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Fast Shape Evolution of TiN Microcrystals in Combustion Synthesis

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ABSTRACT: Single-phase TiN crystalline powder consisting of microcrystals has been prepared by combustion synthesis. During the drastic combustion reaction with a high reaction temperature and rapid heating rate, TiN microcrystals undergo a fast shape evolution process and finally develop into various crystallization shapes, such as quasi-spherical grains, faceted cubes or pyramids, and dendrites. The formation mechanisms of different crystal shapes are discussed in light of basic crystal growth theories. It is proposed that, at the initial stage, quasi-spherical TiN crystals are formed first by diffusion-controlled continuous growth; by a faceting process, flat surfaces then appear in several low-index directions on the quasi-spherical crystals, and at last, well-faceted crystals are produced by two-dimensional nucleation and layered growth. In addition, interesting TiN dendrites are observed, probably arising from the fast cooling rate in combustion synthesis. The dendrites grow quickly in three orthogonal directions, with each growth unit exhibiting a 4-fold symmetry and sometimes a half-octahedral pyramid head.

Introduction

In recent years, the nitrides of transition metals have received increasing attention because of their unique chemical and physical properties. Among these materials, titanium nitride (TiN) is particularly interesting, because of its superior hardness, good thermal stability, high wear resistance, excellent corrosion resistance, and relatively high electrical conductivity. TiN is widely used as a coating material on cutting tools, as a diffusion barrier in microelectronic devices, and as a corrosion and abrasion layer on optical components. In addition, TiN is usually used to fabricate ceramic composite materials to improve mechanical properties.^{1–3}

For these various applications, the surface roughness, film texture, and crystallization shape of TiN will have important influence on its physical properties. Because of that, it is necessary to understand the nucleation and growth kinetics, including the microstructure evolution of TiN crystals under different conditions. A lot of literature have been published on this topic,^{4–8} from experimental studies to theoretical models. Most of these studies, however, were focused on the epitaxial growth of TiN thin films, and up to now, very limited attention^{9,10} has been paid on the crystal growth and shape evolution involved when preparing TiN powders or ceramics.

Combustion synthesis, which is also known as self-propagating high-temperature synthesis (SHS), is a facile and low-cost technique for fabricating a wide range of advanced materials,^{11–13} including various ceramic powders. Because of the expeditious reaction period, fast heating rate, and elevated reaction temperature, combustion synthesis has been proven to be effective in producing ceramic microcrystals with different morphologies, such as fibers, particles, flakes, and whiskers.^{14–17} Combustion synthesis of TiN powders has also been reported,¹⁸ but the work primarily concentrated on how to improve the nitridation of Ti and increase TiN yield, with little attention paid to the crystallization shapes of TiN microcrystals.

In this study, we present single-phase TiN microcrystals with various morphologies prepared by combustion synthesis. The formation mechanisms for different crystallization shapes are discussed in detail, with respect to the special reaction conditions in combustion synthesis.

Experimental Section

Ti powder (99% pure, 300 mesh, General Research Institute for Nonferrous Metals, Beijing, China) and high-purity N₂ (99.9%, Huayuan Gaseous Co., Beijing, China) were used as starting reactants. To reduce the agglomeration of Ti melt and enhance the infiltration of N₂, we used an appropriate amount of TiN powder (self-fabricated by combustion synthesis) as the diluent. At the same time, 3 wt % NH₄Cl (A. R., Beijing Chemical Co., China) was also added to make the sample loose and easy to pulverize.

All the involved raw materials were mixed by agate balls in a plastic jar for 8 h with absolute ethanol as medium. The obtained slurry was dried and sieved. Then the powder mixture was contained in a porous graphite crucible and placed into a reaction chamber for combustion synthesis. The reaction chamber was evacuated to a vacuum of 1×10^{-4} MPa and then inflated with N₂ at a pressure value of 2 MPa. The sample was ignited by passing an electric current through a tungsten coil. The reaction temperature was recorded by a W-Re3/W-Re25 thermocouple, which was directly inserted into the sample and connected with a computer system for data acquisition. The detailed structure of the combustion synthesis equipment has been reported previously.¹⁵

The phase composition of the reaction product was identified by X-ray diffraction (XRD; Rigaku, Japan) using Cu K α radiation, with a scanning rate of 2°/min. The microstructure was examined by scanning electron microscopy (SEM; JSM-6301F, JEOL, Japan) equipped with an energy-dispersive spectroscopy detector (EDS; INCA, Oxford Instrument).

Results and Discussion

The XRD pattern of the combustion product is shown in Figure 1, where all the diffraction peaks arise from TiN and have been indexed. No other impurity phase or residual Ti is detected, revealing that the as-synthesized product is single-phase TiN.

Figure 2 shows the temperature history during the combustion synthesis of TiN. It is clear that once the combustion reaction

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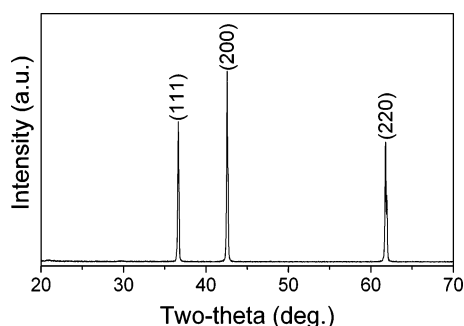


Figure 1. XRD pattern of the as-synthesized TiN product (indexed according to PDF 38-1420).

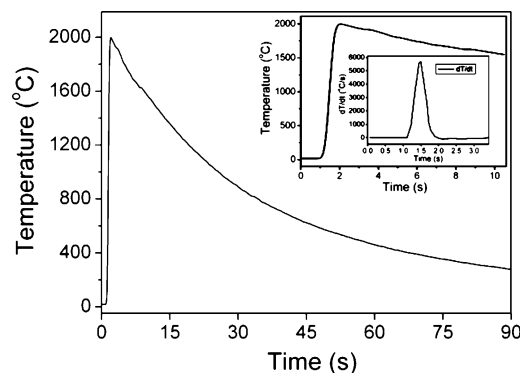


Figure 2. Temperature history during the combustion synthesis of TiN.

is triggered, the nitridation reaction of Ti produces a large amount of heat energy, leading to an abrupt increase in temperature. In no more than 1 s, the temperature is elevated from room temperature to about 2000 °C, and the maximum heating rate is close to 6000 °C/s. Compared with the heating stage, the cooling stage is not as drastic, but the cooling rate is still much higher than those in common sintering techniques. For example, from the apex temperature to around the melting point of Ti (1668 °C), the cooling rate is about 60 °C/s.

Along with the drastic combustion reaction, the TiN microcrystals undergo a fast shape evolution process and finally develop into various morphologies. Several typical crystallization shapes of TiN are shown in Figure 3. It can be seen that in addition to common quasi-spherical grains, well-developed faceted cubic or pyramidal crystals and interesting dendrites have been produced. Similar grain morphologies were also observed in nitride compounds produced by other methods in previous studies.¹⁹ Figure 3e shows a representative EDS result of a TiN microcrystal.

Generally speaking, the final morphology of a crystal depends on both its intrinsic lattice structure and external conditions for growth. The intrinsic factor will lead to the equilibrium crystal shape (ECS) with minimum total surface energy, whereas different external conditions usually force the crystal to deflect from the ECS and develop into various morphologies. The crystal shape is derived from the competition of these two factors and is closely related to the growth kinetics, such as interface property and mass transportation. On the basis of this viewpoint, we discuss the formation mechanisms of the TiN microcrystals with different shapes as follows.

A. Diffusion-Controlled Continuous Growth of Quasi-Spherical TiN Grains. From the temperature history in combustion synthesis shown in Figure 2, one can see that the apex reaction temperature is obviously higher than the melting point of Ti. Therefore, once the combustion reaction starts, Ti

particles in the sample will quickly melt and partially vaporize under the drastic heating rate. As the heating stage is very short, lasting for only about one second, the nitridation of solid Ti is minor, and the reaction between Ti melt and N₂ should be the predominant way of producing TiN.

At the initial reaction stage with high temperature and N₂ pressure, the mass transport is activated and the supersaturation degree is high. And compared with the vapor reaction between Ti vapor and N₂, the nitridation reaction of Ti melt has a lower latent enthalpy. In this case, the interface between TiN crystal and Ti melt is thought to be rough and there is no crucial nucleation barrier for TiN. New TiN nuclei can be formed continuously, and then undergo a fast growth in all directions, with a high reaction temperature and strong driving force. This isotropic growth leads to an equivalent growth rate in different directions, thus producing quasi-spherical grains at last.

Figure 4 illustrates the continuous growth of quasi-spherical TiN crystals briefly. In the N₂ atmosphere with a high-pressure level, some N₂ molecules or N atoms will dissolve into and then react with the Ti melt, creating the initial TiN nuclei. These TiN nuclei, coated by Ti melt, will act as the basis for subsequent nucleation and growth, because the following nucleation on their surface should be easier than homogeneous nucleation in the Ti melt. Therefore, the dissolved N₂ molecules or N atoms will move by diffusion to the interface and then react with Ti. The nitridation reaction can be simply expressed as follows



During the growth of TiN grains, there is no crucial nucleation barrier at the rough interface, and nucleation occurs continuously. In this case, the rate-limited process is diffusion of N₂ or [N] in the Ti melt, and the growth mechanism of quasi-spherical TiN grains can be regarded as being a diffusion-controlled continuous growth. Models for nitrides or carbonitrides that are similar to that given in Figure 4 but associated with solid states have also been reported in previous research work.^{19,20}

For a Ti melt with isotropic surface energy, the minimum total surface energy is equivalent to the minimum surface area at a fixed volume. To reduce its total surface area, the Ti melt always tries to keep a spherical shape, which is inherited by the quasi-spherical TiN grains during the isotropic continuous growth.

For the TiN crystalline phase, however, the situation is different, i.e., the surface energy is not isotropic but anisotropic, varying in different orientations. Accordingly, the minimization of the total surface energy cannot be fulfilled simply by reducing surface area, and the ECS with the minimum total surface energy is not spherical but faceted, bound with the faces with lower surface energy. In this case, to lower the total energy, the quasi-spherical TiN grains will develop flat faces and transform toward the ECS, which is achieved by a faceting process.

B. Analysis of the Equilibrium Crystal Shape (ECS) of TiN. The equilibrium shape of a crystal is the one with the minimum total surface energy, on which the crystal will expose its faces with lower surface energy. Generally, for a crystal, the close-packed faces with larger interplanar spacings have lower surface energy. Experimental observations have revealed that the importance (frequency of occurrence) of a crystal face decreases with its interplanar spacing, which is known as the Bravais–Friedel law.²¹

TiN has a composite face-centered cubic (FCC) lattice like NaCl, as shown in Figure 5a. The list of decreasing interplanar

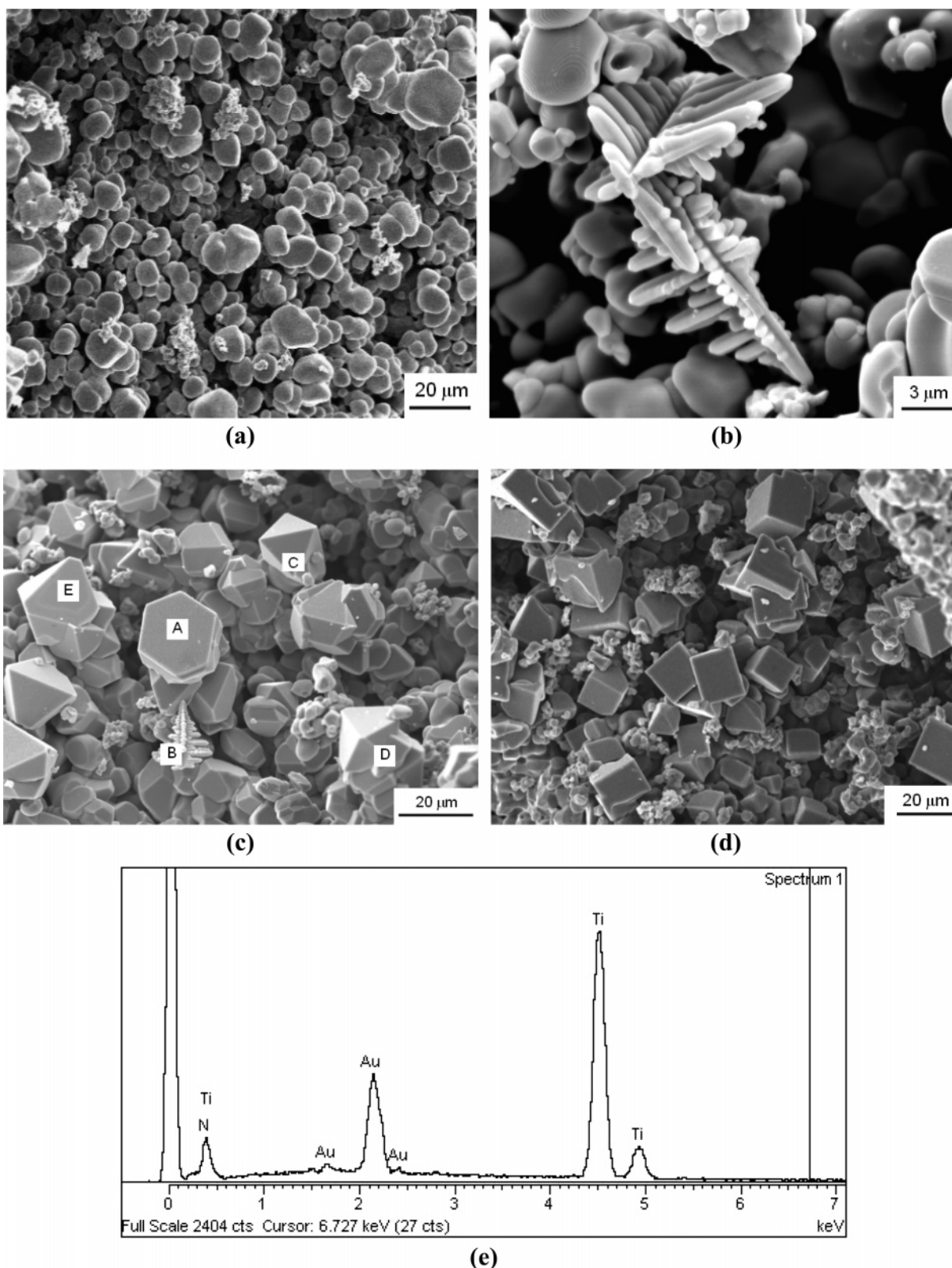


Figure 3. Typical morphologies and EDS result of TiN microcrystals: (a) quasi-spherical grains; (b) dendrites; (c) faceted pyramidal crystals; (d) faceted cubic crystals; (e) EDS of a TiN microcrystal.

spacings for some important crystal faces runs as follows: $\{100\}$, $\{110\}$, $\{111\}$, $\{200\}$, $\{220\}$, $\{222\}$, ...

In the composite FCC lattice of TiN, the elementary growth layers should actually be $\{200\}$, $\{220\}$, and $\{222\}$. According to the Bravais–Friedel law, the importance of these crystal faces should be $\{200\} > \{220\} > \{222\}$. If only the most important

$\{200\}$ faces are exposed, the ECS of TiN should be a cube. In fact, faceted cubic TiN crystals have been observed in the product, as shown in Figures 2 d and 6a.

From a kinetic standpoint, crystal growth is such a process that the reactant atoms in fluid phases are attached and bonded at the crystal surface. The attachment energy or bonding energy

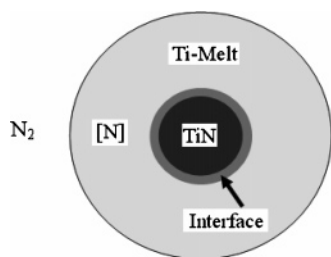


Figure 4. A brief illustration of diffusion-controlled continuous growth of quasi-spherical TiN microcrystals.

can be used to estimate the degree of difficulty for the formation of a new layer. The crystal faces with higher bonding energy usually have a higher growth rate, and during the crystal growth process, they will shrink gradually or even disappear at last. On the contrary, the crystal faces with lower binding energy and growth rates will be reserved in the end as crystal surfaces.

Now let us consider the binding energy for a new atom at $\{200\}$, $\{220\}$, and $\{222\}$ faces in a TiN crystal, with respect to the atom arrangements shown in Figure 5b–d. Although TiN has a lattice structure like NaCl, the bonding ways are different in these two compounds. Here, we regard TiN not as a normal ionic-bonded compound, but as a Hägg phase bonded with covalent and metallic bonds. The metallic bonds are formed among the d electrons of Ti, and the covalent bonds are formed between the d electrons of Ti and the p electrons of N. The metallic bonds are relatively weak, whereas the directional covalent bonds are much stronger. In this way, the bonding energy is mainly determined by the covalent bonds between the new atom and its first nearest neighbors, with a distance of a , shown in the figure. From Figure 5, it can be seen that the number of first nearest neighbors for a new atom should be 1, 2, and 3 at the $\{200\}$, $\{220\}$, and $\{222\}$ faces, respectively. Therefore, with decreasing binding energies, the list of crystal faces runs as: $\{222\} > \{220\} > \{200\}$. Similar results were obtained in a previous study, which reported that the list of crystal faces with decreasing attachment energy runs as $\{111\} > \{110\} > \{100\}$ for several TiN-type crystals.⁹ Because the crystal faces with higher growth rates will shrink and those with lower growth rates will expand during crystal growth, the importance of the above crystal faces should be $\{222\} < \{220\} < \{200\}$, which primarily agrees with the conclusion derived from the Bravais–Friedel law.

For revealing the dependence of the crystallization morphology of a crystal on its lattice structure, we usually consider the periodic bond chain (PBC) theory. According to PBC theory,²¹ the crystal should be bounded by edges parallel to the directions in which there is a continuous chain of strong bonds between the building units. Such a chain is called a PBC, and the crystal can be considered as being an array of PBCs. On the basis of the number of PBCs involved, the crystal faces are divided into three categories, F faces containing two or more PBCs, S faces containing only one PBC, and K faces containing no PBC. These different faces have different growth mechanisms. F faces grow slowly and hence important faces, K faces grow fast and are seldom found on crystals, and S faces are in the middle.

In the TiN crystal structure, there are three PBCs consisting of continuous strong Ti–N covalent bonds, viz. A[100], B[010], and C[001], as shown in Figure 5e. The types of crystal faces can then be identified: $\{200\}$ as F faces, $\{220\}$ as S faces, and $\{222\}$ as K faces. Consequently, with the lowest growth rate, $\{200\}$ faces are most important and will be exposed finally, bounding the cubic crystal shape. With higher growth rates,

$\{220\}$ and $\{222\}$ faces will shrink during crystal growth and at last degrade to edges and corners. By this means, complete cubic TiN crystals can be formed with faceted faces, as shown in Figure 6a.

Because of the variations in growth conditions, of course, sometimes the growing TiN crystals will deflect from their ECS as a perfect cube. Previous studies^{4,8} on the formation of TiN films have shown that the preferred orientation of TiN depends on the incident ion:metal flux ratio, and the nucleation kinetics of TiN is strongly affected by growth temperature and N_2 partial pressure. In the combustion synthesis, the combustion reaction is drastic, with fast heating/cooling rates, and hence the temperature and N_2 pressure, which play important roles in the formation of TiN, may change quickly and remarkably. The oscillations of reaction conditions will change the growth character of TiN crystals and lead to a diversity of crystal shapes. For example, incomplete cubic and pyramidal crystals are also observed, as shown in images b and c of Figure 6. The formation process of these two types of crystals will be further discussed in the following section.

C. Faceting Process of Quasi-Spherical Grains and Formation of Faceted Crystals. As described before, compared to the ECS, the quasi-spherical TiN grains are in a nonequilibrium state with higher energy, and they will thus try to develop flat faces and transform toward the ECS. This transformation is achieved by a faceting process,²² and flat faces are formed on the quasi-spherical grains in several special directions. Figure 7 shows SEM micrographs of the faceting process.

At a first glance, the terraced structure, consisting of a series of layered circular plates, is somewhat similar to the spiral morphology of screw dislocation growth. More careful observations, however, reveal that these terraces are generated by two-dimensional nucleation. As clearly shown in Figure 7a, on the terraced structure, the edges of circular plates are not parts of a spiral curve, but separate and closed circles. At the same time, at the top of the terrace, the smallest plate is flat, without any trace visible, indicating the origin of screw dislocation growth. Therefore, it can be said that the terraced structure has arisen from two-dimensional nucleation. On one layer, when a nucleus grows to a certain size, before it can sweep the whole area in this layer, a new nucleus forms. Accordingly, the lateral growth in each layer and the outward growth in the normal direction take place simultaneously, forming a terraced structure at last.

Figure 8a–c schematically shows the shape evolution of TiN from a spherical grain to a faceted cubic crystal by the faceting process. First, small flat facets appear on the surface of the spherical grain, and then by two-dimensional nucleation, they grow in both the lateral and normal directions, forming the terraced structure. With further growth, two neighboring facets toward different directions will cross and an edge will be created. In the same way, more edge lines can be created, by which the dimensions of the developing cubic crystal are determined. Finally, under a proper condition ensuring that no new nucleation occurs any more but that the lateral growth of terraced faces still progresses, completely flat surfaces are obtained and a faceted crystal is derived.

The above explanation is supported by the SEM micrographs shown in Figure 7. For example, Figure 7a exhibits three terraces (A_1 , A_2 , and A_3) formed in three orthogonal directions, which will develop into three surfaces of a cube. Another faceting grain (II) is shown in Figure 7b, which has shown an obvious tendency to form a cubic crystal. Figure 7b also shows an edge line (L) on a TiN grain (I) formed by the crossing of two terraces (A

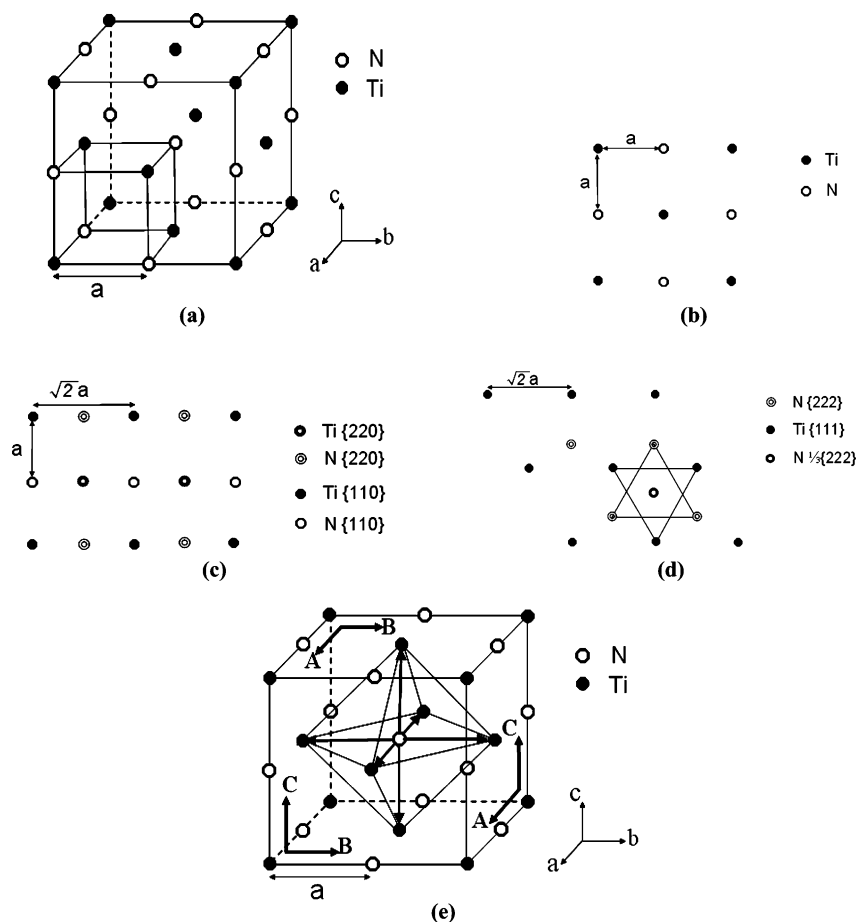


Figure 5. Drawings of the FCC lattice, atom arrangements, and PBC vectors of TiN crystals: (a) FCC lattice structure; (b), (c), and (d) atom arrangements at {200}, {220}, and {222} faces; (e) PBC vectors in a TiN crystal.

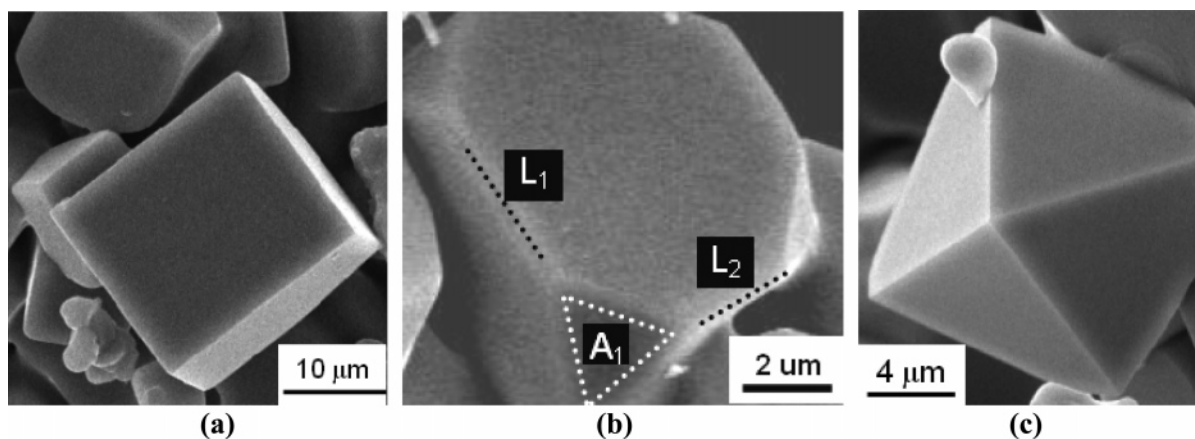


Figure 6. Different crystallization shapes of faceted TiN microcrystals: (a) cube; (b) pyramid as a half octahedron; (c) incomplete cube.

and B). More details for the formation of an edge are shown in Figure 7c, where the crossing and overlapping of two neighboring terraces can be seen clearly. Near the middle overlapped area, the facet boundaries partially become parallel lines, as highlighted by white dotted lines. To some extent, the middle area between two crossing terraces can be regarded as being a small facet at present, which will degrade to an edge line with further lateral growth of the layers on the two terraces.

Sometimes, because of the variations in growth conditions, the growth kinetics of TiN crystals will be modified and the growth rates at some faces may be changed. Consequently, various crystal shapes other than the ECS can be formed. Figure

6b shows an incomplete cube, where {220} faces have degraded to edges, whereas {222} faces still remain as small facets with an equivalent triangular shape (A_1). The formation of this incomplete cube is thought to be caused by the retardation of the growth at the {222} faces. As illustrated in Figure 8d, where the growth rate of {200} faces is $V_A = V_B = V$, and the growth rate of {222} faces is V_T , only when $V_T/V \geq \sqrt{3}$, {222} faces will absolutely degrade to corners and a complete cube can be obtained. Otherwise, if $V_T/V < \sqrt{3}$, {222} faces will be reserved more or less on the incomplete cube. Moreover, if V_T is further reduced to be much lower than V , more significant

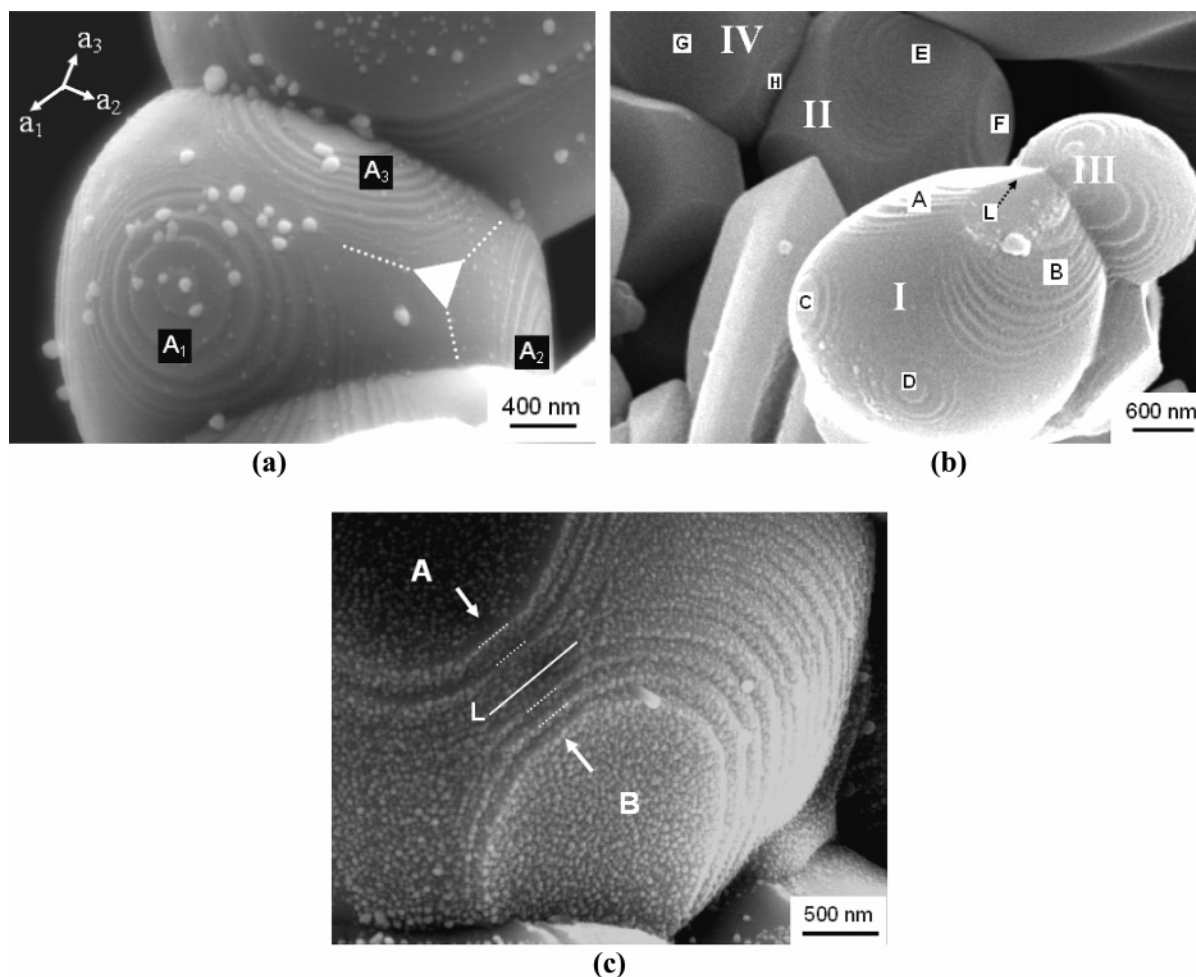


Figure 7. SEM micrographs showing the faceting process of quasi-spherical TiN grains.

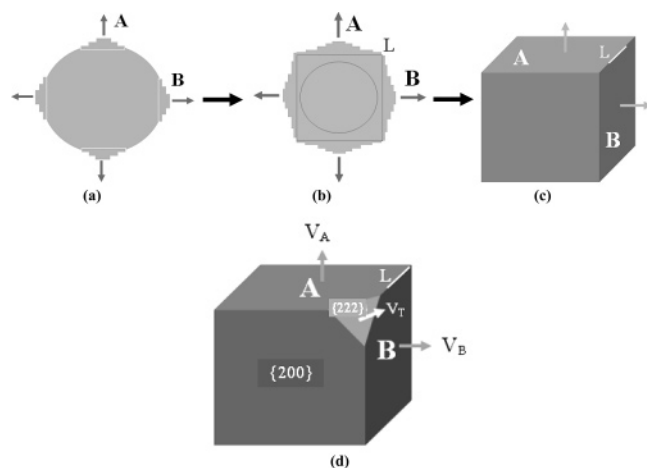


Figure 8. Schematic showing of the faceting process of spherical TiN grains and formation of faceted crystals.

changes in crystal shapes will be effected. In this case, instead of $\{200\}$ faces, $\{222\}$ faces become the most important faces, which will preferentially appear on the surface of quasi-spherical grains at the beginning of the faceting process and be exposed as surfaces on the faceted crystals. Consequently, the final crystal shape will transform from a cube to an octahedron. Figure 6c shows a pyramidal TiN crystal with a 4-fold symmetric character, which can in fact be regarded as a half octahedron.

D. Growth Mechanism of TiN Dendrites. Besides quasi-spherical grains and faceted crystals, TiN dendrites are observed in the as-synthesized product, as shown in Figures 3b and 9. These dendrites exhibit a variety of interesting shapes, such as bamboolike, sharp tooth-like, layered, flowerlike, and treelike morphologies, shown in Figure 9.

Dendrites were first noticed in the microstructure of metal ingots and have attracted much attention in the fields of crystal growth.²³ TiN or TiC dendrites were sometimes observed in the studies on laser surface coating of Ti–Al-based alloys or intermetallics.^{24,25} For the formation of these dendrites generated in rapidly cooled melts, the fast cooling rate plays an important role. Under fast cooling rates, the crystals can develop into various morphologies different to their equilibrium shapes. In the combustion synthesis, with the acute combustion reaction, the drastic temperature variation and fast cooling rate can provide the possibility of the formation of TiN dendrites.

Figure 9a shows a bamboolike dendrite exhibiting a wavy shape at its side faces with many small sharp tips, which is thought to be a feature of the initial growing stage. These tips will then grow larger and form a toothlike morphology or a layered structure, depending on the different forward and lateral growth rates, as shown in images b and c in Figure 9. If from one center, several layered dendrites grow together toward different directions, then a larger flowerlike dendrite is obtained, as shown in Figure 9d. Another kind of growth unit with round tips is shown in the inset in Figure 9e. During the subsequent growth process, these tips can grow forward quickly and develop

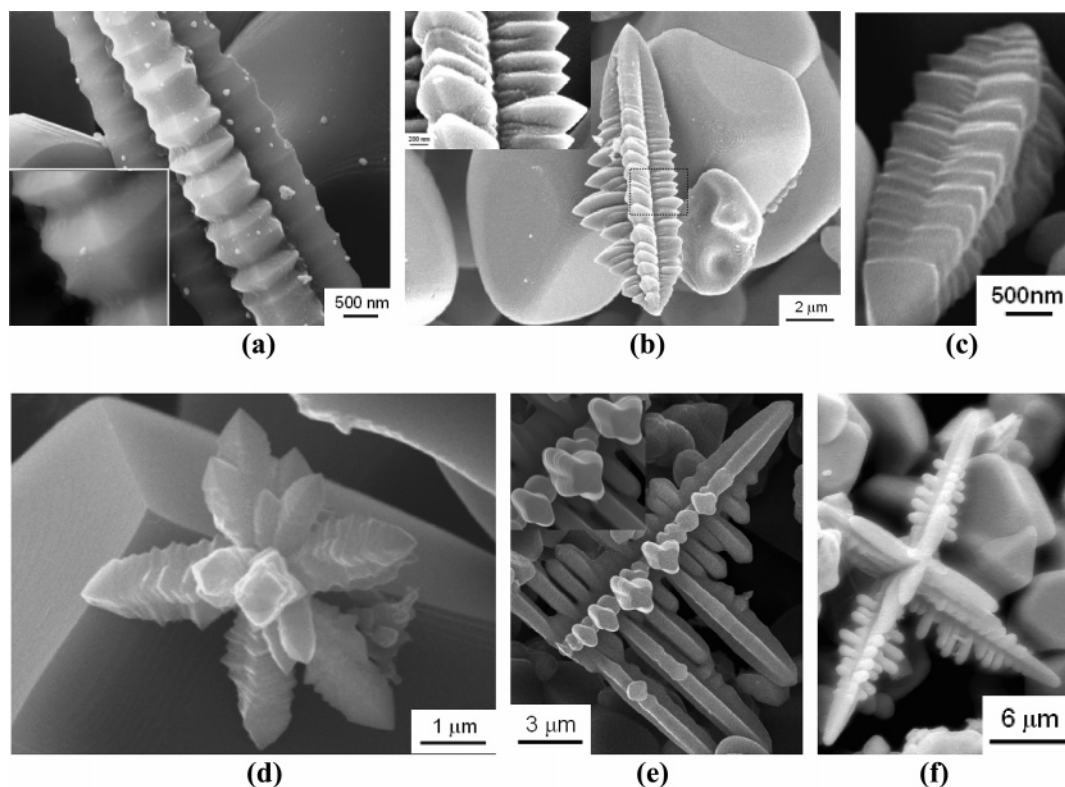


Figure 9. Various morphologies of TiN dendrites.

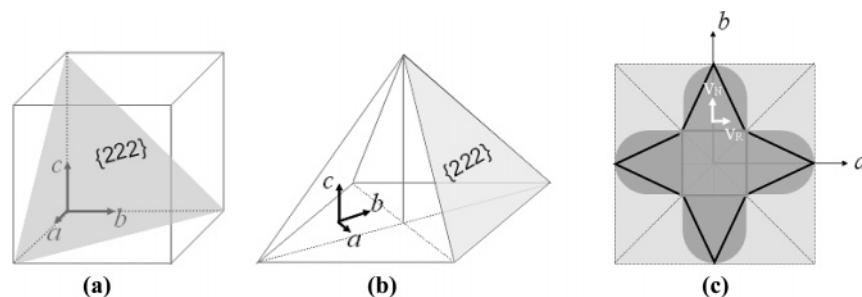


Figure 10. Simple scheme of the growth of TiN dendrites.

into slim branches, and treelike dendrites are produced, as shown in images e and f of Figure 9.

Regardless of the shape of the tips, sharp or round, all of the growth units show a 4-fold symmetry. During the formation of a dendrite, the secondary branches will grow perpendicular to the primary trunk and smaller twigs perpendicular to a branch. From these morphological characters, one can see that the growth of TiN dendrites takes place in three orthogonal directions. One direction is the main growth direction, along which many growth units are connected or partially overlapped, and in the planes normal to this main direction, each growth unit stretches itself in the other two vertical directions.

Now, let us choose the dendrite shown in Figure 9c as an example to explain the above opinion more clearly. Here, the direction in which the dendrite has the largest dimension can be regarded as the main direction. Along this direction, many growth units are connected. Each unit has four acute horns growing in two orthogonal directions perpendicular to the main direction. Another example is shown in Figure 9f, where a typical three-dimensional treelike dendrite can be seen. For this dendrite, the main direction is the one normal to those parallel planes, in which the cross-like growth units extend in two orthogonal directions.

At the same time, the 4-fold symmetric character is noticed on the pyramidal heads of TiN dendrites, as shown in images c and d of Figure 9. These pyramids are very similar to the above-described half octahedron shown in Figure 6c.

On the basis of the above observations and explanations, we suggest a growth mechanism of TiN dendrites. As shown in parts a and b of Figure 10, for each dendrite, the three orthogonal growth directions are parallel to the reference axes, viz. a , b , and c , respectively, and the 4-fold symmetric pyramids are bounded with $\{222\}$ faces. In images c and d of Figure 9, it can be seen that the four base corners of a pyramid and the four acute horns of the growth units are stretching toward the same directions. This orientation relation is consistent with the above suggestion. Figure 10c illustrates the growth process of each unit, occurring in the plane normal to c -axis. Along the directions in a and b , four horns extend simultaneously, and different growth rates in the forward (V_N) and reverse (V_R) directions will lead to different shapes. For example, if the difference between V_R and V_N is small and the ratio of V_R/V_N is constant, the horns will reserve the initial shape during growth process, and if the difference between V_R and V_N is remarkable and V_R is much higher than V_N , the horns will grow very quickly

in the forward direction with the lateral growth limited and will at last develop into slim branches.

Additionally, it should be pointed out that although the dendrites in images c and d of Figure 9 show a layered appearance, their growth units are not real flat layers at all. With more careful observations, one can find that the sharp tip of each acute horn is actually still a small pyramid. In fact, judging only from the intrinsic symmetry of the TiN lattice structure, the three orthogonal directions (parallel to *a*, *b*, and *c*, respectively) are equivalent. If a TiN crystal undergoes equivalent growth in these directions, a three-dimensional eight-pod morphology will be formed, as described for the shape evolution of Cu₂O cubic crystals.²⁶ During the formation of TiN dendrites here, however, the crystal growth in one direction is enhanced, and in this direction, the crystal grows very fast, forming a main chain. Along this chain, many new growth units are produced quickly one after another, with narrow space intervals. In this case, the following growth of each unit in the main direction is strongly limited by simultaneous growth of its neighbors and the growth unit can stretch itself only in the plane normal to the main direction. Consequently, in the main direction, the growth units have smaller dimensions than in the other two directions, and it looks as if they have been pressed in the main direction. Being made of these pseudo-pressed growth units, the dendrites exhibit a layered appearance.

Conclusion

From the above discussions about the formation mechanisms of various TiN crystals, it can be seen that, in association with the drastic combustion reaction, TiN microcrystals undergo a fast shape evolution process. The growth kinetics and final morphology of TiN crystals are determined by the intrinsic crystal structure of TiN and special external conditions in combustion synthesis. Both of these factors are impressive, and their effects are reflected in the different crystal shapes of the TiN product. The TiN crystals try to reach their equilibrium shape with minimized total surface energy and develop into faceted cubes, but the variations of external conditions usually lead them to other shapes. Finally, the complexity of growth conditions provides the TiN microcrystals with a diversity of crystallization shapes. It is proposed that quasi-spherical TiN grains are formed initially by diffusion-controlled continuous growth with rough interfaces. The quasi-spherical grains will then experience a faceting process by two-dimensional nucleation and develop flat surfaces in several special directions. Finally, well-faceted cubic or pyramidal crystals can be formed by layered growth. Additionally, under a fast cooling rate, interesting TiN dendrites are formed by fast growth in three orthogonal directions. Although these dendrites are far from the

equilibrium crystal shape, they exhibit some symmetric character, for example, the 4-fold symmetric pyramid as a half octahedron is observed.

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