Experimental and numerical investigation of the refinement of Hf by EBM

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Abstract. Electron beam melting (EBM) in vacuum is one of the most promising technologies for refining and recycling of metals that react with oxygen when heated. Hf is such a metal. Pure Hf (with a small content of gas and metal impurities) is needed for a variety of applications in the aerospace industry and metallurgy, in the production of components of nuclear reactors, microprocessors, optical components etc. We conducted experiments with the ELIT-60 equipment on Hf ingots at electron beam powers of 12, 15, 17 kW and obtained data about the concentration of impurities by the ICP-MS method. For further understanding and optimizing the Hf refining processes, a non-stationary heat model was applied for numerical simulation of the heat transfer processes. Simulation data about the liquid pool variation during the e-beam treatment was thus obtained. The flatness of the crystallization front shape, which is connected to the structure quality, was investigated by optimization criteria related to the curvature of the liquid/solid boundary curve. We also describe an algorithm for calculation of the criteria. One of the criteria was applied to EBM of Hf for different electron beam powers; the results obtained were confirmed by the experimental data. Combining experimental, theoretical and simulation results, a proper technological regime is proposed for better Hf refining.

1. Introduction

Electron beam melting and refining (EBMR) is a method applied in the special electrometallurgy for production of pure metals and alloys and of new materials [1-6]. The electron beam technologies and, in particular, the technologies for EBMR of metals and alloys have been recognized as a competitive, if not the only, method for obtaining new materials for uses in various fields: nuclear industry, medicine, electronics, instrument engineering, transport, etc. The principle and a description of the EBMR process have been presented in [1, 2, 3, 6]. Computational modeling gives a possibility for a better understanding and investigating the heat transfer mechanisms and can be used for optimizing the electron beam process for obtaining new materials with improved characteristics. In [7], a stationary heat model was described and applied to studying the EBMR process. This mathematical model was extended to a time-dependent heat model with a Pismen-Rekford numerical scheme that is absolutely stable with respect to the time [8].

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A mathematical optimization technique, including a proposition for analytical optimization criteria, their discretization according to the numerical scheme and methods for solving the discrete optimization problems, were proposed and applied as well [8]. In this paper, an optimization problem for achieving flatness of the molten pool shape (liquid/solid metal boundary) is proposed. The criterion is based on calculating the curvature of the liquid/solid boundary which describes the geometry of the molten pool contour and is very important for studying and optimizing the quality of the pure metal obtained after EBMR. The flatness of the liquid/solid boundary is directly connected to the quality of the structure of the metal obtained [3, 6, 8].

2. An optimization problem for EBMR of metals

2.1. Formulation of the optimization problem

The temperature fields during EMBR of metals and alloys in cylindrical ingots are investigated by applying a non-stationary heat model [8]. By \( T(r; z; t) \) we denote the temperature at a distance \( r \), height \( z \) and heating time \( t \), due to the assumed radial symmetry [3, 8].

The flat molten pool shape permits the formation of a vertical dendrite structure and a uniform impurities' displacement toward the ingot top surface. At a fixed moment of heating \( t_f \), the liquid/solid contour can be defined mathematically as a curve:

\[
\Gamma(t_f) = \{(r, z) \mid T(r, z, t_f) = T_{\text{melt}}\},
\]

(1)

where \( T_{\text{melt}} \) is the melting temperature of the investigated metal or alloy.

The following optimization criteria for minimization of the curvature of the crystallization front \( \Gamma(t) \) are defined:

\[
K_{\text{max}}(P_r, r_b, V; t_f) = \max_{s(\Gamma(t))} \left\{ \frac{d \Gamma(t_f)}{ds}(r(s), z(s)) \right\} \rightarrow \min,
\]

(2)

\[
K_{\text{max}}(P_r, r_b, V) = \int_{t_1}^{t_2} \mu(t) K_{\text{max}}(P_r, r_b, V; t) dt \rightarrow \min,
\]

(3)

where \([t_1, t_2]\) is a fixed heating time interval, \( \mu(t) \) is a weight function, \( s \) is a natural parameter for \( \Gamma(t) \) and \( t_f \) is a fixed moment of heating. The temperature field \( T \) is the solution of equation (4) subject to the initial condition (5) and boundary conditions (6-9) for metal samples with height \( H \) and diameter \( D = 2R \), for electron beam radius \( r_b \) and heating time \( F \).

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} + \frac{V}{a} \frac{\partial T}{\partial z} = \frac{\rho C_p}{\lambda} \frac{\partial T}{\partial t}, \quad x \in \Omega = (0, R) \times (0, H) \times (0, F),
\]

(4)

\[
T(x) = T_0(r, z), \quad x \in \Omega_0 = \{x \in \overline{\Omega}: t = 0\},
\]

(5)

\[
\lambda \frac{\partial T}{\partial t}(x) = P(r, t) - \alpha \sigma \left( T^4(x) - T_{\text{room}}^4 \right) - C_p W_r T(x), \quad x \in \{x \in \overline{\Omega}: z = H, t > 0\}
\]

(6)

\[
\lambda \frac{\partial T}{\partial r}(x) = \lambda_2 \frac{\partial T}{\partial r}(x), \quad x \in \{x \in \overline{\Omega}: H - Q \leq z \leq H, r = R, t > 0\},
\]

(7)

\[
\lambda \frac{\partial T}{\partial r}(x) = -\alpha \sigma \left( T^4(x) - T_{\text{room}}^4 \right), \quad x \in \{x \in \overline{\Omega}: 0 < z < H - Q, r = R, t > 0\},
\]

(8)

\[
\lambda \frac{\partial T}{\partial r}(x) = \lambda_2 \frac{\partial T}{\partial r}(x), \quad x \in \{x \in \overline{\Omega}: z = 0, t > 0\}.
\]

(9)
The control variables (on which the criteria depend) are the beam power $P_b$, the beam radius $r_b$, and the casting velocity $V$. $P_b$ is connected with the e-beam energy distribution $P_s$. For a fixed heating time, $t_f$, the beam energy distribution $P_s(r, t_f)$ is a Gaussian-like function and:

$$\int_{[0,R]} \int_{[0,2\pi]} rP_s(r, t_f) drd\varphi = P_b$$

In (4)-(9) $\rho$, [g/m$^3$], is the density of the metal; $C_p$, [W s/g K], is the heat capacity; $\lambda$, [W/m K], is the heat conductivity; $a$, [m$^2$/s], is the heat diffusivity, $a = \frac{\lambda}{\rho C_p}$. The term $\frac{V}{a} \frac{\partial T}{\partial z}$ characterizes the casting, i.e. the heat added by the poured molten metal; $\alpha$ is the metal’s emissivity, $\sigma = 5.6704.10^{-8} [J/ m^2 K^4]$ is the Stefan-Boltzmann constant; $C_p W_i T$ describes the evaporation losses, $T_{room}$ is the room temperature. More details about the heat model (4)-(9) are presented in [8].

2.2. Discretization of the optimization problem and numerical solution methods
The discretization of the problem (4)-(9) is made on the net:

$$W_{h_i h_j} = \{(r_i, z_j, t_n) | r_i = ih_i, z_j = jh_j, t_n = n\tau; i = 0, N, j = 0, M, n = 0, \overline{P}\}$$

by a modified Pismen-Rekfort scheme which is absolutely stable in $\tau$. In the numerical scheme, the approximation of the differential operators in eq.(4) is made via the difference operators

$$\Lambda_{1,r} = (1/r)(r_i-j/2 \eta_{r, j}), \Lambda_{2,r} = T_{z,i}, (V/a)T_{z,j}.$$  For input functions $P_b$ and $V$, the discrete temperature field $\{T_{z,i,j}^{\eta_{M,N}}\}_{i=0}^{\overline{N}}_{j=0}^{\overline{M}}$ is calculated applying the non-stationary heat model [8]. Hence, if the criteria (2) and (3) are approximated over the net (11), the defined analytical problem (2, 4-9) or (3-9) is transformed to a discrete one.

For numerical calculation of the criteria (2) and (3), the curve $\Gamma(t)$ can be approximated by a discrete set of points $\mathcal{G}(t_f)$ at a time $t_f$ (figure 1):

$$\mathcal{G}(t_f) = \{(r_i, z_j); | T_{z,i,j} - T_{\text{melt}} | < \epsilon\}$$

for an apriori fixed $\epsilon > 0$. The choice of $\epsilon$ depends on the steps $h_i, h_j$. Then $\Gamma(t_f)$ can be interpolated using a linear regression method by an analytical function $\Gamma'(t_f)$ (figure 1). After parameterizing the curve $\Gamma'(t_f)$, its curvature $k'(r, t_f) = | \frac{d\Gamma'(t_f)}{ds} (r, z(s)) |$ (figure 1-b) can be easily calculated by an explicit formula in each point of the curve. Usually, the parameter is $r$ and the curvature is calculated via the formula:

$$k'(r; t_f) = \frac{| f''(r; t_f) |}{\sqrt{((f'(r; t_f))^2 + 1)}}$$
For criterion (3), the calculation (13) must be repeated for all points in a regular net of points over the area $D = [r_0, r_{\text{max}}] \times [t_1, t_2]$, where: $r_{\text{max}} = \max\{r \in [r_0; R] | T(r, H, t_f) > T_{\text{max}} \}$, i.e. the radius of the molten pool and $0 < r_0 < r_{\text{max}}$. Then the integral (3) must be calculated by a quadrature or numerically.

![Figure 1](image1.png)

**Figure 1.** (a) An interpolation of the liquid/solid metal contour via a linear regression method; (b) the curvature of the approximated curve, $\| d^2 \Gamma(r(t), z(s)) / ds^2 \|$. The curve is approximated as a polynomial of degree 3 for $\varepsilon = 100K$. The numerical experiment is for Hf ingot with $H = 10\text{mm}$, $R = 30\text{mm}$, $P_b = 12\text{kW}$, $r_b = 10\text{mm}$, $V = 0\text{mm/\text{min}}$, $t_f = 300\text{s}$.

1 - the set $\mathcal{G}(t_f)$, 2 - the curve $\Gamma(t_f)$.

After discretization of the model and implementation of the developed method for calculation of the criterion, a discrete optimization problem has to be solved. For a fixed $P_b$, $r_b$ and $V$, the discrete temperature field $\{T^i_{\nu, j} = \Gamma(t_f)\}$ and the criterion (2)-(3) are calculated. Optimal values of the control parameters are sought for which the criteria (2)-(3) are minimized. For solving the discrete optimization problem obtained, heuristic methods can be applied because the dependence of the criteria on the control variables is implicit [8].

### 3. Results and discussion

Electron beam melting and refining of hafnium was performed using 60 kW equipment (ELIT-60 in the IE-BAS). The feeding material – hafnium chips, were degreased and compacted in the form of disks with a diameter of 60 mm and a height of 10 mm. To investigate the refining processes in Hf recycling, different technological regimes (conditions) were implemented. The ranges studied of the process parameters (electron beam power $P_b$ and refining time $F$) were: $P_b = 12, 15, 17 \text{ kW}$ and $F$ in the range 2-5 min. The beam radius was $r_b = 10\text{mm}$. Using the ICP-MS method, results on the removal of impurities were obtained, namely, the highest purification of Hf ingot was achieved at a beam power of 12 kW and a short processing time [9].

A simulation of the EBM of Hf was made for the above technological regimes. The thermal fields were calculated for all beam powers and the criterion (2) was calculated for $t_f = 1, 2, 3, 4, 5 \text{ min}$. The liquid/solid contour $\Gamma(t)$ was approximated by a linear regression with a polynomial of degree 3.

The function $\Gamma^j$ was parametrized by the radial distance $r$. Thus, the criterion used was:

$$K_{\text{max}}(P_b, r_b, V; t_f) = \max_{r_0(b, t_f)} \left\{ \frac{|f^*(r, t_f)|}{\sqrt{(f^*(r, t_f))^2 + 1}} \right\},$$

(14)
where \( \{(r, f(r; t_f)) : 0 \leq r \leq r_{\text{max}}\} \) is the parametrization of the approximation \( \Gamma' \) of the molten pool contour at the moment \( t_f \), calculated for \( r_b = 10 \text{ mm} \); \( V = 0 \text{ mm/min} \), \( r_1 = 12 \text{ mm} \) and for \( P_b \in \{12kW, 15kW, 17kW\} \). The data obtained for \( K_{1,\text{max}}(P_b, r_b, V, t_f) \) (denoted as \( K_{1,m} \) in Table 1), the depth \( h_m \) of the liquid metal pool, the ratio \( S_m/V_m \) of the melted top surface areas \( S_m \) and melted volume \( V_m \) is shown in Table 1.

Table 1. Calculated parameter values at EBM of Hf.

| \(P_b\) [kW] | \(K_{1,m}\) [mm] | \(S_m/V_m\) [mm\(^3\)] | \(K_{1,m}\) [mm] | \(S_m/V_m\) [mm\(^3\)] | \(K_{1,m}\) [mm] | \(S_m/V_m\) [mm\(^3\)] | \(K_{1,m}\) [mm] | \(S_m/V_m\) [mm\(^3\)] |
|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 12         | 49.2            | 3.67            | 47.60           | 49.7            | 3.67            | 46.64           | 48.4            | 3.67            |
| 15         | 49.2            | 5.8             | 41.87           | 52.3            | 6.00            | 44.29           | 52.1            | 6.00            |
| 17         | 45.8            | 4.61            | 41.25           | 46.8            | 4.61            | 43.44           | 47.4            | 4.61            |

These results allow one to recommend values of the technological parameters in order to optimize the EBM process. The minimal curvature, i.e. the maximal flatness of the molten/solid metal contour, permits the formation of a better structure in the cast ingot; the lowest value of \( K_{1,\text{max}} \) is observed at a heating time \( t_f = 5 \text{ min} \) and electron beam power \( P_b = 12 \text{ kW} \).

The minimal value of the liquid pool depth and high values of the ratio \( S_m/V_m \) and of \( S_m \) ensuring more efficient refining processes (higher purification) are achieved at the same parameters values \((P_b = 12 \text{ kW}; t_f = 5 \text{ min}) \) - Table 1. These recommended regime conditions for obtaining a good quality (structure and composition) of the refined material correspond to the experimental result in [9]. The approximated liquid/solid contour and the graph of the curvature in Fig. 1 correspond to the numerical experiment for the lowest value of \( K_{1,\text{max}}(P_b, r_b, V, t_f) \) achieved at \( P_b = 12 \text{ kW} \) and \( t_f = 5 \text{ min} \). An important advantage of the optimization scheme proposed is that experimental data from a chemical analysis of the impurities' concentrations for different technological regimes are not needed.

4. Conclusions

In this paper, the EBMR process of Hf is investigated experimentally and theoretically (by a non-stationary heat model with a corresponding optimization technique) with the purpose of improving the quality (structure and composition) of the ingots treated. The optimization problem proposed aims to obtain maximum flatness of the liquid/solid metal contour that permits formation of a better structure of the cast metal (vertical dendrite structure and an uniform impurities' displacement toward the top surface of the cast ingot) during EBMR. The maximal curvature of this boundary in terms of the beam power, beam radius and casting velocity is minimized analytically. Simulation results concerning the liquid pool geometry are presented and recommendations are given for appropriate process conditions ensuring better refining processes (higher purification). The technological parameters recommended for obtaining good-quality refined materials correspond to the experimental results showing that the minimal impurities concentrations (higher purification of Hf) are obtained at 12 kW beam power and short heating time for the ranges investigated of the process conditions. The mathematical heat model and the corresponding optimization scheme for achieving maximum flatness of the liquid/solid boundary can be applied to investigating and optimizing the EBMR regimes for different metals without the need of experimental results for the impurities' concentrations.

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