

論文内容の要旨

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This thesis focuses on features of the Zr-N-O system and some particular compounds existed in this system for oxidation of zirconium alloys fuel claddings and application of ZrN as inert matrix for transuranium elements transmutation. The essential focus points are on the ternary diagram of the Zr-N-O system near the Zr-rich corner where equilibrium oxygen partial pressures are relatively low and nano-scale characterization of ZrN, ZrO₂ and β' -Zr₇O₁₁N₂ by transmission electron microscopy. There are three parts in this study: (1) study on the Zr rich corner of the Zr-N-O system by oxidation of nitrated Zr (or separated reaction sequence) and simultaneous oxidation/nitridation of Zr in low oxygen partial pressures, (2) validation of the Zr-N-O system near the Zr-rich corner by a simple sublattice formalism model based on the experiment results. and (3) syntheses of ZrN and β' -Zr₇O₁₁N₂ nanoparticles in relatively high oxygen partial pressures by pulsed wire discharge and characterizations of the synthesized particles using electron energy loss spectrum (EELS), near edge X-ray absorption fine structure (NEXAFS).

In part (1), experiments of oxidation of nitrated Zr and simultaneous oxidation/nitridation of Zr were performed by using redox couples of Mo/MoO₂ and Cu₂O/CuO at a temperature of 1373K. The samples were characterized by X-ray diffraction (XRD), optical microscopy and electron probe micro analysis (EPMA). From the EPMA analysis, phase boundaries were determined between α Zr/Zr(N,O)_{1-x}, ZrO₂/Zr(N,O)_{1-x}, and α Zr/Zr(N,O)_{1-x}/ZrO₂ phases.

For a more comprehensive approach, these experiments data were coupled with a simple sublattice formalism in part (2). In this approach, modelled parameters of three binaries system of Zr(V_a)/ZrN, Zr(V_a)/ZrO and ZrN/ZrO (where Zr(V_a) is pure Zr with vacancies) were applied for the ternary phase modelling. Through this process, the feature of the Zr-N-O system near the Zr-rich corner has been revealed. The stability domains of Zr(N,O)_{1-x} and α Zr were clarified. The former at 1373K is slightly larger than that previously determined by Zainulin et al. at 1773K [15] and is pointing towards the hypothetical zirconium monoxide, ZrO. Furthermore, the stability domain of the hexagonal α Zr phase is significantly extended when both nitrogen and oxygen are dissolved. In the separated reaction sequence with the Cu₂O/CuO redox couple, the oxidation proceeded at both at the surface of ZrN layer and at the interface of Zr(N,O)_{1-x} and α Zr. The oxidation at the interface proceeded faster than the former. The composition of the internal oxide layer and the XRD pattern suggested that this layer was of nitrogen-stabilized t-ZrO₂ and Zr(N,O)_{1-x}.

In part (3), the pulsed wire discharge experiments of Zr in N₂ and N₂/O₂ atmosphere at a total pressure of 100kPa were carried out. Particles of ZrN, Zr₂N were observed in a sample synthesized at a N₂ partial pressure of 100kPa, formations of β'-Zr₇O₁₁N₂ and ZrO₂ were started when O₂ was introduced together with N₂ in the reaction gas mixture, starting at oxygen partial pressure of 1kPa. By bright field image observations EELS and selected area electron diffraction, nanoparticles of ZrN, β'-Zr₇O₁₁N₂ and ZrO₂ were separately characterized. In these syntheses, nanoparticles of β'-Zr₇O₁₁N₂ existed in much smaller size than and different shape from the ordinary spherical nanoparticles of ZrN and ZrO₂. ZrN and β'-Zr₇O₁₁N₂ were investigated comparatively by EELS and NEXAFS. Distinguishable features of N-K edge in ZrN and β'-Zr₇O₁₁N₂ in EELS and NEXAFS, especially the absorption pre-edge in NEXAFS spectra of ZrN were characterized.