Computer simulation of temperature fields in the Cr (film)-Zr (substrate) system during pulsed electron-beam irradiation

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Abstract. The paper presents the results of numerical simulation of the distribution of thermal fields during the formation of Cr-Zr surface alloy using a pulsed low-energy high-current electron beam (LEHCEB). The melting thresholds of the Cr-Zr system for different thicknesses of Cr films were calculated. The melting threshold of the Cr-Zr system increases linearly with increasing Cr film thickness. A linear regression dependency model of the melting threshold on the film thickness is proposed. Evaporation thresholds of the Cr-Zr system for different thicknesses of Cr films were calculated. The evaporation threshold of the Cr-Zr system increases linearly with increasing Cr film thickness. A linear regression dependency model of the evaporation threshold on the film thickness is proposed. The value of the LEHCEB energy density at which the lifetime of the film and substrate are equal is calculated. This value is a maximum value for the effective formation of Cr-Zr. A model of the LEHCEB energy density, at which the lifetime of the film and the substrate are equal, in the form of a third-degree polynomial is proposed.

1. Introduction
Zirconium (Zr) alloys are widely used in the industry, including the nuclear one, as materials to manufacture claddings of fuel elements (FE). With the need to improve the efficiency of nuclear reactors and to increase, within the framework of incident-tolerant fuel, their safety level, new and higher requirements are imposed on the fuel element cladding especially for corrosion and wear resistance. They must be functional not only under normal conditions, but also with the loss of coolant, when their temperature exceeds the standard one by several times. A related issue requiring special attention and solution is the prevention of the steam-zirconium reaction at high temperatures of the coolant, which is in effect in emergency situations when, as a result of intensive hydrogenation with hydrogen, embrittlement of zirconium tubes occurs and cracks appear in them [1]. The steam-zirconium reaction is considered to be the main cause of explosions at both the Chernobyl and Japanese Fukushima nuclear power plants. The solution to this problem could be to modify the surface of the zirconium alloy, from which FE tubes are made by synthesizing highly corrosive and heat-resistant coatings [2]. One way to modify the surface of zirconium alloy is to form a chromium-based coating [3, 4].

The most promising method of forming highly adhesive coatings is the synthesis of surface alloy by the preliminary deposition of the films by the magnetron method and their subsequent mixing with
the substrate in the liquid phase of a low-energy high-current electron beam (LEHCEB) of microsecond duration [5, 6]. The sequence of operations in the formation of the surface alloy is as follows: in a single vacuum cycle, a chromium film of thickness \( h \) (\( \mu \)m) is sputtered onto the substrate, followed by LEHCEB treatment with energy density \( E_s \) (J/cm\(^2\)). The energy density and film thickness of the magnetron sputtering will ultimately determine the thickness of the melt of the film-substrate system, its lifetime and temperature. In total, all this will affect the concentrations of chromium and zirconium in the melt and the intensity of mixing processes of the film and substrate materials in a short pulse exposure time. Optimal parameters for the synthesis of Cr-Zr surface alloy can be determined by computer modeling of the temperature fields in the film-substrate systems.

The present work investigates the influence of the energy characteristics of electron-beam impact on the film (Cr)-substrate (Zr) system on the depth and lifetime of the melt.

2. Modeling

The one-dimensional thermal conductivity equation with appropriate boundary and initial conditions was solved to calculate the temperature field in the film (Cr)-substrate (Zr) system. The melting process was modeled by the effective heat capacity method, and the evaporation process was considered by the thermal fracture model [7, 8]. The real oscillograms of collector current and accelerating voltage of the LEHCEB were used to simulate a pulsed beam of accelerated electrons. Temperature fields were calculated for different LEHCEB energy densities, pulse duration \( \tau \) was 2.5 \( \mu \)s. Calculations were carried out for a single pulse. Table 1 presents the thermophysical properties of the zirconium substrate and chromium film used in calculating the temperature fields in the studied systems. Here \( \rho \), \( c \), \( k \), \( T_m \) and \( L_m \) are density, heat capacity, heat conductivity, melting point and latent heat of melting, respectively. The temperature dependences of thermophysical properties of materials were taken from reference books [9].

| Material | \( \rho \) (kg/m\(^3\)) | \( c \) at 300 K (J/(kg K)) | \( k \) at 300 K (W/(m K)) | \( T_m \) (K) | \( L_m \) (kJ/kg) |
|----------|-----------------|-----------------|------------------|-----------|---------|
| Zr       | 6450            | 279             | 23               | 2125      | 0.286   |
| Cr       | 7200            | 444             | 94               | 2133      | 0.067   |

3. Results

An important energy characteristic of electron-beam exposure is the melting threshold of the film-substrate system. The melting threshold of the Cr (film)-Zr (substrate) system is the lowest value of the electron beam energy density at which complete melting of the film and the beginning of melting of the substrate occur. The melting of the substrate in this case occurs to a small depth, but sufficient to start the process of mixing the elements of the film and the substrate and the formation of the surface alloy. Figure 1 shows the calculated dependence of the melting threshold of the Cr (film)-Zr (substrate) system on the film thickness. The calculation was performed for chromium film thicknesses from 0.25 to 2.5 \( \mu \)m in 0.25 \( \mu \)m increments. The melting thresholds of the pure metals chromium and zirconium are 4.5 and 1.85 J/cm\(^2\), respectively. The melting threshold of the Cr-Zr system at a film thickness of 0.25 \( \mu \)m is 2.05 J/cm\(^2\) and is close to that of pure zirconium. The decrease in the melting threshold of the system of a chromium thin film on zirconium substrates relative to the melting threshold of pure chromium is explained by the low thermal conductivity of zirconium compared to chromium (table 1). The zirconia substrate draws less heat away from the chromium film and makes it easier to melt. The increase in the melting threshold of the system within the analyzed film thicknesses is linear.

Figure 2 shows the dependences of the zirconium substrate melt thickness on the LEHCEB energy density for Cr-Zr systems with chromium film thicknesses of 0.25, 0.5, 1 and 1.75 \( \mu \)m. The chromium film begins to melt first for all cases in question. The melting of both the film and the substrate occurs when the energy values are above the melting threshold. In this case both elements of the system are in
the liquid phase. The energy density of the LEHCEB must be greater than the melting threshold for effective mixing of the film-substrate system elements. The general patterns of changes in melt thickness with increasing LEHCEB energy density for all systems under consideration are observed. As the energy density increases from the melting threshold of the system to some limiting values, a linear increase in melt thickness is observed. Evaporation of materials in this range of energy densities is negligible. Surface evaporation begins to have a significant effect on the temperature regime of the system as the energy density increases further. The calculated melt thickness dependences deviate from a straight line and are well approximated by a function of the natural logarithm. The maximum value of the energy density at which the film-substrate system melts without a noticeable effect of evaporation processes is called the evaporation threshold. The evaporation threshold in figure 2 is indicated by the dashed line. Figure 3 shows the dependence of the evaporation threshold of the Cr-Zr system on the film thickness. A linear increase in the evaporation threshold of the system within the analyzed film thicknesses is observed.

Figure 1. Dependence of the melting threshold of the film (Cr)-substrate (Zr) system on the film thickness.

Figure 2. Dependences of the zirconium substrate melt thickness on the LEHCEB energy density for Cr-Zr systems.

Figure 4 shows the time dependences of the melt thickness at the LEHCEB energy densities corresponding to the melting (a) and evaporation (b) thresholds for the Cr-Zr system with a film thickness of 0.25 μm. When the LEHCEB energy density is 2.1 J/cm², the melting dynamics are as follows (figure 4 (a)). The surface layer of the chromium film begins to melt after 1.092 μs of the start of the pulse energy exposure; the substrate begins to melt after 1.25 μs. The maximum melt depth
reaches 0.28 μm. The total melt of Cr and Zr persists for ~0.84 μs. Then there is a gradual crystallization of the zirconium substrate and the chromium film. Full crystallization of the system occurs after 1.483 μs. The lifetime of the film melt is ~0.391 μs and exceeds the lifetime of the substrate melt.

![Figure 3](image3.png)

**Figure 3.** Dependence of the evaporation threshold of the Cr-Zr system on the film thickness.

When the LEHCEB energy density is 3 J/cm², the melting dynamics are as follows (figure 4 (b)). The surface layer of the chromium film and the zirconium substrate begin to melt simultaneously in 0.8 μs after the start of pulsed energy exposure to the system. The maximum melt depth reaches a value of 1.74 μm after 1.7 μs and persists for 0.3 μs. Then the crystallization of the zirconium substrate begins. Crystallization of the chromium film when the substrate melt is preserved begins after 2.55 μs. Full crystallization of the substrate occurs only after 2.783 μs. The lifetime of the film melt is ~1.75 μs. It is ~0.23 μs shorter than the substrate melt lifetime. The difference between the lifetime of the film and the substrate determines the presence of a sharp-edged section of the profile at times >2.5 μs in the diagram of figure 4 (b). With a further increase in the LEHCEB energy density, this difference increases and the pointed section of the profile becomes more pronounced.

![Figure 4](image4.png)

**Figure 4.** Time dependences of the melt thickness of the Cr-Zr system with a film thickness of 0.25 μm at the LEHCEB energy densities of 2.1 (a) and 3 (b) J/cm².

By the example of the considered time dependences of the melt thickness of the Cr-Zr system with a film thickness of 0.25 μm, we can see that the patterns of changes in the lifetime of the film and the substrate with increasing LEHCEB energy density are different. The lifetime of the film melt is longer than the lifetime of the substrate melt at an energy density close to the melting threshold. If the energy
density is close to the evaporation threshold, then, on the contrary, the lifetime of the substrate melt is longer than the lifetime of the film melt. Consequently, there is a value of the LEHCEB energy density at which the lifetime of the film and the substrate are equal. Figure 5 shows the dependences of the film and substrate lifetime of the Cr-Zr system with film thicknesses of 0.25 and 1.75 μm on the LEHCEB energy density. The film and substrate lifetimes of the Cr-Zr system increase linearly with increasing LEHCEB energy density. The growth line of the film lifetime is more sloping than the growth line of the substrate lifetime. The LEHCEB energy density value at which the film and substrate lifetimes are equal was calculated from the intersection of these lines. The LEHCEB energy densities at which the film and substrate lifetimes are equal were calculated for Cr-Zr systems with film thicknesses from 0.25 to 2 μm in 0.25 μm increments. Figure 6 shows the dependence of the LEHCEB energy density at which the film and substrate lifetimes are equal on the film thickness of the Cr-Zr system. The LEHCEB energy density at which the lifetime of the film and the substrate are equal increases nonlinearly with increasing film thickness of the Cr-Zr system.

![Figure 5](image1.png)

**Figure 5.** The film melt lifetime and the substrate melt lifetime dependences on the LEHCEB energy density for the film thicknesses of 0.25 (a) and 1.75 (b) μm.

![Figure 6](image2.png)

**Figure 6.** Dependence of the LEHCEB energy density at which the film and substrate lifetimes are equal on the film thickness of the Cr-Zr system.

4. Discussion
One of the main characteristics of electron-beam treatment is the LEHCEB pulse energy density. The energy in the pulse should be enough to melt the film material and the surface layer of the substrate and thus form a surface alloy. The minimum energy density value at which the film-substrate system
melts is called the melting threshold. On the other hand, the energy density should not be too high. At high pulse energy densities the temperature of the melt can rise to values at which surface evaporation occurs. The maximum energy density value at which the film-substrate system melts without noticeable effect of evaporation processes is called the evaporation threshold. Another parameter that can be introduced for the Cr-Zr system is the LEHCEB energy density at which the lifetime of the film and substrate are equal. If the condition of equal lifetime of the film and substrate is met, the crystallization process in the system occurs almost simultaneously. Consequently, the LEHCEB energy must not exceed these values to form a homogeneous surface alloy. The energy density values must be within these specified threshold limits for effective surface alloy formation.

As noted, the melting threshold of the Cr-Zr system increases linearly with increasing film thickness (figure 1). The melting threshold of the system tends to infinity with unbounded growth of the film thickness. The dependence of the melting threshold of the considered system on the film thickness for the energy range of the standard mode of operation of the electron-beam machine can be described by a linear regression model:

$$E_{sm}(h) = 1.77 + 1.27h,$$

where $E_{sm}(h)$ is the melting threshold of the Cr-Zr system, $h$ is the film thickness. The linear regression model was calculated by the least squares method.

The evaporation threshold of the Cr-Zr system also increases linearly with increasing film thickness (figure 3). Consequently, the dependence of the Cr-Zr system evaporation threshold on film thickness can also be described by a linear regression model for the energy range under consideration:

$$E_{sv}(h) = 2.7 + 1.27h,$$

where $E_{sv}(h)$ is the melting threshold of the Cr-Zr system, $h$ is the film thickness. The linear regression model was calculated by the least squares method.

Comparing expressions (1) and (2) we can see that the multipliers at $h$ have the same values, only the constants differ. This indicates the same dynamics of growth of the thresholds under consideration as the film thickness increases. In this case, the variation range of energy density values is located from the melting threshold to the evaporation threshold.

Another energy parameter to be highlighted for the Cr-Zr system is the LEHCEB energy density at which the film and substrate lifetimes are equal. The value of this energy density increases nonlinearly with increasing film thickness of the Cr-Zr system (figure 6). The dependence of this parameter on film thickness can be described by a third-degree polynomial:

$$E_{se}(h) = 2.3 + 1.24h - 0.28h^2 + 0.34h^3,$$

where $E_{se}(h)$ is the LEHCEB energy density at which the lifetime of the film and substrate are equal, $h$ is the film thickness. The regression model was also calculated by the least-squares method. The $E_{se}$ curve crosses the evaporation threshold at a film thickness of 1.5 $\mu$m. Consequently, to effectively form a Cr-Zr surface alloy up to chromium film thicknesses of 1.5 $\mu$m, the LEHCEB energy should be between $E_{sm}$ and $E_{se}$, and between $E_{sm}$ and $E_{sv}$ for larger film thicknesses.

5. Conclusion

The following main conclusions can be formulated on the basis of computer simulations of the thermal fields in the Cr(film)-Zr(substrate) system under pulsed electron-beam exposure:

- The melting threshold of the Cr-Zr system is calculated. The melting threshold of the Cr-Zr system increases linearly with increasing Cr film thickness. A linear regression model of the melting threshold on the film thickness is proposed.
- The evaporation threshold of the Cr-Zr system is calculated. The evaporation threshold of the Cr-Zr system increases linearly with increasing Cr film thickness. A linear regression model of the evaporation threshold on the film thickness is proposed.
The LEHCEB energy density at which the lifetime of the film and substrate are equal is calculated. The LEHCEB energy density value must be less than the specified values to effectively form a Cr-Zr surface alloy. The LEHCEB energy density at which the lifetime of the film and substrate system are equal is described as a third-degree polynomial.

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