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Effect of molybdenum on properties of zirconium components of nuclear reactor core

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ABSTRACT

The paper presents results of studies of the effect of Mo on properties of Zr and its alloys. In a structure of binary Zr-Mo alloys and Zr-Nb-Mo alloys a strong and corrosion-resistant phase $ZrMo_2$ additionally appears. In Zr-Sn-Nb-Fe alloys Mo alloying leads to an increase in amount of second phase particles, reduces their dimensions and dissolves in Laves phase particles $Zr(Nb, Fe)_2$. These structural changes led to increased strength of all studied Zr alloys. Alloying by Mo also improves corrosion properties of experimental Zr alloys containing Nb and Sn, the best being alloys with a content of 0.1–0.15% mass of Mo. Adding of 0.1% Mo in standard claddings from the E635 alloy (Zr-Sn-Nb-Fe) notably reduced their hydrogenation and propensity for nodular corrosion. The testing results and their comparison with a literature data made possible to determine the prospects and directions for further work on using of Mo for alloying Zr alloys.

1. Introduction

Commercial zirconium (Zr) alloys (E110, E635, Zircaloy, Zirlo, M5), which successfully operate as structural materials in fuel assemblies (FA) in VVER and PWR reactors, need enhancements of their anticorrosion and mechanical properties taking into account ever increasing strains on reactor components in order to meet current requirements. This refers to hydrogenation of products experiencing temperature of 290–320 °C as a result of interaction with a coolant under pressure of 15–16 MPa and the induced embrittlement, as well as to product's strength and deformation resistance under the action of loads operating as part of FA.

In various periods of time scientists have been repeatedly paying attention to refractory elements, molybdenum (Mo) in particular, used for alloying Zr and its alloys. Mo is a β-Zr phase stabilizer [1,2]. As a result of heating of Zr alloys (Zr-Nb, Zr-Sn, Zr-Sn-Nb) with Mo in (α + β)- or β-phase regions and subsequent annealing in α-region the precipitation of very fine intermetallic compound particles provides alloys with higher corrosion resistance and strength. However, there is still no information on Zr alloys with Mo application in nuclear industry, which is probably due to lack of knowledge to justify the use of such alloys in active zones of nuclear reactors.

In the present work of VNIINM scientists results are reported of studies of the effect of Mo on corrosion and mechanical properties of Zr and its alloys of nuclear reactors components which allowed to define advisability and to develop prospects of further work with Mo for alloying.

2. Material and methods

Structural studies and corrosion and tensile tests were carried out on experimental specimens of cladding tubes Ø 9.15 × 7.73 mm from E635 alloy (Zr-1.2Sn-1Nb-0.35Fe) and E635 alloy with adding of 0.1% mass of Mo (E635 + Mo) made from ingots of ~ 50 kg mass using the standard for E635 alloy technology [3].

Ingots of ~ 200 g mass from Zr-(0–1)Mo, Zr-1.5Sn-0.4Mo, Zr-1Nb-(0–0.4)Mo and Zr-1.2Sn-1Nb-(0–0.1)Mo alloys based on iodide Zr were melted to study the effect of Mo on corrosion and mechanical properties of Zr alloys. The ingots were subjected to cold working, forming strips 0.7–1 mm thick with two different final treatments: annealing at 750 °C, 1 h and quenching in water from ~ 1000 °C with subsequent annealing at 500–550 °C, 3 h.

Structural-phase state study of cladding tubes from E635 and E635 + Mo alloys was conducted using a transmission electron microscope JEM 2000-FXII with an energy-dispersive detector. The experimental method is described in detail in [4].

Corrosion tests of cladding tubes from E635 and E635 + Mo alloys were conducted in autoclaves with different regimes (Table 1).

Corrosion tests of strips from Zr alloys with Mo were conducted in autoclaves with water at temperature of 350 °C and pressure of 17.0 MPa up to 3000 h. In corrosion tests the weight gain was measured and the state and thickness of oxide films was estimated.

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Table 1
Corrosion test regimes of claddings.

Test regime	Environment	Temperature, °C	Pressure, MPa	Testing time, d
1	Water	360	18.6	600
2	Water with 70 ppm [Li]	360	18.6	600
3	Steam	400	10.3	600
4	Water with 300 ppm [O]	360	18.6	150
5	Steam with 540 ppm [O]	320	12	150

Using a method of alloy oxidation with a hard electrolyte in a form of powder containing NiO and Li_2O the propensity of E635 and E635 alloy with Mo for nodular corrosion was studied [5]. The method can be divided into two stages. The first stage is autoclaving of test sample at set corrosive environment at set temperature and pressure until formation of uniform oxide film. The second is exposure of the sample with uniform oxide film in a bath with auxiliary anode and electrolyte. After passing current through the positive (auxiliary anode) and negative (the sample) cathode metal ions leave electrolyte and deposit on the sample at local imperfection of the oxide film where these metal ions form metallic nodules. The propensity of sample for nodular corrosion is estimated by size and quantity of these nodules.

Hydrogen content in all corrosion tests was determined by a melt extraction method using the Leco TCH-600. The method is based on melting of a sample inside a pyro-coated graphite crucible with flux using an electrical impulse. Melting results to releasing of H_2 from the sample. H_2 gas pass through pure heated copper oxide by means of a carrier gas Ar. Here H_2 forms H_2O which fed into infrared detectors by the carrier gas. A method accuracy is ~ 20%.

Yield strength (with 0.2% of residual strain criteria) of the strips from Zr alloys with Mo was determined in tensile tests of flat dog-bone specimens with gauge length 50 mm and initial width 40 mm at temperature of 400 °C using a universal tensile testing machine with a tensile rate in the range of 0.1–10 mm/min. In this range of strain rates all mechanical properties of a particular alloy were the same.

Yield strength (with 0.2% of residual strain criteria) of claddings was determined in tensile tests of tube samples of 150 mm length (the gauge length of sample is 50 mm) at a temperature of 400 °C on a universal tensile testing machine with a tensile rate 0.2 mm/min using industry-based instruction.

3. Results

3.1. Structure of E635 with Mo

Most authors [2,6-8] are inclined to the opinion that Mo is almost insoluble in Zr but forms intermetallic compound $ZrMo_2$, however, it makes ideal solid solutions with Nb and may appear in the form of precipitates containing Nb and Mo [9]. The presence of this compound was observed in the structure of E635 alloy containing 0.1% Mo mass. The same presence of Mo in particles in other Zr alloys containing Nb was also observed [1,10]. Herewith the main role of Mo was noticed [1,10] in refinement and uniforming of the microstructure that contains α-grain, intermetallic compound particles, plates of phases α- and β-Zr after heating in existence region of the phases (α + β).

Since the final treatment of Ø 9.15 × 7.73 E635 alloy claddings is annealing at 580 °C during 2 h the resulting structure is fully recrystallized with an average grain size ~ 3 µm both in E635 and E635 + Mo alloy.

Table 2
Characteristics of Laves phase particles in claddings.

Alloy	Content, % at.				Average size, nm	Concentration, 10^{19} m^{-3}	Max size, nm
	Zr	Nb	Fe	Mo			
E635	35.0	35.0	30		~ 65	~ 7.5	165
E635 + Mo	47.7	36.6	10.5	5.2	~ 50	~ 9.3	156

In the structure of E635 alloy with 0.1% Mo the Laves phase (Zr[Nb, Fe, Mo]$_2$) particles size is notably lower and their concentration is slightly higher compared with an alloy without Mo (Table 2, Fig. 1). By an energy-dispersive microanalysis the presence of 5.2% at Mo in composition of particles was observed.

Laves phase particles with Mo were noticed even in an oxide film of sample after 600 days of corrosion tests in steam at 400 °C and 10.3 MPa.

3.2. Corrosion of Zr alloys with Mo

Annealed binary Zr alloys with 0.10 and 0.15% mass of Mo had notably high corrosion resistance and were corroding during 3000 h with formation of dense oxide films of small thickness (≤ 3 µm). Further increasing of Mo content in binary annealed alloys was accompanied by decreasing of their corrosion resistance (Table 3): light and staining oxide film appears on Zr-0.2Mo alloy after 763 h of tests and on Zr-0.4Mo alloy afore 546 h; light and crumbling oxide film appears on Zr-0.6Mo alloy after 250 h of tests; failure of Zr-1Mo alloy sample was observed after 12 h of tests.

Adding 1% mass Nb to binary alloys with Mo didn't affect the developing of corrosion process in annealed specimens but especially delayed the corrosion process of the alloys after quenching from 1000 °C and subsequent annealing at 500–550 °C (Fig. 2).

Complementary alloying of binary Zr alloys with Mo by Sn (1.5% mass) has a more favorable effect on weakening their corrosion. However, even in this case ternary alloys with Sn had higher corrosion resistance after quenching and subsequent annealing (Fig. 2). During 3000 h of testing in water at 350 °C ternary alloy Zr-Mo-Sn corroded with developing of dark oxide films with the thickness of ~ 4 µm and slight hydrogenation (≤ 0.002% H) (Fig. 2).

An alloy containing Sn and Nb and alloyed by 0.1% mass of Mo also had high corrosion resistance. After annealing the alloy corroded in water at 350 °C with developing dark oxide films and slight hydrogenation (Fig. 2).

In all experiment regimes of corrosion tests, the presence of ~ 0.1% mass Mo in E635 alloy contributed to slighter hydrogenation of the alloy compared with the non-containing Mo alloy (Table 4). The alloy containing Mo forms the same oxide film thickness but accumulates ~ 2 times less hydrogen in the process of corrosion (Fig. 3).

E635 alloy compared with other commercial Zr alloys characterized by high resistance to nodular (focused) corrosion appeared in boiling of the coolant or high oxygen content conditions [11]. The presence of Mo doesn't contribute developing of nodular corrosion. This was confirmed by autoclave tests in water and steam containing oxygen where nodules weren't observed after 150-day test (Table 4). However the presence of Mo in the alloy significantly reduced the propensity for developing nodular corrosion, which was confirmed by the special method (Table 5).

According to phase diagram the intermetallic compound $ZrMo_2$ is present in binary Zr-Mo alloys besides α-solid solution particles. Corrosion behavior and hydrogenation of $ZrMo_2$ was studied in water steam in the temperature range of 300–500 °C. Experiment results showed high oxidation resistance of $ZrMo_2$ accompanied by the absence of its hydrogenation in contrast to other intermetallic compounds ($ZrFe_2$, Zr_2Ni, Zr_2Cu, Zr_4Sn) studied at the same time [12].