The Effects of Aliovalent Elements on Nodular Oxidation of Zr-Base Alloys

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Susceptibility of fuel cladding fabricated from some types of Zr-base alloys to nodular oxidation is an important factor that influences fuel economy, safety-related performance under accident situations, and long-term storage of spent fuel. In earlier years, nodular oxidation in Zircaloy-2 cladding was an important issue for improved BWR fuel performance. Under spent-fuel-pool accident situations in which fuel cladding is heated-up slowly in air or air-rich environment, nodular corrosion followed by breakaway oxidation has been observed for Zircaloy cladding. Recent trend in PWR fuel is increased use of advance cladding fabricated from Nb-containing alloys such as E110, M5, E-635, Zirlo, and MDA. Although corrosion resistance of these fuels under normal operating conditions has been reported to be excellent or superior to that of Zircaloy-4, some of them have been known to be susceptible to nodular oxidation under loss-of-coolant-accident (LOCA) situations. For example, E110 cladding fabricated from Zr-1Nb has been reported to be susceptible to nodular oxidation under LOCA-like transients, either in as-fabricated condition or after service in VVER. Nodular oxidation in E110 leads to excessive hydrogen uptake during LOCA-like transients and subsequent loss of post-quench ductility. In contrast, despite the fact that M5 cladding is fabricated from the nominally same type of Zr-1Nb alloy, it has been reported to be resistant to nodular oxidation under similar conditions, and neither excessive hydrogen uptake nor unexpected ductility loss was observed. Although the chemical composition of E635 and Zirlo is similar, the former has been reported to be susceptible and the latter resistant to nodular oxidation. These observations indicate that the phenomenon of high-temperature nodular oxidation in Nb-containing alloys is sensitive to unknown salient feature(s) of microchemical and microstructural variations, and to assure reliable fuel fabrication and good performance under LOCA situations, understanding the nature of the salient feature(s) is an important step.

In this paper, a mechanistic model has been developed to provide an insight useful to understand the susceptibility of Nb-containing Zr-base alloys to high-temperature nodular oxidation. The model is based on the effect of aliovalent elements (i.e., alloying or impurity element of which valency differs from that of tetravalent Zr in Zr oxide) on the properties of Zr oxide, i.e.: O ion vacancy, stoichiometry, crystal structure, and fracture toughness of oxide. Important aliovalent elements are classified into three groups: (1) double-valent (2+) elements, such as Ca, Mg, K, Ni, Cu, and Ce, (2) triple-valent elements such as Al, Fe, Cr, Y, and La, and (3) penta-valent elements such as Nb and V. When a double- or triple-valent element is incorporated in the oxide, even in very small quantity, the number of O vacancies in the oxide

unit cell increases, keeping the oxide understoichiometric. This is because neutral charge balance in the oxide unit cell is maintained during oxidation in water or steam. Because of understoichiometry, the oxide remains in tetragonal structure of which fracture toughness is significantly greater than that of monoclinic oxide. As a result, a double- or triple-valent element plays an beneficial role in preventing or delaying formation of monoclinic oxide and oxide cracking, thereby rendering the alloy resistant to nodular oxidation. Tin plays a similar role, because its valence states are either SnO (strongly beneficial), Sn_3O_4 (beneficial), or SnO_2 (neutral). In contrast to the undervalent elements, an overvalent element, such as Nb, plays the opposite role at high temperatures. Niobium atoms are readily incorporated in the oxide unit cell at high temperatures, promoting less O vacancy, stoichiometry, monoclinic structure, lower fracture toughness, and hence, higher susceptibility to oxide cracking and nodular oxidation. Effects of volatitility of aliovalent elements at high-temperatures during fabrication, diffusivity in Zr metal, free energy of oxidation, and solubility in Zr oxide are also analyzed to provide a means of determining relative effectiveness of undervalent elements in suppressing the susceptibility to nodular oxidation. The model prediction is then compared to available results of experimental tests. The comparison and discussions are focused on the effects of: (1) fabrication variables and intermetallic precipitates, (2) minor alloying or doping with Cu, La, Y, or Ce, (3) ion implantation of Y, La, or Cr, (4) surface polishing with Cr_2O_3, Al_2O_3, Fe_2O_3, or SiC powders, (5) impurity pickup during production of raw Zr, and (6) Ca and Al pickup during the process of Hf purification for nuclear-grade Zr.