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Differences in Behavior of Sn and Nb in Zirconium Metal and Zirconium Dioxide*

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ABSTRACT

In the beginning days of development of Zr-base alloys for nuclear application, the effort focused on two types of alloy, one based on Zr-Sn system in the west and the other based on Zr-Nb in the east. Although Zircaloy-2 is almost exclusively used for BWR fuel application, alloys used for PWR fuel cladding at this time is more diversified, i.e., Zircaloy-4, Zr-Nb-base alloys such as E110 and M5, and Zr-Sn-Nb-based alloys such as E635, Zirlo, and MDA. Numerous reports indicate that LOCA-related behavior of the three groups of alloys differ significantly, i.e., high-temperature oxidation, hydrogen uptake, beta-to-alpha transformation, and post-quench mechanical properties. For example, susceptibility of fuel cladding fabricated from some Nb-containing alloys to high-temperature breakaway oxidation and hydrogen uptake has been reported to be more pronounced, which influences post-quench ductility significantly. In this paper, fundamental metallurgy concerning the roles of Sn and Nb on LOCA-related processes is reviewed, i.e., structure and properties of Zr dioxide, nature and kinetics of phase transformation, and structure and properties of prior beta (the key load-bearing material from the standpoint of post-quench ductility). A mechanistic model has been developed to provide an insight useful to understand the susceptibility of Nb-containing alloys to high-temperature breakaway oxidation and more pronounced hydrogen uptake. 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 dioxide) on the properties of oxide, i.e., O ion vacancy, stoichiometry, crystal structure, and fracture toughness of oxide. In this model, contrasting effects of Nb and Sn are described. Effects of the two alloying elements on the stability and transformation of beta phase are also evaluated, e.g., solubility of oxygen in beta, nature of the transformation, redistribution of O, H, Nb, and Sn during the transformation, O- and H-induced embrittlement, effect of cooling rate, and mechanical properties of the transformed beta.

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