Structural investigations on the Zr(N,O) phases by means of transmission electron microscopy

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Zirconia, pure or alloyed with aliovalent cations, is a widely used (fuel cells, oxygen sensors, refractories etc.) and intensively studied material because of its outstanding physical properties. A new approach, which has received far less attention both in research and application, is the doping of zirconia with aliovalent anions, in particular nitrogen.

Oxynitrides of zirconium were prepared by nitridation of zirconia pellets in a graphite heated resistance furnace at 1900°C (2 h, nitrogen atmosphere). Specimens for TEM investigations were pre-thinned mechanically by using a tripod tool to the thickness of about 20nm. The following ion etching produced finally large electron transparent area in a sample. TEM experiments were performed at a PHILIPS microscope CM200 (LaB_6, 200kV).

The main frame of this work is to find out the different possible structural modifications of non-stoichiometrical Zr(N,O) compounds depending on the ratio in amounts of N and O, respectively. Beside the well known modifications like γ- (Zr_2N_2O) or β-phase ($Zr_7N_4O_8$) [1,2], oxygen rich phases namely β’- and β’’-phase could be found, which can be described on the one hand by arrangements of numbers of so called BEVAN clusters ($Zr_7N_4O_8$) and Zr_7O_{14} units stacked along [001] direction and on the other hand by certain periodical orderings of vacancies on sites of anions [3]. Such alternating arrangements in the structure, however, induce frequently modulating fringes contrasts observed in TEM images, consequently. From these considerations, different ordered structure models with various possible proportions of anions/vacancies could be suggested and constructed by using the CERIUS simulation software, correspondingly. Comparisons between simulated and experimental received diffraction patterns as well as high resolution images can reveal information about the structure in the local area with such modulating fringes contrasts and specify immediately the local chemical composition, which further can be confirmed by analytical TEM related measurements using EELS or EDX.

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References

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