Densification of reaction bonded O-sialon: A graphical experimental approach for optimising process parameters

G. C. BARRIS, D. KROUSE, C. HATCHWELL
Industrial Research, P. O. Box 31 310, Lower Hutt, New Zealand

A graphical experimental approach, which makes efficient use of experimental data, has been developed for optimising conflicting interactions in a sequential two-stage process. The results are presented in the form of *feasibility graphs*, which provide valuable process design information, including a quantitative measure of the 'robustness' of the proposed process. This method has been developed here for selecting and optimising additives for sintering reaction bonded O-sialon ceramics, but has wider-ranging potential applications.
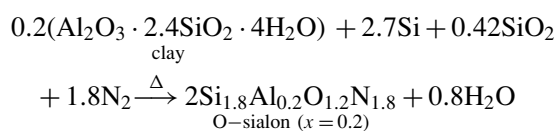© *2001 Kluwer Academic Publishers*

1. Introduction

The problem of optimising processes that involve conflicting interactions and multiple interdependent variables is frequently encountered in all branches of science. A rigorous approach to understanding and optimising such processes would normally require the collection and interpretation of a very large matrix of experimental data. Understandably, much attention has been directed at developing tools to provide the required information from a reduced set of experiments. Here, a new experimental design is developed for the particular case where a primary process variable is involved in conflicting interactions with each stage of an uncoupled sequential two-stage process. This approach makes efficient use of experimental data, and is based on the construction of *feasibility graphs*, which provide valuable process design information. An important feature of this method is that it provides a simple quantitative measure of the robustness of the proposed process, or its sensitivity to variations in production. This concept of robustness is one that is very important for evaluating and designing processes, but is often difficult to define.

The current method was developed for evaluating and optimising additives used for sintering reaction bonded O-sialon ($Si_{2-x}Al_xO_{1+x}N_{2-x}$, $x = 0$–0.2) ceramics. This process can be performed in a single firing, but occurs in two well-defined consecutive steps:

1. reaction of a compacted a mixture of clay, silicon and silica to form O-sialon ($x = 0.2$) by heating under nitrogen [1], e.g.:

$$0.2(Al_2O_3 \cdot 2.4SiO_2 \cdot 4H_2O) + 2.7Si + 0.42SiO_2$$
$$\underset{\text{clay}}{}$$
$$+ 1.8N_2 \xrightarrow{\Delta} 2Si_{1.8}Al_{0.2}O_{1.2}N_{1.8} + 0.8H_2O$$
$$\underset{\text{O-sialon } (x = 0.2)}{}$$

2. sintering of the reacted compact at a higher temperature to form a high density ceramic body.

To be successful the process needs to achieve both *complete reaction* and *high density*, and the reaction stage must be complete before sintering occurs; sintering restricts the access of nitrogen into the body preventing further reaction.

An external limitation that was imposed upon this process was that the sintering temperature should be less than $1600°C$. To sinter O-sialon at such low temperatures it is necessary to use sintering aids. However, common sintering aids such as alkaline earth or rare earth oxides hinder the formation of O-sialon, either by sintering the unreacted compact or sintering the outer reacted zone of the compact, restricting nitrogen access. Adding zirconia (ZrO_2) to the raw mixture along with the sintering aid reduces this inhibiting effect. The aim of this investigation is to identify a suitable sintering aid and to determine suitable concentration ranges for the sintering aid and the zirconia. Note that different sintering aids will tend to sinter the unreacted and reacted compacts at different temperatures.

Two other variables important to this process are the reaction temperature and sintering temperature. Increasing the reaction temperature generally improves the extent of reaction, but will aggravate premature sintering of the unreacted compact if sintering aids are present. Increasing the sintering temperature will improve the sintering, but for this investigation the sintering temperature is restricted to less than $1600°C$. As well as reducing premature sintering, adding zirconia promotes the O-sialon-forming reaction, permitting lower reaction temperatures and therefore lower sintering temperatures [2]. Zirconia also begins to promote sintering at temperatures close to $1600°C$. Understanding and optimising the complex interactions between the type of sintering aid, sintering aid content, zirconia content, reaction temperature and sintering temperature requires careful experimental design and interpretation.

The key feature of this process, which forms the basis of the current experimental design, is the conflicting

effect of the sintering aid on reaction and sintering. By assuming that the sintering temperature is independent of the reaction temperature (an assumption shown to be sufficiently valid), these interactions can be examined separately. The minimum concentration of sintering aid required to achieve adequate sintering can then be determined for different sintering temperatures, and the maximum concentration of sintering aid that still allows complete reaction can be determined for different reaction temperatures. These data are combined to construct feasibility graphs, and the process repeated for different sintering aids and for different zirconia concentrations.

2. Experimental procedure

Two sintering aids were chosen for this investigation, one of which was expected to be effective at higher sintering temperatures (CeO_2) and one which was expected to be effective at lower sintering temperatures (MgO). Zirconia was added as zircon powder ($ZrSiO_4$), with a reduction in the amount of added silica (SiO_2) in the raw mixture to retain the correct overall stoichiometry for forming O-sialon. Preliminary experiments had shown that there is little difference between adding zircon powder, which dissociates during the reaction to form zirconia, and adding zirconia powder. Zircon was chosen because it is less expensive and therefore more attractive as an industrial raw material.

For simplicity, the amount of zircon in each mixture is presented as the theoretical ratio of zirconia concentration to O-sialon concentration in the product ([ZrO_2]/[O-sialon]). [ZrO_2]/[O-sialon] ratios of 0.033, 0.106 and 0.190 (ca. 4, 12 and 20 wt% of the raw mixture) were chosen, the highest ratio representing complete replacement of added silica in the standard O-sialon mixture with silicon and oxygen from the zircon. MgO and CeO_2 were added in [sintering aid]/[O-sialon] ratios between: 0.0023 and 0.023. Control samples were prepared with no additives and with only zircon.

Appropriate mixtures of kaolin clay (<3% alkali and transition metal oxides, $d_m < 0.5$ μm), quartz powder (99.0%, $d_m = 1.45$ μm), silicon metal powder ($d_m = 1.8$ μm) and additives ($ZrSiO_4$ (Aldrich, 97.8%); MgO (SSB, LR); CeO_2 (Aldrich, 99.9%)) were dispersed by strring for ca. 45 min in IPA. The solvent was removed by rotary evaporation, and the mixtures were dried overnight at ca. 110°C. The dried mixtures were granulated by passing them through a 300 μm nylon filter cloth, and formed into blocks (ca. 70 × 40 × 15 mm) by uniaxially pressing at 4 MPa followed by isostatic pressing at 150 MPa. The blocks were dried overnight at ca. 110°C and allowed to cool in a desiccator before measuring the initial weights and dimensions.

The blocks were reacted in batches of 16 in a graphite pot inside a furnace flushed with oxygen free nitrogen at $5.6 \, 1 \cdot min^{-1}$ ($5 \, ml \cdot min^{-1} \cdot g^{-1}$). Within the pot the blocks were stacked on edge in four layers of four blocks, spaced to allow gas access. The samples were heated at $2°C \cdot min^{-1}$ with soaks at 580°C for 2 hours to allow for removal of structural water from the clay, and 1270°C for 2 hours to allow for initiation of the

reaction [1]. From 1270°C, the samples were heated at $1°C \cdot min^{-1}$ to the top temperature (1350°C, 1400°C or 1450°C) and held at temperature for 16 hours. After firing, the apparent porosity was measured for each sample, and the blocks were sliced in half to reveal the depth of O-sialon reaction front. A successful reaction was defined as complete reaction of a 15 mm thick body.

Those blocks which were completely reacted were then sintered by heating at $5°C \cdot min^{-1}$ to 1500°C, 1550°C or 1600°C for 2 hours in a closed graphite pot, in a furnace flushed with oxygen free nitrogen at $0.5 \, 1 \cdot min^{-1}$. Within the pot the blocks were stacked flat with a dusting of BN to prevent sticking. Approximately 4 g ($5 \, g \cdot l^{-1}$) of a milled 1 : 1 molar mixture of Si_3N_4 and SiO_2 was sprinkled around the blocks to provide a SiO-rich atmosphere inside the pot. After sintering, the apparent porosity of each block was measured. The criterion for successful sintering was a final body with zero apparent porosity.

3. Results
3.1. Reaction firings

Graphs of reaction depth versus additive concentration are given in Figs 1–3. Adding ZrO_2 to the reaction mixture promotes the O-sialon reaction (Fig. 1). When used in conjunction with the sintering aids (MgO and CeO_2), ZrO_2 reduces under-reaction caused by the sintering aid (Figs 2 and 3).

In Fig. 2, adding MgO to the reaction mixture inhibits the reaction, causing a decrease in the reaction depth which becomes more pronounced at higher reaction temperatures. With no MgO the reaction depth increases with increasing temperature, but with MgO present the reaction depth decreases with increasing temperature. This causes the crossover in the results shown in Fig. 2a. With a [ZrO_2]/[O-sialon] ratio of only 0.033, the inhibiting effect of the sintering aid prevents all of the blocks from reacting fully, but when the [ZrO_2]/[O-sialon] ratio is increased to 0.190, the reactivity of the blocks improves. Note that the blocks are only 15 mm thick so the top of the graph represents
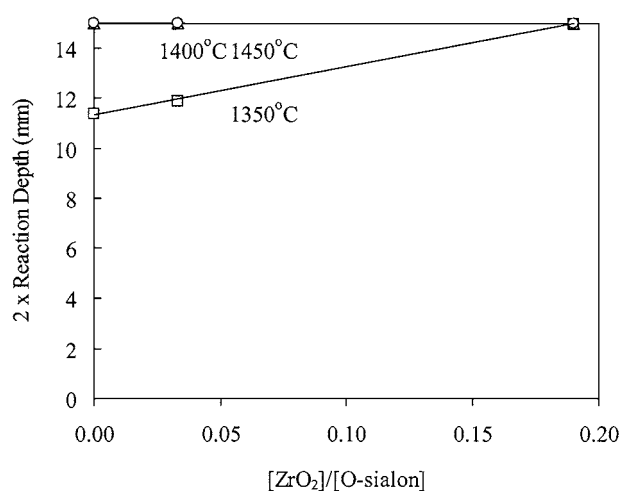

Figure 1 Effect of ZrO_2 concentration on the reaction depth for sample blocks reacted at 1350°C (□), 1400°C (Δ) and 1450°C (○).

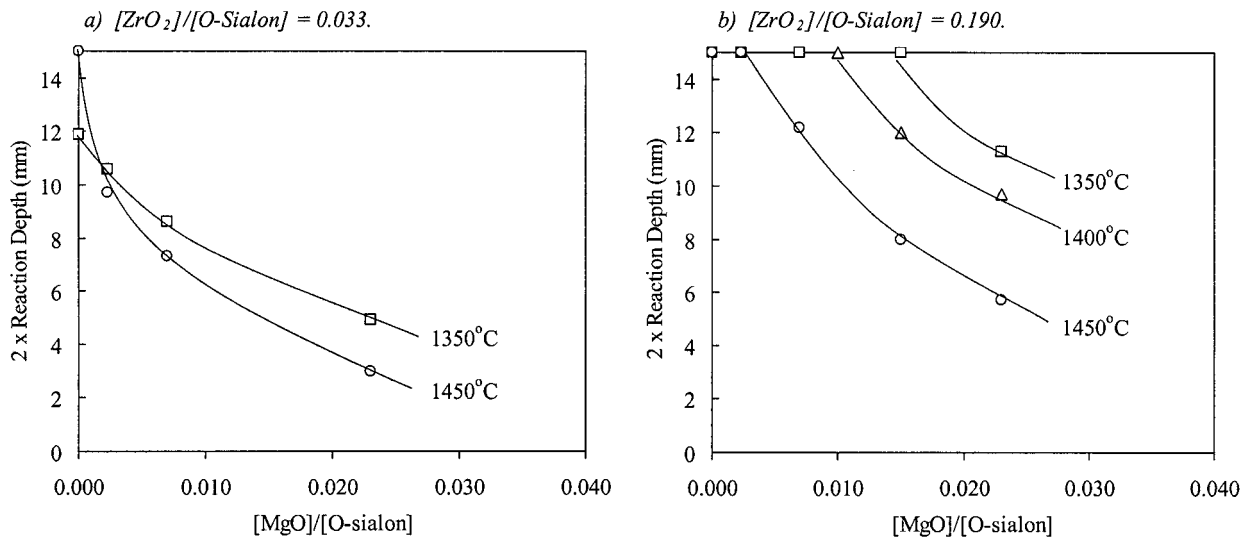a) [ZrO₂]/[O-Sialon] = 0.033.

b) [ZrO₂]/[O-Sialon] = 0.190.

Figure 2 Effect of MgO concentration on the reaction depth for sample blocks containing [ZrO₂]/[O-sialon] ratios of (a) 0.033 and (b) 0.190, and reacted at 1350°C (□), 1400°C (Δ) and 1450°C (○).
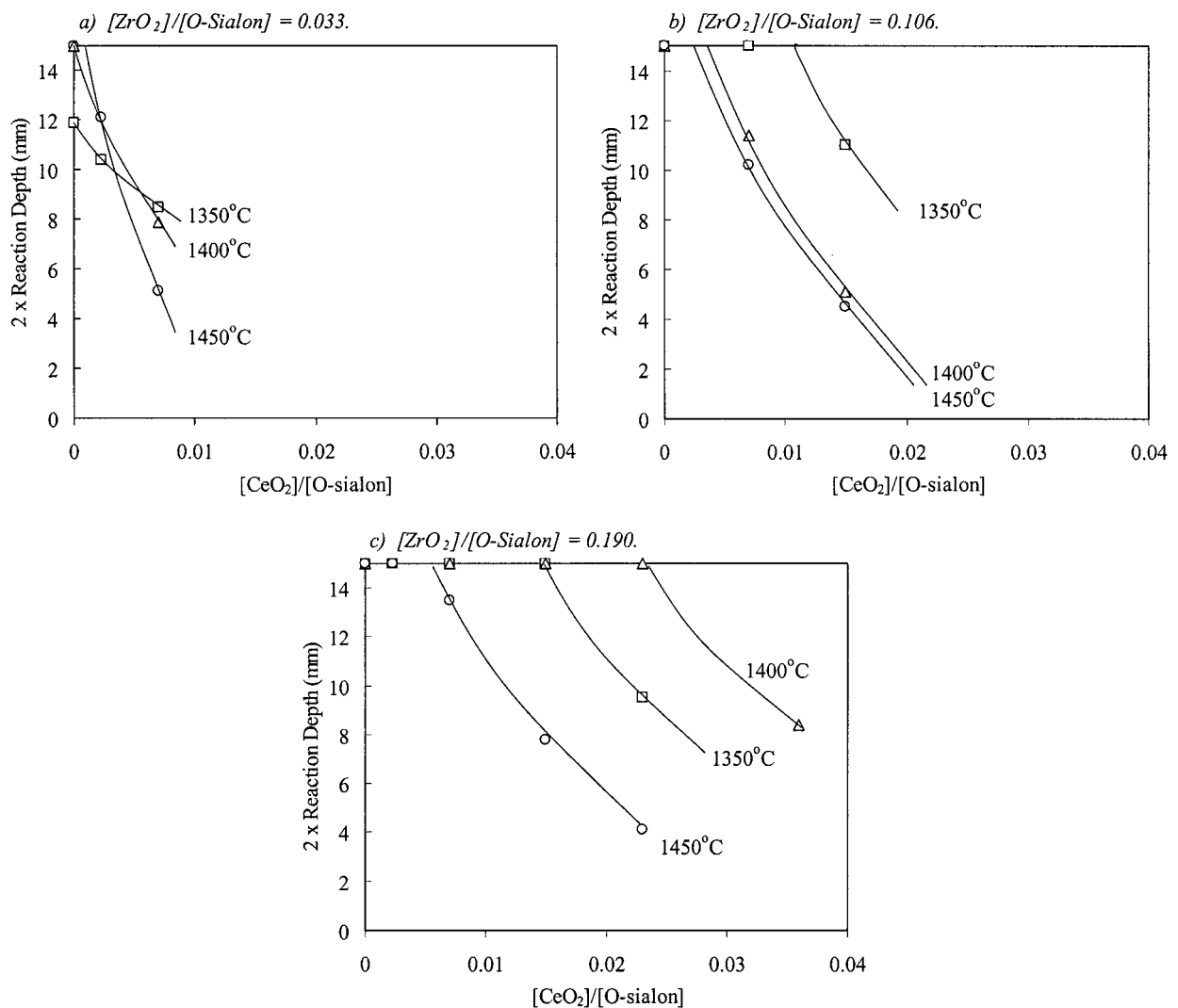
a) [ZrO₂]/[O-Sialon] = 0.033.

b) [ZrO₂]/[O-Sialon] = 0.106.

c) [ZrO₂]/[O-Sialon] = 0.190.

Figure 3 Effect of CeO₂ concentration on the reaction depth for sample blocks containing [ZrO₂]/[O-sialon] ratios of (a) 0.033, (b) 0.106 and (c) 0.190, and reacted at 1350°C (□), 1400°C (Δ) and 1450°C (○).

complete reaction. For [ZrO₂]/[O-sialon] = 0.190, the maximum [MgO]/[O-sialon] ratios that still permit full reaction throughout a 15 mm thick block can be estimated for each temperature (0.015 at 1350°C, 0.010 at 1400°C and 0.003 at 1450°C).

A similar pattern of behaviour was observed for blocks containing CeO₂, but with a notable difference. With a [ZrO₂]/[O-sialon] ratio of 0.190 (Fig. 3c), the extent of reaction *increases* from 1350°C to 1400°C but decreases again by 1450°C. This optimal reaction

temperature arises from the competing effects of increasing temperature promoting the reaction, and increasing temperature promoting inhibition of the reaction by the sintering aid. Presumably CeO_2 forms a higher temperature aluminosilicate eutectic than MgO (ca. 1355°C [3]), and therefore does not inhibit the reaction as severely at 1400°C. An optimal reaction temperature must also exist for MgO in Fig. 2b (close to 1350°C) because experience has shown that reactivity declines rapidly at lower temperatures. With a $[ZrO_2]/[O\text{-sialon}]$ ratio of only 0.033, all of the blocks containing CeO_2 were under-reacted (Fig. 3a). However for $[ZrO_2]/[O\text{-sialon}]$ ratios of 0.106 and 0.190, the maximum $[CeO_2]/[O\text{-sialon}]$ ratios that still allow full reaction could be estimated for each temperature (0.011 at 1350°C, 0.004 at 1400°C and 0.003 at 1450°C when $[ZrO_2]/[O\text{-sialon}] = 0.106$; 0.015 at 1350°C, 0.023 at 1400°C and 0.006 at 1450°C when $[ZrO_2]/[O\text{-sialon}] = 0.190$).

3.2. Sintering firings
Samples cut from the fully reacted blocks from Section 3.1 were sintered at 1500°C, 1550°C or 1600°C. Graphs of the apparent porosity of the sintered blocks versus additive concentration are given in Figs 4 and 5. Note that the sintering data are restricted to compositions that gave full reaction. None of the blocks with $[ZrO_2]/[O\text{-sialon}] = 0.033$ plus sintering aid, and only one of the blocks with $[ZrO_2]/[O\text{-sialon}] = 0.106$ plus sintering aid were fully reacted, so there are no sintering results for these blocks.

Fig. 4 shows that ZrO_2 does have a small influence on sintering at higher temperatures (1550°C and 1600°C), particularly at low concentrations.

Apparent porosities of the reacted and sintered blocks containing MgO and CeO_2 with a $[ZrO_2]/[O\text{-sialon}]$ ratio of 0.190 are plotted in Fig. 5a and b. The symbols indicate the temperatures at which the blocks were reacted, and the sizes of the symbols relate to the sintering temperature. For the poorly sintered blocks, the apparent porosity is strongly affected by the reaction temperature. However, as sintering increases (with increasing sintering aid and higher temperatures), the influence of the reaction temperature on the final porosity becomes very small. Under these conditions, there is little direct interaction between the reaction and sintering temperatures. This supports the earlier assumption that the reaction and sintering stages of the process are sufficiently uncoupled to be treated separately.

In Fig. 5, curves have been fitted to the data for each sintering temperature, and the point where each of these curves meets the x-axis indicates the minimum amount of sintering aid required to achieve zero apparent porosity ($[MgO]/[O\text{-sialon}] = 0.09$ at 1500°C, 0.029 at 1550°C and 0.013 at 1600°C; $[CeO_2]/[O\text{-sialon}] = 0.045$ at 1500°C, 0.019 at 1550°C and 0.008 at 1600°C). In some cases, because of the restricted data, this requires bold extrapolation, and these particular results should be treated with caution.
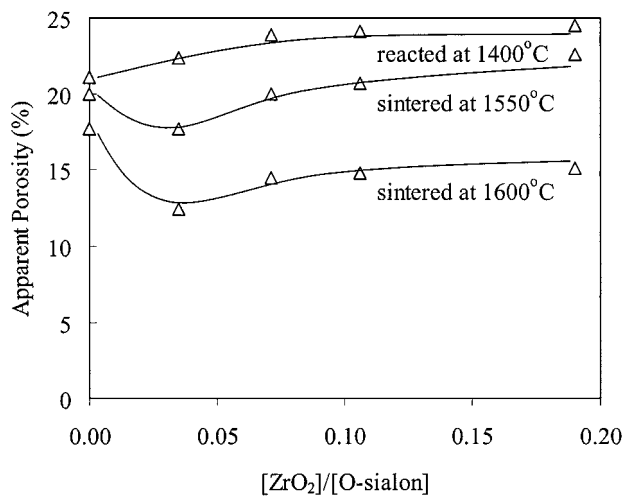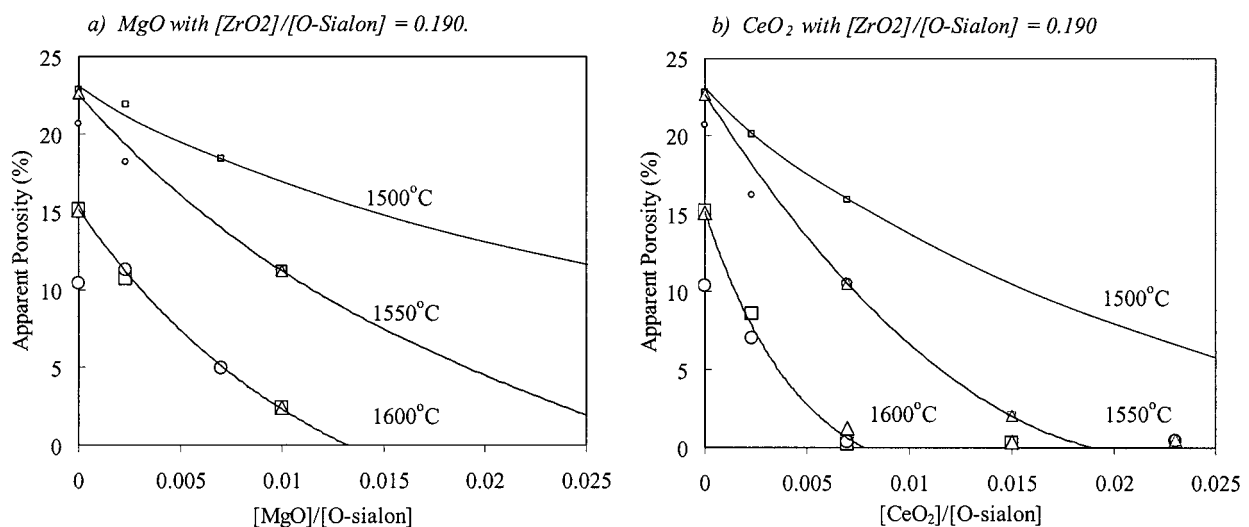

Figure 4 Effect of ZrO_2 concentration on the apparent porosity of sample blocks reacted at 1400°C and sintered at 1550°C and 1600°C.

Figure 5 Effect of (*a*) MgO and (*b*) CeO_2 on the apparent porosity of sample blocks with $[ZrO_2]/[O\text{-sialon}] = 0.190$, reacted at 1350°C (□), 1400°C (△) and 1450°C (○) and sintered at 1500°C (small symbols), 1550°C (medium symbols) and 1600°C (large symbols).

3.3. Feasibility graphs

For MgO and CeO_2 the minimum amounts of sintering aid required to achieve zero apparent porosity at each sintering temperature (from *Section 3.2.*), along with the maximum amounts of sintering aid that still permit full reaction at each reaction temperature (from *Section 3.1.*) are plotted as *feasibility graphs* in Fig. 6. Note that the results presented in these graphs should be regarded with appropriate caution because the data relies upon the interpolations and extrapolations made in Figs 2, 3 and 5.

The feasibility graphs in Fig. 6 allow *feasible concentration ranges* of sintering aid and *minimum feasible sintering temperatures* to be identified for each sintering aid. The feasible range is defined by the minimum amount of sintering aid required to achieve zero porosity (l) and the maximum amount of sintering aid that will still allow full reaction (h) over the complete range of reaction and sintering temperatures. The minimum feasible sintering temperature is defined as the minimum temperature at which a block with the maximum feasible sintering aid (h) can be sintered to zero apparent porosity. These two parameters, the feasible range and minimum feasible sintering temperature, provide
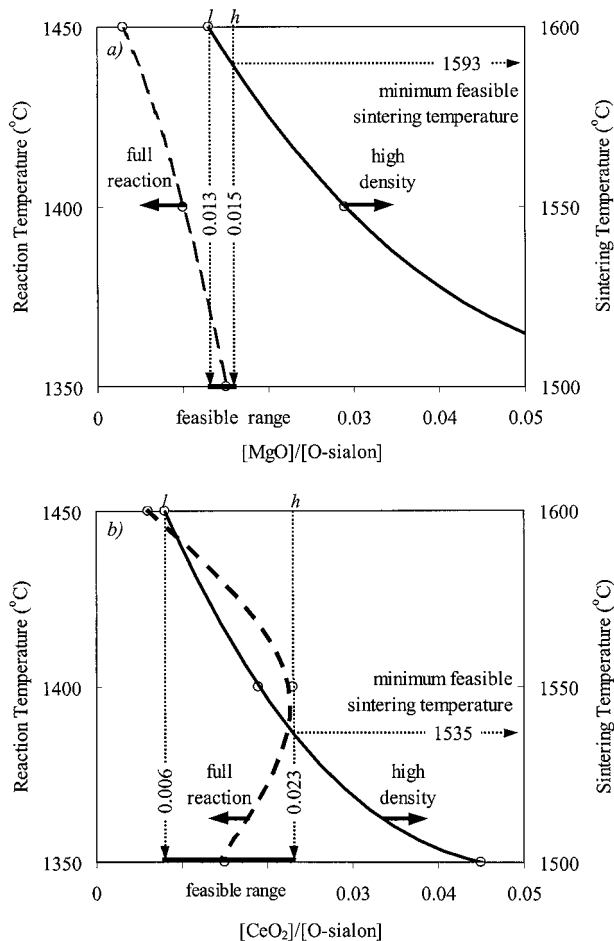
excellent tools for evaluating the performance of different sintering aids.

For a given sintering aid, the extent of the feasibility range indicates the robustness of the proposed reaction bonding-sintering process. For MgO, the feasible range is extremely small ([MgO]/[O-sialon] = 0.013 to 0.015) and slight variations in production could cause product failure. In comparison, the feasible range for CeO_2 is much larger ([CeO_2]/[O-sialon] = 0.006 to 0.023) and allows significant scope for variations in production. The minimum feasible sintering temperature for MgO (1597°C) is also much higher than for CeO_2 (1535°C), making it a less attractive sintering aid. This is surprising because MgO was expected to promote sintering of O-sialon at lower temperatures than CeO_2, but the useful concentration range for MgO is restricted by the need for complete reaction.

As well as allowing different sintering aids to be evaluated, the feasibility graphs in Fig. 6 provide an excellent tool for process design. For example, for a given concentration of sintering aid (s), suitable ranges of reaction and sintering temperatures can be read off the appropriate feasibility graph as shown in Fig. 7. For a robust process, the most suitable values for the sintering aid concentration, reaction temperature and sintering temperature will be near the centres of these ranges.

The feasibility graphs shown in Fig. 6 are for samples with [ZrO_2]/[O-sialon] = 0.109. For CeO_2, as the [ZrO_2]/[O-sialon] ratio is varied from 0.033 to 0.106 to 0.190, the estimated maximum feasible CeO_2 concentration (h) increases from 0.001 to 0.011 to 0.023. Unfortunately no sintering data is available for samples with [ZrO_2]/[O-sialon] = 0.033 and 0.106, but Fig. 4 shows that ZrO_2 has only a small effect on sintering, so the maximum feasible CeO_2 concentration (l) is unlikely to vary significantly with [ZrO_2]/[O-sialon]. Assuming this is the case, Fig. 8 shows the useful combinations of [ZrO_2] and [CeO_2] which will give a successful product; the region where [CeO_2]/[O-sialon] is greater than l and less than h. This graph is based on a succession of approximations and interpolations, but is still useful as a guide.

Figure 6 Feasibility graphs for bodies containing (*a*) MgO and (*b*) CeO_2 with [ZrO_2]/[O-sialon] = 0.190, showing the maximum concentrations of sintering aid that still permit full reaction (dashed lines), and the minimum concentrations of sintering aid required to achieve zero apparent porosity (solid lines). The symbols h and l indicate highest and lowest feasible concentrations of sintering aid which will allow both full reaction and zero apparent porosity.
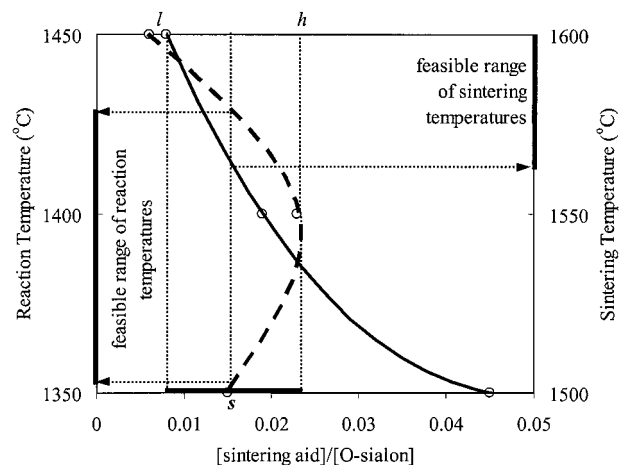

Figure 7 Determining suitable reaction and sintering temperatures for a given sintering aid concentration (*s*).
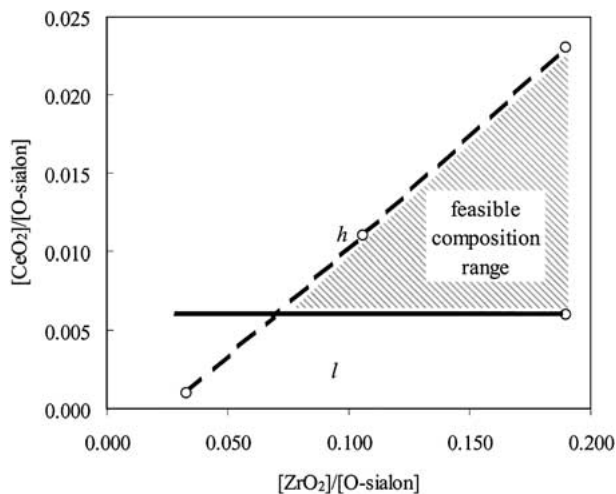
Figure 8 Range of feasible compositions for blocks containing CeO_2 and ZrO_2.

4. Conclusions

A graphical experimental design has been developed to select and optimise combinations of additives for sintering reaction bonded O-sialon. The additives include a sintering aid to promote sintering, and ZrO_2 to reduce the inhibiting effect of the sintering aid on the O-sialon-forming reaction. The experimental approach developed here is based around the conflicting interactions between the sintering aid and the reaction and sintering stages of the process. It makes efficient use of experimental data, and the results are presented in a graphical form, which enables simple selection of optimum process conditions.

As part of the analysis, *feasible concentration ranges* and *minimum feasible sintering temperatures* have been determined for two possible sintering aids (MgO and CeO_2), and have proved useful for evaluating their effectiveness. With $[ZrO_2]/[O\text{-sialon}] = 0.190$, the feasible range of MgO concentrations is very small ($[MgO]/[O\text{-sialon}] = 0.013$ to 0.015), indicating a 'knife-edge' process, whereas the feasible range for CeO_2 is much larger ($[CeO_2]/[O\text{-sialon}] = 0.006$ to 0.023) indicating a much more robust process. The minimum feasible sintering temperature for CeO_2 (1535°C) is also much lower than for MgO (1593°C). CeO_2 is therefore a much more desirable sintering aid. The range of suitable CeO_2 and ZrO_2 concentrations giving both full reaction and zero apparent porosity has also been identified.

The experimental approach developed here has proved to be an excellent tool for process design, and could be useful in a variety of situations that involve a sequential two-stage process and conflicting interactions.

References

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