JOURNAL OF MATERIALS SCIENCE 27 (1992) 2187–2192

Submicronic $MgAl_2O_4$ powder synthesis in supercritical ethanol

M. BARJ, J. F. BOCQUET, K. CHHOR, C. POMMIER
Laboratoire d'Ingéniérie des Matériaux et des Hautes Pressions (CNRS, LP 1311), Université Paris XIII, Avenue J. B. Clément, 93430 Villetaneuse, France

Submicronic $MgAl_2O_4$ powders have been synthesized by decomposition of the double alkoxide $Mg[Al(O\text{-}secBu)_4]_2$ in supercritical ethanol. The influence was studied of various experimental parameters (reaction time and temperature, reactional medium concentration and density) on the main characteristics of the obtained materials. Particularly, sample crystallinity and chemical composition, particle size distribution and mean diameter were investigated by X-ray diffraction, IR spectroscopy, laser scattering and electronic microscopy.

1. Introduction

In much ceramic processing, the most basic step is generally recognized to be the powder elaboration. The quality of the final material depends essentially on some basic properties of the powders to be sintered, such as high purity and chemical homogeneity, small particle size and narrow size distribution. Besides traditional mixing and grinding operations followed by solid-state reactions, non-conventional powder elaboration methods have recently been reviewed [1, 2]. Among these; new techniques using supercritical fluids have been proposed [3–5]. These techniques take advantage of the diffusion properties and the high solvent power of these phases, allowing rapid nucleation and precipitation of solid solute particles after expansion of supercritical solutions. The high density and low viscosity of supercritical fluids are also of interest, for the use of these fluids as reactive media [6].

The spinel $MgAl_2O_4$ is of technological interest particularly for refractory applications. However, solid-state reaction and sintering from single oxides require temperatures as high as 1400–1500 °C [7, 8]. Hydrothermal synthesis does not appear to avoid phase separation and decrease the sintering temperature [9]. Among other routes proposed recently are plasma spray deposition of oxides [10]; low temperature (500–800 °C) spray, and higher-temperature (3000 °C) decomposition of aqueous salt solutions [11]; combustion of metal nitrates and urea in carbohydrazide [12]; freeze-drying of sulphate solutions [13]; and controlled hydrolysis of metal alkoxides [14].

We have recently shown that the decomposition of organometallic compounds in a supercritical fluid can be a new route for submicrometre oxide powder elaboration [15]. We describe the conditions of the alkoxide $Mg[Al(O\text{-}secBu)_4]_2$ reaction in supercritical ethanol, and the influence of various experimental parameters on the obtained $MgAl_2O_4$ characteristics.

2. Experimental procedure

The double sec-butoxide $Mg[Al(OR)_4]_2$ used as starting material was prepared in the laboratory by a previously reported reaction [14] between sec-butanol and a stoichiometric mixture of aluminium and magnesium metals, in the presence of Hg_2Cl_2 as a catalyst. The single alkoxides $Mg(OC_2H_5)_2$ and $Al(OC_2H_5)_3$ are commercial Alfa products. The ethanol ($T_c = 243$ °C, $P_c = 6.13$ MPa) used as reactional medium has a purity better than 99.8%.

The laboratory-made high-pressure reactor was a blind stainless steel cylindrical tube (internal volume about 130 cm^3) with removable caps at each end. One was fitted out with devices allowing temperature and pressure measurements [15]. The observation of the powder formation was realized from a separate experiment in a high-pressure cylindrical optical cell (internal volume about 1 cm^3) closed by sapphire windows. The radiation coming from a He–Ne laser source were sent through the cell and scattered light at 90 ° was collected on a photomultiplier [16].

The obtained powders have been characterized by various techniques : chemical analysis, X-ray diffraction (XRD; Siemens diffractometer using Mo$K\alpha$ radiation), IR spectroscopy (IRS; Perkin Elmer 580), light scattering granulometry (Microtrac 7995–30, Leeds & Northrup), and electronic microscopy (Cambridge 5360).

3. Results

3.1. Metal alkoxide reaction in supercritical ethanol

Metal alkoxides are known to be highly reactive towards water, and thus must be handled with care. The magnesium and aluminium ethoxides are solid materials and poorly soluble in ethanol at room temperature. When heated in supercritical ethanol at about 350 °C, the magnesium derivative leads to the formation of a white crystallized MgO powder. In the same conditions, $Al(OC_2H_5)_3$ transforms into an amorphous solid which, after thermal treatment around 1100 °C, crystallizes as α-Al_2O_3. Differential thermal analysis (DTA) and thermogravimetric studies on these ethoxides have shown decomposition in two main steps, one of them occurring below 200 °C. It is then likely that in our reactor, some partial reaction occurred before the reactional medium was in a supercritical state.

The mixture of the two alkoxides in the stoichiometric ratio $Al/Mg = 2$, when heated at 360 °C in supercritical ethanol, leads to the formation of a white partly crystallized $MgAl_2O_4$ powder. In the reactional medium it is likely that a reaction between the two starting single alkoxides and ethanol first occurs, leading to the double complex $Mg[Al(OC_2H_5)_4]_2$, which further decomposes.

However, because of the solid ethoxides' low solubility at room temperature, and possible deviation with stoichiometry or chemical heterogeneity in the resulting powders, the available double alkoxide $Mg[Al(O\text{-}secBu)_4]_2$ was preferred as starting material. This compound is liquid at room temperature and highly soluble in ethanol, in which some ligand exchange has been demonstrated [17]. We have shown [15] that it decomposes in supercritical ethanol into a more or less crystallized powder according to the experimental conditions. This solid leads to the spinel $MgAl_2O_4$ after thermal treatment around 1100 °C.

The thermal stability of the double alkoxide in ethanol was studied using the 1 cm^3 high-pressure optical cell. The introduced volume (0.3 cm^3) of a solution at 10% corresponded roughly to the critical density of pure ethanol. The scattered light intensity was measured during heating the cell from room temperature up to 350 °C at about 0.5 °C min^{-1} and on cooling (about 0.1 °C min^{-1} between 350 and 240 °C). Fig. 1 shows that during heating, a first maximum on the signal intensity is observed around 250 °C, corresponding to the supercritical phase transition. At 283 °C, a sudden very large increase in scattered light occurs, associated with the formation of solid particles in the supercritical medium. Above about 290 °C, a decrease in the signal intensity indicates that the major phenomenon is now some settling of the powder on the reactor walls. This settling continues during cooling and the only anomaly observed is the reversed supercritical–subcritical phase transition. This experiment shows that the decomposition of the double alkoxide occurs effectively in the supercritical fluid, and that the formation of the solid particles takes place in a short time.

3.2. Elaboration of $MgAl_2O_4$ powder from $Mg[Al(O\text{-}secBu)_4]_2$

The influence of various experimental factors on the main characteristics of the obtained powders was studied. All the experiments were performed in the 130 cm^3 high-pressure stainless-steel reactor. The powders formed in the reactor were sedimented and then oven dried for 12 h at 95 °C before crystallographic, spectrometric and granulometric studies. Experimental conditions of some representative syntheses are summarized in Table I.

3.2.1. Influence of reaction time

Fig. 2 shows the XRD patterns of powders obtained at 360 °C for various residence times and a given filling in the reactor (runs 1–3, Table I). It is clearly seen that the just-formed solid particles are completely amorphous and that a rather limited structural organization of the spinel type is observed after about 1 h. No extra diffraction lines associated with the presence of single metal oxides are evinced. Chemical analyses show Al/Mg and O/Al ratios equal to 2.03 and 2.10, respectively, i.e. very close to that in $MgAl_2O_4$. It should be

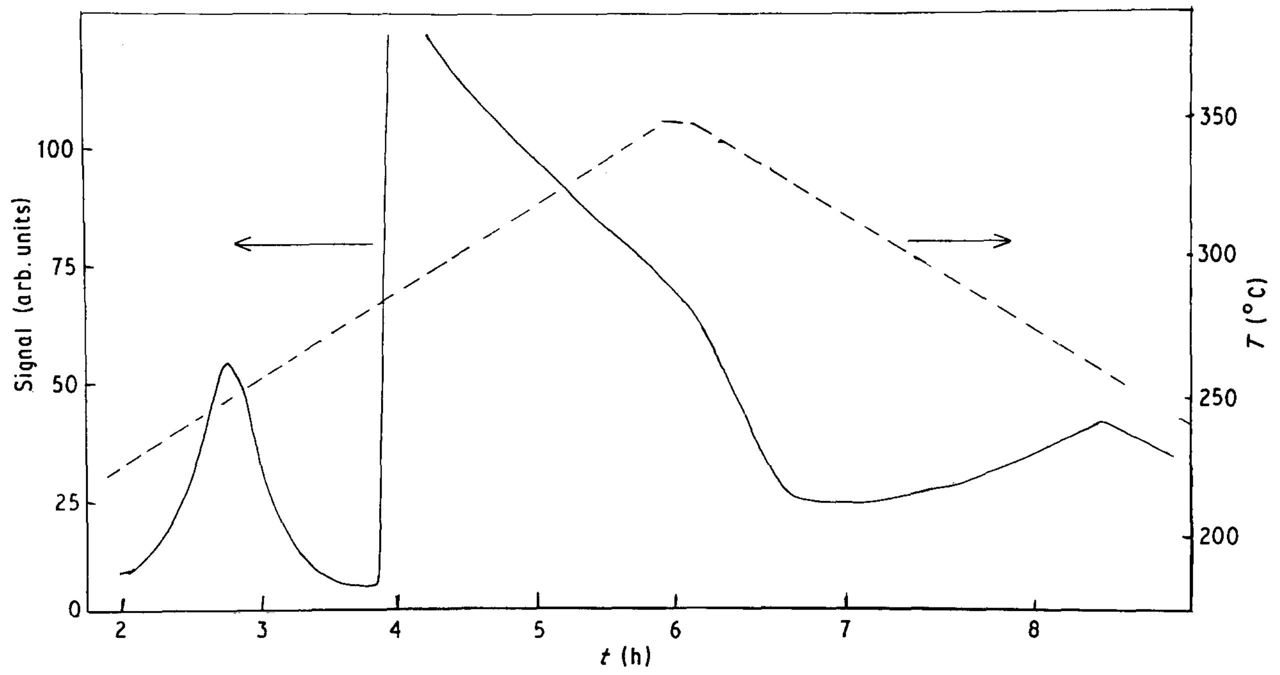


Figure 1 Decomposition of $Mg[Al(O\text{-}secBu)_4]_2$ and powder formation in ethanol from scattered light measurements.

TABLE I Experimental conditions of some representative syntheses in supercritical ethanol

Run Nb	Time (h)	Temperature (°C)	Pressure (MPa)	Volume of ethanol (cm^3)	Composition of solute (vol %)
1	0.5	360	16.2	36	11
2	1	360	16.2	36	11
3	3	360	16.2	36	11
4	7	295	9.8	32	9
5	4.5	360	15.3	32	9
6	6	407	22.5	32	9
7	4	395	20.1	32	16
8	4	360	15.8	32	11
9	4	365	21.3	50	10

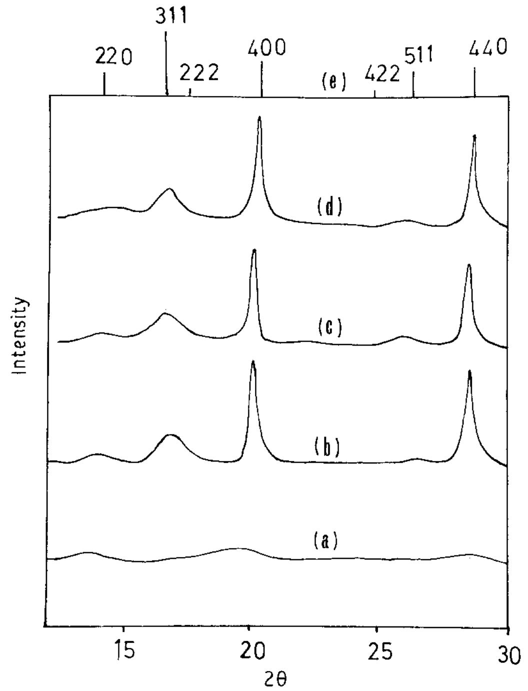


Figure 2 XRD patterns of powders obtained at 360 °C from $Mg[Al(O\text{-}secBu)_4]_2$ for (a) 0.5; (b) 1 and (c) 3 h; (d) from a stoichiometric mixture of $Al(OEt)_3$ and $Mg(OEt)_2$ for 3.5 h; (e) expected lines for spinel $MgAl_2O_4$ [18].

noted that the diagrams Fig. 2b and c are very similar to that of a powder obtained in similar conditions from a stoichiometric mixture of the two single alkoxides (Fig. 2d).

All diffraction patterns of partly crystallized samples show low intensity of the [3 1 1] line, although it is the major line in the spinel spectrum [18]. On the contrary, the [4 0 0] and [4 4 0] lines are the first to appear with significant intensity from the amorphous material. As shown below, it can be noticed that the elementary particle size is very low (some tens of nanometres). The above phenomenon could be explained either by a textural effect along the [4 0 0] and [4 4 0] directions during crystallization or by a long-range ordering first occurring preferentially for cations Mg^{2+} and Al^{3+}. Further structural studies are necessary to confirm this point.

The IR spectra show that the structural organization increasing with time is associated with a decrease in the intensities of O–H and C–H bands, and a narrowing in the 400–800 cm^{-1} frequency range corresponding to metal–oxygen vibrations (Fig. 3). It can then be attributed to a progressive departure of organic radicals from the surface of the solid particles, and a short-range oxygen organization around metal atoms.

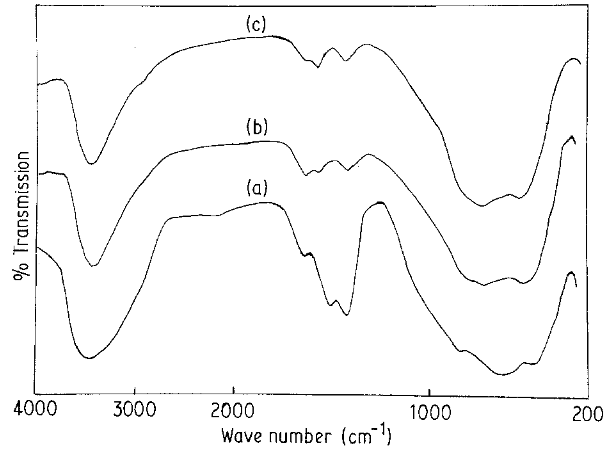
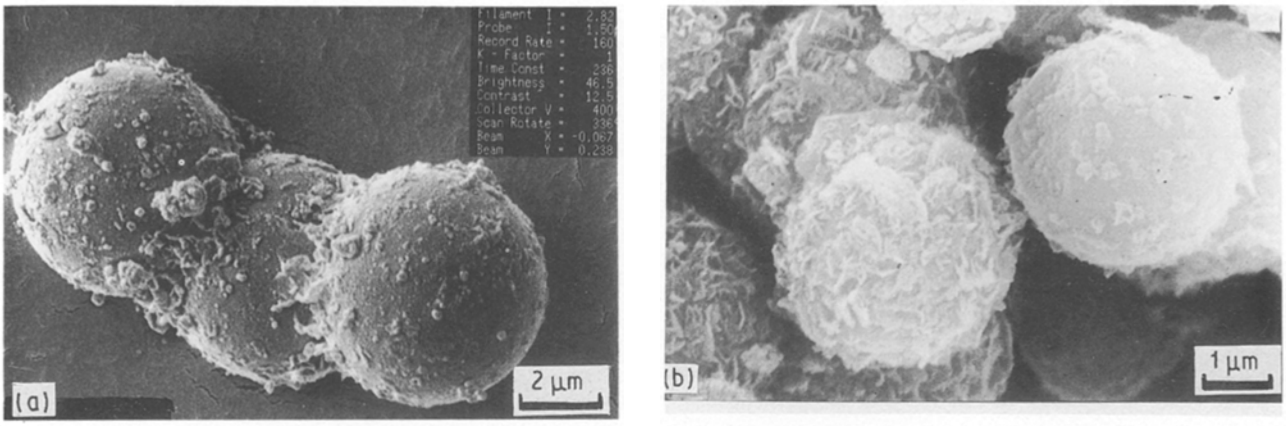


Figure 3 IR spectra of powders obtained from $Mg[Al(O\text{-}secBu)_4]_2$ at 360 °C during (a) 0.5; (b) 1; (c) 3 h.

Granulometric studies by laser light scattering show that both the mean diameter and size dispersion of the observed granules decrease slightly when reaction time increases. They vary from about 1.3–25 μm (mean value around 9.8 μm) to 0.5–9 μm (mean value around 4.3 μm) when going from 0.5–3.0 h. However, SEM shows that these spherical granules are in fact agglomerates of much finer elementary particles, and that their internal structure appears more clearly when crystallization increases (Fig. 4). These micrographs (Fig. 4a and b) are similar to that reported recently by Vollath [11] on powder obtained at an unspecified temperature, by a spray-drying and calcination process, from mixtures of aluminium and magnesium nitrates. However, chemical homogeneity is better in the process presented here. We never observed phase separation or signs of MgO crystallization, because the skeleton of the metal–oxygen bonds, further organized in the spinel structure, is already present in the first-formed amorphous solid (Fig. 2).

3.2.2. Influence of reaction temperature

As seen above, the solid particle formation starts at 283 °C in the supercritical fluid. Fig. 5 compares the



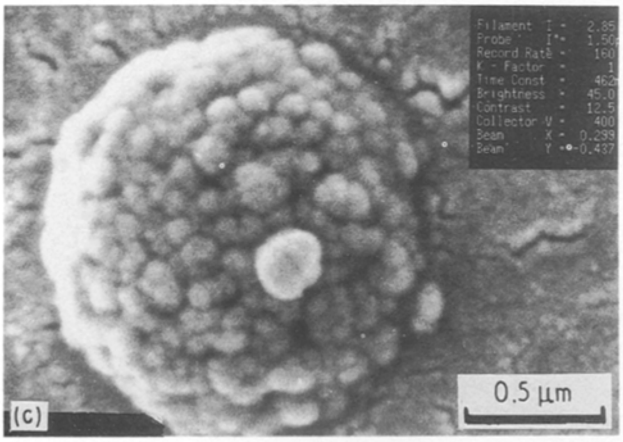


Figure 4 SEM micrographs of powders obtained at (a) 295 °C, 7 h; (b) 330 °C, 1 h; (c) 360 °C, 5 h.

crystallographic behaviour of powders obtained at 295, 360 and 407 °C for reaction times longer than 4 h and similar fillings in the reactor (runs 4–6 in Table I). The solid formed at 295 °C is completely amorphous, and the structural organization increases with temperature.

The IR spectra (Fig. 6), as well as the electron micrographs (Fig. 4), exhibit the same trends as noted above : the increase in solid crystallinity is associated with the loss of organic and OH groups, a better short-range organization of metal–oxygen bonds, and a better definition of the submicrometre elementary particles in the agglomerates.

3.2.3. *Influence of reactional medium*

Powders obtained around 400 °C with the same ethanol filling in the reactor but two different alkoxide concentrations (runs 6 and 7 in Table I) do not show significant differences in their structural organization.

Around 360 °C, for similar reaction times and solute concentrations, the ethanol content in the reactor was increased from 32 to 50 cm^3 (runs 5, 3, 8 and 9 in Table I), leading to a reaction-pressure variation from about 15 to 21 MPa. The increase in fluid density seems to lead to better crystallinity in the solid, and to a slight decrease in the agglomerate size distribution and mean diameter. However, these phenomena need to be confirmed by further experiments.

3.2.4. *Influence of thermal treatment*

When the above partly-crystallized powders are submitted to a thermal treatment for 1 h at around 1100 °C, formation of the spinel structure is reached, as shown in Fig. 5d. Particularly, the relative intensities of XRD lines [18] are now observed. This is associated with a complete loss of the residual organic and OH groups as seen in Fig. 6d. In the IR spectral range corresponding to metal–oxygen vibrations, the expected bands are now well-defined, especially that at 309 cm^{-1} associated with the Al–O bond in the spinel structure [19].

All the treated samples, whatever the experimental conditions of the previous powder formation, show a mean agglomerate size around 3 µm (0.5–7 µm). These agglomerates (Fig. 7a) are easily destroyed when the sample is submitted to an ultrasonic sound treatment. Individual particles of 0.02 µm are then observed by transmission electronic microscopy (TEM) (Fig. 7b).

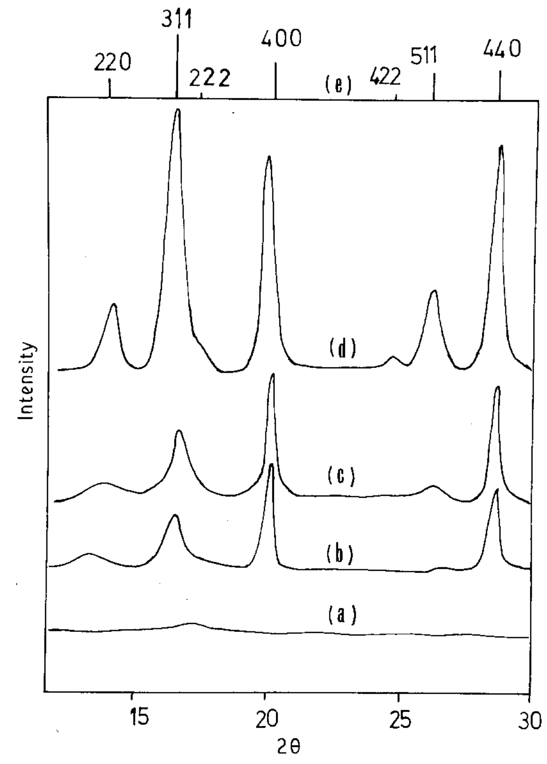


Figure 5 XRD patterns of powders obtained at (a) 295 °C, 7 h; (b) 360 °C, 4.5 h; (c) 407 °C, 6 h; (d) after thermal treatment 1 h at 1100 °C; (e) expected lines for spinel MgAl$_2$O$_4$ powders [18].

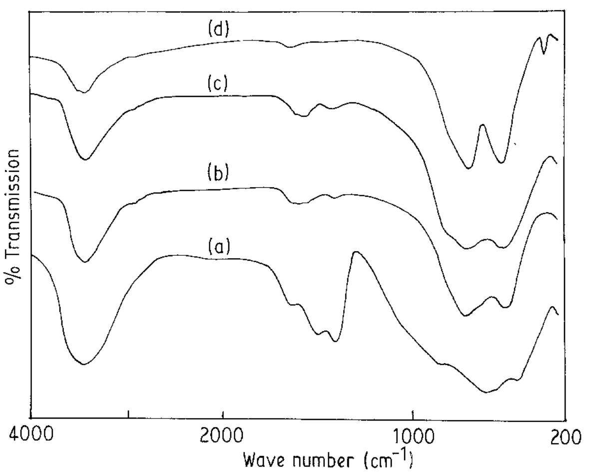


Figure 6 IR spectra of powders obtained at (a) 295 °C, 7 h; (b) 360 °C, 4.5 h; (c) 407 °C, 6 h; (d) after thermal treatment 1 h at 1100 °C.

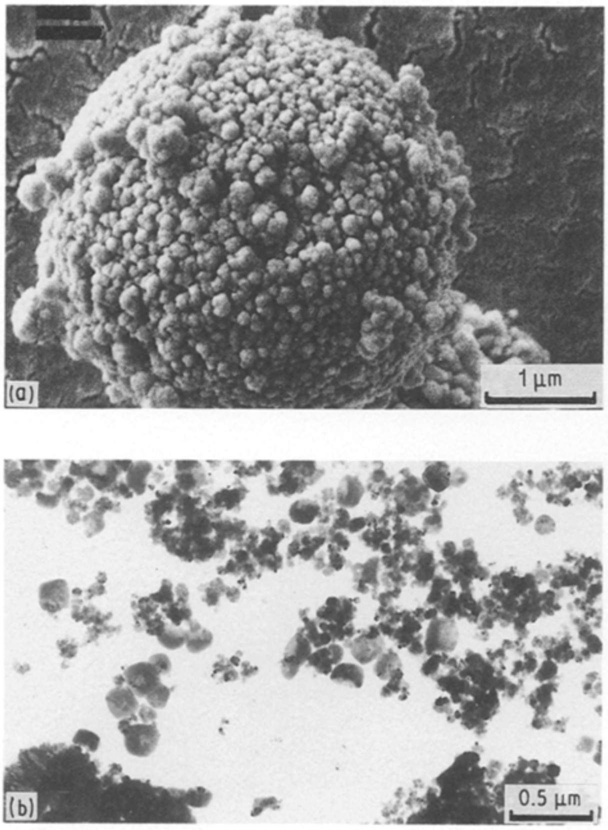


Figure 7 (a) SEM micrograph of powder obtained at 360 °C, 4.5 h and treated 1 h at 1100 °C; (b) TEM micrograph of the same powder after ultrasonic sound treatment.

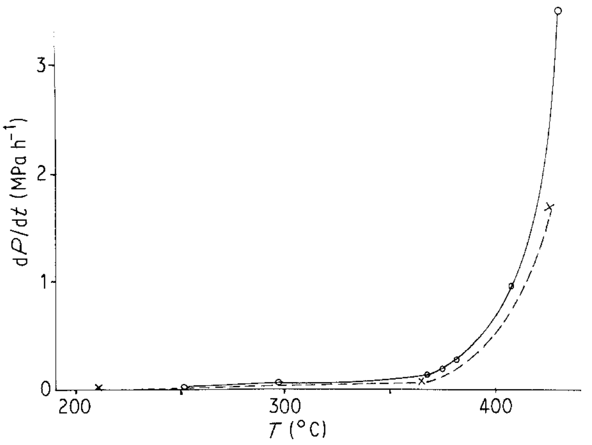


Figure 8 Ethanol decomposition in the stainless steel reactor (—) with and (– – –) without $MgAl_2O_4$ powders.

3.3. Ethanol decomposition

At temperatures above about 300 °C, we observed a continuous pressure drift in the reactor, even after long isothermal residence time (6, 12 or 18 h). The importance of this phenomenon is constant against time and increases rapidly above 360 °C (Fig. 8). This can be attributed to some decomposition of the supercritical solvent. Effectively, pure ethanol heated in the same conditions exhibits the same behaviour and, when coming back to room temperature, a residual pressure was observed, which increased with reaction time and temperature. IRS and gas chromatographic investigations on the solvent then demonstrated the presence of aldehyde and about 10% water.

It is well-known that metal oxides, particularly alumina, play a catalytic role in alcohol dehydration [20]. Fig. 8 shows a faster decomposition of ethanol when solid oxide particles are present. A linear variation of $\ln 1/T\, dp/dT$ against $1/T$ is observed, and the activation energy of ethanol decomposition can then be estimated at about 8.6 kJ mol^{-1}. When this reaction is realized with pure ethanol, the activation energy is found around 34 kJ mol^{-1}.

4. Conclusions

We have shown that metal alkoxides can be decomposed in supercritical ethanol and transformed into submicrometre oxide powders. For the studied double alkoxide $Mg[Al(O\text{-}secBu)_4]_2$, the precise nature of this reaction is not wellknown. A progressive hydrolysis–polycondensation reaction induced by a small amount of water produced in alcohol decomposition is conceivable. However, similar formation of $MgAl_2O_4$ powder was observed with hexane as a solvent, so thermolysing in the supercritical fluid appears likely.

The sintering behaviour of the powders obtained by the new route has been tested: from dilatometric measurements, the sintering phenomenon appears to start at low temperature, around 1000 °C, close to that observed for $MgAl_2O_4$ obtained either by classical sol–gel process from the double alkoxide [15] or by a freeze-drying technique from aqueous solutions of magnesium and aluminium sulphates [13].

The method proposed here would allow the formation of films or thin layers by decomposition of the alkoxide dissolved in a supercritical fluid (below 283 °C) on a substrate placed in this medium and heated at higher temperature.

Acknowledgements

We thank R. Chiron and Professor F. Armanet (Université Paris XIII, Villetaneuse, and Dr A. Dubon (Ecole Supérieure de Physique et Chimie Industrielle, Paris, for taking the SEM and TEM micrographs.

References

1. R. W. RICE, *American Institute of Chemical Engineers J.* **36** (1990) 481.
2. D. W. JOHNSON, *Ceram. Bull.* **60** (1981) 221.
3. D. W. MATSON, R. C. PETERSEN and R. D. SMITH, *J. Mater. Sci.* **22** (1987) 1919.
4. A. TAVANA and A. D. RANDOLPH, *AIChE J.* **35** (1989) 1625.
5. R. S. MOHAMED, P. G. DEBENEDETTI and R. K. PRUD'HOMME, *ibid.* **35** (1989) 325.
6. B. SUBRAMANIAN and M. A. McHUGH, *Ind. Engng Chem. Process Des. Dev.* **25** (1986) 1.
7. R. C. ROSSI and A. M. FULRATH, *J. Amer. Chem. Soc.* **46** (1963) 145.
8. E. KOSTIC, S. J. KISS and D. CEROVIC, *J. Phys.* **47** (1986) 441.
9. P. KRIJGSMAN, J. G. BECHT and J. SCHOONMAN, *Ceram. Engng Sci. Proc.* **9** (1988) 943.
10. H. G. WANG, M. ZU and H. HERMAN, *J. Mater. Sci.* **24** (1989) 4414.
11. D. VOLLATH, *ibid.* **25** (1990) 2227.
12. J. J. KINGSLEY, K. SURESH and K. J. PATIL, *ibid.* **25** (1990) 1305.
13. V. V. PANKOV, M. PAULUS and A. DUBON, *Ann. Chim. Fr.* **7** (1982) 377.
14. K. JONES, T. J. DAVIS, H. G. EMBLEM and P. PARKES, *Mater. Res. Soc. Symp. Proc.* **73** (1986) 111.
15. C. POMMIER, K. CHHOR, J. F. BOCQUET and M. BARJ, *Mater. Res. Bull.* **25** (1990) 213.
16. P. DESMAREST, R. TUFEU, Y. GARRABOS and B. LE NEINDRE, *Chem. Phys. Lett.* **142** (1987) 336.
17. R. C. MEHROTRA and A. MEHROTRA, *Inorg. Chem.* **5** (1966) 342.
18. JCDS, Joint Committee on Diffraction Standards, Powder Diffraction File number 21–1152 (spinel $MgAl_2O_4$) (International center for Diffraction Data, Swartmore, PA, 1971).
19. J. PREUDHOMME and P. TARTE, *Spectrochim. Acta.* **27A** (1971) 1817.
20. A. J. LUNDEEN and R. VAN HOOZER, *J. Amer. Chem. Soc.* **85** (1963) 2180.

Received 7 January
and accepted 7 June 1991