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Synthesis of resins as alpha-alumina precursors by the Pechini method using microwave and infrared heating

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Abstract

A polymeric method based on the Pechini process was successfully used to synthesize alpha-alumina. Different resins have been prepared in order to compare the effect of the heating source (microwave or conventional IR radiation) during the polyesterification reaction, the importance of the starting aluminium salt and the ratios between reactants. The resin precursor and the product powders were fully characterized in order to investigate the polymer decomposition and the characteristic of the resulting alumina. It is concluded that the control of the ethylene glycol to citric acid ratio is important to obtain weak agglomerated particles, which are required to achieve soft porous precursors. Comparing with a conventional infrared source, the 2.45 GHz-microwave heating reduces the polyesterification reaction time to a great extent followed by a solid polymeric resin formation; however, the reaction mechanisms do not change. The best final alumina powder was synthesised by applying the microwave radiation to a precursor resin obtained from the thermal reaction of the aluminium lactate with small amounts of ethylene glycol as the polymerizant agent.

Keywords: Al_2O_3; Microwave heating; Pechini method; Precursors-organic

1. Introduction

Alumina is an advanced material with microelectronic and structural applications, as well as in the technology for thermonuclear fusion reactors. Particularly in this area, alumina ceramic materials are being considered as a promising candidate for dielectric windows on high frequency heating systems due to its very low dielectric losses[1,2] at high frequencies and its radiation resistance.

Anyhow, the lack of a systematic study on the dielectric properties of doped aluminas on an attempt to establish the effect of the processing parameters and the structural features have led the authors to prepare oxide precursors from chemical routes. Uniformed and nanosized starting powders are necessary to obtain dense final sintered bodies, and therefore wet chemical synthesis methods have been usually used in order to achieve high quality oxide powders.[3] Among others, the Pechini synthesis method[4] (also called polymeric precursor process) is a simple powder preparation based on the capability of certain alpha-hydroxycarboxylic acids to form polybasic acid chelates with a large number of cations. Even when the most widely used is the citric acid, the process can be modified by employing some others as lactic or glycolic acids. After chelation between complex cations and citric acid, the polyesterification of an excess of hydroxycarboxylic acid with glycol occurs by slightly heating the solution to form a viscous resin. The final oxide is obtained after drying and calcining the resin. There is a great controversy in the literature to identify the parameters that provide an homogeneous and regular particle morphology.[5] To avoid undesirable particles after heating, the ethylene glycol to acid ratio, the ratio between the acid and the total cations involved in the synthesis, the type of the cation salt and the alpha-hydroxycarboxylic acid used, or its molar concentration must be taken into account.[6]

On the other hand, the microwave enhanced processing is recently being applied in many systems in order to improve the final product.[7,8] Compared to that of an infrared resistence, the more uniform and rapid microwave heat leads to lower process temperatures which are described to give smaller grain size microstructures of the ceramic materials that are noticeably improved in their properties.[9]

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This paper is the first of a serial work to define the synthesis method for low doped aluminas of a wide range of metal cations in order to study its dielectric behaviour. The aim of this contribution is to evaluate the influence of the above mentioned synthesis process variables on the obtention of small and homogeneous particles of ultra pure aluminium oxide. Comparation of the resultant powders when heating the organic precursors by infrared or microwave radiation will allow to establish which of the heating techniques will be useful for industrial applications.

2. Experimental procedure

2.1. Synthesis of the alumina powders

Seven different alumina powders have been prepared following the conventional Pechini synthesis process to which some modifications have been done to compare as described later. The prepared materials are listed in Table 1 and named according to their synthesis differences: "lac" (for aluminium lactate, purity >99%, Fluka Chemie, Switzerland) or "nit" (for nine hidrated aluminium nitrate, purity >99%, Merck Darmstadt, Germany) because of the starting cation salt used; the number refers to the citric acid to ethylene glycol ratio (1 = 0.9, 2 = 1.8, 3 = 3.6); and the ending letters mean the heating procedure used (mw for microwave, ir for infrared). The CA molar and CA/Al^{3+} ratio was maintained constant in all samples in order to compare in the final obtained resin the effect of different raw aluminium salts, the CA/EG ratios and the heating procedure.

Aluminium nitrate or aluminium lactate was dissolved in 100 ml aqueous citric acid solution during stirring. The required amount of ethylene glycol was then added to the solution and heated up to 90 °C. The polyesterification reaction of the reduced solution was promoted at 175 °C by using two different heating sources: a microwave (2.4 GHz, 1500 W) and an infrared resistence. The resultant black powder was then calcined at 1100 °C on a conventional resistance furnace to obtain the alpha-aluminium oxide, although sample nit2-ir was heated at 100 °C steps up to 1100 °C to study the evolution of the resin to the corindum phase. Powders were characterized as follows and compared.

Table 1
Amounts and ratios of reactants added to 100 ml of distilled water

Material	CA (g)	AlLa (g)	EG (ml)	CA/Al^{3+}(molar)	CA/EG(wt)
Lac1/mw	20	10	20	3	0.9
Lac2/mw	20	10	10	3	1.8
Lac3/mw	20	10	5	3	3.6
Lac2/ir	20	10	10	3	1.8
		AlNi(gr)			
Nit2/mw	20	13	10	3	1.8
Nit3/mw	20	13	5	3	3.6
Nit2/ir	20	13	10	3	1.8
Nit3/ir	20	13	5	3	3.6

CA, citric acid; AlLa, aluminium lactate; AlNi, aluminium nitrate; EG, ethylene glycol.

2.2. Characterization methods

The compositional and structural study of the obtained resins after being heated at 175 °C was achieved by means of the following techniques. Thermogravimetry (TG)-differential thermal analysis (DTA) was carried out to evaluate the resins thermal descomposition in air from 175 to 1200 °C at 10 °C/min. (SEIKO TG/DTA 6300). IR spectra were registered on a 1 wt.% pellets with dry KBr (Spectrofotometer Perkin-Elmer 983-G). The residual C and N contents of the resins were studied by the combustion-IR absorption method (LECO CS-244 and C.ERBA EA 1108) as a function of the calcination temperature, which is reached at 5 °C/min and kept constant during 2 h. The crystalline evolution as a function of temperature was investigated by X-ray diffraction (Philips diffactrometer, X-Pert-MPD with CuKα radiation and Si monochromator). Scanning electron microscopy (JEOL JSM 6400 at 20 kV and ADX LINK INCA) was applied to visualise the morphology of the final alumina powders. The granulometric analysis by laser diffraction (MALVERN, Mastersozer System 2.600) and specific surface area (QUANTACHROME, Quantasorb using BET methodology) were determined on the aluminium oxide obtained at calcination temperature of 1100 °C.

3. Results and discussion

3.1. Differential thermal analysis (DTA) results

The typical thermal behaviour observed in all samples is similar to that usually found in polimerized complex resins.[10] In the TG curves (see for example Fig. 1) an intense weight loss is observed from 300 to 500 °C, which is related to the descomposition and removal of the organic material. No significant weight loss was observed for temperatures higher than 600 °C indicating that all the organic material was eliminated.

All resins have a quite similar behaviour when temperature is increased presenting three significant exothermic peaks. Before 300 °C, a broad band appears that can be related with the bridge-type bonding nature of the complex between carboxylate groups and Al ions.[11] The first clear peak is found about 300 °C and is associated with the elimination of many of the organic species involving the hydrocarbon. The one at about 400 °C is associated to polymer charring, while that at 490 °C corresponds to the pyrolysis of the organics. The characteristic endothermic peak about 198 °C was not observed, indicating that there is no excess of ethylene glycol, at the same time that full polimerization reaction have occurred.[12] From 950 to 1200 °C, the broad exothermic peak found is due to the γ to α alumina crystalline transformation, which will be also demonstrated by XRD.

Fig. 1 compares the thermal evolution of two identical resins obtained by a different heating procedure. Both samples follow the same pattern with their three characteristic bands, the only difference being the first band intensity. The spectrum of the microwave heated resin shows a clear and strong band at about 300C, which is a weak shoulder when applying the infrared heating source. In terms of thermal decomposition, it can be concluded that powders obtained when resin is polimerized by using either infrared or microwave sources can be comparable in composition.

Fig. 2 shows two different resins in which the aluminium salt precursor is changed, maintaining the rest of the process parameters identical. Again, the three characteristic thermal processes are present. The difference on the intensity of the peaks is not representative and is due to the different amount of powder weight for the test.

Finally, Figs. 3 and 4 plot the thermal behaviour when the CA/EG is varied. When aluminium nitrate or aluminium lactate are used, the band at about 490 °C disappears as the EG amount decreases and this fact is independent of the heating source applied (Fig. 4).

Two different mechanisms of the pyrolysis reaction are described in the literature[13] when the Pechini process is used which can help to elucidate the resin thermal

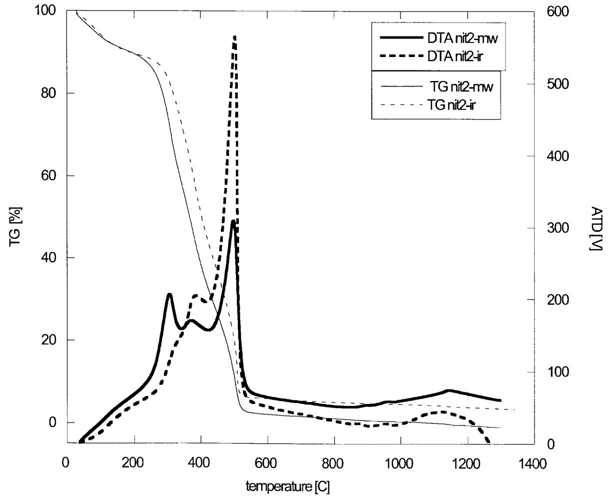

Fig. 1. Thermogravimetric and differential thermal analysis curves comparing samples heated with different power sources: microwave (nit2/mw) and infrared (nit2/ir).

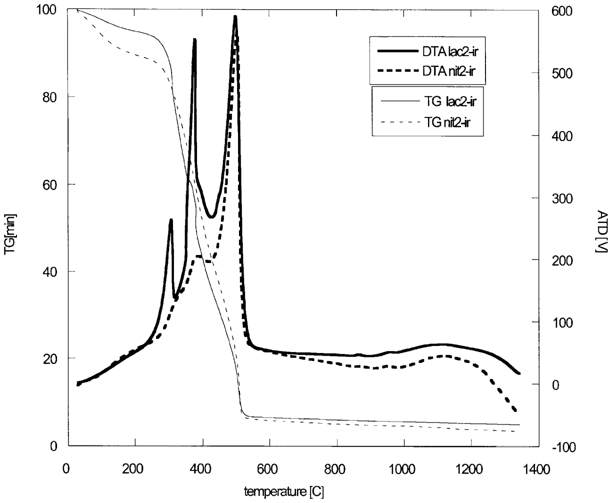

Fig. 2. Thermogravimetric and differential thermal analysis curves comparing samples obtained from different starting compounds: aluminium lactate (lac2/ir) and aluminium nitrate (nit2/ir).

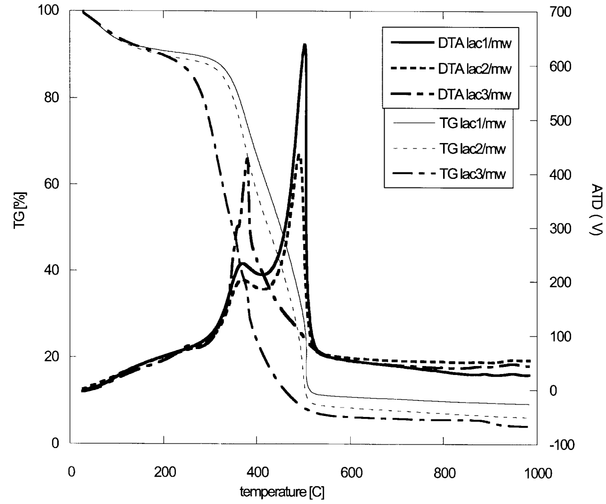

Fig. 3. Thermogravimetric and differential thermal analysis curves comparing samples prepared with an increasing amount of citric acid.

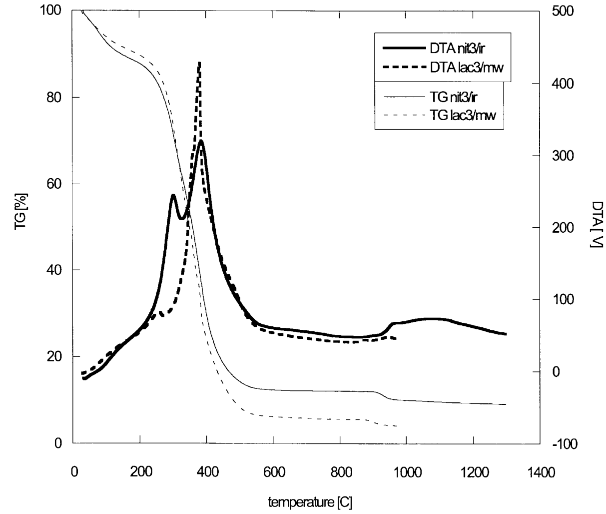

Fig. 4. Thermogravimetric and differential thermal analysis curves comparing samples with different starting salts and heating procedures.

behaviour. The first one is described by a continuous reaction, while the second one is characterised by a two-stage process in which an intermediate decomposition step occurs due to the formation of a stable semi-decomposed precursor consisting of a complex citrate salt. This different thermal behaviour is not related with the reaction mechanism but with the stability of the intermediate compound produced when nitrates are lost. In this case it seems that when the ethylene glycol addition is the lowest, the main species formed seems to be very instable and are decomposed as soon as it is formed.

On the other hand, when the Pechini method is used, it is assumed that most of the polyester chains are broken near 400 °C.[14] In this case, the decrease in ethylene glycol is associated with a decrease in the polymeric chain length. For this reason the peak located at 490 °C disappears or becomes very weak, and the totality of the organic material is eliminated at lower temperatures than in the other cases.

3.2. X-ray diffraction

Taking into account that the discussed IR spectra for all resins are very similar, as well as their thermal evolution, it can be expected that all will present similarities in respect to crystallization. Fig. 5 shows the X-ray diffraction patterns of the nit2-ir powder sample slowly calcined for 2 h at various temperatures. It was found that the product remains amorphous up to 650 °C. Up to 1100 °C the most intense diffraction peaks were identified as γ-alumina major phase together with the presence of weak maximum that could be associated to the monoclinic Θ-alumina phase that it has been refereed in a previous paper [15] depending on the synthesis process used. The patterns at 950 °C show also a small reflection which corresponds to the main reticular space (2086 Å) of an incipient α-alumina structure. After 3 h at 1100 °C, α-alumina is completely formed. The diffraction pattern is extremely sharp indicating the existence of a highly crystalline material.

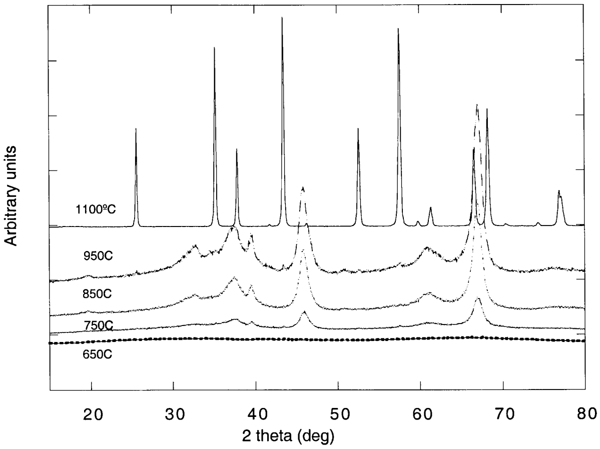

Fig. 5. XRD evolution with calcination temperature of the nit2/ir resin.

It is interesting to comment that this powder sinthesized by the Pechini process needs higher temperatures for the γ-alumina crystallization in comparation with other wet synthesis methods. In this sense, in the sol-gel route γ-alumina is formed from the boehmite phase at about 300 °C,[16] while following the citrate route [17] this phase is obtained at about 600 °C. However, the temperature at which α-alumina is formed (below 1000 °C) is lower. Even more, the temperatures required in this work to form the γ-alumina (referred to a group of transition aluminium oxides) and to obtain the final corundum phase are slightly lower than other authors report for similar conditions.[16]

3.3. IR spectra

Figs. 6 and 7 plot the IR spectra for all the resins prepared at 175 °C. It can be seen that all samples are very similar and the characteristic frequencies, listed in Table 2, do not vary too much between them.

The broad band at about 3400 cm^{-1} is typical of the O–H stretching. The presence of two bands at about 2900 cm^{-1}, which corresponds to C–H stretching, and at 1450 cm^{-1} due to C–H bending vibration, are related with the citrate or lactate ions. The band ranged about 1740 cm^{-1} is reported to agree to the carboxilate anion (COO^-) stretching mode (a covalent carbonyl bond). The last clear band observed is ranged at about 1580 cm^{-1} and can be assigned to the antisymmetric COO^- stretching mode for a bridge-type complex,[18] as well as the band over 1170 cm^{-1} is related to ester bonds type.

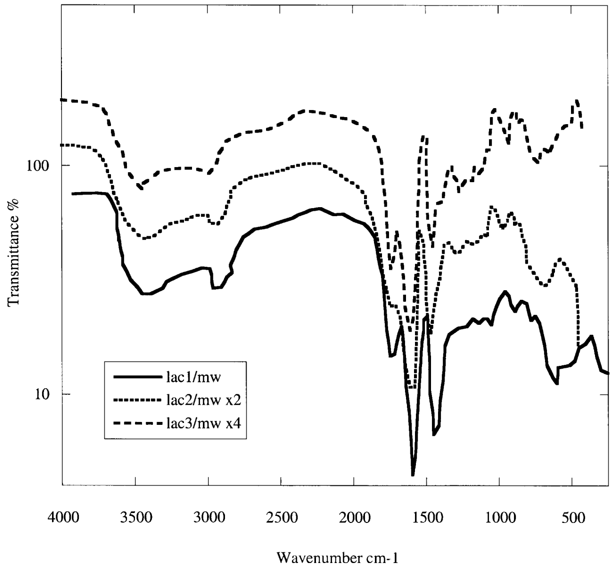

Fig. 6. Optical transmitance spectra in the infrared region comparing samples prepared with an increasing citric acid to etylene glycol ratio.

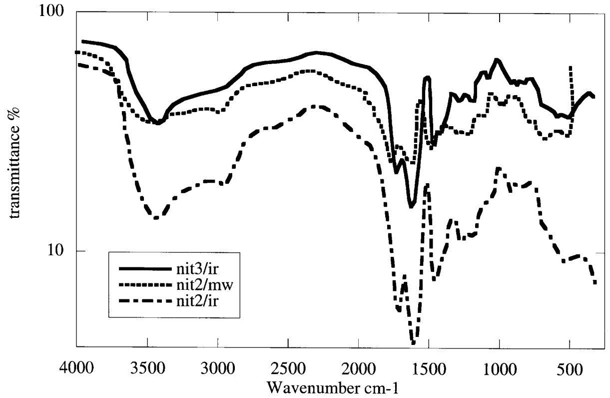

Fig. 7. Optical transmittance spectra in the infrared region comparing samples obtained by applying the two different heating sources: microwave (nit2/mw) and infrared (nit2/ir).

Due to the presence of these bands, it is possible to recognise the ester formation at this temperature by the esterification of the hydroxycarboxylic acid with ethylene glycol.[19]

Taking into account the similar characteristics of all the materials prepared, the thermal evolution by means of the IR spectra has been only checked for nit2- ir. Temperature has been increased from 175 °C up to 1100 °C with a dwell time of 3 h on each step at a heating rate of 1 °C/min. The resulting curves are plotted in Fig. 8 and the characteristic transmittance frequencies are summarised in Table 3.

Although the IR spectrum at 250 °C presents similar bands as that at 175 °C, the decreasing intensity establishes clearly the gradual loss of water and the citrate and carboxylate groups. It is worth noticing the wide band appearing between 500 and 900 cm^{-1}. This region corresponds to the vibrational frequencies of co-ordinated O–Al–O bonds [20,21] and begins to take importance at relative low temperatures.

At 350 °C the pyrolysis process continues as it is demonstrated by the strong intensity decreasing of the carboxylate anions and organic chain bands. The band ranged at about 500–1000 cm^{-1} keep gaining intensity. A small and weak band at 2484 cm^{-1}, which can be related to the OH stretching mode, appears at this temperature while the ether band cannot be noted.

Table 2
Infrared peaks of the studied samples heated at 175 °C

Sample	Characteristic frequency (cm^{-1})					
Lac2-ir	3460	2961	1741	1586	1450	1183
Lac1-mw	3446	2963	1748	1586	1450	1170
Lac2-mw	3437	2976	1732	1594	1449	1173
Lac3-mw	3441	2993	1740	1606	1453	1194
Nit2-mw	3471	2963	1734	1601	1456	1178
Nit2-ir	3431	2965	1729	1602	1451	1172
Nit3-ir	3429	–	1726	1616	1461	1188

The typical bands for the hydrocarbon skeleton and the carboxylate anions have disappeared at 450 °C, and only a trace of the ester band remains at this temperature. These results suggest that most of the organic chains break down between 350 and 450 °C.

The spectra of the resin calcined between 550 and 950 °C show similar features. At all temperatures a well defined peak which emerges at 2341 cm^{-1} and increases with temperature can be observed. Some authors relate this band to the atmospheric CO_2 adsorbed on the metallic cations.[22] The wide band, corresponding to the Al–O bonds, develop into two or three small bands (750, 570 and 460 cm^{-1}, respectively) as temperature increases up to 950 °C. These are the characteristic frequencies of AlO_4 tetrahedra, or more specifically, they can be assigned to some stretching lattice vibrations of interlinked AlO_4 tetrahedra, as occurs in transition aluminas.[19] In the 500 cm^{-1} region, vibrations may be due to some bending motion of the AlO_4 lattice. It is in agreement with the presence of γ-alumina diffractions observed in the XRD pattern from 750 °C.

At 1100 °C, the strong and well defined IR bands observed for Al–O bondings must be explained taking into account the pure XRD reflections of α-alumina observed. In the case of a corundum structure, it is built up only on octahedral AlO_6 and the most characteristic IR feature is the occurrence of two strong bands near 650 and 600 cm^{-1} together with some others of less intensity around 450 and 780 cm^{-1}.[19] The IR bands attributed to the anion vibrations have disappeared at this temperature. The bands of the corundum phase are not completely reproducible but depend on the processing thermal history. Therefore, the band located at 380 cm^{-1} is not refereed by other authors.

It is interesting to note the residual carbon and nitrogen obtained after a LECO analysis and try to relate it

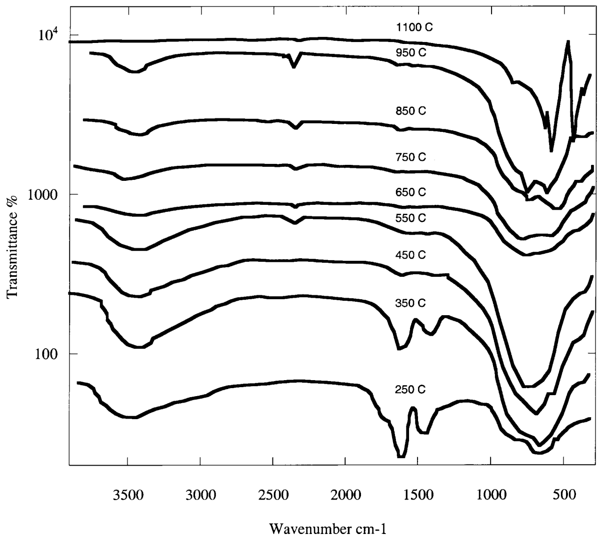

Fig. 8. Optical transmittance spectra in the infrared region of the nit2/ir resin as a function of the calcination temperature.

Table 3
IR-peaks evolution with temperature on the nit-ir sample

Temperature (°C)	Characteristic frequency (cm^{-1})										
175	3431			1602	1451	900–500					
250	3439			1602	1447	900–500					
350	3433	2484		1602	1422	1000–500					
450	3441	2484		–	–	1100–400					
550	3440			–	–	1100–400					
650	3436		2341	–	–	750			–		
750	3437		2341			750			570		
850	3431		2341			750			570		
950	3445		2342			750			570	460	
1100	3441		–				645	610		458	384

with the IR data. Fig. 9 plots the evolution of these light elements as a function of the calcining temperature. A huge weight loss is observed between 250 and 450 °C which agrees with the fracture of the organic chains and the removal of the ester bands observed by ATD. However, the increase on temperature does not provoke the total elimination of carbon which is still present into the γ-alumina structure at 950 °C. The carbon traces can be observed in the IR spectra as a weak band in the frequency range corresponding to the carboxylic anion vibrations. Only at the highest temperature (1100 °C) the carbon content is reduced, although a small amount remains after 3 h of treatment. And longer soaking times are necessary to remove it below 50 ppm level. The slight differences on C-content between the elemental analysis results and TG curves are easily explained taking into account the different heating conditions applied in each case.

3.4. Microstructure and particle size characterization.

Since the DTA results show a significant temperature decrease for the organic material reduction in those resins with a AC/EG relation of 3.6, initial microstructure studies have been performed on a nit3 precursor resin heated up to 175 °C using both heating systems: IR and MW. The as-heated polymeric resin without any subsequent mechanical process present a similar aspect of sharp and irregular-shaped particles (Fig. 10a and b) independently of the power source used. However, the microwave dried one exhibits a most homogeneous scrap size which is explained by means of the non existence of thermal gradients due to, in this case, volumetric radiation–matter interaction.

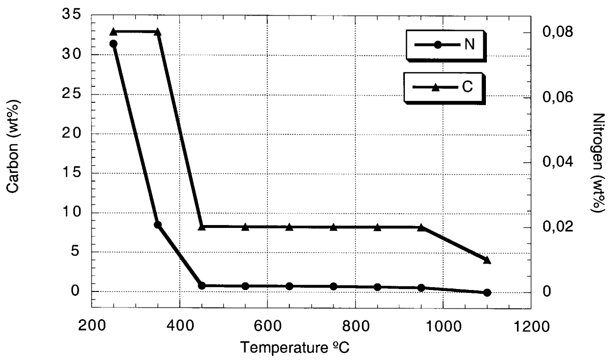

Fig. 9. Carbon and nitrogen elemental analysis in the as-prepared nit2/ir resin.

Granulometric analyses are shown in Table 4. All samples present particle size values for 50% population above 20 microns. After 4 h of attriction milling on a standard sample, as nit2/ir, the agglomerates are significantly broken and the particle size dramatically decreased, maintaining a non negligible population below 3 microns (1.4%) but the specific surface seems not to increase. It is worth mentioning that a similar particle size, as well as the highest specific surface area found without being milled, was obtained on lac3/mw powder (Table 4), indicating the convenience of employing short chain alpha-hydroxy carboxylic acids combined with small amounts of ethylene glycol when the Pechini synthesis is used. Anyhow, the microwave heating seems to have some beneficial effect on agglomerate hardness inducing weaker bondings between pellets that are easily broken after mechanical milling. In terms of particle morphology, best results are obtained when microwave heating is applied on a high citric acid to ethylene glycol ratio resin of a lactate precursor material.

The formation of hard crystalline agglomerates is a problem for all the synthesis related to the Pechini approach. Even in the highest specific surface calcined powder, lac3, great agglomerates can be observed (Fig. 11) that have to be milled during a few hours to break them and to facilitate the following processes, such as sintering. In our case, the high temperatures needed to obtain the corundum phase must be also taken into account. It is interesting to consider some factors that can influence the final powder characteristics and also to explain the differences found in the granulometric data.

In relation with the chelation reaction, it is important to consider the functionality or, in other words, the

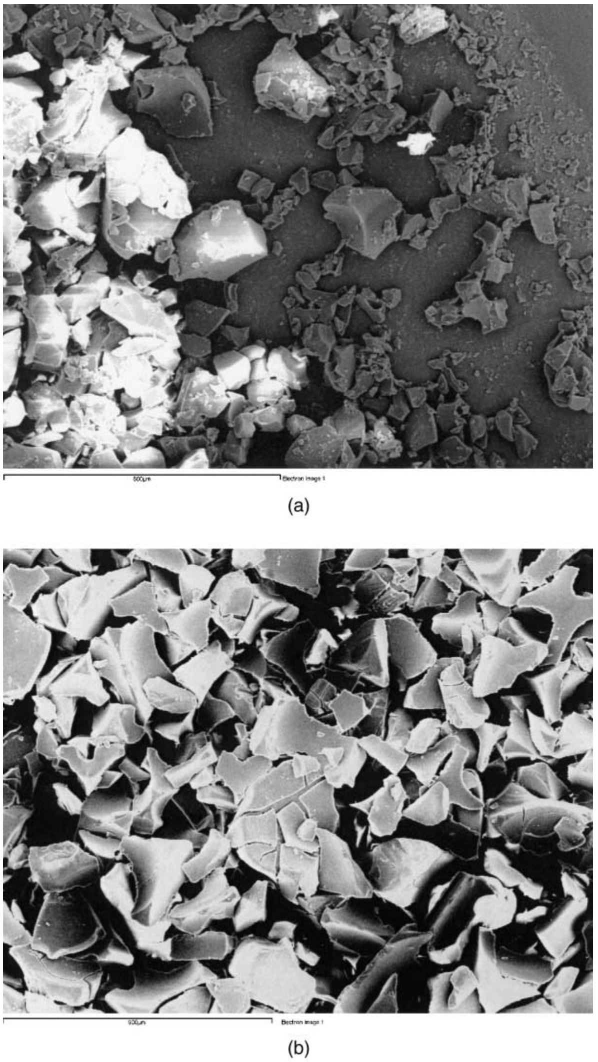

Fig. 10. SEM micrographs of two nit3 resin as-prepared particles heated upto about 175 °C by means of an infrared (a) or a microwave (b) power source.

number of reactive sites that the possible α-polyhydroxycalboxylic acids have able to bond with the metal cations. The molecular structure of the citric acid present three carboxylic groups and one hydroxyl group on a six carbon multisubstituted chain while the much shorter straight-chain of the lactic acid displays only two functional groups. It is known that the number of possible arrangements within amorphous gels increases when the acid functionality increases and can vary in any one batch of precursor,[13] so the citrate acid may form polydentate complexes with the metallic cations in a larger way than the lactic acid.

The subsequent esterification and polymerization reactions will only be possible between the free carboxylic and hydroxyl groups giving rise to spherical and long chain structures when using citric acid. The complex formed between the citrate and the metal ion tends to be fairly stable due to this strong coordination. On the other hand, the metal ion to lactic acid bonding is therefore considered softer because of the inability to form bidentate chelated complexes. After the thermal treatment, it is assumed that the crystalline agglomerates typically follow the morphology established from the resin particles.[10] In the case of lactic acid, it corresponds to the smallest agglomerate size and the highest specific surface area.

Table 4
Granulometric analysis obtained by using a laser diffraction method for as-prepared α-alumina powders

Sample	D (v, 0.5) µm	D (v, 0.1) µm	D (v, 0.9) µm	Ss (m^2/g)
Nit2/mw	19.0	11.2	27.1	3.7
Nit2/ir	19.8	11.6	28.2	6.9
Nit3/ir	33.7	20.9	47.6	9.3
Lac1/mw	19.9	11.7	28.5	3.2
Lac2/mw	21.5	12.6	30.7	7.5
Lac2/ir	23.7	13.9	34.2	4.6
Lac3/mw	4.5	2.7	6.4	14.7
Nit2/ir after milling	5.0	2.6	7.7	4.8

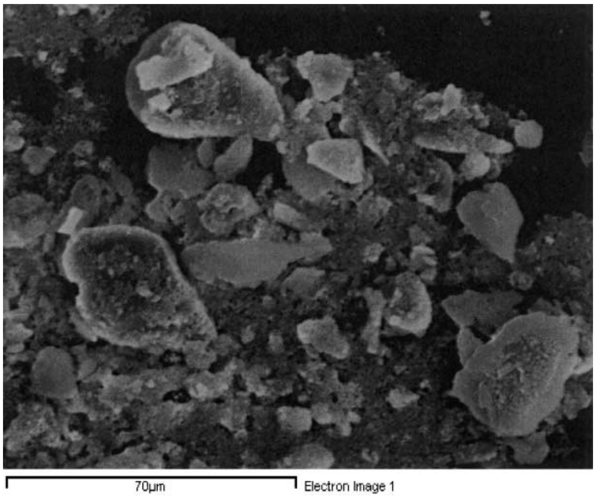

Fig. 11. Aggregates formed on lac3/mw as-calcining at 1100 °C (not milled).

When preparing the lac3 material, the two conditions that seems to give small globular structures ocurred at the same time: a short chain alpha-hydroxycarboxylic acid and low proportions of ethylene glycol. Small additions of ethylene glycol are considered to provide less organic material into the initial solution and so the required calcination temperatures decrease as well as the crystal size and the agglomerate state.

4. Conclusions

Both the different starting aluminium salts and the use of different heating procedures are observed to produce similar resins. However, when a microwave source is incorporated into the process the heating homogeneity significantly increases and those times needed to remove the excess of solvents, to occur the polyesterification reaction, and to form the resin are dramatically reduced from hours to a few minutes. The fact is that microwave radiation does not change the intermediate compounds formed in the Pechini process as it is demonstrated from the IR spectra.

The IR data provide the existence of Al–O bonds just at the resin formation temperature (175 °C). However, the γ-alumina is evident only above 650 °C, while α-alumina is formed at 1100 °C. At 650 °C the γ-alumina phase is too low to be detected by XRD patterns.

A controversy exists between the experimental conditions required to achieve small particles, low carbon content but crystalline corundum phase. The former is fulfilled at low decomposition time and temperatures, however, calcining temperatures above 1000 °C are necessary to reduce the C-content to pmm levels and to reach well-crystallized phase. The use of small additions of ethylene glycol together with short chain hydroxycarboxylic acids has been demonstrated that help to obtain soft particle aggregates. Milling after the 1100 °C calcination could be a second choice to achieve high quality powders with a good sinterability.

Acknowledgements

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