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Organic Gels in the Preparation of Silico-aluminate Powders. I. Mullite

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Abstract

The preparation of mullite powders by the use of organic gels has been studied. In aqueous solution, the silicon alkoxide, TEOS or 3-(triethoxysilyl)-propylamine (TESPA) is directly reacted with a solution of Al salt (nitrate, citrate, chloride or sulphate). When the solution is clear, it is gelled with polyacrylamide and rapidly calcined. The temperature behaviour of the powders has been studied (DTA, XRD, dilatometry). The powder elaborated from Al citrate and TESPA completely crystallizes to mullite at 970°C. In organic solution, a nearly identical result is obtained from ethanolic solution of Al nitrate and TEOS gelled with poly(2-hydroxyethylmethacrylate).

In dieser Arbeit wurde die Herstellung von Mullitpulvern aus organischen Gelen untersucht. Siliziumalkoxid, TEOS oder 3-(Triethoxysilyl)-Propylamin (TESPA) wurde in wässriger Lösung direkt mit einer Al-Salz-Lösung (Nitrat, Zitrat, Chlorid oder Sulfat) versetzt. Sobald die Lösung klar war, wurde sie durch Zugabe von Polyacrylamid geliert und sofort kalziniert. Temperaturabhängige Reaktionen der Pulver wurden durch DTA, XRD und Dilatometrie untersucht. Die aus Al-Zitrat und TESPA hergestellten Pulver kristallisierten bei 970°C vollständig zu Mullit. In organischer Lösung führte in Ethanol gelöstes Al-Nitrat und TEOS durch Poly(2-hydroxyethylmethacrylat) geliertes Material zu nahezu den gleichen Ergebnissen.

L'obtention de poudres de mullite par des gels organiques a été étudiée. En solution aqueuse, un alcoxyde de silicium, TEOS ou triéthoxysilyl-3-propylamine (TESPA) est mis a réagir directement avec une solution de sel d'aluminium (nitrate, citrate, chlorure ou sulfate). Dès que la solution est limpide elle est gélifiée par le polyacrylamide et le gel aqueux est rapidement calciné. Le comportement en température des poudres obtenues a été étudié (ATD, RX, dilatométrie). La poudre préparée à partir de citrate d'aluminium et de TESPA cristallise complètement en mullite à 970°C. En solution organique, un résultat presqu'identique est obtenu à partir d'une solution éthanolique de nitrate d'Al et TEOS gélifiée par le poly(2-hydroxyéthylméthacrylate).

1 Introduction

Among the numerous processes developed for producing ceramic oxide powders, some of them use organic polymers as intermediate auxiliaries between a precursor solution and the oxide powder.

Pechini[1] first prepared perovskite powders by dispersing metallic cations in a polyester resin resulting from polycondensation between ethylene glycol and citric acid. More recently, Micheli[2] has described a precipitation of metal polyacrylate which affords ultrafine powders with high specific surface areas. Another process,[3] more general, has been described, where an organic polymeric network, the polyacrylamide gel, is just used for solidifying a stable aqueous solution where the cations are conveniently complexed by citric acid. The direct calcination of these gels produces ultrafine homogeneous powders. It has been proved to be efficient in various powder compositions of mixed oxides or solid solutions. A more complicated situation results when one cation is not complexed in solution. It is in the case of silicon that this occurs, and it is precisely silicates which constitute an important class of mineral oxides.

The purpose of this paper is to show the essential part played by organic gels in the elaboration of

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silicated powders in aqueous solutions where silicon may not be complexed, and also in silicon and aluminium alcoholic solutions. The present article concerns the case of mullite, $3Al_2O_3.2SiO_2$, while that of cordierite will be presented in a forthcoming paper.

2 Experimental

2.1 Chemicals

Aluminium nitrate ($Al(NO_3)_3.9H_2O$, 98·5%, Merck), aluminium chloride ($AlCl_3.6H_2O$, 98%, Merck) and aluminium sulphate ($Al_2(SO_4)_3.18H_2O$, 99%, Prolabo) are the sources of aluminium. Tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$, 98%, Merck) and 3-(triethoxysilyl)-propylamine (TESPA, $(C_2H_5O)_3Si(CH_2)_3NH_2$, 99%, Merck) are sources of silicon.

For the organic gelation of the solutions, acrylamide (Merck) or 2-hydroxyethylmethacrylate (Merck) are the monofunctional monomers used, and *N,N'*-methylenediacrylamide (Merck) is a bifunctional monomer (crosslinking agent).

α,α'-Azoisobutyronitrile (AIBN, Fluka) or ammonium peroxodisulphate (Merck) are used as radical polymerization initiators and *N,N,N',N'*-tetramethylethylenediamine (Temed, Merck) as radical transfer agent.

2.2 Solutions

The organic solutions are made by dissolving Al nitrate and TEOS in ethanol (96%).

The aqueous solutions are obtained first by dissolving the Al salt (nitrate, chloride or sulphate) in water and then adding the silicon alkoxide. After vigorous stirring, a clear solution is obtained. The concentration of silicon is in the range 0·25–0·4 mol dm^{-3}. The Al citrate solution is obtained by adding citric acid to the nitrate solution (one citric acid per nitrate ion) and then ammonia to adjust the pH to the same level (pH 3) as the nitrate solution before adding the silicon alkoxide.

2.3 Gelation of the solutions by organic polymers and thermal treatment

2.3.1 *Aqueous solutions*

In 100 ml of clear aqueous solutions freshly prepared from Al salt and Si alkoxide, 5 g of acrylamide and 0·5 g of *N,N'*-methylenediacrylamide are first dissolved. The solution is warmed in a water bath with magnetic stirring. Temed (0·1 ml), diluted in water and just neutralized by acid, is added and, as soon as the temperature reaches 80°C, AIBN (0·1 g), previously dissolved in ethanol (1 ml), is introduced. The organic gelation occurs in 1–2 min.

For making gels at room temperature, the solutions are slightly degassed before adding the polymerization initiator, ammonium peroxodisulphate (0·1 g), instead of AIBN, and the gels settle in a few tens of minutes.

The aqueous gels are treated in a microwave oven in order to obtain rapidly a dry residue which is then calcined in a ventilated oven, at 2°C min^{-1} to 750°C and maintained at this temperature for 5 h.

2.3.2 *Alcoholic solutions*

In ethanol, for 100 ml of solution, 10 g of 2-hydroxyethylmethacrylate and 2 g of *N,N'*-methylenediacrylamide are used. AIBN (0·1 g) is the polymerization initiator and the solution is boiled until organic gelation occurs.

The alcoholic gels are dried for 24 h at 80°C and calcined to 750°C as for the aqueous gels.

2.4 Characterization of the powders

The crystalline structures were determined by X-ray diffraction (XRD) on a Philips diffractometer using Cu K-α radiation. Differential thermal analysis (DTA) curves were obtained at 10°C min^{-1} using Pt crucibles and around 250 mg of powder. The specific surface areas of the powders were measured on a Micromeritics Flowsorb II 2300 instrument by the BET method using nitrogen gas. The shrinkage of the powders, isostatically compacted at 200 MPa, was studied on a high-temperature Steram dilatometer.

3 Results and Discussion

3.1 Preliminary results on silica in aqueous solution: Influence of the polyacrylamide gel

TEOS is not directly soluble in water. However, when TEOS is added to an acidic aqueous solution under vigorous mixing to increase the contact surface and thus the reactivity between the two phases, a clear aqueous solution is obtained. In fact, in the presence of such a large excess of water, TEOS is first hydrolysed to silanol monomers. Condensation and crosslinking of these silanols and gelation of the solution follows. The kinetics of these reactions depend on pH, concentration and temperature, as in alcoholic solutions. Examples of processing of silica hydrosols and gels from aqueous solutions have been recently described.[4,5]

Polyacrylamide gel,[6] the most studied hydrophilic gel, is easily made in aqueous medium by radical copolymerization of acrylamide and *N,N'*-methylenediacrylamide.

If a clear aqueous solution obtained from TEOS is divided into two parts (A and B) and one of them (A) is gelled by the polyacrylamide network and both parts are then aged at 90°C in closed vessels, a few days later the solution of part B becomes an opalescent gel of colloidal silica, whereas the polyacrylamide gelled solution A remains clear with only a small amount of syneresis occurring.

When a clear aqueous solution made from an aluminium salt (nitrate or citrate) and TEOS is gelled by polyacrylamide and aged at 90°C in a closed vessel, the gel remains clear, while syneresis also occurs. The expelled liquid, when analysed, contains only aluminium and no trace of silicon.

These experiences show that the polyacrylamide gel inhibits the growth of the silica colloids and immobilizes them in its network while molecular species like salts can migrate, but slowly. The same phenomenon has been described concerning the limitation of growth of silver colloids by polyacrylamide gel.[7] In the case of mullite powder elaboration, these thermal conditions, where chemical segregation is favoured, have been restricted by rapid drying of the gels.

3.2 Mullite powder elaboration

In a preceding work[3] a powder of mullite composition was studied. It was obtained from mixing two stock solutions: one of Al citrate and the other of silica hydrosol obtained from TEOS reacted with a citric acid solution. The resulting solution was gelled by polyacrylamide and the gel calcined to 800°C at the rate of 2°C min^{-1}. The DTA curve revealed two exothermic peaks, of rather weak intensity (Fig. 1): one at 970°C and the other at 1250°C. The XRD diagram of the powder calcined at 800°C showed only the Al–Si spinel phase up to 1250°C, where it converts to pure mullite phase (orthorhombic). This powder is designated M0 in Table 1.

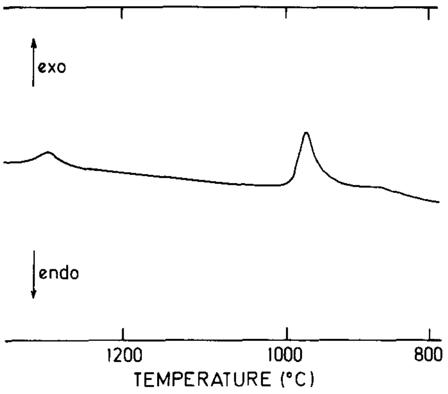

Fig. 1. DTA trace of the M0 powder at 10°C min^{-1}.

A series of new powders has been elaborated from solutions obtained by directly reacting the Si alkoxide (TEOS or TESPA) with an aqueous solution of Al salt (nitrate, citrate, chloride or sulphate). As soon as the mixture is clear, the solution is rapidly gelled by the polyacrylamide in a boiling water bath, the polymerization being initiated by AIBN (samples N1, N2, Ci1 and Ci2; Table 1). For other solutions the gel is made at room temperature by using ammonium peroxodisulphate as polymerization initiator (samples Cl1, Cl2, S1, S2, U1 and U2); in some cases this initiator may produce a tiny quantity of Al sulphate, but this is decomposed during the powder calcination. For the U1 and U2 samples, urea is dissolved in Al nitrate solution in a rather large concentration (4 mol urea/ 1 mol Al nitrate). This produces a pH increase in the

Table 1. Powders prepared and some of their characteristics

Powder	*Al salt*	*Si alkoxide*	*Organic gel*	*Solvent*	*Specific surface areas in $m^2 g^{-1}$ (750°C, 5 h)*	*Crystalline phases*[a] *(950°C, 2 h)*
M0[b]	Citrate	TEOS	polyacrylamide	H_2O	155	S
N1	Nitrate	TEOS	polyacrylamide	H_2O	45	S, m
N2	Nitrate	TESPA	polyacrylamide	H_2O	58	S, m
Ci1	Citrate	TEOS	polyacrylamide	H_2O	195	S
Ci2	Citrate	TESPA	polyacrylamide	H_2O	235	M
Cl1	Chloride	TEOS	polyacrylamide	H_2O	360	S
Cl2	Chloride	TESPA	polyacrylamide	H_2O	350	s, m
S1	Sulphate	TEOS	polyacrylamide	H_2O	310	S, m
S2	Sulphate	TESPA	polyacrylamide	H_2O	300	s, M
U1	Nitrate–urea	TEOS	polyacrylamide	H_2O	300	S
U2	Nitrate–urea	TESPA	polyacrylamide	H_2O	310	S
E	Nitrate	TEOS	pHEMA[c]	Ethanol	60	s, M

[a] S = Spinel; s = weak spinel; M = strong mullite; m = weak mullite.
[b] Obtained as described in Ref. 3.
[c] pHEMA = Poly(2-hydroxyethylmethacrylate).

aqueous gel during the thermal decomposition of urea.

The aqueous gels are then treated in a microwave oven so as to obtain rapidly dry solid residues, which are finally calcined to 750°C at 2°C min^{-1} and maintained at this temperature for 5 h. Light white powders are obtained, agglomerated in fine platelets, with grain sizes around 0·1 μm.

One gel has been made from an alcoholic solution of Al nitrate and TEOS in ethanol. As polyacrylamide is not soluble in ethanol, 2-hydroxyethylmethacrylate was used as organic monomer, with *N*,*N*′-methylenediacrylamide as crosslinking agent, although the latter may be replaced by ethyleneglycol dimethacrylate, and the polymerization initiator being AIBN. This organic gel is more difficult to make than the polyacrylamide one in aqueous solutions. By storing this gel at 80°C for one day a vitreous solid results. This is crushed and calcined to 750°C for 5 h. A white powder is obtained, of much more dense aspect than all those elaborated by the aqueous route.

3.3 Differential thermal analysis and X-ray diffraction

The powders were studied by DTA. All the curves present an exotherm at 970°C, more or less important (Fig. 2), sometimes very strong, and often a second weak exotherm beyond 1200°C. For the powder Ci2 (Al citrate and TESPA) there is only a very intense peak at 970°C. The XRD analysis of this powder shows that it is amorphous up to this temperature. Immediately after this exotherm the powder seems completely crystallized into mullite. Figure 3 reports the XRD diagrams of Ci2 samples for which the heating has been stopped (a) just before and (b) at the beginning of the 970°C peak, but, because of the strong exothermicity of the transformation, the temperature of this second sample reaches more than 1000°C.

To try to quantify the crystallization of the mullite phase, in relation to the intensity of the 970°C exotherm, and to compare the powders, samples of each one were annealed at 950°C for 2 h and further investigated by XRD (Fig. 4). This thermal treatment is sufficient for inducing the transformation observed at 970°C under dynamic heating. If the DTA is run again on such powders, no more exotherm occurs at this temperature.

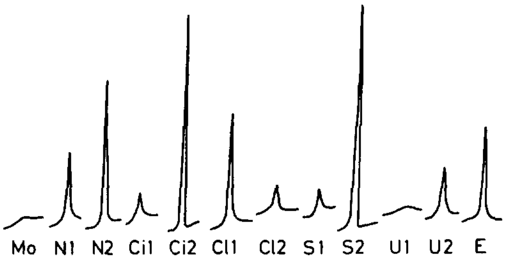

Fig. 2. DTA 970°C exotherms of the powders studied.

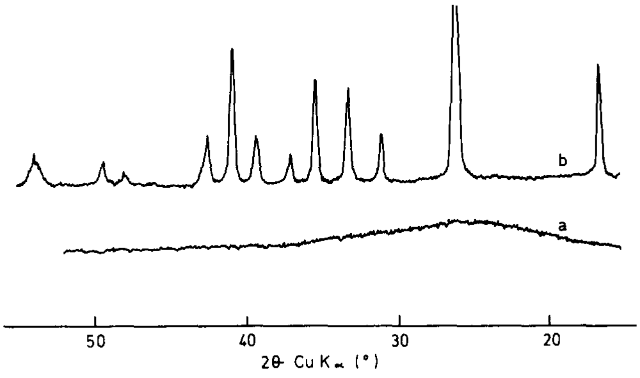

Fig. 3. XRD diagrams of the Ci2 powder. a, just before the 970°C exotherm: amorphous; b, just after the 970°C exotherm: crystalized orthorhombic mullite phase.

For many of these powders (M0, Ci1, Cl1, U1 and U2) there is only the spinel phase after this treatment. For others a beginning of the crystallization into the mullite phase appears in addition to the remaining spinel: N1 and N2 (Al nitrate), Cl2 (Al chloride and TESPA), and S1 (Al sulphate and TEOS), whereas they exhibit apparently uncorrelated exotherm intensities. For the powder E, made from an alcoholic solution (Al nitrate and TEOS), there is an important transformation into mullite, although the exotherm is not very strong. For the powder S2 (Al sulphate and TESPA) the exothermic peak is very strong, the mullite phase is important, although a small amount of spinel remains, and for

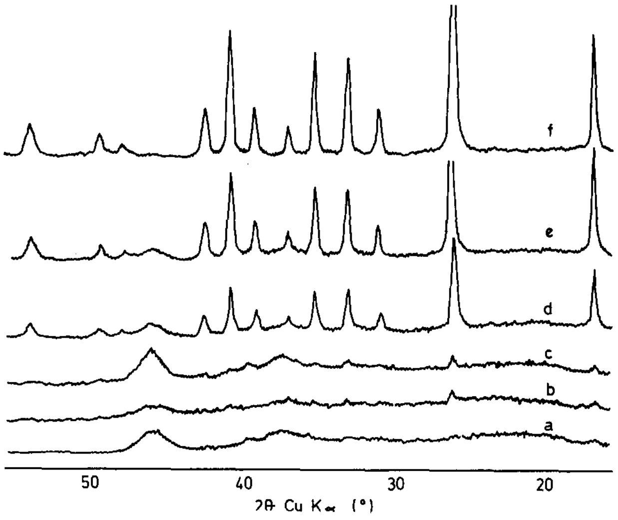

Fig. 4. XRD diagrams of the mullite powders annealed at 950°C for 2 h. a, powders M0, Ci1, Cl1, U1, U2: spinel phase only: b, powder Cl2; c, powders N1, N2, S1; d, powder E; e, powder S2; f, powder Ci2: pure mullite phase (orthorhombic).

the Ci2 sample (Al citrate and TESPA) the exotherm is also very strong and the sample is completely crystallized into mullite.

If the strong exotherm agrees with the crystallization into mullite for the Ci2 powder, this is not the case for the Cl1 powder (Al chloride and TEOS). Although the peak is rather intense, the only transformation discernable by XRD is from an amorphous powder which already has a little spinel phase to only spinel. Other powders, such as M0 or U1 (Al nitrate and urea and TEOS) already have a spinel phase before the 970°C exotherm and apparently no structural modification occurs at this temperature.

Thus there is no direct relation between the 970°C exotherm intensity and the powder crystallization into mullite. The DTA signal intensity must reflect something else at a microscopic level. One hypothesis is that chemical homogeneity is involved, which may be changed by the chemistry of the precursors, and further studies have to be pursued in order to understand the chemistry of the mullite powder elaborations. It can be noted that for each Al salt used, except chloride, the 970°C exotherm is more intense if the starting alkoxide is TESPA instead of TEOS, and for the Al citrate or sulphate the quantity of mullite obtained at this temperature is very much larger. In aqueous medium, a clear solution is obtained much more rapidly with TESPA than with TEOS. The substitution of one ethoxy radical by an aminopropyl one with a basic character makes this alkoxide more soluble in acidic aqueous solutions and thus more reactive with water. Silicic acid $Si(OH)_4$ resulting from the complete TEOS hydrolysis has a propensity to condense, and even if the polyacrylamide network prevents exaggerated colloid growth during the thermal treatment of the gel, the silica network will however develop. TESPA, in contrast, will first be hydrolysed to 3-(trihydroxysilyl)-propylamine ($(HO)_3Si(CH_2)_3NH_2$) which possesses less condensable hydroxy groups than silicic acid and thus will form a less-extended silica network so long as the Si–C bond will not be thermolysed.

When the Si alkoxide is TEOS, the beginnings of crystallization to mullite at 970°C occur when starting with Al nitrate or sulphate, and no trace of the mullite phase is found by XRD with Al citrate or chloride. The 970°C exotherm intensity and the nature of the crystalline phases obtained are thus strongly dependent on the Al salt and Si alkoxide used for making the precursor solution.

The polyacrylamide gels were made in acidic solutions. The attempt to modify the pH *in situ* in the gel when this is heated in an oven, by thermal decomposition of the urea, goes the wrong way; it reduces the exotherm intensity and inhibits the mullite-phase formation.

When the powder is elaborated from the alcoholic solution of Al nitrate and TEOS, gelled by the poly(2-hydroxyethylmethacrylate), a strong exothermic peak occurs, with an important crystallization to mullite at 970°C, but with the presence of a little residual spinel phase.

It must be noted that all these powders, when heated to 1350°C at 10°C min^{-1}, exhibit only the pure orthorhombic mullite phase with no traces of α-alumina or cristobalite.

Chakravorty & Ghosh[8] have recently reviewed the different preparations of mullite by the sol–gel route in alcoholic solution by alkoxide hydrolysis followed by condensation and polymerization, or in aqueous medium by hydrolysis of Al salts in the presence of silica sols. Different thermal behaviours have been observed, with or without the existence of an exotherm at 980°C, more or less intense, resulting in either mullite (orthorhombic) or spinel (cubic mullite) or a mixture of the two phases.

Kanzaki *et al.*[9] produced mullite by spray pyrolysis of a solution made by dissolving Al nitrate and TEOS in a 1:1 water–methanol mixture. Their powder was amorphous and crystallized completely to mullite at 970°C. The methanol was used as cosolvent to favour the dissolution of the TEOS and its hydrolysis by a great excess of water.

Until now mullite had not been produced from a solution made by directly reacting TEOS with an aqueous solution of Al salt. The use of other alkoxides, such as TESPA, has also not been reported previously, and in the same way the use of organic gels such as polyacrylamide or poly(2-hydroxyethylmethacrylate) in the processing of silicate powders is new.

3.4 Specific surface areas

The specific surface areas of the mullite powders elaborated at 750°C are given in the Table 1. These areas are generally high except when nitrate is used as aluminium source. The addition of urea in the nitrate solution significantly enhances the surface area, but reduces the intensity of the 970°C exotherm, and mullite phase does not appear at this temperature.

The elaborations of mullite powders from Al nitrate and citrate have been duplicated and the gels have been directly calcinated to 750°C at 2°C min^{-1} instead of being rapidly reduced to powders in a microwave oven. A reduction of the specific surface areas as well as of the exotherm intensity at 970°C, except for the Ci2 sample (Al citrate and TESPA), has been noted. Thus the rapidity in the transformation of the starting solution to a dry residue seems to be an important factor in the resulting characteristics of the powder. It is why the other powders (sulphate, chloride and nitrate with urea) have been produced from solutions gelled at room temperature and rapidly dried in a microwave oven.

3.5 Dilatometric analysis

The powders were isostatically pressed at 200 MPa without deagglomeration of the platelets and the shrinkage has been measured versus *T* for a constant heating rate of 5°C min^{-1} to 820°C, followed by 2°C min^{-1} to 1250°C. Figure 5 shows the linear shrinkage curves of three powders (Ci2, U1 and Cl1), those of Ci2 and U1 being representative of the extreme behaviours encountered with all the samples. For the three curves the irregularity appearing at 820°C is only due to the change in the heating rate.

For the powder Ci2 (Al citrate and TESPA) there is a shrinkage which is strongly accelerated at the approach of 970°C and then is suddenly stopped at this temperature which corresponds to the crystallization into mullite. Up to 1250°C there is no more densification for this powder.

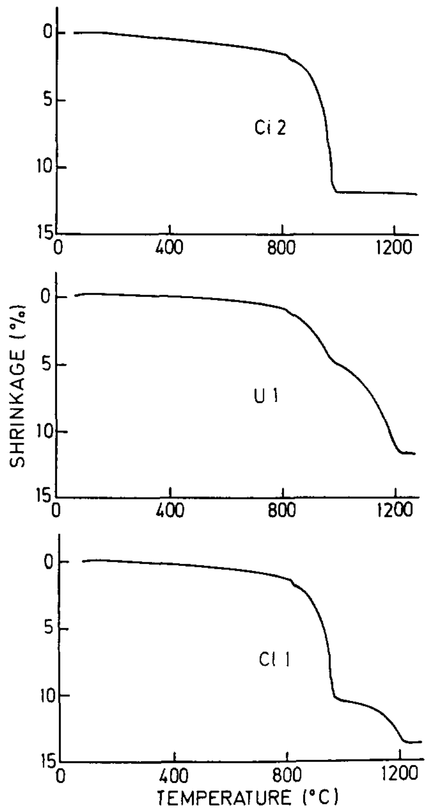

Fig. 5. Linear shrinkage of powders Ci2, U1 and Cl1 versus temperature. Heating rates: 5°C min^{-1} to 820°C, then 2°C min^{-1} to 1250°C.

In the case of the sample U1 (Al nitrate and urea and TEOS) the behaviour is much more progressive with, however, two regions where the shrinkage is accelerated, the first occurring between 900°C and 970°C. The slowing down at 970°C corresponds with the weak exotherm encountered in DTA. At this temperature the only transformation noted by XRD for this powder is from amorphous and spinel to more spinel. The end of the shrinkage at 1220°C corresponds with the accomplishment of crystallization to mullite.

For all the other samples the shrinkage curves are intermediate between these two. There is always a slowing down, more or less sharp, corresponding to the first exotherm on the DTA curve, and a second step of shrinkage beyond 1100°C until complete crystallization into mullite. Generally speaking, the shrinkage acceleration before 970°C is correlated with the intensity of the exotherm, whatever the nature of the crystalline phases developed at this temperature, as observed by XRD. So, for the powder Cl1 (Al chloride and TEOS) (Fig. 5) which transformation through a rather strong exotherm is from amorphous and spinel to only a spinel phase, the densification is fast before 970°C and then sharply reduced, and the second shrinkage step is smaller before the crystallization of mullite. For the powder E, (Al nitrate and TEOS and poly(2-hydroxyethylmethacrylate)), the curve is like that of Ci2 with a sudden stop at 970°C. An important quantity of the powder is then transformed into mullite. There is, however, a small shrinkage beyond 1200°C before the completion of the mullite crystallization.

For all these samples submitted to dilatometric analysis under these conditions, the density remains low at 1250°C and does not exceed 60% of the theoretical value.

Several authors have studied the shrinkage of mullite powders and have observed similar behaviours. The powders or aerogels which crystallize to mullite at 970°C always show an important shrinkage acceleration just before this transformation[10–12] but which beyond this temperature results in completely quenched sintering. It has been claimed[11] that the densification behaviour can be improved by avoiding the mullite formation at low temperature, i.e. 970°C.

4 Conclusion

The polyacrylamide gel process, easy to carry out, has already shown that it is particularly attractive in the production of ultrafine powders of good chemical homogeneity from aqueous solutions where the cations may be complexed by citric acid for instance. It may be considered as an improvement of the original 'amorphous citrate process'.[13] In the case of silicated oxides, when there may not be complexation of silicon in aqueous solutions, the polyacrylamide gel preserves the chemical homogeneity of the powders. A complete crystallization into mullite at 970°C may be obtained from powders elaborated from aqueous solutions by this process.

This concept of organic gel imprisoning a solution is not restricted to the polyacrylamide in aqueous solutions. A powder which transforms almost completely into mullite at low temperature is also obtained from a simple solution of Al nitrate and TEOS in ethanol and gelled by poly(2-hydroxyethylmethacrylate).

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