

Supplementary Materials

Machine-learning optimization of microstructure and mechanical properties in 3D-printed W-alloyed refractory high-entropy alloys

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1. INTEGRATED CALCULATION

1.1. Calculation of the solidification conditions

For laser processing, several important processing parameters, such as laser power P_L and scanning velocity V_b , govern the melt-pool geometry and corresponding solidification conditions (G and V). Therefore, the correlation of a set of given processing parameters with the corresponding G and V should be established. The temperature field was calculated by solving an analytical heat-transfer equation for a moving Gaussian surface heat source, which assumes a semi-infinite body with constant physical properties, no latent-heat release and no convection. More details of the calculations of the solidification conditions can be obtained elsewhere [1, 2]. To facilitate the ML, the solidification conditions (G and V) of melt pools was represented by the characteristic solidification conditions (G_m and V_m), which were calculated as an average over the total depth of the melt pool, Z_{max} , along the symmetrical centerline of liquidus isotherm:

$$G_m = \int_{Z_{max}}^0 G \cdot dZ / |Z_{max}| \quad (1)$$

$$V_m = \int_{Z_{max}}^0 V \cdot dZ / |Z_{max}| \quad (2)$$

1.2. Solidification behavior and microstructure

Rapid solidification behavior depends strongly on the undercooling at dendrite tip, which can be calculated by the Kurz–Giovanola–Trivedi model [3-7]:

$$\Delta T_{tip} = \sum_i (C_{0,i} m_i - C_{l,i}^* m_{v,i}) + 2\Gamma/R \quad (3)$$

$$C_{l,i}^* = C_{0,i} A_i \quad (4)$$

where Γ is the Gibbs–Thomson coefficient, R is the tip radius of dendrites, $C_{l,i}^*$ is the liquid concentration at the dendrite tip, $C_{0,i}$ is the initial alloy composition, $A_i = 1/[1 - (1 - k_{v,i})Iv(Pc)]$, and $Iv(Pc)$ is the Ivantsov function of the solute Péclet number Pc [8, 9]. The Γ of Ti-rich alloys can be set as 1.88×10^{-7} K·m [10], and more details of the evaluation of the A_i can be obtained elsewhere [3, 10, 11]. Once ΔT_{tip} is determined, the size and fraction of the equiaxed grains ahead of solidification r_e and ϕ can be

obtained by Hunt's analytical model, and are given by [12, 13]:

$$r_e = [(1 - \Delta T_n^3 / \Delta T_{tip}^3) \cdot \Delta T_{tip}] / 3G \quad (5)$$

$$\phi = 1 - \exp(-4\pi r_e^3 N_0 / 3) \quad (6)$$

where ΔT_n is the nucleation undercooling of the equiaxed grains. N_0 is the number of nucleation sites (nuclei density). Hunt [12] proposed that fully columnar growth occurs if $\phi < 0.0066$, while fully equiaxed growth occurs if $\phi > 0.49$, *i.e.*, the occurrence of CET. A ΔT_n of 0.75 K was used [10], and the N_0 values were considered within a range from 10^9 to $2 \times 10^{15} \text{ m}^{-3}$ in previous research on the columnar-to-equiaxed transition and a medium N_0 value of 10^{13} m^{-3} was used [14-17]. Comparison between the experimental and calculated results suggested that the use of a N_0 value of $1 \times 10^{13} \text{ m}^{-3}$ is proper. This CET model can well predict the solidification morphology during laser processing [1, 2, 18-28].

Table S1. The phase equilibrium and thermophysical parameters used in the integrated calculation ^a

	0W	2W	4W	6W	8W
$C_{0, \text{Nb}}$ (wt%)	21.7	20.2	19.4	18.0	17.4
$C_{0, \text{W}}$ (wt%)	1.0	8.0	11.5	17.8	20.7
m_{Nb} (K/wt%)	7.3	5.1	4.0	2.0	1.0
m_{W} (K/wt%)	17.5	17.5	17.5	17.5	17.5
k_{Nb}	1.6	1.6	1.6	1.6	1.6
k_{W}	4.8	4.8	4.8	4.8	4.8
$D_{\text{S, Nb}}$ (m^2/s)	1.3×10^{-12}	2.1×10^{-12}	2.6×10^{-12}	3.9×10^{-12}	4.8×10^{-12}
$D_{\text{S, W}}$ (m^2/s)	7.9×10^{-13}	4.7×10^{-13}	3.4×10^{-13}	1.8×10^{-13}	1.5×10^{-13}
T_L (K)	1894.5	2045.0	2107.4	2203.1	2241.8
T_S (K)	1753.3	1754.7	1751.2	1736.2	1723.4
α (m^2/s) ^b	5.68×10^{-6}	5.44×10^{-6}	5.39×10^{-6}	5.21×10^{-6}	5.13×10^{-6}
κ ($\text{W}/\text{m} \cdot \text{K}$) ^b	21.1	21.4	21.6	22.2	22.5
D (m^2/s)	5×10^{-9}				
T_{L0} (K)	1747.8				
T_{S0} (K)	1612.2				

a. The parameters were calculated by the CALPHAD method, which leverages on the TCHEA database integrated in the Thermo-Calc software [29, 30]; b. α and κ are thermal diffusivity and thermal conductivity, respectively, which were used to calculate G and V based on an analytical heat-transfer equation [1, 2].

Moreover, the initial solute content in the solid, $C_{s,i}^*$, at the beginning of the solidification, can be written as [9, 31]:

$$C_{s,i}^* = k_{v,i}C_{l,i}^* = k_{v,i}C_{0,i}A_i \quad (7)$$

To evaluate the microsegregation degree ΔC_i of an element i , the final solid concentration of each solute $C_{s,i}^E$ is also required and there is $\Delta C_i = C_{s,i}^E - C_{s,i}^*$. The final liquid concentration of the solute element i can be obtained by a modified solute redistribution model and written as [31]:

$$C_{s,i}^E = k_{v,i}C_{l,i}^E = k_{v,i}C_{0,i}A_i(2\alpha'_i k_{v,i}A_i)^{\frac{p_i}{q_i}} \quad (8)$$

where $p_i = k_{v,i}A_i - 1$ and $q_i = 1 - 2\alpha_i k_{v,i}A_i$, $\alpha_i' = \alpha_i [1 - \exp(-1/\alpha_i)] - 0.5\exp(-1/2\alpha_i)$, α_i is the dimensionless back-diffusion coefficient of the solute element i , and is written as [9, 31]:

$$\alpha_i = (4D_{s,i}\Delta T')/(\lambda^2 GV) \quad (9)$$

where $\Delta T'$ is the actual (nonequilibrium) solidus-liquidus interval, and λ is calculated by the Kurz–Fisher model [9, 31]:

$$\lambda = 4.3(\Delta T_0 D\Gamma/k)^{0.25} G^{-0.5} V^{-0.25} \quad (10)$$

As described in Eq. (9), calculation of the $C_{s,i}^E$ needs to determine the $\Delta T'$. To obtain $\Delta T'$, a reasonable pseudo-binary simplification for the alloy system is necessary [31]. As aforementioned, the effects of Nb and W are considered together and the current system is regarded as a pseudo-binary system AlTiVZr–X, where the composition X, C_X , is the sum of the compositions of Nb and W. By assuming the liquidus and solidus are straight, equivalent equilibrium liquidus slope, m_e , and partition coefficient, k_e , are given by (Figure S1):

$$m_e = (T_L - T_{L0})/C_X \quad (11)$$

$$k_e = (T_{S0} - T_L)/(T_{S0} - T_S) \quad (12)$$

where T_{L0} is and T_{S0} are liquidus and solidus temperatures of AlTiVZr, respectively. Substituting m_e and k_e into Eqs. (11) and (12), equivalent velocity-dependent liquidus slope, m_{ev} , and partition coefficient, k_{ev} , can be calculated. Accordingly, the $\Delta T'$ can be written as [31]:

$$\Delta T' = m_{ev}(\sum_i C_{l,i}^* - \sum_i C_{l,i}^E) \quad (13)$$

Using Eqs. (7), (8), (9), and (13), the α_i (and the $\Delta T'$) can be solved numerically and ΔC_i can be calculated based on the parameters listed in Table S1.

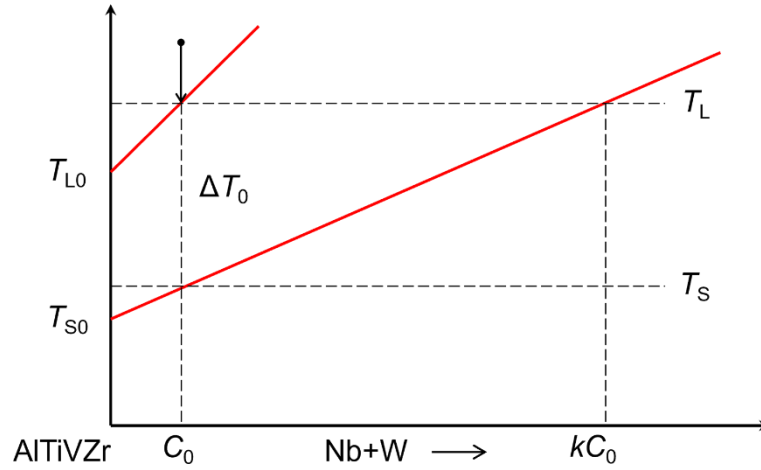


Figure S1. Schematic of a pseudo-binary phase diagram, AlTiVZr–NbW, used to evaluate the solidification parameters of the x W alloys.

Figure S2 shows solidification microstructure features of x W alloys obtained by integrated calculation. As shown in Figure S2a, the CET curve shifts downward with W increasing, implying that a stronger formation trend of equiaxed microstructure exists in the alloy with higher W content. In the processing window for the current calculation, fully columnar microstructure can be obtained in 0W alloy, while such microstructure impossibly exists in 8W alloy (Figure S2b). Similar to grain morphology, W addition exhibits significant effects on many microstructural features (Figure S2c). As W increases, the dendritic tip supercooling ΔT_{tip} , mean size of equiaxed grains d_{GS} and the microsegregation degree ΔC increases. In contrast, the

PDAS λ is insensitive to the change of W content. These comparisons mean that although the increase in W is conducive to the formation of equiaxed microstructure, it may cause other unfavorable changes, such as high microsegregation and brittleness. Therefore, a coordination optimization of processing and W content is important for the development of this new system.

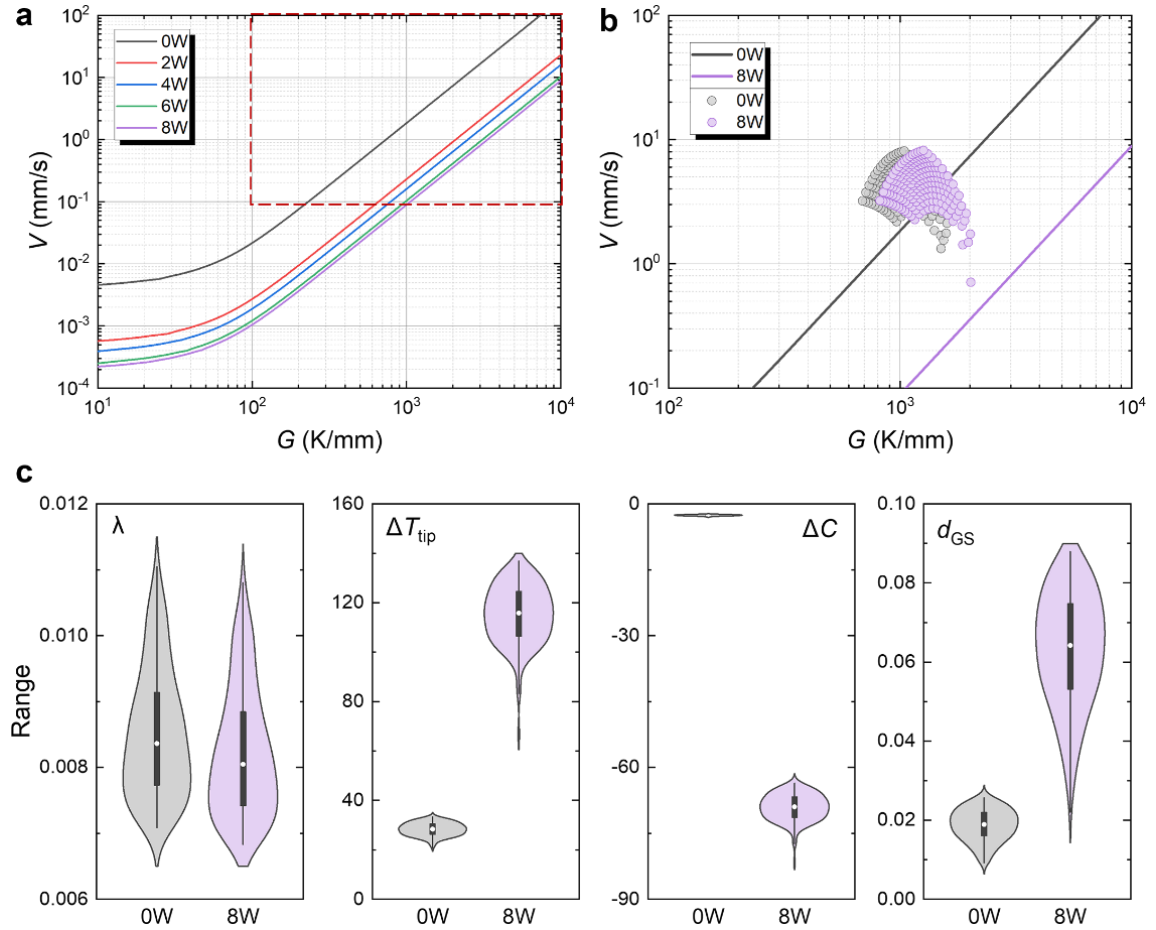


Figure S2. Solidification microstructure features of x W alloys. (a) The CET curves of 0W, 2W, 4W, 6W, and 8W alloys. The processing sets under the CET curves represent the transition to the majority columnar microstructure. (b) Microstructure selection map for the 0W and 8W alloys based on G_m and V_m calculated under the given processing window – the red dash line box marked in (a). (c) Violin plots showing the effects of W content on PDAS λ , constitutional supercooling at dendritic tip ΔT_{tip} , microsegregation degree ΔC , mean size of equiaxed grains d_{GS} , respectively.

1.3. Experimental comparisons

To verify the precision of the integrated calculation, laser remelting experiments were conducted under various processing conditions (Table S2) by a 4 kW LMD system RC-LDM4030 (RAYCHAM Laser Technology Group Co., Ltd.) equipped with a coaxial powder delivery system in an Ar-purged processing chamber with an oxygen content less than 50 ppm. The $(\text{Ti}_{3.6}\text{Zr}_{1.2}\text{V}_{0.8}\text{NbAl}_{0.3})_{100-x}\text{W}_x$, ($x = 2, 4, 6$ and 8 at%) RHEA cast ingots (*i.e.*, 2W, 4W, 6W, and 8W) were chosen as the substrate for laser remelting. These RHEA ingots were prepared by arc melting using pure Ti, Zr, V, Nb, Al and W (>99.95 wt %). Due to the large differences in the melting points of the elements, melting was carried out by placing the raw metal in a water-cooled copper crucible in order of melting point from highest to lowest. To ensure the homogeneity of the melt, each ingot was turned over and re-melted more than 10 times, and the melting time was not less than five minutes each time. Prior to laser melting, the substrates for all experiments were maintained at room temperature and their surfaces were ground with 600-grit SiC paper and cleaned in methanol.

Table S2. The processing parameters (laser power P_L and scanning velocity V_b) used in laser remelting

Sample	P_L (W)	V_b (mm/s)
2W	1200	5
	1400	10
	1600	20
4W	1000	5
	1400	10
	1500	15
	1600	20
6W	1200	15
	1400	10
	1500	5

8W	1600	10
	1000	10
	1200	15
	1400	10
	1500	20

Figure S3 compares the calculated melt-pool geometries with the actual ones. As can be seen, a good agreement between the experimental and calculated melt-pool dimensions, especially the melt-pool widths, can be obtained. This comparison suggests that the solidification conditions calculated by the analytical heat-transfer equation [1, 2] can reasonably represent the actual solidification conditions, and the integrated calculation can give a reliable database for training the ML models.

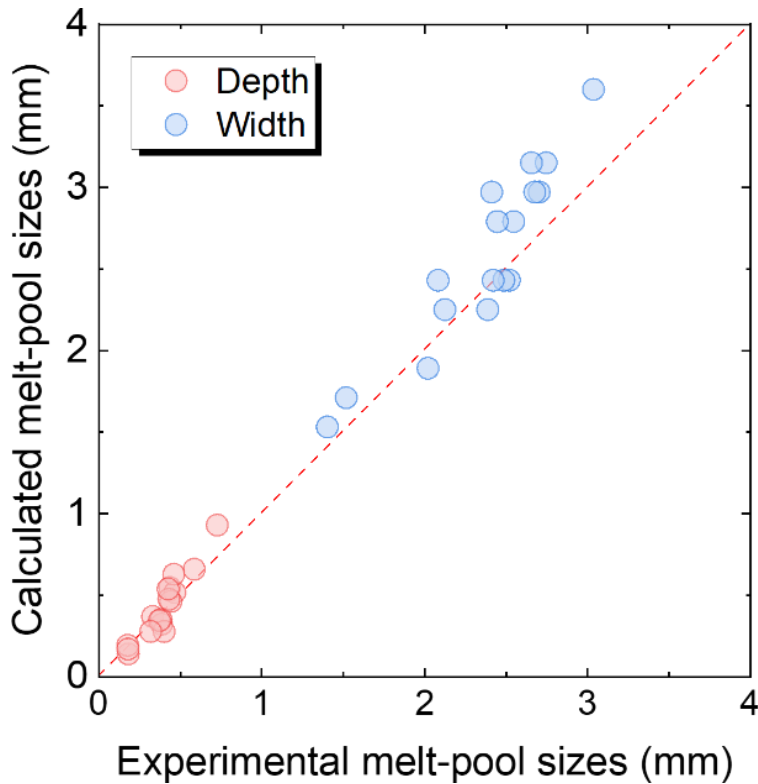


Figure S3. Comparison between the experimental and calculated melt-pool sizes.

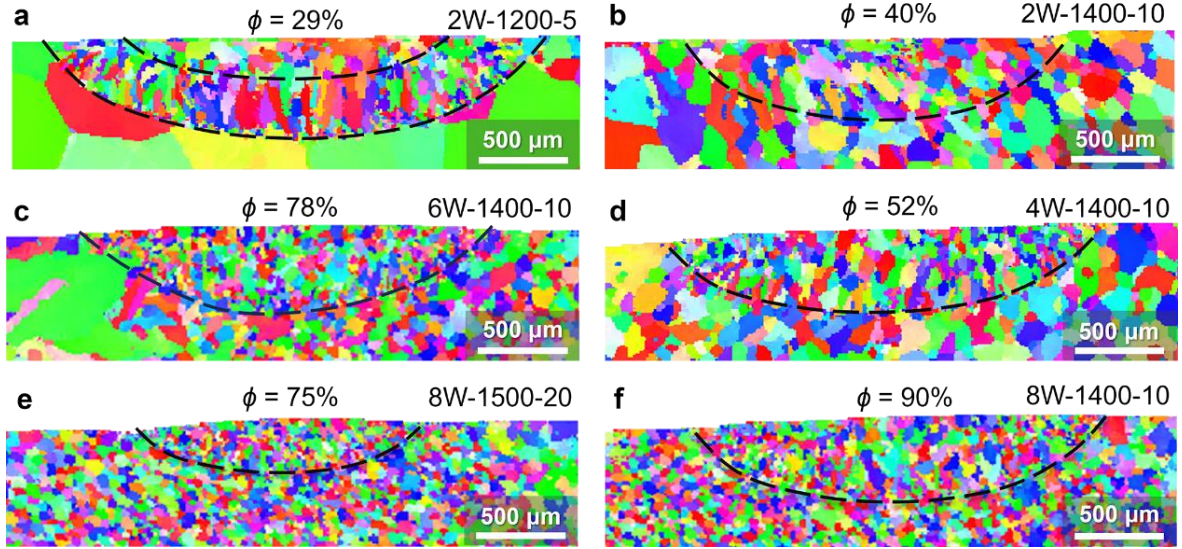


Figure S4. EBSD inverse pole figures showing the solidification grain morphology of laser-remelted x W alloys under different processing conditions. (a) 2W-1200-5, (b) 2W-1400-10, (c) 6W-1400-10, (d) 4W-1400-10, (e) 8W-1500-20, and (f) 8W-1400-10. The ϕ values refer to the volume fractions of equiaxed grains calculated by Hunt's model. The "2W-1200-5" means that the sample is 2W and was performed under a set of laser processing parameters of $P_L = 1200$ W and $V_b = 5$ mm/s.

Figure S4 shows the solidification grain morphology of laser-remelted x W alloys under different processing conditions. In Figure S4a, a microstructure including CET can be seen. This microstructure agrees with the result of the integrated calculation – a $0.66\% < \phi < 49\%$ suggests a morphology mixed the columnar and equiaxed growth. In the same alloy (2W), the trend of columnar growth weakens as ϕ increases to 40% (Figure S4b). Moreover, high W content leads to high ϕ when the processing parameters are the same, as comparison in Figure S4b-d, f, and a ϕ value more than 49% results in a fully equiaxed growth. These trends accord with the results obtained by the integrated calculation (Figure S2a and b), suggesting that the data collected mainly based on integrated calculation can provide an accurate processing–microstructure relationship for ML.

2. ACCURACY COMPARISON IN THE ML MODELS

Figure S5 compares the accuracy of the ML models by the $R^2 - 1$ and MAPE. For the current models, the raw data used to train the ML models were collected by the integrated calculation, which are based on well-developed, experimentally-verified solidification theory calculation rather than scattered experimental data. Accordingly, the almost R^2 values are close to 1 and $R^2 - 1$ values are compared.

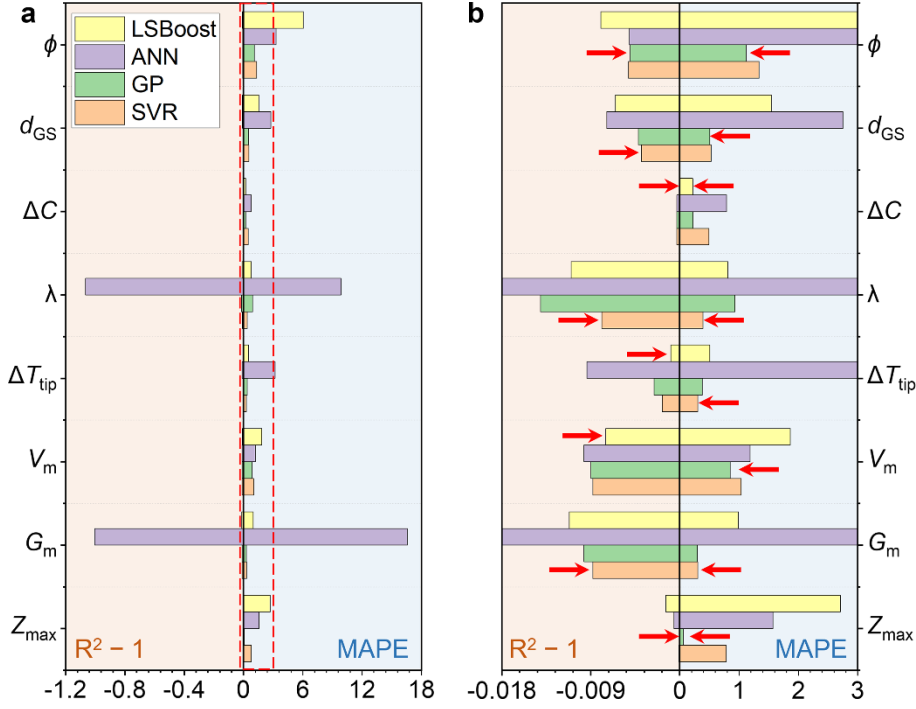


Figure S5. Comparison of the accuracy of the ML models by the $R^2 - 1$ and MAPE. (b) shows a detailed comparison of the red dash line box marked in (a).

As shown in Figure S5b, different surrogate models present different predictive performance for different outputs. Also, for some outputs such as ΔT_{tip} and V_m , the smallest $R^2 - 1$ and MAPE are not be obtained by the same models, which requires a compromise for the model choice. For the most important four microstructural features, λ , ΔC , d_{GS} and ϕ , SVM model can establish the best relationship between the input features and λ , while LSBoost algorithm can accurately predict the ΔC based on the inputs. In contrast, GP method shows superior performance for the prediction of d_{GS} and ϕ . Accordingly, the four models were selected for the inverse design.

REFERENCES

- [1] M. Gaumann, C. Bezencon, P. Canalis, W. Kurz, Single-crystal laser deposition of superalloys: Processing-microstructure maps, *Acta Mater* 49(6) (2001) 1051-1062. DOI: 10.1016/S1359-6454(00)00367-0
- [2] Y.-J. Liang, A. Li, X. Cheng, X.-T. Pang, H.-M. Wang, Prediction of primary dendritic arm spacing during laser rapid directional solidification of single-crystal nickel-base superalloys, *J Alloy Compd* 688(12) (2016) 133-142. DOI: 10.1016/j.jallcom.2016.06.289
- [3] W. Kurz, B. Giovanola, R. Trivedi, Theory of microstructural development during rapid solidification, *Acta Metall Mater* 34 (1986) 823-830. DOI: 10.1016/0001-6160(86)90056-8
- [4] R. Trivedi, W. Kurz, Dendritic growth, *Int Mater Rev* 39(2) (1994) 49-74. DOI: 10.1179/imr.1994.39.2.49
- [5] W. Kurz, Solidification Microstructure-Processing Maps: Theory and Application, *Adv Eng Mater* 3(7) (2001) 443-452. DOI : 10.1002/1527-2648(200107)3:7<443::AID-ADEM443>3.0.CO;2-W
- [6] S. Fukumoto, W. Kurz, Solidification Phase and Microstructure Selection Maps for Fe-Cr-Ni Alloys, *Isij Int* 39(12) (1999) 1270-1279. DOI: 10.2355/isijinternational.39.1270
- [7] M. Vandyoussefi, H.W. Kerr, W. Kurz, Directional Solidification and Delta/Gamma Solid State Transformation in Fe-3% Ni Alloy, *Acta Mater* 45(10) (1997) 4093-4105. DOI: 10.1016/S1359-6454(97)00086-4
- [8] B. Giovanola, W. Kurz, Modeling of Microsegregation under Rapid Solidification Conditions, *Metall Trans A* 22A (1990) 260-263. DOI: 10.1007/BF02656445
- [9] W. Kurz, D.J. Fisher, *Fundamentals of Solidification*, Trans Tech Publications, Switzerland, 1998.
- [10] R. Brooke, D. Zhang, D. Qiu, M.A. Gibson, M. Easton, Compositional criteria to predict columnar to equiaxed transitions in metal additive manufacturing, *Nature communications* 16(1) (2025). DOI: 10.1038/s41467-025-60162-0

- [11] M. Rappaz, W.J. Boettinger, On dendritic solidification of multicomponent alloys with unequal liquid diffusion coefficients, *Acta Mater* 47(11) (1999) 3205-3219. DOI: 10.1016/S1359-6454(99)00188-3
- [12] J.D. Hunt, Steady State Columnar and Equiaxed Growth of Dendrites and Eutectic, *Mater Sci Eng* 65 (1984) 75-83. DOI: 10.1016/0025-5416(84)90201-5
- [13] S.B. Park, Heterogeneous nucleation models to predict grain size in solidification, *Progress in Materials Science* 123 (2022). DOI : 10.1016/J.PMATSCI.2021.100822
- [14] J.D. Hunt, Steady state columnar and equiaxed growth of dendrites and eutectic, *Materials Science and Engineering* 65(1) (1984) 8. DOI :10.1016/0025-5416(84)90201-5
- [15] M. Gaumann, C. Bezencon, P. Canalis, Sing-crystal laser deposition of superalloys processing-microstructure maps *Acta materialia* 46(6) (2001) 12. DOI : 10.1016/s1359-6454(00)00367-0
- [16] T.E. Quested, A.L. Greer, Grain refinement of Al alloys: Mechanisms determining as-cast grain size in directional solidification, *Acta Materialia* 53(17) (2005) 4643-4653. DOI : 10.1016/j.actamat.2005.06.018
- [17] W. Kurz, C. Bezençon, M. Gäumann, Columnar to equiaxed transition in solidification processing, *Science and Technology of Advanced Materials* 2(1) (2001) 185-191. DOI: 10.1016/1359-6454(95)00393-2
- [18] J.M. Vitek, The effect of welding conditions on stray grain formation in single crystal welds – theoretical analysis, *Acta Mater* 53(1) (2005) 53-67. DOI: 10.1016/j.actamat.2004.08.039
- [19] W. Liu, J.N. DuPont, Effects of melt-pool geometry on crystal growth and microstructure development in laser surface-melted superalloy single crystals. Mathematical modeling of single-crystal growth in a melt pool (part I), *Acta Mater* 52(16) (2004) 4833-4847. DOI: 10.1016/j.actamat.2004.06.041
- [20] W. Liu, J.N. DuPont, Effects of substrate crystallographic orientations on crystal growth and microstructure development in laser surface-melted superalloy single

- crystals. Mathematical modeling of single-crystal growth in a melt pool (Part II), *Acta Mater* 53(5) (2005) 1545-1558. DOI: 10.1016/j.actamat.2004.12.007
- [21] T.D. Anderson, J.N. DuPont, T. DebRoy, Stray Grain Formation in Welds of Single-Crystal Ni-Base Superalloy CMSX-4, *Metall Mater Trans A* 41(1) (2009) 181-193. DOI: 10.1016/j.actamat.2004.12.007
- [22] T.D. Anderson, J.N. DuPont, T. DebRoy, Origin of stray grain formation in single-crystal superalloy weld pools from heat transfer and fluid flow modeling, *Acta Mater* 58(4) (2010) 1441-1454. DOI: 10.1016/j.actamat.2009.10.051
- [23] L. Wang, N. Wang, W.J. Yao, Y.P. Zheng, Effect of substrate orientation on the columnar-to-equiaxed transition in laser surface remelted single crystal superalloys, *Acta Mater* 88(4) (2015) 283-292. DOI: 10.1016/j.actamat.2015.01.063
- [24] R. Acharya, R. Bansal, J.J. Gambone, S. Das, A Coupled Thermal, Fluid Flow, and Solidification Model for the Processing of Single-Crystal Alloy CMSX-4 Through Scanning Laser Epitaxy for Turbine Engine Hot-Section Component Repair (Part I), *Metall Mater Trans B* 45(6) (2014) 2247-2261. DOI: 10.1007/s11663-014-0117-9
- [25] R. Acharya, R. Bansal, J.J. Gambone, S. Das, A Microstructure Evolution Model for the Processing of Single-Crystal Alloy CMSX-4 Through Scanning Laser Epitaxy for Turbine Engine Hot-Section Component Repair (Part II), *Metall Mater Trans B* 45(6) (2014) 2279-2290. DOI: 10.1007/s11663-014-0183-z
- [26] Z. Liu, H. Qi, Effects of substrate crystallographic orientations on crystal growth and microstructure formation in laser powder deposition of nickel-based superalloy, *Acta Mater* 87(4) (2015) 248-258. DOI: 10.1016/j.actamat.2014.12.046
- [27] Y.-J. Liang, H.-M. Wang, Origin of stray-grain formation and epitaxy loss at substrate during laser surface remelting of single-crystal nickel-base superalloys, *Mater Design* 102(7) (2016) 297-302. DOI: 10.1016/j.matdes.2016.04.051
- [28] Y.-J. Liang, X. Cheng, J. Li, H.-M. Wang, Microstructural control during laser additive manufacturing of single-crystal nickel-base superalloys: New processing–microstructure maps involving powder feeding, *Mater Design* 130(9) (2017) 197-207.

DOI: 10.1016/j.matdes.2017.05.066

[29] F. Zhang, C. Zhang, S.L. Chen, J. Zhu, W.S. Cao, U.R. Kattner, An understanding of high entropy alloys from phase diagram calculations, *Calphad* 45 (2014) 1-10. DOI: 10.1016/j.calphad.2013.10.006

[30] H.-L. Chen, H. Mao, Q. Chen, Database development and Calphad calculations for high entropy alloys: Challenges, strategies, and tips, *Materials Chemistry and Physics* 210 (2018) 279-290. DOI: 10.1016/j.matchemphys.2017.07.082

[31] Y.-J. Liang, X. Cheng, H.-M. Wang, A new microsegregation model for rapid solidification multicomponent alloys and its application to single-crystal nickel-base superalloys of laser rapid directional solidification, *Acta Mater* 118(10) (2016) 17-27. DOI : 10.1016/j.actamat.2016.07.008