Formation of Cr-Zr gradient layer by magnetron sputtering and ion mixing

Egor B. Kashkarov^{1,*}, Dmitrii V. Sidelev¹, Maya R. Rombaeva¹, Viktor N. Kudiiarov¹ and Anton Lomygin¹

¹ National Research Tomsk Polytechnic University, 30 av. Lenin, Tomsk, 634050, Russia

Abstract. The gradient Cr-Zr layer was formed onto Zr-1Nb substrate by magnetron sputtering of chromium and zirconium targets and ion mixing (Ar⁺ with 25 keV). The distribution of Cr and Zr elements in the deposited coatings was measured by using a glow discharge optical emission spectroscopy. The optimal ion fluence onto the substrate was 8×10^{19} ion/m². At higher ion dose, the intensive sputtering of the deposited coating was observed.

1 Introduction

Zirconium alloy (Zr-1Nb) is one of the most widely used fuel claddings material for light-water and pressurized water reactors. To protect fuel elements from high-temperature oxidation in the case of loss of coolant accident (LOCA) chromium-based coatings can be used [1,2]. This is caused by excellent oxidation resistance, high thermal conductivity (93.9 W/m·K) and low thermal neutron cross section of Cr coatings. Different vacuum plasma techniques such as magnetron sputtering, arc evaporation and others can be used for deposition of protective coatings [3,4]. However, due to high heating rate of the fuel cladding at LOCA conditions, the protective coating can peel-off from a zirconium substrate due to the difference in linear expansion coefficients ($\alpha_{Zr} = 7.8 \times 10^{-6}$ 1/K, $\alpha_{Cr} = 9.2 \times 10^{-6}$ 1/K). Moreover, the transition of zirconium from α - to β -phase (at the temperature ~ 1136 K) and strong oxidation of the coating are also possible. So, the adhesion of the deposited coating on the fuel cladding should be strong. For this task, many technological approaches can be used, for example, preliminary substrate heating [5], substrate biasing [6], deposition interlayers between substrate and protective film [7], etc.

Surface modification of nuclear fuel cladding should be realized at minimal thermal flux to prevent a phase transformation of the Zr-1Nb. Thus, it is preferable to deposit a gradient Cr-Zr layer by magnetron sputtering combined with Ar⁺ ion mixing [8,9]. In this case, only surface layers will be modified without a significant change of substrate temperature. The main goal of this study is to determine the ion mixing parameters to form gradient Cr-Zr layer onto the Zr-1Nb substrate.

* Corresponding author: egor_kashkarov@mail.ru

2 Experimental part

2.1 Materials and methods

The gradient Cr-Zr coatings were deposited using a vacuum ion-plasma installation equipped with two magnetron sputtering systems with disk ($\varnothing 90$ mm) targets of Cr (99.95%) and Zr (99.95%), an ion implanter with a hollow cathode [10], an ion source with closed electron drift, planetary rotated substrate-holder and quartz thickness tester (Mikron-5, Izovac Ltd.). The scheme of the installation is shown in Fig. 1. More details about the plasma equipment are presented in [11]. The base pressure was 5×10^{-3} Pa. The working pressures were 0.3 and 0.1 Pa for magnetron sputtering and ion mixing, respectively. The distance from magnetron sputtering systems to substrate was 100 mm, from ion implanter to substrate – 250 mm.

Fig. 1. The scheme of the ion-plasma installation.

The pieces of polished Si (100) and Zr-1Nb ($20 \times 20 \times 2$ mm³) were used as the substrates. The Zr substrates were prepared by polishing and grinding machine with SiC paper (P4000), then it were cleaned in an ultrasonical bath with alcohol during 20 min. Before the depositions, all substrates were also treated in Ar atmosphere by ion source with closed electron drift (accelerated voltage – 2.5 kV, discharge current – 40 mA, pressure – 0.1 Pa, time – 15 min). The modes of films deposition and its ion irradiation are presented in next Sections.

To determine the distribution of Cr and Zr elements in the deposited coatings, a glow discharge optical emission spectroscopy (GD-Profilier-2, Horiba Ltd., Japan) was used. The analysis was performed at the following parameters: discharge power – 40 W, pulse frequency – 1 kHz, duty factor – 0.0625, atmosphere – Ar (99.999%), pressure – 650 Pa.

2.2 The selection of ion fluence

Firstly, the deposition rates of Cr and Zr films by magnetron sputtering in Ar (99.99%) atmosphere were determined. For this purpose, thickness of the deposited coatings was measured by Micro Measure 3D Station (optical profilometer) and then it was calibrated for the quartz thickness tester to enable of control films thickness during the deposition process.

The selection of ion fluence was based on the analysis of Cr and Zr distributions at the interface of Cr films and Zr-1Nb substrate after irradiation (Table 1). For this, 14 nm-thick Cr films were deposited onto polished Zr-1Nb and, then, irradiated by 25 keV Ar⁺ ions with ion fluence of 2×10¹⁹, 8×10¹⁹ and 2×10²⁰ ion/m². Such thickness of the films is equal to the projective range of 25 keV Ar⁺ in a chromium that was calculated by TRIM [12].

Table 1. The parameters of deposition and irradiation of Cr coatings onto Zr-1Nb substrate.

№	Deposition parameters	Irradiation parameters	t_{ion}, s	$\Phi, ion/m^2$	h_{sput}, nm
Cr-1	$U_{dep}=514\text{ V}, I_{dep}=0.58\text{ A}, P=300\text{ W}, t_{dep}=3\text{ min}$	$j_{ion}=0.205\text{ mA/cm}^2$ $U_{ion}=25\text{ kV}, p=0.1\text{ Pa}$	5	2×10^{19}	1.1
Cr-2			20	8×10^{19}	4.4
Cr-3			49	2×10^{20}	10.7

Note: U_{dep} – discharge voltage; I_{dep} – discharge current; P – power, t_{dep} – deposition time; j_{ion} – ion current density; U_{ion} – voltage; p – pressure; t_{ion} – irradiation time; Φ – fluence, h_{sput} – thickness of the sputtered layer.

Surface sputtering of the deposited coatings can be observed in the case of ion mixing. The thickness (h_{sput}) of the sputtered layer for different ion fluences can be estimated based on the formula:

$$h_{sput} = \frac{V}{S_{sample}} = \frac{S \cdot M \cdot j \cdot t_{ion}}{q_e \cdot \pi \cdot N_A \cdot \rho}, \tag{1}$$

where V – volume of the sample, cm³; S_{sample} – square of the sample, cm²; S is the sputtering coefficient of irradiated material, atom/ion ($S_{Cr} = 4.47$ atom/ion, $S_{Zr} = 2.24$ atom/ion); M is the molar mass of irradiated material, g/mol; j is the ion current density, mA/cm²; t_{ion} is the irradiation time; q_e is the elementary charge, C; N_A is the Avogadro number, 1/mol; ρ is the density, g/cm³.

Fig. 2 presents the Cr and Zr distributions in Cr film/Zr-1Nb substrate before and after irradiation at different ion fluences Φ .

Fig. 2. The distributions of Zr and Cr in the deposited coatings before and after irradiation at different ion fluences Φ .

The intensity of the Cr signal decreased with increasing ion fluence that is caused by film sputtering. It is good correlated with the calculations of h_{sput} . Moreover, the width of the Cr signal increased at Φ equal to 2×10^{19} and 8×10^{19} ion/m² that indicate ion mixing of Cr and Zr atoms at the interface of Cr film and Zr-1Nb substrate. The significant reduction of the Cr signal is observed at the fluence of 2×10^{20} ion/m². In this case, the mixing of Cr and Zr atoms and sputtering of the mixed layer are occurred. Since the thickness of the formed layer should not be significantly reduced, the ion fluence $\Phi = 8 \times 10^{19}$ ion/m² was chosen as the most relevant to forming the gradient Cr-Zr layer.

3 The formation of the gradient Cr-Zr coating

Two samples of the gradient Cr-Zr coatings were prepared by means of magnetron sputtering of Cr and Zr targets without/with ion mixing. The detailed deposition process is shown in Fig. 3.

Fig. 3. The formation of the gradient Zr-Cr coating with ion mixing (indicated here at.%).

The first sample was irradiated ($\Phi=8 \cdot 10^{19}$ ion/m²) between deposition of each Cr-Zr layer, the second sample was deposited only by co-sputtering of Cr and Zr targets in Ar atmosphere without ion mixing. The distribution of Cr and Zr atoms in the prepared samples is presented in Fig. 4.

Fig. 4. Distribution of Zr and Cr in the gradient Cr-Zr coatings: non-treated – without ion mixing; ion-treated – with ion mixing between deposition of each Cr-Zr layer.

The thickness of the sputtered layer during ion mixing with a fluence of $8 \cdot 10^{19}$ ion/m² was estimated, according to the equation (1). The total thickness of sputtered layer was 18.9 nm. However, to calculate the sputtering coefficient of the multicomponent film (Cr-Zr with different at), the following equation was used:

$$S = \sum_{i=1}^n C_i \cdot S_i, \quad (2)$$

where C_i is the volume concentration of the element, $C_i = 0 \dots 1$; S_i is the sputtering coefficient of the element.

It is obvious that the area of the signal from Cr atoms significantly decreased for ion-treated Cr-Zr sample due to film sputtering. The application of ion mixing leads to shift of Zr distribution to the surface of the irradiated sample. Nevertheless, the analysis of the distribution of Cr and Zr in both samples (non- and ion-treated) indicates on the both deposition modes can be used to form the gradient Cr-Zr coating. For future task, the role of the gradient Cr-Zr layer in adhesion of Cr to the Zr-1Nb substrate should be analyzed.

4 Conclusion

The gradient Cr-Zr coatings were formed on the Zr-1Nb substrates by co-sputtering of Cr and Zr targets using magnetron sputtering systems and without/with ion mixing by 25 keV Ar⁺ ions. In view of the sputtering of treated surface, the ion fluence of $8 \cdot 10^{19}$ ion/m² was chosen to perform ion mixing process. Layer-by-layer deposition of Cr and Zr together with ion mixing results in the shift of Zr distribution to the surface of the gradient layer. Sputtering of the surface has the significant role on the elemental distribution for ion mixing processes.

This research was funded by Russian Science Foundation, research project No. 19-79-10116.

References

1. C. Tang, M. Stueber, H.J. Seifert, M. Steinbrueck, *Corros. Rev.*, **35**, 141-165 (2017)
2. J. Bischoff, C. Delafoy, C. Vauglin, P. Barberis, C. Roubeyrie, D. Perche, D. Duthoo, F. Schuster, J.-C. Brachet, E.W. Schweitzer, K. Nimishakavi, *Nucl. Eng. Technol.*, **50**, 223-228 (2018)
3. D.V. Sidelev, E.B. Kashkarov, M.S. Syrtanov, V.P. Krivobokov, *Surf. Coat. Technol.*, **369**, 69-78 (2019)
4. A.S. Kuprin, V.A. Belous, V.N. Voyevodin, V.V. Bryk, R.L. Vasilenko, V.D. Ovcharenko, E.N. Reshetnyak, G.N. Tolmachova, P.N. V'yugov, *J. Nucl. Mater.*, **465**, 400-406 (2015)
5. R.C. Vega-Morón, G.R. Castro, D.V. Melo-Máximo, J.V. Méndez-Méndez, L. Melo-Máximo, J.E. Oseguera-Peña, A. Meneses-Amador, *Surf. Coat. Technol.*, **349**, 1137-1147 (2018)
6. A.M. Engwall, S.J. Shin, J. Bae, Y.M. Wang, *Surf. Coat. Technol.*, **363**, 191-197 (2019)
7. E.B. Kashkarov, N.N. Nikitenkov, M.S. Syrtanov, Yu.I. Tyurin, Z. Le, *J. Surf. Invest.*, **9**, 1277-1280 (2015)
8. A. Arranz, *Applied Surf. Science*, **258**, 3264-3268 (2012)
9. S. Tobbeche, A. Boukhari, R. Khalfaoui, A. Amokrane, C. Benazzouz, A. Guittoum, *Nucl. Instrum. Methods B*, **269**, 3242-3245 (2011)

10. D.R. Emlin, N.V. Gavrilov, P.V. Tretnikov, V.F. Nasyrov, A.Z. Timerbaev, IOP Conf. Ser. J. Phys., **830**,012050, (2017)
11. D.V. Sidelev, M. Bestetti, G.A. Bleykher, V.P. Krivobokov, V.A. Grudinin, S. Franz, A. Vincenzo, Y.L. Shanenkova, Surf. Coat. Technol., **350**, 560-568 (2018)
12. J.F. Ziegler, J.P. Biersack, U. Littmark, *Transport of Ions in Matter (IBM Research, Yorktown Heights, NY, 1991)*