REVIEW OF A BOOK BY SREĆKO STOPIĆ: SYNTHESIS OF METALLIC NANOSIZED PARTICLES BY ULTRASONIC SPRAY PYROLYSIS

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Summary:

Nanotechnology belongs to the key innovative technologies for powder production. Ultrasonic spray pyrolysis is a versatile method for the formation of nanosized particles of metals, oxides and composites. This work deals with Ag, Cu and Au nanoparticles formed by ultrasonic spray pyrolysis using the horizontal and vertical reactor. Furthermore, a direct synthesis of Ru-TiO_2 and RuO_2-TiO_2 nanoparticles with the core and shell structure was investigated. The molar fractions of precursors, solvent type, and the process temperature play the crucial role in the formation of core and shell structures. Moreover, the influence of the reaction parameters (temperature, residence time, solution concentration and ultrasonic frequency) on the morphological characteristics of the prepared nanoparticles was studied. A decrease in the solution concentration decreases the final nanoparticle size. An increase in temperature from 150°C to 1000°C leads from an irregular form to a more spherical one. Subsequently, a model of metallic nanoparticle formation from an aerosol droplet could be proposed. Using ultrasonic spray pyrolysis, ideal spherical metallic particles were obtained at temperatures above the melting point. A scanning mobility particle sizer (SMPS) was used for the on-line determination of nanoparticle size distribution. The collection of nanosized particles was

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performed in an electrostatic field. The scale up of the ultrasonic spray pyrolysis method was successfully applied for the synthesis of silver powder from a water solution of silver nitrate.

Key words: *metal, powders, synthesis, ultrasonic spray pyrolysis.*

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Introduction

This book "Synthesis of metallic nanosized particles by ultrasonic spray pyrolysis" by Srecko Stopic was published by Shaker Verlag, Kohlsheid, Germany. It belongs to the written literature from the Institute for Process Metallurgy and Metal Recycling of the RWTH Aachen University in Germany. This work represents the collected activities in nanotechnology performed by Dr. Srecko Stopic at the IME Process Metallurgy and Metal Recycling of the RWTH Aachen University between 2003 and 2013. His activities during this period revolved around three important hydrometallurgical processes:

1. dissolution of metal from ores into a solution during high pressure leaching in an autoclave (Stopić, Friedrich, 2011, pp.29-44)
2. neutralization/precipitation processes for cleaning wastewaters using a cascade line and an electrocoagulation reactor (Pavlović, et al, 2007, pp.518-522),
3. synthesis of metals from different solutions for producing submicron and nanosized powders by using ultrasonic spray pyrolysis (Stopic, 2013, pp.1-15).

This work deals with the third part of the above-mentioned research and describes the synthesis of metallic and oxidic particles from the precursor solution using the ultrasonic spray pyrolysis method (USP). Owing to the ability to control the process parameters such as the ultrasonic frequency, the concentration of the solution, the residence time of the aerosol, the gas flow rate and the reaction temperature, it is possible to produce powders with morphologies that satisfy even more demanding requirements of advanced engineering materials (Song, et al, 2011, pp.210-215). As a final step, the thorough collection of the small amount of collectable nanosized metallic particles in an electrostatic field or the improvement of the collection process itself, represent some of the most challenging tasks concerning ultrasonic spray pyrolysis.

A significant improvement of the powder characteristics (smaller particle size and a more spherical form with a higher specific surface area) was obtained by the application of an ultrasonic atomizer for the preparation of aerosols. The USP process was carried out using powerful ultrasound on the corresponding water solution of metallic salts such as silver nitrate, copper sulphate, ruthenium chloride and gold chloride, forming the aerosol with a constant droplet size, which depends on the characteristics of the liquid (surface tension, density and viscosity) and the frequency of the ultrasound (Bogovic, et al, 2011, pp.455-459). The produced aerosols were transported into the hot wall tubular vertical and horizontal reactor, thus enabling the chemical reaction in a very small volume of a droplet in order to form submicron and nanosized powder. Spherical, non-agglomerated, nanosized particles of metals (Cu, Ag, Au), and mixed metal/oxides particles (Ru/TiO_2 and RuO_2/TiO_2) were produced with new and improved physical and chemical characteristics. The high costs associated with small USP facilities, producing large quantities of uniform, nanosized (submicron) metallic particles, limit the use of generated nanomaterials in many practical applications.

This book was written in English and partially in German language (only the summary of this book) and contains 8 chapters, 120 pages, 84 figures, 16 tables and 100 cited references.

Description of chapters

The first Chapter „Nanotechnology“ written on ten pages focuses on: nanoparticles (properties and synthesis), different spray pyrolysis methods and commercial application and perspectives. The word “Nano” (symbol n) is derived from the Greek meaning dwarf, and was firstly officially confirmed as a standard in 1960 denoting a factor of 10^{-9}. It is frequently encountered in science and electronics for prefixing units of time and length. Nanostructured materials have shown an explosion of scientific and industrial interest over the last few decades. These unique powders are distinguished from conventional polycrystalline micron materials by their fine crystallite sizes. A significant higher fraction of atoms are located at the surface of nanosized powders in comparison to conventional prepared powders. This structural characteristic is responsible for the enhanced reactivity of nanoparticles compared to submicronic powders. Changes in properties at the nanosized level have especially an impact on: electrical (higher conductivity in ceramics), magnetic (increase of coercivity down to a critical grain size), mechanical (enhanced ductility, toughness, and formability of ceramics), and optical (increase in luminescent efficiency of semiconductors) characteristics. The synthesis of nanoparticles contains two different strategies: “Top-Down” and “Bottom-Up“. The „Top-Down” approach is based on mechanical grinding of initial powders to small dimensions. The meaning of “Bottom-Up” is related to the physicochemical preparation methods (synthesis in the gas and liquid phase). Ultrasonic spray pyrolysis includes the formation of single droplets of the precursor solution in a form of an aerosol and a subsequent thermal decomposition in a hot wall tubular reactor for metal powder production. For the reasons of simplicity, ultrasonic spray pyrolysis was used for the production of metallic particles, oxides and composite materials.

The second chapter "State of the art in the synthesis of nanosized powder" was written on twelve pages. This chapter contains the introduction, the general principles of ultrasonic spray pyrolysis, the aerosol synthesis route, ultrasonic-modulate two fluid atomization and nanoparticles in modern life. Nanoparticles are mostly used in medicine, automotive industry, catalysis and environmental protection. Gold nanoparticles are used in destroying tumors (Rudolf, et al, 2012, pp.195-212). Nanosilver has become one of the most commonly used powders in consumer products. It is used as an antibacterial material in filters for air and water purification, also in t-shirts, as well as in conductive nanoinks for printed circuits, sensors, and catalysts.

The third chapter "Mechanism and kinetics of nanosilver production by ultrasonic spray pyrolysis" contains the introduction followed by the description of the decomposition of silver nitrate in the horizontal reactor and the thermochemical analysis of the decomposition of silver nitrate, as well as the experimental work and its procedure, results and discussion with a model of nanoparticle formation. A differential thermal and thermalgravimetric analysis of the decomposition of silver nitrate in nitrogen was performed by different heating rates (5, 10, 20, 40°C) using a Derivatograph NETZSCH STA 409 with α -Al_2O_3. The calculated value of the activation energy for the heating rates between 5°C· min^{-1} and 40°C·min^{-1} was E_A= 137 kJ·mol^{-1}, which confirms that the decomposition of silver nitrate is a chemical rate controlled process depending on the reaction temperature. Pure silver nanoparticles were prepared by the ultrasonic spray pyrolysis of aqueous solutions of silver nitrate in the nitrogen atmosphere at a new vertical reactor technology line with improved productivity of powder and the on-line measurement of nanoparticles. The reduction of silver nitrate and the final sintering of silver nuclei took place almost instantly at 600°C.

The fourth chapter "Synthesis of copper nanoparticles by ultrasonic spray pyrolysis" was written on ten pages. The aerosol generation by the ultrasonic spray of copper-solutions followed by the hydrogen reduction pyrolysis is suitable for the synthesis of spherical, non-agglomerated and uniform nanopowders of copper with particle sizes from D = 30 - 700 nm. Copper sulphate and copper acetate were both suitable for preparing copper powder using the ultrasonic spray pyrolysis method. It was confirmed that both precursor materials (copper sulphate and copper acetate) allow the production of fully spherical and dense particles of a size between 100 nm and 700 nm. In comparison to copper sulphate, the use of copper acetate enables a complete reduction even at 800°C. HCOOH can be used to provide a reductive atmosphere in situ during spray pyrolysis and thus makes it unnecessary to use gaseous H_2. The use of $CuSO_4$ may result in sulphur contamination, the risk of CuAc is the formation of sticky surfaces due to the presence of organics. The increase of the reaction temperature from 800 to 1000°C leads to a complete hydrogen reduction of the solution of copper sulphate. The increase of the precursor concentration increases the final particle size and the uniformity of the obtained Cu-powder. On the powder surface, a thin oxide film is present (a protective layer of Cu_2O). Nanoparticles are mostly used in catalysis and against different bacteria.

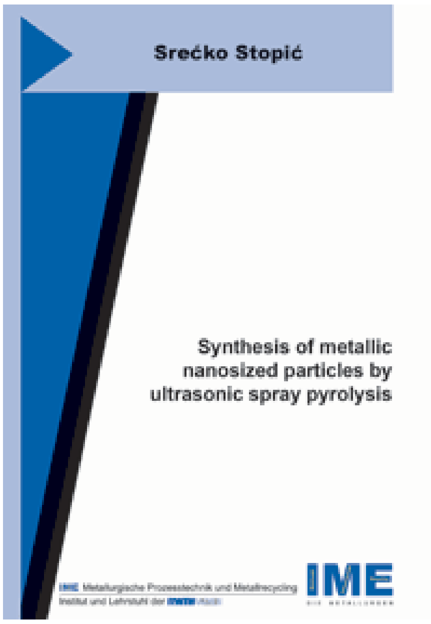
The fifth chapter "Synthesis of gold nanoparticles by ultrasonic spray pyrolysis" was also written on ten pages. Spherical and cylindrical nanosized particles of gold were synthesized by the ultrasonic atomization of chloride-nitrate solutions based on gold alloying elements (Cu, Ag, Zn and Ni) and a decomposition of the obtained solution at temperatures between 300°C and 800°C in the hydrogen and nitrogen atmosphere (Đokić, et al, 2012, pp.528-538). A new methodology was proposed for gold recovery from jewellery scrap. After the leaching of jewellery scrap in chloric acid/nitric acid, the formed solution was investigated in an ultrasonic generator. The subsequent ultrasonic spray pyrolysis of the obtained solution in the hydrogen atmosphere produces nanosized gold particles.

The sixt chapter "Synthesis of nanoparticles based on ruthenium-titania by ultrasonic spray pyrolysis" was reported on 13 pages. Ideally spherical nanoparticles of Ru/TiO2, of an average diameter between 10 and 800 nm, were prepared in a single-step ultrasonic spray pyrolysis process at 800°C. A core-and-shell structure was revealed by the FIB and SEM analysis. The performed EDS analysis has shown that the majority of the core consists of titanium oxide, while the shell is predominately composed of ruthenium (Stopic, et al, 2013, pp.3633-3635). Spherical RuO2/TiO2 particles with a mixed core-and-shell structure were prepared in a single step spray pyrolysis process, as potential candidates for a catalytic application. The molar ratio of the fractions of the precursors, a solvent type and the process temperature play the crucial role in the formation of the core-and-shell structures of RuO2/TiO2. Spherical nanosized core-shell RuO2-TiO2 particles were prepared by a novel multi step variant of ultrasonic spray pyrolysis. The comparison of the results from the EDX analysis with a hard-sphere model confirmed a nearly perfect core-and-shell structure of the particles. Further investigations shall be directed towards the process optimization of the reaction parameters in order to obtain tailored core-shell nanoparticles.

In the reported conlusions, the nanosized particles of silver, gold, copper, Ru/TiO_2 and RuO_2/TiO_2 with the core- and shell structure were described. Different precursors of metal salts: copper sulphate, copper acetate, silver nitrate, ruthenium-chloride and chloroauric acid were successfully used for the synthesis of metallic particles. Tetra-n-butilorthotitanat as a precursor was used for the formation of titanium oxide. Different mechanisms of the nanoparticle synthesis were described. Generally, the main influences of the parameters on the particle size were reported. Notably, the part "from the horizontal laboratory reactor to the scale up of the USP-method" was briefly described. The industrial scale for nanopowder production using ultrasonic spray pyrolysis contains: 1) system of five aerosol ultrasonic generators PRIZNano, 2) high-temperature furnace with five wall-heated reactors, 3) two electrostatic filters, and 4) vacuum system (Matula, et al, 2013, pp.1-5).

Conclusions

This book was written in English and partially in German language. The content of this book contains 8 chapters, 120 pages, 84 figures, 16 tables and 100 references. This book describes in details: importance of nanotechnology, principles of ultrasonic spray pyrolysis and other methods for the synthesis of nanosized particles, application of nanosized particles, USP synthesis of nanosized particles of silver, gold, copper, Ru/TiO_2 and RuO_2/TiO_2 and partially the scale up of ultrasonic spray pyrolysis.



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ОБЗОР КНИГИ СРЕЧКА СТОПИЧА «СИНТЕЗ НАНОЧАСТИЦ МЕТАЛЛОВ УЛЬТРАЗВУКОВЫМ РАСПЫЛИТЕЛЬНЫМ ПИРОЛИЗОМ»

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ОБЛАСТЬ: химические технологии
ВИД СТАТЬИ: обзор
ЯЗЫК СТАТЬИ: английский

Резюме:

Нанотехнология является ключевой иновационной технологией в производстве порошковых изделий. Распыление порошков ультразвуковым пиролизом имеет широкое применение в сфере образования частиц нанопорошковых металлов, оксидов и композитов.

Данная работа освещает процессы образования наночастиц серебра, меди и золота методом ультразвукового пиролиза, с использованием горизонтального и вертикального реакторов. Исследуется прямой синтез наночастиц на основе $Ru-TiO_2$ и RuO_2-TiO_2 со структурой ядро-оболочка. Молярный состав прекурсора, вид растворителя и средняя температура играют важную роль в образовании частиц, имеющих такую структуру. В работе представлен анализ воздействия реакционных свойств (температура, время задерживания, концентрация раствора и частота ультразвука) на морфологические характеристики наночастиц.

Повышение температуры от 150°C до 1000°C может вызвать, как деформирование частицы, так и образование сферической частицы. В работе также рассматривается новая модель образования металлических наночастиц из капли аэрозоля.

В процессе распыления ультразвуковым пиролизом идеальные сферические частицы образуются при температуре ниже точки плавления. Для сортировки величины частиц на основании траектории движения частиц в электростатическом поле используется устройство, данные которого отслеживаются в режиме онлайн.

Сбор наночастиц проводится в электростатическом поле. Рост производственных объемов порошковых изделий, изготовленных методом ультразвукового распылительного пиролиза способствовал успешному внедрению данного метода для синтеза порошка серебра из раствора серебра нитрата.

Ключевые слова*: металл, порошки, синтез, ультразвуковой распылительный пиролиз.*

PRIKAZ KNJIGE SREĆKA STOPIĆA: SINTEZA NANOČESTICA METALA ULTRAZVUČNIM RASPRŠIVANJEM U USLOVIMA PIROLIZE

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OBLAST: hemijske tehnologije
VRSTA ČLANKA: prikaz
JEZIK ČLANKA: engleski

Sažetak:

Nanotehnologija pripada ključnim inovativnim tehnologijama za proizvodnju prahova. Raspršivanje prahova ultrazvučnom pirolizom višestruko je korišćeno za formiranje čestica nanoprahova metala, oksida i kompozita. Ovaj rad odnosi se na nanočestice srebra, bakra i zlata, formiranih ultrazvučnom pirolizom korišćenjem horizontalnog i vertikalnog reaktora. Direktna sinteza nanočestica na bazi $Ru-TiO_2$ i RuO_2-TiO_2 sa strukturom sastavljenom od jezgra i ljuske dalje je ispitivana. Molarni udeli prekursora, tip rastvarača i procesna temperatura imaju odlučujuću ulogu u formiranju čestica sa ovom kombinovanom strukturom. Zatim, ispitivan je uticaj reakcionih parametara (temperatura, vreme zadržavanja, koncentracija rastvora i frekvencija ultrazvuka) na morfološke karakteristike pripremanih nanočestica. Uvećanje temperature od 150°C do 1000°C vodi od jednog nepravilnog oblika do proizvodnje sfernih čestica. Nakon toga, bio je predložen model formiranja metalnih nanočestica od kapi aerosola. Korišćenjem procesa raspršivanja preko ultrazvučne pirolize idealno sferne čestice dobijene su na temperaturi ispod tačke topljenja. Uređaj za određivanje raspodele veličine čestica korišćenjem različite pokretljivosti čestica u elektrostatičkom polju korišćen je za on-line analizu tokom proizvodnje čestica. Sakupljanje nanočestica izvršeno je u elektrostatičkom polju. Uvećanje proizvodnje prahova raspršivanjem ultrazvučnom pirolizom uspešno je primenjeno za sintezu prahova srebra iz vodenog rastvora srebronitrata.

Ključne reči: metal, prahovi, sinteza, raspršivanje ultrazvučnom pirolizom.

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