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Editors
A. Antić-Jovanović and S. Anić

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MECHANICALLY ACTIVATED CERIA

S. Zec and S. Bošković

Institute of Nuclear Science Vinča, Materials Science Laboratory, 11001 Belgrade, POB 522, Serbia and Montenegro

Abstract

The reduction of comercial and mechanically activated CeO_2 powder at 1200 °C in an argon atmosphere was examined by XRD. Mechanical activation of oxide powder was performed by milling in a vibratory mill for different lengths of time. During 30 min of milling it came to the greatest change in crystallite size, as well as of lattice distortion of CeO_2 while after 60 min of activation effect of milling on the CeO_2 properties was negligible. Fired CeO_2 was partly reduced but firing of 60 min milled CeO_2 produced only CeO_{2-x} with lattice parameter a = 0,550 nm.

Introduction

Studying of ceria - CeO_2, has been intensified recently, due to its wide range of applications[1]. CeO_2 is important in a various fields of technology including optoelectronics, microelectronics, catalysis, solid oxide fuel cells, corrosion protection, ceramics sintering etc. The main attention is paid to the oxygen transport ability of ceria as a result of the presence of oxygen vacancies, due to different cerium ion valent states, tetravalent and trivalent, in non-stoichiometric CeO_{2-x} ($0<x<0.3$). Defect fluorite structure is formed due to the presence of oxygen vacancies [2]. Different procedures (chemical proceses, solid solutions, etc.) were applied with the aim to obtain ultrafine ceria powders and to improve the degree of the ceria reduction [3]. As no evidence of the influence of mechanical activation on the formation of CeO_{2-x} was found in the literature we have investigated in the present paper the reduction of mechanically activated ceria.

Experiment

Commercial oxide powder CeO2 (Aldrich, purity 99,9 %, particle size < 5 μm) was mechanically activated in vibratory mill, Pulverisette 9(Fritsch), made of tungsten carbide (WC). Oxide powder batch of 10 g were milled 2, 15, 30, 45, 60, 90 and 120 min applying the vibration speed of 1450 rpm. The activated mixture and non-activated oxide powder were pressed into pellets (diameter 10 mm) under 35 MPa. Pellets were fired in an Astro furnace in the flowing argon atmosphere at 1200 °C, 1 hour. Cooling of pellets were done under argon together with furnace down to the room temperature. X-ray powder diffraction (XRD) analysis was performed by Siemens D500 diffractometer using Ni-filtered CuKα radiation and scanning speed of 0.02 º2θ/s. XRD data were processed with Diffracplus software while the lattice parameters were refined by Wincell program. Crystallite size (D) and lattice distortion

(ε) were determined on the base of FWHM (full width at half maximum) of diffraction peaks using Cauchy expression [4].

Results and Discussion

Lattice parameter change as a function of milling time of the cubic CeO_2 unit cell was not observed. Rapid decrease in CeO_2 crystallite size up to 34 nm in comparison with 140 nm measured in non-activated oxide powder occurred in the first 2 min of milling. During 30 min of milling the greatest change of crystallite size as well as lattice distortion of CeO_2 (Fig. 1) was observed, due to its particles fragmentation and lattice defects formation. After 60 min of activation, effect of milling on the CeO_2 crystallographic properties was negligible. CeO_2 fired 1 h at 1200 °C in argon was partly reduced, so that two phases were present according to the related XRD pattern (Fig. 2a), CeO_2 phase with lattice parameter a = 0,541 nm and smaler quantity of the second one, non-stoichiometric CeO_{2-x} with lattice parameter a = 0,548 nm. Firing of 60 min milled CeO_2 for 1h at 1200 °C produced only CeO_{2-x} (Fig. 2b), which lattice parameter a = 0,550 nm corresponding to the expansion of the unit cell of 1.8% compared to the unreduced cell.

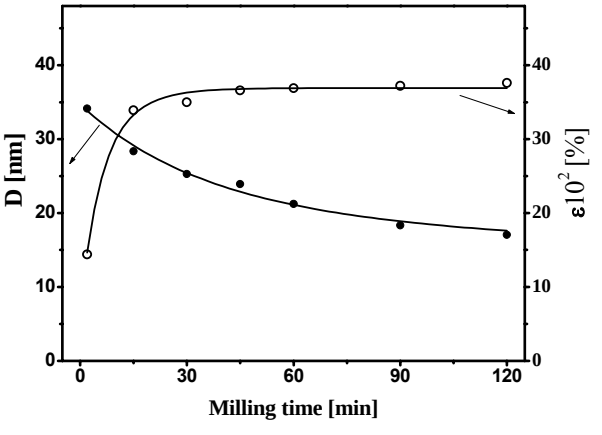

Fig. 1 CeO_2 crystallites size (D) and lattice distortion (ε) as a function of milling time

These resultes designate that activation of CeO_2 by milling accelerates its reduction proces and makes it more effective on heating. Through the particles fragmentacion, crystallite size decrease and the lattice defects got introduced. Mechanical activation affects also the surface structure of the CeO_2 powder because in the activated ceria heated at 1200 °C mobility of oxygen ions was higher, release of oxygen from the crystal lattice was easier and followed by oxygen vacancis formation as well as reduction of the part of tetravalent cerium into trivalent. Therefore, the mechanical activation can be applied as prosperous procedure in the redox reaction of ceria.

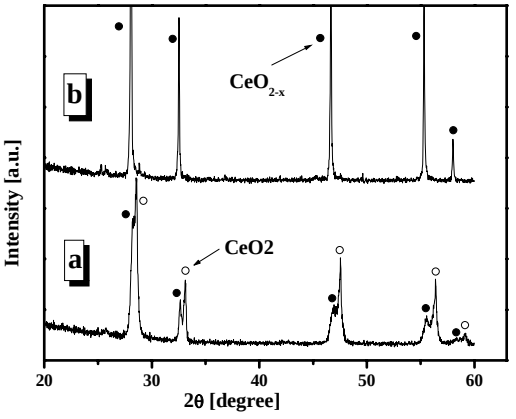

Fig. 2 XRD patterns of a) non-activated and b) 60 min activated CeO_2 fired at 1200 °C in argon.

Conclusion

The major change in crystallite size and lattice distortion of the CeO_2 powder occurred within 60 min of milling in a vibratory mill while the lattice parameter of CeO_2 was not affected by milling. Ceria fired 1 h at 1200 °C in argon was partly reduced into non-stoichiometric CeO_{2-x} with lattice parameter a = 0,548 nm but firing of 60 min milled ceria for 1h at 1200 °C produced only CeO_{2-x} with lattice parameter a = 0,550 nm. Activation of CeO_2 by milling accelerates its reduction proces and makes it more effective upon heating. In the mechanicaly activated ceria mobility of oxygen ions is higher and the release of oxygen atoms was followed by reduction of the part of tetravalent into trivalent cerium ions, and consequently by oxygen vacancies formation.

Acknowledgment

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References:

[1] A. Trovarelli, M. Boaro, E. Rocchini, C. Leitenburg, G. Dolcetti, J. Alloy and Compo., 2001, 323-324, 584.
[2] A. Gotte, K. Hermansson, M. Baudin, Surface Science, 2004, 552, 273.
[3] Y. Zhou, M. N. Rahaman, Acta Mater., 1997, 45, 3635.
[4] B. Lönnberg, J. Mater. Sci., 1994, 29,3224.