TECHNICAL ARTICLE





Engineering the Surface Melt for In-Space Manufacturing of Aluminum Parts

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Aluminum alloys are among the top candidate materials for in-space manufacturing (ISM) due to their lightweight and relatively low melting temperature. A fundamental problem in printing metallic parts using available ISM methods, based on the fused deposition modeling (FDM) technique, is that the integrity of the final printed components is determined mainly by the adhesion between the initial particles. Engineering the surface melt can pave the way to improve the adhesion between the particles and manufacture components with higher mechanical integrity. Here, we developed a phase-field model of surface melting, where the surface energy can directly be implemented from the experimental measurements. The proposed model is adjusted to Al 7075-T6 alloy feedstocks, where the surface energy of these alloys is measured using the sessile drop method. Effect of mechanics has been included using transformation and thermal strains. The effect of elastic energy is compared here with the corresponding cases without mechanics. Two different geometric samples (cylindrical and spherical) are studied, and it is found that cylindrical particles form a more disordered structure upon size reduction compared to the spherical samples.

Keywords additive manufacturing, in-space manufacturing, phase-field modeling, phase transformation

1. Introduction

For future interplanetary missions, the further away from Earth, the harder it will be to take all the supplies and redundant parts the astronauts might need. Thus, a primary requirement for such missions is robust ISM capability for advanced and lightweight materials. NASA has successfully printed polymer parts using the fused deposition modeling (FDM) technique on International Space Station (ISS). This technology is widely utilized in polymer printing, where the melt extrusion process is employed to deposit filaments of thermal plastics in a predetermined pattern. It was recently converted to print metallic components, in which the printer prints metal/polymer composite filament and then debinds and sinters the produced

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portions to make compact metal parts (Ref 1). The ISM techniques for printing metallic parts are still under development (Ref 2). In the microgravity environment of ISM, the traditional powder-based additive manufacturing methods that rely on gravitational force to hold the feedstock particles together face critical challenges, including (i) preparation of a powder layer with a controlled thickness, (ii) avoiding the flowing of feedstock powder in the print space upon deposition of each feedstock layer or upon direct hit by the energy source. The presence of "Solidification Using a Baffle in Sealed Ampoules (SUBSA)" on the ISS allows heating of the samples up to 850°C (Ref 3). This existing capability makes the FDM technique the most promising method for ISM printing of metallic parts. The current sintering facility at ISS can heat samples as high as 600°C, which would enable the making of aluminum parts with FDM. One critical technical challenge associated with FDM is printing parts with high integrity that is directly related to the formation of surface melt for loosely packed metallic powders.

Reported experimental and atomistic simulations indicate size dependence of melting temperature (Ref 4,5). When a particle size reduction under a critical value is reached, melting temperature deviates from the bulk value due to the increased surface-to-volume ratio (Ref 6). Classical molecular dynamics simulations of BCC single-crystal iron nanoparticles revealed a nucleation temperature of 300K below the melting temperature while melting, and nucleation temperatures were decreased with particle size (Ref 7). Ultrasensitive thin-film differential scanning calorimeter of ultrathin Al films revealed sizedependent melting point depression for Al cluster radius (Ref 8). Melting of Al nanoparticle core inside a strong Al shell was investigated. Two opposite phenomena of reduction in melting temperature with particle size and increment in melting temperature due to pressure build-up in Al core were studied (Ref 9).

The phase-field approach has already been utilized to understand various material problems such as solidification, strain-accommodating solid-state transformations, and surface diffusion (Ref 10). The method has an increasing interest because it overcomes some of the limitations of sharp interface models. This technique avoids applying boundary conditions at an interface that is mathematically difficult and computationally expensive. Instead, it uses additional internal variables, called order parameters, to model the interfaces and microstructure of the material (Ref 11-18). The method captures intermediate phases and applies to particles with a size comparable to the solid-melt interface width. With no interface tracking or remeshing, the phase-field method is computationally more efficient than sharp interface methods. It can also be combined with material databases such as Thermo-Calc (Ref 19) to predict various phases that form during the printing process (Ref 20-21). The interface and defect energies can be determined using atomistic simulations (Ref 22-30) to determine the free parameters of the phase-field model (Ref 31-34).

Ginzburg and Landau developed the thermodynamic theory explaining phase transformation kinetics in materials (Ref 35). It was found that interface thickness increases with temperature and becomes infinite at critical temperature (Ref 36). Surface melting much below melting temperature was observed along with the change in the crystal's shape toward equilibrium shape due to hydrodynamic flow along the surface (Ref 37). A phasefield model is presented to study the coherent microstructure evolution in elastically anisotropic systems with significant elastic modulus inhomogeneity (Ref 38). The size dependency of nucleation in single-crystal nanoparticles was presented using phase-field theory, including surface energy, chemical reactions, and coherency strain. Also, an observation on surface wetting was presented, which shows nucleation occurs when surface wetting becomes unstable (Ref 39).

We pursued a combined theoretical and experimental approach to improve the binding between the sintered particles of metallic parts made using the FDM process by tailoring the surface melt thickness. We developed a unique phase-field model of surface melting that allows direct implementation of the surface energy from experimental measurements and allows controlling the surface width and energy. Here, we used Al 7075 alloy as the model material due to its extensive use in the aerospace industry. We consider two feedstock particle geometries to study the surface melt thickness. Interface propagation, the effect of mechanics, and interface width/energy on the formation and stability of the surface melt are studied. A comparison between two different geometric samples with/ without elasticity is presented.

2. Phase-Field Potential and Kinetic Equations

We developed a phase-field model in the polar coordinate system, satisfying the stability conditions at all temperatures and stresses. The polar order parameter Υ is introduced here to develop thermodynamic potentials for two phases, where $\Upsilon=0$ indicates the origin or the reference phase (melt) and $\Upsilon=1$ is solid. We consider two axisymmetric samples, i.e., a spherical and a cylindrical feedstock particle. The developed Helmholtz free energy with the elastic, thermal, double-well barrier, and gradient energies is $\psi = \psi^e + \psi^\theta + \breve{\psi}^\theta + \psi^\nabla$, where local energy, ψ^l , is $\psi^l = \psi^e + \psi^\theta + \breve{\psi}^\theta$ (Ref 13,16,17). The elastic energy, ψ^e , in terms of total strain, ε_e , elastic strain, ε_e , transformation strain, ε_t , and thermal strain, ε_θ , is

$$\begin{split} \psi^{e} &= 0.5\varepsilon_{e} : \sigma; \varepsilon = \varepsilon_{e} + \varepsilon_{t} + \varepsilon_{\theta}; \varepsilon_{t} = \overline{\varepsilon_{t}}(\varphi(\Upsilon)); \varepsilon_{\theta} \\ &= (\alpha_{m} + \Delta \alpha q(y, a)(\theta - \theta_{e}))I, \end{split} \tag{Eq 1}$$

where $\overline{\epsilon_t}$ is the transformation strain that transforms the elemental volume of solid to melt under $\sigma = 0$, i.e., $\overline{\epsilon_t} = \frac{1}{3} \epsilon_{0t} I$. α_m is the thermal expansion coefficient of melt and $\Delta \alpha$ is the change in thermal expansion coefficient upon melting (Ref 40). The bulk and shear moduli of the material will also vary upon phase transformation as $K(\gamma) = K_m + \Delta Kq(\Upsilon, a)$, and $\mu(\gamma) = \mu_m + \Delta \mu q(\gamma, a)$. We assumed the shear modulus of the melt, μ_m , to be approximately zero (Ref 41).

The other energy terms are defined as follows (Ref 42):

$$\begin{split} \psi^{\theta} &= G_0^{\theta}(\theta) + \Delta G^{\theta}(\theta) q(\Upsilon, 0); \quad \breve{\psi}^{\theta} = A^{S0}(\theta) \Upsilon^2 (1 - \Upsilon)^2; \\ \psi^{\nabla} &= 0.5 \Big[\beta^{so} |\nabla \gamma|^2 \Big] \end{split}$$
(Eq 2)

The change in thermal energy of phases is

$$\Delta G^{\theta}(\theta) = \Delta G^{\theta}_{S0} = -\Delta s_{S0} \left(\theta - \theta^{S0}_{e}\right).$$
 (Eq 3)

The solid-melt energy barrier coefficient is

$$A^{S0}(\theta) = A^{S0}(\theta) = A_c^{S0}(\theta - \theta_c^{S0}).$$
 (Eq 4)

It determines the region of stability of the phases, and θ_c^{S0} is the critical temperature, and we assume $A_c^{S0} = -3\Delta s_{S0}$ (Ref 43). The solid-melt gradient energy coefficient is $\beta^{S0} = (6E^{S0}\delta^{S0})/P$, where P=2.415. Interpolating function qis defined as $q(y,a) = ay^2 - 2(a-2)y^3 + (a-3)y^4$. This fourth-degree polynomial is the lowest degree polynomial that satisfies all the stability conditions (Ref 16).

Here, "a" is a free parameter of the model material that describes the profile of the property variation across the interface. We assume a=3, i.e., equivalent to a symmetric property variation profile across the interface unless stated otherwise. Applying an irreversible thermodynamic procedure based on the first and second laws of thermodynamics and assuming a linear relation between thermodynamic deriving forces and the rate of change of the internal variables (order parameters), we derived the Ginzburg – Landau (GL) kinetic equation as

$$\frac{1}{L_{\Upsilon}}\frac{\partial \Upsilon}{\partial t} = -\frac{\partial \psi^l}{\partial \Upsilon} + \nabla \cdot \left[\beta^{S0} \nabla \Upsilon\right].$$
 (Eq 5)

where ∇ is in the deformed state, which leads to the following boundary conditions:

$$\frac{\partial \psi}{\partial \nabla \gamma} . n = \beta^{S0} \nabla \gamma . n = -\frac{d\gamma}{d\Upsilon}, \ \sigma_n = \frac{2\gamma(\Upsilon)}{R} + \overline{p}$$
(Eq 6)

where n is the unit normal to the boundary, σ_n is the normal component of the surface stress, R is the mean radius of the particle, and \overline{p} is the external pressure. The surface energy as a function of the order parameter is defined as, $\gamma(\Upsilon) = \gamma_l + \Delta \Upsilon q(\Upsilon)$, where γ_l is the surface energy of melt

and $\Delta\Upsilon$ is the change in the surface energy upon melting. Substituting the energy terms and their definitions, the GL equation is

$$\frac{1}{L_{\Upsilon}} \frac{\partial \Upsilon}{\partial t} = \nabla . \left[\beta^{S0} \nabla \Upsilon \right] - 2\Upsilon (1 - \Upsilon) \left[6\Delta G^{\theta}(\theta) \Upsilon + A^{S0}(\theta) (1 - 2\Upsilon) \right] - 0.5\sigma : \varepsilon_e \frac{\partial q(y, a)}{\partial \Upsilon}.$$
(Eq 7)

The GL equation can be solved in an infinite sample analytically neglecting the elasticity, where the

$$\Upsilon(x) = \left[1 + \exp\{-P(x - x_0)/\delta^{S0}\}\right]^{-1}.$$
 (Eq 8)

The interface energy can be calculated by calculating the excess energy with respect to the bulk solid ψ_s and melt ψ_0 phases,

$$E^{50} = \int_{-\infty}^{\Upsilon=0.5} (\psi - \psi_0) dx + \int_{\Upsilon=0.5}^{\infty} (\psi - \psi_s) dx.$$
 (Eq 9)

Here, $\psi = \psi^{\theta} + \breve{\psi}^{\theta} + \psi^{\nabla}$; $\psi_0 = (\psi^{\theta} + \breve{\psi}^{\theta})_{\Upsilon=0}$; $\psi_s = (\psi^{\theta} + \breve{\psi}^{\theta})_{\Upsilon=1}$. Substituting Eqs. (2)-(4) in Eq. (9), considering the analytical solution Eq. (8), the interface energy is calculated as follows:

$$E^{S0} = \frac{1}{6} \sqrt{2\beta^{S0} \left[A^{S0}(\theta) - 3\Delta G^{\theta}_{S0}(\theta) \right]}.$$
 (Eq 10)

Interface energy as a function of position for the cylindrical and spherical samples, respectively, is

$$E = \left(\int_{0.01}^{0.5} (\psi - \psi_0) r dr + \int_{0.5}^{0.99} (\psi - \psi_S) r dr\right) / r$$
 (Eq 11)

$$E = \left(\int_{0.01}^{0.5} (\psi - \psi_0) r^2 dr + \int_{0.5}^{0.99} (\psi - \psi_S) r^2 dr\right) r^2$$
(Eq 12)

The analytical solution of the GL Eq. (7) also leads to a relationship for the interface width, which is defined as the inverse of the maximum slope of the strain profile at the interface (Ref 44),

$$\delta^{S0} = \{ dq [\Upsilon(x), 3] / dx \}_{\max}^{-1}$$

$$\delta^{S0} = p \sqrt{\beta^{S0} / [2A^{S0}(\theta) - 3\Delta G^{\theta}_{S0}(\theta)]}$$
 (Eq 13)

The choice of the interpolation function q(x,a) instead of the order parameter itself is because the order parameter does not have any physical meaning. In contrast, q represents the variation of properties across the interface. The value of "a" in q(x,a) is chosen to be 3, leading to symmetric property variation across the two phases and the natural choice when such information is not available experimentally. Here, p=2.415 and is constant. Using the analytical solutions, Eqs. (10) and (13), we defined two dimensionless parameters, i.e., (i) ratio of solid-vacuum to solid-melt interface energy KE. We have investigated the effect of these two parameters, which can be tweaked by alloying the feedstock material, on the formation and stability of the surface melt.

3. Surface Tension Measurements

An Al7075-T6 plate (Kaiser Aluminum, USA) and high alumina matrix sheets RS-99R of dimensions 72.6 mm × 72.6 mm ×3.2 mm (ZIRCAR Refractory Composites, Inc.) were utilized to measure the surface tension of the Al7075-T6 alloy using the Sessile Drop method (Ref 45). Three cuboid-like Al 7075-T6 samples were cut and ground to an average of 7.3 mm \times 5.2 mm \times 5.2 mm using a 320-grit size silicon carbide paper. Next, aluminum oxide refractory sheets of 57 mm \times 36 mm \times 3.5 mm were cut and used as the sample base in the furnace. The surface tension of the Al 7075-T6 sample is measured by conducting three sessile drop experiments under vacuum $(10^{-3}-10^{-4})$ Torr) using the SCA 20 software module of the OCA 25-HTV 1800 video-based contact angle (CA) measuring and contour analysis system for high temperatures and vacuum (DataPhysics Instruments, Germany).

The samples were heated to 750 °C at a heating rate of 5 °C/ min to form an elliptical-shaped droplet and held isothermally at 750°C for 30 min. Sample profiles were recorded at one frame per second. Note that the solidus and liquidus temperatures of Al 7075-T6 alloy are ~477 and 635.0°C, respectively. A profile fit was conducted to determine the contact angle and calculate the surface tension using the Laplace–Young profile method. The method requires a known sample density, which was calculated by estimating the sample volume via the profile.

The measurement was repeated with three samples to estimate the surface tension values as a function of temperature and contact angle. For each sample, the variation of surface tension and distribution during the isothermal period (\sim 1800 images) were determined with each test resulting in a normal distribution with a standard deviation of less than 2 mN/m. Likewise, the aggregated results provide a statistical mean of 0.134 J/m² with a standard deviation of 3.45 mN/m.

4. Sintering and Characterization

Aluminum 7075 metal powders, supplied by AMERICAN ELEMENTS, magnesium powders with a purity above 99%. polyethylene oxide (PEO) powders, polypropylene (PP) powders, and stearic acid (SA) are used to mimic the FDM process at ISS. The polymer binder consists of PP, PEO, and SA in a mass ratio of 6:3:1. In this study, we focus on the role of feedstock characteristics on the formation of surface melt and, thus, the density of printed parts. We consider a printed green body with a 1:9 mass ratio of the total polymer to Al-7075 powder, mimicking the final stages of sintering that the role of surface melt dominates. The effect of print parameters, such as feedstock flowability, is not studied here. The polymer binder mixture was dissolved in an appropriate amount of toluene before the Al 7075 powders were added to achieve good mixing of polymer with the metal powders. To ensure that the polymer binder was fully dissolved in toluene, the toluene solution was heated to 100 °C. After fully dissolving the polymer binder in toluene, the Al 7075 powders were first added and dispersed in an ultrasonic shaker for 5 minutes before an additional 30 minutes of electromagnetic stirring was carried out. Finally, after all the solution was evaporated slowly at room temperature for 36 hours, Al-7075 powders coated with



Fig 1 Effect of Mg content on samples' porosity. SEM images of Al-7075 samples sintered at 620 °C for 4h. (a) pristine Al7075 sample, (b) Al7075 with 1%Mg sample, (c) Al7075 with 2%Mg sample. Pores are designated in red using ImageJ software, indicating reduction in density of pores upon Mg addition.

polymer binder were collected as the precipitates. The same procedures were used to coat magnesium powders with polymer binders. The mass ratio of the total polymer binder to magnesium powder is also 1:9.

To ensure that all large polymer agglomerates were removed, only powder particles less than 75 μ m in diameter were selected. An 8000M Mixer/Mill® High-Energy Ball Mill machine (Spex SamplePrep) was used to mix the Al-7075/ polymer powder with different weight percentages of magnesium/polymer powder (1% and 2%) for one hour. In this mixing process, no grinding balls were applied. Disk-shaped specimens with a diameter of 12.7 mm and a thickness of 2 mm were prepared using the mixed powders in a hot compression process with a temperature and pressure of 150 °C and 20 MPa, respectively. Before sintering, a debinding process at 300 °C for 30 minutes in the air was applied. The sintering process consists of two stages: Stage 1 is to heat the specimen to 500 °C for two hours with a heating rate of 10 °C/min, and stage 2 is to further heat the specimen to 620 °C for four hours with a fixed heating rate of 5 °C/min. All the sintering process was performed in an MTI KSL-1100X Muffle Furnace.

Scanning electron microscope (SEM) and ImageJ software were utilized to investigate the distribution of the polymers in the matrix and microstructures, indicating a significant reduction in the number of pores upon Mg addition (Figure 1). The average pore area of the Al-7075 sample, the Al-7075 plus 1%Mg sample, and the Al-7075 plus 2%Mg sample is 1.98 ± 0.22 , approximately 1.53 ± 0.36 , and $1.17\% \pm 0.19\%$, respectively, relative to the overall area. The average particle size for the Al-7075 sample, the Al-7075 plus 1%Mg sample, and the Al-7075 plus 2%Mg sample is approximately 9.55 \pm 3.90, 9.89 \pm 3.11, and 11.21 μ m \pm 3.47, respectively. The sintered samples were also tested for density using the Archimedes method. The average density of the Al-7075 sample, the Al-7075 plus 1%Mg sample, and the Al-7075 plus 2%Mg sample is approximately 2.47g/cm3 \pm 0.07, 2.49g/cm3 ± 0.06 , and 2.56g/cm3 ± 0.03 , respectively.

In contrast to our experimental measurements, the addition of lighter Mg particles shall reduce the density of sintered parts. Thus, the only viable hypothesis explaining the increase in the density of printed parts is the reduction in the porosity of asbuilt samples, as marked by red in Figure 1. Although direct experimental measurement of a surface melt using in situ experimental techniques upon alloying is ideal, such experiments are highly challenging if at all possible. Furthermore,



Fig. 2 Effect of Mg content on mechanical characteristics (microhardness). Adding Mg results in the increase in the surface energy, a thicker surface melt, better densification, and improved mechanical performance. Adding 2% Mg increased the microhardness by $\sim 20\%$.

such experiments are generally performed under a high vacuum environment, changing the surface melt stability range compared to the real processes. Here, we considered two possible avenues for alloying, e.g., with Mg, to increase the thickness of the surface melt, i.e., adding Mg (i) increases the interface energy ratio of the solid alloy surface to its melt (parameter *KE* in the model), and (ii) increase the ratio of surface melt width to the solid surface width (parameter 1/KD in the model). We investigated both cases in our simulations.

We further investigated the effect of Mg content on the mechanical performance of sintered samples using microhardness indentation tests at a load of 500 g, Figure 2. The hardness increases from 58.82 ± 2.10 HV0.5 to 69.68 ± 1.13 HV0.5 as the Mg content increases from 0 to 2 wt.%. Increasing the element Mg content will increase the surface energy and, thus, the thickness of the surface melt, which promotes the densification process and increases the hardness of the specimen.

5. Material Specifications

We considered Al 7075 as our model material with the following specifications (Ref 46-50): kinetic coefficient, $L_{\Upsilon} = 400$ m.s/kg, solid-melt interface width $\delta_{S0} = 1nm$, solid-melt interface energy $\gamma_l = 0.134$ J/m², critical temperature for the loss of stability of melt and turning into solid, $\theta_c = 379.1K$, density, $\rho_0 = 2710$ kg/m³, change of entropy, $\Delta s_{S0} = -35.46$ kJ/m³, K, bulk modulus, $K_m = 41.3GPa$, shear modulus, $K_s = 71.1GPa$, thermal expansion coefficients of melt and solid, $\alpha_m = 4.268$ 10⁻⁵K⁻¹ and $\alpha_s = 3.032$ 10⁻⁵K⁻¹ and volumetric transformation strain, $\varepsilon_{0t} = 0.06$. It should be noted that the value of $\Delta \Upsilon$ varies upon changing the KE.

6. Numerical Implementation

The GL kinetic and elasticity equations are solved using the commercial finite element software package COMSOL Multiphysics (Ref 51) without applying any external force. A relative calculation error of 1e-4 is used with a mapped mesh of quadratic Lagrange elements with five to eight elements perinterface width, ensuring a mesh-independent solution. The time scale of the simulations is on the order of magnitude of 1 ns. The microstructure evolution is predicted by solving the GL Eq. (7) using a time-dependent solver with the implicit timestepping method. An initial time step on the order of 1 ps is chosen, where the solver automatically selects subsequent integration time steps. A stationary solver is used to solve the stationary GL equations and find the critical nucleus associated with the maximum energy of the structure. A nonlinear solver is used that is an affine invariant form of the damped Newton method.

7. Results and Discussion

The relative ratios of interface width and energy for both melt and solid phases, KD and KE, determine the formation and stability range of the surface melt, which can be tailored by alloying the feedstock. Here, we investigate the effect of KD, KE, temperature, and particle size on the formation and stability of the surface layer melt. We described the effect of temperature in terms of the degree of overheating/underheating by defining a parameter $K_{\theta} = \theta - \theta_e$.

The variation in the energy barrier height between the solid and melt as a function of the order parameter Υ is plotted in Fig. 3(a), (b) for different KE and KD values at solid/melt equilibrium temperature, revealing its increase upon decrease (increase) in KE (KD). Figure 3(c) shows the variation in the local energy upon changing the temperature for KE=KD=1. We also investigated the effect of KD and KE on the critical



Fig. 3 Energy landscape as a function of Υ . Local potential ψ^l vs Υ is plotted for different KE at $K_{\theta}=0$ (a), KD at $K_{\theta}=0$ (b), and K_{θ} for KD=KE=1 (c). The energy barrier between the solid and melt increases by reducing (increasing) KE (KD).



Fig. 4 Range of metastability temperature. Instability temperature versus KD at KE = 1 (a) and KE at KD=1 (b), indicating a linear increase in the range of metastability temperature as a function of KD and a nonlinear decrease in this range upon increasing KE. The negative temperatures indicate the degree of stability at 0K, i.e., the lower the critical temperature for loss of stability of melt, the more stable the melt.



Fig. 5 Structure of spherical- and rod-shaped feedstock particles as their size becomes comparable to the interface width. Spherical samples of radii 3 nm (a) and 1 nm (b), and cylindrical samples of radii 3 nm (c), 1 nm (d) are considered at equilibrium temperature for KE=2 and different KD values. Rod-shaped feedstock materials are more prone to the formation of melt.

temperature for the loss of stability of homogenous solid and melt phases. Figure 4 revealed a linear (nonlinear) increase in the metastability range of temperatures as a function of KD (KE).

Atoms located on the surface experience a different environment than those within the bulk of the material. Thus, it is expected that the feedstock properties depend on the size and geometry of its constituents. We considered two particle geometries, rod and spherical, and studied their structure as their size became comparable with the solid-melt interface at equilibrium temperature (Figure 5). Our results indicate that the structure of rod-shaped feedstocks is more sensitive to their size and the value of KD. Thus, elongated particles could be melted at a lower temperature.

We further investigated the effect of interface position on its energy. Here, the interface position corresponding to the location of a sharp interface is where the order parameter Υ =0.5. These calculations are performed by placing the interface at different locations across samples of 200nm in diameter, by choosing different x_0 values in Eq. (8) Calculations are performed for KD=2, and KE=2, with mechanics, at different temperatures. For the spherical sample, Fig. 6(a), interface energy decreases close to the core, followed by a sudden increase at the position range of $0\sim10$ nm near the center of the particle. At the outer surface of the particles, range $90\sim100$ nm, the interface energy monotonously increases. The largest undercooling temperature results in the largest reduction in the interface energy close to the core and the largest increase in the surface energy close to the outer surface. Thus, there is a crossover between interface energy and temperature dependency. For cylindrical samples, Fig. 6(b), the interface energy reduces close to the core at undercooling temperatures while converging to the same value on the surface. Thus, while the surface energy is a strong function of temperature for spherical samples, it becomes temperature-independent for rod-shaped samples.

We further studied the effect of KD on the critical nucleus's energy, where the critical nucleus was found by solving the stationary GL equation and elasticity equations using an affine invariant form of the damped Newton method with initial conditions close to the final configuration of the critical nucleus. Our results indicate a peak in the critical nucleus



Fig. 6 Interface energy at a function of interface position. Two sample geometries, (a) plot at different temperatures for spherical (a) and cylindrical (b) sample. Results are obtained for a 100-nm sample considering mechanics and changing temperature above and below equilibrium melting temperature θ_e . Both parameters KD and KE considered being 2 for the simulations.



Fig. 7 Energy of melt critical nucleus vs. KD. Critical nucleus energy for the two sample geometries (a) spherical and (b) cylindrical samples with a radius of 100 nm are calculated considering cases with and without elastic energy for KE=1 and various KD values. Elastic energy plays a key role, specifically at low KD values.

energy at KD value 0.3, which gradually declines when elastic energy is considered. In contrast, neglecting the elastic energy, the energy of the critical nucleus is lower for all KD values (Figure 7), emphasizing the vital role of elastic energy in the formation of the surface melt.

We further studied the size dependence of common spherical feedstock particles. We revealed that melting temperature is size-dependent, and its degree of dependence is a function of KD and KE. Melting temperature becomes a weak function of size for particles with a diameter larger than 40nm (Figure 8). With the increase in interface width, a decrease in melting temperature was observed, while decreasing the interface energy reduced the melting temperature. However, the melting temperature increased by ~30% when the interface energy of solid-vacuum is 60% of solid-liquid interface energy, Fig. 8(b), getting close to the critical temperature for the loss of stability of the homogeneous solid phase.

8. Conclusion

We developed a phase-field model of melting with the correct thermodynamic formulation of the surface tension. The proposed model is solved numerically using the finite element technique to investigate the effect of various parameters that alloying can control on the formation and stability of the surface melt to enable the ISM of metallic parts using the FDM technique. We used Al 7075 as our model material and studied the effect of elasticity and feedstock size and shape on the stability of surface melt. We introduced two key dimensionless parameters, ratios of solid-vacuum to solid-melt interface energies and width, KE and KD, respectively.

Our results revealed that the energy barrier between the two phases is a function of KD and KE. The range of metastability of the surface melt is shown to be a direct linear function of KD and an inverse function of KE. We further found that the



Fig. 8 Melting temperature as a function of feedstock particle size. Particle radius vs. melting temperature for different KD (a) and KE (b) values for spherical feedstock particles.

structure of the feedstock material is a strong function of their geometry when their size becomes comparable with the solidmelt interface width. The interface energy of melt was shown to be a strong function of the interface location and undercooling temperature, where the surface energy is larger at lower temperatures in spherical feedstock particles. The surface energy is almost independent of temperature in the case of rod-shaped feedstock particles.

Furthermore, the energy of the critical nucleus also reduces upon the increase of KD and upon increasing the elastic energy contribution and is more significant for spherical particles than the rod-shaped ones. Finally, we showed a strong dependence of melting temperature on the feedstock particle size, specifically for particles of a diameter smaller than 80 nm and when KD is reduced. The results presented here provide a fundamental understanding of the role of alloying on the formation and stability of the surface melt, which has a direct implication in printing high-quality components using FDM for ISM.

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