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316L FFF binder development and debinding optimization

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Abstract

Fused Filament Fabrication (FFF) technology is used to create metal parts in this paper. A binder formula is developed for 316L stainless steel powder, composed of polypropylene (PP), styrene ethylene butylene styrene (SEBS) and paraffin wax (PW). The binder is mixed with the 316L stainless steel powder to produce mixture which is then extruded into filament. The optimum binder formula, PP:SEBS:PW = 5:2:2, is obtained by orthogonal experiment. After optimization, mixture viscosity is reduced, filament tensile strength is guaranteed, rigidity is improved. The filament can be printed by a desktop FFF printer to obtain green parts. Binder within the green parts can be sufficiently removed by solvent and thermal debinding, and the shape of printed parts can be maintained well. After sintering, shrunken 316L stainless steel parts can be created, some pores distributed inside. With finer metal powder, the relative density of sintered part can be increased to 96%. The research ideas of this paper can provide effective methods for the development and optimization of binder.

1. Introduction

Additive Manufacturing (AM) is also known as 3D Printing [1]. The main advantage of AM over traditional manufacturing processes is that it breaks through the complexity constraints of geometry and materials [2]. Fused Filament Fabrication (FFF) is currently the most widely used extrusion AM technology, using a variety of polymer filament materials, and in recent years has been gradually used in the manufacture of metal and ceramic components. When powders of more than 20 vol% are added into polymer to obtain high loading mixture, the interaction between powder particles cannot be ignored [3]. Mixtures with more than 45 vol% powder loading can be used to produce metal or ceramic components and have been proved by the PIM process [4, 5]. In this paper, the FFF technology, used to manufacture metal or ceramic components, is called FFF Plus technology.

FFF Plus consists of three main processes: printing, debinding and sintering, as shown in figure 1. The filament continues to melt and is squeezed out of the nozzle by the rear unmelted part. The molten thermoplastic material is extruded from the nozzle, deposited and solidified on the printing platform to form a two-dimensional printed layer. The second layer is deposited on top of the first layer, and the three-dimensional structure is obtained by repeatedly superimposed layer by layer. The 3D structure obtained in the printing stage is called green part. Solvent debond part is obtained after solvent debinding. Grey part is obtained after the total removal of polymer by thermal debinding, and then the final shrunken metal or ceramic component is obtained by sintering. There is no laser, powder or volatile matter in the whole printing process. The cost of the equipment is low and it is suitable for a variety of filament materials.

The binder formula is the core of FFF Plus, and improper selection will cause problems such as powder agglomeration, green part warping, and debinding difficulty [6, 7]. When in molten state, mixture of binder and powder should have good fluidity and formability, to ensure smooth extrusion and stable filament diameter. After repeated heating during mixing, extruding or printing, the molten mixture should still be able to flow through the printer nozzle without any blocking. Besides, it must have sufficient viscosity to adhere to the
platform. After cooled and solidified, the mixture should have sufficient strength and toughness to ensure filament winding/unwinding and green part shape maintaining. In order to reduce the thermal debinding time, part of the binder components should be removed during solvent debinding to obtain connected pores for subsequent thermal debinding. Finally, it is necessary to make sure the remained binder can be removed during thermal debinding and the grey part retain its original shape.

Binder components can generally be divided into three categories according to their purposes: (1) backbone material, accounting for 0–50 vol% of binder mixture, maintaining green part shape after solvent debinding; (2) solvent soluble material, accounting for 50–90 vol% of binder mixture; (3) additives, such as dispersant, compatilizer, stabilizer, promoting uniform and stable powder distribution in binder, accounting for 0–10 vol% of binder mixture \[8\]. Composition and dosage of the binder formula are often avoided in publications or patents. Actually, binder formulation for PIM is of great reference value to FFF Plus. The latter one has lower requirements on mixture fluidity and requires the mixture to solidify faster after cooling. Most binder formulations contain at least two components, as shown in table 1.

Solvent debinding can effectively promote the removal of binder, reduce or even eliminate bubbling and cracking that easily coming in thermal debinding or sintering process \[24\]. Solvent debinding effect is mainly determined by the solvent itself, temperature, and soaking time. In general, the higher the temperature is, the higher the debinding efficiency will be. While too fast solvent debinding often leads to the green part cracking. The removal sufficiency can be guaranteed by lowering the temperature but increasing the soaking time, and the crack tendency can be reduced at the same time.

Thermal debinding effect is mainly affected by heating strategy. The higher the temperature, the faster the binder decomposes. The heating rate needs to be controlled. If the temperature rises too fast, the thermal

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### Table 1. Examples of binder formulations.

| Backbone | Soluble binder | Additive | Application | Ref.  |
|----------|----------------|----------|-------------|-------|
| PE       | PW             | SA       | PIM         | [9]   |
| HDPE     | PW, EVA        | SA       | PIM         | [10]  |
| HDPE     | PW, MW         | SA       | PIM         | [11]  |
| PP       | PEG            | —        | PIM         | [12]  |
| PP       | PW             | SA       | PIM         | [13–15] |
| PP       | WAX            | Plasticizer, tackifier | FFF Plus | [16] |
| PP       | Elastomer, PW  | Plasticizer | FFF Plus    | [17] |
| PP       | TPE            | —        | FFF Plus    | [18]  |
| LDPE     | —              | —        | FFF Plus    | [19]  |
| gPO      | TPE            | —        | FFF Plus    | [20]  |
| EVA      | —              | SA       | FFF Plus    | [21]  |
| AA-HDPE  | PW, SEBS       | SA       | FFF Plus    | [22]  |
| PMMA     | Elvax450, PLA, PEG | SA | FFF Plus | [23] |

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*Figure 1. Schematic diagram of FFF Plus process and material morphology of each stage.*
decomposition will be too fast, so that the decomposed matter cannot escape through the tiny pores in time, which will lead to the bubbling and a large number of holes in the sintered parts [25].

The key factors affecting sintering are temperature, holding time and atmosphere [26, 27]. The general sintering temperature is 70%–90% of the melting point of the sintering material, the holding time is adjusted according to the actual sintering results, and the atmosphere is selected according to the material property. Stainless steel is usually sintered in argon, nitrogen, or hydrogen atmosphere [28].

FFF Plus is a new additive manufacturing method for metal and ceramic materials. Existing literature is often limited to the study of printing or debonding. Besides, the development of binder for 316L stainless steel is rarely reported, and the tensile strength of filament is relatively low, indicating that the binder needs to be modified [19]. This paper mainly focuses on binder formula development, taking into account the printing, debinding and sintering processes. First the coarse 316L stainless steel powder is used in formula optimization experiment, then the fine 316L stainless steel powder is used to conduct experiments concerning particle size and powder loading capacity. The research provides effective methods for development and optimization of binder for FFF Plus.

2. Materials and methods

2.1. Metal powder

The 316L stainless steel powder used in the experiment is supplied by HEBEI JINGYE GROUP, and its chemical composition is shown in table 2. The morphology and particle size distribution are shown in figure 2. The powder shape is approximately spherical. In the coarse powder, the number of particles with size less than 30.8 μm accounts for 50%. In the fine powder, the number of particles with size less than 10 μm accounts for more than 50%.

| Table 2. Chemical composition of 316L stainless steel (wt.%) |
|------------------|---|---|---|---|---|---|---|---|
| C | Si | S | P | Mn | Cr | Ni | Mo | Fe |
| 0.019 | 0.61 | 0.007 | 0.008 | 0.4 | 16.82 | 11.99 | 2.51 | Bal |

Figure 2. (a), (c) Morphology and (b), (d) diameter distribution of 316L stainless powder. (a), (b) coarse powder, (c), (d) fine powder.
2.2. Binder and selection criteria

The basic properties of binder components developed in this paper are shown in table 3. As backbone material, PP has high elastic modulus, high melting point, and low thermal expansion coefficient, which is conducive to the shape maintenance, after printing and solvent debinding. SEBS can improve the viscosity of the mixture and increase the dispersion stability of metal powder in binder. PW can improve the fluidity of the mixture, it has good wettability with 316L stainless steel powder, and is easy to be removed from the green part. SA can reduce the agglomeration of metal powder and improve the mixing efficiency.

Table 3. Binder composition and density of the components.

| Component | Chemical formula | Density (g cm\(^{-3}\)) | Provider    |
|-----------|-----------------|--------------------------|-------------|
| PP        | \([\text{CH}_2\text{CH}(\text{CH}_3)]_n\) | 0.92                     | ALADDIN     |
| SEBS      | —               | 0.91                     | KRATON      |
| PW        | \(C_n\text{H}_{2n+2}\) (20<n<240) | 0.9                      | PETRO CHINA |
| SA        | \(C_{18}H_{36}O_2\) | 0.87                     | PT. SUMI ASIH |

Figure 3. TG and DSC curves of binder components.

Figure 4. Schematic diagram of a torque mixer.

Table 4. Factors and levels of orthogonal experiments.

| Factor       | Level 1 | Level 2 | Level 3 |
|--------------|---------|---------|---------|
| \(V_{PP}\text{ (cm}^3\)) | 12.5    | 10      | 7.5     |
| \(V_{SEBS}\text{ (cm}^3\)) | 10      | 7.5     | 5       |
| \(V_{PW}\text{ (cm}^3\)) | 7.5     | 5       | 2.5     |
| \(V_{SA}\text{ (cm}^3\)) | 5       | 2.5     | 0       |

\(V_{PP}\): volume of PP; \(V_{SEBS}\): volume of SEBS; \(V_{PW}\): volume of PW; \(V_{SA}\): volume of SA

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The differential scanning calorimetry (DSC) and thermogravimetric (TG) curves of binder components are shown in figure 3. The temperature corresponding to the first endothermic peak of each component is the melting point of the component. It can be seen that the melting points of PP, PW and SA are 179 °C, 72 °C and 70 °C respectively. SEBS is a tri-embedded copolymer, and its melting point is not obvious. The mixing temperature should be greater than the melting point of each component in the binder, that is, at least above 179 °C. At the same time, in order to avoid the decomposition of components, the temperature should be as low as possible, so the mixing temperature is set as 180 °C. And according to the experiment, the SEBS has been melted at this temperature.

Considering the characteristics of PP, SEBS, PW and SA, three volume dosage levels are set for the four components. The factor-level table is shown as table 4. The orthogonal table L9(34) is used, shown as table 5.

| No. | V_{PP} (cm³) | V_{SEBS} (cm³) | V_{PW} (cm³) | V_{SA} (cm³) |
|-----|--------------|----------------|--------------|--------------|
| 1   | 12.5         | 10             | 7.5          | 5            |
| 2   | 10           | 7.5            | 5            | 5            |
| 3   | 7.5          | 5              | 2.5          | 5            |
| 4   | 7.5          | 7.5            | 7.5          | 2.5          |
| 5   | 10           | 10             | 2.5          | 2.5          |
| 6   | 12.5         | 5              | 5            | 2.5          |
| 7   | 12.5         | 7.5            | 2.5          | 0            |
| 8   | 10           | 5              | 7.5          | 0            |
| 9   | 7.5          | 10             | 5            | 0            |

*V_{PP}: volume of PP; V_{SEBS}: volume of SEBS; V_{PW}: volume of PW; V_{SA}: volume of SA

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Considering the characteristics of PP, SEBS, PW and SA, three volume dosage levels are set for the four components. The factor-level table is shown as table 4. The orthogonal table L9(34) is used, shown as table 5.

### 2.3. Preparation of mixture
Add 316L stainless steel powder and binder components into the mixer (HAAKE Rheomix OS), controlling the metal powder loading to be 50 vol%. The internal rotor rotates and stirs to disperse the metal powder in the binder, as demonstrated in figure 4. After the torque fluctuation is minimum, a uniform mixture is obtained. The specific operations are as follows: preheat the mixer up to 180 °C, set rotating speed at 60r min⁻¹, add 316L stainless steel powder and SA into the mixer, mixing for 5 min, add PP into the mixer, mixing for 5 min, add SEBS and PW into the mixer, mixing for 30–50 min. After mixing, the mixture is cooled to room temperature and cut into particles with a diameter of about 5 mm as the raw material for subsequent filament extrusion. The mixture viscosity is measured using a rotational rheometer (HAAKE Mars III) at 220 °C.

### 2.4. Filament production
The mixture is extruded into filament by a single screw extruder (Wellzoom). The filament is then wounded and collected by the spooling device after air cooling or water cooling, as shown in figure 5. Set the heating temperature at I in the middle section as 170 °C, the temperature at II near the exit as 165 °C, and the screw speed as 35r min⁻¹. To ensure the uniform distribution of metal powder, the cross section of the filament is observed by scanning electron microscope (SEM). The filament mechanical properties are tested by universal tensile testing machine.
2.5. Printing

A desktop 3D printer (WANHAO Duplicator 4S) is used to test the printability of the filament. The nozzle diameter is 0.8 mm, the nozzle temperature is set as 220 °C, the substrate temperature is set as 110 °C, the layer thickness is set as 0.1 mm, the printing speed is set as 10 mm s\(^{-1}\). The printing continuity, bonding between printed layers, bonding between first printed layer and the substrate, are observed. SEM is used to observe the micromorphology of the green part.

2.6. Solvent debinding

As shown in figure 6, in order to remove part of the binder to get connected pores, the printed green part is placed back up on the wire mesh and immersed in cyclohexane at 70 °C/60 °C for solvent debinding. After 6 h/18 h, the solvent debond part is taken out, dried and weighed. The removal extent of soluble binder components is evaluated by weight loss percentage. SEM is used to observe the micromorphology of the solvent debond part.

Table 6. Binder composition of orthogonal experiments.

| No. | \(V_{PP}/V_b\) | \(V_{SEBS}/V_b\) | \(V_{PW}/V_b\) | \(V_{SA}/V_b\) | \(V_{S}/V_b\) |
|-----|----------------|----------------|----------------|--------------|--------------|
| 1   | 0.36           | 0.29           | 0.21           | 0.14         | 0.64         |
| 2   | 0.36           | 0.27           | 0.18           | 0.18         | 0.63         |
| 3   | 0.38           | 0.25           | 0.13           | 0.25         | 0.63         |
| 4   | 0.30           | 0.30           | 0.30           | 0.10         | 0.7          |
| 5   | 0.40           | 0.40           | 0.10           | 0.10         | 0.6          |
| 6   | 0.50           | 0.20           | 0.20           | 0.10         | 0.5          |
| 7   | 0.56           | 0.33           | 0.11           | 0.00         | 0.44         |
| 8   | 0.44           | 0.22           | 0.33           | 0.00         | 0.55         |
| 9   | 0.33           | 0.44           | 0.22           | 0.00         | 0.66         |

\(V_{PP}\): volume of PP; \(V_{SEBS}\): volume of SEBS; \(V_{PW}\): volume of PW; \(V_{SA}\): volume of SA; \(V_{S}\): volume of soluble binder components; \(V_b\): volume of binder

Figure 6. Schematic diagram of solvent debinding.

Figure 7. Viscosity diagram of the mixtures at different shear rates.
2.7. Thermal debinding and sintering
The thermal debinding temperature is determined by TG and DSC tests. Thermal debinding and sintering are performed in a tubular furnace. The atmosphere in the furnace is 2.5 vol% hydrogen – 97.5 vol% argon mixture/pure hydrogen. SEM is used to observe the micromorphology of the grey part. The density of sintered part is measured by Archimedes drainage method and metallographic structure is observed with optical microscope.

3. Results and discussion

3.1. Evaluation of the mixtures
Except PP, the other components in the binder are soluble in cyclohexane [29, 30]. The calculated volume fraction of each component in the binder and the volume fraction of soluble components are shown in table 6.

The internal friction of a material against flow in the molten state, as well as the conversion of mechanical energy to thermal energy, is expressed in terms of viscosity, which reflects the fluidity of the material [31].
smaller the viscosity, the better the fluidity. The viscosity of the 9 groups of molten mixtures is shown in figure 7. When the shear rate is within the range of 0.1/s-100/s, the mixture viscosity decreases with the increase of shear rate, that is, the mixture has the characteristic of shear thinning [32]. No.5 mixture has the highest viscosity and No.8 mixture has the lowest viscosity, which is directly affected by the dosage of SEBS and PW. The shear thinning effect of No.9 mixture is the most obvious, because the dosage percentage of SEBS in this binder formula is the largest, which naturally reflects the characteristics of SEBS.

3.2. Evaluation of the filaments

The 9 rolls of filaments extruded from the 9 groups of mixtures all have smooth surfaces and can be spooled/unspooled at room temperature, as shown in figure 8(a). The spring has been adjusted before printing to make the FFF printer suitable for the feeding of the newly developed filament. After feeding and withdrawing, the rollers leave an imprint on the filament. And the filament stiffness is evaluated by the ratio of the imprinted section’s thickness to the original filament diameter. As illustrated in figure 8(b), the diameter is measured at section d, the thickness is measured at section h. The softening deformation at section ha is large due to heat affect, and it is not in the measurement range. The measurement results are shown in table 7.

The stress-strain curves of 9 rolls of filaments are shown in figure 9. No.5 filament has superior elongation due to higher dosage percentage of SEBS and lower dosage percentage of PW. No.6, 7, 8 filaments have greater stiffness and strength due to higher dosage percentage of PP. While No.2, 3 filaments have the lowest tensile strength, due to the high dosage percentage of SA.

3.3. Evaluation of printing performance

Figure 10(a) shows the print adhesion of the initial two layers. The viscosity of No.5 mixture is too high, so it is difficult to be extruded from the nozzle during printing. At the same time, this mixture tends to stick to the outside of the nozzle, causing the inadhesion to the platform. Figure 10(b) shows the morphology of solvent debond parts, having been immersed in cyclohexane for 6 h at 70 °C. No.8 mixture contains the highest dosage percentage of PW, No.9 mixture contains the highest dosage percentage of SEBS, all leading to poor formability. No.7 mixture can keep the green part shape perfectly, due to the highest dosage percentage of PP. Because of the low strength, No.2, 3 filaments cannot be stably extruded out of the nozzle during printing, so that there are many conspicuous pores in No.2, 3 parts.
3.4. Evaluation of solvent debinding
After solvent debinding, the weight loss of the green part is shown in table 8. The soluble binder in No.9 green part has not been completely removed, due to the high dosage percentage of SEBS. It can also be seen from figure 10(b) that there is obvious wire mesh imprint on the surface of No.9 solvent debond part, indicating the insufficient shape retention. For the other parts, the soluble binder is considered to have been removed completely, and small amount of metal powder has fallen off at the same time. Taking No.6 binder formula as an example, there is 25 vol% pore in the solvent debond part, that is, the PP decomposition products can escape outside the part through the massive connected pores, during thermal debinding.

3.5. Evaluation of thermal debinding and sintering
According to figure 11(a), TG curve and DSC curve of 9 groups of mixtures have the same overall trends. The thermal decomposition mainly occurs in two stages, the first one occurs at 220 °C-350 °C, the second one occurs at 350 °C-480 °C. The first stage decomposition of No.7 mixture is not obvious for the low dosage of PW and SA. The mixture absorbs heat from the initial heating moment. The heat absorption increases first and then decreases. After the weight keeping stable, the mixture no longer absorbs heat. The heating strategies for thermal debinding and sintering are designed according to DSC-TG curves. The strategy 1 is selected, as shown in the red curve in figure 11(b). The solvent debond parts are kept at 370 °C for 1 h and 440 °C for 2 h to fully remove the residual binder. Then the grey parts are sintered at 1350 °C for 4 h. The sintered parts are shown in figure 10(c). All the 8 printed parts can be sintered successfully, shrinking to some extent, without bubbling or cracking. It is worth noticing that the surface of the parts sintered in 2.5 vol% hydrogen−97.5 vol% argon mixture atmosphere turns green, and their shrinkage is limited, shown as No.1, 2, 6, 7, 8, 9 in figure 10(c). This is because the reducibility of the mixed gas is not enough and the presence of oxides Cr₂O₃ hinders the densification of the sintered parts [33].

3.6. Component dosage optimization
Since all the printed parts can be sintered, and the viscosity is the decisive factor of whether the printing can be done, and the filament must have enough strength to ensure the printing continuity, the mixture viscosity and filament strength are then taken as the measurement indexes to optimize the binder formula using intuitive analysis method, which is the most commonly used analysis method in orthogonal experiment. K(L n) of Factor m is the sum of measurement index corresponding to Level n of Factor m. R of Factor m is the range of K(L n) corresponding to Factor m. The smaller the R value of Factor m is, the smaller the influence of the level change of this factor on the test results is. Therefore, the order of influence degree of each factor can be determined according to the R value.

During printing process, the filament is heated and melted in the nozzle and extruded by the rear unmelted filament, as illustrated in figure 1. The shear rate of the molten mixture can be calculated by equation (1):

\[ \gamma = \frac{2d^2}{15D^3} V \]  

(1)

where, \( d \) is the diameter of the filament, \( D \) is the diameter of the nozzle, \( V \) is the filament feeding speed.
It is considered that the molten mixture is an incompressible fluid, then:

$$V = \frac{D^2}{6} \frac{U}{d^2}$$  \hspace{1cm} (2)

where, $U$ is the printing speed, then:

$$\gamma = \frac{2U}{15D}$$  \hspace{1cm} (3)

Therefore, when the printing speed is 10–100 mm s$^{-1}$, the shear rate is about 1.7–17 s$^{-1}$. Viscosity of 9 groups of mixtures at the shear rate of 9.2 s$^{-1}$ is taken as index, as shown in table 9, to conduct intuitive analysis. The values of $K$ and $R$ are shown in table 10. Since the measurement index is viscosity, the level corresponding to the minimum $K$ value is the optimal level. When PP is at level 3, SEBS is at level 3, PW is at level 2, and SA is at level 3, the viscosity is the lowest. It can be seen from the $R$ value that SA dosage has the greatest influence on mixture viscosity. The viscosity index analysis results are shown in table 13.

The tensile strength of the filament is shown in table 11. The values of $K$ and $R$ are shown in table 12. Since the measurement index is tensile strength, the level corresponding to the maximum $K$ value is the optimal level. When PP is at level 1, SEBS is at level 2, PW is at level 1, and SA is at level 3, the tensile strength is the highest. It can be seen from the $R$ value that SA dosage has the greatest influence on filament tensile strength. The tensile strength index analysis results are shown in table 13.

The optimal component dosage levels obtained by the two measurement indexes separately are inconsistent, so it should be considered comprehensively according to the influence of the two factors. The influence of PP dosage on the filament tensile strength is greater than that on the mixture viscosity, so PP(L1) is the most suitable for the comprehensive performance. The influence of SEBS dosage on the mixture viscosity is greater than that on the filament tensile strength, so SEBS(L3) is the most suitable for the comprehensive performance. Similarly, the influence of PW dosage on the mixture viscosity is greater than that on the filament tensile strength, so PW(L2) is the most suitable for the comprehensive performance. The filament tensile strength and the mixture viscosity is most affected by SA dosage, and the optimal levels of which obtained by the two single factor analyses above is the same, so SA(L3) is the most suitable for the comprehensive performance. In summary, the optimal component dosage is PP(12.5 ml)-SEBS(5 ml)-PW(5 ml)-SA(0 ml), that is, the optimum volume ratio of the binder components is $\nu_{PP} : \nu_{SEBS} : \nu_{PW} = 5:2:2$. 

### Table 9. Viscosity of the mixtures ($\gamma = 9.2$ s$^{-1}$).

| No. | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|-----|------|------|------|------|------|------|------|------|------|
| Viscosity/(Pa.s) | 9043.96 | 5675.60 | 4977.83 | 12991.86 | 23011.95 | 9173.01 | 8609.57 | 3385.28 | 4997.85 |

### Table 10. $K$ and $R$ of the factor-level tests, mixture viscosity as measurement index.

| Factor | PP  | SEBS | PW  | SA  |
|--------|-----|------|-----|-----|
| K(L1)  | 26826.54 | 37053.76 | 25421.1 | 19697.39 |
| K(L2)  | 32072.83 | 27277.03 | 19846.46 | 45176.82 |
| K(L3)  | 22967.54 | 17536.12 | 36599.35 | 16992.7 |
| R      | 9105.29 | 19517.64 | 16752.89 | 28184.12 |

### Table 11. Tensile strength of the filaments.

| No. | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|-----|------|------|------|------|------|------|------|------|------|
| Stress/MPa | 1.90 | 1.67 | 1.34 | 2.31 | 1.96 | 2.58 | 3.65 | 2.92 | 2.41 |

### Table 12. $K$ and $R$ of the factor-level tests, filament tensile strength as measurement index.

| Factor | PP  | SEBS | PW  | SA  |
|--------|-----|------|-----|-----|
| K(L1)  | 8.13 | 6.27 | 7.13 | 4.91 |
| K(L2)  | 6.55 | 7.63 | 6.66 | 6.85 |
| K(L3)  | 6.06 | 6.84 | 6.95 | 8.98 |
| R      | 2.07 | 1.36 | 0.47 | 4.07 |
3.7. Performance verification

The mixture is prepared according to the optimum binder formula, which is then extruded into filament. Since coarse powder is used, and the powder loading is 50 vol%, the mixture is marked as L50. The viscosity of L50 is tested, and the result is shown as curve O in figure 7. The filament tensile test result is shown as curve O in figure 12.

**Figure 12.** (a) Image of green parts after binder optimization and SEM images of (b) green part, (c) solvent debound part, (d) thermal debound part.

**Table 13.** Single-index analysis results and the corresponding suitable composition.

| Index             | Order of influence degree | Suitable composition                  |
|-------------------|---------------------------|---------------------------------------|
| Viscosity         | SA > SEBS > PW > PP       | PP(L3)-SEBS(L3)-PW(L2)-SA(L3)         |
| Tensile strength  | SA > PP > SEBS > PW       | PP(L1)-SEBS(L2)-PW(L1)-SA(L3)         |

**Figure 13.** Diagram of torque variation during compound mixing.
The TG-DSC test results are shown as curves TG and DSC in Figure 11(a). Obviously, the molten mixture viscosity is reduced significantly. The filament rigidity is enhanced. The TG curve of L50 looks like that of PP. The green parts printed with the L50 filament have clear outline, and do not contain any pores, as shown in Figure 12(a). The microscopic morphology of the green part is shown in Figure 12(b). The 316L stainless steel powder particles are wrapped by binder and uniformly dispersed in the mixture. Figure 12(c) shows the microscopic morphology of the cross section of the solvent debond part after having been immersed in cyclohexane for 6 h at 70 °C. It can be seen that due to the removal of a large amount of soluble binder, pore network has been formed inside the part, which provides conditions for the coming thermal debinding.

After thermal debinding in hydrogen atmosphere, the grey part then is heated to 850 °C, holding for 30 min, the microscopic morphology of which is shown in Figure 12(d). The binder has been totally removed, and the sintering neck has been formed between the particles, which is strong enough to maintain the original part shape.

3.8. Influence of particle size and powder loading

With the same optimum binder formula, it is found that the maximum loading capacity of coarse powder can only reach 50 vol%, and that of fine powder can reach 60 vol%. Further addition of 316L stainless steel powder will cause the filament to break easily. After mixing for a period of time, the torque fluctuation gradually decreases, as shown in Figure 13, indicating that the metal powder and binder have been fully mixed. The reason why the torque value still tends to decrease is that after mixing for a long enough time, the mixture and the rotor
will slip, and the effect of continuing mixing is limited. Obviously, the torque of fine powder mixture is greater than that of coarse powder mixture, and the higher the powder loading, the greater the torque. The reason is that fine powder has a larger specific surface area and can cohere to the binder more firmly\cite{34}. The higher the powder loading, the greater the friction inside the mixture, which is manifested as the greater torque.

* L50: coarse powder mixture with loading of 50 vol%; S50: fine powder mixture with loading of 50 vol%; S55: fine powder mixture with loading of 55 vol%; S60: fine powder mixture with loading of 60 vol%.

Scanning analysis of iron and chromium elements on the section of S50 filament is carried out, and the results are shown in figure 14. Fine metal powder particles have been evenly mixed in the binder. Thermal debinding and sintering are performed using heating strategy 1 in figure 11 (b). The L50 part can be successfully sintered, as shown in figure 15. However, there are numerous holes in the S50 part, because the binder has not been sufficiently removed. It is difficult to debind fine powder mixture and the solvent debinding time needs to be extended. Some cracks are found on the side of the S50 solvent debond part, after solvent debinding for 12 h at 70 °C. So the solvent debinding temperature is set as 60 °C, and the duration time is set as 18 h.

Different heating strategies are selected to conduct thermal debinding and sintering on S50 parts, as shown in figure 15. It can be seen that heating strategy 4 is the most suitable one for S50, and there are the least bubbles and holes on the sintered part’s surface. Using the same strategy, there is only a slight bulge on the surface of S55 sintered part, without any visible bubbles or holes, and the S60 part can be perfectly sintered. The reason is that, the higher the powder loading, the less binder volume percentage in the green part, and the easier to totally remove the binder during thermal debinding.

The linear shrinkage along length direction and the density of the sintered parts are shown in table 14. It can be seen that the shrinkage of fine powder part is greater than that of coarse powder part, and the higher the

### Table 14. Linear shrinkage and density of block samples.

| No. | Lg  | Lsol | Lsin  | Lsol/Lg | Lsin/Lg | Rho/(g cm\(^{-3}\)) | Relative density |
|-----|-----|------|-------|---------|---------|---------------------|-----------------|
| L50 | 17.64 | 17.41 | 15.28 | 0.99    | 0.87    | 5.958               | 0.75            |
| S50 | 17.25 | 17.3  | 14.5  | 1.00    | 0.84    | 7.135               | 0.90            |
| S55 | 17.58 | 17.58 | 14.97 | 1.00    | 0.85    | 7.534               | 0.95            |
| S60 | 17.42 | 17.65 | 15.02 | 1.01    | 0.86    | 7.632               | 0.96            |

* Lg: length of green part; Lsol: length of solvent debond part; Lsin: length of sintered part.

![Figure 16. Metallographic structure of (a)L50, (b)S50, (c)S55, (d)S60, all sintered at 1350 °C for 4 h.](image-url)
powder loading is, the higher the sintered part’s density will be. The full density of 316L stainless steel is 7.93 g cm\(^{-3}\) [28], so the highest relative density of the sintered parts is 0.96. Besides, it is noted that the size change during solvent debinding is not obvious, therefore the initial green part shape can be maintained well.

The metallographic structure of the sintered parts is shown in figure 16. Due to the large particle size of the powder, the huge gap between the powder particles in L50 part could not be effectively removed by diffusion in the sintering stage, so there are a lot of pores remained. It is difficult to remove the binder in S50 part, and the residual binder swells and decomposes rapidly in the later heating stage, resulting in bubbles and large holes. Because the powder loading of S55 and S60 is increased, the binder volume percentage is relatively reduced, so it is easier for debinding. In particular, there are no large pores in the microstructure of S60, and the remained pores can be further removed to a certain extent by optimizing sintering process. This paper mainly focuses on the development of binder, the sintering process will not be discussed further.

4. Conclusions

In this paper, a new additive manufacturing method for 316L stainless steel powder was studied. The binder formulation is developed and optimized based on the whole process procedure. The conclusions are as follows:

Both the mixture viscosity and the filament tensile strength is most affected by SA dosage percentage. Without adding SA, the 316L stainless steel powder can still disperse evenly in the binder. The volume ratio of each binder component in the optimal formula is PP:SEBS:PW = 5:2:2. The viscosity of the molten mixture prepared according to the optimum formula is significantly reduced, compared with the orthogonal experiment result. The rigidity of filament extruded from the optimal mixture is improved, and the filament tensile strength can meet the requirement for spooling/unspooling at room temperature. With a desktop FFF printer, the filament can be printed into green parts easily.

With the same optimum binder, the maximum loading capacity of coarse powder can reach 50 vol%, and that of fine powder can reach 60 vol%. Compared with the coarse powder, it is more difficult to debind the fine powder mixture. But when the powder loading is higher, the difficulty of binder removal is reduced.

The S60 green part is immersed in cyclohexane for 18 h at 60 °C to sufficiently remove the soluble binder. Taking heating strategy 4, the S60 solvent debond part is kept at 370 °C for 4 h and 420 °C for 4 h to fully remove the residual binder. The S60 grey part is sintered at 1350 °C for 4 h in pure hydrogen. Finally, the sintered 316L stainless steel part with 96% relative density is obtained, containing no bubble or cracking.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

X F Kan was in charge of the whole experiments, and wrote the initial manuscript; D C Yang assisted with analyses; Z Z Zhao revised the manuscript; J Q Sun revised the final manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Gibson I, Rosen D and Stucker B 2015 Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing 2nd edn (New York: Springer)
[2] Hegah H A 2016 Design for additive manufacturing of composite materials and potential alloys: a review Manuf. Rev. 311
[3] Gonzalez-Gutierrez J, Duretek I, Kukla C, Poljsak A, Bek M, Emri I and Holzer C 2016 Models to predict the viscosity of metal injection molding feedstock materials as function of their formulation Metals 6 129
[4] German R M (ed) 1994 Powder Metallurgy Science Metal Powder Industries Federation 2nd edn (New Jersey: Princeton)
[5] German R M 2012 Metal powder injection molding (MIM): key trends and markets Handbook of Metal Injection Molding ed D F Heaney (Philadelphia: Woodhead Publishing) 1–25
[6] Tseng W J and Hsu C K 1999 Cracking defect and porosity evolution during thermal debinding in ceramic injection moldings Ceram. Int. 25 461–6
[7] Shivashankar T S, Enneti R K, Park S J, German B M and Atre S V 2013 The effects of material attributes on powder–binder separation phenomena in powder injection molding Powder Technol. 243 79–84
[8] Gonzalez-Gutierrez J, Cano S, Schuschnig S, Kukla C, Sakpota J and Holzer C 2018 Additive manufacturing of metallic and ceramic components by the material extrusion of highly-filled polymers: a review and future perspectives Materials 11 840
[9] Huang R, Rassi E, Kim M, Jo K, Lee S, Morscher G N and Choi J 2021 Material extrusion and sintering of binder-coated zirconia: comprehensive characterizations Additive Manufacturing 45 102073
[10] Cheng J, Wan L, Cai Y, Zhu J, Song P and Dong J 2010 Fabrication of w–20wt.%Cu alloys by powder injection molding J. Mater. Process. Technol. 210 137–42
[11] Ye Y, Qiao L, Zheng J, Ying Y, Li W, Yu J, Che S and Jiang J 2017 Effect of microcrystalline wax on the solvent debinding of the Sr-ferrite ceramics prepared by powder injection molding Eur. Ceram. Soc. 37 2105–14
[12] Lee S H and Jeung W Y 2001 Anisotropic injection molding of strontium ferrite powder using a PP/PEG binder system Journal of Magnetics & Magnetic Materials 226 1400–2
[13] Hwang K S and Hsieh Y M 1996 Comparative study of pore structure evolution during solvent and thermal debinding of powder injection molded parts Metallurgical & Materials Transactions A 27 245–53
[14] Sahli M, Lebied A, Gelin J–C, Barriere T and Necib B 2015 Numerical simulation and experimental analysis of solid-state sintering response of 316L stainless steel micro–parts manufactured by metal injection molding Int. J. Adv. Manuf. Technol. 79 2079–92
[15] Shen T, Xiong H, Li Z, Zhang L and Zhou K 2021 Fused deposition fabrication of high-quality zirconia ceramics using granular feedstock Ceram. Int. 47 34352–60
[16] Kalita S J, Rose S, Hosick H L and Bandypadhyay A 2003 Development of controlled porosity polymer–ceramic composite scaffolds via fused deposition modeling Materials Science & Engineering C 23 611–20
[17] Bandypadhyay A, Das K, Marusich I and Onagorowa S 2006 Application of fused deposition in microstructure metal-ceramic composites Rapid Prototyping Journal 12 121–8
[18] Lengauer W et al 2019 Fabrication and properties of extrusion-based 3D-printed hardmetal and cermet components Int. J. Refract. Met. Hard Mater 82 141–9
[19] Sadaf M, Bragaglia M and Nanni F 2021 A simple route for additive manufacturing of 316L stainless steel via Fused Filament Fabrication J. Manuf. Processes 67 141–50
[20] Gonzalez G J, Cano S, Ecker J, Kitmantel M, Arbeiter F, Kukla C and Holzer C 2021 Bending properties of lightweight copper specimens with different infill patterns produced by material extrusion additive manufacturing, solvent debinding and sintering Applied Sciences 11 7262
[21] Hadian A, Koch L, Koberg P, Sarraf F, Liersch A, Sebastian T and Clemens F 2021 Material extrusion based additive manufacturing of large zirconia structures using filaments with ethylene vinyl acetate based binder composition Additive Manufacturing 47 10227
[22] Cano S, Gonzalez-Gutierrez J, Sakpota J, Speerck M and Kukla C 2019 Additive manufacturing of zirconia parts by fused filament fabrication and solvent debinding: selection of binder formulation Additive Manufacturing 26 117–28
[23] Barmore B 2017 Fused Filament Fabrication of Filled Polymers for Metal Additive Manufacturing, (Oregon State University)
[24] Fan Y L, Hwang K S, Wu S H and Liao Y C 2009 Minimum amount of binder removal required during solvent debinding of powder-injection-molded compacts Metall. Mater. Trans. A 40 768–79
[25] Thompson Y, Gonzalez-Gutierrez J, Kukla C and Feller P 2019 Fused filament fabrication, debinding and sintering as a low cost additive manufacturing method of 316L stainless steel Additive Manufacturing 30 100861
[26] Chasougou L, Hryha E and Nyborg L 2013 Effect of process parameters on surface oxides on chromium–alloyed steel powder during sintering Mater. Chem. Phys. 138 405–15
[27] Oumar M A and Subuki I 1988 Sintering characteristics of injection moulded 316L component using palm-based biopolymer binder Sintering – Methods and Products ed V Shatokha (Rijeka: Intech Europe) pp 127
[28] Do T, Bauder T J, Suen H, Rego K, Yeom J and Kwon P 2018 Additively Manufactured Full-Density Stainless Steel 316L With Binder Jet Printing, Proc. of the ASME 2018 13th Int. Conference on Metal Forming Science and Engineering Conf., Texas (https://doi.org/10.1115/ MSEC2018–6681)
[29] Zaky M T, Soliman F S and Farag A S 2009 Influence of paraffin wax characteristics on the formulation of wax-based binders and their debinding from green molded parts using two comparative techniques J. Mater. Process. Technol. 209 5981–9
[30] Ovejero G, Pérez P, Romero M D, Díaz I and Díez E 2009 SEBS triblock copolymer–solvent interaction parameters from inverse gas chromatography measurements Eur. Polym. J. 45 589–94
[31] Strivens T A 1999 14 – an introduction to rheology Woodhead Publishing Series in Metals and Surface Engineering, Paint and Surface Coatings ed R Lambourne and T A Strivens 2nd (Woodhead Publishing) 350–74
[32] Ahn S, Park S J, Lee S, Atre S V and German R M 2009 Effect of powders and binders on material properties and molding parameters in iron and stainless steel powder injection molding process Powder Technol. 193 162–9
[33] Ohmi T 1996 Formation of chromium oxide on 316L austenitic stainless steel Journal of Vacuum Science & Technology A Vacuum Surfaces & Films 14 2505–10
[34] Fu S Y, Feng X Q, Lauke B and Mai Y W 2008 Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites Composites Part B: Engineering 39 933–61