Formation of a Cr-Zr surface alloy using a low-energy high-current electron beam

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Abstract. The paper investigates the regularities of the formation of Cr-Zr surface alloy using a low-energy high-current electron beam (LEHCEB). The influence of the electron-beam processing parameters and the magnetron deposition parameters on the elemental composition of the formed Cr-Zr surface alloy is estimated. It is shown that, for all considered modes, there is a general tendency to a decrease in the chromium content in the surface alloy with an increase in the energy density or the LEHCEB processing pulse number. The thickness increase of the chromium film applied in one cycle or the surface alloy total thickness increase leads to an increase in the chromium content in the surface alloy. The LEHCEB processing parameters, namely the energy density and the number of pulses, have a greater effect on the chromium content during the formation of the Cr-Zr surface alloy in comparison to the magnetron sputtering parameters, namely the deposited film thickness and the formed surface alloy thickness. A linear regression model that describes the chromium content in the surface alloy depending on the film thickness, the surface alloy total thickness, the number of pulses and the pulse energy density is proposed.

1. Introduction
Zirconium-based alloys are widely used in modern nuclear power engineering due to a set of exceptional properties, such as high neutron transparency, acceptable mechanical properties, and good corrosion resistance. In regular operation of nuclear power plants, zirconium alloys satisfy the basic requirements for reactor materials. However, under emergency conditions such as a loss of coolant accident (LOCA), zirconium is subject to significant degradation. Temperatures beyond 700°C cause an uncontrolled oxidative reaction of zirconium and water (steam) with the generation of heat and hydrogen gas [1]. Reducing the rate of oxidation of Zr at high temperatures is one of the key problems associated with increasing the accident stability of nuclear power plants. Considerable efforts are directed at improving the operational properties of zirconium alloys through the application of protective coatings [2, 3]. The most likely candidates among them are chromium-containing coating. Nevertheless, there are several problems in the application of coatings, among which the most relevant are their discontinuity, low adhesion, as well as the mutual diffusion of elements between the materials of the substrate and the coating. One of the methods that allow the formation of uniform coatings with good adhesion is the method of forming surface alloys [4].
Surface alloy was formed using low-energy high-current electron beam of microsecond duration (LEHCEB). Surface alloy structure and properties strongly depend on its formation mode [4–6]. The surface alloy formation mode selection is not an easy task, since in the general case it is a function of four variables. These variables are: LEHCEB parameters (pulse energy density \(E_\text{s}, \text{J/cm}^2\)) and pulse number \(N\)), and magnetron deposition parameters (deposited film thickness \(h, \mu\text{m}\)) used for subsequent LEHCEB treatment and surface alloy total thickness \(H, \mu\text{m}\), which is determined by the number of repeated magnetron sputtering and LEHCEB treatment iterations). Each of these variables contributes to the desired surface alloy quality and in its own way affects the surface alloy formation process.

The paper investigates the regularities and estimates effects of outlined parameters on the formation of a Cr-Zr surface alloy and its chemical composition.

2. Experimental Setup

Cr-Zr surface alloy was formed using “RITM-SP” facility [7]. The following surface alloy formation procedure was used: Cr film with a thickness of \(h, \mu\text{m}\) is deposited onto substrate; than substrate-film system is treated by \(N\) pulses of LEHCEB with the pulse energy density of \(E_\text{s}, \text{J/cm}^2\); deposition and LEHCEB treatment alternating repetition take place \(m\) times until the surface alloy total thickness reaches the value of \(H = h \times m, \mu\text{m}\). All the procedure was performed in a single vacuum cycle. Substrates with dimensions in millimeters 15×15×2 were made of Zr (99.9 wt.%). Films were deposited using Cr (99.95 wt.%) target magnetron sputtering, deposition rate 11 ± 2 µm per hour.

LEHCEB treatment and films magnetron deposition parameters will ultimately determine the melt thickness of the film-substrate system, its lifetime and temperature. All this together will affect the chromium and zirconium concentration in the melt and the intensity of the film and substrate materials mixing processes in a short time of pulsed treatment. Cr-Zr surface alloy Cr concentration is chosen as main criteria of formed surface alloy since it has the main effect on surface alloy physical properties.

To assess the particular parameter effect on the chromium concentration in the samples surface layer, the surface alloys were formed in the modes with this parameter variations, the rest parameters were fixed. Samples surface elemental analysis was carried out by energy dispersive X-ray spectroscopy (EDS) with an accelerating voltage of 30 kV.

3. Results

There is Cr-Zr surface alloy Cr concentration dependency on LEHCEB pulse energy density shown in figure 1. Formation modes are grouped, for each colored group Cr film thickness \(h\), surface alloy total thickness \(H\), LEHCEB treatment pulse number \(N\) are fixed. Pulse number for all the modes is 4. LEHCEB energy density \(E_\text{s} = 2.7, 3.9 \text{ and } 4.3 \text{ J/cm}^2\). There is a general tendency to a decrease in the chromium content in the surface alloy with an increase in the LEHCEB energy density. For the modes with the film thickness \(h = 0.25 \mu\text{m}\), and surface alloy total thickness \(H = 1 \mu\text{m}\) Cr concentration decreases from 71 to 38% at the pulse energy density \(E_\text{s} = 2.7 \text{ and } 3.9 \text{ J/cm}^2\) respectively. For the modes with the same film thickness \(h = 0.25 \mu\text{m}\), and surface alloy total thickness \(H = 2 \mu\text{m}\) Cr concentration decreases from 45 to 29% at the pulse energy density \(E_\text{s} = 3.9 \text{ and } 4.3 \text{ J/cm}^2\) respectively. For the modes with the film thickness \(h = 0.5 \mu\text{m}\), and surface alloy total thickness \(H = 1 \mu\text{m}\) Cr concentration decreases from 82 to 67 and then to 55% at the pulse energy density \(E_\text{s} = 2.7, 3.9 \text{ and } 4.3 \text{ J/cm}^2\) respectively.

There is Cr-Zr surface alloy Cr concentration dependency on LEHCEB pulse number shown in figure 2. Formation modes are grouped, for each colored group \(h, H, E_\text{s}\) are fixed. Pulse number \(N\) = 2, 4 or 8 pulses. There is a general tendency to a decrease in the chromium content in the surface alloy with an increase in the LEHCEB pulse number. For the modes with the film thickness \(h = 0.25 \mu\text{m}\), surface alloy total thickness \(H = 1 \mu\text{m}\) and energy density \(E_\text{s} = 3.9 \text{ J/cm}^2\) Cr concentration decreases from 38 to 22% at the pulse number \(N = 4\) and 8 pulses respectively. For the modes with the film thickness \(h = 0.5 \mu\text{m}\), the same surface alloy total thickness \(H = 1 \mu\text{m}\) and energy density \(E_\text{s} = 3.9 \text{ J/cm}^2\) Cr concentration decreases from 71 to 54 and then to 22% at the pulse number \(N = 2, 4\)
and 8 pulses respectively. For the modes with the same film thickness $h = 0.5 \, \mu m$, and the same surface alloy total thickness $H = 4 \, \mu m$, but higher energy density $E_s = 4.3 \, J/cm^2$ Cr concentration decreases from 87 to 52% at the pulse number $N = 2$ and 4 pulses respectively.

Figure 1. Cr-Zr surface alloy Cr concentration dependency on pulse energy density. Other formation parameters are fixed for each colored group, colors correspond to set of parameters - $h; H; N$, where $h$ – Cr film thickness in $\mu m$, $H$ – surface alloy total thickness in $\mu m$, $N$ – LEHCEB treatment pulse number.

Figure 2. Cr-Zr surface alloy Cr concentration dependency on pulse number. Other formation parameters are fixed for each colored group, colors correspond to set of parameters - $h; H; E_s$, where $h$ – Cr film thickness in $\mu m$, $H$ – surface alloy total thickness in $\mu m$, $E_s$ – LEHCEB pulse energy density in J/cm$^2$.

There is Cr-Zr surface alloy Cr concentration dependency on surface alloy total thickness shown in figure 3. Formation modes are grouped, for each colored group $h$, $N$, $E_s$ are fixed. Surface alloy total thickness $H = 1$, 1.5 or 2 $\mu m$. There is a general tendency to an increase in the chromium content in the surface alloy with an increase in the surface alloy total thickness. For the modes with the film thickness $h = 0.25 \, \mu m$, pulse number $N = 4$ pulses and energy density $E_s = 3.9 \, J/cm^2$ Cr concentration increases from 38 to 45% at the surface alloy total thickness $H = 1$ and 2 $\mu m$ respectively. For the modes with the same film thickness $h = 0.25 \, \mu m$, the same energy density $E_s = 3.9 \, J/cm^2$ but pulse number $N = 8$ pulses Cr concentration increases from 22 to 33 and then to 45% at the surface alloy total thickness $H = 1$, 1.5 and 2 $\mu m$ respectively. For the modes with the film thickness $h = 0.5 \, \mu m$, pulse number $N = 8$ pulses and energy density $E_s = 3.9 \, J/cm^2$ Cr concentration increases from 22 to 38% at the surface alloy total thickness $H = 1$ and 2 $\mu m$ respectively.

There is Cr-Zr surface alloy Cr concentration dependency on deposited Cr film thickness shown in figure 4. Formation modes are grouped, for each colored group $H$, $N$, $E_s$ are fixed. Deposited Cr film thickness $h = 0.25$, 0.5 or 1 $\mu m$. There is a general tendency to an increase in the chromium content in the surface alloy with an increase in deposited Cr film thickness. For the modes with the surface alloy total thickness $H = 1 \, \mu m$, pulse number $N = 4$ pulses and energy density $E_s = 3.9 \, J/cm^2$ Cr
concentration increases from 38 to 54 and then to 63% at the Cr film thickness $h = 0.25$, 0.5 and 1 µm respectively. For the modes with the same surface alloy total thickness $H = 1$ µm, pulse number $N = 8$ pulses and energy density $E_s = 3.9$ J/cm$^2$ Cr concentration increases from 22 to 59% at the Cr film thickness $h = 0.25$, 0.5 and 1 µm respectively. For the modes with the surface alloy total thickness $H = 1.5$ µm, pulse number $N = 8$ pulses and energy density $E_s = 3.9$ J/cm$^2$ Cr concentration increases from 33 to 60% at the Cr film thickness $h = 0.25$ and 0.5 µm respectively.

![Figure 3](image3.png)

**Figure 3.** Cr-Zr surface alloy Cr concentration dependency on surface alloy total thickness. Other formation parameters are fixed for each colored group, colors correspond to set of parameters - $h; N; E_s$, where $h$ – Cr film thickness in µm, $N$ – pulse number, $E_s$ – LEHCEB pulse energy density in J/cm$^2$.

![Figure 4](image4.png)

**Figure 4.** Cr-Zr surface alloy Cr concentration dependency on Cr film thickness. Other formation parameters are fixed for each colored group, colors correspond to set of parameters - $H; N; E_s$, where $H$ – surface alloy total thickness in µm, $N$ – pulse number, $E_s$ – LEHCEB pulse energy density in J/cm$^2$.

4. Discussion
LEHCEB pulse energy density is one of the most important parameters for film-substrate system treatment. Pulse energy density should be enough energy to melt both film and substrate near surface layer thereby form surface alloy. The minimum value of the pulse energy density at which the film-substrate system melts is called the melting threshold. On the other hand, the energy density should not be too high. Too high pulse energy density can lead to melt overheating and even evaporation from the surface. The maximum value of the pulse energy density at which the film-substrate system melts without significant evaporation is called the evaporating threshold. Effective surface alloy formation can be performed using pulse energy density in range from melting threshold to evaporating threshold.

Pulse energy density increase leads to film-substrate system parameters values increase, namely melt thickness, melt lifetime and temperature. Melt thickness increase leads to substrate material concentration increase, melt temperature increase leads to mass transfer velocity increase, which in the complex leads to the chromium content decrease in the formed surface alloy (figure 1).
LEHCEB pulse duration is about 2.5 us. Materials melt during this time and film-substrate system mixing occur. Pulse number increase leads to increased integral melt lifetime and intense materials mixing resulting in decreased surface alloy Cr concentration (figure 2). Moreover, pulse number increase leads to higher surface alloy homogeneity.

Melt threshold and evaporation threshold are strongly depend on deposited film thickness. Thresholds values are proportional to deposited film thickness. Therefore for fixed LEHCEB parameters increased Cr film thickness leads to decreased substrate material concentration and increased Cr concentration at the same time (figure 4). Pulse energy density and film thickness are interconnected and their different combinations can lead to opposite effect.

All the analyzed parameters effect on surface alloy properties and quality. As it mentioned before pulse energy density and film thickness are interconnected. To keep in the range of thresholds we should increase or decrease film thickness and pulse energy density simultaneously. Therefore, surface alloy thickness maximum is limited by LEHCEB maximum parameters. These limitations can be overcome by layer-by-layer surface alloy formation by multiple magnetron deposition followed by electron-beam treatment. Number of such layers and their thickness will define surface alloy total thickness. It is obvious, that Cr concentration in each next layer would depend on materials concentration in previous layer. Since with an increase in the number of layers, a sequential redistribution of a certain amount of substrate material occurs, then with an increase in the surface alloy total thickness, the Cr concentration increases (figure 3).

As it seen it is very significant to consider both LEHCEB and magnetron deposition parameters, and this task is not trivial. It is possible to partially overcome the difficulties in surface alloy formation mode choosing using a multiparametric statistical model. Cr-Zr surface alloy atomic Cr concentration can be expressed as a function of four variables. Variables independence and their effect linearity is supposed for the following formula:

$$Cr(h, H, N, E_s) = 167 + 38.5h + 8.7H - 4.6N - 32.2E_s,$$

(1)

where $Cr(h, H, N, E_s)$ is Cr concentration in percent, $h$ is the film thickness in µm, $H$ is the surface alloy total thickness in µm, $N$ is the pulse number, $E_s$ is the pulse energy density J/cm². This model makes it possible to estimate the chromium concentration for the given parameters of the surface alloy formation mode with an accuracy of up to 10%.

5. Conclusion
The following main conclusions can be formulated, based on formation mode effect on the chromium content in the Cr-Zr surface alloy studies, experimental data statistical and regression analysis:

- For all considered modes, there is a general tendency to a decrease in the chromium content in the surface alloy with an increase in the energy density or the LEHCEB processing pulse number.
- The thickness increasement of the chromium film applied in one cycle or the surface alloy total thickness increasement leads to an increase in the chromium content in the samples near surface region.
- The LEHCEB processing parameters, namely the energy density and the number of pulses, have a greater effect on the chromium content during the formation of the Cr-Zr surface alloy in comparison to the magnetron sputtering parameters, namely the deposited film thickness and the formed surface alloy thickness.
- A linear regression model that describes the chromium content in the surface alloy depending on the film thickness, the surface alloy total thickness, the number of pulses and the pulse energy density is proposed.

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References

[1] Kim H H, Kim J H, Moon J Y, Lee H S, Kim J J and Chai Y S 2010 J. Mater. Sci. Technol. 26 827–32
[2] Pint B A, Terrani K A, Yamamoto Y and Snead L L 2015 Metallurgical and Materials Transactions E 2 190–6
[3] Pint B A, Terrani K A and Rebak R B 2019 Proceedings of the 18th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors (Portland: Springer) pp 1451–60
[4] Markov A, Yakovlev E, Shepel’ D and Bestetti M 2019 Results in Physics 12 1915–24
[5] Batrakov A V, Markov A B, Ozur G E, Proskurovsky D I and Rotshtein V P 2008 Eur. Phys. J.-Appl. Phys. 43 283–8
[6] Bytsenko O A, Steshenko I G, Panov V A, Tishkov V V and Markov A B 2020 Periódico Tchê Química 17 459–68
[7] Markov A B, Mikov A V, Ozur G E and Padei A G 2011 Instrum. Exp. Tech. 54 862–6