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Binder removal from injection moulded zirconia ceramics

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Abstract

Binder removal from a wax-based zirconia ceramic moulding has been investigated in terms of solid content of the mouldings (45–55 vol%), heating rate (0.5–5°C min^{-1}), sample form (powder and block), and sample thickness (0.5–5 mm). Experimental results show that the samples with lower surface-to-volume ratio or more solid content has greater restriction to binder transport which reduces binder removal kinetics to a significant extent. Such a transport restriction can be minimised or eliminated by using the sample in a powdered configuration. The behaviour of binder pyrolysis is considerably modified by the presence of inorganic particles, which may be considered as a result of catalytic reaction. Activation energy of pyrolysis of the binder is evaluated directly based on the existing kinetics models through the use of the resulting weight loss–temperature curve. The activation energy for evaporation obtained is smaller than that for thermal degradation suggesting that for the binder with low molecular weight currently employed, evaporation may be considered as a dominant mechanism for binder removal. This finding is also in well agreement with literature results. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

1. Introduction

The removal of organic vehicle from ceramic injection-moulded body has long been known as the most time-consuming stage and is one of the critical steps in determining the microstructural optimum of the green body as well as the sintered product. In practice, thermal pyrolysis is currently the most frequently-used method for binder removal purpose. The removal of organic vehicle by thermolysis involves several basic mechanisms including evaporation, thermal degradation, and oxidative degradation [1,2]. As ambient temperature is raised, binder components may usually degrade into fragments of varying molecular structures; some of them are in a gaseous state, some of them are liquified with a relatively low viscosity characteristic, and some of them having a critical chain length can be evaporated directly without further degradation. However, such molecular chain fragmentation/scission due to thermolysis may be less pronounced when the binder component that employed has relatively low molecular weight over which the binder can be evaporated without degradation, e.g. chain scission [2,3]. In most practical instances, all those mechanisms may concurrently be taken place and this makes the analysis and modelling of the binder removal extremely difficult.

For a given injection-moulded body, diffusion/migration of binder component from the interior to the outer regions of the body while subjecting to thermolysis plays a critical role in transport kinetics, which finally affects the kinetics of binder removal [4,5]. In general, binder transport takes place by either diffusion (in gaseous and liquid phases) or migration by capillarity, or by a combination of both. The binder diffusion in gaseous phase has a relatively higher rate by about 3–4 orders of magnitude than that in liquid phase [6], the latter thus becomes a limited-step in binder removal. Capillary migration according to the analysis of Barone and Ulincy [7] is likely to dominate in most of the binder removal processes even when the ambient temperature is high that gaseous transport becomes important. In this communication, a low-molecular-weight binder system containing paraffin wax and polyolefin-type polymer was used for ceramic injection mouldings, processing variables such as heating rate, sample thickness, sample form, and ceramic powder content were investigated in order to gain a better understanding for process

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variables control and optimisation. The activation energy for the pyrolysis of the binder was also evaluated.

2. Experimental procedures

Low-molecular-weight organic binder composed of paraffin wax, polyolefin-type polymer, and stearic acid in a weight ratio of 7:3:1 was used as major ingredient, minor ingredient, and lubricant, respectively. The wax-based zirconia ceramic blends with zirconia (HSY3.0, 0.25 mm in average particle size) content of 45–55 vol% was prepared using ball mill to homogenise the blend with chloroform as medium. The organic components can be dissolved entirely into the medium and the resulting ceramic slurry was dried in air under a vigorously stirring condition to ensure blend homogeneity. The blend was compounded and kneaded through an extruder (Model 70-20vex-6, KCK Industrial Co.), following injection into a cavity of $5\times5\times40\,\text{mm}^3$ dimension with a barrel temperature series of 70–120–140–150–180°C. The injection pressure is 50 MPa and mould temperature is 45°C.

The moulded articles of varying solid contents were cut into different thicknesses, i.e. 0.5 and 5 mm and subjected to thermal gravimetric analysis (TGA) under flowing nitrogen (200 ml min^{-1}). The heating rate was in the range of 0.5 to 5°C min^{-1}.

3. Results and discussion

3.1. Weight-loss behaviour

Fig. 1 shows the weight-loss behaviour of the moulded articles ($5\times5\times5\,\text{mm}^3$ cubes) in comparison with the behaviour of pure organic binder (prepared under the same condition described above excluded the addition of zirconia powder). The pure organic binder appears to exhibit a more stable weight-loss characteristic than that in the presence of inorganic powder because the weight-loss curve spreads over a wide range of temperature for the pure binder. The chemical nature of the binder has been largely modified by the zirconia powder. Similar phenomena were also observed in a study by Masia et al. [8] and which is believed to be a result of catalytic reaction between organic and inorganic components. Initially, the weight-loss curve for the pure binder exhibits a higher degree of binder removal than those for powder blends. As further increase in temperature, the powder blends show a steeper weight-loss characteristic. The temperature for the crossover of the TGA curves between the powder blends and the pure binder increases with solid loading, i.e. 225, 250, and 270°C for 45, 50, and 55% loadings, respectively. This increase in crossover temperature with increasing solid content may be due to the change in degradation rate, burnout mechanism, or diffusion path, or their combinations.

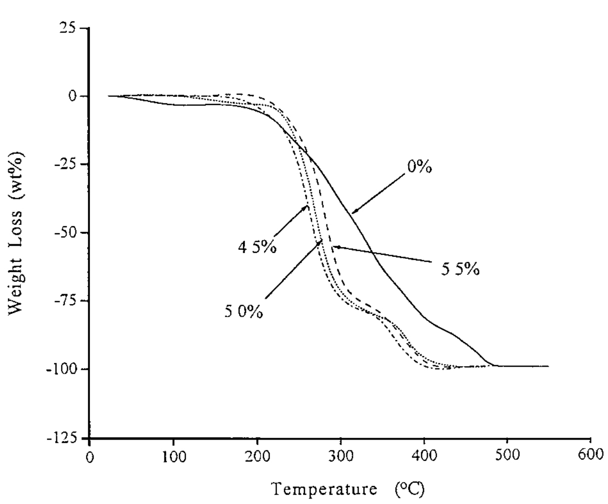

Fig. 1. Effect of solid content on the weight-loss behaviour of wax-based zirconia mouldings (at a heating rate of 0.5°C min^{-1}).

In general, two major weight-loss steps were observed in the TGA curve for the as-moulded specimen. The first stage of major weight loss occurs in the temperature range of ~250 to 300°C and the second, ~350–400°C. The percentage of weight loss at the first stage of binder removal is closely equivalent to the initial content of binder wax. It can therefore be reasonably considered that the first stage of binder pyrolysis is resulting dominantly from the removal of binder wax. Although definite evidence for the determination of pyrolysis mechanism is currently insufficient for the first stage binder wax removal, analogous investigations on examining the pyrolysis of such a low-molecular-weight wax suggested to be an evaporation controlled [3]. On this basis, evaporation may reasonably be assumed to be a dominant mechanism for the wax removal. The second stage of weight loss, accordingly, is attributed dominantly to the removal of the low-molecular-weight polymer. Since the polymer has a chemical structure comparable to polyolefin and has an average molecular weight below 4500 , according to an earlier study on the thermal degradation of polyolefin by Wright et al. [3], the pyrolysis of the currently-used polymer may be controlled by thermal degradation. The weight-loss curves for the moulded articles shift in approximately 20–30°C interval to higher temperature region as the solid content increases in 5 vol% interval. Such an increase in temperature associated with the increased solid content may be caused by an increase in transporting length, that is, a higher solid content implies smaller pore channels and a higher degree of tortuosity.

If the binder diffusion/migration from the interior to the outer region of the moulded article were dominant throughout the binder thermolysis process, it can be simply verified by using samples of differing thicknesses and Fig. 2 shows the resulting weight-loss curves. Both curves for samples of varying thicknesses show an identical shape which suggests that the mechanism for binder removal may be identical [2]. Obviously, the thinner sample is subjected to a greater weight loss in comparison to the thicker sample at a given temperature; for instance at 300°C, the 0.5 mm-thick sample illustrates an approximately 20% higher weight loss than that of the 5 mm-thick sample. This difference in weight-loss behaviour is primarily due to the variation in surface-to-volume ratio ($^S/V$) between the specimens. The smaller specimen, having an $^S/V = 4.8\,\mathrm{mm}^{-1}$, provides a shorter path length and a larger area per unit volume for the binder to be transported and to be removed in comparison to the thicker one, having an $^S/V = 1.2\,\mathrm{mm}^{-1}$ [4]. The inward diffusion of oxygen to accelerate oxidative degradation should be important for binder removal [9], however, this may be negligible in the current investigation (only about 50 ppm of oxygen in the flowing nitrogen).

Based on this understanding, we postulated that if the diffusion/migration path were minimised or completely eliminated, the rate of binder removal will be significantly enhanced and this is verified by using a powdered sample, which was obtained by comminution of the moulded article, as denoted in Fig. 2. The weight loss of the powdered sample shows a considerably lower weight loss below 275°C in comparison to the others. The crossover of the powdered TGA curve can be characterised as the melt of binder in a thermal environment which causes the powder to form an agglomerate configuration. The powdered specimen then loses its original characteristic from being having a relatively large $^S/V$ of approximately $30\,000\,\mathrm{mm}^{-1}$, to a relatively low ratio that may lie between 1.2 and $4.8\,\mathrm{mm}^{-1}$ above 275°C. Under such circumstance, the pyrolytic behaviour for the powdered specimen is more likely to behave as a block. As a matter of fact, a large block form of the debound powdered specimen was seen at a later examination which supports this assumption. The diffusion/migration path developed within the agglomerate further reduces transport kinetics and consequently suppresses the binder removal to a considerable extent.

The influence of heating rate on the binder removal is illustrated in Fig. 3 for 50% solid loading. In general, the weight-loss curves shift to a higher temperature with increasing heating rate, but the shape of the weight-loss curve remains roughly the same without interruption by the change in the heating rate. This indicates that the variation in the heating rate in this study range appears to have little or relatively minor effect on pyrolytsis behaviour. Similar behaviour was also reported by Mutsuddy et al. [2]. In fact, in most of the binder pyrolysis events, higher heating rate tends to deteriorate the green microstructure by generating different degrees of micro- and macro-scale defects due to the rapid degradation of the binder to form gaseous products during a short period of time within the moulded articles. However, visual examination of the specimens used for TGA tests shows no macro-scale defects present even under a relatively high heating rate of 5°C min^{-1}. This may be due to the evolution of interconnected pore channel at the initial period of binder removal [10] after which the gaseous products generated at higher temperature can be rapidly removed without causing extensive internal pressure buildup.

3.2. Activation energy

Evaporation as well as thermal degradation are primarily dominant pyrolytic mechanisms responsible for the binder removal in current binder system. However, as indicated by Wright et al. [3], as the molecular weight of the binder decreases, the proportion of the molecules

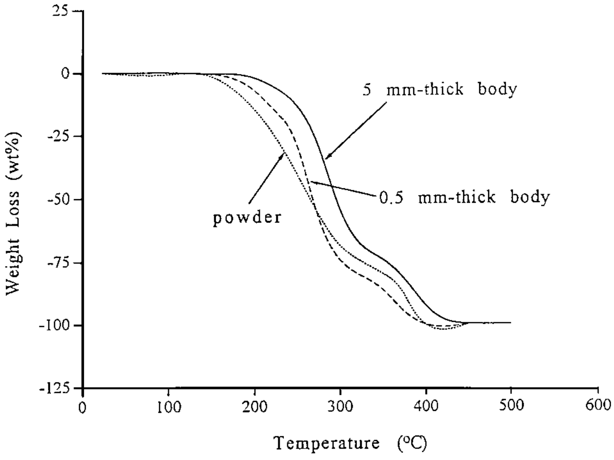

Fig. 2. Effect of sample form and sample thickness on the weight-loss behaviour (at aheating rate of 0.5°C min^{-1}).

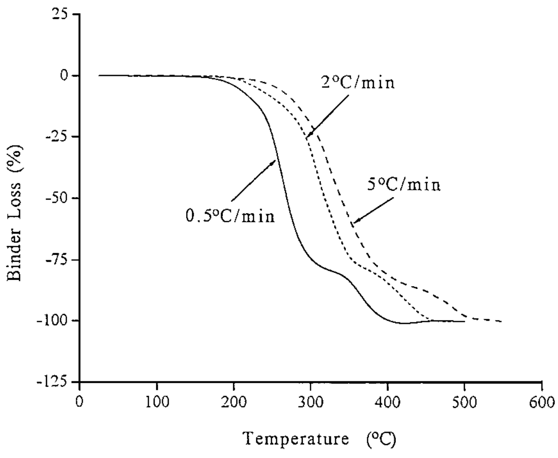

Fig. 3. Effect of heating rate on the weight-loss behaviour of the cube mouldings.

close to or less than a critical length for evaporation increases, and evaporation can then be considered as the only mechanism for binder removal. However, the critical length for this polymer associated with its gaseous products at or above the decomposition temperature can not be determined at present. Therefore, the forthcoming analysis of the activation energy of the binder pyrolysis will then be detailed separately.

The activation energy of evaporation can be derived directly from the weight-loss curve by the method of Dickens who considering the evaporation to be zero order [11] and in this case

$$(\mathrm{d}x/\mathrm{d}T)_{\mathrm{T}} = K_{\mathrm{e}} \tag{1}$$

where the rate of weight loss ($\mathrm{d}x/\mathrm{d}T$) at a given temperature can be obtained by estimation of the slope of the weight-loss curve and K_{e} is rate constant which can be related to

$$K_{\mathrm{e}} = K_{\mathrm{eo}}\exp(-E_{\mathrm{e}}/RT) \tag{2}$$

where E_{e} is the activation energy for evaporation, R is the universal gas constant, and T is the absolute temperature.

The activation energy of evaporation can be obtained by plotting ln ($\mathrm{d}x/\mathrm{d}T$) vs $1/T$ as illustrated in Fig. 4 for the pure binder and the powdered blend, and which is listed in Table 1. The corresponding temperature range of 150–275°C over which the relationship is linear in Table 1 suggests to be a result of evaporation for the low-melting components, i.e. wax and stearic acid in this case. The activation energy of evaporation for the powdered blend is slightly lower than that for the pure binder over this temperature region and this is primarily due to the fact that the former specimen provides a larger $^{\mathrm{S}}/\mathrm{V}$ ratio than that for the latter specimen. A more plausible reason could be a possible catalytic reaction which may even take place during blend preparation. Both possibilities tend to promote evaporation kinetics. However, a significant increase in activation energy, i.e. 72.3 kJ mole^{-1}, was found in the moulded specimen. This increase in activation energy may be due to a considerable reduction in $^{\mathrm{S}}/\mathrm{V}$ ratio associated with additional diffusion/migration effects.

Table 1
Activation energy (in kJ mole^{-1}) for thermal degradation and evaporation for the injection-moulded materials

Materials	Thermal degradation	Evaporation
Pure binder	35 (150–350°C) 178 (400–450°C)	34.6 (150–235°C)
Powdered blend	36.6 (150–275°C) 220 (350–400°C)	28.5 (150–235°C)
Moulded compact (55%)	74.8 (225–300°C) 185 (350–400°C)	72.3 (225–275°C)

A similar methodology is used to evaluate the activation energy for the thermal degradation of the polymer binder. It is assumed that such thermal degradation is of first-order kinetics as that observed for the degradation of polyolefin polymer reported by Wright et al. [3]. For the first-order reaction, the rate of weight loss is related to the remaining weight by [12],

$$(\mathrm{d}x/\mathrm{d}T)_{\mathrm{T}} = K_{\mathrm{d}}D_x \tag{3}$$

where D_x is the remaining binder weight within the test sample and K_{d} is the rate constant for degradation which has similar form as defined in Eq. (2). The activation energy for thermal degradation can thus be deduced directly by plotting ln ($\mathrm{d}x/\mathrm{d}T/\mathrm{D}x$) vs 1/T. Fig. 5 shows the activation energy plot for the pure binder and the powdered specimen. The resulting energy

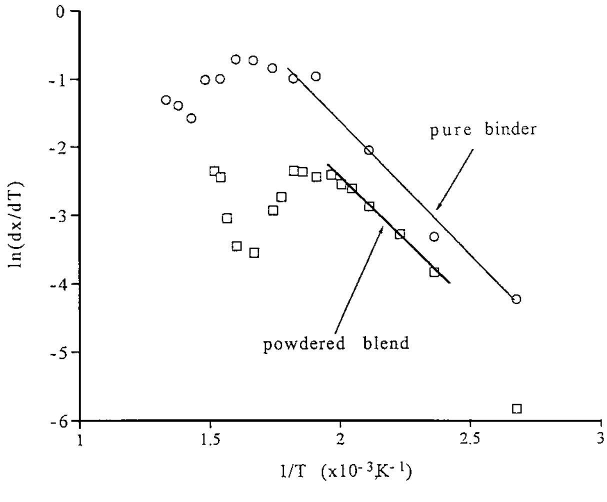

Fig. 4. Arrhenius plot for the evaluation of the activation energy of evaporation for the pure binder and powdered blend samples.

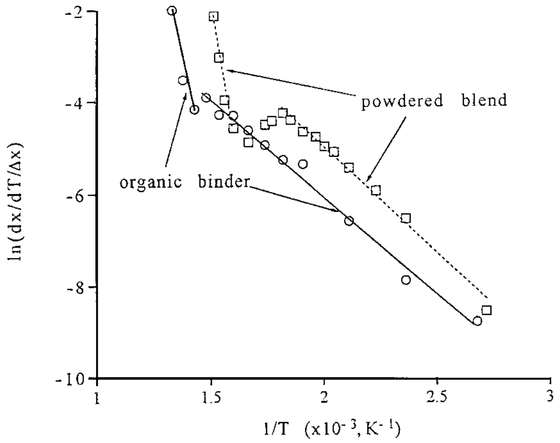

Fig. 5. Arrhenius plot for the evaluation of the activation energy of thermal degradationfor the pure organic binder and powdered blend samples.

values associated with corresponding temperature range is given in Table 1. Both the pure binder and the powdered blend show nearly identical activation energies of thermal degradation over the temperature of 150–275°C. In comparison, the activation energy is slightly greater for degradation than for evaporation, which reflects that the binder tends to be removed by evaporation. This finding is consistent well with the argument given by Wright et al. [3] who have particularly emphasised that evaporation will tend to be a dominant mechanism of binder removal for a low-molecular-weight organic binder.

The activation energy of thermal degradation for the 55% moulded specimen was higher, i.e. more than twice in comparison to the others over a temperature range of approximately 225–300°C. The decomposition mechanism for the binder with or without the presence of inorganic species is unclear at present and is believed to be relatively complex. Based on the identical blend formulation, it is reasonable to assume that this increase (which is similar to that observed for the evaporation mechanism previously mentioned) in degradation energy may not be the result of a catalytic reaction (which would supposedly reduce the energy required for degradation) but could be a result of diffusion/migration effects. The slightly higher energy value for thermal degradation in comparison to that for evaporation further implies an evaporation-dominant weight loss characteristic. According to the discussion of Wright et al. [3], this result may not be impossible because the gaseous products of the decomposed polymer may have a molecular size that is smaller than some critical length.

In Fig. 5, an additional linear proportion in the plot is found at a higher temperature range, e.g. 350–400°C. Based on the same principle as defined in Eq. (3), the activation energy of degradation can then be calculated and is also given in Table 1. The activation energy of thermal degradation is generally higher by an order of magnitude in the higher temperature region than in the lower temperature region for all types of specimen geometries employed in this study. These energy values are of the same order in magnitude as that observed for the thermal degradation of low-density polyethylene [3] (i.e. 196–209 kJ mole^{-1} over a similar temperature range).

The influence of solid loading of the moulded body on the activation energy of the thermal degradation has been evaluated and appears to be small, e.g. ~80 kJ mole^{-1} for 45% and 75 kJ mole^{-1} for 55% loading over the temperature range of 225–300°C. This result implies that the weight-loss behaviour (in the temperature range of interest) due to variation in solid loading (Fig. 1) can hardly be accounted for by a thermal degradation mechanism only. An acceleration of binder removal rate by catalytic reaction due to the incorporation of inorganic particles indicate a reduction in the overall activation energy. The experimental findings of thermal degradation seems to fail in accounting for this argument at first sight. On the other hand, evaporation appears to provide a reasonable explanation of this weight-loss behaviour not only for its reasonable change (getting smaller) in the activation energy due to the presence of inorganic particles, but also by its apparently lower activation energy in comparison with that for thermal degradation.

4. Conclusions

Binder removal from wax-based zirconia ceramic injection mouldings was investigated in terms of a variety of processing variables such as heating rate, solid content, sample thickness, and sample form. The weight-loss behaviour is strongly affected by solid content as well as specimen thickness and these findings indicate a pronounced effect of binder diffusion/migration from the interior to the surface region of the sample. Such a diffusion/migration effect restricts the transport capability of the binder out of the specimens to a significant extent and eventually causes a reduction in binder removal kinetics. Activation energy of thermal degradation and evaporation of the binder during thermolysis has been evaluated. The lower activation energy of evaporation in comparison with that of thermal degradation strongly implies that for the low-molecular-weight binder system currently employed, evaporation may be a dominant mechanism for the binder removal.

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