Microwave assisted preparation and sintering of Al_2O_3, ZrO_2 and their composites from metalorganics

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Controlled pyrolysis of $Al(OBu^s)_3$, $Zr(OPr^n)_4$ and their mixtures in ethyl acetate induced using microwaves of 2.45 GHz frequency has been carried out. Microwave irradiation yields second-stage precursors for the preparation of respective oxides and their composites. It is observed that the microwave irradiation has a directive influence on the morphology of the ultimate oxide products. Al_2O_3, ZrO_2 and the two composites 90% Al_2O_3–10% ZrO_2 and 90% ZrO_2–10% Al_2O_3 are also found to be sintered to very high densities within 35 min of microwave irradiation by the use of β-SiC as a secondary susceptor.

Use of microwaves for the synthesis and processing of ceramic materials has attracted much attention recently. Microwave methods offer several advantages such as unique synthetic pathways, rapid heating rates, short processing durations, low power requirements, product uniformity, *etc.*[1–9] We have reported rapid and clean methods of synthesis of β-SiC[10] AlN,[11] MoO_2,[12] *etc.* using microwaves. We have also achieved very rapid sintering of ZrO_2–CeO_2 ceramics using microwave irradiation.[13] Metalorganics such as metal alkoxides, amides, imides, esters, *etc.* are generally employed as precursors for preparation of high purity ceramic powders. Use of alkoxides for the preparation of oxides through sol–gel techniques is widely established.[14] We have found that direct pyrolysis of metalorganics by conventional heating is unsuitable for powder production because it gives rise to non-uniform powder morphology. Several other technological problems have been reported to be associated with complete combustion using conventional heating methods.[15] However, when microwave irradiation is employed, very rapid and volumetric heating of metalorganic liquids is achieved. This can be expected to result in the formation of products of good structural and morphological uniformity. Microwave pyrolysis is known to be superior to conventional heating as it is self-regulating (microwave absorption characteristics change drastically once the susceptor is chemically altered) and therefore products having uniform particle size distribution can be expected to form. Further microwave heating can be used with advantage in the preparation of ceramic composites because of the differential susceptibilities (and hence the heating rates) of the different precursors used in their preparations to generate unique morphologies.

There is, however, very little known in the literature with regard to the use of microwaves in the preparation of ceramic powders and composites starting from organic precursors. In this paper we report our investigation on the unique influence of microwave irradiation of organic precursors during the preparation of ceramic composites of ZrO_2 and Al_2O_3. We have also examined the sintering of Al_2O_3–ZrO_2 composites by microwave irradiation and using a secondary heater.

Experimental

The experimental set-up used for microwave heating is an ordinary kitchen microwave oven (Batliboi Eddy, India) operating at a frequency of 2.45 GHz and a maximum output power level of 980 W. We have chosen as organic precursors $Al(OBu^s)_3$ and $Zr(OPr^n)_4$ (Fluka AG, H-9470, Buchs). For the preparation of the composites calculated quantities of the precursors were mixed in ethyl acetate and a uniform solution was made. However for the preparation of pure Al_2O_3 and ZrO_2, the precursors were used directly. Precursors were placed in Borosil glass beakers and in the first stage of the experiment precursors were decomposed by microwave irradiation in the oven for brief periods. Within a few minutes of heating (see later) we observed a rapid increase in the viscosity of the precursors leading to formation of a foam-like product in the beakers. Further exposure to microwaves did not cause any change in the foam-like products. There was no further increase in temperature or further decomposition. The oven was switched off and the foam-like powder was collected from the beaker.

Powders were characterized by X-ray diffraction studies (Philips X-ray Diffractometer, model PW 1050/70, Cu-Kα radiation, $\lambda = 1.5418$ Å), thermogravimetry and differential thermal analysis (CAHN Instruments, California, USA, heating rate 10 K min^{-1}, in air) and particle size distribution (Micrometer Photosize, SKC 2000) (Table 1).

In the second stage, the powders were heated to 1673 K (only to 1473 K in the case of Al_2O_3) in air, with a heating rate of 10 K min^{-1} in a conventional furnace (Thermolyne 46100). X-Ray diffraction studies were also performed on powders recovered from various temperatures. Transmission electron microscopy (JEOL-200CX TEM) was used to characterize the completely crystallized composites. The composite powders were ultrasonically dispersed in acetone medium. A drop of the suspension was placed on the holey carbon film, supported on a copper grid and the bright field images were recorded.

In the third stage, the crystallized powders were subjected to sintering again in the microwave oven by a method described earlier[13] using β-SiC as a secondary heater. Sintered products were characterized using scanning electron microscopy (Cambridge Instruments, Stereoscan 360).

Results and Discussion

Pure alkoxides

We first consider the effect of microwave irradiation of the metalorganics. Both $Al(OBu^s)_3$ (ASB) and $Zr(OPr^n)_4$ (ZIP) appear to produce fumes when irradiated and become viscous liquids. This results in the formation of foam-like solids designated ASB-F and ZIP-F respectively. The products were scraped from the beakers and the scraped materials were powdery (very fine particles) and are produced by irradiation after only a few minutes. Combined TG-DTA of the powders

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Table 1 Microwave preparation conditions and the compounds formed

starting material	exposure duration^a/min	product	colour	particle size/μm
Al(OBu^s)$_3$	7+7+7+7	Al_2O_3	white	0.72
Zr(OPr^n)$_4$	7+7	ZrO_2	yellowish white	0.41
Al(OBu^s)$_3$+Zr(OPr^n)$_4$+MeCo$_2$Et +MeCo$_2$Et	7+7+7+7	90Al_2O_3–10ZrO_2	white	0.75
Al(OBu^s)$_3$+Zr(OPr^n)$_4$+MeCO$_2$Et	7+7	10Al_2O_3–90ZrO_2	yellowish white	0.73

[a] The microwave power (560 W) was briefly interrupted every 7 min to examine the nature of the contents in the beaker.

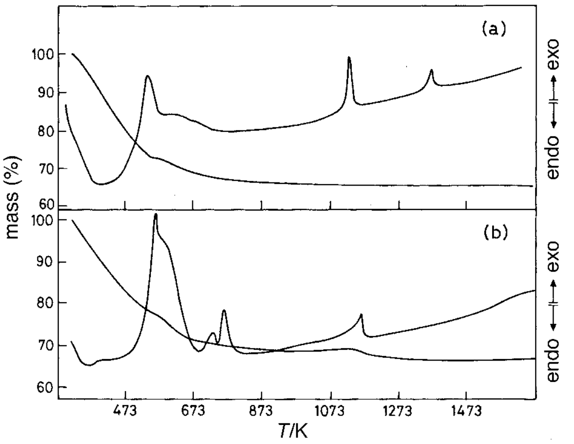

Fig. 1 Combined TG-DTA of microwave obtained powders of (a) ASB-F and (b) ZIP-F (see text for definition of ASB-F and ZIP-F)

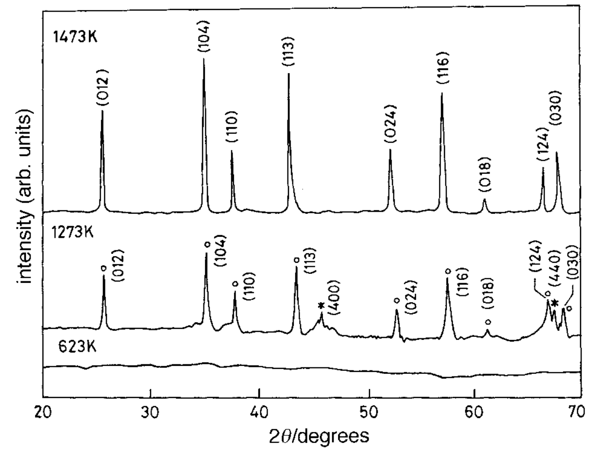

Fig. 2 X-Ray diffractogram of ASB-F heated to various temperatures (Cu-Kα radiation, $\lambda = 1.5418$ Å; ○, α-Al_2O_3; *, γ-Al_2O_3)

is shown in Fig. 1. The loss of mass for ASB-F is gradual and most of the mass loss (25%) occurs below 500 K, corresponding to the first fairly large endotherm in the DTA. The remaining part of the mass loss occurs well below 873 K which corresponds to the region of a minor exotherm in DTA. The mass of the residual product is 65% of the original and remains constant up to 1473 K. The DTA suggests that there are two smaller exotherms in this region occurring at 1173 and 1273 K, respectively. For ZIP-F the first endotherm is rather shallow and extends to *ca.* 493 K and the mass loss is *ca.* 21%. The remaining mass loss occurs in small shallow steps and no further loss occurs beyond 1173 K. These step-like losses are associated with one large initial and two smaller subsequent exotherms.

The first endotherm observed during heating of both ASB-F and ZIP-F can be associated with the loss of water (H_2O). The total mass loss for ASB-F (35%) is almost equal (34.6%) to the mass loss expected if ASB-F is $Al(OH)_3$. The negligible difference may be due to residual organics which are burnt out in the region 473–673 K. However, for ZIP-F the exotherm in this region is large and the final yield is only 67%, which is much less than would be expected if ZIP-F corresponded to $Zr(OH)_4$ (77.4%). Thus, microwave-irradiated material ZIP-F contains a significant proportion of undecomposed organics. It was noted in the IR spectrum (not shown) that there was a significant amount of residual ZIP in the ZIP-F. The spectra of both ASB-F and ZIP-F exhibited H_2O related absorptions at 3300 and 1600 cm^{-1}.

We have examined XRD of the initial and heated powders of ASB-F and ZIP-F. Both are amorphous up to 623 K (Fig. 2 and 3). For ASB-F the XRD of the sample heated to 1273 K (just above the second exotherm in DTA of Fig. 1) was found to be crystalline and could be indexed to a mixture of α- and γ-Al_2O_3. A cubic unit cell ($a = 7.90$ Å) and a trigonal unit cell ($a = b = 4.758$ Å, $c = 12.991$ Å) were used to index the γ- and α-Al_2O_3 structures respectively. The high-temperature small exotherm around 1373 K observed for alumina can be associated with a transition of the small amount of γ-Al_2O_3 to α-Al_2O_3 since samples cooled from 1473 K gave XRD typical of α-Al_2O_3 (Fig. 2) only. Generally, under conventional conditions, the transition of γ- to α-Al_2O_3 occurs at 1373 K.[16] For ZIP-F, however, the major product was found to be cubic (c) ZrO_2 at 843 K [with monoclinic (m) ZrO_2 as a minor phase]. A cubic unit cell ($a = 5.09$ Å) was used to index cubic ZrO_2 while a monoclinic unit cell ($a = 5.146$ Å, $b = 5.213$ Å, $c = 5.311$ Å, $\beta = 99.20$) was used to index monoclinic ZrO_2.

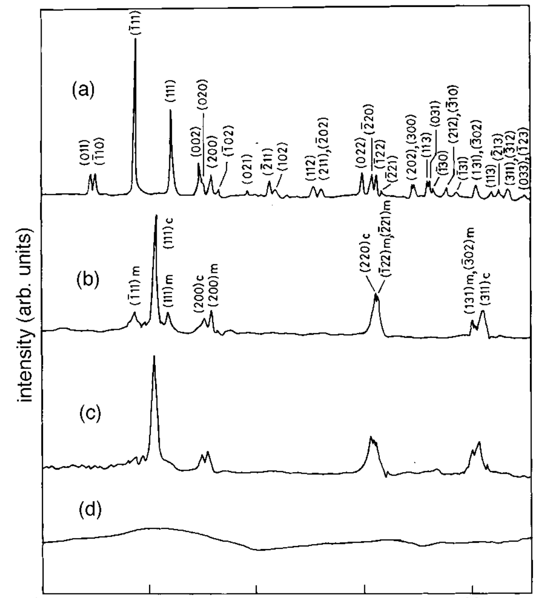

Fig. 3 X-Ray diffractogram of ZIP-F heated to various temperatures (Cu-Kα radiation, $\lambda = 1.5418$ Å). (a) 1673 K, (b) 843 K, (c) 743 K, (d) 623 K.

Conventionally, under atmospheric conditions, ZrO_2 undergoes the following transformation sequences before it melts,[17]

$$\text{monoclinic} \xrightarrow{1443\ \text{K}} \text{tetragonal} \xrightarrow{2646\ \text{K}} \text{cubic} \xrightarrow{2953\ \text{K}} \text{liquid}$$

A metastable cubic phase of ZrO_2 was also observed at 673 K before the formation of stable monoclinic ZrO_2 at 1273 K in crystallization studies of zirconia gels.[18]

The crystallization appears to start around 700 K, just at the beginning of the first of the twin peaked exotherms in the DTA (Fig. 1). In fact, the XRD at 743 K (middle of the twin exothermic peaks) reveals incomplete crystallization. Samples heated to 1673 K revealed that only monoclinic ZrO_2 (Fig. 3) was present. We are therefore led to believe that the exotherm at 1173 K is associated with a cubic to monoclinic transformation of ZrO_2 while the exotherm in the region 723–773 K could be largely due to burning (oxidation) of either strongly attached organic fragments or oxidation of any residual carbon formed during the rapid initial combustion of organics in insufficient oxygen.

The above observation suggests that the alkoxides ASB and ZIP do not decompose in a single step to their respective oxides by microwave irradiation. The extent of residual organics in the amorphous powder products ASB-F and ZIP-F are also different (higher in ZIP-F) at the stage where microwave interaction almost ceases. Both ASB-F and ZIP-F contain some water and their masses suggest that there is enough for formation of $Al(OH)_3$ ($AlOOH \cdot H_2O$?) or $Zr(OH)_4$ [$ZrO \cdot (OH)_2 \cdot H_2O$? or $ZrO_2 \cdot 2H_2O$?]. In the second stage of furnace heating ASB-F and ZIP-F are converted to oxides at higher temperatures. The various steps leading to the formation of oxides are visualized as follows.

$$Al(OBu^s)_3 \xrightarrow{\text{microwaves}} [Al(OH)_3(AlOOH \cdot H_2O?) +$$

$$\text{little organic residue}] \xrightarrow{623\ \text{K}} \text{amorphous } Al_2O_3$$

$$\xrightarrow{1273\ \text{K}} [\alpha\text{-}Al_2O_3 + \gamma\text{-}Al_2O_3] \xrightarrow{1473\ \text{K}} \alpha\text{-}Al_2O_3$$

$$Zr(OPr^n)_4 \xrightarrow{\text{microwaves}} [Zr(OH)_4? \text{ (or } ZrO \cdot (OH)_2 \cdot H_2O$$

$$\text{or } ZrO_2 \cdot 2H_2O\ ?) + \text{organic residue}] \xrightarrow{623\ \text{K}}$$

$$\text{amorphous } ZrO_2 \xrightarrow{843\ \text{K}} [c\text{-}ZrO_2 + m\text{-}ZrO_2] \xrightarrow{1173\ \text{K}} m\text{-}ZrO_2$$

Thus ASB-F and ZIP-F are actually second-stage precursors for the formation of oxides.

Mixture of alkoxides

We have also noted in our experiment that the time required to obtain the dry foam-like product ASB-F was 28 min compared to only 14 min for ZIP-F. We attribute this to the significant difference in the microwave susceptibilities of two alkoxides themselves since the decomposition products do not couple to microwaves effectively. However the difference may also arise from different thermal stabilities of the alkoxides. The presence of a high level of remnant organics in ZIP (which decomposes faster) suggests that thermal instability may not be the cause. On both counts we expect microwave decomposition of the alkoxide mixture to produce a mixture of fine amorphous powders since the microwave assisted decomposition rates are different. The tendency of ZIP to be associated with a greater proportion of remnant organics may also help differentiation of ASB-F and ZIP-F phases. Compositions of the two Al_2O_3–ZrO_2 composites examined were $90Al_2O_3$–$10ZrO_2$ (CA) and $90ZrO_2$–$10Al_2O_3$ (CZ) respectively. We found that the time required to obtain foam-like powders (second-stage precursors) was 28 min for the alumina-rich mixture (CA-F) and 14 min for the zirconia-rich mixture (CZ-F).

The powders CA-F and CZ-F were then directly heated to 1673 K and kept at that temperature for 2 h. The X-ray diffraction patterns of the resulting oxide composites are shown in Fig. 4. It is evident that, upon heating, CA-F gives a composite product which consists of tetragonal ZrO_2 particles (a tetragonal unit cell with $a = b = 5.12$ Å and $c = 5.25$ Å was used to index tetragonal ZrO_2) in an α-Al_2O_3 matrix while CZ-F gives an α-Al_2O_3 dispersion in monoclinic ZrO_2.

Fig. 5 shows transmission electron micrographs of CA and CZ composites. In the TEM of the CA composite, ZrO_2 particles (dark) are seen to be finely dispersed in α-Al_2O_3 matrix. The diameters of ZrO_2 particles vary from 3 to 35 nm. On the other hand in CZ composites only large crystallites of ZrO_2 were seen and Al_2O_3 particles could not be identified with certainty. The X-ray evidence from Fig. 4 however clearly suggests that formation of a ZrO_2–Al_2O_3 solid solution does not occur. We do not consider the possibility that CA-F and CZ-F are actually solid solutions which decompose to give rise to composites at higher temperatures because there are no reports of such ready formation of solid solutions during thermal decomposition of alkoxide mixtures.

We therefore note that microwave heating of the alkoxides influences the nature of the final products. This is due to differential microwave susceptibilities and to a certain extent differences in quantities of undecomposed organics. It has been observed by Yoshimatsu *et al.*[19] that a fine distribution of ZrO_2 particles can result by decomposition of a zircanoaluminium compound under optimum conditions. The procedure of Yoshimatsu *et al.*[19] and the present procedure can not be compared although the product morphologies are similar. The composite preparation is achieved here starting from homogeneous liquid mixtures of alkoxides and therefore a dehomogenization step must be involved in the formation of the observed composite. This we attribute tentatively to the differences in the microwave characteristics.

Microwave sintering

Another focus of this work has been to show that ceramics which are normally microwave inert at low temperatures such as Al_2O_3, ZrO_2 and ZrO_2–Al_2O_3 can still be sintered remarkably rapidly in microwaves by a technique which employs a

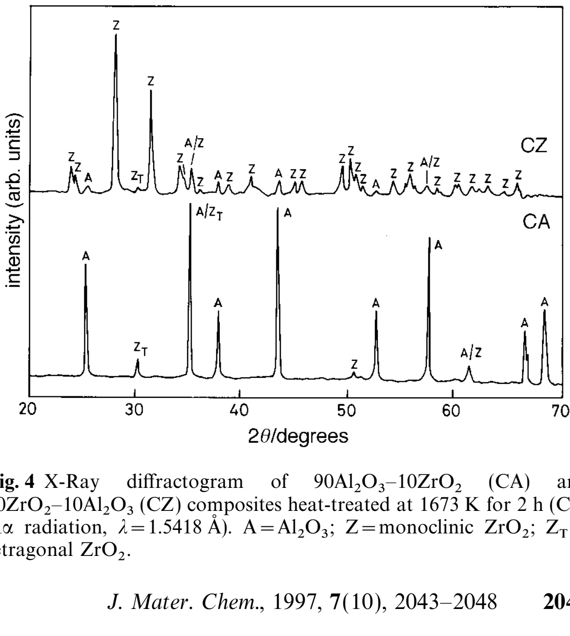

Fig. 4 X-Ray diffractogram of $90Al_2O_3$–$10ZrO_2$ (CA) and $90ZrO_2$–$10Al_2O_3$ (CZ) composites heat-treated at 1673 K for 2 h (Cu-Kα radiation, $\lambda = 1.5418$ Å). A = Al_2O_3; Z = monoclinic ZrO_2; Z_T = tetragonal ZrO_2.

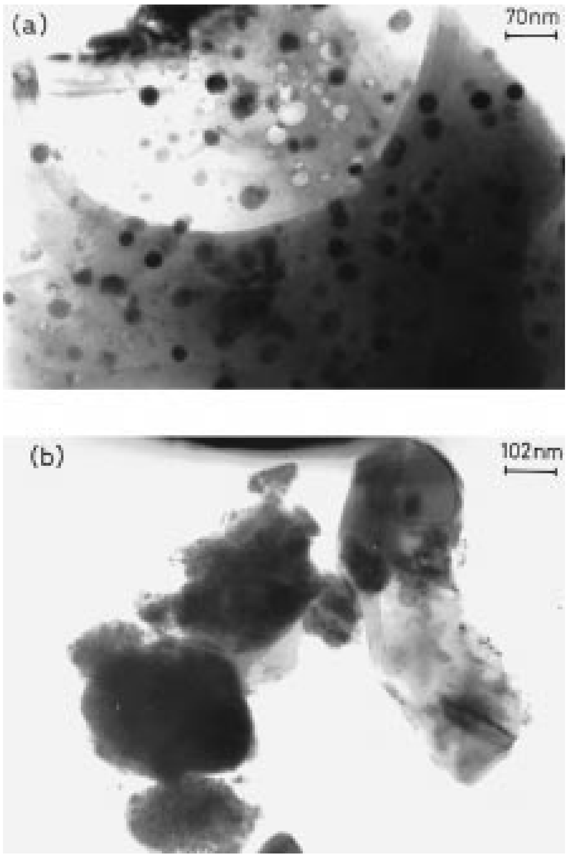

Fig. 5 TEMs of (a) CA composite (dispersion of ZrO_2 particles is seen clearly in the Al_2O_3 matrix), and(b) CZ composite

secondary heater. In this 'hitch-hiking' approach low-temperature microwave inert materials are embedded in other strongly microwave active materials (secondary heater) and subjected to microwave irradiation. The critical requirement is that the material of the secondary heater is chemically unreactive with the material to be sintered. In the present case Al_2O_3, ZrO_2 and Al_2O_3–ZrO_2 composite samples were first pelletized under 196 MN m^{-2} pressure to obtain 10 mm diameter pellets of approximately 3 mm thickness using 1% poly (vinyl alcohol) as a binder. These pellets were surrounded by β-SiC powder in a silica crucible (*ca.* 10 g of β-SiC is sufficient) and the crucible was placed inside a microwave oven. In the present set-up 35 min was required for complete sintering of the pellets.

Details of the microwave sintering procedure with the use of the secondary heater has been described earlier.[13] The temperature of β-SiC used as a secondary heater reaches initially about 1073 K. The temperature of the pellet also rises, as a consequence, to nearly 1000 K. Around this temperature the ceramic materials themselves couple well to microwaves. Efforts were made to monitor temperatures of the pellet surface by quickly interrupting the microwaves and inserting a Pt–Pt13%Rh thermocouple. The maximum temperatures of the pellets were usually attained after *ca.* 15 min of exposure and are given in Table 2. The densities of the pellets were also measured after 35 min of sintering (Table 2).

Pure Al_2O_3 could be sintered to $\geqslant$95% of its theoretical density in under 35 min using microwaves: this, we believe, is extraordinary. Pure ZrO_2 pellets sintered well but developed visible cracks upon cooling due to the well known tetragonal to monoclinic transformation. Pellets of Al_2O_3–ZrO_2 composites also sintered well but to a maximum of only *ca.* 90% theoretical density.

Alumina can be sintered to a high density when a small amount of MgO is added.[20] Addition of 3% Y_2O_3 with zirconia resulted in tetragonal zirconia polycrystals (TZP) having very good mechanical properties.[21] The effect of adding MgO to Al_2O_3 and Y_2O_3 to ZrO_2 on the microwave sintering was examined. Using sintering durations as above with the addition of 3% MgO as a sintering aid, Al_2O_3 was found to sinter to 97% of its theoretical density. ZrO_2 also sintered to 98% of its theoretical density with the addition of 3% Y_2O_3. SEM micrographs of sintered Al_2O_3 (without and with 3% MgO), ZrO_2 and the two composites (both with 3% Y_2O_3) are shown in Fig. 6 and the corresponding densities, sintering temperatures and other relevant data are given in Table 2. The flaky morphology of the sintered high density Al_2O_3 is similar in both cases, with or without the additives, and agrees well with the microstructures reported in the literature.[9] The microstructure of ZrO_2 consists of multifaceted particles with virtually complete elimination of enclosed porosity accounting for its high density. The SEM images of the sintered composites are quite similar to the morphology of the major components in the composite in their respective pure states. Particles of the two different phases in the composites, however, are not so clearly distinguished.

Conclusions

Two observations of this work are significant to ceramic science and both are related to the use of microwaves. First microwave irradiation has a direct influence on the structure of the initial powders obtained from metalorganic mixtures used as precursors in the preparation of composites. This eliminates the need to employ the rather slow and tedious sol–gel route to make composites starting from metalorganics. Also, the metalorganics upon microwave irradiation yield second-stage precursors for the preparation of ceramic composites. Secondly, the rate of sintering of composites in microwaves is fascinating in the novel 'hitch-hiking' heating process where use is made of a secondary microwave susceptor. It is possible to achieve very high densities of products in extremely short times.

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Table 2 Data related to sintering[a] of Al_2O_3, ZrO_2 and their composites by microwave irradiation

sample	green density/g cm^{-3}	sintered density/g cm^{-3}	relative density(%)
Al_2O_3	2.60	3.78	95
$Al_2O_3+3\%MgO$	2.58	3.85	97
ZrO_2	3.80	5.65	96
$ZrO_2+3\%Y_2O_3$	3.81	5.73	98
$(90Al_2O_3–10ZrO_2)+3\%\ Y_2O_3$	2.70	3.89	95
$(90ZrO_2–10Al_2O_3)+3\%Y_2O_3$	3.56	5.4	96

[a] Microwave power = 980 W, sintering duration = 35 min, maximum temperature = 1773 K.

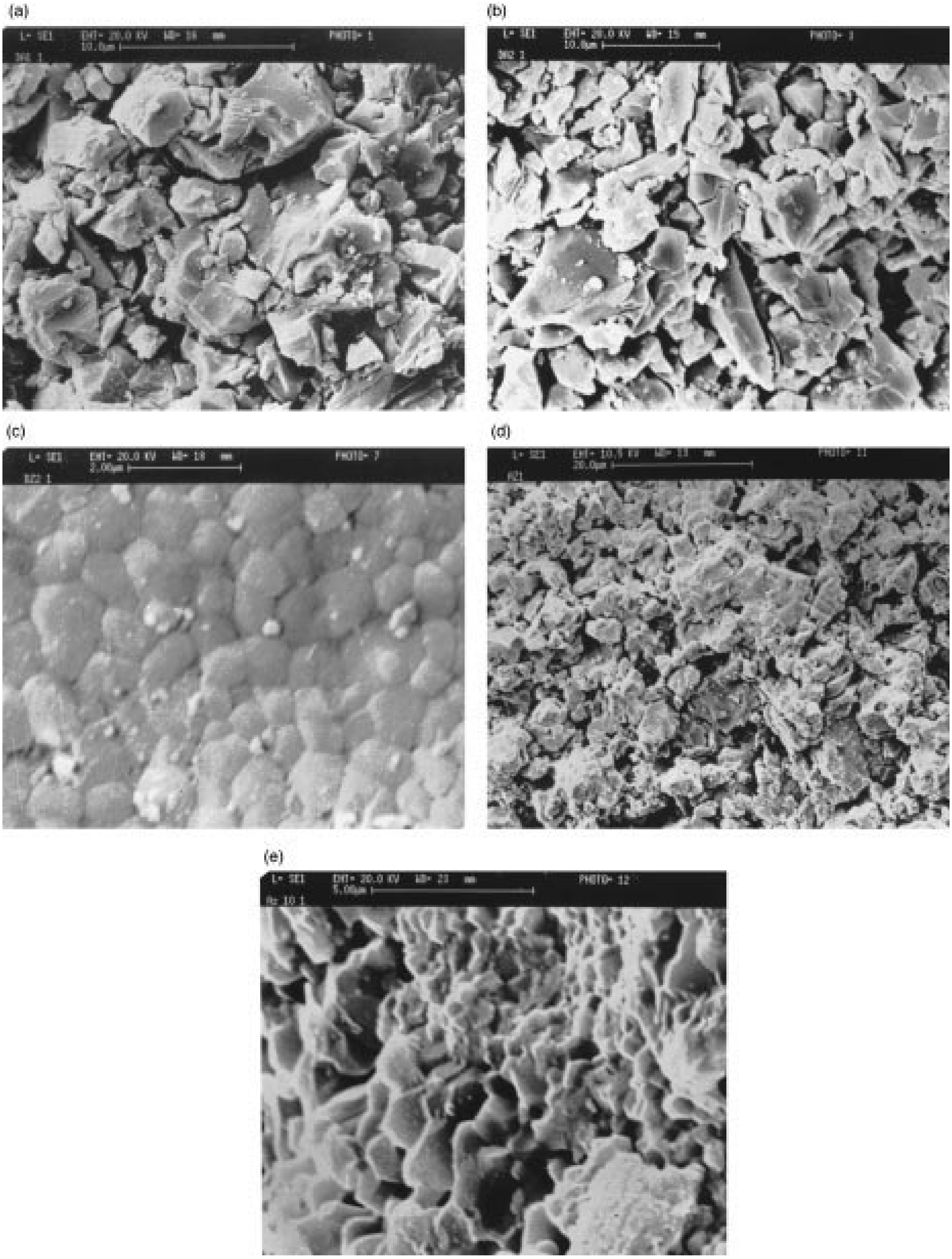

Fig. 6 SEMs of freshly fractured surfaces of microwave sintered (a) Al_2O_3, (b) Al_2O_3 (3% MgO), (c) ZrO_2 (3% Y_2O_3), (d) $90Al_2O_3$–$10ZrO_2$ and (e) $90ZrO_2$–$10Al_2O_3$ composites

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