printing technology, the effect of different proportion of binder formula on the product performance was studied:

1) The surface tension, bonding effect and nozzle life of the adhesive were tested, and the optimal scheme was obtained for the preparation of porous titanium.

2) In order to improve the overall performance of the printed parts, the debinding sintering research was carried out to determine the sintering temperature.

3) After degreasing and sintering, the parts were aged for different periods at 550°C, and the performance test for different treatment hours showed that with the increase of treatment time, the density, porosity and compressive strength of the parts decreased.

Acknowledgments
This work was financially supported by Key University Science Research Project of Jiangsu Province (18KJA460006), Priority Discipline Construction Program of Jiangsu Province (2016-9), Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (2020-9), Key R&D plan of Jiangsu Province (BE2018010-4), Science and technology project of Gangzha District (GZKJ2018ZLK013), Science and technology project of Nantong (JCY19123, JC2018144).

References
[1] Chen Weiping, Lin Youxi, Huang Jie, et al. Analysis and Prospect of 3D printing development. Tool technology, 2019, pp. 10-14.
[2] Wang Yuqi. Research on the application and development of 3D printing technology, Modern manufacturing technology and equipment, 2019, pp. 138-139.
[3] Zhang Diyu, Yang Jianming, Huang Dazhi, et al. Development and research status of 3DP 3D printing technology, Manufacturing technology and machine tools, 2017, pp. 38-43
[4] Yang Jianming, Gu Hai, Chen Jinsong, et al. Study on water-based binder system for 3D printing of metal, Modern manufacturing engineering, 2019, pp. 36-40.
[5] Wang Pengcheng, Yang Bin, Li Qiao, Huang Yongcheng. Preparation technology and physical properties of metal materials based on 3DP, World nonferrous metals, 2017, pp. 285-286.
[6] Feng Chendong, Xia Yu, Li Xiang, Wang Chengtao. Microstructure and mechanical properties of 3D printed porous titanium scaffold, Medical biomechanics, 2017, pp. 256-260.
[7] Yang Jianming, Tang Yang, Chen Jinsong, et al. 3D printing of metal parts by 3DP method with light curing adhesive, Mechanical design and manufacturing, 2019, pp. 123-125 + 130.
[8] El-Hajje A, Kolos E C, Wang J K. Physical and mechanical characterisation of 3D-printed porous titanium for biomedical applications, Journal of Materials Science: Materials in Medicine, 2014, pp. 2471-2480.