Effect of the particle size and solids volume fraction on the thermal degradation behaviour of Invar 36 feedstocks

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ABSTRACT

Degradation kinetics and the thermal stability of Invar 36 powder injection moulding feedstocks (PIM) based on cellulose acetate butyrate (CAB) and polyethylene glycol (PEG) binders were investigated using simultaneous thermogravimetric analysis (STA) and differential scanning calorimetry (DSC). The initial decomposition temperature (IDT) and the integral procedure decomposition temperature (IPDT) were used to analyse the thermal stability of the binder system as a function of the solid loading content and powder particle size. The degradation kinetics was studied, and the process apparent activation energies were assessed using isoconversional methods. All the methodologies revealed changes in the thermal degradation behaviours of the feedstocks for solid loadings that were previously determined to correspond to optimal solid loadings using other experimental procedures. The studies also contrast previous similar findings with a ceramic powder. Therefore these results strengthen the proposal of thermodynamic degradation studies of feedstocks as an alternative or complementary technique to determine optimal solid loading contents in metal injection moulding (MIM).

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1. Introduction

Powder injection moulding (PIM) is one of the main manufacturing processes used to produce small parts with complex geometries, thin walls and in large production batches [1]. This technology is applied to a wide variety of ceramics (commonly referred as ceramic injection moulding, CIM), metals (also referred as metal injection moulding, MIM) and combinations thereof [2]. The process consists of mixing a fine powder material with different polymer-like compounds, the so-called binder system. The binder system provides sufficient fluidity to the newly created feedstock to allow mould filling during injection. However, it will be removed during the subsequent debinding process, thus it has to allow an easy extraction. The binder system must be added in such quantities so as to optimise the process conditions and time required.

Elimination of the binder system out of the green body is the bottle neck in MIM processes and a critical and delicate step. It requires tailored optimisation of the time–temperature cycle in order to be economical and effective while avoiding faults like undesirable blistering [3]. For multi-component binders obtaining optimal thermal cycles is a difficult task that conventionally has been performed by "trial and error". However recent works propose to investigate the binder decomposition kinetics in order to identify points of rapid weight loss to avoid green parts damage, to speed up the debinding process and lower the overall cost [4–6].

The thermal burn out of organic components during debinding processes of MIM feedstock is intricate. There are several decomposition mechanism involved which are also dependant on several factors. Transport and elementary reactions steps could be rate limiting during debinding. Transport mechanisms would become more influential with increasing sample thickness, whereas in thin specimens such as in micro pieces, polymer decomposition kinetics would play a predominant role [7].

In previous works [8] we have proposed thermogravimetric analysis as an alternative to determine optimal solid loading for ceramic feedstocks while studying their thermal stability and decomposition kinetics. In this work same methods are contrasted with metallic powders. Calorimetric and thermogravimetric analyses were performed to study the thermal decomposition of an Invar 36 alloy ($Fe_{0.64}Ni_{0.36}$) feedstocks composed of cellulose acetate butyrate (CAB) and polyethylene glycol (PEG) binders in an

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inert nitrogen atmosphere. Binder and feedstock temperature stability and decomposition kinetics were investigated using integral procedure decomposition temperature (IPDT) and isoconversional methodologies, respectively. A number of isoconversional methods were used, and their convenience discussed.

Several Invar 36 feedstocks consisting of mixtures with different proportions of constituents were investigated. The volume fractions of metallic powders as well as the powder particle sizes were varied in this study. These variations allowed the effect of the effective powder surface on the interactions of CAB and PEG molecules with Invar 36 particles and the channel volume used to remove volatiles to be elucidated. The degradation of the binder system was studied to evaluate the extent of the influence that particles exert on the decomposition of CAB and PEG. The results reveal changes in the thermal degradation behaviour with solid loading and particle size. Based on these findings, we have contrasted the suitability to determine the optimum solid loading conditions using thermogravimetric tools.

2. Thermal stability studies

The initial decomposition temperature (IDT) and the integral procedure decomposition temperature (IPDT) were used to analyse the thermal stability of the binder system as a function of the solid loading content and particle size. The IDT indicates the apparent thermal stability of binder system with regard to the maximum feedstock processing rate and moulding temperatures. The IDT is determined by the onset weight loss in the TGA curves of the different feedstocks. In this work IDT corresponds to the temperature at which the 2% in mass of the organic compounds was lost. The IPDT determined from the residual weight fraction in the TGA is a reproducible datum that can be consistently determined for diverse materials and represents both a truly comprehensive index of intrinsic thermal stability and a real temperature that has practical significance. The method for calculating the IPDT is proposed by Doyle [9,10] and converts the area under the TGA curve into a value that approximately represents the characteristic end-of-volatilisation temperature, T_{a^*} (Eq. (1)):

$$T_{a^*}[\text{o}C] = A^* \cdot \left(T_f - T_i\right) + T_i, \tag{1}$$

where A^* is the area under the TGA curve within the evaluated temperature range (defined by initial temperature T_i and the final temperature T_f) and normalised with respect to both the residual weight and temperature. However, the IPDT takes into account the amount of refractory or non-volatile residues at T_f by means of the coefficient K^*. Therefore, the method to calculate the IPDT is described in Eq. (2):

$$\text{IPDT}[\text{o}C] = A^* \cdot K^* \cdot \left(T_f - T_i\right) + T_i. \tag{2}$$

A representation of the areas S_1, S_2 and S_3 used to calculate $A^*[A^* = (S_1 + S_2)/(S_1 + S_2 + S_3)]$ and $K^*[K^* = (S_1 + S_2)/S_1]$ is shown in Fig. 1. In these cases, the IPDT represents the inherent thermal stability of the binder system and describes the entire binder degradation process in terms of the decomposition and vaporisation of the different volatiles taking into account differences in the solid loading percentages. The higher the IPDT is, the more thermally stable the feedstock is. Thus, the binder components will resist higher temperatures until complete volatilisation occurs.

From the IPDT definition, it is clear that this value will be influenced by the selection of initial and final temperatures. To the best of the authors knowledge there is not a standard that defines where to set these temperatures. Hence, there is a limitation of using IPDT value when different systems are compared. In this
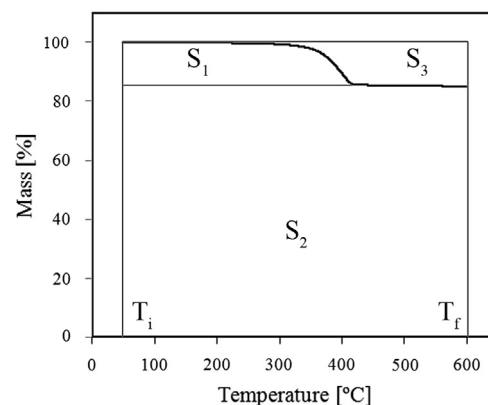

Fig. 1. Scheme of the areas $S1$, $S2$ and $S3$ for the IPDT assessment.

work initial temperature was selected approximately considering the 20% below the IDT, which resulted to be 50 °C. For the final temperature, approximately the 20% above the end of degradation temperature was selected, which resulted to be 600 °C. For comparison purposes this limits were maintained when determining the IPDT of different feedstocks and binder system components.

3. Degradation kinetic studies

A thorough discussion about the convenience of using model-free isoconversional methods to analyse thermal decomposition of MIM feedstocks could be found in the work of Salehi et al. [7]. Model-free methods turn out to be the most reliable way to determine kinetic parameters of thermally activated complex processes, because the prior knowledge of the reaction mechanism is not necessary [11]. These methods are based on studying the degree of conversion with respect to temperature at different heating rates. The degree of conversion for a certain temperature α is defined as the ratio of the actual weight loss $m(T)$ to the total weight loss, as expressed in Eq. (3):

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_\infty}. \tag{3}$$

The variables m_0 and m_∞ correspond to the initial and final masses, respectively. In the model free methods apparent activation energy is calculated directly from the TGA curves. The term apparent activation energy comes for the uncertainty of the physical process associated to this activation energy. Activation energy most likely takes into account several different processes occurring at the same time. The rate of degradation, $d\alpha/dt$, is assumed to depend on the temperature and weight of the sample. Therefore, the main advantage of eliminating the necessity of a kinetic model is clouded by the influence of the sample mass and size in the apparent kinetics parameters calculated. Furthermore these parameters could be influenced by the thermal lag across the specimen [12]. To reduce possible errors regarding size and mass, samples of similar dimensions and masses were employed. It is assumed for the thin disks employed that the binder removal rate is predominantly determined by decomposition rates of organics and not by transport processes.

In literature a wide variety of non-isothermal models could be found. The lack of agreement among kinetic parameters calculated from the same set of experimental data using different methods of mathematical analysis is disturbing. It has been shown that the causes for these differences are due to the intrinsic nature of the methods. In this work Flynn–Wall–Ozawa (FWO) and Kissinger–