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Structural evolution in polyolysed hybrid organic-inorganic alumina gels

F. TOUATI, N. GHARBI*
Laboratoire de Chimie de la Matière Condensée I.P.E.I.T, 2 Rue Jawaher Lel Nehru-1008 Monfleury B.P 229, Tunisia

PH. COLOMBAN
CNRS, LASIR, 2 rue Henri Dunant, 94320 Thiais, France

New material gels obtained by reaction of the aluminum sec-butoxide with propan-1,2-diol at room temperature without using a catalyst or adding water, have been pyrolyzed at different temperatures under argon and in air. The obtained products have been characterised by various methods (X-ray, IR and Raman spectroscopies, SEM and density measurements) to determine their structures. Corundum is formed at 1450°C when the material is heat-treated under argon, but this phase is obtained rapidly at temperatures above 1000°C for the xerogel pyrolysed in the air. *© 2000 Kluwer Academic Publishers*

1. Introduction

The oxides of aluminum materials find numerous applications in ceramics, refractories, abrasives due to their high hardness, chemical inertness, high melting point, involatility and resistance to oxidation and corrosion [1–5]. α-Al_2O_3 is widely used in the microelectronics industry as it is an electrical insulator and a good heat conductor.

Many studies dealt with the preparation of alumina gels by the process of hydrolysis of aluminum alkoxides and the peptization of the hydroxide [6–10]. It has already been shown that aluminum alkoxides react with chelating agents, such as acetylacetone or ethylacetoacetate, giving rise to new molecular precursors [11, 12]. On the other hand, several studies have illustrated the additive influence on the chemical process [13, 14]. Nevertheless, it has been reported previously that ethylene glycol is used as a solvent and a reducing agent for the chemical preparation of metallic powders from various inorganic precursors [15], and as stabilizing agents of metallic alkoxides [10]. Alternative processing methods for the preparation of advanced ceramics are under study as a means of overcoming difficulties encountered in the traditional fabrication routes. Despite the great progress which has been made in powder science within recent years, the fabrication of ceramics without the use of powders and combining different routes have retained the attention of ceramists. The use of gels is an alternative powder-free fabrication route especially for composites, ceramic matrix which has been successfully developed on the laboratory scale [16, 17]. The availability of a liquid precursor giving a gel without addition of water may be very interesting for the gelation within the worm fibre yarns.

In a previous work, ^{27}Al, ^{13}C MAS-NMR and infrared spectroscopy studies have clearly shown that exchange between aluminum alkoxide and propan-1,2-diol may occur at room temperature to give hybrid organic-inorganic gel without the use of any catalyst and without addition of water [18]. Interest in the use of diols with metal alkoxide arises from their tendency to slow down the high reactivity of alkoxide towards the moisture; to form highly polymeric derivates which have applications in several domains as ceramic, optic, catalyst, etc; to allow the formation of composite Al_2O_3—carbon graphitic at low temperature, that could be considered as a new material in ceramic field.

It has already been shown that α-Al_2O_3 phase is formed by pyrolysis of alumina gels at temperatures ranging between 1000°C and 1300°C [19–27].

In this paper, we report the structural and morphological study of new hybrid organic-inorganic aluminum gel pyrolyzed under argon and in air at different temperatures using Raman and infrared spectroscopies, X-ray diffraction and scanning electronic microscopy techniques.

2. Experimental

The starting material used was aluminum tri-sec-butoxide $Al(OBu^s)_3$. It was dissolved in CCl_4. Propan-1,2-diol was added to the obtained 0,2 M solution. The mole ratio of the diol to the aluminumn alkoxide was represented by $k = n\text{diol}/n\text{Al}$. The mixed solution (volume = 10 ml) was stirred for about ten minutes in a closed bottle at room temperature. While stirring, the solution became gradually viscous to give a gel. The obtained gel was monolithic and transparent. In a previous

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* Author to whom all correspondence should be addressed.

study, we have shown that time of gelification is affected by the nature of diols and the molar ratio k [18].

Xerogels were obtained after drying of gels at 100°C for 24 hours to evaporate a maximum of solvent. These xerogels were pyrolysed in an electric furnace at different temperatures, up to 1450°C under argon (quality U: O_2 content <5 ppm) and oxidised up to 1000°C in air (heating rate: 200°C/h, during of treatment is 3 hours under argon and 24 hours in air). A platinum crucible was used for thermal treatments. The samples obtained were characterised by different techniques.

The Raman measurements were obtained with an XY Dilor spectrograph equiped with CCD mosaic detector using power illumination of 1mW ($\lambda = 458$ nm).

IR spectra were recorded on 1720 and 983 Perkin Elmer spectrometers using KBr pellets and Nujol emulsions between CsI windows.

The morphology of samples was determined by scanning electronic microscopy (SEM) using Cambridge Instruments Stereoscan 120.

The identification of the solid phases was performed by X-ray diffraction (XRD) using X-ray powder diffractometer (Philips PW 1729 using Cu-Ka radiation).

The density of the samples was determined by Archimedes method. The reported values are the average of three determinations in all the cases.

3. Results and discussion

3.1. Evolution at the molecular scale

Raman and infrared spectroscopies were valuable tools for studying the structural transformations on a molecular scale which progressively occur during the sol to gel evolution and subsequent thermal treatment of materials before their crystallisation.

Fig. 1 compares the IR spectrum of the gel dried at 100°C with those of pure propan-1,2-diol and solution of aluminum tri-sec-butoxide. Strong modifications were observed in all the characteristic regions: 2800–3000 cm^{-1} (ν_{CH}), 1300–1500 cm^{-1} (δ_{CH}), 900–1200 cm^{-1} ($\nu_{\text{C-O}}$ and $\nu_{\text{C-C}}$) and 400–800 cm^{-1} ($\nu_{\text{Al-O}}$). This means that diol reacts with the alkoxide giving an organic-inorganic gel.

Fig. 2a shows the Raman spectrum of xerogel trated at 100°C in air. The 1460 and 1373 cm^{-1} bands correspond to torsion and stretching modes of -CH_3 of the chain of propan-1,2-diol interbedded between aluminum atoms. The band at 1135 cm^{-1} is assigned to the C-C vibration. The presence of two bands at 1082 and 838 cm^{-1} might be due to the vibrations of Al-O-C groups contained in the network gel. The bands between 400 and 800 cm^{-1} could indicate the formation of Al-O-Al bands.

Fig. 2b and c show the Raman spectra of black samples obtained from xerogels pyrolysed at 500 and 1000°C under argon. These spectra show only two intense and broad bands at 1604 and 1360 cm^{-1} assigned to carbon precipitates. The relative intensity of the bands ($I_{1604} > I_{1360}$) indicates the graphitic state of the carbon precipitates [28]. Fig. 2d gives the Raman spectrum of xerogel heat-treated at 1400°C under argon. The 378, 418, 432, 450, 578, 645 and 750 cm^{-1} Raman bands indicate the formation of α-Al_2O_3 phase [29]. The intensity of the peaks at 1360 and 1604 cm^{-1} was reduced. Then the quantity of carbon in the material was reduced.

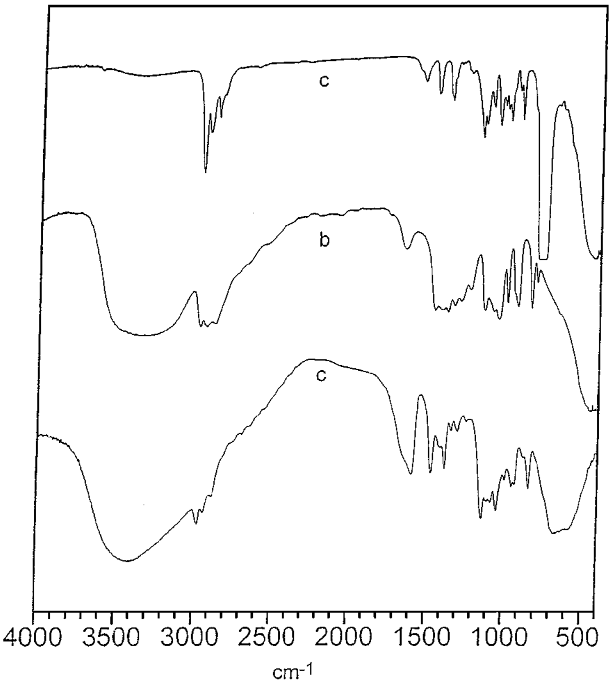


Figure 1 IR spectra of: solution of Al(OBu^s)$_3$ (a), propan-1,2-diol (b) and xerogel (c).

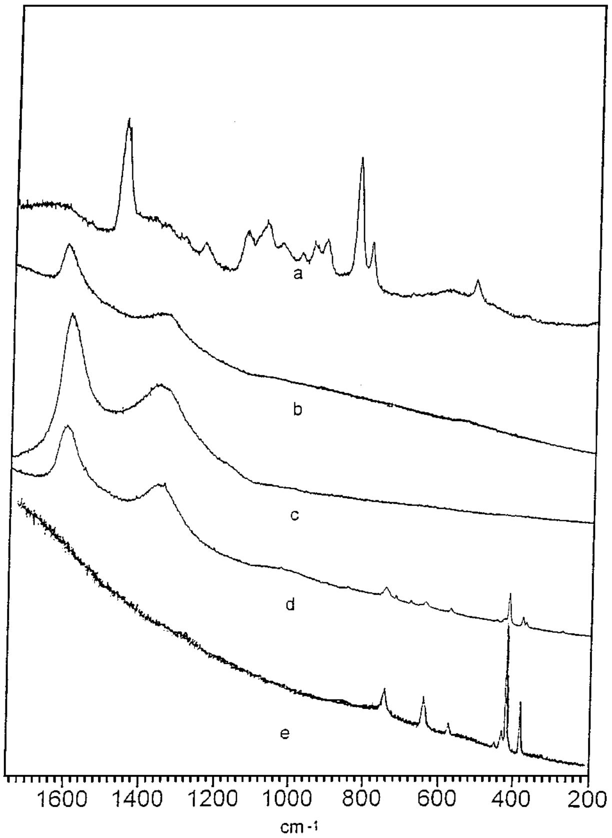


Figure 2 Raman spectra of gels pyrolyzed under argon at various temperatures: 100°C (a), 500°C (b), 1000°C (c), 1400°C (d) and 1450°C (e).

Raman spectrum of xerogel pyrolyzed at 1450°C under argon (Fig. 2e) shows the disappearance of carbon

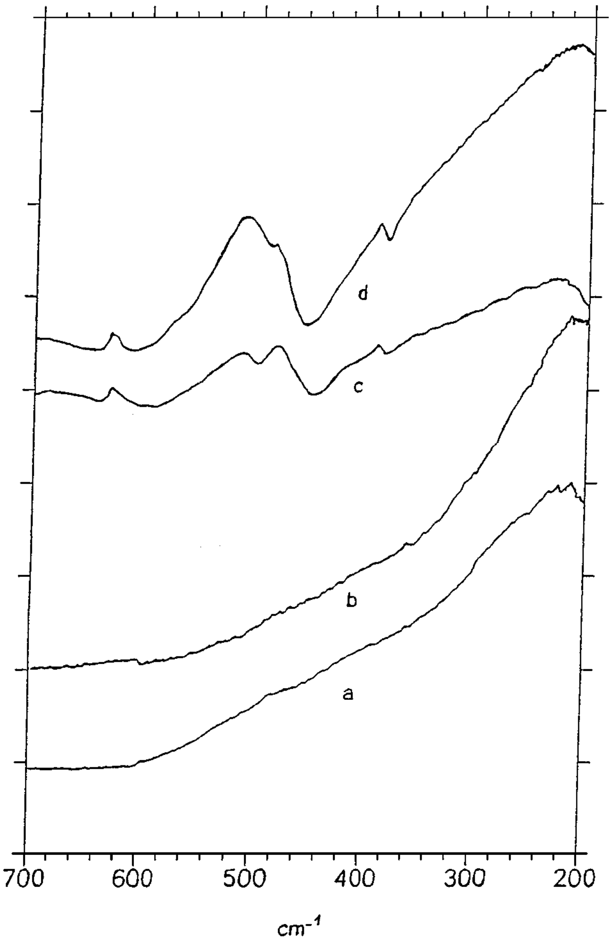


Figure 3 IR spectra of gels heated at different temperatures under argon: 500°C (a), 1000°C (b), 1400°C (c) and 1450°C (d).

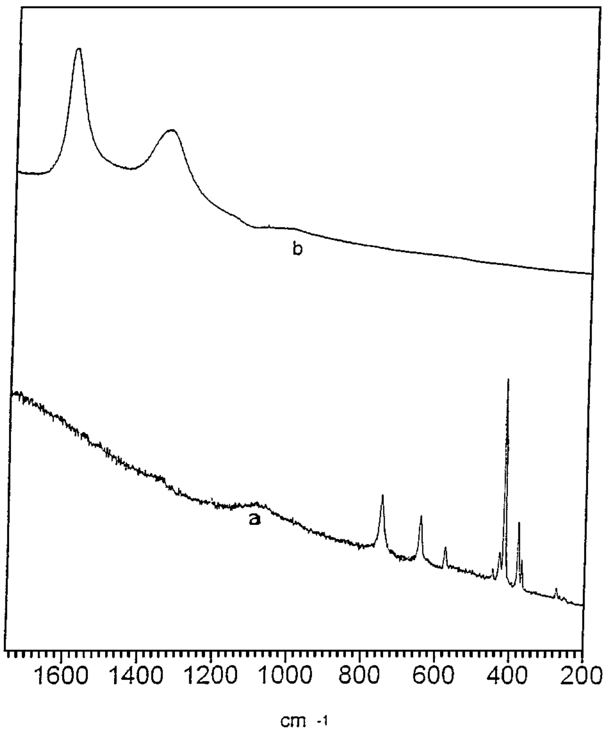


Figure 4 Raman spectra of gels pyrolyzed at 1000°C in various atmospheres: under argon (a) and in air (b).

precipitates (absence of peaks at 1360 and 1604 cm^{-1}) and the presence of α-alumina phase.

IR spectra of xerogels fired in inert atmosphere(argon) at different temperatures are reported in Fig. 3. The spectra of materials pyrolysed at 500 and 1000°C don't present bands at about 350 and 560 cm^{-1} as observed on amorphous optically clear gels prepared by very slow hydrolysis of Al-sec-butoxide [30] (Fig. 3a and b). The absence of well defined 360, 480 and 620 cm^{-1} peaks characteristic of Al(OH)$_3$ and AlOOH phase is consistent with the achievement of a polymeric (Al-O(C))$_n$-materials. The IR bands observed at 383, 451, 492, 594, 635 and 720 cm^{-1} for the materials heat-treated at 1400 and 1450°C (Fig. 3c and d) are consistent with the presence of α-Al$_2$O$_3$ phase [31].

Raman and IR spectra of the xerogel heat-treated at 1450°C are similar to those of α-Al$_2$O$_3$. They show all the bands of the corundum compound [32] which is characterised by a very intense Raman line at 418 cm^{-1} and a well-defined IR band at 451 cm^{-1} [33].

The colour and stucture of the samples heat-treated were conditioned by furnace atmosphere. Indeed, at 1000°C the xerogel obtained with $k = 1, 5$ pyrolysed under argon is black and has an amorphous structure. On the other hand, the sample synthetised with $k = 1, 5$ fired at 1000°C in air has a white colour. The Raman spectrum of this sample (Fig. 4) present relatively intense peaks at 380, 418, 432, 450, 644 and 751 cm^{-1} which are considered as characteristic of to α-Al$_2$O$_3$ phase [29]. In comparison with the "classical" alumina gels obtained by hydrolysis of aluminum tri-sec-butoxide and using a catalyst, alpha phase is observed only above 1200°C when the starting material is bayerite, whereas conversion from boehmite powder begins below 1050°C according to previous studies [30, 34].

3.2. Ordering and crystallisation

X-ray diagrams of the fired samples under argon are presented in Fig. 5. The dried gel powders are amorphous at $T < 1000$°C. At about 1100°C two broad peaks as well as others of low intensity, were detected. They correspond to metastable γ-alumina [35] and to the beginning of crystallization of α-Al$_2$O$_3$ phase. Complete tansformation to α-alumina is achieved around 1450°C.

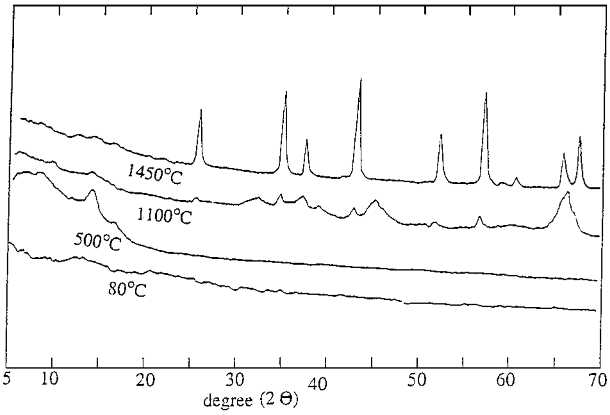
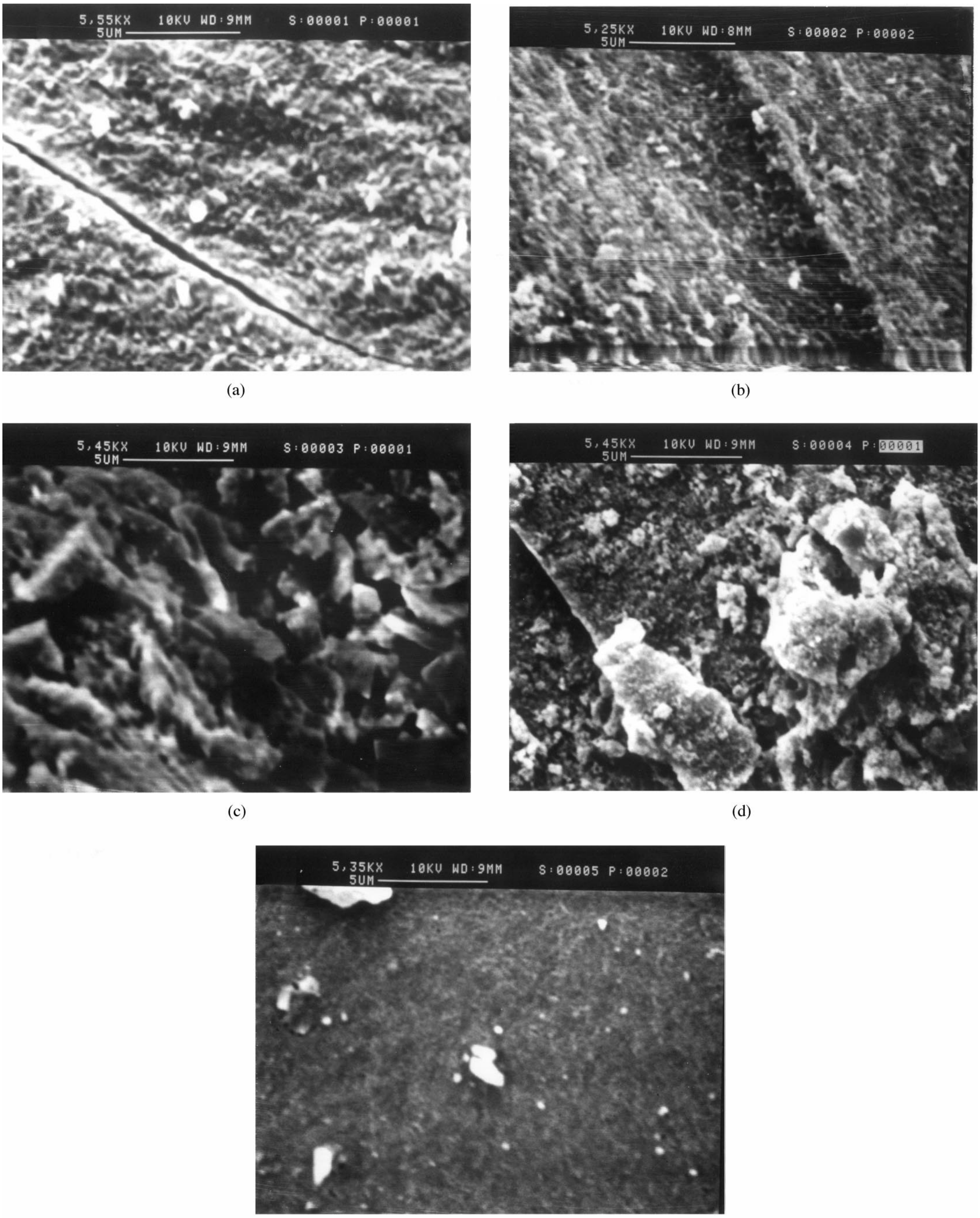


Figure 5 X-ray powder diagram of gels heated under argon at: 100°C (a), 500°C (b), 1100°C (c), 1450°C (d).



(a) (b)

(c) (d)

(e)

Figure 6 SEM of pyrolyzed products at various temperatures under argon: 100°C (a), 500°C (b), 1000°C (c) and 1400°C (d). At 1000°C in air (e).

The crystallisation behaviour of the xerogel powder heat-treated at 1000°C in air was studied. X-ray diagram of this sample show three small peaks of low intensity, wich can be attributed to γ-alumina phase. Other intense peaks correspond to the formation of α-Al_2O_3 phase.

3.3. Microstructure and densification

Microstructures of xerogels pyrolyzed at 100°C, 500°C, 1000°C and 1400°C under argon and this fired in air at 1000°C are respectively shown in Fig. 6 a–e. The SEM of materials heat-treated at different temperatures under argon show that all the samples exhibit small pores except those pyrolyzed at 1000°C. The smallest pore size is due to the densification phenomena and to entrapping the pores inside the α-Al_2O_3 grains [22]. Indeed, on heating the xerogel, OH groups on the particules liberate the water and the organic groups present in the network xerogels submitted to combustion reactions. However, these pores collapse gradually as the temperature increases. On further heating, sintering of

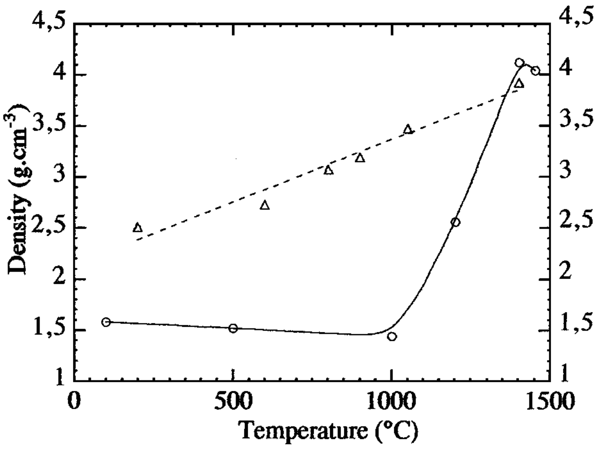


Figure 7 Plots of density versus thermal treatment temperature for: hybrid alumina gel pyrolyzed under argon (○) and inorganic alumina gel heated in air (△).

particles occurs, forming aluminum oxide wich may cause the collapse of the fine pores [19]. It is interesting to compare the evolution of the pores within the present materials to the results reported by Wilson and Stacey [36]. They have shown that the thermal treatment of materials in air is accompanied by changes in the morphology and distributions of the pores, that having regular orientations and spacings. This regularity is maintained during heat treatment. Such regularity is not observed in our materials.

The result of SEM micographs analysis is in agreement with a previous work on the textural properties of fired materials [18].

The values of density of samples heat-trated under argon at different temperatures are determined (Fig. 7). This result shows three temperature ranges in which the density changes:

– From above 300°C to 1000°C, the sample is black, the density decreases progressively. This could be due to the disappearance of OH and the traces of organic groups and to the increase in the size of the pores [20].

– Between 1000°C and 1400°C, the colour of the sample turns from black to grey. At the same time, the density increases. Indeed, in this temperature range, residual graphitics fixed in the network disappear, pores shrink and crystallisation progresses [37].

– Above 1400°C, the product obtained has a white colour, the density decreases from 4.12 to 4.04 g·cm^{-3}. The last value corresponds closely to the theoretical density of α-Al_2O_3. The decrease of the density is due to the growth phenomenon of grains [38]. Therefore, the material corresponds to pure α-alumina.

The results of the density evolution during the pyrolysis of hybrid alumina gel are compared with those of V. Vendange's in the case of alumina gels prepared by very slow hydrolysis [39]. Fig. 7 clearely shows that the density of hybrid gel remains lower than that of inorganic gel. This is consistent with the formation of hybrid organic-inorganic material. Indeed, the existence of organic chains linking the aluminum atoms gives a less condensed network. The sample pyrolysed at 1000°C under air has a white colour. Its density reaches 3.92 g·cm^{-1}. This is closely in agreement with the density value of α-alumina. X. Yang *et al.* [22] prepared gels at 90°C by the hydrolysis of Al sec-Butoxide in excess water and peptization with HNO_3 and indicated that the density of materials annealed in air at 1150°C is 3.94 g·cm^{-3} corresponding to the theoretical density of α-Al_2O_3.

4. Conclusion

The thermal behaviour of gels, prepared from aluminum secondary butoxide and propan-1,2-diol was investigated. The comparison between the IR spectra of the xerogel and those of starting materials show that the reaction occured and an organic-inorganic gel was formed. A structural investigation of materials performed by X-ray, IR and Raman spectroscopies, SEM and density measure, show that the thermal behaviour of products pyrolysed under argon was different to the materials heat-treated in air. Indeed, at 1450°C, α-Al_2O_3 was obtained for the materials heat-treated under argon, but this phase was obtained above 1000°C in the case of the materials treated in air.

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