

PREPARATION OF ALUMINA MATRIX FOR CERAMIC COMPOSITES BY SOL-GEL METHOD

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SUMMARY: •-Alumina ($\bullet\text{-Al}_2\text{O}_3$) is a typical delegate of oxide ceramics, which owns many excellent properties, such as high melt point, excellent high temperature stability, good heat and electrical properties, etc. It is widely applied in industry fields at many aspects. It may also be a kind of good high temperature structure material for its high strength and modulus at high temperature.

The sol-gel method is chosen to prepare Al_2O_3 matrix in order to fabricate •-Alumina matrix composite reinforced by three dimensional carbon fiber braided preform. Some Al_2O_3 sols are prepared by hydrolysis aluminum salt or aluminum alkoxide, then, the sols prepared can infiltrate into the preform. Thus gelation and pyrolysis in the preform can be carried out. After pyrolysis, Al_2O_3 matrix composite reinforced by carbon fiber woven preforms could be obtained.

KEYWORDS: alumina (Al_2O_3) matrix, sol-gel method, aluminium isopropoxide, aluminium nitrite, aluminium chloride

INTRODUCTION

•-Alumina ($\bullet\text{-Al}_2\text{O}_3$) is a typical delegate of oxide ceramics, which owns many excellent properties, such as high melt point, excellent high temperature stability, good heat and electrical properties, etc. It is widely applied in industry fields at many aspects. It is also a kind of good high temperature structure material for its high strength and modulus at high temperature.

The traditional processing to prepare bulk alumina material is so-called hot-press method. A new processing, which is called as sol-gel method, to prepare bulk oxide ceramic materials, has been developed since the end of 1970s [1-3]. Sol-gel method to prepare Al_2O_3 possesses the following three steps. First, hydrolyzing aluminum salt or aluminum alkoxide in order to obtain a sol; then, condensing and drying the sol for the purpose of obtaining a gel; finally, pyrolyzing the gel at high temperature under inert atmosphere protection for getting the final ceramic product. Preparation of Al_2O_3 from this processing is of the following advantages [1]. (1) The final ceramic product compositions can be precisely designed through controlling

those of pre-ceramic sols. (2) The pyrolysis temperature is lower than that of hot-press processing. (3) Through infiltrating the sols into fibers or fiber woven preforms, and together with the following gelation and pyrolysis, some ceramic matrix composite materials reinforced by continuous fibers or fiber woven preforms, which is similar to the polymer pyrolysis processing.

In the present paper, first of all, three sols were prepared by hydrolyzing aluminum isopropoxide ($\text{Al}(\text{o-Pr}^i)_3$), aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), respectively. Then, the influences of processing parameters, such as reactant concentrations, hydrolysis reaction temperature, and hydrolysis reaction time, on the sol properties, gelation conditions, and the pyrolysis product properties were investigated. Finally, an α - Al_2O_3 matrix composite material reinforced by carbon fiber woven preform was prepared by infiltrating the sol into the preform, together with the following gelation of the sol, and pyrolysis of the green body pre-composite at high temperature and under an inert atmosphere protection.

EXPERIMENTAL METHOD

Raw materials and their specifications

Raw materials used and their specifications was shown in Table 1.

Table 1. Raw materials and their specifications

Raw materials	Formula	Specifications	Characters
aluminum isopropoxide	$\text{Al}(\text{o-Pr}^i)_3$	AR	white powder
aluminum nitrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	AR	colorless crystal
aluminum chloride	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	AR	colorless crystal
deionized water	H_2O	—	colorless liquid
aluminum powder	Al	CR	gray powder

Preparation and characterization of sols

Preparation of sols

In a three-neck circular bottom flask, quantitative amount of deionized and double-distilled water was added and heated to 80° , then quantitative of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was added piece by piece with stirring. During the reaction, Al powder was added in order to adjust the aluminum ion concentration. The hydrolysis reaction was, from a to z, carried out under a refluxing condition. After a transparent and stable sol was obtained, the reaction was completed.

Characterization of the sols

The sols were qualitatively identified by Dindaer effect. Then infrared (IR) analysis was used to further identify and to characterize the sol structures.

The relative viscosity was considered as a key parameter to characterize the sol processing

property for infiltrating fibers or fiber preforms. It was defined as the ratio of the time that the sols flowed over the U-viscometer deadline to that the deionized water did.

Gelation conditions of the sols out- or insider the preforms

A little of sols previously prepared was placed on a glass surface and then put into an oven, then held in different time at different temperature to obtain the continuous crack-free and semi- transparency or transparency gel. The gelation conditions obtained can be considered as a reference for gelation of the sols in a three dimensional carbon fiber braided preform. So, the gelation conditions of the sol infiltrating into the preforms were investigated according to the reference. Then, the gel structures were identified and characterized with infrared (IR) analysis.

Pyrolysis of the gels out or insider the preform and pyrolysis product characterization

Determination of the gel pyrolysis processing conditions

Three gels from three different sols, without or with a little of short carbon fibers, were put into three crucibles respectively, then heated with a DSC apparatus from room temperature to 1250 ° under N₂ atmosphere. From the DSC analysis result diagrams, one can determine the gel pyrolysis processing conditions to prepare the composites.

Structural analysis of the pyrolysis products

Some analyses were used to identify and characterize the pyrolysis product structures, infrared (IR) analysis for the molecular structures and XRD for the crystal structures. The pyrolysis product thermal properties were investigated with TG-DTA apparatus (Rigaku Thermal, Made in Japan).

RESULTS AND DISCUSSIONS

Preparation of alumina sols

The alumina sols which were suitable for infiltrating a three dimensional carbon fiber braided preform in order to prepare alumina matrix composite materials should meet the following demands. (1) low viscosity to overcome the difficulties during the infiltration and to promote the infiltrating efficiency; (2) higher ceramic yields to shorten the infiltration-gelation-pyrolysis cycles of composite preparation. In general, lower viscosity sols are of a lower sol concentration, which would lengthen the preparation cycles.

Therefore, it is necessary to obtain a compromise between the viscosity and the concentration. In the present paper, the following factors which affect the compromise were investigated: (1) Concentration of aluminum ions, represented by R, which is mole ratio of water to aluminum ions ($R = \text{Mol}(\text{H}_2\text{O})/\text{Mol}(\text{Al}^{3+})$); (2) hydrolysis reaction temperature (T); (3) hydrolysis reaction time (t). The influences of the three factors upon the sol properties were investigated.

Influence of Water/reagent Ratio (R) upon the sol properties

The sol system via $\text{Al}(\text{o-Pr})_3$ was used to prepare an Al_2O_3 coating, both on the carbon fiber

surfaces and on the composites, as an oxidation resistant. The other two sol systems were used to prepare an Al₂O₃ matrix for composite preparation. All results were shown in Table 2.

From Table 2, one can see that the value of R for the sol used as coating should be equal to 100. Otherwise, the coating prepared via Al(o-Pr)ⁱ₃ sol system hydrolysis would be either too thick to be of crack-free, or too thin to be continuous [4]. The value of R for the sols used to prepare Al₂O₃ matrix, via Al(NO₃)₃ and AlCl₃ systems, must be over 8, which can give a lower viscosity and a higher ceramic yield for the composite preparation.

The relation between the concentration (R) and the relative viscosity (•), described with an example of the sol via Al(o-Pr)ⁱ₃ hydrolysis, was shown in Fig.1. In Fig.1, the abscissa is the reactant ratio (R), and the ordinate stands for the relative viscosity (•) (The trends when R<50 were conjectured).

Table 2. Influence of concentration upon the sol properties

Number	Ratio R	Sol systems	Uses	Characters	Precipitation properties	Relative viscosity
No.11	150	Al(o-Pr) ⁱ ₃	coating	white translucent	>30days	1.30
No.12	100	Al(o-Pr) ⁱ ₃	coating	white translucent	>30days	1.71
No.13	85	Al(o-Pr) ⁱ ₃	coating	white translucent	>15 days	1.89
No.14	50	Al(o-Pr) ⁱ ₃	coating	white muddy	<7 days	21.5
No.21	6	Al(NO ₃) ₃	matrix	gray semi-solid	immediately	--
No.22	8	Al(NO ₃) ₃	matrix	gray-yellow glutinous	<7 days	1.70
No.23	9	Al(NO ₃) ₃	matrix	light-yellow translucent	>15 days	1.36
No.24	10	Al(NO ₃) ₃	matrix	light-yellow translucent	>30 days	1.25
No.31	6	AlCl ₃	matrix	gray semi-solid	immediately	--
No.32	8	AlCl ₃	matrix	clay-yellow glutinous	<7 days	6.39
No.33	9	AlCl ₃	matrix	light yellow liquid	>15days	2.41
No.34	10	AlCl ₃	matrix	light yellow liquid	>30days	2.04
No.35	11	AlCl ₃	matrix	light yellow liquid	>30days	1.79

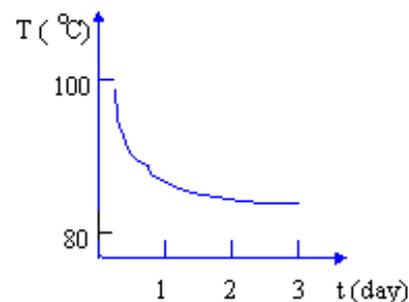
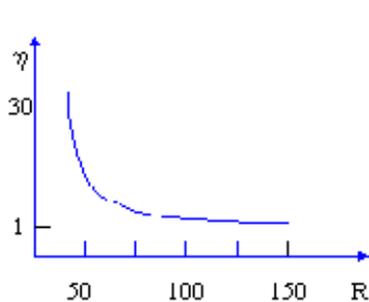


Fig.1 Relation between reactant ratio (R) and relative viscosity (•) Fig.2 Relation between hydrolysis temperature (T) and refluxing time (t)

From Fig.1, one can see that • would linearly decrease after the R>75; but • would dreamily increase before R<50. In fact, greater the value of R, higher the sol concentrations. A higher sol concentration enhances the probability of condensation reaction in sol solution. Similar relations between • and R of the other sol systems were found, we didn't describe any more here.

Influence of temperature (T) upon the properties of sols.

The relation between hydrolysis temperature and reaction refluxing time was shown in Fig.2. For the sol system via $\text{Al}(\text{o-Pr}^i)_3$, although $\text{Al}(\text{o-Pr}^i)_3$ was hard to hydrolysis, it was found in the present paper that a sol formation is much more sensitive to hydrolysis temperature than reaction time. When the hydrolysis temperature ranged from 90° to 95° ($R = 100$), the required time were from 12hrs to 8 hrs, which was significantly reduced being compared to the previous research results [5](Yoldas et al.). Then a transparent and stable sol could be obtained

For the sol system via $\text{Al}(\text{NO}_3)_3$, the hydrolysis reaction could be described by the following equation:



It was possible that hydrolysis product H^+ would slow down the hydrolysis reaction. In general, high temperature benefited the hydrolysis reaction. Hydrolysis reaction was difficult to occur when temperature lower than 90° . But, when temperature higher than 95° , a foam would be formed because hydrolysis product NO_3^- would be decomposed. So the optimum hydrolysis temperature should range from 90 to 95° .

For the sol system via AlCl_3 , the hydrolysis reaction could be described by the following:



The experiment showed that AlCl_3 was easier to hydrolysis than $\text{Al}(\text{NO}_3)_3$. Cl^- is an ion strongly much more sensitive to moisture than the other ones and Al^{3+} is vulnerable by water. Furthermore, HCl produced is easy to vaporize, which benefited reaction. To prevent the reaction from being too rapid and from vaporizing HCl , the optimum hydrolysis temperature range should be from 85 to 90°C . Otherwise, either a foam or an unstable $\text{Al}(\text{OH})_3$ deposition would be formed. The aim to add aluminum powder was adjusting the sol concentration of aluminum ion. The aluminum powder was dissolved in the solution and became a part of the AlOOH sol.

The influence of refluxing time (t) upon the properties of the sols

For the two sol systems via $\text{Al}(\text{o-Pr}^i)_3$ and $\text{Al}(\text{NO}_3)_3$, hydrolysis reaction couldn't complete if refluxing time was too short. For the first one, it was a system hard to hydrolysis. Then, high hydrolysis temperature and long refluxing time were required and optimum conditions for the sol preparation were $R=100$, $T=95^\circ$, and $t=8\text{hrs}$. For the second one, when the reaction time was too long, the produced HNO_3 would be vaporized, and the sol system acid degree would be gradually decreased, thus the sol was easy to condense and $\text{Al}(\text{OH})_3$ particles would be formed. The optimum conditions for the sol preparation were $R>8$, $T=95^\circ$, and $t=30\sim 60\text{min}$.

The influence of refluxing time upon the transparency and stability of the sol via AlCl_3 hydrolysis was greater than that via $\text{Al}(\text{NO}_3)_3$ hydrolysis. In fact, AlCl_3 was easy to hydrolysis and the produced HCl was easy to vaporize, which means that the time for sol preparation of this system was shorter than that of the other ones and the system viscosity would be increased due to an acid degree diminution. Further more, the system stability would be decreased. The optimum conditions for the sol preparation were $R>8$, $T=90^\circ$, and $t<20\text{min}$.

Gelation of the sols out or inside the preforms

The temperature influences upon gelation of the sols out or inside the preforms were investigated in the present paper. It was necessary to raise gelation temperatures, slowly and stage by stage, to form crack-free gels. The results were shown in Tables 3 and 4, respectively. The gelation temperatures of $\text{Al}(\text{o-Pr}^i)_3$ and AlCl_3 sol systems were higher than those of $\text{Al}(\text{NO}_3)_3$ sol system, and the gelation time of $\text{Al}(\text{o-Pr}^i)_3$ and AlCl_3 sol systems was also longer than that of $\text{Al}(\text{NO}_3)_3$ sol system. Though AlCl_3 and $\text{Al}(\text{NO}_3)_3$ sol systems had a same R value, the former requires higher gelation temperature and longer gelation time than the later because the former was of strong moisture absorbent ions Cl^- .

Table.3 Influences of temperature and time on gelation of the sol outside the preforms

Sol systems	Temperature (°)	Time (min)	Gelation situations
$\text{Al}(\text{o-Pr}^i)_3$	< 60	>60	Better gels could be obtained
	60•70	>45	Little cracks in the gels
	> 70	<30	Large amount of cracks in the gels
$\text{Al}(\text{NO}_3)_3$	< 30	>60	Better gels could be obtained
	30•40	>30	Little cracks in the gels
	> 40	<30	Large amount of cracks in the gels
AlCl_3	< 80	>120min	Better gels could be obtained
	80•85	>90min	Little cracks in the gels
	> 90	<60min	Large amount of cracks in the gels

Table 4 Gelation conditions for the sols inside the preform

System	Gelation temperature (°)	Time (hour)
$\text{Al}(\text{o-Pr}^i)_3$	<60	>8
$\text{Al}(\text{NO}_3)_3$	<30	>4
AlCl_3	<80	>8

Characterization of the gel pyrolysis products

IR analysis of the gels

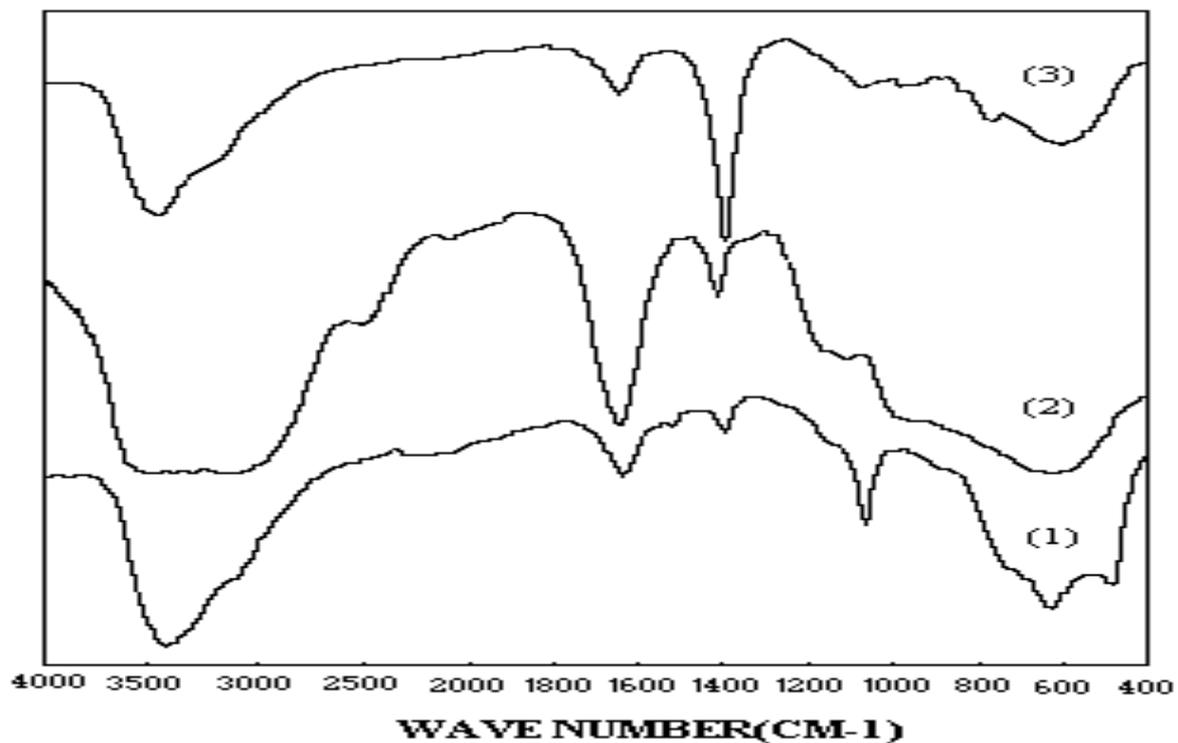


Fig.3 Infrared spectra of the gels

The IR spectra of the various gels were shown in Fig. 3. Marks (1) (2) and (3) indicated the sol via $\text{Al}(\text{o-Pri})_3$, AlCl_3 , and $\text{Al}(\text{NO}_3)_3$ hydrolysis, respectively. According to Refs.[1,3,5,6], the H_2O molecular vibration, OH stretching(3079cm^{-1}) and bending(3262cm^{-1}) vibration of AlOOH are at 3500cm^{-1} , AlOOH vibration is at 1630cm^{-1} , OH stretching vibration of pseudogibbsite ranges from 1155 to 1070cm^{-1} , Al-O-Al stretching and H_2O vibration range from 750 to 400cm^{-1} . It showed that the hydrolysis products were AlOOH sol. The condensation reaction from the sols to the gels were shown in Ref.6.

Thermal analysis of gels

The TG and DTA curves of three gels were shown in Figs.4 and 5, respectively.

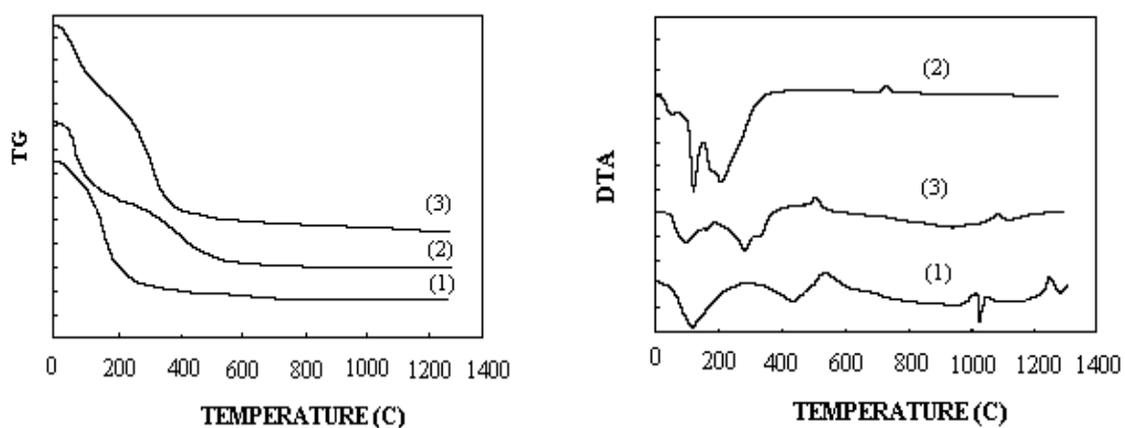


Fig.4 TG curves of three gels

Fig.5 DTA curves of three gels

The weight loss of three gels was basically finished after 600° (see Fig.4). It means that the pyrolysis process could be finished before 600°, which was in accordance with the results of Ref.[1,3]. However, there also existed endothermic and exothermic peaks after 600° (see Fig.5). It showed that the process after 600° was phase transformation. According to Y. H. Chiou's work and Refs.[1,3,5-6], the transition temperature to •-Al₂O₃ ranges from 1100 to 1260°. The ceramic yields of three gels were shown in Table 5

Table 5 Ceramic yields of the three gels

marks	gel systems	R	Ceramic yield (wt %)
(1)	Al(o-Pr ¹) ₃	100	64.15
(2)	AlCl ₃	8	33.18
(3)	Al(NO ₃) ₃	8	44.15

XRD analysis of pyrolysis products

The main crystal structures of the gel pyrolysis products were shown in Table6.

It is well known that Al₂O₃ has almost ten kinds of crystal structures, but only the •-Al₂O₃ is the most stable. According to Refs.[1,3,5], the conversion process from AlOOH gel to Al₂O₃ ceramic could be finished before 600°. The gel would condense its molecules with each other to form Al₂O₃ network, losing its residuary water. The reaction could be described by the following equations:

Table 6. Main crystal structures of the gel pyrolysis products

Number	Systems	Pyrolysis conditions	Pyrolysis temperature (°)	Main cristral(s)
(1)	AlCl ₃	N ₂	600	•-Al ₂ O ₃
(2)	Al(o-Pr ¹) ₃	Air	600	•-Al ₂ O ₃
(3)	AlCl ₃	Air	600	•-Al ₂ O ₃
(4)	AlCl ₃	Air	1260	•-Al ₂ O ₃ • •-Al ₂ O ₃
(5)	Al(o-Pr ¹) ₃	Air	1260	•-Al ₂ O ₃ • •-Al ₂ O ₃
(6)	Al(NO ₃) ₃	Air	1260	•-Al ₂ O ₃
(7)	pure Al ₂ O ₃	AR	—	•-Al ₂ O ₃
(8)	Al(NO ₃) ₃	N ₂	600	•-Al ₂ O ₃ • •-Al ₂ O ₃
(9)	Al(NO ₃) ₃	Air	600	•-Al ₂ O ₃
(10)	AlCl ₃ *	N ₂ • C _f	1260	•-Al ₂ O ₃
(11)	Al(NO ₃) ₃ *	N ₂ • C _f	1260	•-Al ₂ O ₃

note: * fetched from the composites.



So, it was shown that the last pyrolysis products was •-Al₂O₃ no matter which route and pyrolysis conditions were selected. All of the three gels could be converted into •-Al₂O₃ before 1260°. It was also true when the gel was inside the preform, which indicated that the carbon fibers did not inhibit conversion of •-Al₂O₃ to •-Al₂O₃. But, according to Ref.[4,6], 14.3% volume shrinkage would occur from •-Al₂O₃ to •-Al₂O₃.

Pyrolysis products at 600 and 1260°, and under different atmosphere (air or N₂) were investigated. XRD patterns of pyrolysis products under different conditions were shown in Fig.6. The main results were also summarized in Table 6.

CONCLUSIONS

The sol-gel method was useful to prepare α -alumina matrix composite reinforced by three dimensional carbon fiber braided preform.

Some Al₂O₃ sols were prepared by hydrolysis aluminum salt or aluminum alkoxide. The optimum conditions for sol preparation via Al(o-Pr)ⁱ₃ hydrolysis were R=100, T=90~95°, and t=12~8hrs, the obtained sol was suitable for coating preparation. The optimum conditions for sol preparation via Al(NO₃)₃ hydrolysis were R•8, T=90~95°, and t=30~60min. The optimum conditions for sol preparation via AlCl₃ hydrolysis were R•8, T=85~90°, and t<20min. The latter two obtained sols were suitable for preparation of the composite matrix.

Then, the sols, prepared and being of suitable viscosity, could infiltrate into the carbon fiber woven preform. Thus gelation and pyrolysis in the preform could be carried out under controlled conditions (suitable temperature and time, heating procedures and protection atmosphere, etc.). After pyrolysis, an α -Al₂O₃ matrix composite reinforced by carbon fiber woven preform could be obtained.

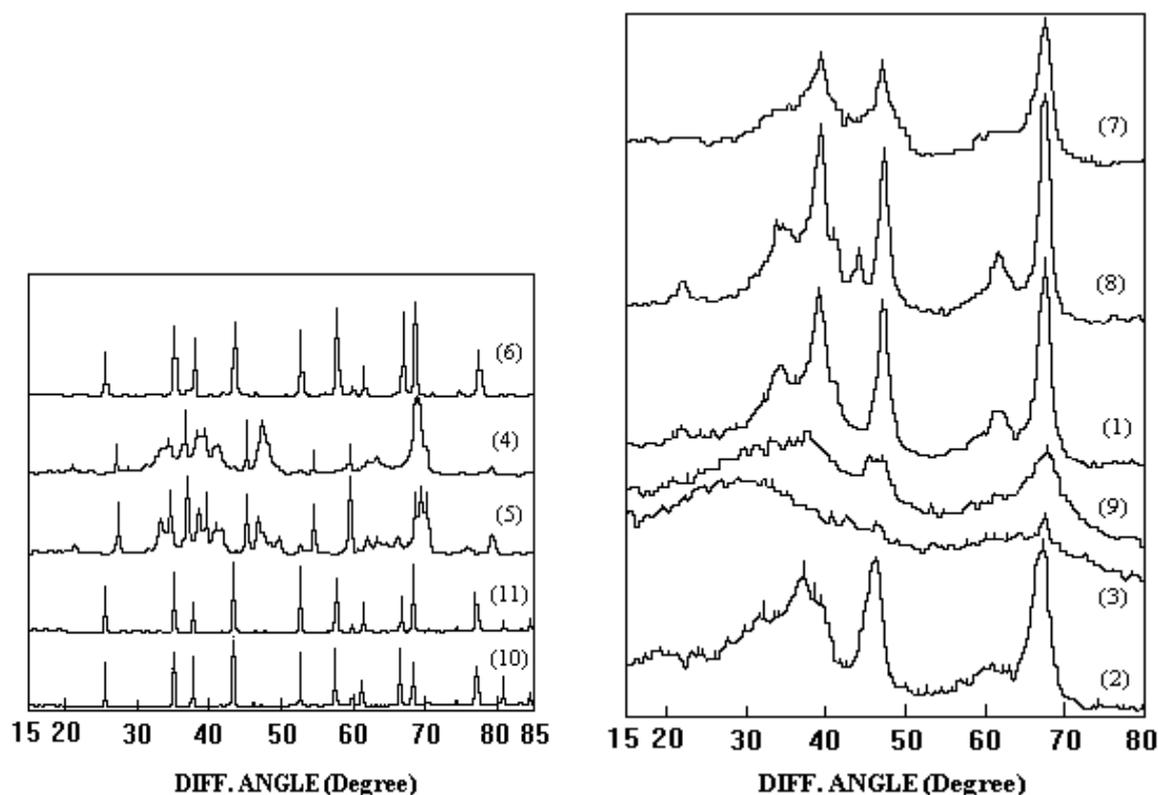


Fig.6. XRD patterns of pyrolysis products under different conditions

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