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Nucleation mode selection during formation and growth of molten removal particles in Al_2O_3 ceramics laser cutting

Yonghao Luo[a,*], Xuyue Wang[a,*], Yebing Hu[b,*]

[a] School of Mechanical Engineering, Dalian University of Technology, Dalian 116023, PR China
[b] School of Materials Science and Engineering, Dalian University of Technology, Dalian 116023, PR China

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ABSTRACT

Because of the multiple selections on different crystalline faces in nucleation process of α-alumina, it is necessary to confirm the nucleation mode and growth mechanism of molten removal particles produced by alumina ceramics laser cutting. A model based on driving force of Helmholtz and Gibbs free energies is built to compare different critical nucleation sizes and corresponding nucleation barriers among several crystal planes. The calculation shows that when alumina ceramic is cooled and solidified from a molten state, the material is preferably nucleated in the parallelepiped model with extension and stack along the $(11\bar{2}0)$ plane. X-ray diffraction and scanning electron microscopy detections are taken to verify the nucleation mode that the morphologies thereof are shown as corners of an octahedron or edges of hexagons in different section directions. A pyramid stacking growth mode of spherical particles is proposed to coincide with the hollow micro morphology. The analysis concludes this model is feasible and it makes contribution to the potential application of removal particles for the field of ceramic powder metallurgy during laser processing.

1. Introduction

As the by-product of alumina ceramics laser cutting, the molten removal can be divided into following forms: the first is the spherical particles cooled and blown away from substrate by the assistant gas; the second is the adhering slag condensed on the lower surface; and the third is the residual molten layer in kerfs [1]. It is particularly special that the molten removal particles during alumina ceramic laser cutting have some unique features such as relatively high sphericity, centralized particle sizes and universal hollowness [2]. Mishra et al. [3] used a developed jet wheel atomization based spray dryer to produce alumina powder with analysis of the density, particle size and flowability behavior. Chen et al. [4] prepared nano α-Al_2O_3 powder by flash thermal spray method and investigated the wear resistance of the particles. Geng et al. [5] introduced a facile method to fabricate closed-cell alumina ceramics by binding hollow alumina spheres with high-temperature binder. Because these properties of size, sphericity and hollowness are superior to the alumina microspheres prepared by means of common sintering or spray [6–9], it is profound to study the formation of molten removal particles generated by laser processing.

Generally speaking, with the increasing temperature in melting process of alumina, the transitional metastable phase will be carried out an irreversible phase transformation by lattice reconstruction to form a more stable α phase [10]. The nucleation of α-Al_2O_3 has a variety of forms such as hexagonal prism, quadrangular, triangular prism, octahedron and hexahedron. Scholars have taken a series of researches based on modeling and experimental method to study the formation of these morphologies [11–13]. Hounslow et al. [14] established two families of mathematical models for the kinetics of granule nucleation and predicted the growth of micro powder. Boumaza et al. [15] prepared α-Al_2O_3 powders by calcination of boehmite or gibbsite. The specific signatures are investigated through X-ray diffraction, scanning electron microscopy, thermal analysis and cathodoluminescence. Yang [16] calculated the thermodynamics for homogeneous nucleation of alumina and pointed out that the formation many single-alumina particles with different shapes, including spherical, dendritic, flower, plate-like, and irregular is due to different growth mechanisms.

Due to the multiple selections on different crystalline faces in nucleation process of α-Al_2O_3, it is necessary to confirm the nucleation mode and growth mechanism of molten removal particles produced by alumina ceramics laser cutting. In this paper, a nucleation modeling is carried out based on driving force of Helmholtz and Gibbs free energies. The potential barrier of the nucleation of alumina on different crystalline faces is compared by the calculation. Through the observation by X-ray diffraction and scanning electron microscopy, the component and sectional microstructure of cutting products are obtained to verify the

* Corresponding authors.
E-mail addresses: luoyonghao@mail.dlut.edu.cn (Y. Luo), wbzzd@dlut.edu.cn (X. Wang), huyebingdlut@163.com (Y. Hu).

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Nomenclature

Δg	driving force for nucleation
ΔG	Gibbs free energy
V	nucleation volume
σ	surface tension
r	crystal nucleus radius
ΔF	Helmholtz free energy
Δf_v	free energy decrease caused by nucleation unit volume
γ_{xyz}	surface energy of a core crystal plane (xyz)
A_{xyz}	area of a core crystal plane (xyz)
a	lattice constant
a_c	critical nucleation size
G_c	nucleation barrier
r_e	unit cell span

model and reveal the growth mechanism of spherical particles. The modeling provides a theoretical support on the formation of α-Al_2O_3 particles in ceramics laser cutting. It is also a potential way of manufacturing method that can be used in the field of ceramic powder metallurgy.

2. Theoretical model

2.1. Driving force for nucleation of α-Al_2O_3 molten removal particles

The driving force for nucleation of alumina ceramic melt removal particles is derived from the difference of free energy between the crystalline phase and the parent phase. On the other hand, the creation of new surface by the formation of a new phase causes free energy to increase. Therefore, in an over cold liquid phase, when a new phase of spheroidal solid is formed, the total energy of every object in the nucleation course is changed into:

$$\Delta g = -\frac{\Delta G}{V}\cdot\frac{4\pi}{3}r^3 + \sigma\cdot 4\pi r^2, \tag{1}$$

where the first item refers to volume energy, the second item refers to interface energy, ΔG refers to Gibbs free energy accompanied by the occurrence of phase transformation, V refers to molar volume, σ refers to surface tension, and r refers to crystal nucleus radius. The volume energy is in direct proportion to the nucleation volume, namely, the larger the nucleation volume is, the larger the decrease of free energy is; and the surface energy is in direct proportion to the nucleation surface area, namely, the smaller the surface area is, the smaller the increase of free energy due to nucleation is, and the more stable the crystal nucleus is.

As shown in Fig. 1, when the size of the crystal nucleus is below critical radius r_c, the increase of surface energy is greater than the decrease of volume energy, and free energy is changed rightwards and upwards. Thus, the crystal nucleus is in a thermodynamic unstable state to be decomposed easily. At this moment, the new solid phase particles are in metastable state, and may be immediately eliminated even being generated. Such state is called incipient crystal in material science [17]. Moreover, once the particle size is greater than the critical radius r_c, the decrease of volume energy is greater than the increase of surface energy, and free energy is changed rightwards and downwards, the crystal nucleus becomes stable in thermodynamics to grow and form solidified melt particles. It can be seen that at a small radius, because specific surface area change is more significant than specific volume change, surface energy plays a dominant role. In contrast, with the growth of grains, volume change is more significant, and volume energy plays a dominant role [18].

The ΔG_c corresponding to critical nucleation size r_c is called nucleation barrier. To reduce the nucleation barrier, crystals are always nucleated in the shape of lowest surface energy. For isotropic crystals, the critical nucleation shape thereof is sphere, because sphere has the minimum surface area when volume is constant. However, for most crystals, because of anisotropy caused by crystal structures and chemical bonds, surface energy of various crystal surfaces are different, and even different greatly. Thus, most critical nucleation shapes of crystals are polyhedron.

2.2. Nucleation mode selection of alumina ceramic removal particles

During laser cutting of alumina ceramic, most melting products (including removal particles, adhering slag and residual molten layer) still keep the α-phase state. For the α-Al_2O_3 crystal form, the energy of the $(0001)(1\bar{1}00)(10\bar{1}0)(11\bar{2}0)$ crystal plane thereof is lower than others as demonstrated [19]. The crystal nucleus is easy to extend and stack in these several crystal boundary directions when growing, as shown in Fig. 2.

The change in polyhedron nucleation energy may be expressed using a Helmholtz function as demonstrated [20]:

$$\Delta F = -V\Delta f_v + \sum \gamma_{xyz}A_{xyz}, \tag{2}$$

where ΔF refers to Helmholtz free energy change, V refers to nucleation volume, Δf_v refers to free energy decrease caused by nucleation unit volume, γ_{xyz} refers to surface energy of a core crystal plane (xyz), and A_{xyz} refers to the area of this surface. α-Al_2O_3 is in a hexagonal close packed (HCP) crystal form, and lattice constant a = b ≠ c (ideal lattice index c = 1.633a, for alumina material, c ≈ 2.729a).

When crystal nucleus is nucleated by taking (0001) plane as a core surface (hexagonal prism shape), the Helmholtz energy thereof is changed into:

$$-V\Delta f_v + \sum \gamma_{xyz}A_{xyz} = -\left(2.73\times\frac{3\sqrt{3}}{2}\right)a^3\Delta f_v + (3\sqrt{3} + 6\times 2.73)a^2\gamma_{(0001)}. \tag{3}$$

Since the critical size corresponds to an extreme point of ΔF, after derivation performed on this equation:

$$-\left(2.73\times\frac{9\sqrt{3}}{2}\right)a^2\Delta f_v + (6\sqrt{3} + 12\times 2.73)a\gamma_{(0001)} = 0, \tag{4}$$

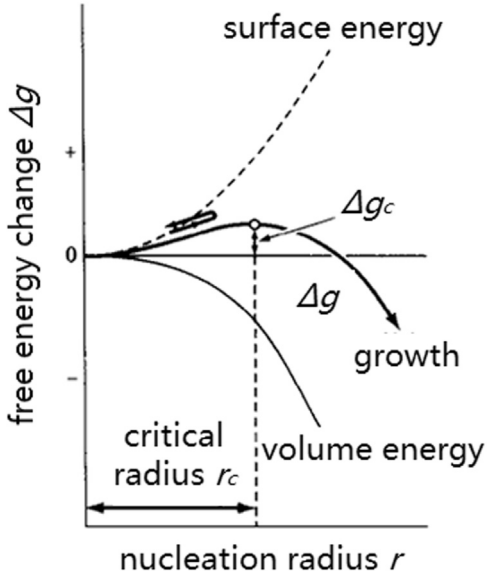

Fig. 1. Change of free energy in nucleation course.