The mechanism of formation of surface micro- and nanostructures in the AlCoCrFeNi high-entropy alloy during electron-beam treatment

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The paper is devoted to a study of the formation of submicron and nanosized cellular crystallization structures on the surface of a high-entropy AlCoCrFeNi alloy irradiated by high current electron beams with the energy density varying from 10 to 30 J/cm² and a pulse time of 200 μs. The study revealed that the combination of thermal, evaporation-capillary and thermoelectric instabilities induces the formation of submicro- and nanodimensional cellular structures similarly to high-entropy alloys. The proposed dispersion equation was analyzed to detect the conditions for the generation of this instability. The importance of the evaporation process was investigated by finding a solution to the heat problem with phase transformations. The temperature distribution over time calculated at different distances from the surface of the alloy samples demonstrated that the surface temperature is lower than the evaporation temperature for the energy density \( E_s < 30 \) J/cm², therefore, the term of evaporation in the dispersion equation was ignored for these values of the energy density. The analysis of the dispersion equation showed that for \( E_s = 30 \) J/cm², the wavelength \( \lambda_m \) with the maximal growth rate of perturbations on the melt surface gains a value in the submicro-and nano-range, provided that the thermoelectric coefficient equals to ~4 – 10 V/K, and the pressure of evaporation is ~10⁵ Pa. If we exclude thermoelectric effects, these values \( \lambda_m \) are observed for the pressure of evaporation ~10¹¹ Pa. The wavelength \( \lambda_m \) was revealed to decrease according to a power law as the beam energy density increases.

Keywords: high-entropy alloys, AlCoCrFeNi, electron beam treatment, thermocapillary instability, thermoelectric effect.

УДК: 532.5; 539.8

Механизм формирования поверхностных микро- и наноструктур в высокоэнтропийном AlCoCrFeNi сплаве при электронно-пучковой обработке

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Изучено формирование структуры ячеистой кристаллизации субмикро- и наноразмерного диапазона на поверхностии высокоэнтропийного сплава AlCoCrFeNi при воздействии низкоэнергетических сильноточных электронных пучков с плотностями энергии от 10 до 30 Дж/см² и длительностью импульса 200 мкс. Установлено, что также как и для двух- и трёхкомпонентных сплавов причиной образования субмикро- и наноразмерных ячеистых структур является комбинированная неустойчивость, которая включает в себя термо-, испарительно-капиллярную и термоэлектрическую неустойчивость. Для выявления условий зарождения этой неустойчивости анализировались предложенное в предыдущих работах авторов дисперсионное уравнение. Роль процесса испарения выявлялась путем
решения тепловой задачи с уче том фазовых переходов. Расчеты распределения температур по времени на различных расстояниях от поверхности образцов данного сплава показали, что при значении плотности энергии $E_s < 30$ Дж/см$^2$ температура поверхности не достигает температуры испарения, поэтому при данных значениях плотности энергии испарительный член дисперсионного уравнения не учитывался. Результаты анализа дисперсионного уравнения показали, что при $E_s = 30$ Дж/см$^2$ длина волны $\lambda_m$, на которую приходится максимум скорости роста возмущений поверхности расплава, принимает значение, находящееся в субмикро и нанодиапазоне, при условии, что значение термоэлектрического коэффициента будет составлять $\sim 4 \text{--} 10$ В/К, а значение испарительного давления $\sim 10^5$ Па. Если не учитывать термоэлектрические эффекты, то такие значения $\lambda_m$ наблюдается только при испарительном давлении $\sim 10^{11}$ Па. Показано, что $\lambda_m$ уменьшается с ростом плотности энергии пучка электронов по степенному закону.

Ключевые слова: высокоэнтропийные сплавы, AlCoCrFeNi, электронно-пучковая обработка, термокапиллярная неустойчивость, термоэлектрический эффект.

1. Introduction

In recent years, the effect of concentrated energy flows, e.g. low energy high current electron beams on high-entropy alloys with different chemical formulae, has been the subject of many research works [1–5]. These works have demonstrated that multiple irradiations of CrFeCoNiMo and CoCrFeNiMo$_{0.2}$ alloys by an electron beam with an energy density of 4 J/cm$^2$ and a pulse time of 1.5 μs induces the formation of a fusion zone. Moreover, its thickness expands with the increasing number of pulses [1,2]. The structure of this zone comprises crystals with an average size of 109 nm. Several authors [3–5] revealed that high-entropy alloys (HEAs) synthesized in selective electron-beam melting are characterized by high mechanical properties, which are possible due to the formation of micro-and nanodimensional structures and phases. One of the most probable mechanisms responsible for their forming is thought to be various hydrodynamic instabilities, e.g. the Mullins-Sekerka instability [6], thermocapillary instability [7,8] and the Kelvin-Helmholtz instability [9,10]. An assumption was made [11,12] that micro- and nanostructure phase states develop in multicomponent alloys owing to the evolving combination of thermal, concentration-evaporation and thermoelectric instabilities. This study investigates the effect of an electron beam with the energy density from 10 to 30 J/cm$^2$ and a pulse time of 200 μs on the AlCoCrFeNi high-entropy alloy (chemical composition, mass.%: 15.64 Al, 7.78 Co, 8.87 Cr, 22.31 Fe, 44.57 Ni). A principal method to analyze the structure of a material surface was selected scanning electron microscopy. Fig. 1 provides findings of an SEM-analysis carried out on the surface irradiated by an electron beam with an energy density of 30 J/cm$^2$. It is apparent from this figure that a cellular structure ranging

![Image](image.png)

**Fig. 1.** Structure of a high-entropy alloy irradiated by an electron beam with an energy density of 30 J/cm$^2$ (SEM-image of the irradiated surface (a), SEM-image of the fracture surface (arrows show the direction of electron beam irradiation) (b), histogram of the grain size distribution of the irradiated surface (c), cross-section TEM-image of the irradiated surface(d)).
from 225.83 to 618.87 nm was formed on the treated surface. The dimensional distribution of cells displays one maximum in the range from 300 to 350 nm.

The cross-section of the samples (Fig. 1) was analyzed, and a conclusion was drawn that the modified layer is a product of the electron-beam treatment. The thickness of this layer depends on the height of the crystallization columns and increases with the growing energy density of an electron beam.

2. Results and Discussion

As discussed above, the formation of micro-and nanodimensional structure and phase states on the surface during electron-beam treatment is induced by the combination of thermal-capillary, concentration-capillary and thermoelastic instabilities. We assume that this instability arises when an electron beam is applied to high-entropy alloys. The significant role of thermoelastic convection for the formation of a cellular crystallization structure is traced in the thickness of the molten layer ~1–20 μm. As stated in previous studies [13,14], thermoelastic effects fail to be neutralized totally by the thermocapillary convection if a concentrated flow of energy is supplied from above. When determining the thermoelastic coefficient, we proceed from the assumption that the convective flow, intensifying the thermocapillary effect, is of significant importance for the transfer of charge in the liquid state [12].

The dispersion equation, proposed earlier in [12], is used to determine conditions under which the combined instability is most likely to develop:

\[ R_T - R_E - R_V - R_\sigma = 0, \]  
\[ R_T = \frac{\omega^2}{\rho \nu} \left( \frac{1}{2} \left( \frac{1}{k_1} + \frac{1}{k_2} \right) \right) \left( 2 \omega_A + \omega_0 + \omega_0^2 \right) + \frac{4 \omega^2 \omega_A^2 k_1}{k}, \]  
\[ R_E = -\omega E_0 \omega_0 \left( \frac{1}{k_1} + \frac{1}{k_2} \right) + \frac{1}{2 \omega_A \omega_0} \left( 1 + \frac{k_1}{k_2} \right), \]  
\[ R_V = \omega_0 \omega_0 \left( \frac{1}{k_1} + \frac{1}{k_2} \right) \left( \frac{1}{2} \left( \frac{1}{k_1} + \frac{1}{k_2} \right) \right) + 2 \omega_0 \omega_0 \left( \frac{1}{k_1} + \frac{1}{k_2} \right) + \frac{4 \omega^2 \omega_A^2 k_1}{k}, \]

where \( R_T, R_E, R_V, R_\sigma \) — capillary, thermocapillary, thermoelastic and vapour dispersion equation respectively, \( \omega_T = \sigma / \nu k^2 \) — viscosity frequency, \( \omega = \sigma / \nu k^2 \) — capillary frequency, \( \omega_0 = \rho / \nu k^2 \) — vapour-capillary frequency, \( \delta = \frac{1}{2 \omega_A} \left( \frac{1}{k_1} + \frac{1}{k_2} \right) \).

Prandtl number, \( \sigma_\sigma \) — surface tension at a temperature of material melting \( T_m \), \( \sigma_\sigma \) — temperature coefficient of the surface tension, \( \rho \) — density, \( \nu \) — kinematic viscosity, \( \chi \) — temperature coefficient, \( G_0 \) — gradient of temperature, where \( \varepsilon \) — dielectric permittivity, \( \varepsilon_0 \) — electric constant, \( E_0 \) — electric field strength on the stable horizontal surface of a liquid. Provided that \( Pr < 1 \) the Eq. (1) is written:

\[
\frac{\omega_T \cdot Pr}{2} \left( 2 \omega_A + \omega_0^2 \right) \left( \omega + 2 \omega_A \right) \left( 1 - \frac{k_1}{k} \right) + \frac{\omega_T \cdot Pr}{2} \left( 2 \omega_A + \omega_0^2 \right) \left( \omega + 2 \omega_A \right) \left( 1 - \frac{k_1}{k} \right) + \\
\omega \left( \omega^2 + 2 \omega_A \omega_0 + 4 \omega_0^2 \right) \left( 1 - \frac{k_1}{k} \right) - \omega_0 \omega_0 \omega_0 \left( 1 - \frac{k_1}{k} \right) \omega_0 + \omega_0 - \\
- \omega_0^2 \left( \omega^2 + 2 \omega_A \omega_0 + \omega_0^2 \right) + \frac{4 \omega \omega_0 \omega_0^2 k_1}{k} = 0.
\]

Substituting \( z = \frac{k_1}{k} \) and \( \omega = \omega_0 \left( z^2 - 1 \right) \), the Eq. (2) is stated:

\[
C^2 + 2 \left( z^2 - 1 \right) C_2 + 2 C_4 + \left( z^2 + 2z + 3 \right) \left( z^2 - 1 \right) C_3 = \\
- 2 \left( z^2 + 1 \right) C_4 - \left( z + 1 \right)^2 \left( C_2^2 + \left( z^2 + 1 \right)^2 - 4z \right) = 0,
\]

where \( C = \omega / \omega_0, C_1 = \omega_0 / \omega, C_2 = \omega_0 / \omega, C_3 = \omega_0 / \omega_0 \). As proposed earlier [12], such solutions are selected, which meet the condition \( \text{Re} \left( \omega \right) > 0 \) and \( \text{Re} \left( z \right) > 0 \). In these cases, the growth rate of perturbations \( \alpha = \text{Re} \left( \omega \right) > 0 \). The data for calculations is given in Table 1.

The values of specific heat of fusion and evaporation in the first approximation are determined according to the mixture rule: \( X = \sum_{i=1}^{n} x_i \), where \( a_i \) — volume percentage of an \( i \)-component in the alloy, \( x_i \) — specific heat of fusion (specific heat of evaporation) for an \( i \)-component of the alloy. The temperature gradient is found as in [12]: \( G_c = \left( q - q_{out} \right) / \kappa \), where \( q = E / T_m \) — energy density of an electron beam, \( E_0 \) — surface energy density of an electron beam, \( q_{out} \) — evaporation-conditioned surface energy density, \( \kappa \) — thermal conductivity of a liquid metal. The role of evaporation for the power density [15] is calculated as follows:

\[
q_{out} = 10^7 \left( \frac{2 \pi \kappa}{\rho v} T_m \right) \exp \left( \frac{A_{out}}{k_B \left( 1/T_m - 1/T_v \right)} \right),
\]

where \( A_{out} \) — work function of an atom escaping from the melt, \( k_B \) — Boltzmann constant, \( m \) — atomic mass, \( T_m \) — evaporation temperature.

The role of evaporation in the formation of nanostructures was calculated according to the previously proposed heat model [16], which considers this phase transformation. Fig. 2 provides the data on the temperature distribution over time at various depths from the irradiated surface at 30 J/cm².

It can be apparent from the data in this figure that the temperature on the irradiated surface is equal to the temperature of evaporation for this value of the energy density, whereas no evaporation is observed for any other values of the energy density below 30 J/cm². Therefore, for \( E < 30 \text{ J/cm}^2 \) we consider \( \omega = 0 \).

Further, it is necessary to find the minimum wavelength, which initiates the combined instability. For this purpose, the solution (3) is determined in \( z^2 = 1 \pm iC + \Theta \). As a result,
Table 1. Thermal physical properties of AlCoCrFeNi systems [17–20].

| Symbol / dimension | Property                        |
|-------------------|--------------------------------|
| $T_m$, K          | Melting temperature            |
| $T_v$, K          | Evaporation temperature        |
| $\rho_v$, kg/m$^3$| Solid phase density            |
| $\rho_l$, kg/m$^3$| Liquid phase density           |
| $\rho_s$, kg/m$^3$| Vapor phase density            |
| $\nu$, 10$^{-3}$m/s| Viscosity                     |
| $\chi$, 10$^{-3}$m/s| Thermal diffusivity           |
| $\sigma$, N/m    | Surface tension                |
| $\sigma_v$, 10$^{-5}$N/(m·K) | Temperature coefficient of surface tension |
| $\kappa_s$, W/(m·K) | Thermal conductivity of solid phase|
| $\kappa_l$, W/(m·K) | Thermal conductivity of liquid phase|
| $\kappa_v$, W/(m·K) | Thermal conductivity of vapor phase|
| $L_v$, kJ/kg     | Specific heat of melting       |
| $L_e$, kJ/kg     | Specific heat of evaporation   |

The numerical solution of the dispersion Eq. (3) showed that the maximum value of the perturbation growth rate under these conditions falls on the wavelengths of 380 and 530 nm (Fig. 3a, curve 1 and 2). Considering thermoelectric effects, the wavelength attributed to theorigination of instability is 225 nm (Fig. 3a, curve 3) for an evaporation pressure of 10$^{11}$ Pa and a thermoelectric coefficient of 4.3 V/K; this outcome is in line with experimental data.

The maximum growth rate is recorded for a wavelength of 430 nm; it differs slightly from the SEM data of the cellular structure. As mentioned above, the presented results are obtained in the low-frequency approximation by finding a solution to Eq. (3). We turn to the discussion of numerical solutions to full dispersion Eq. (1). This equation is a cumbersome algebraic equation of the 16$^{th}$ degree with respect to $\omega$, so we omit it here. The study considers only such roots of Eq. (1), which meet the condition $\text{Re}(\omega) > 0$ and $\text{Re}(\sigma) > 0$, $\text{Re}(\kappa) > 0$. As numerical solution shows, the equation has two roots. In both cases, the instability arises at $\lambda > 220$ nm, and the maximum growth rate is registered for a wavelength of 430 nm (Fig. 3b, curve 1); this is in line with the experimental data and solutions of Eq. (3).

This fact allows one to conclude that the low-frequency approximation is adequate (3). If evaporation is not taken into account, the wavelength at which the maximum growth rate is observed is the same as at an evaporative pressure of $\sim 10^{11}$ Pa. This allows us to conclude that the thermoelectric instability prevails over the evaporation-capillary instability in this range of vapour recoil pressures. The most noticeable effect of evaporation becomes at an evaporative pressure of $\sim 10^{10}$ Pa (Fig. 3b, curve 2). The maximum growth rate, in this case, will be observed at a value of $\lambda = 450$ nm.

Fig. 4 demonstrates the correlation between the wavelength with the maximum growth rate and the energy density varying from 10 to 30 J/cm$^2$. This figure shows that the growing energy density $E_v$ brings about a decrease in the wavelength according to the power-law $\lambda_m = 583.16 \cdot E_v^{-2.125}$ (correlation coefficient 0.999); therefore, the most likely expected sizes of the cellular crystallization structure will be reduced. This correlation allows optimizing the processing conditions of high-entropy alloys by low energy high current electron beams.

![Fig. 2. Temperature distribution vs. time throughout the depth for the energy density $E_v = 30$ J/cm$^2$.](image-url)
Still, it necessitates the research into the role of the concentration of alloying elements for the surface tension of the alloy under study and the determination of the diffusion coefficients in these alloys.

3. Conclusion

The study establishes that thermoelectric phenomena significantly affect the initial stage of thermocapillary flow instability in a high-entropy alloy melt irradiated by electron beams. The critical outcome of the study is that evaporation-capillary instability is possible only for the energy density of 30 J/cm² and higher. The correlations between the growth rate of perturbations at the plasma-melt boundary and the wavelengths display one maximum only, which is recorded in the submicro- and nanometer range for the thermoelectric coefficient $\gamma \geq 4$ V/K. Due to the obtained results, the mechanism responsible for forming surface micro-and nanostructures represents the combination of thermal, evaporation-capillary and thermoelectric instabilities. They can be relevant for determining the optimal conditions of electron-beam processing high-entropy alloys to form micro-and nanostructures. The further development of the model can be related to the consideration of concentration-capillary effects.

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