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Microstructure evolution of ceramic materials during solidification from melts in high-gravity combustion synthesis

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ABSTRACT

A variety of bulk ceramic materials were prepared via melt-casting by high-gravity combustion synthesis, and the microstructure evolution during solidification was investigated. Most single-phase ceramics like Al₂O₃, YAG, and MgAl₂O₄ showed a faceted crystal shape because they have higher melting entropies. The cooling condition had an evident influence on the solidification process, resulting in different microstructures. As an example, a strongly textured structure consisting of well-arranged faceted crystals was observed in the surface layer of Al₂O₃ samples. Compared with single-phase ceramic materials, multiphase eutectic ceramics have lower melting temperatures and can provide more opportunity for tailoring microstructures. From the experimental results, the microstructure of eutectic ceramics was related with the volume fraction of each component, and various eutectic structures with submicron interphase spacings were produced such as lamellae, fibers, and three-dimensional interpenetrating frameworks. No cracks were found at the interface between different phases in the eutectic ceramics, indicating an excellent interfacial bonding strength.

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1. Introduction

In contrast to metals and alloys, which are generally produced by casting from melts, polycrystalline ceramics are generally fabricated by sintering from fine powders. For the melt-casting of ceramics, two major technical obstacles are involved. The first one is the difficulty in preparing stable and homogeneous ceramic melts because most ceramic materials have extremely high melting points and some decompose instead of melting at elevated temperatures. Therefore, the melting of ceramic materials is often realized by efficient heating media such as high-frequency induction, lamp mirror furnaces and lasers [1–5]. Another obstacle in the melt-casting of ceramics is exaggerated grain growth during solidification from hot melts. A large grain size is usually not desirable in ceramic materials because it will impair the mechanical strength. In order to obtain fine microstructure, multiphase eutectic ceramics are more frequently prepared than single-phase ceramics [6–8].

The preparation of bulk ceramics by direct solidification can be carried out by unidirectional solidification in a container or pulling of a solid from a melt meniscus [9,10]. The Bridgman method is a suitable technique for preparing large samples, where the ingot size is limited only by crucibles. By this technique, ceramic melts are contained in molvbdenum, tungsten or iridium crucibles, and unidirectional solidification is realized by slowly pulling the crucibles off the hot region. The apparent thermal gradients in the Bridgman technique are generally below 10 °C/mm, which results in growth rates of <100 mm/h and interphase spacings of >10 μ m. Another approach is the Czochralski method, in which crucibles are also required but direct contact between crucibles and growing materials is avoided. In addition, the floating-zone method is often used to prepare eutectic ceramics such as Al₂O₃/YSZ (Y₂O₃stabilized ZrO₂), Al₂O₃/YAG (Al₅Y₃O₁₂ garnet) and Al₂O₃/YAG/YSZ [11–13]. This method does not require crucibles, and a relatively small volume of sample is melted by high-frequency induction or lasers. In the floating-zone method, larger thermal gradients up to 10³ °C/mm can be attained, leading to higher growth rates and smaller interphase spacings below 1 µm. Other methods for solid pulling from a melt meniscus include edge-defined film-growth and micro-pulling down [14-16], which can provide thermal gradients of 10² °C/mm.

Despite the differences in technical details, all the abovementioned methods require an external heating source to achieve high temperatures for melting ceramic materials. In contrast to these methods, a furnace-free technique called high-gravity combustion synthesis has been recently reported to prepare bulk ceramics by direct solidification [17,18]. By this technique, highly

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Table 1

Nominal chemical compositions and calculated phase compositions of the ceramic samples prepared by high-gravity combustion synthesis.

Sample	Nominal chemical composition (mol%)	$T_{m/e}$ (°C)	Calculated phase composition (vol%)	$T_{\rm ad}$ (°C)
Al_2O_3	Al_2O_3	2054	Al_2O_3	2884
YAG	62.5 Al ₂ O ₃ +37.5 Y ₂ O ₃	1950	YAG	2593
$MgAl_2O_4$	50 Al ₂ O ₃ +50 MgO	2135	MgAl ₂ O ₄	2476
YA-1	80 Al ₂ O ₃ +20 Y ₂ O ₃	1825	59 YAG+41 Al ₂ O ₃	2859
YA-2	95 Al ₂ O ₃ +5 Y ₂ O ₃	1825	84 Al ₂ O ₃ +16 YAG	2884
AZ	62 Al ₂ O ₃ +37 ZrO ₂ +1 Y ₂ O ₃	1860	67 Al ₂ O ₃ +33 ZrO ₂	2678
YAZ	65 Al ₂ O ₃ +16 Y ₂ O ₃ + 19 ZrO ₂	1715	49 YAG+37 Al ₂ O ₃ +14 ZrO ₂	2678

 $T_{m/e}$: melting point for single-phase ceramics or eutectic points for multiphase eutectic ceramics; T_{ad} : calculated adiabatic temperature.

exothermic aluminothermic reactions are utilized to realize high temperature and produce ceramic melts. At the same time, a highgravity field is applied to accelerate the separation between ceramic and metallic melts and removal of gas bubbles from the melts. After cooling and solidification, bulk ceramics are obtained together with metallic ingots. In high-gravity combustion synthesis, the heat energy created by chemical reactions is used for melting ceramic materials, and thus external heating source is not necessary. At the same time, combustion reactions progress very quickly and the whole synthesis process lasts only tens of seconds. Accordingly, high-gravity combustion synthesis can offer a fast and economical way to prepare bulk ceramics. Up to now, high-gravity combustion synthesis has been applied to prepare a variety of ceramic materials, including single-phase ceramics, multiphase eutectic ceramics, glasses and glass-ceramics [19–25].

For preparing bulk ceramics by high-gravity combustion synthesis, microstructural evolution during solidification plays an important role in determining the structure and properties of the solidified samples, and a systematic study on this problem is necessary for the manipulation of microstructure and optimization of processing parameters. This paper makes a detailed investigation on microstructure evolution during the solidification of ceramic melts in high-gravity combustion synthesis. The effects of phase composition and cooling conditions on the solidification process and microstructural development are discussed for both single-phase and multiphase eutectic ceramic materials.

2. Experimental

Commercial powders of Al, NiO, Y_2O_3 and ZrO_2 were used as raw materials. The Al powder had a purity of >99% and an average

particle size of 2–3 μ m, and the oxides were analytical-grade reagents. The Al and NiO powders were used to produce Al₂O₃ by the aluminothermic reaction of 2Al + 3NiO = Al₂O₃ + 3Ni. The nominal chemical compositions of all the samples are listed in Table 1.

The raw materials were mixed in ethanol and homogenized by planetary ball milling for 1 h, and then dried at 80 °C for 8 h to prepare a uniform mixture of reactant powders. The powder mixture was cold-pressed into a round compact and loaded into a graphite crucible. The crucible was coated by carbon felt and then put into a steel vessel. The vessel was mounted on a Ni-based superalloy rotator, which was placed in a closed reaction chamber. A schematic illustration of the equipment is shown in Fig. 1(a).

The reaction chamber was evacuated to a vacuum of <100 Pa and then the rotator was started. By centrifugation, a high-gravity field was induced. The strength of the high-gravity field was evaluated by a high-gravity factor of g'/g, where g' and g mean the centrifugal acceleration and normal gravitational acceleration, respectively. In this work, a high-gravity factor of 900 was applied. The high-gravity field could be modulated by controlling the rotation frequency of the rotator. When the designed high-gravity factor was reached, the combustion reaction was triggered by passing an electric current through a tungsten coil closely above the sample. In the reaction, a large amount of heat energy was created and the products were melted. Then, ceramic and metallic melts were separated in a high-gravity field because of their density difference. After cooling and solidification, bulk ceramic samples and Ni ingots were obtained in graphite crucibles, as sketched in Fig. 1(b). Fig. 1(c) shows the photographs of some asprepared ceramic samples as well as a Ni ingot.



Fig. 1. A schematic illustration of the equipment for high-gravity combustion synthesis and photographs of as-prepared samples: (a) a simple drawing of the equipment, where the high-gravity field is induced by centrifugation and the high-gravity acceleration is calculated by $g' = \omega^2 \cdot (R_1 + R_2)/2$; (b) bulk ceramics and Ni metal ingot obtained in the graphite crucible; (c) photographs of some ceramic and glass samples as well as the Ni ingot prepared by high-gravity combustion synthesis.

The prepared ceramic samples were machined and then characterized. The phase assemblage was identified by X-ray diffraction (XRD; D8 Focus, Bruker, Germany). The microstructure was examined by scanning electron microscopy (SEM; S-3400, Hitachi, Japan), and chemical analysis for selected areas was carried out by energy dispersive spectroscopy (EDS; INCA, Oxford Instrument, UK).

3. Results and discussion

High-gravity combustion synthesis is a complex process including combustion reaction, phase separation, and solidification. Combustion reactions generally progress very quickly and last no more than 10 s. During the reactions, much heat energy is released, leading to an abrupt increase in temperature, and the products occur in a molten state. Then, phase separation happens, which involves the separation between ceramic and metallic melts and removal of gas bubbles from the melts. Finally, solidification takes place during a cooling and bulk ceramic samples are obtained together with Ni ingots.

To realize the melt-casting of ceramics by high-gravity combustion synthesis, it is required that the reaction temperature exceeds the melting or eutectic points of the ceramic materials. For the materials studied in this work, the adiabatic temperatures are all much higher than the melting or eutectic points, as shown in Table 1. Consequently, the ceramic samples are expected to be produced by solidification from melts instead of powder metallurgy.

In this work, both single-phase and multiphase eutectic ceramics were prepared by high-gravity combustion synthesis, as shown in Table 1. In the samples, no Al or NiO was found, indicating that the aluminothermic reaction of $2AI + 3NiO = A - I_2O_3 + 3Ni$ was almost complete. In the XRD patterns of the ceramic samples, diffraction peaks of Ni were not found. EDS analysis revealed that the content of Ni in the samples was below 1.0 wt%. From these results, the phase separation between Ni and ceramic melts was almost finished.

The prepared ceramic samples showed a diversity of microstructures, including faceted crystals, skeletal crystals, and fibrous, lamellar and three-dimensional interpenetrating eutectic structures. Associated with SEM observations, the microstructural evolution during solidification for single-phase ceramics and multiphase eutectic ceramics will be discussed respectively as follows.

3.1. Single-phase ceramics

3.1.1. Al₂O₃

Single-phase Al₂O₃ ceramics can be prepared by high-gravity combustion synthesis from the aluminothermic reaction of 2Al + 3NiO = Al₂O₃ + 3Ni. For this reaction, the adiabatic temperature reaches the boiling point of Ni (2884 °C). The vaporization of Ni is not desirable as this will increase the porosity in the solidified samples. In order to decrease the reaction temperature, Al₂O₃ powder is often added as diluent in the thermite reaction. With increasing content of Al₂O₃ diluent, the adiabatic temperature for the reaction of 2Al + 3NiO + xAl₂O₃ = (1 + x)Al₂O₃ + 3Ni decreases, as plotted in Fig. 2. When too much diluent is added (x = 1.6), the adiabatic temperature decreases to below the melting point of Al₂O₃ (2054 °C). Considering the fact that the actual reaction temperature is lower than the adiabatic one because of heat dissipation, an appropriate content of diluent is expected as $0.2 \le x \le 0.6$.

During the solidification of ceramic melts, the driving force for liquid-solid transformation and growth rate of solid phases are closely related to the under-cooling degree. For this reason, the microstructure evolution during solidification depends on thermal



Fig. 2. The relationship between the adiabatic temperature and the proportion of diluent for the combustion reaction of $2AI + 3NiO = AI_2O_3 + 3Ni$.

gradient in melts. By high-gravity combustion synthesis, the cooling and solidification of ceramic melts occur in a graphite crucible (Fig. 1(b)). With a good thermal conductivity, the graphite crucible is a major source of heat dissipation. In this case, a thermal gradient occurs in the radial direction in melts, where the temperature decreases from the center to the side. With such a thermal gradient, solidification will take place first at the side and then develop into the center. This is verified by SEM observation, as shown in Fig. 3, where the growth direction of Al₂O₃ crystals is nearly parallel to the radial direction.

Besides crucibles, another source of heat dissipation is the fast gas flow above the surface of melts under the condition of highspeed rotation. In this case, a thermal gradient also existed in the axial direction in the melts. This thermal gradient caused a directional solidification from the surface to the center, as shown in Fig. 4. Some huge rod-like crystals up to 1 mm growing along the axial direction were observed. The formation of these crystals can be probably attributed to the coupling of combustion reaction with the high-gravity field, because both the propagation of combustion wave and the high-gravity force (G') occur in the axial direction, where enhanced mass transportation and heat transfer are expected.

During solidification, Al₂O₃ showed a strong tendency to develop into faceted crystals, even in large dendrites, as shown in Fig. 5. This agrees well with the Jackson's criterion on interface structures and crystal growth modes in solidification of melts. According to the Jackson's criterion [26], the interface structure is identified by an interface roughness parameter defined as $\alpha = A \cdot \Delta S_m / R$, where ΔS_m is the melting entropy, *R* is the gas constant, and A is a crystallographic parameter equal to the ratio between the number of bonds parallel to the surface and the total number of bonds. For a solidification process, if $\alpha < 2$, the liquid/ solid interface is atomically rough and non-faceted interface is expected. If $\alpha > 2$, the interface is atomically smooth and faceted interface is produced because the crystal growth is limited by nucleation rate. The melting entropies of ceramic compounds investigated here are listed in Table 2. For Al₂O₃, $\Delta S_m/R = 5.74$, and A is estimated to be 0.5–1, giving $\alpha > 2$. Therefore, atomically smooth interface structure should be involved during the solidification of Al₂O₃, resulting in faceted crystals.

For the solidification of ceramic materials like Al_2O_3 with large melting entropies, the energy barrier for nucleation is high, and the crystal growth is thought to take place by two-dimensional nucleation and growth. With as-existing crystals as nucleation sites, new nuclei form and grow up. By iterative nucleation and



Fig. 3. SEM images showing varying microstructures in the radial direction in Al₂O₃ samples.



Fig. 4. SEM images showing varying microstructures in the axial direction in Al₂O₃ samples.



Fig. 5. SEM images and EDS results of Al₂O₃ dendrites.

growth, large faceted crystals will be produced with a sufficient material supply from the melt at the early stage of solidification. When the solidification is close to the end, however, solid phase is predominant and the melt becomes isolated. In this wise, material supply for solidification is limited and incomplete growth of faceted crystals takes place, resulting in a terraced morphology, as shown in Fig. 6.

At the surface of some Al_2O_3 samples, bright layers with a thickness of nearly 0.5 mm were produced. These layers were not entirely smooth but consisted of small flakes with different

Table 2	
Melting entropies of ceramic materials involved in this work.	

Compound	$\Delta S_{\rm m} (\mathrm{J} \mathrm{mol}^{-1} \mathrm{K}^{-1})$	$\Delta S_{\rm m}/R$
Al ₂ O ₃	47.72	5.74
YAG	122.38	14.72
$MgAl_2O_4$	81.64	9.82
ZrO ₂	29.51	3.55



Fig. 6. Terraced structures observed in as-prepared Al₂O₃ samples.

orientations. The width of the flakes varied in the range of 3-5 mm, and each flake was composed of orderly arranged faceted Al_2O_3 crystals, as shown in Fig. 7. Such strongly textured structure was also verified by XRD analysis. As shown in Fig. 8, an evident difference in relative intensities of the diffraction peaks was observed between the XRD patterns of the flakes and that of a powder sample.

The formation of the strongly textured structure can be attributed to two reasons. One is the intrinsic faceted growth character of Al₂O₃, and the other is the particular solidification condition at the melt surface, which is characterized by fast cooling and free growth. Under high-frequency rotation, the gas flow sweeping the melt surface causes fast cooling and induces rapid solidification as well as crystal growth. On the other hand, crystal growth at the melt surface is not constrained by crucible, and thus the Al₂O₃ crystals can grow freely. It is thought that the strongly textured structure has been produced by parallel continuous growth. At first, individual primary nuclei are precipitated in the melt and with different orientations. Then, based on each primary nucleus, more nuclei occur and grow with an orientation identical to the basis. Finally, by continuous nucleation and growth, an array of crystals with the same orientation is produced, which is recognized as a flake on a macroscopic scale. By the assembly of such flakes, a strongly texture structure is obtained.

In the prepared Al₂O₃ samples, skeletal crystals were also observed, as shown in Fig. 9. To some extent, the skeletal crystals can be regarded as intermediate products from incomplete growth of faceted crystals. The skeletal crystals are possibly induced by fast cooling at melt surface. On one hand, fast cooling often results in large under-cooling degree and high growth rate of crystals. On the other hand, fast cooling means a short lifetime of melt, which can lead to the lack of material supply. Without sufficient material supply, the imperfections created during fast crystal growth cannot be timely repaired, leading to the occurrence of skeletal crystals.

In contrast to the surface, in the center part of samples, rather dense microstructure was obtained. In the fracture surface of the center part, typical cleavage planes are visible, as shown in Fig. 10. Few secondary particle inclusions were found inside the Al_2O_3 crystals. From EDS analysis for six individual crystals with different size and morphology (e.g., Figs. 5 and 6), the atomic ratios of Al and O are 59.5–60.5% and 39.5–40.5%, respectively, showing a good consistency with the nominal composition of Al_2O_3 .

3.1.2. YAG

Besides Al₂O₃, YAG is another example of single-phase ceramics prepared by high-gravity combustion synthesis. YAG can be prepared from the reaction of $10Al + 15NiO + 3Y_2O_3 = 2Y_3A-I_5O_{12} + 15Ni$. For this reaction, the calculated adiabatic temperature is 2593 °C, which is much higher than the melting point of YAG (1950 °C). Therefore, it is feasible to carry out the melt-casting of YAG ceramics by high-gravity combustion synthesis.

Fig. 11 shows SEM images of as-prepared YAG ceramics, without or with glass additives. In pure YAG ceramics without



Fig. 7. SEM images showing the strongly textured structure at the surface of Al₂O₃ samples.

additives, coarse grains were produced and some of them were larger than 500 μ m. At the boundary areas of the coarse grains, large cavities up to 100 μ m were present. In the samples with 5 wt% SiO₂ or 10 wt% Si–Al–Ca–O glass additives, both the porosity and grain size were greatly reduced. The reduction of porosity and



Fig. 8. XRD patterns of as-prepared Al_2O_3 samples: (a) pulverized powder; (b–d) flakes in the surface layer.

grain size contributed to a higher hardness. For example, the Vickers hardness of the YAG sample with 10 wt% Si–Al–Ca–O glass additive was 8.7 ± 0.2 GPa, which was 21% higher than that $(7.2 \pm 0.4$ GPa) of pure YAG samples with prepared by high-gravity combustion synthesis.

The above results show that, during the melt-casting of YAG ceramics, proper additives are helpful to reduce the porosity and limit grain growth. In the solidified YAG samples, the porosity comes from two sources. One is the shrinkage cavities created during fast solidification of the melt, and the other is the gas bubbles not removed from the melt. The densities of YAG solid and melt are 4.552 and 3.688 g/cm³, respectively [27]. In this case, the solidification of YAG melt is accompanied by a volume shrinkage of 19%. Under a fast cooling rate and with a short lifetime of melt, the volume shrinkage is difficult to be fully compensated, which causes shrinkage cavities. Such shrinkage cavities can be filled by additives with lower melting temperatures than YAG. When the solidification of YAG is over, the additives still keep a liquid state and can feed into the shrinkage cavities. Additionally, with a longer lifetime than YAG melt, the additive melt can accommodate gas bubbles and reduce the porosity of solidified YAG samples.

The effect of additives in limiting grain growth of YAG can be attributed to depressed grain boundary migration. In high-gravity combustion synthesis, YAG melt is intersected by the additive melt and divided into smaller sections. Among these sections, mass transportation and heat transfer are greatly blocked. In this way, the grain growth of YAG is restricted into a smaller volume, reducing the occurrence of huge grains. Moreover, in each small section, YAG grains are separated by the additive melt and grain



Fig. 9. SEM images of skeletal crystals in as-prepared Al₂O₃ samples.

boundary migration is pinned, which is helpful to limit grain growth.

Similar to Al_2O_3 , YAG also has a high melting entropy of $\Delta S_m/R = 14.72$ (Table 2) and thus is expected to undergo faceted crystal growth. This has been verified by SEM observation showing faceted polyhedron YAG crystals (Fig. 11). Especially, a regular polyhedral morphology was observed for the crystals growing in cavities with no spatial constraint.

Besides polyhedral faceted crystals, other crystallization shapes were also found in the prepared YAG samples. At the boundary areas or the surface of some large faceted crystals, smaller grains or thick dendrites occurred, as shown in Fig. 12. The smaller grains did not fully develop or show regular faceted morphology. The dendrites were composed of ultrafine crystallites below 1 μ m, and some crystallites were only ~100 nm. The exact mechanism for the formation of the dendrites is not clear yet. Perhaps they have developed from isolated fractions of melt under a large undercooling degree.

3.1.3. MgAl₂O₄

Other than Al_2O_3 and YAG, $MgAl_2O_4$ is also an important singlephase ceramic material prepared by high-gravity combustion



Fig. 10. SEM images of fracture surface of Al₂O₃ samples showing typical feature of cleavage planes.



Fig. 11. SEM images of as-prepared YAG samples: (a) with no additives; (b) with 5 wt% SiO₂; (c-f) with 10 wt% Si-Al-Ca-O glass.

synthesis. MgAl₂O₄ can be synthesized from the reaction of 2Al + 3NiO + MgO = MgAl₂O₄ + 3Ni. For this reaction, the calculated adiabatic temperature is 2476 °C and higher than the melting point of MgAl₂O₄ (2135 °C). In this way, the melt-casting of bulk MgAl₂O₄ ceramics can be realized by high-gravity combustion synthesis.

Typical SEM images of as-prepared MgAl₂O₄ ceramics are shown in Fig. 13. At the sample surface, a porous structure was produced, consisting of equiaxed crystals $>100~\mu m$ and large cavities. In the center, a relatively dense structure was obtained with plate-like crystals with a width $>10~\mu m$. At the boundaries of the plate-like crystals, smaller grains and pores existed. The



Fig. 12. Different crystallization morphologies observed in YAG samples: (a and b) mixed microstructure with fine crystallites distributed at the boundary regions of the large crystals; (c-f) thick dendrites produced at the surface of large crystals.



Fig. 13. SEM images of as-prepared MgAl₂O₄ samples: (a and b) porous structure with coarse crystals observed at the surface of samples; (c) dense structure with plate-like crystals obtained in the center of samples; (d) faceted MgAl₂O₄ crystals with an octahedral shape.

different structures observed at the surface and in the center of samples are related to different solidification conditions, including under-cooling degree and spatial constraint for crystal growth.

MgAl₂O₄ has a melting entropy of $\Delta S_m/R = 9.82$ (Table 2), which is between those of Al₂O₃ and YAG. From the Jackson criterion, MgAl₂O₄ should also undergo faceted crystal growth. This is confirmed by SEM observation showing faceted MgAl₂O₄ crystals with an octahedral shape, as shown in Fig. 13(d).

3.2. Multiphase eutectic ceramics

In addition to single-phase ceramics, multiphase eutectic ceramics can also be prepared by high-gravity combustion synthesis. Compared with single-phase ceramics, multiphase eutectic ceramics have two advantages. At first, the eutectic point of two or more phases is usually lower than the melting point of each individual phase. That is to say, eutectic systems have lower melting temperatures than single-phase systems. Eutectic melts have a longer lifetime, which is desirable for phase separation and removal of gas bubbles. On the other hand, multiphase eutectic ceramics can offer more opportunity for tailoring the microstructure. In single-phase ceramics, only one phase is involved and the microstructure is characterized by grain size and morphology of that phase. In multiphase eutectic ceramics, however, two or more phases co-exist, and the microstructure is affected by more factors, including the proportion, size and morphology of each phase. For example, in eutectic ceramic materials, a change in proportions of the components often induces a transition of microstructure.

In comparison with single-phase ceramic materials, multi-phase eutectic ceramics will show more complicated behaviors in microstructure evolution during solidification. Here, both binary and ternary eutectic ceramics have been prepared by high-gravity combustion synthesis, and their microstructure evolution characteristics during solidification from melts are discussed as follows.



Fig. 14. XRD pattern of the YAG-Al₂O₃ eutectic ceramic sample (YA-1).

3.2.1. YAG-Al₂O₃

The first example of binary eutectic ceramics is the YAG-Al₂O₃ system. In this system, two compositions were studied, including a eutectic one (YA-1) and a hypoeutectic one (YA-2), as shown in Table 1. For both the compositions, the calculated adiabatic temperatures are much higher than the eutectic temperature as well as the melting points of Al_2O_3 and YAG.

Fig. 14 shows the XRD pattern of the sample YA-1, which was composed of major YAG and minor Al_2O_3 . This phase composition is consistent with that expected from the binary phase diagram shown in Fig. 15. By calculation from the nominal chemical composition, the volume fractions of YAG and Al_2O_3 are 59% and 41%, respectively. The sample YA-2 also consisted of YAG and Al_2O_3 , except that the major phase was Al_2O_3 . By calculation, the volume fractions of Al_2O_3 and YAG in YA-2 are 84% and 16%.

In the samples YA-1 and YA-2, different microstructures were obtained, as shown in Fig. 16. YA-1 showed typical fine eutectic structures with interphase spacings $< 1 \mu$ m, but in YA-2 large Al₂O₃ crystals were produced and eutectics occurred only at the



Fig. 15. A simplified phase diagram of the Al₂O₃-Y₂O₃ binary system.



Fig. 16. SEM images of YAG–Al₂O₃ eutectic ceramic samples: (a and b) uniform and fine eutectic structure observed in YA-1 with a eutectic composition; (c–e) mixed structure with large primary Al₂O₃ crystals and fine eutectics observed in YA-2 with a hypoeutectic composition; (f and g) EDS spectra for Al₂O₃ and YAG crystallites, as marked with "1" and "2", respectively in (e).



Fig. 17. XRD pattern of the Al₂O₃-ZrO₂ eutectic ceramic sample (AZ).

boundaries of the large crystals. The different microstructures observed in YA-1 and YA-2 should be attributed to the different volume fractions of Al_2O_3 and YAG in them. According to the binary phase diagram, for YA-1 with a eutectic composition, the eutectic reaction "liquid \rightarrow YAG + Al_2O_3 " takes place during the whole solidification process, leading to a homogeneous eutectic structure. For YA-2 with a hypoeutectic composition, during solidification primary Al_2O_3 crystals will be precipitated first. The precipitation of Al_2O_3 causes a segregation of Y_2O_3 in the liquid, whose composition gradually changes along the liquidus line (AE line in the phase diagram in Fig. 15). When the composition of the liquid reaches the eutectic point, eutectic reaction occurs with further cooling and continued solidification. Consequently, the

final structure of YA-2 is made up of primary Al_2O_3 crystals and YAG-Al_2O_3 eutectics at the boundaries of the primary crystals.

3.2.2. Al₂O₃-ZrO₂

Another example for binary eutectic ceramics prepared by high-gravity combustion synthesis is the Al_2O_3 – ZrO_2 system. From the Al_2O_3 – ZrO_2 phase diagram, the eutectic composition was selected, as shown in Table 1, where 1 mol% Y_2O_3 was added to stabilize the tetragonal structure of ZrO_2 . For the eutectic composition, the calculated adiabatic temperature is 2678 °C and higher than the eutectic point of 1860 °C.

Fig. 17 shows XRD pattern of the as-prepared Al_2O_3 -ZrO₂ eutectic ceramic sample (AZ). From the pattern, the sample was composed of Al_2O_3 and ZrO₂. In the sample, both polymorphs of ZrO₂ were observed, with either tetragonal or monoclinic lattice structure. The occurrence of monoclinic ZrO₂ can be attributed to the relatively low concentration of Y₂O₃. From the nominal chemical composition of the sample AZ, the volume fractions of Al_2O_3 and ZrO₂ are calculated to be 67% and 33%, respectively.

The microstructure features of the Al₂O₃–ZrO₂ eutectic ceramic sample existed on different size scales, as shown in Fig. 18. On a larger scale, the sample consisted of colonies with an average size of >10 μ m. In the center of each colony, the eutectic structure was unaffected, but at the boundaries the eutectic structure became irregular. The interphase spacing in the center (<1 μ m) was much smaller than that at the boundaries.

During the solidification of eutectics, the interphase spacing is determined by the balance of two opposite energy contributions.⁹ On one hand, transverse diffusion of solutes must occur over greater distance for thicker lamellae or fibers, therefore, favoring smaller interphase spacings. On the other hand, the interfacial energy associated to interphase boundaries will increase as the width of lamellae or fibers decreases, thus favoring larger



Fig. 18. SEM images of Al₂O₃-ZrO₂ eutectic ceramic samples: (a and b) an overview of colonies; (c) and (d) fine eutectic structures in a colony.

interphase spacings. In general, the interphase spacing is related with under-cooling degree and growth rate, which can be expressed as:

$$\lambda \Delta T = C_1$$
 and $V \lambda^2 = C_2$,

where λ is the interphase spacing, ΔT is the under-cooling degree, V is the growth rate, C_1 and C_2 are the constants [28]. From the formulae, a greater under-cooling degree is expected in the center than that at the boundaries of the colonies in the Al₂O₃–ZrO₂ eutectic ceramics.

According to the model proposed by Hunt and Jackson [28], the microstructure of binary eutectics depends on the melting entropies of the components. If the large-volume component has a high melting entropy ($\alpha > 2$) and the minor one has a small melting entropy ($\alpha < 2$), a "complex regular" microstructure will be produced, which shows many features of the lamellar or fibrous eutectic microstructure. In this work, the Al₂O₃-ZrO₂ eutectic sample possesses a phase composition of 67%Al₂O₃ + 33%ZrO₂ in volume fraction. The large-volume component of Al₂O₃ has a higher melting entropy of $\Delta S_m/R$ = 5.74, and the minor ZrO₂ has a lower melting entropy of $\Delta S_m/R$ = 3.55. In this case, the eutectic sample showed a complex microstructure, where both fibrous and lamellar features were observed, as shown in Fig. 18(c and d). In the fibrous structure, fine ZrO₂ fibers with a width of 100-200 nm were embedded in a continuous Al_2O_3 matrix. The lamellar structure was somewhat incomplete, which was more exactly a mixture of lamellar and fibrous features.

The microstructure of binary eutectics is usually connected with the volume fractions of the two components. It was reported that [29], if the surface energies are isotropic or with no significant anisotropy, the fibrous structure is stable when the volume fraction of the minor component is below 32%, and when the fraction is >32% a lamellar structure will be produced. This prediction has been proved by experimental results on several metal eutectics, where a lamella-to-fiber transition takes place at



Fig. 19. XRD pattern of the YAG-Al₂O₃-ZrO₂ eutectic ceramic sample (YAZ).

the volume fraction of \sim 30%. In the Al₂O₃–ZrO₂ eutectic ceramic sample prepared in this work, the volume fraction of the minor component (ZrO₂) is 33%, which is almost the critical point for the transition between the two structures. As a result, both fibrous and lamellar structures were obtained in the sample.

Another factor affecting the microstructure of eutectics is the growth rate. During the solidification of eutectic ceramics, microstructure evolution is generally related with the thermal gradient, concentration gradient, and growth rate. For given thermal and concentration gradient values, the solidification mechanism depends on growth rate. When the growth rate is below a critical value, planar growth front is stable, and with increasing growth rate shallow cells will occur as a secondary phase. The microstructure transition from coupled to cellular and then to shallow cells with increasing growth rate has been observed in Al₂O₃–ZrO₂ system [11]. In this work, the discrepancy



Fig. 20. SEM images showing the eutectic structures in YAG-Al₂O₃-ZrO₂ ternary eutectic ceramics.

in the growth rates of different parts is probably one of the reasons responsible for the diversity of microstructures observed in the Al_2O_3 -Zr O_2 eutectic ceramic sample.

3.2.3. YAG-Al₂O₃-ZrO₂

Besides binary eutectic systems, $YAG-Al_2O_3-ZrO_2$ ternary eutectic ceramics have also been prepared by high-gravity combustion synthesis. The eutectic composition was determined according to the $Al_2O_3-Y_2O_3-ZrO_2$ phase diagram and reported in Table 1. For the eutectic composition, the calculated adiabatic temperature is 2678 °C, which is much higher than the eutectic point of 1715 °C.

The XRD pattern of as-prepared YAG–Al₂O₃–ZrO₂ eutectic sample (YAZ) is shown in Fig. 19. The sample consisted of YAG, Al₂O₃ and tetragonal ZrO₂, with no occurrence of monoclinic ZrO₂. By calculation from the nominal chemical composition, in the sample YAZ, the volume fractions of YAG, Al₂O₃ and ZrO₂ are 49%, 37% and 14%, respectively.

In the YAG–Al₂O₃–ZrO₂ eutectic sample, a typical colony structure was observed, as shown in Fig. 20. Most colonies had a size of >30 μ m and some were larger than 100 μ m. In the center parts of the colonies, two microstructure features were found, including lamellar and three-dimensional interpenetrating structures. The eutectic structures were composed of YAG and Al₂O₃ crystallites with interphase spacings of <1 μ m, and ultrafine ZrO₂ particles were distributed at the interface between YAG and Al₂O₃. At the boundaries of the colonies, larger interphase spacings were observed.

In the YAG–Al₂O₃–ZrO₂ ternary eutectic system, YAG and Al₂O₃ have higher melting entropies and ZrO₂ has a lower one. In the sample of YAZ, YAG was the major phase with a volume fraction of 49%, and the minor Al₂O₃ and ZrO₂ had volume fractions of 37% and 14%. According to the model proposed by Hunt and Jackson [29], Al₂O₃ and ZrO₂ will form lamellar and fibrous structures, respectively. The experimentally observed microstructure in the sample YAZ was basically consistent with the prediction, except for the occurrence of the three-dimensional interpenetrating structure.

For the solidification of multiphase eutectic ceramics, thermal residual stress is usually a problem of consideration. In high-gravity combustion synthesis, eutectic ceramics are prepared by direct solidification from hot melts. During solidification, two or more phases with different thermal expansion coefficients are grown simultaneously. The thermal expansion mismatch will cause thermal strain in the eutectic ceramics. The strain cannot be relaxed by plastic deformation, which is limited in ceramic materials, and hence thermal residual stress is induced. The residual stress depends on the thermal expansion mismatch of different phases, cooling rate, and morphological features of the eutectic structure. As an example, the residual stress in Al₂O₃-Y₂O₃-ZrO₂ ternary eutectics grown by the laser-heated floating-zone method has been studied [30], where the compressive residual stress in Al₂O₃ was measured to be 160-300 MPa. In the YAG-Al₂O₃-ZrO₂ eutectic ceramics prepared here by high-gravity combustion synthesis, no cracks were observed at the interfaces between different phases, indicating an excellent interfacial bonding strength.

4. Conclusion

Both single-phase and multiphase eutectic ceramics were prepared by high-gravity combustion synthesis. According to the microstructural features observed in as-prepared samples, the microstructure evolution mechanism during solidification was studied. For most single-phase ceramic materials like Al_2O_3 , YAG and $MgAl_2O_4$ with high melting entropies, a faceted crystal growth mode was operative in solidification, which is consistent with Jackson's criterion on interface roughness. The solidification process strongly depended on cooling conditions, and the discrepancy in cooling conditions for different parts of samples resulted in a diversity of microstructures. As an example, a strongly textured layer composed of orderly arranged faceted crystals was observed at the surface of Al_2O_3 samples. In the solidification of YAG ceramics, the incorporation of proper glass additives was helpful to decrease the porosity and reduce grain growth.

Compared with single-phase ceramics, multiphase eutectic ceramics have lower melting temperatures, which is desirable for phase separation and removal of gas bubbles. In addition, eutectic ceramics consist of multiple components and can provide more opportunity for tailoring microstructures. From the experimental results, the microstructure of eutectic ceramics was related with the volume fractions of components, and various eutectic structures were produced such as lamellae, fibers, and threedimensional interpenetrating frameworks. The eutectic structures showed interphase spacings on a submicron scale. In the eutectic ceramics, no cracks were found at the interface between different phases, indicating an excellent interfacial bonding strength.

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