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WATER TREATMENT AND WATER CHEMISTRY

Simulating the Corrosion of Zirconium Alloys in the Water Coolant of VVER Reactors

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Abstract—A model for predicting the corrosion of cladding zirconium alloys depending on their composition and operating conditions is proposed. Laws of thermodynamics and chemical kinetics of the reactions through which the multicomponent zirconium alloy is oxidized in the reactor coolant constitute the physicochemical heart of the model. The developed version of the model is verified against the results obtained from tests of fuel rod claddings made of commercial-grade and experimental zirconium alloys carried out by different researchers under autoclave and reactor conditions. It is shown that the proposed model adequately describes the corrosion of alloys in coolants used at nuclear power stations. It is determined that, owing to boiling of coolant and its acidification in a VVER-1200 reactor, Zr–1% Nb alloys with additions of iron and oxygen must be more resistant to corrosion than the commercial-grade alloy E110.

Keywords: reactor, VVER, zirconium alloys, water chemistry, simulation, thermodynamics, chemical kinetics, prediction of corrosion

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Corrosion of zirconium alloys in the water coolant used in nuclear power installations is determined by the totality of internal factors (the chemical composition and structural state of material) and external factors (irradiation conditions, water chemistry, heat removal, etc.).

The following conclusions can be drawn from the well-known data on corrosion of zirconium alloys operating in water coolants used at nuclear power stations (NPSs):

(i) Surface temperature, pH value of water at temperature t (pH_t), and the presence of oxidizers and other admixtures in it have an essential effect on corrosion.

(ii) The corrosion rate depends on the alloy composition and conditions under which the tests are carried out: the rate of corrosion occurring in an autoclave may differ from that in a reactor by a factor of 3–5.

(iii) The corrosion processes occurring in different parts of fuel assemblies (FAs) have different patterns depending on the operating conditions (in a single-phase flow, during boiling, in slits, etc.).

(iv) In the region of high burnup values, the corrosion processes occurring in all parts of FAs made of E110 and E635 alloys used in VVER and RBMK reactors are quasi linear but have different rates.

In the general case, the zirconium and zirconium alloys corrosion processes that take place in water and steam at elevated temperatures are characterized by two periods "before a turning point (pre-turn)" and "after a turning point (post-turn)". The thickness of oxide film generated for the time τ can be described in a simplified way by the following expression [1]:

$$h = k\tau^n, \quad (1)$$

where k and n are constants. For the "pre-turn" period, $n \approx 0.5$, and for the post-turn period, $n \approx 0.5$–1.0.

The oxide film formation process in the "pre-turn period" is described by a parabolic dependence. This black-colored film consists of a nonstoichiometric oxide ZrO_{2-x} and has good protective properties. As the content of oxygen increases in the "post-turn" period, this oxide transforms into a stoichiometric dioxide initially having a gray color, which then becomes white as the film thickness increases. This white-colored dioxide has almost no protective properties. If the oxidation process continues for a long period of time, the oxide layer may become severely cracked and exfoliated, and local kinds of corrosion can appear. The oxide film formation process in the "post-turn" period can be described by a linear dependence.

In empirical models simulating the corrosion of zirconium alloys, the oxidation process is considered as a thermally activated one. Such models describe systems the corrosion rate in which is mainly determined by the corrosiveness of one of the reacting participants, namely, water. On other words, these models have been developed for strictly defined conditions of operation and for one selected alloy [1, 2].