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The current status of zirconium alloys fuel cladding

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Abstract.
Properties such as corrosion and radiation resistance of zirconium alloys fuel claddings for nuclear reactors and ways to improve them are considered. The need to ensure high radiation and corrosion resistance and reliability of fuel claddings for the safe operation of pressurized water reactors of NPPs under operating conditions is substantiated. The use of sponge zirconium as the base of the alloys provides safety criteria under LOCA conditions. Optimization of the Fe content in the Zr-1%Nb alloy leads to increased corrosion resistance in the coolant and resistance to radiation growth during irradiation.

Keywords:
zirconium alloys
fuel cladding
corrosion
radiation resistance
Fe content
sponge zirconium

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Zirconium alloys have widely been used in the nuclear power industry of various countries (Ukraine, Canada, USA, France, Japan, etc.) include alloys Zircaloy-2, Zircaloy-4, ZIRLO, E110, E125, E635, M4, M5, MDA, and others. In the USA, Canada, and Western Europe, two main zirconium alloys are used for fuel element cladding, shrouds and channels of light-water and heavy-water reactors: Zircaloy-4 and Zircaloy-2, and the first is mainly used for fuel element for pressurized water reactors (PWR), the second – for boiling water reactors (BWR) [1, 2]. Zr-1%Nb alloy are the materials for cladding and structures and used in pressurized water reactors VVERs and provide reliable operation of fuel elements and fuel assembles in existing reactors and serves as a basis for new modifications. The advanced PWR cladding alloys are Nb-containing alloys: ZIRLO and M5. In Canadian heavy water reactor designs the pressure tubes are made from Zr-2.5%Nb.

In Table 1 shows the chemical composition of some zirconium alloys. These alloys, with Zr as the dominating constituent, enables a combination of desirable properties, e.g., high mechanical strength, high melting point (1852 °C), high corrosion resistance and a low absorption cross-section for thermal neutrons (0.18 barn). The latter is a key advantage of Zr over most other structural materials, and is necessary for the use of low-enriched nuclear fuel.

Table 1

Nominal composition of some fuel cladding alloys

Cladding alloy	Nominal composition (wt.%)
Zircaloy-2	Zr-1.5 Sn-0.2Fe-0.1 Cr-0.05Ni-0.12 O
Zircaloy-4	Zr-(1.3-1.5)Sn-0.2Fe-0.1 Cr-0.12 O
E110	Zr-1Nb (O ≈ 0.05-0.07)
M5	Zr-1Nb-0.12 O
E635	Zr-1Nb-1.2Sn-0.4Fe (O ≈ 0.05-0.10)
ZIRLO	Zr-1Nb-1Sn-0.1 Fe-0.12 O

All contemporary fuel cladding of water-cooled thermal neutron reactors contain 97-99% zirconium. Minor amounts of other elements are added to optimize the desired properties, e.g., Sn, Fe, Cr, Nb and Ni. Most of those have a low solubility in Zr, leading to the formation of precipitates,

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secondary phase particles (SPPs). The number density, size distribution and chemical composition of these SPPs play a major role for the in reactor performance of a cladding alloy, e.g., creep, growth, corrosion and hydrogen pickup.

The modern generation of cladding is capable of supporting fuel with 5% ^{235}U enrichment, corresponding to a burn-up (a measure of the extracted energy) of up to 75 MWd/kg U, fuel rod average. 5% ^{235}U is effectively an upper enrichment limit for water-cooled thermal neutron reactors fuel in most countries, and an increase will require a significant licensing effort. On the other hand, mixed oxide fuels (MOX, containing several % of plutonium) have no equivalent upper bound to the fissile content.

Zirconium-based fuel cladding materials have served the nuclear power industry well over a 50 year time period. They have been subject to an intense evolution and development process in fuel performance and reliability (e.g., life time, temperature, surface heat flux and neutron fluence).

The life limit of Zr-based cladding is usually determined by its corrosion properties, i.e., oxidation in the hot reactor coolant, and in particular the associated absorption of hydrogen. At hydrogen concentrations above the limit for solid solution in Zr, zirconium hydride precipitates will form. Those have a relatively poor mechanical strength and are brittle at room temperature, meaning that excessive hydrogen can reduce the mechanical strength and ductility of cladding. Both oxidation resistance and the hydrogen pickup depend on material composition and processing as well as operating conditions, and often also change with the accumulated fast neutron fluence.

Irradiation leads to several gradual changes on the microstructural level of the material, e.g., a buildup of dislocation loops and dissolution of the secondary phase particles, coupled to redistribution in the Zr matrix of atoms knocked out from the SPPs. These changes influence the in-reactor performance of the material, adding to the challenge of optimization.

Neutron irradiation leads to a redistribution of alloying elements between the matrix and the precipitates, and to changes in the α-solid solution composition. These changes

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affect accumulation and mobility of irradiation defects, anisotropy and formation of vacancy <c>-component dislocation loops. The appearance of <c>-loops usually correlates with the irradiation induced growth (IIG).

The irradiation induced growth phenomenon is a significant research area for zirconium alloys, which are used as cladding and structural materials in fuel assemblies in reactor-cores [3]. IIG refers to the volume-conservative shape change, which occurs during neutron irradiation; the cladding expands in the axial direction and shrinks in the radial direction [4]. This growth is one of the main limiting factors in the lifespan of fuel assemblies.

Irradiation-induced growth is well correlated to the evolution of dislocation loops in the material. At low fluences, irradiation-induced point defects collapse into vacancy and interstitial a-type dislocation loops on mostly first order prismatic planes with a Burgers vector of $b = \frac{1}{3}\langle 11\bar{2}0\rangle$ [5]. Upon further irradiation, c-component vacancy dislocation loops form on the basal plane, which have a Burgers vector of $b = \frac{1}{6}\langle 20\bar{2}3\rangle$.

Irradiation induced growth is well correlated to the evolution of dislocation loops in the material. At low fluences, irradiation-induced point defects collapse into vacancy and interstitial <a>-type dislocation loops on mostly first order prismatic planes. Upon further irradiation, <c>-component vacancy dislocation loops form on the basal plane [5].

Alloy chemistry can significantly alter the observed irradiation induced growth and particularly the point at which breakaway growth occurs. That's why, the role of Fe has been investigated with particular interest, as Fe dissolves from pre-existing SPPs during irradiation and is a fast diffusing element in Zr, potentially sitting interstitially within the Zr lattice and interacting with point defects generated during irradiation [6].

In Zr-Sn, Zr-Nb and Zr-Sn-Nb alloys the addition of more Fe led to a decrease in growth strain. Also showed data from the BOR-60 test reactor, which indicated that increased Fe leads to a lower IIG strain in variants of the E635

Nb-containing alloy.

Alloying elements should positively influence the corrosion resistance of products under operating conditions in the reactor and provide the necessary mechanical properties and reliability of products during operation [7, 8]. Numerous works have shown that alloying of zirconium with iron is promising in developing alloys for high temperatures. The increase of the iron content in the zirconium alloy provides the material of the cladding tubes with the required resistance to creep and strengthening under irradiation. In addition, the alloying of Zr-1%Nb alloy with iron increases its corrosion and radiation resistance in the conditions of the operation of a nuclear reactor.

Ar^{2+} ions irradiation of the Zr-1%Nb alloy with different Fe content showed that increasing the Fe concentration leads to the decrease in the size of the interstitial dislocation loops and a slight increase in their density [9]. During irradiation, the Fe release from the precipitates of the Laves phase, diffuse through the matrix and form secondary radiation-induced fine precipitates, which delay in <c>-type dislocation loops nucleation responsible for the acceleration of radiation growth. The Fe alloying of the alloys of the system Zr-Nb contributes to the suppression of the phenomenon of radiation growth in commercially effective ranges of radiation doses [9].

When Zr-based alloys are exposed to O, various sub-oxides are formed in a concentration gradient from the metal to ZrO_2 on the surface of the material. The thickness of the ZrO_2 layer will increase with increasing environmental exposure time and temperature [10]. The reaction of zirconium and its alloys with an oxidizing atmosphere is generally characterized by two distinct stages. During the first stage, the kinetics of oxidation can be described by a quasi-parabolic relationship; the oxide scale formed is black or possesses an iridescent appearance, and is very compact and protective in nature. During the second stage the rate of oxidation is linear and, in place of the black adherent film, the metal and its alloys become covered with a friable grey oxide which tends to spall. Usually, at this stage, a rapid deterioration of the metal and its alloys takes place. The

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change-over from the first to the second stage of oxidation is termed "transition" or "breakaway". This is usually one of the most prominent features of the oxidation of zirconium and its alloys.

Study of the influence of air-thermal oxidation temperature on the micromorphology, structure, and composition of the modified surfaces of the Zr-1%Nb alloy has been established that at a temperature of 500-600 °C oxide films are formed that are characterized by high strength and density [11]. The thickness of such coatings is 2-7 μm, the roughness parameter R_a is not more than 0.1 μm. The corrosion rate increases sharply at temperatures above 700 °C and characterized by fast oxidation and a number of oxide coating defects such as cracks and pores (Fig. 1). Transition from the protective oxide coating to the flake it off occurs for relatively short time after which the Zr-1% Nb alloys are oxidized with increased rate to complete destruction.

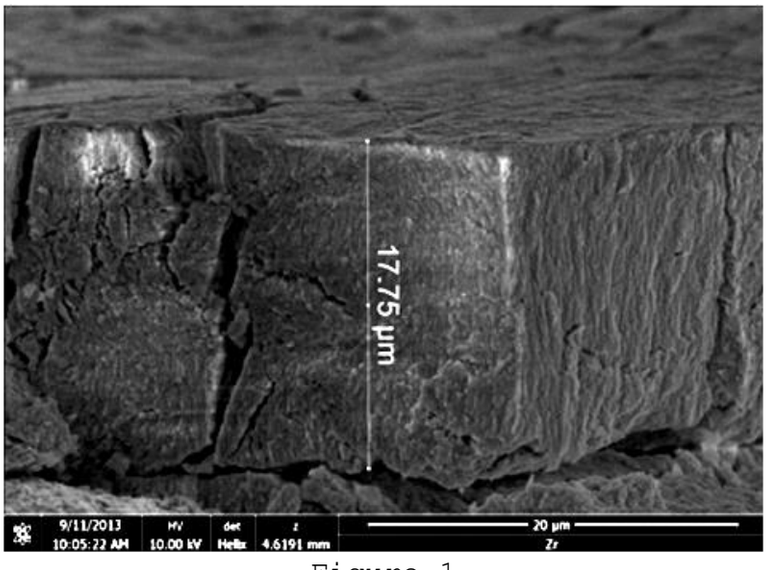

Figure 1
Image of the coating formed on the surface of the Zr-1%Nb alloy at 700 °C

Aqueous corrosion of conventional Zr alloys is a process, which involves breakdown of the oxide layer and adsorption/ingress of H. In short, at temperatures that far

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exceed nominal fission reactor operation (≥500 °C), aqueous corrosion will be problematic. Therefore, alternative alloys or barrier coatings will need to be utilized in these cases.

Previously, long-term corrosion tests of samples of the Zr-1%Nb alloy with different Fe content in water of a chemical composition similar to the primary coolant in reactor VVER-1000 (temperature 350 °C, pressure 16.5 MPa) were carried out [12]. Mathematical processing of the results of these researches has detected that the dependence of the corrosion rate *V (Fe, T)* at a fixed *T* has a pronounced oneextreme character (Fig. 2), and indicates the presence of an optimal value of Fe content localized around 0.10 wt. % [13]. The Zr-1%Nb alloy with this Fe content has the highest corrosion resistance under operating conditions of the VVER-1000 core. Increasing or decreasing of the Fe content in the Zr-1%Nb alloy leads to an increase its corrosion rate. This Fe content too provides acceptable values of microhardness of the alloy. Additional iron doping of the Zr-1%Nb alloy within the specified limits does not leads to change-over to the "breakaway" oxidation, ensuring high corrosion resistance.

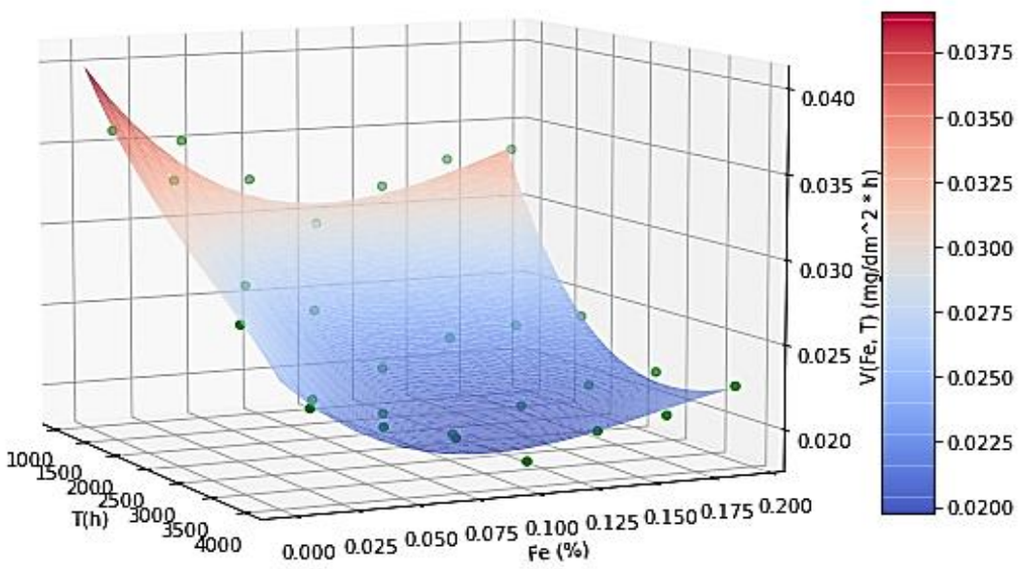

Figure 2

The dependence of the corrosion rate *V (Fe, T)* of zirconium alloy samples at a fixed exposure time *T*

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Zirconium alloys corrode relatively rapidly in steam at the elevated temperatures encountered during a design base LOCA (loss of coolant accident), e.g., caused by a large coolant pipe break. Corrosion resistance of Nb-containing alloys under normal operating conditions is excellent or superior to that of Zircaloy-4, some of them (E110 and E635) have been known to be susceptible to nodular oxidation under LOCA situations [14]. High-temperature nodular oxidation leads to excessive H uptake and premature loss of post-quench ductility. In contrast, despite the fact that M5 cladding is fabricated from nominally the same type of Zr-1%Nb alloy, the alloy has been reported to be resistant to nodular oxidation under LOCA-like conditions, and neither excessive H uptake nor premature ductility loss was observed.

In contrast to their conventional counterparts, the modified E110 and E635 alloys fabricated using sponge Zr (Zr feedstock produced with Kroll process) performed similar to M5, and ZIRLO, and were not susceptible to nodular or "breakaway" oxidation at high temperature in LOCA-relevant conditions [15].

The technology of magnesium-thermal production of spongy zirconium in laboratory installations has been studied. The processes for obtaining spongy zirconium are considered: reduction of zirconium tetrachloride and high-temperature vacuum sublimation of the reaction mass [16, 17]. The change in the content of impurities during the refining of magnesium-thermal the zirconium sponge was investigated using the electron beam melting method. It is shown that the content of impurities, except for gaseous ones, in the obtained sponge and the quality of metal zirconium slightly differ from the sponge zirconium of other manufacturers. The results of the research can be used to develop a domestic industrial magnesium-thermal technology for the production of spongy zirconium and equipment for its production.

Thus, to improve the performance properties of zirconium alloys fuel cladding, it is necessary to optimize the iron content for increases corrosion resistance in the coolant and resistance to radiation growth, and also use zirconium sponge as the alloys base, since such alloys meet safety criteria under LOCA conditions.

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