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ELABORATION OF ULTRAFINE MULLITE POWDER AND STRONG ADVANCED CERAMICS FROM SOL-GEL METHOD

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ABSTRACT

The physical-chemical aspects of powders production in the system of Al_2O_3-SiO_2-MeO using the sol-gel method have been studied. The processes of crystallization, sintering and microstructure of mullite powder and mullite-based ceramics depend on the homogeneity of initial compositions The dense mullite ceramics with the bend strength of 300 MPa has been obtained from the powder with the grain size of 185 Å, characterized by the lowest crystallinity degree. The powders with high degree of crystallinity can be used for as catalyst carriers or gas absorbers for porous mullite ceramics.

INTRODUCTION

According to the available literature the ultrafine mullite powders obtained by sol-gel method are considered to be most promising materials.

These powders are very often produced from alcoholates of corresponding metals (1) or from SiO_2 sols and aluminium salts mixtures (2). As a rule the synthesis of mullite in such compositions occurs through intermediate phase formation i.e. aluminosilicate spinel which is being formed at 950 - 1000°C and transforms into mullite at 1100°C (3,4).

The hydrolysis rate of initial components considerably influences the mullite crystallization during thermal treatment (5).

The purpose of these investigations is the production of mullite powders from ethyl silicate and aluminium chloride mixtures excluding spinel phase and the production of dense and porous mullite ceramics.

THE INITIAL MATERIALS AND PREPARATION OF COMPOSITION

Aluminium chloride and ethyl silicate containing 32 - 34 % of SiO_2 as well as pure tetraetoxysilane have been used for principal investigations. In order to obtain sol the ethyl silicate was hydrolised by stoichiometric water amount with addition of acid catalyst. The organic solvent have not been used.

The initial compositions have been prepared by two methods (Fig.1). The first group of compositions has been obtained by hydrolysis of ethyl silicate and aluminium chloride. The hydrolyzates have been cured for several days at 5 - 10 ^{0}C.

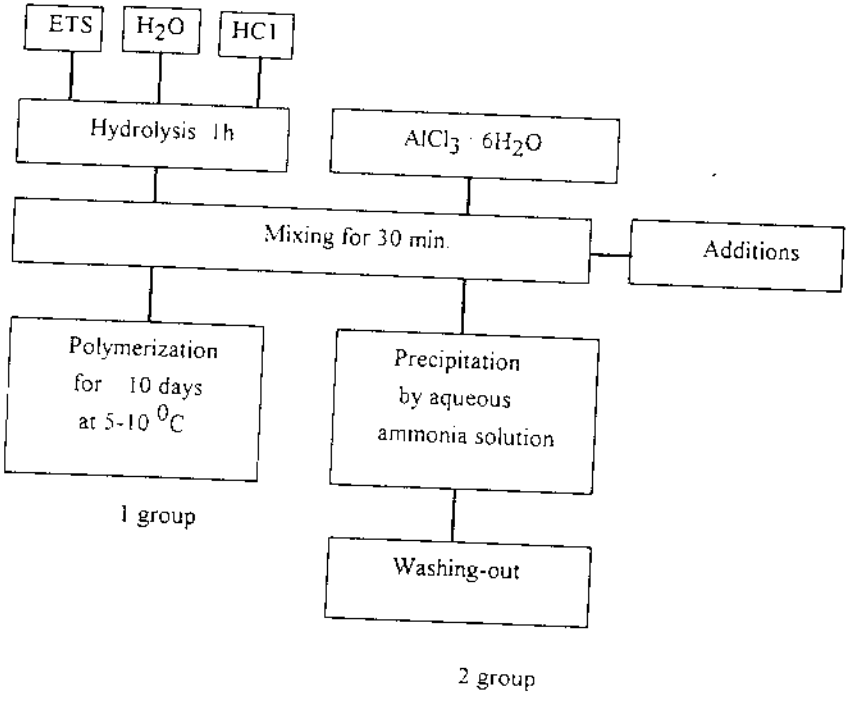

Fig.1. The scheme of sol-gel composition preparation.

The second group of compositions has been prepared using the method of precipitation of quick-obtained hydrolysate by aqueous ammonia solution with further washing-out of ammonium chloride. Following this the gel compositions have been subjected to thermal treatment at 900 - 1450 ^{o}C (Temperature gap - 100^{o}C) being cured for 0,5- 6 hours. The obtained powders have been ground by corundum balls during 30 min.

INVESTIGATION TECHNIQUES

The differential-and-thermal analysis (DTA) of gels was made in air using OD-103 instruments of Paulic F.-Paulic I.-Erdey P. system. The temperature was increased at a rate of 10 ^{o}C/min. The infra-red absorption spectra have been studied in the range of 400 - 4000 cm^{-1} using IRS-29 spectrophotometer. The monocrystalline KBr has been used as a standard.

The phase composition has been studied in the CuK_{α} radiation using DRON-3 X-ray apparatus. The mullite phase lattice parameters (reflexes 110 and 220) have been determined in FeK_{α} radiation. The powders have been subjected to microscopic investigation using polarising microscope (Leningrad optico-mechanical corporation). The structure of mullite ceramics has been studied using electronic microscope.

INVESTIGATION RESULTS

1.The synthesis of ultrafine mullite powders.

The thermal treatment of aluminium chloride leads to the formation of aluminium oxide. The latter remains in amorphous state up to 800^{o}C and then it is transformed into γ - Al_2O_3. At 1170 ^{o}C γ- Al_2O_3 is transformed into α- Al_2O_3. The ethyl silicate has amorphous state up to 1000 ^{o}C.

The main product of ethyl silicate hydrolysis is polysilicon acid, to which correspond the bands of IR-spectra at 470,800,950 and 1080 cm^{-1}. Besides, the gel contains small amount of polyetoxysilanes to which corresponds a band at 1350 - 1450 cm^{-1}.

The IR-spectra (Fig.2) show the polymerization character of sol-gel compositions belonging to the first group and its transformation during thermal treatment.

The composition not subjected to thermal treatment is a mixture of polysilicon acid (bands 470,800,950 and 1080 cm^{-1}), aluminium chloride (bands 600,830 cm^{-1}) and polyetoxysilanes (bands 1450-1500 and 2900-3000 cm^{-1}).

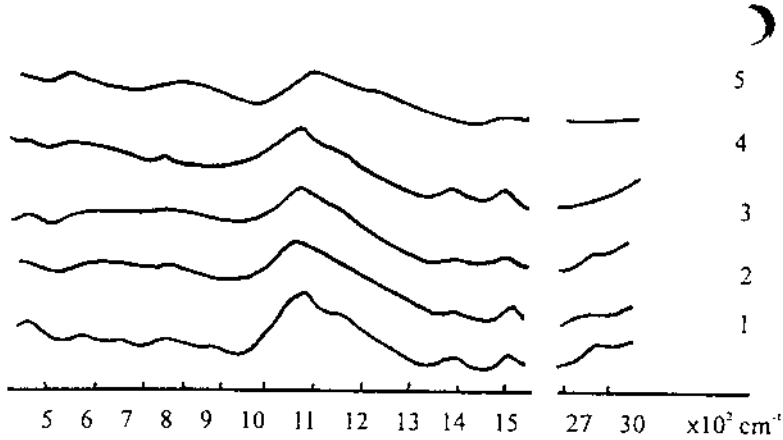

Fig.2. IR-spectra of compositions subjected to slow thermal treatment at (°C) : 1 - 20; 2 - 500; 3 - 700; 4 - 900; 5 - 1000.

The disappearance of 950 cm^{-1} band with increase of temperature is accounted for the decomposition of polysilicon acid with release of amorphous SiO_2 to which correspond bands at 470,300 and 1080 cm^{-1}. In the same conditions the decomposition of aluminium chloride and formation of its amorphous oxide is accompanied by complete absorption in the area of 600 - 800 cm^{-1}.

With increase of thermal treatment up to 1000°C the mullitization process is accelerated. This is shown by clearer bands of IR-spectrum at 600, 750 and 1250 cm^{-1}.

The first mullite crystals are formed at 550°C. After thermal treatment at 1200°C (6 hours) the mullite output was equal up to 83 wt.% . The table shows the calculated lattice parameters and synthesized mullite formula as well as the size of mullite crystalline blocks that have been formed in the process of synthesis.

The composition subjected to thermal treatment at 960°C possesses the lowest degree of mullite crystallinity. The size of its blocks is 185 Å. A composition subjected to thermal treatment at 1200°C has the highest degree of mullite crystallinity (ermal size is 443 Å). It is established that mullite is formed in very small amounts and only from homogeneous gels at high rates of thermal treatment under low temperatures (900 - 1000°C).

The synthesized mullite represents the aggregation of small crystals (up to 6 μm) which are bonded with each other by glass envelopes and have direct contact.

Table

Mullite lattice spacing and the Al_2O_3:SiO_2 ratio

№	Additions	Therm. treat. ^0C	Curing time, hour	a, Å	Medium size of grains Å	Approximate formula
1	MnO_2, SrO_2	1200	6	7,538(2)	443	$3Al_2O_3 \cdot 2SiO_2$
2	MgF_2	1200	6	7,527(3)	405	$3Al_2O_3 \cdot 2SiO_2$
3	without ad.	1200	6	7,540(4)	-	$3Al_2O_3 \cdot 2SiO_2$
4	MgF_2	960	6	7,591(5)	185	$2Al_2O_3 \cdot SiO_2$

The silica glass has nonuniform distribution in the mullite matrix. It forms both the envelopes around mullite crystalls and single inclusions. The change of its amount is in inverse proportion to temperature and duration of thermal treatment.

With increase of temperature and of thermal treatment the degree of mullitization of this composition also increases.

The amorphous Al_2O_3 and Al_2O_3 in the form of different crystalline transient forms is present in small amounts in these compositions.

2. The production of structural mullite ceramics.

The mullite ceramics was produced from powders by hot moulding for 30 min. at 1100 - 1550 ^0C. The powders were obtained by thermal treatment of compositions at 180,950 and 1100 ^0C.

THE DISCUSSION OF RESULTS

The starting point of mullite formation was determined petrographically at 550 ^0C (cured for 2 hours) due to the introduction of modifying agents. The X-ray photograph confirms the mullite formation only at 900 ^0C.

The output of mullite sharply increases with increase of temperature of thermal treatment. The differences in the values of mullite lattice constant can be accounted first of all for Al_2O_3 content in synthesized phase. The divergence of their values from linear dependence can be explained by different thermal prehistory of mullite production.

The design formula for crystalline powders after thermal treatment at 1200 ^0C is $3Al_2O_3 \cdot 2SiO_2$ (Table). It doesn't matter what dopants have been used. This formula corresponds to one for stoichiometric mullite.

The thermal treatment of sol-gel compositions at lower temperatures (less than 960°C) leads to the deviation of Al_2O_3:SiO_2 ratio from stoichiometric one in the synthesized crystalline phase.

The compositions are preferrebly to be subjected to thermal treatment at 1200 °C in order to obtain crystalline ultrafine powder. The mullite powder obtained at low heating temperatures can be used in production of hot moulded mullite ceramics. The mullite lattice is subjected to rearrangement ordering of its structure. The mechanical disturbance of homogeneity of the second composition explains the onset of mullite formation during thermal treatment by 100-150 °C higher temperatures during washing out of gel from NH_4Cl (Fig.3).

The ultrafine mullite powders of different aggregate state and dispersion can be used for different purposes. The aggregated nonground powders with specific surface of 51m^2/g are suggested as catalyst carriers.

The mullite powders obtained by different techniques and subjected to grinding in planetary mill during 10 - 30 min have been used for production of dense structural mullite ceramics.

It is established that the powders obtained during thermal treatment of sol-gel compositions of the first group at temperature not higher than 950 °C with lower degree of mullite crystallinity can be used for production of mullite ceramics with dense structure and relatively high strength(up to 300 MPa). The mullite ceramics is obtained in the processes of hot moulding at 110 - 1550 °C.

The complete mullitization of the above mentioned powder was already observed during pressurized sintering (30 - 50 MPa) at 1100 °C independently of prehistory of powder preparation. The temperature of hot moulding was increased up to 1550 °C in order to increase the density and strength of mullite ceramics. A 100 % mullitization of used powders has been reached.

The aggregated mullite powders (the size of grains is 405 Å), that was ground for 10-30 min have been used for production of porous transparent mullite ceramics.

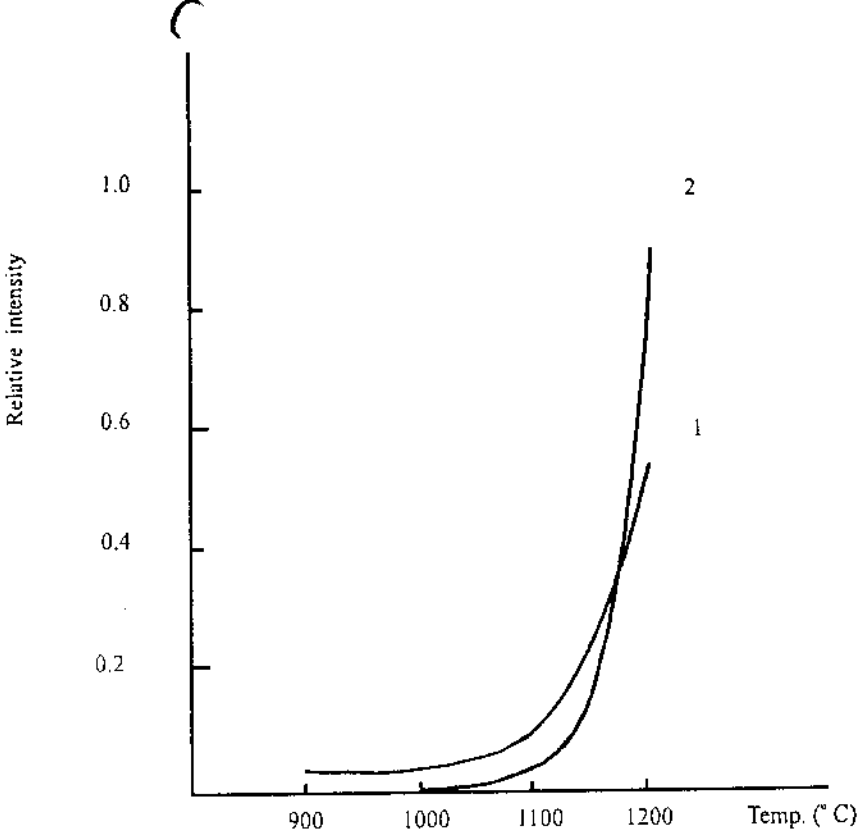

Fig.3. The formation of mullite from first and second sol-gel compositions as a function of thermal treatment temperature.

CONCLUSION

It is shown that ethyl silicate and aluminium chloride compositions can be used for production of pure mullite powders. The onset of powders crystallization from sol-gel compositions is noted at 550 - 600 ^{o}C. The complete mullitization (96 - 99 %) of powders takes place at 1200 ^{o}C. The optimal parameters for thermal treatment of compositions have been defined. The mullite powders with different sol-gel prehistory can be used for production of mullite materials.

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