

**NON-DESTRUCTIVE TESTING OF A Zr-1Nb ZIRCONIUM ALLOY WITH A PROTECTIVE Cr/Mo THIN LAYERS COATING FOR THE PRODUCTION COMPONENTS OF CORROSION-RESISTANT FOR NUCLEAR REACTORS**

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**Abstract**

The study explores the effectiveness of Cr- and Cr/Mo-coated Zr-1Nb zirconium alloys. The coatings, deposited through magnetron sputtering, provided protection during high-temperature oxidation. The Mo sublayer prevented Cr-Zr interdiffusion. The study used various NDT methods to evaluate the structural soundness and effectiveness of Cr/Mo coatings. Results showed that Cr/Mo coatings significantly enhance the long-lastingness and dependability of zirconium alloy components in emergency situations.

Keywords: Non-destructive testing (NDT); chromium and molybdenum; zirconium alloy; in situ XRD; magnetron sputtering; corrosion resistance; nuclear reactors.

**Introduction**

The safety and efficiency of nuclear reactors heavily depend on the performance of their core components, which are often subjected to extreme conditions. Zirconium-based alloys are widely used in the nuclear power industry for manufacturing corrosion-resistant core components in fuel claddings and other structural components of pressurized water reactors due to their low thermal neutron capture cross-section, high corrosion and radiation resistance, and acceptable mechanical properties. However, their susceptibility to oxidation under high-temperature conditions poses significant challenges. Chromium and molybdenum coatings have emerged as promising solutions to enhance corrosion resistance and mechanical integrity of these alloys [1, 4].

The Fukushima Daiichi nuclear power plant accident highlighted the drawbacks of zirconium alloy claddings, as oxidation reactions can become self-sustaining in steam at temperatures above 860 °C. To improve the performance of Zr-based alloys under normal operation and potential accidental conditions, two main strategies are considered: replacing zirconium-based alloys with other structural materials or using surface modification technologies to form protective coatings without changing the bulk properties of zirconium-based alloys.

One way to solve this problem is to develop a new type of Cr-based protective coating with a barrier sublayer that can prevent Cr-Zr interdiffusion. Multilayer protective coatings have been suggested to enhance resistance to cracking under high-temperature conditions, but thin multilayer CrN/Cr coatings have a short-term effect and should be improved. Molybdenum is also a promising barrier layer used to prevent mutual diffusion of Cr-Zr in reactors, but further studies on oxidation kinetics and behavior of Cr-Mo and Mo-Zr interlayers are needed [2, 3].

**Materials and methods**

Zr-1Nb zirconium alloy (Zr balance, 0.9–1.1 wt% Nb, 0.06–0.1 wt% O) samples with dimensions of 15 × 15 × 2 mm were used as substrates. The samples were grinded and polished using SiC paper (P600 → P1200 → P2500 → P4000). Single-crystal polished Si (110) substrates were also used as substrates for coating deposition.

The deposition of coatings was performed by magnetron sputtering using the ion-plasma installation developed in Tomsk Polytechnic University. In this paper, bilayer Cr (8 μm)/Mo (3 μm) and single-layer Cr (8 μm) coatings were deposited. Chromium coatings were deposited using a multi-cathode magnetron sputtering with direct current (DC) power supply. Chromium targets (Ø 90 mm) had a purity of 99.95 %. The deposition mode of the Cr coatings was selected according to the previous studies. The deposition parameters are presented in Table 1.

Table 1 –The deposition parameters of Cr and Mo layers

Layer	$Q$ , W/cm <sup>2</sup>	$j_s$ , mA/cm <sup>2</sup>	$t$ , h	$T_{max}$ , °C
Cr	39	65	2.5	319
Mo	39	18	2.8	187

**Note:**  $Q$  – discharge power density;  $j_s$  – current density on a substrate;  $t$  – deposition time;  $T_{max}$  – maximum deposition temperature.

Microstructure of the samples before and after HT oxidation was analyzed by scanning electron microscopy (SEM) using MIRA3 (Tescan, Brno, Czech Republic) with energy dispersive spectroscopy (EDS) attachment Ultim Max 40 (Oxford Instruments, High Wycombe, UK). Structure and phase composition were investigated by X-ray diffraction (XRD) using diffractometer XRD-7000S (Shimadzu, Kyoto, Japan) in a Bragg-Brentano configuration with CuK $\alpha$ -radiation (wavelength  $\lambda=1.54$  Å) at 40 kV and 30 mA. The PDF4+ 2021 database and Sieve software were used to identify phase composition of the samples.

### Results

Figure 1 shows cross-section SEM images of Cr and Cr/Mo coatings on Si substrates.

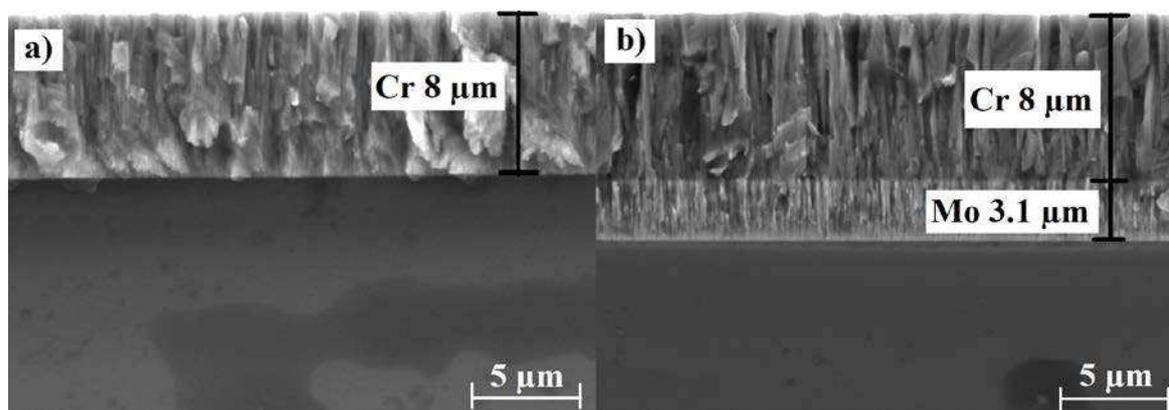


Figure 1. Cross section SEM images of Cr (a) and Cr/Mo (b) coatings deposited on Si substrates

The single-layer Cr coating had a thickness of 8  $\mu\text{m}$ , while the Cr/Mo coating had a thickness of 11  $\mu\text{m}$ . Both layers have a dense columnar microstructure, with Mo sublayer having thinner columns. Chromium columns do not increase over coating thickness.

The XRD study reveals that uncoated Zr alloy samples contain only  $\alpha$ -Zr phase with a hexagonal close packed lattice, while single-layer Cr-coating samples have only  $\alpha$ -Cr phase with body-centered cubic lattice. HT oxidation results in a two-phase system of  $\alpha$ -Cr and Cr<sub>2</sub>O<sub>3</sub>, with an increase in Cr<sub>2</sub>O<sub>3</sub> content up to 60 minutes. Cr-Mo coating samples have only  $\alpha$ -Cr phase, as X-rays do not penetrate the Mo sublayer through the outer 8 $\mu\text{m}$ -thick Cr layer. Cr<sub>2</sub>O<sub>3</sub> phase formation in single-layer Cr coating samples and Cr<sub>3</sub>Mo phase formation at high temperatures are also observed. The increase in oxide phase content was observed after 60 minutes of HT oxidation test.

Figure 2 shows the diffraction patterns of uncoated, Cr- and Cr/Mo-coated Zr alloy samples depending on oxidation time.

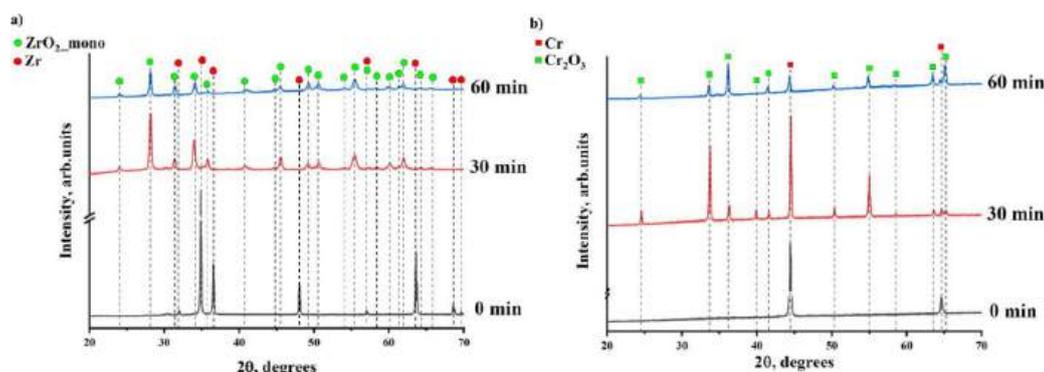


Figure 2. Diffraction patterns of uncoated (a), Cr-coated (b) after oxidation in air at 1100 °C

The uncoated Zr alloy shows the highest weight gain, increasing from 36 to 93 mg/cm<sup>2</sup> over 60 minutes. Coated samples have lower gains, with Cr/Mo coating increasing weight gain with oxidation time. Single-layer Cr coatings offer better oxidation resistance. Figure 3 shows the weight gain for the uncoated, Cr- and Cr/Mo-coated Zr alloy samples oxidized in air at 1100 °C varying based on the oxidation time.

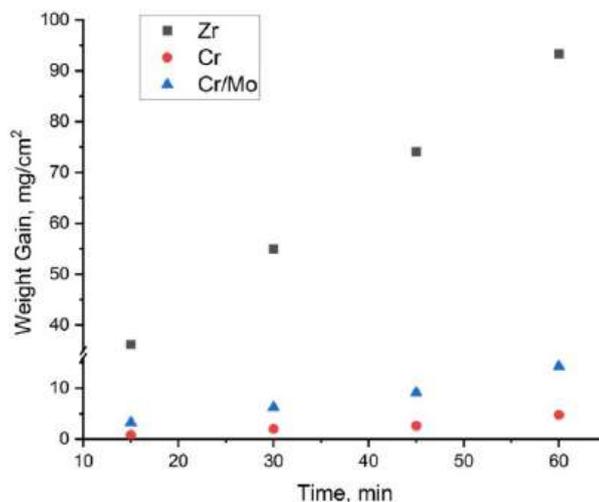


Figure 3. Weight gains of the uncoated, Cr- and Cr/Mo-coated Zr alloy after oxidation at 1100 °C as a function of oxidation time

To understand the reasons for the observed effects, further research is needed, in particular structural studies – Scanning electron microscope (SEM), optical microscopy, X-ray Diffraction (XRD) before and after HT oxidation and in situ X-ray diffraction up to 1250 °C, four-probe resistivity measurements, and thermal electromotive force (EMF).

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