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CERAMICS INTERNATIONAL

Ceramics International 41 (2015) 11598-11604

www.elsevier.com/locate/ceramint

Review paper

Application of urea precipitation method in preparation of advanced ceramic powders

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Received 21 May 2015; received in revised form 5 June 2015; accepted 5 June 2015 Available online 16 June 2015

Abstract

Urea precipitation method has been developed as an important approach for the preparation of inorganic particles with defined morphology and composition. In present work, we provide survey of the technological developments and achievements mainly on the application of the urea precipitation method in preparation of advanced ceramics powders. Stable pH obtained during the thermal decomposition of urea in aqueous solution make it quite promising for the precise composition control of ultrafine powders. The decomposition mechanism of urea in aqueous solution is discussed before a systematic description of its application in the preparation of monodispersed particles with unary/binary composition. Clear decomposition mechanism of urea provides researchers a possibility to analyze the evolution process of ultrafine particles from its initial forming period. Finally, the application potential and future prospects of this method, such as preparation of core–shell particle with designed composition and precipitation kinetics study, are outlined.

Keywords: Urea precipitation method; Advanced ceramics powders; Decomposition mechanism

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1. Introduction

Urea, as the first manmade organic compound synthesized from inorganic starting materials, has been performing

important role in many areas such as agriculture, chemical industry, medical care, laboratory analysis, etc. [1–9]. The successful synthesis of urea is also considered the starting point of modern organic chemistry [10]. In 1895, Walker and Hambley [11] first called attention to the reversibility of Wöhler's classic synthesis. After that, investigation on the decomposition of urea in aqueous media has then been performed by many investigators including Fawsitt [12,13],

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http://dx.doi.org/10.1016/j.ceramint.2015.06.032 0272-8842/© 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Werner [14,15] and Price [16], etc. At that time, a precise control of pH in the separation of metals by precipitation as hydroxides, hydrous oxides or basic salts from their aqueous solution is necessary [17,18]. Although a precise control of the precipitant can be achieved via fine regulation of its applied dosage, the uncertainty of its terminal pH makes its hard to prepare precipitant with defined composition. Hobart and Ning Kang [19] discovered in 1937 that the decomposition of urea in aqueous solution would finally lead to solution with stable pH (see Fig. 1). Precipitate of aluminum salt was obtained via the urea precipitation method (UPM) in their work. After that, UPM has been developed as an important method for the synthesis of precipitate from metal ions in aqueous solution [20]. That provided scientists novel approach to prepare fine powders with regular microstructure [21]. With the development of nanotechnology in recent years, requirement for the precise control of well defined particle make this method even attractive. Among which, progresses that have been made in the areas of advanced ceramics [22-26], especially transparent ceramics, are significantly promoted by wet chemical precipitation technology.

Considering its advantageous application in the preparation of ultrafine powders, this paper provides a survey of the technological developments and achievements mainly on the application of UPM in the preparation of advanced ceramic powders. We will focus on the following areas to give a comprehensive review on the application of UPM in the ceramic related processes: decomposition mechanism, preparation of monodispersed particles with unary/binary composition, and finally the application potential and future prospects of this method.

2. Precipitation mechanism and analysis on typical powder synthesis

Shaw and Franks [27,28] studied the decomposition of urea in aqueous solution in detail. The reaction was shown to be first order with respect to urea. Besides, it is proved that urea molecules exists in the aqueous solution in form of monomolecule. No diamer (2 urea) or more conjugated molecules can be formed. That information is quite important since it offers evidence for a clear decomposition mechanism from its starting point. In situ decomposition of urea releases precipitaing ligands (mainly OH⁻ and CO₃²⁻) homogeneously into the



Fig. 1. Schematic illustration of pH evolution during UPM [17-19,43].

reaction system, avoiding localized distribution of the reactants and thus making it possible to precisely control the nucleation and growth of the precipitate.

2.1. Preparation of monodispersed unary particles

During the urea precipitation process, precipitating ligands were released into the aqueous solution at a rate that can be well controlled via the temperature variation. What is more important, concentration of the ligands can be extremely uniform at different parts of the aqueous solution. An explosive nucleation can be achieved at a relative high temperature, usually at temperatures higher than 83 °C [29,30]. Different from diffusion controlled growth of nucleus, primary particles homogeneously formed in this process aggregate to form larger particles (see Fig. 2), thus make it even attractive for the preparation of spherical particles [31].

By taking advantage of those unique conditions, a variety of inorganic particles with uniform size and well-defined morphologies have been synthesized in recent 30 years [29–34]. The importance of well-defined fine particles has been recognized in numerous applications. Major significance of monodispersed particles may be attributed to the uniformity in physico-chemical properties of individual in a dispersed system, which allows us to directly correlate the properties of the whole system with those of each particle and facilitates.

A typical work was accomplished by Matijević [21], in which work colloidal particles of lanthanide compound were prepared by aging the lanthanede salt solutions at elevated temperatures in the presence of urea. Colloidal particles of lanthanide compound with different composition and morphology were achieved via altering the aging temperature and time. It is worthy to mention his work in 1988 about the preparation of yttrium system [29]. In that work, Egon discussed the precipitation process of yttrium ions in neutral and basic aqueous solution.

In neutral circumstance, yttrium ions hydrolyze to YOH $(H_2O)_n^{2+}$ [35,36]

$$Y^{3+} + (n+1)H_2 O \rightleftharpoons YOH(H_2 O)_n^{2+} + H^+$$
(1)

The precipitation of the yttrium basic carbonate therefore could be described by the following reaction:

$$YOH(H_2O)_n^{2+} + H_2O + CO_2 \to Y(OH)CO_3 \cdot xH_2O + 2H^+ + (n-x)H_2O$$
(2)



Fig. 2. Growth and aggregation process of particle formed during UPM.

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