Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 1379–1384

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Solution combustion synthesis of α-Al_2O_3 using urea

V.D. Zhuravlev[a,*], V.G. Bamburov[a], A.R. Beketov[b], L.A. Perelyaeva[a], I.V. Baklanova[a], O.V. Sivtsova[a], V.G. Vasil'ev[a], E.V. Vladimirova[a], V.G. Shevchenko[a], I.G. Grigorov[a]

[a]*Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences, Pervomaiskaya 91, Yekaterinburg 620990, Russia*
[b]*Ural Federal University named after the first President of Russia, B. N. Yeltsin, Mira 21, Yekaterinburg 620002, Russia*

Received 6 March 2012; received in revised form 23 July 2012; accepted 23 July 2012
Available online 31 July 2012

Abstract

The processes involved in the solution combustion synthesis of α-Al_2O_3 using urea as an organic fuel were investigated. The data describing the influence of the relative urea content on the characteristic features of the combustion process, the crystalline structure and the morphology of the aluminium oxide are presented herein. Our data demonstrate that the combustion of stable aluminium nitrate and urea complexes leads to the formation of α-alumina at temperatures of approximately 600–800 °C. Our results, obtained using differential thermal analysis and IR spectroscopy methods, reveal that the low-temperature formation of α-alumina is associated with the thermal decomposition of an α-AlO(OH) intermediate, which was crystallised in the crystal structure of the diaspore.

Keywords: Combustion synthesis; α-Al_2O_3; Urea

1. Introduction

Corundum (α-Al_2O_3) compounds and its composites have a wide range of applications in various industrial areas such as high-density ceramics [1,2], biocompatible ceramics [3], and thermal barrier coatings with low thermal conductivities [4,5].

Solution combustion synthesis is a fast and effective method for producing fine and nanosized oxide powders [6–8]. This method has also been successfully applied to the production of alumina [9–15] and other Al-based compounds [16–25].

The SCS process is based on redox reactions between metal salts and reducing agents such as glycine [12,14,16,21] or urea [9–12,17,18,24,25]. Generally, an organic reducing agent should also be a complexing agent. For example, glycine (NH_2CH_2COOH) is a complexing agent for a number of metal ions because it contains a carboxylic acid group at one end and an amino group at the other end [16]. In an acidic medium, aluminium nitrate forms a complex with urea via a reaction of the NO_3^- anion with the urea amino group. As a result, during the evaporation of the reaction solution, the gelation prevents the divided salting-out of the solution components and facilitates the formation of an easily flammable xerogel and the initiation of combustion or the solution combustion synthesis reactions.

The combustion temperature can be calculated a priori from the available thermodynamic data for various reactants and products [17,18,25,26] according to the following equation:

$$T_{ad} = T_o + (\Delta H_r - \Delta H_p)/C_p$$

where H_r and H_p are the enthalpies of formation of the reactants and products, respectively; C_p is the heat capacity of the products at a constant pressure, and T_o is 25 °C. Nevertheless, the calculated T_{ad} is typically much higher than the objective peak temperature generated in a combustion reaction (the so-called "flame temperature", T_f) as a result of factors such as the loss of heat by radiation, incomplete combustion, the transfer of heat to the air, heat exchange, the shape of the reaction vessel, and the heat supply rate [22,23]. Such dependence of the solution combustion synthesis process on the secondary experimental conditions alters the properties of the oxides obtained using the same reducing agent and requires further study.

*Corresponding author. Tel.: +7 343 374 50 05; fax: +7 343 374 44 95.
E-mail address: zhvd@ihim.uran.ru (V.D. Zhuravlev).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.07.078

The combustion temperature is not determined only by the specific heat of combustion of the internal fuel used. The fuel-to-oxidiser ratio, φ, may also control the combustion temperature directly or indirectly, thus influencing the resulting powder properties [26]. The deviation from the stoichiometric amounts of the reducing agent can be expressed in fractions of unity. What is appealing is that, unlike the thermolysis reaction, when a stoichiometric ratio of oxidiser and reductant is used, the combustion of a reaction mixture consisting of nitrates proceeds without the formation of nitrogen oxides:

$$2Al(NO_3)_3 + 5(NH_2)_2CO = Al_2O_3 + 8N_2 + 5CO_2 + 10H_2O \quad (2)$$

According to Mukasyan et al. [27], the dependence of the synthesis on φ is described by different mechanisms:

- Smouldering Combustion Synthesis (SCS): an excess of oxygen in the reaction mixture is present and stifles the reaction, $\varphi \sim 0.4$–0.7.
- Volume Combustion Synthesis (VCS): the reaction occurs in the solution volume and results in the formation of a homogenous solid, $\varphi \sim 0.8$–1.1.
- Self-propagating High-temperature Synthesis (SHS): when $\varphi \sim 1.2$–2 (fuel-rich regime), the reaction is locally ignited and propagates as a combustion wave in a self-sustained manner throughout the reaction volume. In this regime, atmospheric oxygen is required for a complete combustion between the fuel and the metal nitrates. Additionally, when $\varphi < 0.3$–0.4, thermolysis occurs, and when $\varphi \gg 2.0$, the combustion usually becomes intermittent and ceases in the absence of an external heat supply.

If the syntheses of aluminium oxide are the sol–gel method using carboxylic acids [28,29] or ammonia [30,31], the resulting precursor is usually converted into corundum annealing at 800–1300 °C. In the reactions of aluminium nitrate with glycine, as a rule, there is a formation of an amorphous product, which upon annealing up to 600–800 °C transforms into γ-Al_2O_3 [13–15]. The annealing temperature for α-Al_2O_3 should be above 1000 °C. However, α-Al_2O_3 is formed after the combustion reaction of aluminium nitrate with urea [10–12]. But the presence in the reaction mixture combustion aids increasing gas production or ballast of a solid phase, reducing the actual temperature of the process and leads to the synthesis of θ-Al_2O_3 [17,18].

Analysis of publications [10–12], shows that the interaction of aluminium nitrate with urea is poorly understood. In particular the unknown cause of the lack of smouldering combustion synthesis in the reactant mixture when $\varphi < 0.8$ [27]. In this article, we have investigated the conditions of the synthesis of α-alumina powders near the stoichiometric fuel/oxidant ratio ($\varphi \sim 0.8$–1.2) using urea as a fuel and aluminium nitrate as an oxidiser.

2. Experimental

Aluminium nitrate, $Al(NO_3)_3 \cdot 9\,H_2O$ (99.0%), and urea, $(NH_2)_2CO$ (99.8%), were used as the initial salts. The reaction solutions contained 228 g/dm^3 of $Al(NO_3)_3$ and varying amounts of urea. The synthesis was performed in an open cylindrical reactor using an aluminium alloy 1 dm^3 in volume. The reaction mixture was heated through the bottom of the reactor by means of an electric heater with a power of 1.5 kW. The temperature in the reaction zone was recorded using a special programme with the use of a Pt/Pt-10Rh thermocouple.

The powder X-ray diffraction (XRD) patterns of the obtained materials were recorded using Cu Kα monochromatic radiation. The morphology of the powders was studied via scanning electron microscopy using an SEM Tesla BS-301 that was upgraded into a digital instrument. A differential thermal analysis (DTA) was performed using a Shimadzu DTG-60 instrument with a heating rate of 10 °C/min. The IR absorption spectra of the powder samples prepared in the form of tablets with caesium iodide (CsI) were recorded using an IR Fourier spectrometer Vertex 80 (Bruker) in the 4000–400 cm^{-1} frequency range. The specific surface area of the aluminium oxide powders was determined using the BET method for the thermal desorption of nitrogen using a Tri Star 3000V 6.03A instrument.

3. Results and discussion

Urea forms sufficiently stable complex compounds with many substances including metal salts. The composition of aluminium nitrate complexes can vary from $Al(NO_3)_3 \cdot 2(NH_2)_2CO \cdot nH_2O$ to $Al(NO_3)_3 \cdot 3(NH_2)_2CO \cdot nH_2O$ depending on the urea/aluminium nitrate ratio. Under acidic conditions, urea precipitates in the form of salts, for example, with a nitric acid such as $(NH_2)_2CO\ HNO_3$. Urea nitrate decomposes explosively upon heating, but heating pure urea leads to its decomposition at a temperature of 168 °C [32]. The combination of these properties makes urea a very attractive component of the combustion synthesis reactions.

The bulk xerogel forms upon evaporation of the free water from the urea and aluminium nitrate solutions with $\varphi = 1$ at temperatures below 100 °C. In the IR spectrum of the xerogel (Fig. 1, curve II), absorption bands associated with the urea–Al^{3+} complex and absorption bands in the 3200–3050 cm^{-1} range are observed instead of bands arising from the stretching vibrations of primary amides (NH_2) at 3455 and 3352 cm^{-1} (Fig. 1, curve I) [33–35]. This shift of the absorption bands indicates the coordination of the urea molecules by the Al^{3+}. The frequency of the deformation vibrations of NH_2 decreases from 1466 cm^{-1} in the spectrum of urea to 1407 cm^{-1} in the spectrum of the xerogel. A significant decrease in the absorption intensity (1682-1601 cm^{-1}) of the band that is attributed to the oxygen-based vibrations of the CO–NH_2 group in the amide I moiety during the formation of the xerogel occurs as a