Effect of Crystal Growth Angle and Solidification Rate on Molten Zone Stability in Zone Melting of High-Melting-Point Metals: Postprint

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Abstract

A stability analysis of the molten zone height in electron beam zone melting of high-melting-point metals Nb, W, Ta, Mo, and Ir was conducted. It was found that when zone melting specimens of the same size, the ranking of achievable stable molten zone heights was Nb > Mo > W > Ta > Ir. The calculated crystal growth angles for these five metals were in the range of 8°–13°. It was discovered that the non-zero growth angle plays a dominant role in the molten zone height for large-sized specimens, while the actual crystal growth angle of metals is related to the interface growth mechanism. When the growth mechanism is rough interface growth, the growth angle changes little with increasing zone melting solidification rate; whereas for the dislocation growth mechanism, the growth angle decreases with increasing zone melting solidification rate; if the facet growth mechanism is operative, the growth angle decreases significantly at low speeds and increases with increasing solidification rate. Employing a relatively high solidification rate (approximately 1 mm/min) is beneficial for controlling the variation in crystal growth angle and molten zone height for Ir and Mo, which is basically consistent with experimental results on Mo zone melting single crystal growth.

Full Text

Introduction

Single crystals of refractory metals W, Mo, Nb, Ta, and Ir and their alloys are widely used in many high-tech fields such as electronics, electrical engineering, aviation, aerospace, and medicine due to their excellent comprehensive properties [1~3]. In particular, W and Mo single crystals have become ideal emitter materials for space reactor ion energy converters because of their superior high-temperature fatigue resistance, low ductile-to-brittle transition temperature, high vacuum work function, small thermal neutron capture cross-section, low electrical resistivity, and good compatibility with nuclear materials, and have been successfully applied in TOPAZ-type space reactors. Nb single crystals are currently being developed and applied as acceptor materials for thermionic fuel elements. For Ir single crystals, they serve as the best epitaxial growth substrates for diamond materials [4], and single-crystal yttrium aluminum garnet (with a melting point near 2000 °C) pulled from Ir single crystal crucibles exhibits high quality with a service life reaching 2500–3000 h [5].

All these metals W, Mo, Nb, Ta, and Ir are high-melting-point materials, with Ir having the lowest melting point at 2443 °C and W reaching as high as 3370 °C. Consequently, no suitable crucibles are available for melt-based single crystal growth, making the crucible-free electron beam floating zone method (EBFZM) the only viable option. This method is also the most effective technique for preparing refractory metal single crystals [6]. To date, using this technology, refractory single crystals of W and Mo with diameters exceeding 30 mm have been successfully prepared both domestically and internationally [7,8]. Since the key to EBFZM processing of refractory metal single crystals lies in maintaining the stability of the molten zone, which is sustained by surface tension and closely related to alloy density, it is noteworthy that among these five metals, Ir has the highest solid metal density at 22.42 g/cm^3—17% greater than that of W (19.35 g/cm^3) and double that of Mo (10.2 g/cm^3). Therefore, preparing Ir single crystals is considerably more challenging than growing W and Mo single crystals. Moreover, zone stability is also intimately related to the crystal growth angle [9]. Although successful preparation of W and Mo single crystals has been reported, the relationship between the crystal growth angle and zone stability for these five metals has not yet been investigated.

This work first discusses the stability of the molten zone in EBFZM from a theoretical perspective, then calculates the crystal growth angles of the aforementioned five high-melting-point metals, elucidates the roles of the growth angle and solidification rate on zone stability, and obtains reasonable ranges for zone height and solidification rate in refractory metal single crystal growth. These findings not only provide valuable guidance for the growth of Nb, Ta, and Ir single crystals but also serve as a useful reference for other refractory metal crystal growth processes.

1 Theoretical Model

[Figure 1: see original paper] presents a schematic diagram of the electron beam floating zone method for refractory metals, where Fig. 1a shows the molten zone shape during upward solidification and Fig. 1b shows that during downward solidification. In the figure, a represents the crystal growth angle, which varies among different materials. For semiconductor Si, a is approximately 10°–11° [10], while for InSb, a ranges from 25°–30° [11]. The magnitude of a significantly affects the shape and stability of the molten zone. For both zone configurations shown in Fig. 1, when the zone height exceeds a certain value, the hydrostatic pressure generated by the zone height cannot be balanced by the surface tension of the liquid metal, leading to zone collapse and failure of the crystal growth experiment. Therefore, investigating the effect of the growth angle on zone stability is crucial for floating zone crystal growth.

During steady-state crystal growth by EBFZM as depicted in Fig. 1, if we neglect the centrifugal force caused by crystal rotation (the rotation speed during crystal growth is typically 1-2 r/min, and the resulting centrifugal force is at least one order of magnitude smaller than surface tension [9]), the hydrostatic pressure generated by the zone height must be supported by the surface tension of the molten metal. Consequently, the following force balance relationship exists in the molten zone:

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where g is the surface tension of the zone-melted metal (numerically equal to the liquid/vapor surface energy), R_1 and R_2 are the two principal radii of curvature of the molten zone (shown in the cross-section in Fig. 1b), r is the density of the liquid metal, g is the gravitational acceleration, and z is the vertical coordinate corresponding to the zone height.

2 Results Analysis and Discussion

2.1 Simplified Case with Zero Growth Angle

Under simplified conditions, if the molten zone shape is a cylinder of uniform diameter ($R_1 = R_2 = R$) and the zone side remains vertical (i.e., the crystal growth angle $a = 0$), we have:

(1) $a = 0$

At this time, Eq. (1) can be transformed into:

The liquid metal surface tension can thus support a molten zone height of:

When R , we have h . From Eq. (3), it is evident that as the zone radius R decreases, the stable zone height increases. When R , h , which is clearly unreasonable because as the zone height increases, the molten zone will self-contract under surface tension into a spherical shape to reduce surface area and minimize the total system free energy. This phenomenon is known as Rayleigh instability [12]. According to the Rayleigh instability criterion, the molten zone will not contract into a sphere when the zone height satisfies the following condition:

The equality in Eq. (4) gives the maximum stable zone height. When h exceeds the value given by Eq. (4), the zone itself will disintegrate. Table 1 lists the physical parameters of the five high-melting-point metals [13,14]. Figure 2 [Figure 2: see original paper] shows the calculated stable growth zone height curves for the five metals using the parameters from Table 1 in combination with Eqs. (3) and (4), where the maximum supportable zone height (h) is:

Since the zone height caused by Rayleigh instability in Eq. (4) is directly proportional to the zone radius, while the zone height stabilized by surface tension in Eq. (3) is inversely proportional to the zone radius, these two curves intersect at a point shown by the intersection of the two dashed lines in Fig. 2. To the left of the intersection point, the surface tension-stabilized zone height is much greater than that caused by Rayleigh instability; therefore, in this region, the floating zone height is primarily determined by Rayleigh instability effects. To the right of the intersection point, the Rayleigh instability-induced zone height gradually increases, while the surface tension-supported zone height decreases with increasing zone size. Consequently, to the right of the intersection point, the stable floating zone height depends on the magnitude of surface tension. At the intersection point, the corresponding zone height (h) should be: , so for the case of $a = 0$, the stable floating zone height is:

Additionally, the data in Table 1 reveal that the surface tensions (g) of high-melting-point metals differ only slightly, whereas their densities vary significantly. Therefore, metals with lower density can support larger zone heights under surface tension. For example, the liquid metal density of Nb is 7.83 g/cm^3, while that of Ir is 20 g/cm^3. When zone-melting samples of the same size, the surface tension can support a Nb zone height 2.5 times that of Ir. Thus, the ranking of surface tension-stabilized floating zone heights in Fig. 2 is Nb > Mo > W > Ta > Ir.

Furthermore, based on Eq. (5) and assuming $a = 0$, the maximum zone heights for high-melting-point metals Nb, Mo, Ta, W, and Ir are calculated to be 13.7, 11.9, 10.1, 10.2, and 8.4 mm, respectively (Table 1). These values correspond to the vertical coordinates of the intersection points in Fig. 2, with the associated horizontal coordinates (zone radii) being below 2.5 mm. This indicates that for stable zone-melting of large-diameter samples, the achievable crystal growth zone height must be correspondingly reduced.

2.2 Non-zero Growth Angle Case

Since when $a = 0$ the zone side is vertical, the zone shape is identical to the grown crystal shape. However, experimentally obtained crystal dimensions are not necessarily the same as the zone shape, indicating that the actual crystal growth angle a during solidification can be non-zero. Moreover, existing experimental results for Mo single crystal growth show that when zone-melting large-diameter samples, the stable growth zone height can exceed 5 mm [15], which is larger than the results shown in Fig. 2, demonstrating that the crystal growth angle can enhance zone stability to some extent. For α , we can analyze the following cases:

Considering only one principal radius of curvature (2) α :

Substituting the mathematical expression for the R_1 principal radius of curvature into Eq. (1) yields:

3 2 =

Combining with the coordinates in Fig. 1b:

[1 + (d r = -tan(π r^2 = d) = - 1 α , substituting Eqs. (8) and (9) into Eq. (7) gives:

r (-tan

where β r = - . Substituting Eq. (8) into Eq. (10):

Combining with the coordinates in Fig. 1b (since the molten zone is symmetric, only half of the zone is analyzed) and integrating Eq. (11):

2 gz g cos 1 = π is the actual growth angle in zone-melted crystal growth. Therefore, Eq. (13) can be rewritten as:

g sin

Considering these two parts separately, the final surface tension-supportable zone height (h) is:

- 2π 1 = 0 g sin 1 $\neq$ 0 g sin 1 $\neq$ 0 1 = 0

Additionally, research [16] has shown that the actual crystal growth angle relates to the solidification rate as follows:

$V^{-1\ 3}$

where ΔT and V are the undercooling and solidification rate during metal solidification growth, respectively; α is the crystal growth angle at zero solidification rate, which is related to the solid/liquid interface energy (g) and liquid/vapor surface energy (g) [17]:

Based on the solid/liquid interface energy and liquid/vapor surface energy values in Table 1, the calculated crystal growth angles α for the five metals range from 8.4° to 12.7°, showing relatively small differences. Among these five metals, only W has reported experimental growth angle values [8] of 20° ± 5°. The calculated W growth angle from Table 1 is 12.0°, which is close to the minimum measured value of 15° but deviates significantly from the maximum value of 25°.

lv sin exp(-

where is the kinetic coefficient for continuous growth mechanism, is the kinetic coefficient for dislocation growth mechanism, and coefficients A and B are kinetic coefficients for faceted growth. In high-melting-point metal zone growth, all three mechanisms are possible. For instance, in Mo single crystal growth, rough interface growth yields (111)-oriented single crystals, whereas faceted growth produces polycrystalline structures, with significantly different crystal orientations obtained through different interface growth mechanisms [19].

2.3 Effect of Solidification Rate on Growth Angle and Zone Height

Given that Mo single crystal growth has been experimentally reported while Ir single crystal growth is more challenging, we analyze these two metals as examples. Figure 3 [Figure 3: see original paper] shows the relationship between zone stability height and zone radius for the two metals at zero solidification rate, based on Eqs. (14) and (15). For small zone radii, the zone height calculated from Eq. (15) is much greater than that from Eq. (14), indicating that small-diameter samples primarily exhibit vertical side walls ($a = 0$). For large zone radii, the results from Eqs. (15) and (14) are similar. In crystal growth, according to metal solidification theory, V follows the relationship [18]:

The results demonstrate that non-zero growth angles dominate the zone height support for large-diameter samples. Thus, utilizing non-zero growth angles enables zone-melting of large-diameter samples, which explains why needle-eye and pedestal techniques can grow large single crystals. For semiconductor Si, the needle-eye technique can produce Si single crystals 200 mm in diameter with zone heights around 16 mm [17]. Specifically for the metals Mo and Ir in this work, when the zone radius reaches 20 mm, Eq. (15) yields zone heights of 7.4 mm for Mo and 4.6 mm for Ir, while Eq. (14) gives 6.3 mm and 4.1 mm, respectively. The small difference indicates that both equations can provide zone height parameters for zone growth of large-diameter zones.

Further considering the effect of solidification rate on crystal growth angles for Ir and Mo, Fig. 4 [Figure 4: see original paper]a and b illustrate this relationship. Parameter values for Eq. (18) are taken from reference [18]: for Ir in Fig. 4a, $k = 1$, $mc = 1$, $ms = 10^{-2}$, $A = 10^2$, $B = 1$; for Mo, $k = 1.5$, $mc = 0.9$, $ms = 6.94 \times 10^{-3}$, $A = 10^3$, $B = 2$. Despite slight parameter differences, the influence of solidification rate on growth angles is essentially consistent for both Ir and Mo.

For the rough interface continuous growth mechanism, the actual crystal growth angles of Ir and Mo change little with increasing solidification rate. For the dislocation growth mechanism, the growth angles of both metals decrease with increasing solidification rate. In contrast to rough interface and dislocation mechanisms, during faceted growth, the actual growth angles of both metals decrease significantly at low solidification rates and then increase with further rate increases.

Considering that actual solidification rates generally range from 0.1 to 1.0 mm/min [1], if the rate continues to increase, the growth mechanism transitions from dislocation or faceted growth to rough interface growth [20]. Therefore, the dislocation and faceted growth mechanisms in Fig. 4 can only operate at low solidification rates. Within the normal rate range of 0.1–1.0 mm/min, rough interface and dislocation growth mechanisms have minor effects on the actual growth angle, whereas faceted growth causes substantial angle variations. These conclusions align with experimental observations: in Mo single crystal growth [7], faceted growth results in highly non-uniform sample dimensions (changing growth angle), while rough interface or dislocation growth produces uniformly sized crystals (stable growth angle).

Similarly, the effect of solidification rate on growth angle influences the supportable zone height. Figure 5 [Figure 5: see original paper] shows the stable zone heights for Ir and Mo under different growth mechanisms. Within the 0.1-1.0 mm/min rate range, Ir and Mo with rough interface growth can support zone heights of 4.8 mm and 7.8 mm, respectively, whereas under faceted growth, they can only support 3.6 mm and 4.6 mm. As the solidification rate increases, the supportable zone height also increases. Therefore, to achieve single crystal growth of high-melting-point metals Ir and Mo, a higher solidification rate is preferable to avoid very low rates. Within the normal range of 0.1–1.0 mm/min, different growth mechanisms for Ir show slight variations: for dislocation growth, the supportable zone height decreases from 4.8 mm to 4.5 mm; rough interface growth shows almost no change; and faceted growth increases from 3.6 mm to 4.2 mm. These trends also apply to Mo zone growth, demonstrating that a higher solidification rate (approximately 1.0 mm/min) not only minimizes growth angle variation and improves sample uniformity but also benefits the supportable zone height.

2.4 General Discussion

When the growth angle is non-zero and both principal radii of curvature are considered, Eq. (1) becomes a nonlinear equation that cannot be solved analytically; only numerical methods can obtain the relationship between zone height and growth angle, requiring further detailed discussion. This calculation applies the growth angle to the EBFZM crystal growth process for high-melting-point metals, correlating it with zone stability height and solidification process parameters (pulling rate) and linking it to interface growth mechanisms. This research reveals that the appearance of stray crystals in refractory metal single crystal growth may have multiple causes, highlighting the importance of process control. Given that no experimental methods currently exist to detect different growth mechanisms in high-temperature melt crystal growth, the theoretical prediction that small zone height changes can alter the growth mechanism cannot yet be experimentally verified. However, theoretical studies conducted under these experimental limitations contribute to a better understanding of EBFZM crystal growth for refractory and high-melting-point metals, providing guidance for subsequent precise control of crystal growth processes.

Conclusions

(1) The crystal growth angles of high-melting-point metals Nb, W, Ta, Mo, and Ir were calculated to be in the range of 8°–13°. When zone-melting samples of the same size, the ranking of stable zone heights is Nb > Mo > W > Ta > Ir. For large-diameter samples, non-zero crystal growth angles dominate zone height stability.

(2) The actual crystal growth angles of high-melting-point metals Nb, W, Ta,

Mo, and Ir are related to the interface growth mechanism. For rough interface growth, the growth angle changes little with increasing solidification rate; for dislocation growth, the growth angle decreases with increasing solidification rate; and for faceted growth, the growth angle decreases significantly at low rates and increases with increasing solidification rate. Employing a higher solidification rate (approximately 1.0 mm/min) is beneficial for controlling growth angle variation and stabilizing zone height.

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