Identification of debinding behaviours for 316L stainless steel feedstocks during thermal debinding stage

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Abstract :

During the preparation of 316L stainless steel feedstock, binders are often added to increase the strength of the green part. The binders need to be removed prior to densification of the stainless steel components. In this paper, a thermal debinding has been set up and carried out under nitrogen atmosphere by subjecting the feedstocks to heating cycles. The 5 µm 316L stainless steel feedstocks, by increasing powder volume loadings from 60 to 64 %, are studied and compared to each others. The feedstocks are heated up to 500°C in a thermo gravimetric analyser at different heating rates varying from 2 to 10°C/min. The weight binder loss is recorded with respect to temperature. A kinetic model assuming a first order reaction rate is used to set up the present experimental results.

Key words: 316L stainless steel, binders, thermal debinding, thermo gravimetric analyser, kinetic model.

Résumé :

Pendant la préparation des mélanges polymères-poudres d'acier inoxydable 316L, destinés au moulage par injection de poudres, des liants sont souvent ajoutés pour augmenter la résistance et la cohésion du composant injecté. Ces liants doivent être éliminés juste avant l'étape de densification par diffusion solide des composants en acier inoxydable. Dans cette étude un déliantage thermique sous une atmosphère d'argon a été réalisé avec différents mélanges et pour différentes cinétiques. Les mélanges de poudres 316L de granulométrie 5 µm ont été élaborés avec différents taux de charge correspondant respectivement à 60, 62 et 64%, puis testés et identifiés. Ils sont testés jusqu' à 500°C dans un analyseur thermo gravimétrique pour différentes cinétiques de chauffage correspondant à 2,5 et 10°C/min. La perte du liant éliminé est enregistrée en fonction de la température. Un modèle cinétique, prenant en compte une réaction de premier ordre, est utilisé afin de vérifier les résultats expérimentaux obtenus.

Mots clés: Acier inoxydable 316L, polymères, déliantage thermique, analyseur thermo-gravimétrique, modèle cinétique.

1 Introduction

During the last recent years, 316L stainless steel powders are commonly used in Powder Injection Molding (PIM). These powders are largely used associated to their capabilities to be sintered to high density [1]. Powder injection molding (PIM) is a cost effective processing technology with high volume production for small, complex and accurate parts. The process is a combination of conventional powder technology and plastic injection molding. The technology is commonly named as metal injection molding (MIM) or ceramic injection molding (CIM), depending on whether metal or ceramic powders are used. The PIM process includes mixing of either metallic or ceramic powders with a binder to elaborate a feedstock, injection molding to form a green part with the required shape by pushing the feedstock to flow into and fill a mold cavity under pressure, debinding to form a brown part by removing the binder components and then solid state sintering by diffusion to get near full density [2].

In PIM, the debinding stage is a critical step for forming a desired shape. This step requires two main specific characteristics for the binder system used. The first one is to provide an easy flow of the particles into the die cavity during molding, wax polymers which generally have low viscosity meet well this demand;

the second one is to avoid separation between powders and polymers during the preparation of feedstock and molding, and pure waxes are not sufficient with this respect. For this reason, most of binder systems contain at least two components; the added polymeric components lead to increase the viscosity in order to hold the component shape after cooling time [3]. Consequently, polypropylene has been used as the first binder component system to keep the component shape after injection molding and debinding. The second binder component system is a wax that improves the flowability of the mixture and that can be removed in early stages of debinding leaving open pores that allow the gaseous products of the remaining polymer to diffuse out of the structure, the additive surfactant stearic acid has been added to facilitate powder wetting by lowering the surface energy of the binder-powder interface. At the end of debinding stage, the binder has to be fully decomposed before sintering with low ash content. For processing the binder must be inexpensive and environmental friendly [4]. In general, the kinetic models proposed for the kinetics of polymeric materials thermal decomposition are in principle based on consideration of the variation in the mass amount of the material in a time function, so a kinetic model assuming a first order reaction rate will be used to build a physical model and to set up numerical simulations of the debinding cycle. This study is designed to investigate thermal stability of the 316L stainless steel compounds by means of simultaneous thermal thermogravimetry differential analysis (TG-DTA).

2 Experiments and methodologies

2.1 Powders and binders characteristics

The metallic powders used in this analysis are composed of gas atomized spherical Stainless 316L steel powder with a density equals 7.9 g/cm^3 [5].The physical properties and chemical composition of the powders are related in table 1. Fig.1 exhibits a scanning electron microscope (SEM) of the powders. One can notice in Fig.1 that most particles are mainly spherical or elliptical, which is well appropriated for injection molding. A binder system based on paraffin wax has been prepared. The minor component is polypropylene. The characteristics of the binder components are summarised in table 2. The stainless steel powders mixture has been then mixed with the binder for the different powder loadings at 160°C during 30 minutes.

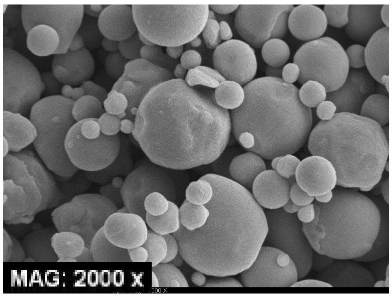

FIG. 1 – SEM photograph of 316L stainless steel powders (D_{50}=3.4 µm) used in the proposed investigations.

TAB. 1 – Physical and chemical properties of the 316L stainless steel powders.

	D_{10} [µm]			D_{50} [µm]	D_{90} [µm]		Density [g.cm^{-3}]		
316L Stainless 5 µm	1.8			3.4	6.0		7.9		
Element	C_r	Ni	Mo	Mn	Si	C	P	S	Fe
Content (%)	17.4	10.4	2.5	1.2	1.64	0.021	0.015	0.006	Bal

TAB. 2 – Characteristics of the polymer ingredients used for the binder system.

Binder components	Density [g.cm^{-3}]	W (%)	Decomposition range (°C)
Paraffin Wax (PW)	0.91	22	180 to 320
Polypropylene (PP)	0.95	16	420 to 480
Stearic Acid (SA)	0.89	2	220 to 320

2.2 Feedstock thermal decomposition measurements

The debinding process was carried out with thermal debinding using thermogravimetry (TG) and differential thermal analysis (DTG). All the tests were carried out using a model TGA thermogravimetric analyser (©Setaram) with temperature range from 25 to 500°C with heating rates corresponding to 2, 5 and 10°C/min, under dynamic nitrogen atmosphere (20 mL/min). Sample masses were about 100 mg and each sample was heated in Platinum crucibles. TG gives the variation of the weight binder loss (percentage) against temperature and DTG is employed to obtain the derivative curve peaks in order to identify the exact temperature for which one get a complete decomposition.

3 Results and discussion

3.1 Characterisation of thermal debinding behaviour of 316L stainless

The TGA of feedstocks help to design the thermal debinding cycles. Figure 2 shows the weight binder loss–temperature plots corresponding to three different heating rates for 316L stainless steel feedstock with powder volume loading 60%. The TGA curves exhibit two stages, corresponding to the thermal decomposition of low-molecular-weight binder components (PW+ SA) and high-molecular-weight binder components (PP). As shown in figure 2, for the different heating rates one has quite the same removed binder quantity (80% of the initial binder weight has been removed). Each stage is described by two kinetic parameters in an Arrhenius-type equation (1). These parameters are activation energy (E) and preexponential factor (A).

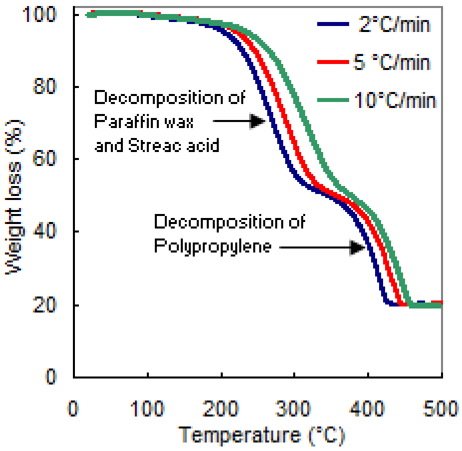

FIG. 2 – Weight binder loss vs. temperature with powder volume loading equals to 60%.

The apparent activation energy (*E*) needs to be determined. The activation energy for polymer decomposition can be determined from DTG curve data using both methods developed by Ozawa [6] and Kissinger [7] based on the temperature $T_{\max}$ at which the maximum rate of weight binder loss occurs at various heating rates as follows:

$$\frac{d}{dt}\left(-\frac{d\varepsilon_b}{dt}\right)=0 \text{ and } T=T_{\max} \tag{1}$$

where $t, \varepsilon_b, T_{\max}$ stand, for time, mass fraction of binder and maximal temperature, respectively.

Figure 3 shows two local maxima for the rates of weight binder loss and corresponding temperatures at different heating rates for the 316L stainless steel feedstock with powder volume loading equals to 60%, under the condition of constant heating rate β.

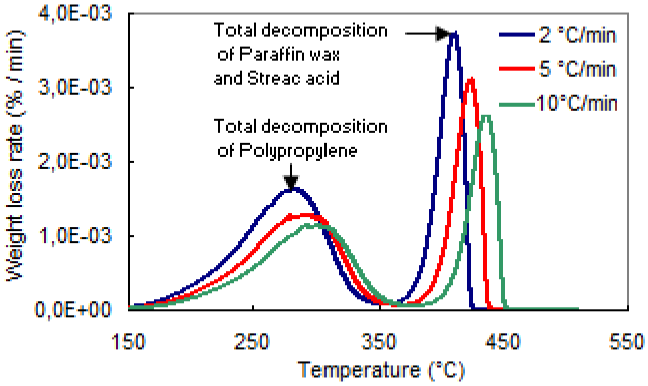

FIG. 3 – Weight binder loss rate at different heating rates with powder volume loading 60%.

3.2 Effect of powder volume loading

Figure 4 relates the effect of powder volume loading on the decomposition temperature of the binder system at three different heating rates. The data presented in figure 4 shows two main stages in the variation of decomposition temperature whatever the heating rate, that as the powder volume loading was increased from 60 to 62 %, the decomposition temperature of the feedstocks was shifted to higher temperatures. When the powder volume loading ranges between 62 and 64 %, the decomposition temperature is almost constant. Therefore, the feedstock with powder volume loading of 60% is the most sensitive to temperature; the thermal degradation of the binder system for this feedstock is quite fast which may lead to the distortion of components during debinding stage. Figure 5 presents the weight binder loss versus temperature for different powder volume loadings at different heating rates, it can be shown that the weight binder loss (%) of binder for feedstocks loaded at 60, 62 and 64 % is 80, 73 and 73%, respectively, after they decompose. The rate of binder decomposition is greater than the one obtained for 62 and 64 %. On the other hand, the decomposition temperature of the binder system is strongly increased when the heating rate increases from 2 to 5°C/min.

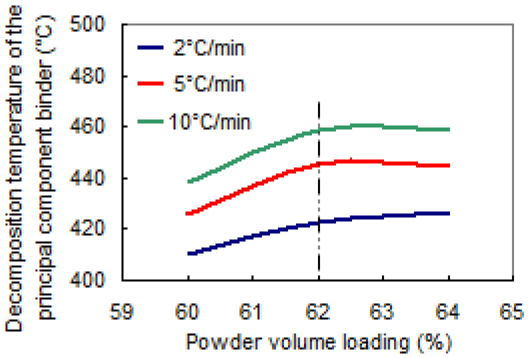

FIG. 4 – Binder decomposition temperature vs. powder volume loading.

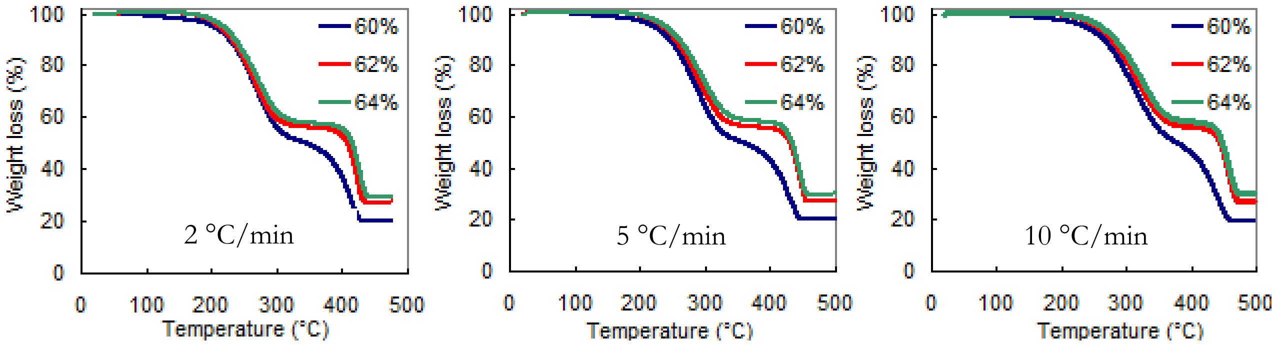

FIG. 5 – Binder loss (in weight) vs. debinding temperature for different powder volume loadings at different heating rates.

3.3 Simulation of thermal debinding behaviour of 316L stainless

Depolymerization can be described by a first-order reaction kinetics. The remaining weight fraction of a polymer ε_b is expressed as [8]:

$$\frac{d\varepsilon_b}{dt} = -K\varepsilon_b \tag{2}$$

where t is the time and K is the constant rate associated to thermal degradation and follows an Arrhenius equation*:*

$$K = A\exp\left[-\frac{E}{RT}\right] \tag{3}$$

where A is the preexponential factor, *E* is the apparent activation energy for thermal degradation, R is the gas constant and T is the absolute temperature. In combining equations (1) and (2), the rate of binder decomposition, r, can be represented as

$$r = -\frac{d\varepsilon_b}{dt} = A\exp\left[-\frac{E}{RT}\right] \tag{4}$$

The solution to equation (4), for a linear heating rate, β is expressed as:

$$\frac{\varepsilon_b}{\varepsilon_{b_0}} = \exp\left[-\frac{A}{\beta}\left\{\frac{\left(\frac{RT^2}{E}\right)\exp\left(-\frac{E}{RT}\right)}{1+\frac{2RT}{E}} - \frac{\left(\frac{RT_0{}^2}{E}\right)\exp\left(-\frac{E}{RT_0}\right)}{1+\frac{2RT_0}{E}}\right\}\right] \tag{5}$$

where: ε_{b0} is the initial mass fraction of binder and T_0 is the initial temperature. As TGA curves exhibit two sigmoids, corresponding to the thermal decompositions of low-molecular-weight binder components (PW+SA) and high-molecular-weight binder's components (PP). Each sigmoid is described by the following parameters in table 4, subscripts 1 and 2 associated to E and A denote first and second reaction step, respectively. The interrelation between (*E*) and (*A*) observed by Seong-Jin et al. for titanium powder [9] is quite similar to the one observed in the present work.

TAB. 4 – Thermal decomposition properties of 316L stainless feedstocks

Powder volume loading	60%	62%	64%	Used Method
A_1 (S^{-1})	1.02E+07	4.82E+05	4.95E+05	Kissinger
A_2 (S^{-1})	6.94E+17	1.09E+13	3.20E+15	Kissinger
E_1 (kJ/mol)	91.001	80.33	81.57	Ozawa
E_2 (kJ/mol)	223.98	179.48	205.41	Ozawa

Figure 6 relates the weight binder loss versus temperature corresponding to the powder volume loadings 60, 62 and 64% for heating rates 2, 5 and 10°C/min, respectively. One can notice that there is a small difference between the model path and the experimental one. On the other hand, one get the same values of decomposition temperatures for the two binder components which are very important for the debinding kinetics. Through knowing the activation energy and preexponential factor values of the used feedstocks, the model can quantify the thermal debinding behaviour for the new heating rates.

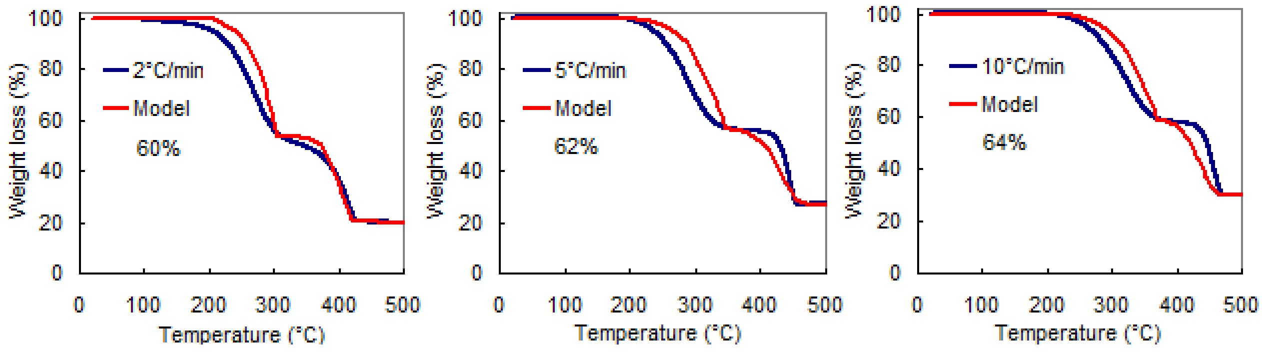

FIG. 6 – Comparison of weight binder loss vs. temperature using both the experiments and the proposed model, for different heating rates.

4 Conclusions

The thermal debinding kinetics for the 316L stainless steel based feedstock, with different powder volume loadings at different heating rates, was investigated using (TG/DTA). It is shown that there is a significant influence of the heating rate and powder volume loading on the thermal debinding behaviour of the different feedstocks.

The results showed that the weight binder loss (%) for feedstocks corresponding to 60, 62 and 64 % is 80, 73 and 73%, respectively, after complete decomposition. On the other hand, the decomposition temperature is sharply increased when the heating rate increases from 2 to 5°C/min.

Activation energies (*E*) and preexponential factors (*A*) for the decomposition were calculated by Ozawa and Kissinger methods, respectively. For the activation energy, 60 and 64% loaded feedstocks show high values and are much more sensitive than 62% feedstock. Therefore, the control of temperatures such as heating rate should be monitored accurately for 60 and 64%. The experimental feedstock loaded at 62% can be well debinded with a heating rate that varies between 5 and 10°C.

It is also shown that the present experimental results are in good agreement with the proposed physical model that is mainly based on the activation energy, preexponential factor and heating rate values, respectively. The model can properly describes the thermal debinding behaviour for new heating rates, corresponding to different powder volume loadings.

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