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Study of magnesium aluminate spinel formation from carbonate precursors

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Abstract

The aim of the presented work was to study formation of magnesium aluminate spinel precursor powder during the co-precipitation of magnesium and aluminium nitrate with ammonium carbonate and its thermal transformation to spinel powder. After precipitation, the only crystalline phase is $NH_4Al(OH)_2CO_3{\cdot}H_2O$ (ammonium dawsonite). The second one, $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ (hydrotalcite) appears during ageing. As found by DTA-MS and HT-XRD measurements, co-existence of both phases in very close contact results in their easier decomposition. On the base of the results obtained the scheme of phase transformations of co-precipitated precursor leading to formation of $MgAl_2O_4$ is proposed.

Keywords: Spinels; Powders-chemical preparation; Calcination; $MgAl_2O_4$

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is one of the best-known and widely used polycrystalline materials. It possesses a good combination of features like high melting point, good mechanical strength, low dielectric constant and high resistance against both alkali as well as acids.[1] This makes it popular in many industrial applications, e.g., in chemistry, metallurgy and electronics. Spinel ceramics is commonly used as isolative and refractory material. Chemical inertness makes it an ideal candidate for ultrafiltration membranes.[2] Polycrystalline $MgAl_2O_4$ also finds application as humidity sensor[3] or insulating material for fusion reaction cores.[4] Another field of possible uses opens fabrication of transparent $MgAl_2O_4$ ceramics. In this form it is attractive alternative to relatively expensive and difficult to produce $MgAl_2O_4$ monocrystals. Optical applications of transparent spinel include infra-red windows and passive Q-switch of lasers.[5]

It is well known that good properties of ceramics are the result of properly chosen formation processing and sintering conditions as well as the favorable properties of starting powder. It is not possible to obtain good, uniform and porosity-less ceramics, which is essential for optical applications without using very reactive, pure and non-agglomerated powder. As previous studies proved,[6–8] these characteristics are typical for $MgAl_2O_4$ powders prepared by co-precipitation with ammonium carbonate. Until now, there is no work describing in details the processes taking place during precursor formation by this method and its decomposition leading to nanometric spinel powder. The attempt to study this problem is undertaken in present work.

2. Experimental

2.1. Powders processing

Magnesium aluminate precursor powder was prepared by co-precipitation using carbonate route similarly to that proposed by Li et al.[6–8] Briefly, an aqueous solutions of 0.15 mol aluminum nitrate and 0.075 mol magnesium nitrate (analytical grade, purchased from Polskie Odczynniki Chemiczne) were prepared. 200 ml of both solutions were mixed and heated to

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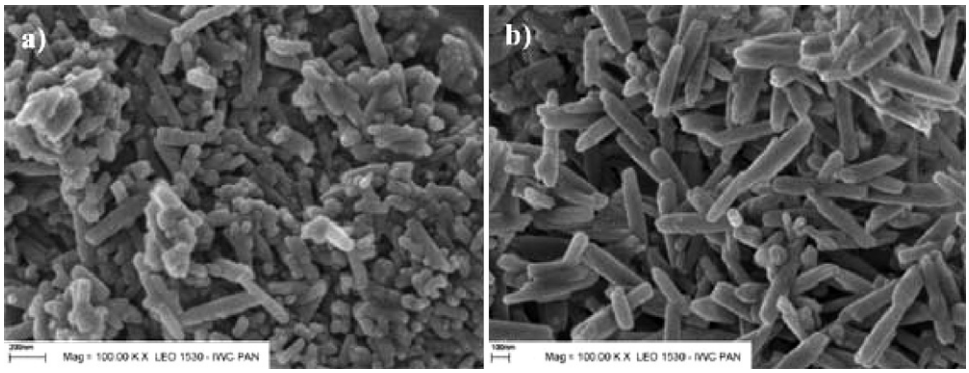

Fig. 1. SEM pictures of $MgAl_2O_4$ precursor powder (a) before ageing and (b) after ageing.

50 °C. Mixture was added drop by drop with 7 ml/min speed to stirred 600 ml of 1.5 mol ammonium carbonate (analytical grade, Chempur) solution at the same temperature. To maintain pH of solution equaled 9.8, ammonia water was added. After precipitation, suspension was aged for 17 h at processing conditions. The resultant powder was two times washed by decantation using water and then centrifugally separated and rinsed with ethanol (Alchem LINE-Etoh CLEAR). This procedure was repeated two times. Finally, the precursor powder was dried at room temperature.

$NH_4Al(OH)_2CO_3{\cdot}H_2O$ and $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ separately as well as its mixtures with different mass ratios (2.1:1 and 1:1) than for magnesium aluminate spinel stoichiometry (2.6:1) were also prepared in similar way. In all cases precipitation temperature was set on 50 °C and pH on 9.8. Aluminum nitrate solution of 0.15 mol concentration (for $NH_4Al(OH)_2CO_3{\cdot}H_2O$) or its mixture with 0.075 mol magnesium nitrate water solution (for $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ and $NH_4Al(OH)_2CO_3{\cdot}H_2O$–$Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ mixtures) were added dropwise to 1.5 mol ammonium carbonate solution. After precipitation all suspensions were aged for 17 h, washed with water and rinsed with ethanol.

2.2. Powders characterization

Specific surface of precursor powder was measured by BET method (Nova 1200e, Quantachrome Instruments). Differential thermal analysis coupled with thermogravimetry and mass spectroscopy of evolved gasses (SDT 2960, TA Instruments with QMS Thermostar, Balzers) were conducted in He atmosphere (5N purity). Powders morphology was observed by scanning electron microscope (LEO1530).

The XRD ex situ measurements were carried out on Siemens D5005 diffractometer using Ni filtered Cu Kα radiation (=1.5418 A), scintillation detector and commercial DiffracPlus Software. The X-ray tube was operated at 40 kV and 40 mA settings. The *in situ* diffraction measurements employed INEL CPS 120 position sensitive detector with a flat graphite monochromator and in-lab designed environmental XRD camera.[9] The camera used a flat sample mounting with a sample powder spread over porous glass slab mounted on a steel heater. The measurements used asymmetrical geometry with incident angle set between 10° and 20°. Data conversion and analysis of pattern evolution with time was done using a laboratory written software INEL. The *in situ* measurements employed XRD camera fed with helium (5N purity) with the sample heated up to 773 K using linear temperature program and the heating rate of 1 K/min. A series of XRD patterns were collected starting from room temperature with each pattern collected for 5 min, every 5 min.

3. Results and discussion

As a result of co-precipitation and ageing of suspension, a white and loose precursor powder of high (389 m^2/g) specific surface has been obtained. Powder consisted of two crystalline phases: $NH_4Al(OH)_2CO_3{\cdot}H_2O$ (ammonium dawsonite) and $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ (hydrotalcite) with molar ratio equal to 10:1. As it was found, crystalline powder particles were formed in two steps. After co-precipitation only ammonium dawsonite was detected by XRD as a crystalline phase. Chemical analysis of powder and a filtrate proved that in the applied conditions precipitation was complete for both cations. Crystalline hydrotalcite appeared after ageing of suspension at reaction conditions (pH 9.8, $T = 50$ °C). Phase change of precursor powder was followed by its morphology change. As seen in Fig. 1a two kinds of particles were found before ageing: the spherical ones with diameter of 50–80 nm approximately and rod-like particles with thickness below 100 nm and length of 200–400 nm. After ageing, spherical particles almost disappeared and the rod-like particles were found (Fig. 1b).

DTA and MS results of $NH_4Al(OH)_2CO_3{\cdot}H_2O$ and $Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4H_2O$ powders obtained separately and $MgAl_2O_4$ precursor are presented in Figs. 2 and 3. DTA of hydrotalcite (Fig. 2) is similar to described by Yang et al.[10] There are two wide endothermic effects with minima at 210 and 390 °C. MS results (Fig. 3) show that in the first decomposition step mostly H_2O is lost. At this moment metastable phase of structure similar to hydrotalcite (interlayer distance changed from 3.0 to 1.8 Å) named by Kanezaki "phase II" is formed.[11] Second endothermic effect is strongly asymmetric, which suggests two processes overlapping. It is confirmed by MS results. While the water is being removed evenly and gradually, much more complicated is ionic current course of CO_2. CO_2 starts to evolve together with H_2O, however, the maximum of its