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CONTROLLED-RATE THERMAL ANALYSIS
Study of the process of super hard material debinding

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Abstract

Binder burnout has been carried out by a controlled heating programme which depends on the composition of the binder system used. The present paper gives the principle of constant decomposition rate thermogravimetry, which falls within controlled-rate thermal analysis, and the advantage of this technique when evolved gas analysis is used in discriminating the process of super hard material burnout by comparison with the conventional linear heating method is described. In this technique, the sample temperature is varied to maintain a constant rate of mass loss by control of the heating of the infrared image furnace. Since the constant decomposition rate control (CDRC) allows a much better control of the sample environment, which generally depends on the rate of gas evolution, it is possible for uniform conditions to exist throughout the sample, and the total burnout time can be reduced considerably without crack formation. The efficiency of this CDRC was proved by the obtained temperature *vs.* time curve and SEM observations of the heat-treated sample after the debinding process.

Keywords: binder burnout, CDRC, CRTA

Introduction

A general technique for the production of ceramics is the injection molding of ceramic powder plasticized with organic binders. Organic binders are desirable for ceramics processing because they impart strength and plasticity to ceramic green bodies to be retained in the desired shape before firing. During firing, organic binders should be completely removed from the body. This removal of organic binders, generally called 'binder burnout', is performed by evaporation and thermal decomposition of the polymeric binder.

It is very important to control the binder burnout process carefully, in order to prevent the development of flaws and to minimize carbon residues which may

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alter the desired properties of the final product. If the heating rate is too rapid, defects may occur; cracking, voids and pores may then be produced in the final product and the mechanical properties can be badly affected. For these reasons, the burnout of the organic binder used to form ceramics materials is recognized as one of the most important processes in the industry. It would be desirable to perform binder burnout so as to remove the binders more rapidly than with the present methods.

Studies on binder burnout are generally performed by continuous mass decrease using thermogravimetry (TG). This means that the mass signal is a good measure of the burnout stages. Binder burnout is typically performed with a temperature – time schedule as follows. Initially, the temperature is raised quickly to a level where binder burnout starts, and it is subsequently programmed at a very low constant heating rate up to a level where burnout is almost complete. In order to achieve optimum binder burnout, the controlled-rate thermal analysis (CRTA) technique is very useful. Various kinds of feedback control of the furnace temperature via mass sensoring have been proposed [1].

The CRTA technique has been proved to be useful in both TG and dilatometric studies [2]. The aim of CRTA is to obtain thermoanalytical curves that are independent of the experimental arrangement (e.g. sample mass, crucible shape and granulometry). In this technique, the temperature of the sample is controlled by monitoring the reaction rate in thermal decomposition or shrinkage during sintering. The CRTA technique has been examined by several laboratories, using TG to improve the kinetic evaluation of the reactions and transformations. Historically, the CRTA technique was in fact introduced *via* quasi-isothermal TG (Q-TG) [3] or quasi-isothermal thermal analysis [4], stepwise isothermal analysis (SIA) [5] and constant decomposition rate thermal analysis (CDRTA) [6]. These techniques have often been considered to be different from each other, but it was held that they have fundamentally the same nature in a sense. Also, we have devised a dynamic rate control (DRC) method which belongs in CRTA. This method gives a very high resolution or 'separation power', and we earlier reported that it was an especially effective technique for the dehydration of inorganic salts [6] and the analysis of the thermal decomposition of a polymeric material by means of combined TG-gas chromatographic/mass spectrometric analysis (TG-GC/MS) [8].

Binder burnout has been carried out in many ceramic fabrication processes, but fundamental studies are scarce. Further, many cases are achieved empirically. The basic data are thought to be useful for the design of optimum burnout control, and to clarify the mechanism of ceramics debinding [9, 10].

In this study, we proposed a new concept of the constant decomposition rate control (CDRC) method, in which the principle of the DRC method is extended to the present purpose, and we described that the coupling of controlled-rate TG and MS is a useful technique as optimum heating control for binder burnout.

Principle of constant decomposition rate control (CDRC)

In a first attempt, the CRTA technique was an on-off control [11]. This type of control is quite easy with modern microprocessor controllers. However, the main disadvantage of this method is the large noise generated on the TG signal with the on-off control. To overcome this problem, we have developed a new concept of the controlled heating rate, called CDRC.

The basis for the algorithm of CDRC is described below. In the CDRC technique, the rate of decrease in mass dW/dt, is monitored and changed into a rate of temperature increase such that dW/dt remains constant. This principle can easily be extended on analogy to the DRC algorithm. Consequently, the heating rate in CDRC, and the DRC mode, are controlled in such a way that the absolute value of the rate of sample temperature decrease is expressed as a monotonous function of the decrease in sample mass, and hence the heating rate is controlled so as to be decreased promptly as the mass loss occurs.

The rate of decrease in mass (first derivative of TG signal) is successively computed, and the heating control is carried out according to the following equation:

$$V = V_m[(S_m - S)/S_m]^y \qquad (1)$$

Here, V is the heating rate dT/dt, V_m is the maximum heating rate and S is the rate of decrease in mass, dW/dt. Also, S_m is a constant pre-selected rate of decrease in mass and the exponent y acts as a local sensitivity coefficient of V *vs.* S.

As concerns the physical meaning of Eq. (1), when S is zero (i.e. the sample mass does not change), V is exactly fixed to V_m. The value of V becomes small with increasing value of S, and when S equals S_m, V becomes zero, whereupon the heating control changes to be isothermal. On the other hand, if S, goes up to over S_m, V becomes negative, and hence the actual control turns to cooling. This technique provides a smooth control without compulsory pumping of the temperature.

Experimental

Sample

Binder contents of about 8% (1–2% ethyl alcohol, 4% plasticizer and 2–3% polyvinyl resin) were added to super hard material consisting primarily of 70–80% WC, 1–2% TaC and 10% Co, in which the particle sizes were $1-10\times10^{-6}$ m. The material was then thoroughly blended. This mixture was molded to a size of 4.5 mm o.d.×1.5–0.6 m long by a pressure of about 20 MPa, using a piston extruded molding machine, and then cut out to the prescribed dimension. The sample of about 500 mg was heated in a platinum pan from ambient temperature to 500°C in an inert helium atmosphere, with a normal purge flow rate of 100 ml min^{-1}.

Measurements

A Rigaku TAS-300 TG-DTA 8110D thermogravimetry (single sample holder type) differential thermal analyser upgraded with a dynamic TG-DTA module was used to measure the mass profile. This dynamic TG-DTA can be used in both standard (constant heating rate) and high-resolution modes, including DRC, SIA and CDRC, in which the rate of sample heating is dependent on the rate of loss in sample mass. The furnace responsiveness is quite important, to give precise temperature measurement and to improve the separation ability. For purposes of improvement of the responsiveness, an infrared image furnace unit was used instead of a conventional type, which utilizes a relatively high heat capacity and resistivity heater. This furnace response effect competes with the heating generated from the infrared image heating elements to permit moderately rapid heating or cooling of the sample, based on the requirements of the control system to achieve high burnout rates. Consequently, the rates of mass loss are ultimately limited by the furnace response time, and the furnace temperature therefore oscillates about the setpoint of the rates of mass loss. When resistance heating elements are used, the higher the rate of constant mass loss, the more difficult is to control this heating system. Hence, the burnout is generally performed by using lower setpoint rates below $1\times10^{-4}\%\ s^{-1}$ to avoid steep temperature oscillations brought about by temporary control system imbalance. Further, in the present unit, one sensor attached directly to the sample controls the heating and cooling rates, and also measures the temperature. This furnace can be heated (and cooled) at a precise heating rate from the conventional values of 0.5–20°C min^{-1} up to the much higher 100°C min^{-1}. This combined ability of measuring the sample temperature directly and using the same sensor for the precise control of furnace heating and cooling rates facilitates thermoanalytical studies in both the high-resolution mode and the normal standard mode. The mass change signal detected by the TG control circuit is fed back to an automatic temperature control system. Here, the signal of heating rate according to the control parameters from the CPU is calculated in succession, and is supplied as a control current to the infrared image furnace.

The dynamic TG-DTA was connected with a Shimadzu PARVUM (QP-5000) gas chromatography – quadrupole mass spectrometer (GC-MS), using a Rigaku TG-MS interface to create in integrated simultaneous TG-DTA/GC-MS system. The simultaneous TG-DTA/GC-MS configuration is shown schematically in Fig. 1. This original TG-DTA/GC-MS system can be used for two kinds of interface modes. They are distinguished between continuous sampling (direct coupling mode), in which a purge gas stream is continuously recorded with a TG-DTA signal as a function of time or temperature for 'on-line' analysis, and intermittent sampling (trap coupling mode), in which a portion of the evolved gases is collected over a chosen temperature range and then analysed 'off-line'. GC separation of the degradation products was achieved by using a 30 m×0.25 mm i.d.×0.25 μm film thickness DB-1 fused silica capillary column

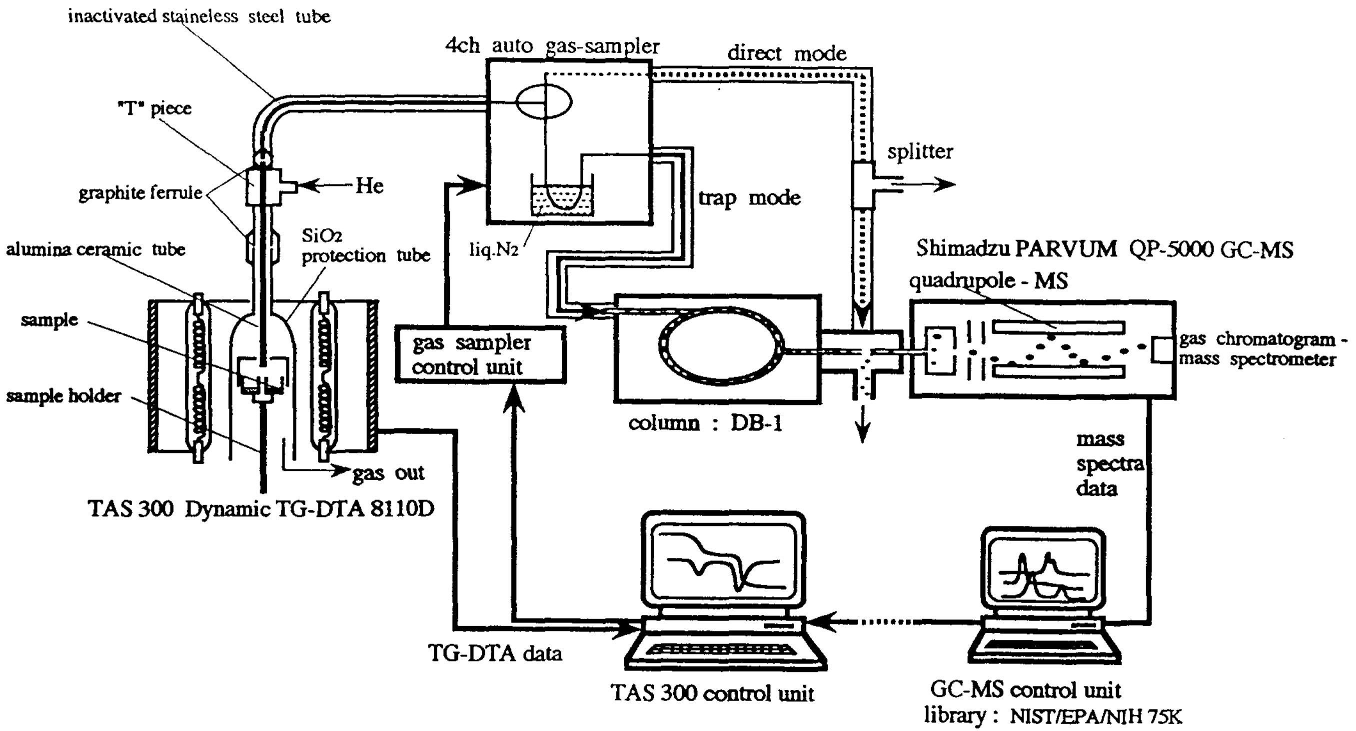

Fig. 1 Schematic diagram of a simultaneous TG-DTA/GC-MS installation

(supplied by J & W Scientific) and the GC was temperature programmed from 30 to 280°C at a rate of 10°C min^{-1}. Peak identification was primarily carried out by the GC-MS system in the electron ionization (EI) mode. The library search was a procedure that compares the spectrum of an unknown compound against a library of reference spectra, using the NIST/EPA/NIH chemical structures database.

The instrumentation has been described in more detail elsewhere [8]. The cross-section of the heat-treated samples after burnout was examined by using a JEOL JXA-733 scanning electron microscope (SEM).

Results and discussion

Figure 2 shows the TG, DTG (derivative weight loss, % s^{-1}) and temperature curves of a sample heated at a high heating rate of 15°C min^{-1}. The sample gradually and continuously decomposed, with several burnout stages between 100 and 450°C. Corresponding to the decomposition of the binder content of the sample, the mass loss is observed to have a maximum rate of about 12×10^{-3}% s^{-1} at around 300°C. This DTG profile may be indicative of a particular chemical structure fragment. Figure 3 shows the intensity of the main mass chromatogram (MC) and mass spectrum obtained at the total ion current (TIC) peak, with maximum intensity at 16.5 min. The mass spectrum at this time corresponds to that of dibutyl phthalate. The main mass fragments observed are characterized as follows: *m/z* 18 is H_2O, 28 is N_2 or CO, 44 is CO_2 and 149 is

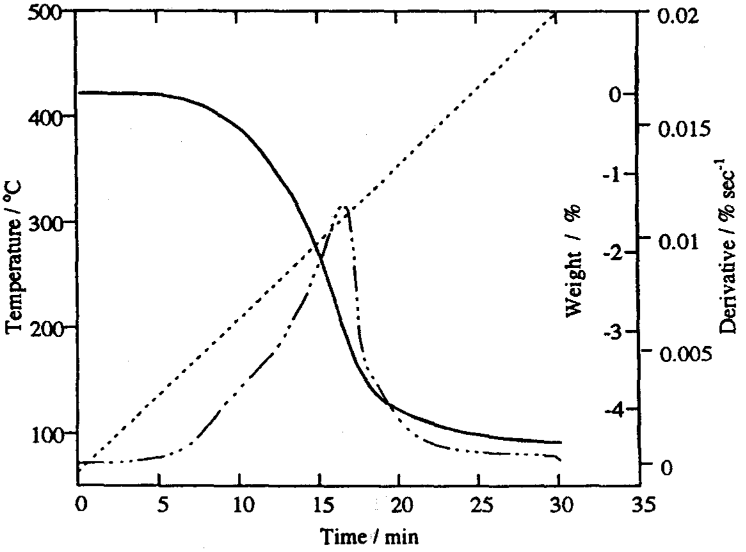

Fig. 2 Overall TG and DTG curves for conventional binder burnout at 15°C min^{-1}.
— Mass-Time, — · · · — Deriv.-Time, · · · · · Temp.-Time

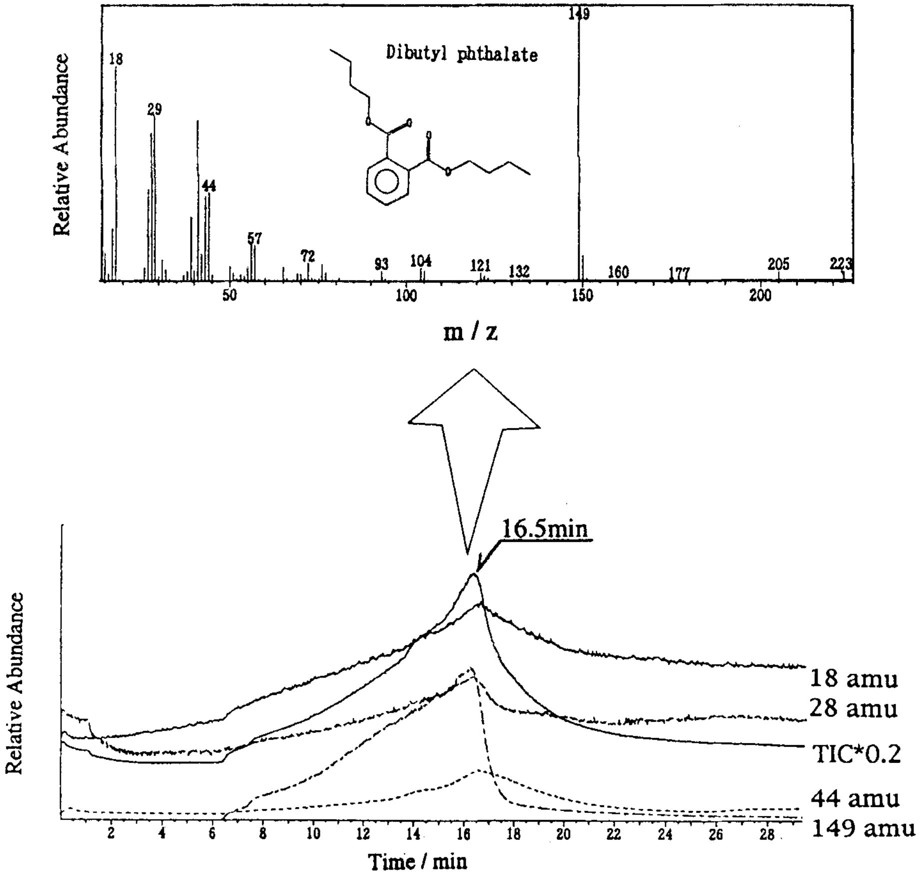

Fig. 3 Main MC curves and mass spectra in TIC at 16.5 min

the base peak of dibutyl phthalate. Figure 4 shows the TG-GC/MS pyrogram for the decomposition components collected at 300°C, corresponding to a maximum DTG curve with a linear heating rate. The low boiling components at times up to 14 min are expected to be formed mostly from alcohol or poly(vinyl butylal). The characteristic components derived from the phthalic acid used as plasticizer are observed for the high boiling components after 20 min. The TG-MS combination is therefore helpful in assessing volatilization behaviour in the debinding process.

From these results, the enhancement of *m/z* 149 on the production of dibutyl phthalate occurs with rising temperature. Figure 5 shows the TG, DTG and temperature curves as a function of time, compared with MS data collected on a time basis and transformed to a temporal display of the intensity of the specific MC of *m/z* 149.

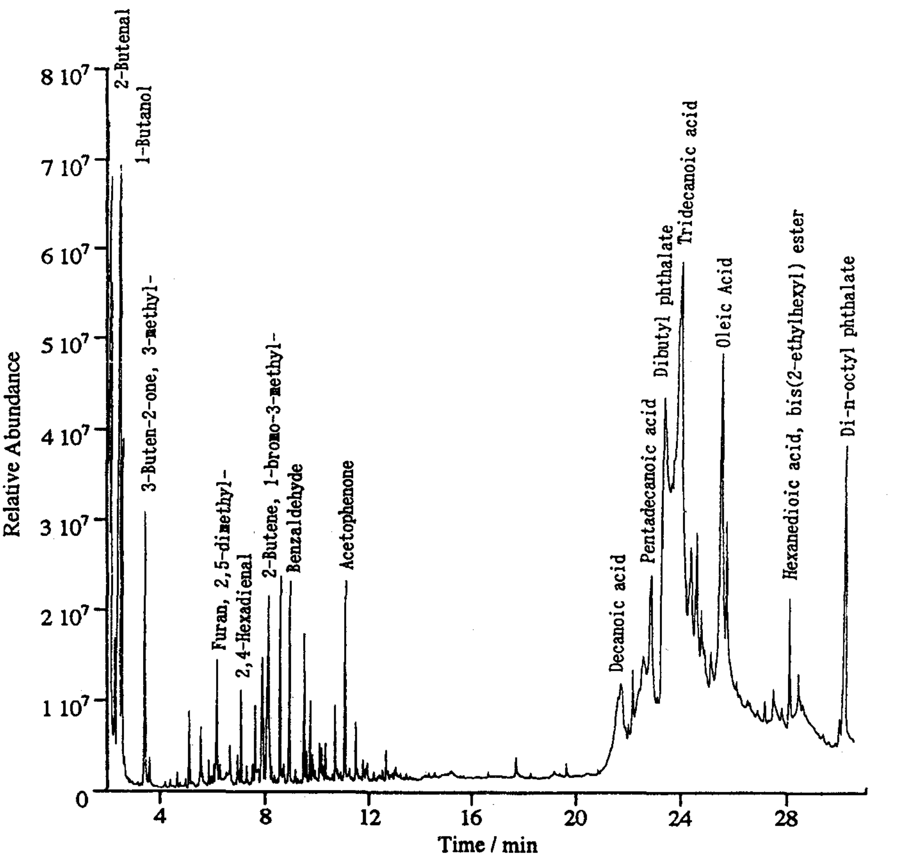

Fig. 4 TG-GC/MS pyrogram for the decomposition components at 300°C

Such being the case, the linear heating rate experiments result in problems of pressure and temperature gradients within the sample. With this type of experiment, the rate of mass loss passes through a maximum near the midpoint of a reaction step. On the other hand, the volatile products are produced throughout the sample body and must diffuse to the surface. The binder content near the surface of the body can be removed faster than that near the center. This has been mentioned as a cause of subsequent crack formation due to large shrinkage differences between the surface and the interior. On adjustment of the heating rate to the limit, this maximum peak can also give rise to unrealistically long experiments. The heating rate has to be chosen so that is sufficiently low to avoid excessive temperature gradients.

The CDRC technique can offer a workable approach that improves the burnout process without sacrificing time. As shown in Fig. 3, however, when the

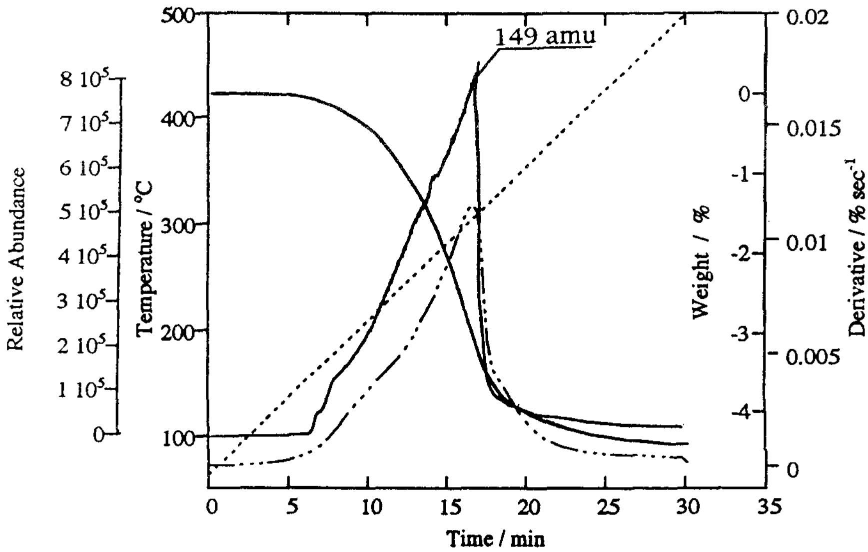

Fig. 5 Overall TG and DTG curves and MC curve of *m/z* 149 for conventional binder burnout at 15°C min^{-1}. — Mass-Time, — · · · — Deriv.-Time, · · · · · Temp.-Time

binder content decomposes to comparatively low molecular species such as CO and CO_2, mere monitoring of the constant mass loss rate can not detect the steep gas evolution and, ultimately, defects within the sample may be unavoidable. To sum up, just because the rate of mass loss is maintained constant, it does not follow that the gas is produced at a uniform rate. What matters is rather that the gas evolution from the molding, together with the thermal decomposition of the organic binders, is controlled so as to indicate a uniform gas evolution rate. To overcome this problem it is essential to know the characteristics of a qualitative and quantitative nature of the decomposition components. Hence, introduction of the EGA technique is particularly valuable, in that it provides direct chemical information about these debinding processes, followed by the physical technique of TG. Results of the MC and TIC curves, together with temperature – time, mass – time and derivative – time curves obtained with this opimal control, are presented in Fig. 6. Here, the CDRC was terminated when the sample temperature setpoint reached the level of 130°C, where the normal temperature program of 10°C min^{-1} was continued. The switchover point from temperature to mass control was selected in the range of the onset of binder burnout, which was determined from a prior TG in Fig. 2. The mass loss percentage was controlled to decrease linearly at a high burnout rate of 5×10^{-3}% s^{-1}. As seen in the profiles, in practice the shape of the obtained DTG is analogous to that of the TIC, except that the TIC intensity is temporarily varied towards an increasing temperature region at around 22.5 min due to the decomposition to the low molecular components.

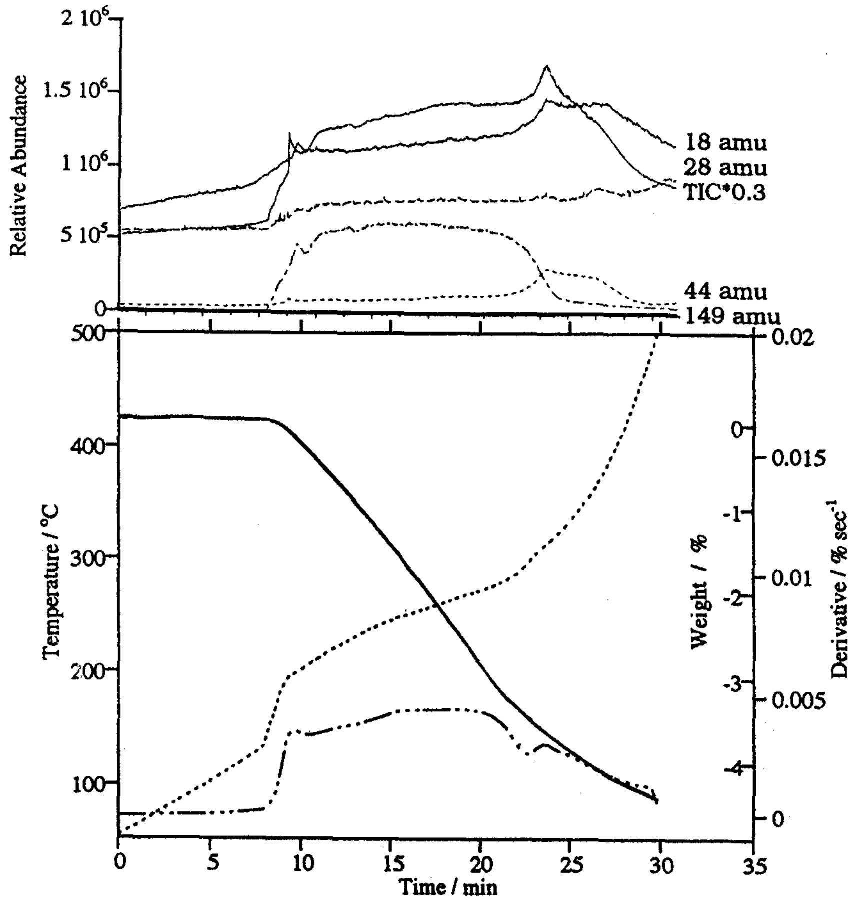

Fig. 6 Overall TG, DTG and MC curves for CRC binder burnout — Mass-Time, — · · · — Deriv.-Time, · · · · · Temp.-Time

Inspection of the results clearly reveals the advantage of this TG-MS technique in terms of controlling the amount product gas which this method maintains constant. Additionally, it is obvious that the CRDC technique maintains constant the rate of production of *m/z* 149, which predominantly influences this debinding process and is capable of inhibiting the steep evolution of low molecular species. Also, Figs 2 and 6 demonstrate that significant improvements in the burnout process can be achieved, yet both experiments took a similar amount of time to cover the same temperature range.

In order to prove the effectiveness of the presented results, the cross-section of the heat-treated sample after burnout was examined by SEM. Figure 7 shows a comparison of the examinations in the two experiments. The observations under the conventional conditions demonstrate fairly large cracks, and inhomo-

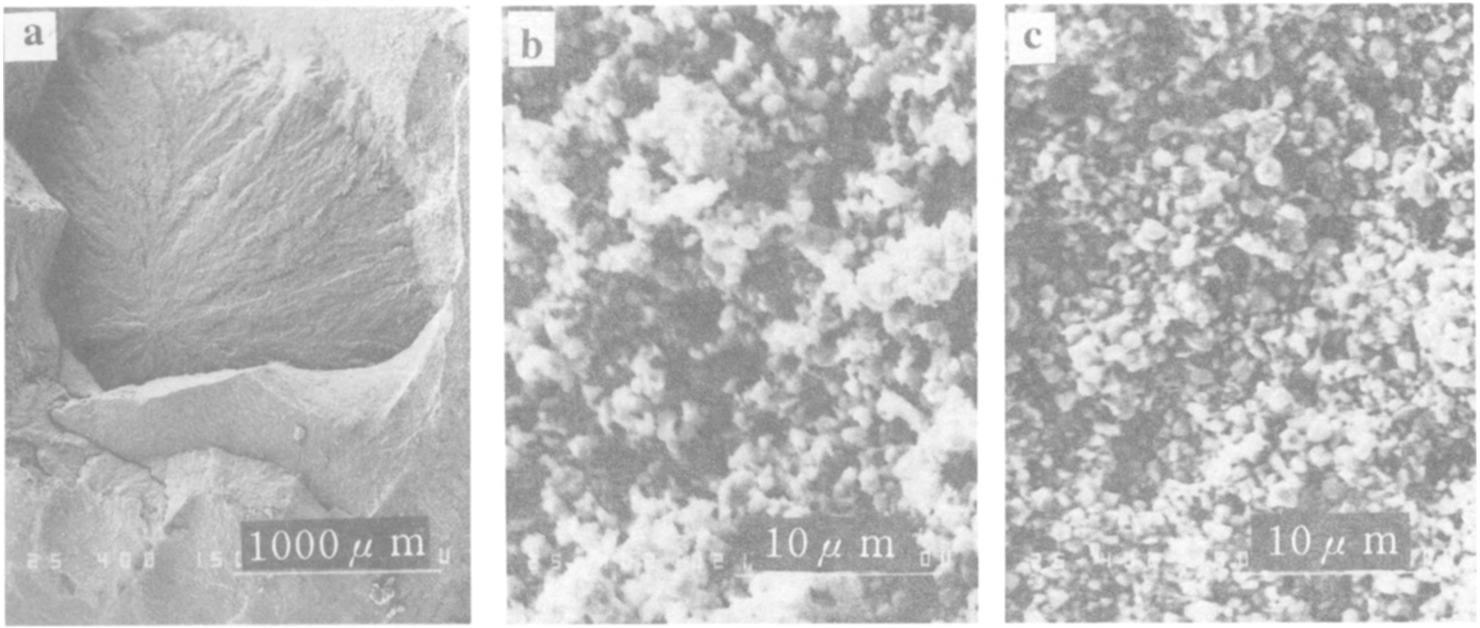

Fig. 7 Comparison of SEM microstructural analysis between different heating processes for a constant heating rate of 15°C min^{-1} and CRC. (a) 15°C min^{-1}; cross-section, (b) 15°C min^{-1}; near surface, (c) 15°C min^{-1}; core

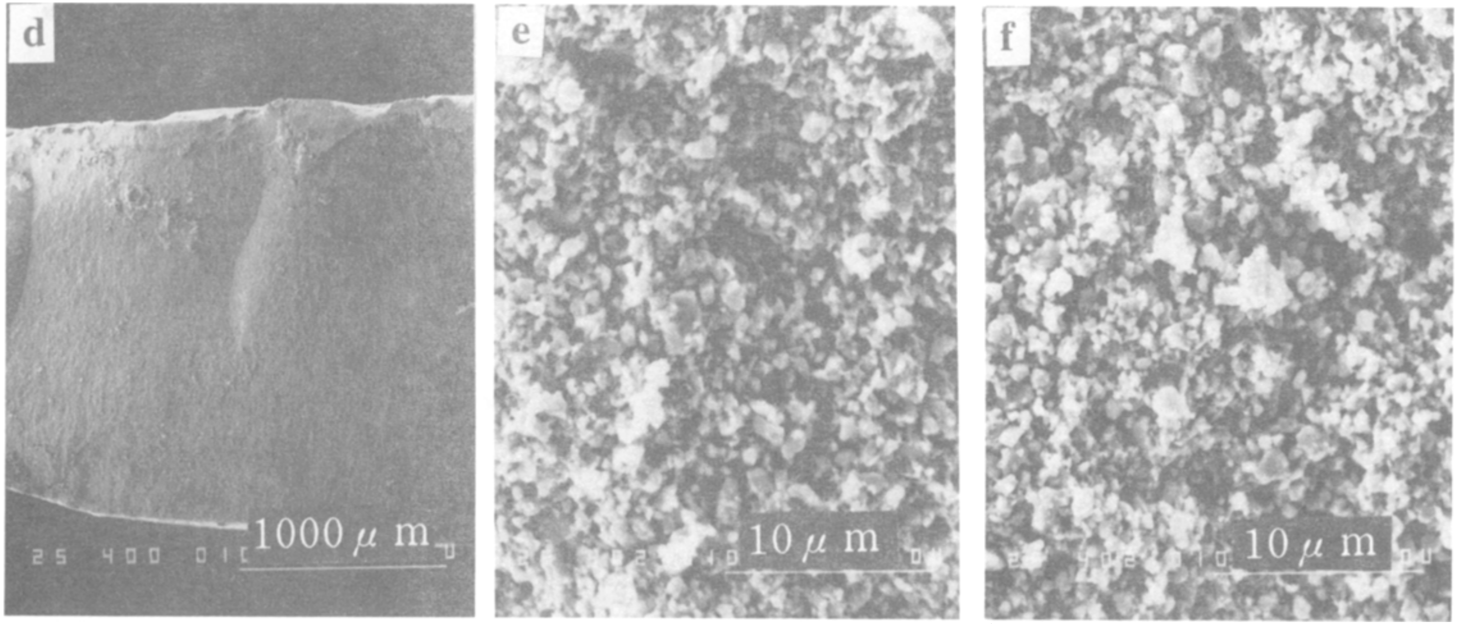

Fig. 7 Comparison of SEM microstructural analysis between different heating processes for a constant heating rate of 15°C min^{-1} and CRC. (d) CRC; cross-section, (e) CRC; near surface, (f) CRC; core

geneities in the pore sizes and densities were observed between the surface and the core structure. In contrast, due to the temperature control, which appeared to occur with only a moderate temperature increase in the CDRC, the examination results can be explained in terms of the optimum technique without any crack formation, and the pore sizes and densities between the surface and the core structure appeared very homogeneous.

The present approach ensures that an optimum burnout control (temperature – time schedule) is obtained automatically for each batch. This means that CDRC can be taken such that a considerable spread in product and binder burnout properties can be allowed without the need for reoptimization using a programming heating curve.

Conclusions

The CDRC technique proved to be a powerful tool to establish the optimum conditions for binder burnout of ceramic green body. One advantage is that CDRC enables a more precise control of the uniformity of the reaction environment, which broadly consists in controlling the product gas pressure, and the temperature and pressure gradients within the sample. In this technique, the rate of mass loss is monitored and changed into a rate of temperature increase such that it remains constant. By the present method, since a higher constant decomposition rate can be attained than that in the conventional method, the total burnout time can be reduced considerably. It is concluded that the mass data obtained simultaneously by means of TG give a good account of the control of the gas amount produced, which the CDRC maintains constant, and the debinding processes can prevent the formation of defects within the sample by the elimination of binders. Consequently, as the selectivity of available binders is broadened, it is highly possible to get more complex shapes or dimensions which are ordinarily difficult to mold. It is ensured that the CDRC experiment takes the minimum possible time compatible with obtaining the desired results. This technique will be used in an available large-scale system as a commercially industrial furnace, possibly making use of adaptive control.

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