

# The transformation of the oxide coatings of aluminum by imitation factors of nuclear power plants

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## Abstract

The authors present the results of a study on kinetics of hydrogen generation by heterogeneous compositions with aluminum exposed to  $\gamma$ -irradiation in air, in different aqueous solutions at room temperature and high temperature annealing. It has been found that hydrogen generation kinetics depends on the  $\gamma$ -irradiation dose, temperature and aqueous medium chemistry. Changes in hydrogen generation kinetics are due to transformations of aluminum oxide coatings influenced by factors simulating the NPP conditions. The effect of metal oxide coating transformations should be considered in predicting the corrosion resistance of NPP structural materials.

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*Keywords:* Aluminium; Aluminium oxide; Water; Hydrogen; Irradiation dose; Generation kinetics; Annealing; Oxide coating transformation.

## Introduction

In nuclear power plants (NPPs) the high corrosion resistance of structural materials is provided by passivating oxide coatings which protect the pure metal against direct contact with water and steam. Thus, zirconium and zirconium alloys are covered with a layer of zirconium oxide ( $ZrO_2$ ), and aluminum and aluminum alloys are covered with a layer of aluminum oxide ( $Al_2O_3$ ). In the case of aluminum, it has been found that if the surface oxide coating ( $Al_2O_3$ ) is removed in alkaline solutions, aluminum effectively reacts with water to generate hydrogen and a solid product [1-3]. An analysis of hydrogen storage in heterogeneous hydro-reactive compositions with aluminum has shown that the hydrogen generation kinetics indicates transformations of surface aluminum oxide coating when reacting with a catalyst, water and ambi-

ent oxygen. Therefore, the study of the kinetics of hydrogen storage in compositions containing structural materials with oxide coatings can be used to determine the transformations of surface aluminum oxide coatings under the integral action of factors simulating the NPP conditions, i.e. ionizing radiation, high temperatures, water coolant, and ambient oxygen.

The authors present the results of the investigation of the kinetics of hydrogen generation by heterogeneous hydro-reactive compositions containing aluminum previously exposed to radiation and thermal treatment. For this purpose, aluminum samples were exposed to  $\gamma$ -irradiation ( $^{60}Co$ ) at room temperature and in aqueous media simulating the PWR coolant. The samples of  $\gamma$ -irradiated aluminum were subsequently thermolized at 320 °C in air. Based on the studied hydrogen storage kinetics, assumptions were made about the surface aluminum oxide layer transformations in simulating the operational conditions of structural materials in the reactor coolant [4]. Aluminum is studied as a model metal as against zirconium: within the electrochemical series of metals aluminum and zirconium are placed nearby (the standard electrode potential of aluminum and zirconium are 1.66 V and 1.59 V, respectively). Extensive literature for example [5-17] devoted to the study of the physical properties of aluminum oxide.

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## Experimental technique

Commercial aluminum samples were taken for research in the form of aluminum powder with a specific surface area of  $1.6\text{ m}^2/\text{g}$  (brand PAP-2, GOST 5494-95). Aluminum powder particles have a plate form and are covered with a thin oxide and fatty film. The powder bulk density is about  $0.15\text{--}0.30\text{ g/cm}^3$ , the active aluminum content is  $85\text{--}93\%$ . The average thickness of aluminum powder petals is approximately  $0.25\text{--}0.50\text{ }\mu\text{m}$ ; the average linear dimension is  $20\text{--}30\text{ }\mu\text{m}$ . To activate aluminum, sodium meta-silicate crystallohydrate salt was used ( $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$ ) with a melting temperature of  $48\text{ }^\circ\text{C}$  and hydrolysis constant of  $10^{-3}$ .

The aluminum powder was placed in thick-walled glass vessels of 500 ml and irradiated by  $\gamma$ -source  $^{60}\text{Co}$  with 1.0, 2.0 and 5.0 mGy doses at a specific absorption rate of 1.5 Gy/s. In air, distilled water, boric acid solution (5 g/l of 20% acid content), and boric acid and potassium hydroxide solution (pH=8) the samples were irradiated with a dose of 1.0 mGy. Annealing of the source and  $\gamma$ -irradiated aluminum samples was performed at  $320\text{ }^\circ\text{C}$  in air, in a muffle furnace SNOL-4/900 as follows: Annealing of a sample for about 6 h, then holding at room temperature for approximately 17 h, repeated annealing for 6 h, etc. to achieve the desired annealing duration.

The study of the hydrogen storage kinetics includes the following procedures. The reaction mixture was prepared by thoroughly mixing the aluminum powder (initial,  $\gamma$ -irradiated, and annealed) and sodium meta-silicate crystallohydrate in a certain ratio with the addition of distilled water. The mixture sample weight was loaded into a glass bulb of 500 ml with a tube for removing hydrogen through the water into the measure cell. The reaction vessel was placed into a thermostat and heated to a specified temperature. Hydrogen generation was monitored by measuring the amount of hydrogen evolved in the measure cell.

## Results and discussion

The process of forming the aluminum oxide ( $\text{Al}_2\text{O}_3$ ) layer on the aluminum surface is two-sided, i.e. on one side of this layer the reaction occurs on the surface dividing two solids: aluminum and aluminum oxide layer; while on the other side, the solid layer of aluminum oxide, water and ambient oxygen. The formed oxide dissolves excess stoichiometric aluminum, water and oxygen; and the aluminum oxide layer is a two-sided non-stoichiometric phase. In air, two fluxes of charged particles move from each side of the layer: A flux of metal and electrons moves from the metal side; a flux of oxygen ions and holes moves from the gaseous phase. The oxide layer thickness increases due to the flux of cations and anions [18].

The resulting aluminum oxide film with a thickness from 1 to 100 nm consists of two layers: an inner compact crystalline layer adjacent to the metal and outer porous layer [19]. The high mechanical strength of the oxide film is provided by the inner crystalline layer with a thickness of 1–3 nm, tightly contacting with the metal. The upper loose layer of the film

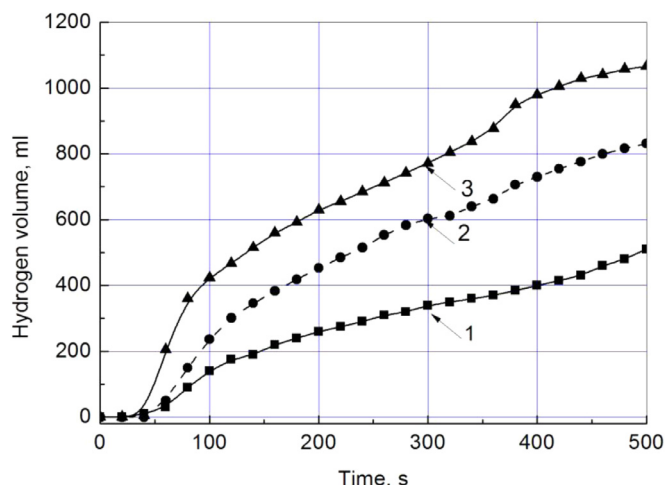
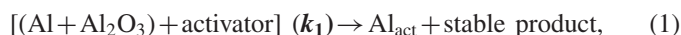


Fig. 1. Dependence of evolved hydrogen amount on reaction time: 1. Composition with initial aluminum; 2, 3. Compositions with aluminum,  $\gamma$ -irradiated in air at room temperature with 1 and 2 mGy, respectively. Composition content: 1 g of aluminum, 2 g of sodium meta-silicate crystallohydrate and 10 g of distilled water.

with the structure of bayerite ( $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ ) is monoclinic hydroxide.

In our experiment, the heterogeneous composition of “solid aluminum–aluminum oxide layer–water, oxygen” is exposed to direct  $\gamma$ -irradiation, the impact of energy transmitted from aluminum to the oxide layer in the form of excitations and charged particles as well as the impact of ambient oxygen, intermediate active particles and stable products of water radiolysis. Based on the studied kinetics of hydrogen generation in compositions containing aluminum previously exposed to radiation, thermal and chemical treatment, we can make assumptions about the nature of aluminum oxide layer transformations induced by these factors.

On the kinetic curves describing the dependence of hydrogen generated by the composition with initial and  $\gamma$ -irradiated aluminum, sections can be distinguished related to the three stages of solid-phase reactions: initial, basic and final (Fig. 1). A characteristic feature of the initial stage is the induction period during which the hydrogen generation process is slow. This is due to the fact that aluminum is covered with an oxide layer ( $\text{Al}_2\text{O}_3$ ) which prevents the direct contact of reagents, i.e. pure aluminum and water. The presence of the quasi-stationary oxide layer is due to the simultaneous occurrence of three competing processes with similar rates: on the one hand, the destruction of the oxide layer ( $\text{Al}_2\text{O}_3$ ) when interacting with the chemical activator in an alkaline medium to form activated aluminum (without the oxide layer) and a stable product:



On the other hand, the recovery of the aluminum oxide layer due to the rapid reaction of activated aluminum with oxygen:



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