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Solution combustion synthesis of α-Al_2O_3 using urea

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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.

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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:

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

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 $\varphi \geqslant 2.0$, 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

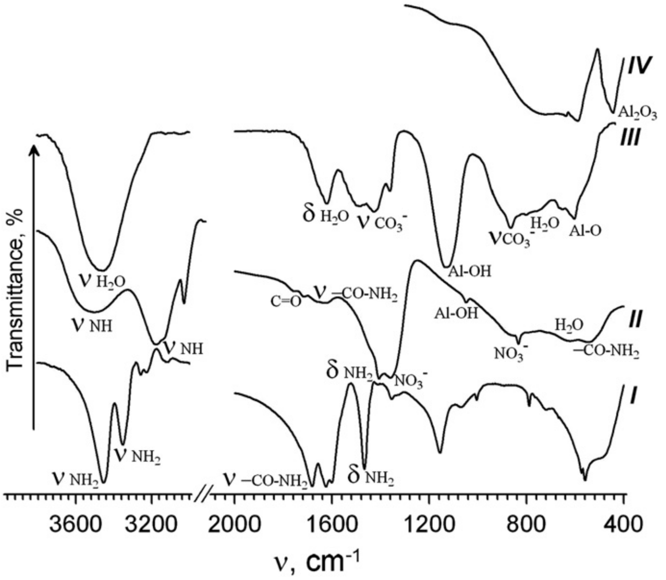

Fig. 1. Infrared spectra: I—urea; II—xerogel; III–reaction product ($\varphi=0{,}6$); IV–Al_2O_3 (900 °C).

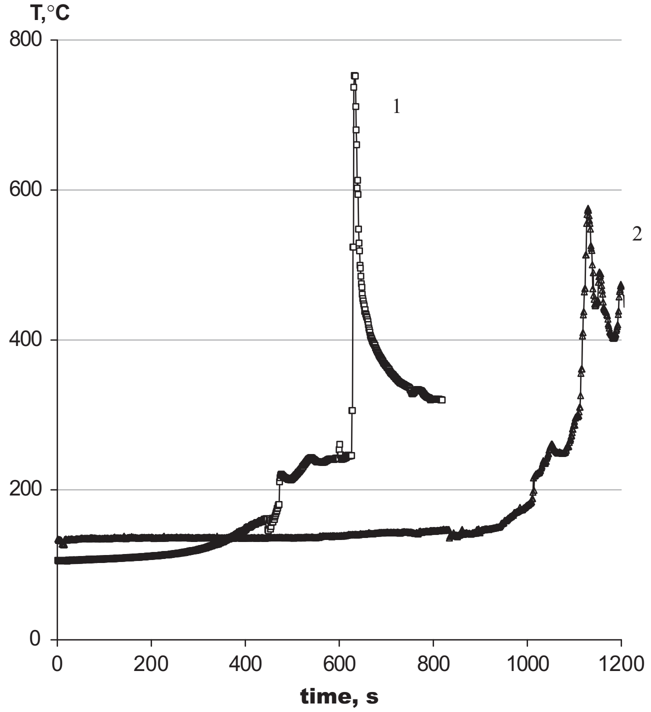

Fig. 2. Thermal change in the combustion zone in the synthesis of Al_2O_3 with urea (1) and glycine (2).

result of an interaction involving the carboxyl oxygen that leads to a weakening of the C═O bond in the ligand molecule and the disappearance of the 1682–1601 cm^{-1} lines in the resulting spectrum (Fig. 1, curve II) [33,34]. This observation is consistent with the presence of two reaction centres in the urea molecule. In the IR spectrum of the xerogel, the weak absorption bands of the unreacted urea are also observed.

In addition to the absorption bands related to urea, the most intense band in the IR spectrum of the xerogel is the absorption band of the nitrate ion at 1359 cm^{-1} (Fig. 1, curve II), which is located in the characteristic frequency region of 1380–1350 cm^{-1}. In addition, a small amount of cyanic acid is generated as a product of urea decomposition in the xerogels, which is indicated by the absorption bands at 1735 and 1715 cm^{-1} [33].

The samples were synthesised using a fuel-to-oxidiser ratio in the range of $\varphi=0.6$–1.2. During heating, the initial solution dries and becomes a white powder with a solid crust ($\varphi=0.6$) or a hat with the appearance of whipped cream ($\varphi=0.8$–1.2) on its surface. The bulk material is formed stepwise at temperatures from 148 to 250 °C, which is followed by ignition and a temperature increase in the combustion zone up to 750 °C (Fig. 2). The formation of aluminium oxide at $\varphi=0.8$–1.2 is a typical case of volume combustion synthesis. A lack of fuel in the mixture when $\varphi=0.6$ leads to a decrease in the peak reaction temperature to 600 °C, an increase in the decomposition time and an instability of the combustion process. Absorption bands due to water (3458, 1622 cm^{-1}), CO_3^{2-} groups (1484, 1362, 865 cm^{-1}), Al–OH (1131 cm^{-1}), and Al_2O_3 (700–600 cm^{-1}) are observed in the IR spectra of the prepared samples (Fig. 1, curve III) [35]. The DTA indicated that the powder obtained from the reaction solution with $\varphi=0.6$ (Fig. 3a) is composed primarily of $Al(OH)_3$. This

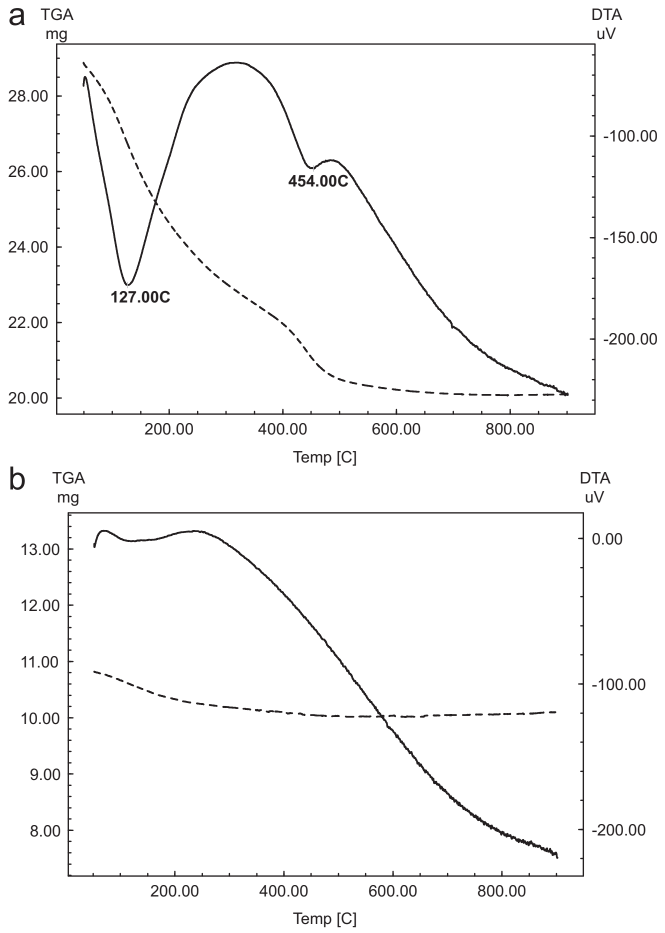

Fig. 3. The DTA/TG curves of the aluminium oxide powders after the synthesis with urea: (a) $\varphi=0.6$ and (b) $\varphi=1.0$.

composition is indicated by an endothermic effect at 128 °C (Fig. 3a) that corresponds to the decomposition of $Al(OH)_3$ and a second endothermic effect at 454 °C that corresponds to the decomposition of AlO(OH). The weight loss observed in the DTA is 30.4%, which is only 88% of the theoretical value for the decomposition of $Al(OH)_3$. Approximately 12% of the sample mass is Al_2O_3. The predominance of aluminium hydroxide in the powder phase can be (a) a consequence of hydration of the formed aluminium oxide nanopowder in the process of cooling or (b) the result of parallel CS processes of the urea–nitrate complex and the thermolysis of aluminium nitrate. Typically, oxidation–reduction reactions are very active in the $\varphi = 0.6$–0.9 modes of smouldering combustion and volume combustion [26].

Most likely, the displacement of the intensive interaction of aluminium nitrate with urea into the region of $\varphi > 1.0$ is associated with the unique character of urea as a complexant.

AlO(OH) powders adopt the crystal structure of corundum at relatively low annealing temperatures of 600–800 °C for 1–2 h. It is known that the dehydration of $Al(OH)_3$ is influenced by the crystalline modification of this complex and can occur in two ways [36]:

$$\mathrm{Al(OH)_3}\xrightarrow{150\,^{\circ}\mathrm{C}}\gamma\text{-AlO(OH) (boehmite)}\xrightarrow{300\,^{\circ}\mathrm{C}}\gamma\text{-}\mathrm{Al_2O_3} \quad (3)$$

$$\mathrm{Al(OH)_3}\xrightarrow{150\,^{\circ}\mathrm{C}}\alpha\text{-AlO(OH) (diaspore)}\xrightarrow{420\,^{\circ}\mathrm{C}}\alpha\text{-}\mathrm{Al_2O_3} \quad (4)$$

The implementation of this process in accordance with Eq. (4) and the crystal structure of the annealed powder are revealed by the endothermic effect at 454 °C that is observed in the DTA/TG curves of the sample obtained by combustion of the reaction solution with $\varphi = 0.6$ (Fig. 3a). Furthermore, the powders produced by the combustion of the reaction solutions with $\varphi = 0.8$–1.2 consisted of α-Al_2O_3 (Fig. 4) with a specific surface area of 52–54 m^2/g. The weight loss that occurred upon heating the solutions to 900 °C was 2.7–6.3% depending on the urea content, and the shape of the TG curve was typical for water desorption (Fig. 3b). The formation of the crystal structure of the corundum powders obtained via SCS with a stoichiometric amount of glycine required additional annealing at a temperature not lower than 900–1000 °C, whereas the temperature of formation of α-Al_2O_3 via SCS with urea was 750 °C (Fig. 2). Under similar conditions, the temperature of the combustion mixture of aluminium nitrate with glycine reached only 570 °C (Fig. 2), and the product consists of an amorphous aluminium oxide and carbon [14].

The aluminium oxide obtained by combustion with urea at $\varphi = 1.2$ was white in colour with a greenish tint and did not contain carbon impurities, whereas the use of glycine with a relatively high carbon content resulted in an increase in the carbon content of the final product [14]. Such an advantage of urea as a fuel may be explained by the absence of carbon–carbon bonds in the urea molecule. Our calculations indicated that in the reactions of $Al(NO_3)_3 \cdot 9H_2O$ with urea, the adiabatic combustion temperature is 1279 °C, and with glycine, this temperature is 1470 °C. We can assume that this difference is due to the

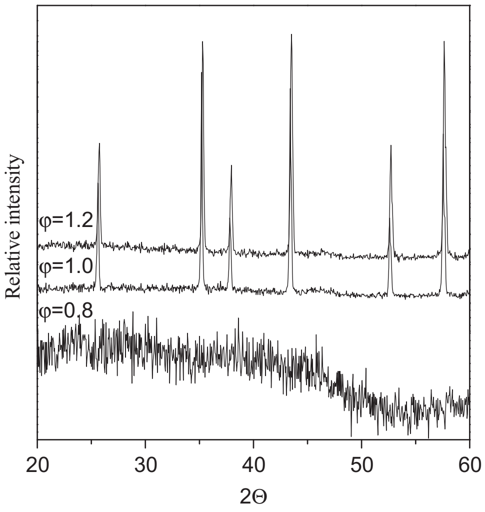

Fig. 4. XRD patterns of the powders prepared using urea.

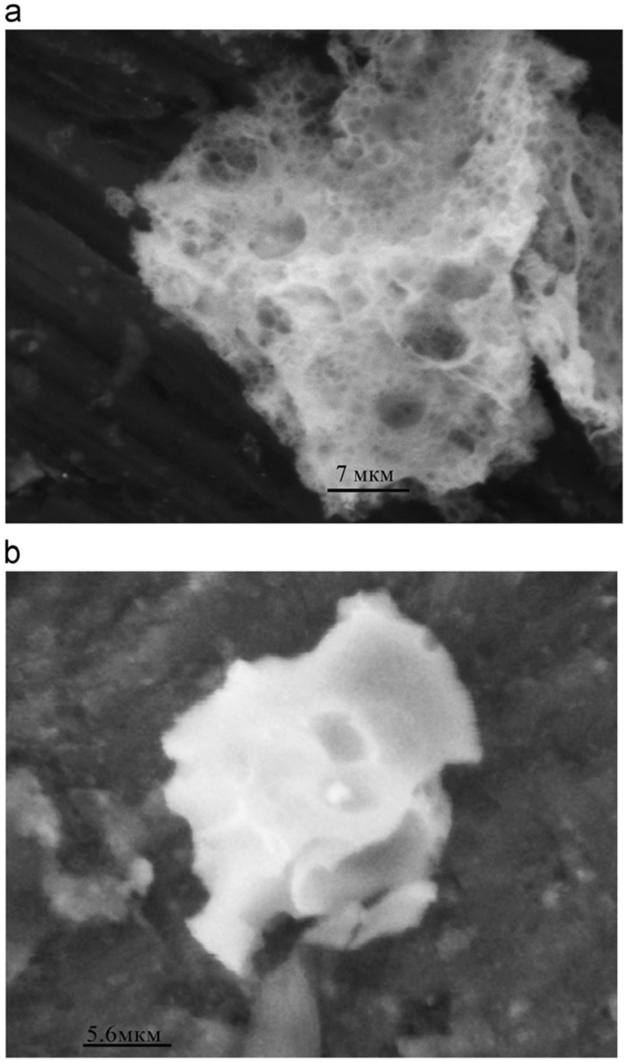

Fig. 5. The morphology of the aluminium oxide particles obtained with glycine (a) and urea (b).

lower strength of coordination complexes of urea compared with the aluminium nitrate–glycine mixture.

The powders obtained in the SCS reactions are highly agglomerated. The solidity, size and structure of the agglomerates depend on the process conditions and the type of fuel used. The morphology of aluminium oxide powders obtained with urea significantly differs from that of the powders obtained with glycine (Fig. 5). The agglomerates of aluminium oxide particles (glycine) have a friable structure (Fig. 5a). However, the particle aggregates in the aluminium oxide powder obtained with urea are denser, larger and more durable without visible cellular structure (Fig. 5b).

4. Conclusions

The use of urea as a chelating component and inner fuel facilitates the single-stage synthesis of fine α-Al_2O_3 powder of the form $(NH_2)_2CO:Al(NO_3)_3=2.0$–$3.0$, which leads to the formation of stable complex compounds. The purported reason for the formation α-Al_2O_3 is the generation of an α-AlO(OH) intermediate in the crystal structure of the diaspore during the combustion reactions of the aluminium nitrate–urea mixture. Increasing the actual temperature of the flame and the full burnout of carbon resulted in a relatively low strength of the chelate bonds in the aluminium nitrate and urea complexes.

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