INTRODUCTION

Ni-based single crystal superalloys are currently the main thrust materials in hot end of the industrial gas turbines. However, even for the most advanced alloys, that is, the 4th or 5th generation Ni-based single crystal, their properties would degrade sharply if the temperature exceeds 1150°C. In order to solve this problem, many potential high-temperature materials were explored. For instance, directionally solidified oxide eutectic crystals, such as Al₂O₃/ZrO₂, Al₂O₃/GdAlO₃, Al₂O₃/Y₃Al₅O₁₂, etc., have been extensively studied.

SHORT COMMUNICATION

Investigation on the leading phase of Al₂O₃/Y₃Al₅O₁₂ eutectic crystals prepared by directional solidification

Yujie Zhong¹,² | Shengjie Wang¹ | Yangru Liu¹ | Qian Gao¹ | Kuikui Wang³ | Xu Wang⁴

¹School of Materials Science and Engineering, Xi’an Shiyou University, Xi’an, China
²Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, South China University of Technology, Guangzhou, China
³Laboratory of New Fiber Materials and Modern Textile, Growing Basis for State Key Laboratory, College of Materials Science and Engineering, Institute of Materials Science and Environment, Qingdao University, Qingdao, China
⁴School of Materials Science and Engineering, Xi’an University of Technology, Xi’an, China

Correspondence
Xu Wang, School of Materials Science and Engineering, Xi’an University of Technology, 5 South Jinhua Road, Xi’an 710048, China. Email: xuwang@xaut.edu.cn

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Abstract
The leading phase of eutectic materials has an effect on the solidification behavior and further influences on their properties. Many studies have been carried out on the leading phase of metal/metal and nonmetal/metal eutectic alloys. Nevertheless, few studies were focused on no-metal/no-metal eutectic materials. In the present work, the leading phase in the Al₂O₃/Y₃Al₅O₁₂ eutectic crystal during solidification was investigated by electron back-scattered diffraction and discussed according to the classical solidification theory. It is observed that the Y₃Al₅O₁₂ was the leading phase. The leading phase was determined by the wetting angle and the undercooling. At a given wetting angle, the Y₃Al₅O₁₂ would be the leading phase when the undercooling exceeds the critical value.

KEYWORDS
Al₂O₃/Y₃Al₅O₁₂ eutectic crystals, eutectic solidification, leading phase, undercooling

1 | INTRODUCTION

Ni-based single crystal superalloys are currently the main thrust materials in hot end of the industrial gas turbines. However, even for the most advanced alloys, that is, the 4th or 5th generation Ni-based single crystal, their properties would degrade sharply if the temperature exceeds 1150°C. In order to solve this problem, many potential high-temperature materials were explored. For instance, directionally solidified oxide eutectic crystals, such as Al₂O₃/ZrO₂, Al₂O₃/GdAlO₃, Al₂O₃/Y₃Al₅O₁₂, etc., have been extensively studied.
Al$_2$O$_3$/Er$_3$Al$_5$O$_{12}$ and Al$_2$O$_3$/Y$_3$Al$_5$O$_{12}$ (YAG) eutectic crystals, have attracted great interest because of their potential applications at ultra-high temperatures. These materials have superior flexural strength at temperature close to their melting point, good oxidation, and creep resistance.

Eutectic growth in crystals/alloys involving the nucleation and coordinated growth of two or more phases from one liquid phase has always been the topic of interest. Nucleation conditions usually determine the solidification evolution of a liquid melt. Two phases do not nucleate at the same time in eutectic alloys. There must be a leading phase, which nucleates and grows preferentially. However, there are no uniform conclusions as to the cause of the leading phase formation in eutectic alloys. For instance, in the metal/metal eutectic alloys, the component possessing smaller dynamic undercooling might nucleate first and act as the leading phase. However, for nonmetal/metal eutectic alloys, such as Al/Si eutectics, Si is usually considered as the leading phase though it has a higher dynamic undercooling (1-2°C) than that of Al (0.02°C). That is attributed to constitutional supercooling in the alloys and detailed interpretation can be found in Ref. 18. For nonmetal/nonmetal eutectic systems, such as Al$_2$O$_3$/YAG eutectic crystals, in which both phases have high melting entropies, the leading phase has not yet been studied in detail. Understanding the leading phase and nucleation during solidification is the kernel parameters for the microstructure optimization of the engineering ceramics. It can also ensure their excellent properties for the as-grown crystals, so that it is necessary to study the leading phase in Al$_2$O$_3$/YAG binary eutectic crystals.

Herein, we investigated the leading phase of Al$_2$O$_3$/YAG eutectic crystals with two kinds of seed bars used. It is found that the leading phase of the Al$_2$O$_3$/YAG eutectic crystal is determined by the wetting angle and the undercooling. At a given wetting angle, the Y$_3$Al$_5$O$_{12}$ would be the leading phase when the undercooling exceeds the critical value. This finding is of clear significance for the microstructure optimization and design of the Al$_2$O$_3$/YAG eutectic crystal.

2 | EXPERIMENT PROCEDURE

Nano-Al$_2$O$_3$ and Nano-Y$_3$O$_5$ powders purchased from Beijing Yosoc Science& Technology Co. Ltd were mixed at a mole ratio of 79:21 and ball milled for 10 hours. Precursors were prepared with a pressure of 50 MPa for 30 minutes. Next, the precursors were sintered at 1550°C for 2 hours. Directional solidification was carried out with an optical floating zone (OFZ) furnace with 4 × 3 kW xenon lamps in vacuum environment. The withdraw rate was 10 mm/h. Crystals were prepared with up to 10 mm in diameter and ~120 mm in length. In order to start the solidification, a polycrystalline Al$_2$O$_3$ bar and a single crystal bar (c-axis sapphire) were used as the seeds.

The as-prepared samples were sectioned by a diamond saw along the growth direction. The samples were ground with SiC paper until 2000# and further polished down to 2.5 μm diamond paste.

The microstructure was observed with scanning electron microscopy (SEM, LEO, Supra35). The orientation was successfully determined by electron back-scattered diffraction (EBSD, NordlysNano).

3 | RESULTS AND DISCUSSION

The microstructure between the seed bar (polycrystal Al$_2$O$_3$) and Al$_2$O$_3$/YAG eutectic crystals is shown in Figure 1. A layer of the YAG with 1-2 μm in thickness was identified on the seed crystal. The preliminary results indicate that the leading phase to nucleate and crystallize is the cubic YAG and then the trigonal alumina. The typical coupled eutectic growth morphology was observed afterward.

Specimens were prepared for EBSD investigation to further study the relationship between the seed bar and Al$_2$O$_3$/YAG crystals. Firstly, a polycrystalline alumina bar was used as the seed. Figure 2A shows the EBSD band-index micrographs at the interface between the seed bar and Al$_2$O$_3$/YAG eutectic crystals. The dark area is Al$_2$O$_3$, and the gray area is the YAG. Figure 2B shows the corresponding EBSD orientation maps of Al$_2$O$_3$. In order to show the relationships clearly, the EBSD map of the YAG is not shown. It can be observed that the YAG (the white area) is the leading phase to crystallize on the seed. It is worth noting that the orientation of Al$_2$O$_3$ in the as-prepared eutectic crystals is totally different with the orientation of the Al$_2$O$_3$ seed. Namely, the epitaxial growth of Al$_2$O$_3$ does not occur, which indicates that Al$_2$O$_3$ is not the leading phase. Otherwise, the Al$_2$O$_3$ in the eutectic...
crystal would grow epitaxially along the seed and the orientation would be the same as the seed.\textsuperscript{21}

For comparison, a $c$-sapphire was used as the seed bar. Figure 3 shows the EBSD map between the $c$-sapphire and the eutectic crystal. The white area in Figure 3A is the YAG. The morphology of Al$_2$O$_3$ in the eutectic is quite different from that of the $c$-sapphire. The interface between the $c$-sapphire and the eutectic is straight. These results further demonstrate that the YAG is the leading phase during solidification. In this part of the work, the liquid ceramic zone was soaked for 1 minute to ensure that the $c$-sapphire was melted. Therefore, the orientation relationship of Al$_2$O$_3$ in the eutectic is the same as that of the $c$-sapphire. The goal is to verify the effect of interfacial energy on microstructure, and results can be found in Ref.\textsuperscript{7}

The heterogeneous nucleation rate, $I$, is described by terms involving the rate of atom attachment to the growing nucleus, the concentration of clusters, and the activation barrier for nucleation.\textsuperscript{22} As reported by Yan et al,\textsuperscript{23} the phase with larger $I$ is more likely to be the leading phase. The value of the nucleation rate of binary Al$_2$O$_3$/YAG eutectic can be calculated based on the classical nucleation theory\textsuperscript{20}:

$$I = 10^{32} \exp \left( - \frac{\Delta G_0^0 + \Delta G_d}{k_B T} \right)$$  \hspace{1cm} (1)

where $\Delta G_0^0$ is activation energy for the nucleation of the critical cluster radius, $\Delta G_d$ is activation free energy for diffusion across S/L interface, and $k_B$ is Boltzmann constant, $1.38 \times 10^{-23}$ J/K. $\Delta G_0^0$ can be written as\textsuperscript{20} follows:

$$\Delta G_0^0 = \left( \frac{16\pi}{3} \right) \left( \frac{\sigma^3}{\Delta s_f T^2} \right) f(\theta)$$ \hspace{1cm} (2)

where $\sigma$ is S/L interfacial energy, $\Delta s_f$ is entropy of fusion, $\theta$ is wetting angle, and $f(\theta) = (2 + \cos \theta) (1 - \cos \theta)^3/4$ is wetting angle factor.

![EBSD band-index micrographs (A) and inverse pole figure of Al$_2$O$_3$ (B) of the longitudinal interface between the polycrystalline alumina seed bar and Al$_2$O$_3$/YAG eutectic ceramics](image1)

![EBSD orientation micrographs of the longitudinal interface between $c$-sapphire and Al$_2$O$_3$/YAG eutectic ceramics and the corresponding inverse pole figures (inserted) of Al$_2$O$_3$ (A) and the YAG (B), respectively](image2)
The nucleation rates of Al₂O₃ and the YAG are calculated using the parameters listed in Table 1. For heterogeneous nucleation, the wetting angle factor shows striking effects on the nucleation rate. Since wetting condition is good between nucleus (either Al₂O₃ or the YAG) and the substrate (Al₂O₃), that is, small θ, two cases of \( f(θ) = 0.01 \) where \( θ = 30° \) and \( f(θ) = 0.001 \) where \( θ = 15° \) are considered. The results are presented in Figure 4. The nucleation rate of the YAG becomes higher than that of Al₂O₃ when the undercooling is more than 97°C for \( f(θ) = 0.001 \) or 317°C for \( f(θ) = 0.01 \).

According to Figure 4, the competitive nucleation behavior between Al₂O₃ and the YAG changes when the undercooling Δ\( T \) exceeds a critical value. In the OFZ technique, the temperature of the liquid eutectic is higher than 1820°C (melting point). The temperature of the alumina seed (substrate) is about 1000°C. High undercooling is expected in the process. Therefore, the nucleation rate of the YAG is larger than that of Al₂O₃, and the cubic YAG is expected to nucleate from the melt first and forms as a leading phase during directional solidification.

### CONCLUSIONS

In summary, the leading phase in Al₂O₃/YAG eutectic crystals during solidification was investigated with a polycrystalline Al₂O₃ bar and c-sapphire as the seed, respectively. The YAG was the leading phase. The heterogeneous nucleation rate was calculated based on the classical nucleation theory. The leading phase was determined by the wetting angle and the undercooling. At a given wetting angle, the YAG might be the leading phase when the undercooling exceeds the critical value.

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### ORCID

Yujie Zhong [https://orcid.org/0000-0002-5902-3771]
Xu Wang [https://orcid.org/0000-0001-9935-5984]

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