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学位論文題目	Synthesis and Characterization of Ultrafine Crystals of Zirconia and Titania by the Solvothermal Reactions (ソルボサーマル反応によるジルコニア及びチタニア微結晶の合成と特性評価)
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論 文 内 容 要 旨

Zirconia and titania ceramics possess excellent physical and chemical properties and can be found wide application as functional materials. In order to use these ceramics in industry it is important to develop the technology to synthesize the powders with well-controlled stoichiometry, purity, agglomeration state, particle size and crystallinity. From the view point of economy and environmental problem it is also required to develop energy and resource saving and environmentally friendly technologies for the production of materials. The solvothermal process has all the advantages of wet-chemical processes, which are suitable to control the stoichiometry, purity, agglomeration state, particle size, crystallinity of products. The objectives of the present study is to design and develop new techniques for the preparation of advanced inorganic materials such as zirconia and titania via solvothermal reactions in aqueous and / or nonaqueous solvents. The results of the investigations were summarized as follows:

CHAPTER 1 General Introduction

Chapter 1 surveyed the basic physical chemistry, application and theories of zirconia and titania ceramics; mentioned the chemical synthesis of ceramic powders, advantages of solvothermal reaction and its application on the synthesis of ceramics; clarified the purposes of the present study.

CHAPTER 2 Crystallization and Characterization of Ceria and Yttria Co-Doped Zirconia

Chapter 2 described the crystallization behavior of amorphous ZrO_2 gels in air and liquid media such as water, n-hexane, and methanol over a range of temperatures. The kinetics of crystallization in water, n-hexane and methanol could be adequately described by the surface chemical reaction controlled shrinking core model with activation energies of 40.4, 44.8, and 52 kJ mol^{-1} , respectively. Softly agglomerated CeO_2 and Y_2O_3 co-doped zirconia powders were fabricated by crystallizing amorphous gels of the mixtures of end members and intermediate compositions along with the tie-lines joining 12 mol% CeO_2 -doped ZrO_2 (12Ce-88 ZrO_2) to 2 mol% Y_2O_3 -doped ZrO_2 (2Y-98 ZrO_2) and 12Ce-88 ZrO_2 to 3 mol% Y_2O_3 -doped ZrO_2 (3Y-97 ZrO_2) in supercritical methanol at 250°C for 5 h and supercritical drying. The powders could be sintered to full theoretical density at low temperature around 1200°C. 12Ce-88 ZrO_2 /2Y-98 ZrO_2 and 12Ce-88 ZrO_2 /3Y-97 ZrO_2 alloys containing less than 25 mol% 2Y-98 ZrO_2 and 3Y-97 ZrO_2 caused no noticeable tetragonal to monoclinic phase transformation by annealing in water at 200°C for 50 h. 12Ce-88 ZrO_2 /2Y-98 ZrO_2 and 12Ce-88 ZrO_2 /3Y-97 ZrO_2 alloys containing 10 mol% 2Y-98 ZrO_2 and 25 mol% 3Y-97 ZrO_2 , respectively, possessed excellent mechanical properties and thermal stability of tetragonal phase in moist atmosphere.

CHAPTER 3 Crystallization and Characterization of Ceria and Yttria Co-Doped Zirconia / Alumina Composites

In Chapter 3, Ceria and yttria co-doped tetragonal zirconia (Ce, Y- ZrO_2)/alumina composites containing 5-30 mol% alumina were fabricated by low temperature sintering at 1200-1400 °C using powders prepared by crystallizing amorphous gel precursors in supercritical methanol at 250 °C for 5 h and supercritical drying. Two compositions, one containing 10.8 mol% CeO_2 and 0.2 mol% Y_2O_3 , designated as (10.8Ce, 0.2Y)- ZrO_2 , and other containing 9.0 mol% CeO_2 and 0.75 mol% Y_2O_3 , designated as (9Ce, 0.75Y)- ZrO_2 , were used as end members for the preparation of the composites. The addition of alumina inhibited grain growth of zirconia during sintering and reduced the sinterability but improved the thermal stability of tetragonal zirconia in moist atmospheres. The fracture strength and fracture toughness values of (10.8Ce, 0.2Y)- ZrO_2 /Al₂O₃ composites were higher than those of (9Ce, 0.75Y)- ZrO_2 /Al₂O₃. Composites of (10.8Ce, 0.2Y)- ZrO_2 /5 ~ 10mol% Al₂O₃ sintered at 1300°C for 5 h

possessed excellent fracture strength, fracture toughness and thermal stability of tetragonal phase in moist atmosphere.

CHAPTER 4 Crystallization and Characterization of Ceria and Alkaline Earth Metal Oxide Co-Doped Zirconia

In Chapter 4, cheaper MgO and CaO were used as stabilizer in Ce-ZrO₂ instead of more expensive Y₂O₃. CeO₂ and MO (M=Mg, Ca) co-doped zirconia powders were prepared by crystallizing amorphous gels of the mixtures of end members and intermediate compositions along the tie-lines joining 12 mol% CeO₂ doped ZrO₂ (12CeO₂-88ZrO₂) to 9 mol% MgO doped ZrO₂ (9MgO-91ZrO₂) and 12CeO₂-88ZrO₂ to 12 mol% CaO doped ZrO₂ (12CaO-88ZrO₂) in supercritical methanol at 250°C for 5 h and supercritical drying. The compacts of (CeO₂, MO)-ZrO₂ powders were sintered to almost theoretical density at low temperature (1200 ~ 1250°C). Sintered bodies consisting of 10~15 mol% 9MgO-91ZrO₂ or 25 mol% 12CaO-88ZrO₂ possessed excellent mechanical properties and showed no noticeable tetragonal to monoclinic phase transformation on annealing in water for 50 h at 200°C.

CHAPTER 5 Preparation of Porous Ceria-Doped Tetragonal Zirconia Ceramics by Capsule Free Hot Isostatic Pressing

Chapter 5 investigated the normal sintering and capsule free hot isostatic pressing (HIPing) of 12CeO₂-88ZrO₂ powder at 1100 ~ 1200°C using different starting powders. The sintering mechanism of capsule free HIPing was proposed. Porous 12CeO₂-88ZrO₂ ceramics with ~35 % open porosity, micropore diameter of ~23 nm and a narrow pore size distribution were fabricated by capsule free hot isostatic pressing at 1100°C using the powders crystallized in methanol followed by supercritical drying. The porosity increased with decrease in HIPing temperature and was accompanied by a steady decrease in fracture strength.

CHAPTER 6 Crystallization and Characterization of Titania Powders

Chapter 6 described the crystallization behavior of amorphous titania gels which prepared by dissolving TiCl₄ to NH₄OH-CH₃OH-H₂O mixed solution and hydrolysis of titanium(IV) tetraisopropoxide. Microcrystalline anatase was fabricated by crystallizing amorphous TiO₂ gels in methanol, n-hexane and water at 140 ~ 200°C which were much lower than the crystallization temperature in air. The kinetics of crystallization in water, n-hexane and methanol could be adequately described by the surface chemical reaction controlled shrinking core

model with activation energies of 89.1, 88.0, and 206 kJ mol⁻¹, respectively. Crystallization in water was much faster than in methanol and n-hexane, but the sinterability of powder prepared in water was poorer than that prepared in organic solvents. The addition of requisite amounts of water to organic solvents was found useful in promoting crystallization of gel without loss of powder sinterability. The crystallite size of anatase prepared in water was larger than that prepared in organic solvents. The crystallized powders were capable of efficient hydrogen evolution following band gap irradiation in the presence of a sacrificial hole acceptor such as methanol. The photocatalytic activity of powder crystallized in methanol was superior to those prepared in water and air.

CHAPTER 7 Photocatalytic Properties of Titania Prepared by the Solvothermal Reactions of Protonic Layered Tetratitanate

Chapter 7 investigated the phase transformation behavior of the protonic layered tetratitanate, H₂Ti₄O₉ · nH₂O, in air, water, methanol and ethanol. H₂Ti₄O₉ · nH₂O transformed in steps to H₂Ti₈O₁₇, monoclinic TiO₂, anatase and rutile. All products remained fibrous morphology similar to that of K₂Ti₄O₉ used as a starting material, however, the phase transformation temperature and the microstructure of the products changed significantly depending on the heating environment. Nanosize crystals of TiO₂ possessing high crystallinity could be obtained by the solvothermal reactions using water, methanol and ethanol as reaction media. The photocatalytic activity of titania prepared by solvothermal reactions in water and alcohols at 200 ~ 325°C was much higher than that prepared by calcination in air. The solvothermal reactions using methanol and ethanol were much more efficient in increasing the photocatalytic activity than when water was used. When the titania formed by the solvothermal reaction in methanol was heated in air, the photocatalytic activity decreased with increasing temperature; however, the powders possessed higher photocatalytic activity than those produced directly by calcining the protonic layered tetratitanate at the same temperature without a solvothermal treatment.

CHAPTER 8 Summary and Conclusions

Chapter 8 summarized the main conclusions. In the present thesis, the solvothermal reaction process is established as a new method for preparation of ultrafine ceramic powders with soft agglomeration and high crystallinity. The zirconia and titania powders prepared by solvothermal reactions exhibit excellent physical and chemical properties. It is expected that the solvothermal reaction method will be widely applied in preparation of various functional materials.

審査結果の要旨

本論文は、アルコール等の非水溶媒を反応溶媒として用いるソルボサーマル反応によるジルコニア及びチタニアセラミックス微結晶の合成及び得られた微結晶の特性評価を行なったもので、全編8章よりなる。

第1章は緒論で、本研究の背景と従来の研究を述べることにより本論文の目的を明らかにしている。

第2章は、高強度高靱性材料として注目されているセリアおよびイットリア固溶ジルコニアに関するもので、ソルボサーマル反応によるジルコニアゲルの結晶化の速度論的解析を行ない、結晶化機構を解明すると共に、ソルボサーマル反応によるゲルの結晶化及び超臨界乾燥による高分散性ジルコニア微結晶粉末の調製プロセスを確定している。また、ジルコニアセラミックスの特性の組成依存性についても調べ、優れた機械特性と熱安定性を有するセリアおよびイットリア固溶正方晶ジルコニアセラミックスの創製に成功している。

第3章では、セリアおよびイットリア固溶ジルコニアにアルミナを複合化すると、ジルコニアの粒成長が抑制されるとともに粒子分散強化機構により機械的特性および熱安定性が向上し、優れた三点曲げ強度及び破壊靱性を有する複合体の調製ができることを明らかにしている。

第4章では、高価なイットリアの代わりに安価なアルカリ土類金属酸化物を用いたセリア固溶正方晶ジルコニアの機械特性の改善について述べている。

第5章では、ソルボサーマル反応によるセリア固溶ジルコニア微結晶粉末を用いて、カプセルフリーHIP法により、優れた機械的特性、熱安定性、高开気孔率および狭いポアサイズ分布を有するメソポア多孔体の合成に成功している。また、焼結機構、焼結体の空孔率と機械的特性との関係を明らかにしている。

第6章では、ソルボサーマル反応によるチタニアゲルの結晶化の速度論的解析を行ない、結晶化機構を明らかにしている。得られたチタニア微結晶の焼結特性と光触媒活性について調べ、光触媒活性は比表面積及び結晶化度に依存することを明らかにした上で、市販の高活性チタニアより1.9倍優れた活性を有するチタニア光触媒の創製に成功している。

第7章では、繊維状四チタン酸を前駆体として用い、ソルボサーマル反応による相変態挙動を明らかにし、生成されるチタニアの光触媒活性に及ぼす結晶化溶媒の影響を解明している。また、四チタン酸を前駆体とするソルボサーマル反応により、市販の高活性チタニアより1.1倍優れた活性を有する繊維状チタニア光触媒の創製に成功している。

第8章では、第2章から第7章までを総括した。

以上要するに本論文は、ソルボサーマル反応によるセラミックス材料の新規合成法について検討したものであり、結晶成長や水を媒介とする水素結合による粒子間架橋及び毛細管力による凝集を制御し、形態及び凝集の制御された微結晶粉末の合成法を開発し、得られた微結晶の工学的利用のための特性が大きく向上することができたもので、材料工学及び新材料開発に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。