

Ab initio Density Functional Theory thermodynamics study of α -aluminum oxide grain boundaries doped with reactive elements

by

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Abstract

Thermal barrier coatings (TBCs) are applied extensively in gas-turbine engines to protect them from the harsh operating environment and enable them to function at elevated temperatures. The growth of thermally grown oxide (TGO) in TBCs can be significantly decelerated through adding less than 1 wt.% of reactive elements (REs) in the scale-forming alloys. This phenomenon is significant as it delays the failure of the TBCs and extends the lifetime of the gas-turbine engines. However, the mechanisms behind how the REs influence the growth of this oxide are unclear. Therefore, it is necessary to understand the underlying impact of the REs to further improvement of the TBCs. In this thesis, focusing on the aluminum oxide (Al₂O₃) as TGO, an *ab initio* computational study was performed using density functional theory (DFT) calculations to examine the influence of singly- and co-doped Hf, Y, and Zr at a Σ 3 twin grain boundary (GB) and a Σ 13 twin GB in α-Al₂O₃. Five energetically favorable models with different REs were constructed for each GB. The impact of the dopants on the electronic structure of these models, as well as the segregation of oxygen vacancy (V_0^{2+}) and aluminum vacancy (V_{Al}^{3-}) were investigated. Our results show that some dopants and co-dopants changed the electronic structure of the GBs and the segregation of vacancies at those regions remarkably, which can be correlated to experimental observations of suppressed oxide growth by the same REs. The findings in this work suggest that REs modify the segregation energies of V_0^{2+} through altering the electronic structure and the electrostatic interactions around GBs. On the other hand, there are not sufficient results from this study to explain the changes brought by the REs on the segregation of V_{Al}^{3-} , suggesting that it is likely affected by other factors, such as interactions between ions and the strain effect. To summarize, this work demonstrates that the electronic properties at GBs are important characteristics to be investigated to gain insight into the effect of REs on the growth of TGO.

Résumé

Les revêtements à barrière thermique (TBCs) sont largement utilisés dans les moteurs à turbine à gaz pour les protéger des conditions d'exploitation difficiles et leur permettre de fonctionner à des températures élevées. L'oxyde obtenue par croissance thermique (TGO) dans les TBC peut être considérablement ralentie par l'ajout de moins de 1 % en poids d'éléments réactifs (REs) dans les alliages formateurs d'oxyde. Ce phénomène est important car il retarde la défaillance des TBC et prolonge la durée de vie des moteurs à turbine à gaz. Toutefois, les mécanismes qui expliquent comment les REs influencent la croissance de cet oxyde ne sont pas clairs. Il est donc nécessaire de comprendre l'impact sous-jacent des REs pour améliorer davantage les TBC. Dans cette thèse, une étude de calcul *ab initio* axée sur l'oxyde d'aluminium (Al₂O₃) comme le TGO a été réalisée à l'aide de calculs de théorie de la fonctionnelle de la densité (DFT) afin d'examiner l'influence des dopage et codopage du Hf, du Y et du Zr à une limite de grain (GB) désigné par Σ 3 et à une GB désigné par Σ 13 dans l' α -Al2O3. Cinq modèles énergétiquement favorables avec différents RE ont été construits pour chaque GB. L'impact des dopants sur la structure électronique de ces modèles, ainsi que la ségrégation de la lacune d'oxygène (Vo²⁺) et de la lacune d'aluminium (VAI3-) ont été étudiés. Nos résultats montrent que certains dopants et codopants ont modifié la structure électronique des GB et la ségrégation des lacunes dans ces régions de manière remarquable, ce qui peut être corrélé aux observations expérimentales de la suppression de la croissance de l'oxyde par les mêmes REs. Les résultats de ce travail suggèrent que les REs modifient les énergies de ségrégation de Vo²⁺ en altérant la structure électronique et les interactions électrostatiques autour des GBs. En revanche, les résultats de cette étude ne sont pas suffisants pour expliquer les changements apportés par les REs sur la ségrégation de la V_{Al}³⁻, suggérant qu'elle est probablement affectée par d'autres facteurs, tels que les interactions entre les ions et l'effet de déformation. En somme, ce travail démontre que les propriétés électroniques des GB sont des caractéristiques importantes à étudier pour mieux comprendre l'effet des REs sur la croissance du TGO.

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Contribution of Authors

Chu Yang Li is the author of all the chapters presented in this thesis. He completed this work under supervision by Prof. Jun Song and Dr. Kuiying Chen. They helped define the concept, gave feedback on the computational results, as well as reviewed and edited the writing of this thesis.

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List of abbreviations

APT: atom probe tomography CMAS: calcium magnesium alumina silicate CTE: coefficient of thermal expansion DFT: density-functional theory DOS: density of states EB-PVD: electron beam physical vapour deposition ELF: electron localization function GB: grain boundary GGA: generalized gradient approximation GGA-PBE: generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange functional LDA: local density approximation MD: molecular dynamics PAW: projector augmented-wave method PDOS: partial density of states PO₂: partial pressure of oxygen **RE:** reactive element TBC: thermal barrier coating TGO: thermally grown oxide VASP: Vienna Ab initio Simulation Package V_{Al}³⁻: aluminum vacancy with a charge of 3- V_0^{2+} : oxygen vacancy with a charge of 2+ XC: exchange-correlation YSZ: yttria-stabilized zirconia

1 Introduction

Gas-turbine engines are a type of engine that uses internal combustion of pressurized gas to generate electricity or kinetic energy. These engines, which are world standards for aircrafts and power generation, possess advantages like high efficiency and power output, good resistance to elevated temperature and pressure, low maintenance, low carbon dioxide emission, desirable performances under cyclic operations, and lower cost compared to other alternatives [1]. Despite these advantages, scientists and engineers are still attempting to make gas turbines more efficient by increasing the inlet temperature of the gases. This modification enables the gases to expand further, thereby moving the turbine with greater pressure. The turbine entry temperature has risen from around 1000 °C in the 1940's to roughly 1700 °C in present days. As a result, the fuel consumption of aircrafts has reduced by around 50% [2]. Since such elevated temperature exceeds the melting point of the superalloy components in gas turbines, a thermal barrier coating (TBC) is conventionally employed to protect these components from degrading. Therefore, whether the entry temperature of gases can be increased further hinges on developing TBCs that can sustain higher heat.

TBCs have been used extensively in high-temperature environments, such as aircraft engines and power generation plants, to protect the metallic components of the superalloy substrates from heat and corrosion during operation. TBCs normally have three constituents: a ceramic top coat that provides thermal insulation, a bond coat that connects the superalloy substrate and the ceramic top coat to lessen the thermal mismatch, and a layer of thermally grown oxide (TGO) located between the bond coat and the top coat, which is developed during manufacturing and engine operations due to the diffusion of oxygen through the top coat [3]. When applied on jet engine blades, TBCs maintain a thermal gradient that enables the substrate alloy to operate at temperatures above its melting point to enhance the efficiency of the engine [3]. Although TBC has desirable characteristics that benefit gas-turbine engines, its full potential has not yet been realized. Accordingly, TBC continues to generate growing interest from scientists as the number of yearly publications on this material increased by over 75% from 2011 to 2021 [4]. One major limitation of this coating is its premature spallation failure, which is partially attributed to the excessive growth of TGO at operating temperatures. Thermal mismatch strain builds up as the oxide layer keeps thickening during thermal cycles. Once the strain energy exceeds the interface strength, the TBC spalls and the superalloy substrate is then exposed to the heat [5], [6]. As a result, controlling the growth rate of the TGO, which usually consists of Al₂O₃, is crucial for improvement on the durability of TBCs.

The growth of Al₂O₃ in TBC can be alleviated and the oxidation resistance of this coating can be enhanced by adding less than 1 wt.% of reactive elements (REs), such as Ce, Hf, Y, and Zr, in Al₂O₃ – scale forming bond coat [7], [8], [9]. This phenomenon is called the "RE effect". Over the past decades, notable progresses have been made on assessing how REs assert influence on the growth of TGO. Pint suggested that larger RE ions diffuse more slowly than Al ions, thereby blocking the diffusion of the latter and slowing down the oxide growth [10]. This proposition is called the dynamic-segregation theory. However, it was later discovered that there are exceptions to it, and several other hypotheses have been made since. For instance, Yoshida et al. claimed that the ionic bond strength of RE-O also contributes to the RE effect [11]. GB strengthening due to increased O coordination number, as well as the ionic size mismatch induced by the REs also constitute factors behind the RE effect [12]. Moreover, co-doping of certain REs have been shown to give rise to stronger RE effect than doping those REs separately [13], [14], [15]. For that reason, the synergy of co-dopants is also worth investigating. Several possible causes of this synergistic effect have been proposed, including the combination of RE effect from both REs [13], stronger physical blocking and chemical interactions with Al ions induced by two REs [14], and the interactions between both REs [16]. All in all, although the beneficial impact of adding REs in bond coats are well-documented, there is still no consensus on a scientific explanation of its mechanisms.

Conventionally, scientists conduct experiments to investigate the influence of REs on the mass gained of oxides or the diffusivity of O or Al. With the advances in computational methods, more and more researchers were drawn to use calculations based on density functional theory (DFT) to study this topic at the atomistic scale, which is hard to achieved by experiments. The results from several DFT studies completed in recent years indicated that the electronic density of states (DOS) of the GB affects diffusivity of oxygen, which in turn alters the growth of oxide scale [17], [18]. Since these computational studies provide a new insight for the investigation of the "RE effect", a DFT study on the influence of selected REs on the growth of Al₂O₃ and their synergistic effect is carried out in this study. More specifically, the objectives of this work are to analyze the effect of singly doped and co-doped Hf, Y, and Zr on (1) the electronic structure of a Σ 3 GB and a Σ 13 GB of α -Al₂O₃ and, (2) the segregation of oxygen and aluminum vacancies at these two GBs.

This thesis is structured as follows. Chapter 2 consists of a comprehensive review of relevant literature on TBC, α -Al₂O₃ GBs, state-of-the-art studies on the "RE effect", as well as the current understanding of this topic. Chapter 3 comprises the methodology and the parameters of the DFT calculations. The results from the DFT calculations are presented and discussed in chapter 4. Lastly, Chapter 5 summaries this study and provides suggestions for future work.

2 Literature Review

2.1 Overview of TBC Systems

The TBC is a multi-layer coating system providing protection to the underneath metallic substrate against corrosion, erosion, and extreme temperature in the hot gas stream inside gasturbine engines. It enables the metallic components to operate at temperatures well above their melting temperatures to achieve improved performance and efficiency for the gas-turbine engines for applications in aerospace, electronics, automobile, and nuclear industries [3], [6]. This thesis mainly focuses on the application of TBCs on turbine engine components made of nickel-based superalloys, for which a state-of-the-art TBC is typically composed of three layers, namely top coat, TGO and bond coat, as schematically illustrated in Figure 1.



Figure 1. A schematic view of the three layers in a TBC system.

2.1.1 Top Coat

On the superalloy substrate, the thermal barrier coating is the outermost layer of a thermal barrier coating system, and it functions primarily as a heat shield against the combusted jet fuel, as illustrated earlier in Figure 1. This layer is also called the top coat. The key requirements for this material are, among others, low thermal diffusivity, good phase stability, and strong resistance against oxidation and corrosion [3]. The thickness of the top coat typically ranges from 100 to 400 µm. In current practices of turbine engines, to effectively protect the substrate from heat attack, the top coat must decrease the temperature by around 200°C across the span of its thickness. The common top coat candidates able to fulfill such need are ceramics like titania, zirconia, alumina, and porcelain [3].

Yttria-stabilized zirconia (YSZ) has been considered a well-suited top coat material with desirable properties including low density, low thermal conductivity, high thermal-expansion coefficient, high resistance to corrosion, high melting point, and good manufacturability [6]. In addition, YSZ exists in a stable tetragonal phase at operating temperatures of turbine engines, thus preventing excessive stress buildup during phase transitions and enhancing resistance to thermal cycling [19]. Another advantage of YSZ entails in its fabrication process. For application on gas turbine blades in jet engines, TBC is fabricated through the electron beam physical vapor deposition (EB-PVD) process. Since Y₂O₃ and ZrO₂ have similar vapor pressures, it is attainable to deposit a uniform columnar layer of YSZ through EB-PVD. On the contrary, alternate TBC materials are composed of oxides with different vapor pressures, resulting in non-uniform structures [20]. Pratt & Whitney incorporated the EB-PVD YSZ top coat into their Gen III TBC system in 1987 [21]. This material improved the blade durability by a factor of three compared to its predecessors. The ideal concentration of Y₂O₃ is within the range of 6-8 wt.%, as adding this

quantity of Y_2O_3 to ZrO_2 enables the TBC to have the most optimal thermal cycle life [22], [23]. Consequently, YSZ with 6-8 wt.% Y_2O_3 has been the prevailing material of choice for top coat since its initial development [19]. Even nowadays, although there have been significant research efforts [24], [25], [26] to further innovate the top coat material, e.g., search for material candidates with lower thermal conductivities than YSZ with 6-8 wt.% Y_2O_3 , it remains the preferred material of choice in major TBC systems [27].

2.1.2 Bond Coat

The top coat is not directly applied on the Ni-based superalloy substrate since top coat is porous and thus oxygen can permeate it during engine operation and subsequently oxidize the superalloy, which would render the TBC prone to early failure [6]. To avoid this, a bond coat is deposited on the substrate before the top coat. The bond coat is an alumina forming metallic layer located between the top coat and the superalloy substrate, as displayed in Figure 1. Its primary functions consist of providing adhesion between the top coat and substrate, reducing mismatch of coefficient of thermal expansion (CTE) between them, as well as offering the necessary oxidation resistance [20], [28]. In particular, the bond coat provides the oxidation resistance by promoting stable growth of TGO, which will be described in the section below.

Two types of corrosion resistance coatings are commonly used as bond coats in the TBC systems [29]: the first is MCrAIY, in which M refers to the base material (Ni, Co, or Fe), and the second type is NiAl-based bond coat, which is currently the more popular choice owing to its lower cost and simpler fabrication process. Compared to MCrAIY, Pt-modified NiAl is also more oxidation resistant [5]. In addition, the NiAl compounds can exhibit sufficient melting temperatures, e.g., the melting point of an NiAl compound with 50 at.% Ni is about 1638 °C, which

is high enough for the operation environment in gas turbine engines [30]. Because of these desirable properties, NiAl-based bond coats are extensively used in TBC systems.

2.1.3 Thermally Grown Oxide (TGO)

A thin layer of TGO forms at the bond coat/top coat interface during deposition of the bond coat and operation of the jet engine due to oxidation of NiAl and/or MCrAIY. The TGO undergoes slow growth into a layer of α -Al₂O₃. This oxide scale has low oxygen ionic diffusivity among known oxides and is effective in slowing down further oxidation of the bond coat, thus providing excellent oxidation resistance for the superalloy substrate [6]. Plus, the slow growth rate of TGO also leads to slow crack rate of the TGO/bond coat interface, thereby enhancing its interfacial adhesion [31]. As such, TGO is also beneficial for the durability of the TBC system [32]. One of the most important attributes of TGO to consider in the engineering practices is its growth rate, as the excessive thickening of TGO is believed to be the primary trigger of the spallation of TBCs. It has been reported that for the commonly used TBCs, a thickness of TGO exceeding 10 μ m is enough to cause spallation failure of the TBC [6]. In general, the optimal thickness for TGO immediately after deposition of the bond coat is 0.3-1.0 μ m [20].

When being exposed to hot gas stream, oxidation of NiAl-based bond coat begins to take place at around 700 °C through outward diffusion of aluminum ions and inward diffusion of oxygen ions along the grain boundaries of alumina, whereas the rate of lattice diffusion is negligible in the formation of TGO [33]. The outward transport of aluminum ions results in their interaction with oxygen and formation of new oxide at the scale/gas interface; the inward diffusion of oxygen ions interacts with aluminum ions to generate alumina at the scale/metal interface [34]. The thickening of the oxide scale requires the supersaturation of vacancy, which can be presented as follows [35]:

$$2V_{Al}^{\prime\prime\prime} + 3V_{0}^{*} + 2Al_{Al}^{\times} + 3O_{0}^{\times} \to Al_{2}O_{3}$$
(2.1)

The formation of alumina involves several metastable phases and its stable α phase. The transformation of phases of Al₂O₃ reportedly follows the sequence shown below [36]:

$$\gamma \to \delta \to \theta \to \alpha \tag{2.2}$$

Although the above sequence was not fully proven, all of those transient phases can be observed on all alumina forming alloys at oxidation temperatures below 1000 °C [37]. The formation of α-Al₂O₃ is likely caused by a combination of direct nucleation on NiAl at elevated temperatures and the transition of θ -Al₂O₃ to α -Al₂O₃. The inward diffusion of oxygen controls the growth of α -Al₂O₃, while the outward diffusion of aluminum is the dominant factor for the growth of θ -Al₂O₃ [32]. Through oxygen transport along alumina grain boundaries, the metastable alumina nuclei grow until a layer of stable α-Al₂O₃ forms underneath the metastable scale. The inward diffusion of oxygen promotes the growth of TGO at the oxide/bond coat interface. As the scale thickens, small grains that grow slowly merge with the adjacent grains with bigger sizes that grow faster. Eventually, the size of grains in the scale increases, and the grain boundary area reduces. As a result, the diffusion coefficient of oxygen at grain boundaries gradually decreases and the oxide undergoes a slow and stable growth [38]. The aluminum oxide in the α phase has higher mass density and lower growth rate compared to the other transient phases, making it the ideal phase for oxidation resistance [32]. The oxidation of NiAl-based bond coat is illustrated in Figure 2. The TGO layer continues to thicken slowly during the operation of the jet engines, which eventually leads to the failure of the TBC.



Figure 2. Illustration of the alumina scale growth on NiAl-based bond coat [32].

2.2 Factors affecting Lifetime of TBC Systems

2.2.1 Causes and Mechanisms of TBC Failure

In TBC systems, failure can occur at the interface between TGO/bond coat or the one between TGO/top coat, while it is more likely to happen at the latter [6]. During aircraft engine operation, the spallation of the TGO and the subsequent failure of TBCs can be attributed to a variety of factors. For instance, the surface of the bond coat roughens during thermal cycles due to aluminum depletion and decomposition of the β phase of the material, which creates separations between the bond coat and the top coat that leads to the failure of TBC [39]. Other common factors also include external mechanical damage, calcium magnesium alumina silicate (CMAS) - induced erosion, hot corrosion, spallation, and delamination of the thickened TGO among others [3].

One dominant cause of breakdown of TBC systems is the excessive growth of TGO during thermal cycles [6], [40]. When the oxide layer thickens during thermal cycles, the thermal expansion mismatch strain between the TGO and bond coat also increases. This strain energy is proportional to the scale thickness. During the cooling phase of a cycle, this thermal mismatch

between layers results in high compressive residual stresses in the oxide layer. Once the thickness of the TGO layer exceeds a threshold value, the compressive stress induces the formation of crack tips at the TGO/BC interface [3]. These cracks ultimately lead to delamination and spallation of the TGO, which resulted in the failure of the coating system. A schematic illustration of the evolution of cracks during the thermal cycles can be seen in Figure 3 [41]. The growth of TGO also progressively depletes aluminum in the bond coat, which can cause formation of other oxides that damage the structural integrity of the TGO and amplify local oxidation, thereby accelerating the breakdown of the TBC coating [6]. With the critical role of TGO in the failure TBC, it is crucial in ensuring a slow and stable growth of TGO, a topic that has motivated great research efforts, elaborated in the next section below.



Figure 3. Cross-sectional images of evolution of cracks at different stage in a TBC system. The top layer with a columnar structure is the top coat, the layer beneath the oxide film is the bond coat. [41].

2.2.2 Suppression of TGO Growth by REs

As mentioned previously, grain boundaries in TGO can play a crucial role for diffusion of oxygen and the growth of the oxide scale. A grain boundary is essentially an interface between two grains of atoms oriented in different directions. Unlike the bulk lattice, atoms along grain boundaries are arranged in an irregular pattern. There is more free volume present in the grain boundaries than in the bulk, thus enhancing diffusion of atoms [38]. For example, Heuer et al. reported that the diffusion coefficient of oxygen at grain boundaries is in the order of 10⁶ times higher than in bulk lattice at around 1500 °C, which is within the range of operating temperatures of gas turbines [35]. Similarly, other studies also observed or reported that the diffusion coefficient of oxygen at grain boundaries higher than that of bulk diffusion, which is illustrated in Figure 4 [42], [43]. Despite the general facilitation in oxygen diffusion by grain boundaries, it has been shown that the degree of facilitation depends on the geometric characteristics of grain boundaries, which can render variation in the oxygen diffusivity by up to three orders of magnitude [44].



Figure 4. Comparison of diffusion coefficients in bulk (Do), subboundary (D"o), and GB (D'o) between undoped and Y-doped alumina [43].

Doping a small amount (typically < 1 wt.%) of REs in the alumina-forming bond coat is a proven method to effectively slow down the growth of TGO [7], [8], [9]. This phenomenon is called the "RE effect". All the REs that reduce the scale growth rate tend to segregate to the grain boundaries in the TGO [8]. For example, an image generated by atom probe tomography (APT) illustrating segregation of Zr along the grain boundaries in an alumina sample is shown in Figure 5 [45]. The concentration of dopants at the GBs depends not only on the RE species, but also their depth within TGO. Grain boundaries are important for the REs to suppress scale growth, because the doping of these elements is only effective in the presence of GBs: spallation occurred in a single-crystalline NiAl sample doped with 0.05 at. % Hf after undergoing 15 hours of cyclic oxidation, while a polycrystalline sample did not spall even after 100 hours, as exhibited by the change of mass on different samples in Figure 6 [46]. On this graph, the gap between the mass gain of the single-crystalline sample and its mass change indicates spallation of the scale. Since grain boundaries are necessary for the REs to suppress the growth of TGO, knowing how REs act at the grain boundaries is the key to understanding their beneficial effect.



Figure 5. An APT image showing two GBs segregated with Zr in an alumina sample [45].



Figure 6. Mass gains on NiAl samples doped with different RE at 1200 °C in air [46].

2.3 Current Understanding of the RE Effect on Scale Growth

The initial discovery of RE effect on scale growth can be dated back to the 1950's, when it was discovered that the durability of chromia-forming heater alloys could be enhanced by adding minor amounts of cerium to these materials [7]. Since then, there have been continuous efforts in exploring the use of RE in engineering practices in relation to scale growth, some of which are summarized in [8], [47]. Nowadays, it is widely recognized that adding < 1wt.% of certain elements (mostly REs) is beneficial for the durability of chromia and alumina - forming alloys,

as both oxides protect the substrate from further oxidation. Such elements include Hf, Y, Zr, La, Ce, Sc, among others, and are termed the RE elements due to their large negative free energies of formation of oxides. The beneficial outcome of doping REs is therefore called the "reactive element effect" or the "RE effect" [7], [8], [9].

So far, it is known that RE dopants demonstrate at least the following favorable roles in alumina-forming alloys: improving scale adherence through interactions with sulfur and other impurities; inhibiting grain coarsening and maintaining parabolic scale growth; suppressing outward diffusion of aluminum ions; altering electronic conductivity [33], [48]. The RE effect is crucial for extending the lifetime of alumina-forming alloys used in jet turbines and nuclear fuel cladding materials. However, despite being used extensively in commercial applications, the mechanistic understanding behind the RE effect on the growth of Al₂O₃ is still not complete. Some notable studies on this topic are summarized in the following subchapters.

2.3.1 Experimental Studies

Experimentally, it was first known that the addition of REs impeded the growth of chromia at elevated temperatures, while the RE effect on the growth of alumina was not explicitly confirmed until around 2000 [8]. Several studies were carried out in the 1970's to investigate the doping of REs to Ni-Cr alloys. Strafford and Harrison doped 0.5 wt.% of different elements in Ni-15 wt.% Cr alloys and reported that Y, Sm, V, U, and Zr reduced oxidation rates of the metals at 900 °C [49]. Kvernes investigated the high-temperature corrosion of several Ni-Cr-Al alloys with addition of between 0.005 wt.% and 0.7 wt.% yttrium [50]. The author showed that adding 0.1 wt.% of Y resulted in the slowest oxide growth, which he attributed to the change in oxide microstructure induced by doping. Similarly, Ecer and Meier looked into the impact of adding minute amount of Ce in Ni-50Cr alloys [51]. They reported that between 800 to 1100 °C, Ce reduced the oxidation

rate of chromia while also increasing scale adherence and decreasing its tendency of spallation. The authors suggested that the beneficial effects of doping Ce stemmed from its interactions with oxide grain boundaries and its suppression of grain growth. Furthermore, a review written by Whittle and Stringer in 1980 summarized three plausible mechanisms that might inhibit the growth of chromia: (1) dopants modify the Cr_2O_3 atomic structure, thereby reduce the cation diffusion rate; (2) dopants can form compounds that partially block the oxide/alloy interface; and (3) dispersoids containing dopants inhibit movement of chromium in short-circuit diffusion (i.e. grain boundary diffusion) [52]. To sum up, the benefits of doping various elements in different Ni-Cr alloys were partly quantified, and some mechanisms were proposed in the 1970's. However, due to the lack of advanced analytical techniques and sufficient experimental evidence, researchers could not come up with a general theory for the RE effect on TGO growth.

In recent years, the effectiveness of reactive elements in reducing alumina growth have been acknowledged, and their important role in TBC applications have prompted more researchers to direct their attention towards this topic [47]. Several REs that exhibit desirable effect on aluminaforming alloys have been identified. Li et al. [53] studied the mass gain of oxide on NiAl alloys that are doped with different REs at 1200 °C in air. The results demonstrated that Dy, Hf, Zr, and Y reduced the rate of oxidation significantly. On the contrary, La accelerated the growth of oxide compared to the undoped sample (Figure 7). In another work by Yan et al. showed that Hf and Zr both slowed down the thickening of oxide scale, but La and Dy had the opposite impact (Figure 8) [54]. On the other hand, excessive amount of REs can be detrimental to the stability of alumina. For instance, Guo et al.'s study illustrated that doping 0.5 mol.% of Dy in NiAl caused severe internal oxidation that significantly intensified the oxidation, as revealed by the mass gains of NiAl samples shown in Figure 9. Although the experimental process differs in different studies, there is prominent evidence of the beneficial RE effect on growth of alumina. However, a systematic mechanistic understanding of the RE effect, such as the interaction between REs and the host atoms and the influence of REs on the local atomic environment, on scale growth on alumina-forming alloys remains largely missing, despite extensive efforts of research on this topic leading to different mechanisms proposed, as further elaborated in the following paragraphs.



Figure 7. Mass gains on NiAl samples doped with different RE at 1200 °C in air [53].



Figure 8. Mass changes of several NiAl alloy samples doped with REs during 100 h oxidation [54].



Figure 9. Mass gains of NiAl samples during 1h cyclic oxidation at 1200 °C [55].

In addition to the above extensive experimental work, there have been many experimental studies focusing on mechanistic understanding, many of which took the GB diffusion and oxide growth rate as the focal point. Pint made notable progress on this topic as he proposed the dynamic-segregation theory based on experimental observations [10]. The theory states that since the larger RE ions diffuse more slowly compared to the aluminum ions, these dopants inhibit the short-circuit

diffusion of Al along the GBs and thereby reduce the scale growth. However, several other works demonstrated that Hf is more powerful than Y in reducing growth of oxide, as shown in Figure 7, despite the fact that Hf has a smaller ionic radius [53], [56]. Therefore, size of the RE ions is not the only factor contributing to the RE effect. To clarify these inconsistencies, Pint also argued that Hf is more effective than Y as the former has a larger effective ionic radius [57]. However, this theory still does not constitute a general mechanism behind the effect caused by REs. Furthermore, it was also revealed that Y led to increased Al GB diffusivity, indicating that it did not impose a blocking effect on the ion transport along grain boundaries [58]. Evidently, this theory does not apply to all the REs and experimental conditions.

Since the proposition of the dynamic-segregation theory, more studies have been carried out to examine different aspects of the RE effect pertaining to oxide growth. Nakagawa et al. observed that doping of Y decreased GB diffusivity by a factor of 10 compared to the undoped crystals, which the authors attributed to the "site blocking" mechanism [59]. Indeed, it appears that this mechanism is fitting for the influence of yttrium on growth of alumina. In another study, the doping of less than 0.1 wt.% of Dy, Hf, Zr, Y, and La in NiAl on its cyclic oxidation at 1200 °C was investigated [53]. It was reported that all but La have significantly hindered the growth of alumina, which was quantified by mass gain as illustrated in Figure 7. However, as shown in Figure 10, La has the largest radius but the La-doped sample had the highest mass gain; on the other hand, Hf is the smallest ion, yet the Hf-doped sample had the lowest mass gain. This graph shows that dopant cation size is inversely proportional to the RE effect, revealing that the dopant size is not a the only decisive factor. As a result, the authors recommended that the interaction of dopants and Al should be examined to better understand how REs affect TGO growth. In another paper, Yan et al. claimed the solubility of the REs also plays a role as RE-rich precipitates are prone to internal oxidation

that accelerates scale growth [54]. In their tests, the mass gain from high-temperature oxidation of the NiAl samples with different RE dopants was measured. The results showed that doping 0.05 at.% of Hf and Zr led to decreased rate of oxidation, while doping the same amount of Dy and La had the opposite effect, as displayed in Figure 8. It is worth noting that Dy exhibited contradictory impacts on the oxidation rate in Yan et al.'s study [54] compared to the one conducted by Li et al. [53], which demonstrated that Dy was effective in slowing down the scale growth (Figure 7). This discrepancy indicates the RE effect might also depend on experimental and operating conditions, as the same element might reduce scale growth under condition and enhance oxidation under another condition.



Figure 10. Total mass gains (specimen + spall) for RE-doped NiAl alloys plotted versus dopant ion size after 300, 1 h cycles (the La-doped alloy after 200, 1 h cycles) at 1200° C in air [53].

Several other meaningful studies on the RE effect were elucidated with respect to the GB transport of ions. It was revealed in Nakagawa et al.'s study that diffusivity of oxygen in pristine alumina GBs varied by up to 10³ times in different GB configurations [44]. Therefore, it is also possible that the diffusivity of oxygen might also differ in different RE-doped alumina, implying

that atomic structure also influences the RE effect. Yoshida et al. examined the impact of RE oxides on Al₂O₃ grain boundary diffusivity [11]. Their findings suggested that the ionic bond strength around the GB is an important factor that influence the GB diffusion of polycrystalline alumina. Similarly, Matsudaira et al. also attributed the retardation of GB diffusion of Al and oxygen to the strengthening of bonds at grain boundaries [12]. Their study showed that the transport of oxygen is inhibited by strengthening of bonds between Al and O as well as by the "site-blocking" effect. Besides, the authors also proposed that the diffusion of Al is delayed by the GB strengthening caused by the increase in oxygen coordination number of REs. Furthermore, Rehman et al. also reported evidences that contradicted the dynamic-segregation theory [56]. The authors observed that Hf was more effective in suppressing oxidation kinetics than Y and Ce, while both elements have larger ionic radius than Hf. The authors attributed these findings to two possible reasons: (1) Hf ions have the strongest adhesion at the GBs, so the diffusion of Hf is the slowest; and (2) Y and Ce are more likely to react with oxygen to form binary oxides. As a result, less Y and Ce ions are present at the GBs to suppress diffusion. Again, these results reflected the complex nature of the RE effect as there are numerous factors that play a role in oxide growth.

Several researchers suggested that co-doping REs can further enhance the dopant effect, as single-dopants have low solubility in β -NiAl [12], [14], [53]. Accordingly, co-doping should also be included in studies on the RE effect. Several combinations of co-doping have been identified to be more powerful in reducing oxide growth than doping the same REs separately. In the case of co-doping Dy-Hf, Hf-Zr, Hf-La, and Y-La, all the combinations greatly reduced the oxidation rate, as presented by mass gain on the NiAl samples in Figure 11. In that study, co-doping of Hf-Zr and Y-La exhibited better inhibition of scale growth than the corresponding single-doping, which resulted in lower mass gain [14]. The authors attributed this beneficial synergistic effect to the

stronger "blocking effect" and chemical interaction induced by co-doping. Kim et al. also demonstrated in their paper that doping Hf with Y is more effective than doping Y by itself [15]. The observations from their study are exhibited in Figure 12, which shows the cross section of alumina (dark area in the image) on Ni-20Al-5Cr (at. %) alloys. One can see the sample with 0.1 at.% Hf and 0.05 at.% Y oxidizes more slowly than the sample with 0.05 at.% Y. The weight changes of the tested alloy samples confirmed the visual observation of the cross-sectional images, as displayed in Figure 13. These results also indicated that Hf is the more dominant dopant between these two. Lan et al. also showed that co-doping Pt with Dy is more effective in slowing oxide growth than doping Pt only [13]. This phenomenon is demonstrated by the inferior mass gain on the alloy sample doped with Pt and Dy (Figure 14). The authors ascribed this beneficial co-doping effect to the co-segregation of REs, but they did not give further detail on the specific mechanism. However, it was reported in another article that co-segregation is neither a sufficient nor necessary condition for the synergistic effect [16]. It was instead suggested that the interaction between RE ions is the main cause of it. Similar to the research on single doping of REs, there is not yet a consensus on the co-doping effect either. Further investigation will be required to unveil the mechanisms of how these RE dopants affect growth of TGO.



Figure 11. The square of mass gains (sample + spall) for NiAl alloys with various RE additions during 100 h cycles at 1200 °C in air [14].



Figure 12. Cross-sectional images of Ni–20Al–5Cr (at.%) alloys with additions of reactive elements at

1150 ° C [15].



Figure 13. Weight changes of reactive element-doped Ni–20Al–5Cr (at.%) alloys as a function of isothermal exposure time at 1150 °C in air [15].



Figure 14. Isothermal oxidation kinetics curves of different samples [13].

Overall, though the enormous experimental work clearly demonstrated the complex nature of the RE effect where many different factors, such as bonding, ionic size, and interaction between ions, were found to play a role in affecting the oxide growth. Contradicting results exist as the experimental parameters and conditions varied in those studies. Consequently, there are still many puzzles remaining, with the dominant mechanisms of the RE effect not pinpointed.

2.3.2 Computational Studies

As discussed in the previous section, a conclusive understanding of the RE effect has yet to be established based on findings from experimental studies, where inconsistent conclusions were drawn on the influence of RE dopants from experimental investigations under different conditions. In recent years, computational modeling and simulations have emerged as a powerful method in parallel to experimentation in the research, design, and development of materials. Computational methods can be more streamlined than experiments, thereby complementing experiments and allowing studies to be carried out more efficiently and trial and error to be reduced. Computational research also requires less cost than experimental studies owing to the simplicity of its set up. In
addition, computational studies allow direct investigation of small-scale phenomena, e.g., at lattice or even atomic level, a scale typically not accessible by experiments. Such small-scale capability also enables more fundamental and thus mechanistic understanding of the RE effect. There have been different computational methods employed over the years for studying the RE effect, with the notable ones being molecular dynamics (MD) and first-principle methods like density functional theory (DFT). In the MD method, atoms are regarded as the fundamental particles, so the system can be described as atom-atom interactions using Newton's equations of motion [60]. MD is conventionally employed to calculate the time-evolution of atoms. On the other hand, the first-principle methods treat nuclei and electrons as the foundational particles, thereby revealing information at the subatomic scale [60]. This method focuses on the electronic and magnetic properties of the material, and the system is expressed by quantum mechanics. Particularly for chemical bonding, electronic structure, and energetics, the DFT method has been the most prevailing one used since its calculations focus on electrons. Several DFT studies have been carried out to provide new insights of the RE effect, which are discussed below.

The modification of bonding and electronic structure at the grain boundaries due to RE dopants might play a significant role in altering the thickening of oxide scale. It was reported in a DFT study that Y forms strong ionic bonds with neighboring O atoms in a Y-doped Al₂O₃ Σ 13 GB, which showed a correlation between strong Y-O bonds and slow oxide growth [61]. Heuer et al. proposed that the RE dopants inhibit the oxidation by modifying near-band edge GB defect states rather than blocking of diffusion pathways [62]. Therefore, the impact brought to the GB electronic properties by the dopants deserve more attention. In another study, it was shown that Y segregation at a Σ 7 GB induced a significant reduction in the concentration of near-band edge states in the Y-doped bi-crystal, as illustrated by the partial density of states (PDOS) of oxygen in the undoped

and Y-doped GB in Figure 15 [17]. The decreased number of PDOS near the valence band maximum implies a reduction in hole conductivity, which might be the reason behind the slow oxide growth. However, Chen et al.'s research indicates that the above mechanism is limited to the GB configuration used in that study, but not all GBs in general [18]. The authors reported that in an alumina GB with different atomic structure, REs created localized states in the band gap near the conduction band minimum but had little impact on states near valence band maximum (Figure 16). The reduced oxidation rate was thus attributed to the positively charged RE dopants expelling V_0^{2+} via Coulomb repulsion. A similar conclusion was drawn from another research, in which Boll et al. argued that RE (IV) dopants expel oxygen vacancies from the grain boundaries and remove the impurity states that facilitate the conduction of electrons [63]. In summary, a correlation between the changes in GB electronic structure and the RE effect has been demonstrated in the above studies, but further investigation is needed to resolve the discrepancy of their conclusions.



Figure 15. PDOS of oxygen of the GBs with no dopant (top) and with Y (bottom) [17].



Figure 16. The densities of states of the Σ 7a and Σ 7m GB simulation cells in the presence of single substitutional dopants of different types [18].

DFT studies also revealed that REs modified diffusion kinetics and energetic properties, which also contributes to the RE effect. For instance, the energetics and kinetics of oxygen diffusion at undoped alumina GBs showed a connection to the atomic structure of the alumina GB [64]. Although no RE-doped GB was investigated in the study, this discovery might imply that the RE effect on oxygen diffusion also changes from GB to GB. This approach can also be applied to examine RE-doped alumina GBs in the future. Furthermore, DFT calculations showed that doping Hf and Zr separately both increase the segregation energy of oxygen vacancies at two configurations of alumina Σ 7 GB (Figure 17) [18]. A positive value of segregation energy indicates that it would not be energetically favorable for the oxygen vacancy to segregate at the GB. As the growth of alumina is largely mediated by GB diffusion of ions, such change of energetics would theoretically lead to slow oxide formation. In another *ab-initio* computational study, it was reported that doping Hf increased migration energy barrier of aluminum vacancies in bulk alumina [65]. Although this focused on the bulk of alumina, the same method can be applied on its grain boundaries. All in all, DFT is a fitting and effective tool to investigate the diffusion of vacancies in aluminum oxide, both energetically and kinetically. So far, there exist only a limited number of computational studies that have covered few GBs and dopants. Plus, investigation of co-doping of REs is largely lacking. Therefore, there is not yet a comprehensive understanding of the impact of REs on electronic properties or GB diffusion.



Figure 17. V_0^{2+} segregation energies at oxygen sites coordinated to substitutional RE dopant sites in two GBs [18].

2.4 Summary of Research Gaps

The previous studies have significantly advanced the knowledge of the RE effect on hightemperature oxidation of alumina-forming alloys through experiments and computations. Multiple RE species and pairs of co-doping that showed effectiveness in suppressing growth of alumina have been identified. Several mechanisms through which the REs reduce rate of oxidation have been proposed. Many researchers believe that the RE dopants blocking GB sites physically, which in turn blocks oxygen or aluminum diffusion, is a contributing factor to the RE effect. However, this blocking effect is not the only cause. Other possible factors include chemical interactions between ions, GB atomic structure, strength of RE-O bonds, GB electronic structure, repulsion of vacancies by REs, and vacancy migration barrier.

Nonetheless, there remain multiple fronts where mechanistic understanding is still elusive, such as the exact role of REs in inhibition of oxide scale growth, influence of operating conditions on the efficacy of REs, how the GB structure affects the RE effect, what causes the synergy of codoped REs, why some REs are more effective than the others, etc. Among those, understanding the role of REs in reducing the oxide growth would be crucial for optimizing the performance of TBCs and transferring this knowledge to be used on other commercial alloys. As mentioned above, it is known that the REs can influence the growth of aluminum oxide through numerous mechanisms. Conventionally, experimental investigations on the RE effect emphasize on the mass gained of the oxide and the diffusivity of the ions. Since it has been proposed that the RE effect can be associated with the electronic structure of the system, combining experiments and DFT study on the electronic structure of the RE-doped aluminum oxide can provide a more comprehensive understanding of the role of REs. Currently, there exist some limitations in DFT studies on the RE effect at the GBs of aluminum oxide. Firstly, the previous studies only focused on selective GB models, so it is unclear whether the same RE effect generalizes to different GBs. Moreover, co-doping of REs has largely been neglected in DFT studies, so there is little mechanistic understanding of the synergistic effect between some co-dopants. Consequently, these limitations should be addressed in future DFT studies by considering more GBs and co-dopants.

3 Methodology

Despite the extensive research efforts on oxidation mechanisms of alumina-forming alloys at elevated temperatures, there is still lack of general agreement on this topic. Thus, more work remains necessary to achieve a better mechanistic understanding. As previously discussed in chapter 2 on the subject of the "RE effect", *ab-initio* DFT calculations based atomic-scale modeling has been proven as a powerful method to complement the traditional experimental studies, as it allows the inspection of alumina at the microscopic level that is difficult to achieve by experimentation.

Work in this thesis focuses on alumina GBs under the influence of RE doping, specifically investigating two important aspects of the "RE effect", namely the impact of RE doping on (1) electronic structure and (2) vacancy segregation at the GBs in alumina. For this study, Hf, Y, and Zr are incorporated into two different GBs by substituting Al atoms, and the appropriate models with different arrangement and combination of dopants are selected based on consideration of energetics. The resultant electronic structures and segregation energies of vacancies in these models are then examined.

3.1 Model Construction

The two GBs studied are $\Sigma 3$ (10 $\overline{10}$) and $\Sigma 13$ (10 $\overline{14}$) twin boundaries, constructed as the representatives of α -Al₂O₃ grain boundaries for this work. These two GBs are selected as they were observed in experiments and also examined in some previous studies [66], [67], [68], [69], [70], [71]. Such selection also allows us to compare our results with some benchmarks previously established.

The model of the $\Sigma 3$ (1010) GB is adapted from a previous study of its structure through DFT calculations and transmission electron microscopy (TEM) by Fabris et al. [72]. Figure 18 schematically illustrated the model, which is comprised of 180 atoms, with 72 Al atoms and 108 O atoms in an orthorhombic supercell. The supercell is defined by three orthogonal vectors $\mathbf{e}_1 = [10\overline{1}0]$, $\mathbf{e}_2 = [\overline{1}2\overline{1}0]$, $\mathbf{e}_3 = [0001]$, with the corresponding supercell dimension of 35 Å, 4.8 Å, and 13.1 Å respectively. The GB is built by rotating one half of the bulk structure by 180° around the $[10\overline{1}0]$ axis with respect to the other half. More specifically, this model corresponds to the screwrotation model proposed in the study by Fabris et al., as the most stable configuration for this GB [72]. The supercell is fully periodic, but with 5 Å of vacuum space added to both sides of the model along the \mathbf{e}_1 direction to prevent image interactions between GBs.



Figure 18. Schematic view of the $\Sigma 3$ (1010) GB. The Al atoms are colored in grey, and the O atoms are in red. The bottom image is viewed along the e_2 direction, while the top image is projected in the e_3 direction. The dash line highlights the grain boundary.

The $\Sigma 13$ (1014) boundary is constructed based on the models proposed by Fabris and Elsässer [73], as well as by Azuma et al. [61]. The supercell consists of 120 atoms, including 48

Al atoms and 72 O atoms, defined by the vectors $\mathbf{e}_1 = [\overline{2}021]$, $\mathbf{e}_2 = [1\overline{2}10]$, and $\mathbf{e}_3 = [50\overline{5}4]$. The supercell dimensions along those directions are 7.05Å, 4.80Å, and 42.92Å respectively. The GB is built by cutting the bulk corundum structure with a (10 $\overline{1}4$) plane and rotating one half of the bulk 180° around [50 $\overline{5}4$] with respect to the other half. This configuration has an O-termination structure with glide mirror symmetry. A schematic view of this GB is displayed in Figure 19.



Figure 19. Schematic view of the $\Sigma 13$ (1014) GB. The Al atoms are colored in grey, and the O atoms are in red. The bottom image is viewed along the e_1 direction, while the top image is projected in the e_2 direction. The dash line highlights the grain boundary.

3.2 Computational Details

All the DFT calculations are carried out through the Vienna Ab initio Simulation Package (VASP) using generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange functional (GGA-PBE) [74], [75], [76]. The electron-ion potentials were defined by the projector augmented-wave method (PAW) [77]. The plane-wave energy cut-off was set to 500 eV. During structural relaxations, the models were relaxed until the atomic forces were below 0.02 eV/ Å and the total energies were less than 10^{-4} eV. A gamma-centered mesh of 5 × 3 × 1 and 6 × 10 × 1 k

points were applied for the Σ 3 and Σ 13 GBs, respectively. For electronic structure calculations, the spacing between k points is 0.1/Å.

3.3 Ab-initio Calculations

In the sections below, the essential computation aspects of *ab-initio* calculations employed in this thesis work are described in detail.

3.3.1 Density Functional Theory

Density-functional theory (DFT) is an *ab-initio* computational method, particularly for studying electronic structures of atoms and molecules. It is a quantum-mechanical technique and its significancy lies in its simplification of the complex electron-electron interactions in manyelectron systems through representing them with an effective one-electron potential that only depends on the electron density [78]. The fundamental concept behind this method is solving a single-particle version of the Schrodinger's equation below:

$$i\hbar\frac{\partial\Psi}{\partial t} = \left(\frac{-\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\Psi$$
(3.1)

where *i* is the imaginary number, \hbar is the reduced Planck constant, Ψ is the wavefunction, *t* is time, $\frac{-\hbar^2}{2m}\nabla^2$ is the kinetic energy term, and $U(\vec{r})$ represents the electrostatic potential energy. This equation can be solved iteratively, as there is an interdependency between the electron density, the wavefunction, and the electrostatic potential [79]. To solve this equation, an initial guess of electron density is defined to solve for $U(\vec{r})$. With this potential term, equation 3.1 can be solved to find the wavefunctions. Next, the electron density can be calculated using these wavefunctions. This calculated electron density is then compared with the initial trial electron density. This iteration terminates once the desired accuracy is reached. Computationally, the above equation can be solved as an eigenvalue problem for which the solution are wavefunctions (Ψ) that only depend on three spatial variables representing the coordinates of each electron [79], as shown below in equation 3.2:

$$E\{\Psi\} = \widehat{H}\{\Psi\} \tag{3.2}$$

where $E = i\hbar \frac{\partial}{\partial t}$ and $\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + U(\vec{r})$. The electrostatic potential energy term, $U(\vec{r})$, is composed of electron-nuclear interactions, pseudopotentials, and electron-electron interactions. While the electron-nuclear interactions, pseudopotentials, and the kinetic energy term in the Hamiltonian operator (\hat{H}) can be calculated individually, the electron-electron interactions are solved through DFT self-consistent calculations iteratively with the help of an exchangecorrelation (XC) functional to approximate the exchange-correlation energy density. The accuracy of DFT calculations largely depends on the functionals involved, but there is not yet a universal approximation method suitable for all chemical systems [78]. Therefore, it is important to understand which functionals to apply in the calculation.

Some XC functionals exist in simple forms, while others are more complex and have more capabilities. The local density approximation (LDA) was the first method proposed and the simplest functional. This approximation method only depends on the energy per particle of an electron gas with uniform spin densities, which can be calculated accurately. This technique has long been a popular functional for researchers as it gives precise approximation for solids and solid surfaces [80]. However, LDA also has significant drawbacks. These functionals typically overestimate atomization energies and bond strength in solids, resulting in several errors, such as small lattice constant, overestimated cohesive energies, as well as underestimated energy gaps in semiconductors and insulators [78], [80]. Some of the errors produced in LDA can be corrected

by the generalized gradient approximation (GGA), which not only account for the electron density, but also its gradient at each point. With this change, GGA reduces several error terms and usually yields more accurate results than LDA [81]. There is only one form of LDA, but GGA exist in different forms as some of the popular ones being PW91, PBE and RPBE [78]. It is worth noting that the PBE form of GGA is commonly used in DFT studies of the α -Al₂O₃ system, as seen in several research articles published in recent years [18], [63], [62]. PBE is a universal GGA that works for a wide range of systems [81]. Consequently, this functional is applied in this work.

3.3.2 Electron Localization Function

Electron localization function (ELF) is a method devised by Becke and Edgecombe to calculate the probability of finding localized electron groups in a region, which enables characterization of bonding and shell structure [82]. The value of ELF is defined as follows [82]:

$$ELF = \left[1 + \left(\frac{D_{\sigma}}{D_{\sigma}^{0}}\right)^{2}\right]^{-1},\tag{3.3}$$

in which

$$D_{\sigma} = \sum_{i}^{\sigma} |\nabla \psi_{i}|^{2} - \frac{1}{4} \frac{|\nabla \rho_{\sigma}|^{2}}{\rho_{\sigma}}, \qquad (3.4)$$

and

$$D_{\sigma}^{0} = \frac{3}{5} (6\pi^{2})^{\frac{2}{3}} \rho_{\sigma}^{\frac{5}{3}}, \qquad (3.5)$$

where D_{σ} represents the spherically averaged σ -spin pair probability, and D_{σ}^{0} denotes the corresponding value for the homogeneous electron gas, which is the fully delocalized state. $\sum_{i}^{\sigma} |\nabla \psi_{i}|^{2}$ is the kinetic energy density, and ρ_{σ} is the σ -spin electron density matrix. The value of ELF ranges from 0 to 1, with 1 indicating perfect localization (low probability of an electron seeing another electron of the same spin), and 0.5 signifying electron-gas like pair probability (perfect delocalization) [83].

3.3.3 GB Energy

One critical metric in assessing the stability of a GB is its formation energy. The formation energy of a GB at 0 K, γ , can be defined by the following equation [84], [85]:

$$\gamma = \frac{E_{GB} - E_{bulk}}{A},\tag{3.6}$$

where E_{GB} is the energy of a GB without dopant, and E_{bulk} is the energy of an undoped oxide bulk in the same supercell. The cross-sectional area of the GB is denoted by *A*.

3.3.4 Segregation Energy of REs

The likelihood of the REs segregating to the alumina GBs compared to staying in the bulk is quantified by their segregation energy, E_{seg} , which is defined as

$$E_{seg} = (E_{RE-GB} - E_{GB}) - (E_{RE-bulk} - E_{bulk}),$$
(3.7)

where E_{RE-GB} is the energy of GB doped with RE, E_{GB} is the energy of a GB without dopant, $E_{RE-bulk}$ is the energy of bulk α -Al₂O₃ doped with RE, and E_{bulk} is the energy of an undoped bulk [71], [86]. The dopants are doped substitutionally to the Al sites. A negative value of E_{seg} suggests that RE prefers to segregate to the GB.

3.3.5 Binding Energy

In the case of a RE-doped alumina, there may be necessity to consider the interaction between the RE atoms when they are within close vicinity. In such situation, the interaction between two dopants can be evaluated by their binding energy, E_b, defined as

$$E_b = E_{RE1-RE2} - E_{RE1} - E_{RE2} + E_{GB}, (3.8)$$

where $E_{RE1-RE2}$ is the energy of a GB doped with two REs, E_{RE1} is the energy of a GB with one RE, E_{RE2} is the energy of a GB with the other RE, and E_{GB} is the energy of a GB with no dopant [86], [87]. A negative value of E_b indicates attraction between the two REs, meaning it is energetically favorable for these two atoms to co-segregate in the GB.

3.3.6 Segregation Energy of Vacancy

To evaluate the tendency of an oxygen or aluminum vacancy to segregate along the GBs, the segregation energy of selected vacancies, E_{seg-V} , are calculated following the equation below:

$$E_{seg-V} = E_{V-GB} - E_{V-bulk}, ag{3.9}$$

in which E_{V-GB} represents the energy of a GB model with a vacancy at the GB, and E_{V-bulk} is the energy of a GB model with a vacancy at its bulk region, which is approximately 10 Å away from the GB. A negative value of E_{seg-V} reveals the vacancy is energetically favorable to segregate to the GB [18], [64].

4 Research Findings and Discussion

4.1 Atomic GB Structures with and without REs

The atomic structures of both GB models used this study, i.e., the $\Sigma 3$ (10 $\overline{1}0$) and the $\Sigma 13$ (10 $\overline{1}4$) twin boundaries are validated through comparing with data from published studies [72], [73], [88], [89], [90] on the structure of these GBs. The two main parameters used in our validation are (1) the GB energy γ , and (2) the nearest-neighbor distances between Al and O atoms at the GBs. These two parameters characterize the energetics and the atomic arrangements of a GB. The calculated values and the ones in literature studies are compared in Table 1. Though general agreement can be seen from Table 1, small discrepancy between the two set of values is also observed. Such discrepancy can be attributed to the discrepancies between the settings used in different DFT simulations, such as convergence criteria, algorithm, number of atoms, number of fixed atoms, among others. These factors can lead to different studies having slightly different GB energies and bond lengths.

It is also worth noting that though ideally one would like to use GB models with a higher number of atoms to better represent GBs in real materials, in practice we are limited by the computational resources. The Σ 3 and Σ 13 GB models in our work consist of 180 and 120 atoms, respectively. As previously discussed, calculations using these models yield close results with the literature studies. In addition, preliminary calculations were performed to confirm the good convergence of our results with respect to the supercell size.

GB	Parameters	Present study	Literature
$\Sigma 3(10\overline{1}0)$	γ (J/m²)	0.26	0.30 [72]; 0.25 [88]; 0.27 [89]
	Rang of Al-O bond length (Å)	1.79 - 2.07	1.79 – 2.04 [72]
14)	γ (J/m²)	2.45	2.44 [73]; 3.06 [90]
Σ13(10	Rang of Al-O bond length (Å)	1.88 – 1.99	1.84 – 1.99 [73]

Table 1. Properties of the relaxed $\Sigma 3$ and $\Sigma 13$ GB models.

4.1.1 Segregation of Single Dopants in Σ 3 and Σ 13 GBs

In the Σ 3 GB, 12 Al sites near the GB were selected as candidate sites for substitutional defects created by the RE dopants, which are numbered in Figure 20 (a). The segregation energy of each RE is listed in Table S1 in Appendices. A negative value indicates that the dopant is energetically favored to segregate at the GB Al site, while a positive value indicates the opposite. One can see that it is energetically advantageous for these REs to segregate to most GB Al sites, with the most preferred Al site for all three elements to segregate being site #2. To understand this segregation tendency, we examine the sizes of RE elements and Al. The ionic radius of Al is 67.5 pm, while the ionic radii of Hf, Y, and Zr are 72 pm, 73 pm, and 104 pm, respectively. Due to their large sizes compared to Al, mechanically the REs would favor locations with more free volume. The Al sites in the middle of the GB are the ones with most free volume, and consequently become favorable locations for RE segregation. This relationship between the segregation tendency and ionic radius mismatch has also been confirmed in other studies [69], [91]. The tendency of REs segregating to GB is also in good agreement with experimental observations. For instance, Gemming reported the experimental observation of Y segregation to Σ 3 twin boundary [92], and

Chen et al. reported the segregation of Hf, Y, and Zr in six synthesized α -Al₂O₃ GBs with the grain misorientation ranging from 53 to 90° [45].

At the $\Sigma 13$ GB, eight Al sites near the GB were selected as substitutional sites for the RE dopants, as illustrated in Figure 20 (b). The segregation energy of each RE at each Al site is tabulated in Table S1 in Appendices, showing that it is thermodynamically favorable for all dopants to segregate to these Al sites. The lowest segregation energy for Zr is obtained by replacing Al at site #1, while the lowest segregation energy for Hf and Y is from the substitutional defect at Al site #3. Again, the REs preferred to segregate to the Al sites that are the closest to the GB, which can be attributed to its large space compared to the bulk region.



Figure 20. (a) Schematic view of the $\Sigma 3$ (1010) GB along the [1210] direction, and (b) schematic view of the $\Sigma 13$ (1014) GB projected in the [1270] direction. The Al atoms are colored in grey, and the O atoms are in red. The dash lines indicate the GB.

4.1.2 Co-segregation of Dopants in Σ 3 and Σ 13 GBs

Moreover, to assess the feasibility of co-segregation of REs, all three combinations of codoping, such as Hf-Y, Y-Zr, and Hf-Zr, were examined. The Σ 3 GB models with co-dopants were created by adding a second RE substitutionally to the three most energetically stable GBs, each one with a different RE occupying the Al site #2. For example, due to Hf having a lower segregation energy compared to Y, Hf is fixed at site #2, and Y is placed in eight other different atomic sites (Al site #5 to Al site #12) to create eight GB models with Hf-Y co-doping. The same procedure was also carried out to create eight GB models for Hf-Zr and Y-Zr. The lowest binding energy between two REs among the eight GB structures for each co-doping pair is shown in Table 2. The negative binding energies of Hf-Y and Y-Zr pairs suggest there is attractive interaction between the co-dopants, while the positive binding energy of Hf-Zr reveals the repulsion between these two elements. It is thus not thermodynamically favorable for the latter co-doping pair to form in the GB. As a result, co-doping of Hf and Zr was not considered in the subsequent calculations. Co-doping of Hf-Y and Hf-Zr have been observed in experimental studies, meaning that it is possible to fabricate these co-doped GBs in practice [15], [16]. To summarize, one undoped Σ 3 GB model and five Σ 3 GB models doped with the following REs were chosen for further investigation: (1) Hf at #2, (2) Y at site #2, (3) Zr at site #2, (4) Hf at site #2 with Y at site #8, (5) Zr at site #2 with Y at site #9. The mean atomic separations between the RE dopants and the neighboring oxygen atoms in the Σ 3 GB models are summarized in Table 3. The maximum bond length considered in this study is 3 Å, as this distance includes the separation of between these REs and the coordinated oxygens seen in other studies [18], [93]. The structural distortion induced by the REs are illustrated by the increased length of RE-O bonds compared to the corresponding

Al-O in the undoped GB, which can be attributed to the larger ionic radii of the REs and the difference in their electronic charges.

The same approach taken for the Σ 3 GB was also applied for the Σ 13 GB to examine all the co-doping combinations. It was revealed by the negative binding energies in Table 2 that there are attractive interactions between Hf and Zr, as well as Y and Zr. Both co-doping scenarios have been observed experiments by He et al. [16], so it is feasible to have these co-dopants to segregate in a GB of α -Al₂O₃ in practice. Therefore, one undoped Σ 13 GB structure and five Σ 13 GB models with the following dopants were selected for further analyses: (1) Hf at site #3, (2) Y at site #3, (3) Zr at site #1, (4) Zr at site #1 with Y at site #8, (5) Hf at site #2 with Zr at site #1. The mean atomic separations between the RE dopants and the surrounding oxygen atoms in the Σ 13 GB models are listed in Table 3. The longer bonds in the doped GBs might be caused by the larger ionic radii of the REs and the difference in their electronic charges.

GB	REs	E _b (eV)	GB	REs	E _b (eV)
((Hf-Zr	0.541	Σ13(10 <u>1</u> 4)	Hf-Zr	-0.481
3(101	Hf-Y	-0.228		Hf-Y	0.014
M	Y-Zr	-0.330		Y-Zr	-0.220

Table 2. The lowest binding energy for each pair of RE co-dopants at Σ *3 GB and* Σ *13 GB.*

GB	RE	RE-O separation (Å)	GB	RE	RE-O separation (Å)
$\Sigma 3(10\overline{1}0)$	Undoped	1.949	$\Sigma 13(10\overline{1}4)$	Undoped	1.855
	Y	2.303		Y	2.338
	Hf	2.069		Hf	2.263
	Zr	2.077		Zr	2.209
	Zr (in Zr-Y)	2.263		Zr (in Zr-Y)	2.336
	Y (in Zr-Y)	2.297		Y (in Zr-Y)	2.476
	Hf (in Hf-Y)	2.077		Hf (in Hf-Zr)	2.162
	Y (in Hf-Y)	2.408		Zr (in Hf-Zr)	2.321

Table 3. Mean bond lengths of RE-O in the Σ *3 GB and the* Σ *13 GB.*

4.2 Electronic Structure

4.2.1 Density of States (DOS)

The electronic structure of a GB has implications on its local bonding environment and charge distribution, which make an impact on GB diffusion and thereby oxide growth [62], [65]. The electronic DOS of the pure and doped Σ 3 GB are displayed in Figure 21. The Fermi energy is indicated by the black dashed lines. The impact of different REs on the DOS can be revealed through comparing the differences between the DOS of the undoped GB [Figure 21 (a)] and the GBs with dopants [Figure 21 (b)-(f)]. The addition of Y introduces some localized impurity states inside the band gap at ~ 5 eV, which is shown as a sharp peak on the graph. This peak is likely attributed to the hybridization of the Y d-states and the O p-states, as indicated by the overlapping of their respective peaks at around 5.5 eV. As a result, more energy states are available for electron conduction in the Y-doped GB compared to the pristine GB. However, this impact appears to be

marginal, as the rest of the DOS plot remains largely unchanged. These changes induced by Y on DOS of the GB have also been reported in other theoretical studies of doping Y into the bulk [94] and a Σ 7 GB of α -Al₂O₃ [18]. The slight influence of Y on the DOS might be due to its low concentration in the model, since only one atom of Y was added to the GB. However, Y atoms occupy on average around 60% of an atomic monolayer at the GB, so its impact on the oxide growth and the electronic structure could potentially be more prominent in real materials [58]. Similarly, all the other dopants and co-dopants also give rise to new energy states near the conduction band. These changes are caused by the hybridization of the d-state of the REs and the p-state of the neighboring O's, as indicated by the overlap of their peaks at energies above the Fermi level. These new localized states are also related to the longer RE-O bonds compared to the Al-O bonds, as listed in Table 3. As the bond length changes, the distribution of electrons also changes, which might lead to new energy states. In addition, adding these REs also causes a significant shift of the occupied states towards lower energy levels, illustrating the substantial doping effects generated by these REs. The doping of REs in Al₂O₃ sometimes results in shift of the DOS due to the transfer of electrons from the RE to its neighboring O atoms. For instance, doping Hf in a NiAl-Al₂O₃ interface also causes a downward shift of the occupied states in the DOS plot (figure 4 in [95]). Since the formation of alumina involves transport of ions, the downward shift of the DOS also implies that it is potentially harder for electron transfer to occur. Therefore, the hole conductivity is reduced, and the diffusion-controlled oxide growth is hindered. In experimental studies, Hf, Zr, Hf-Y, and Y-Zr have all shown to have favorable effects on slowing down the growth of α -Al₂O₃ scale [15], [16]. Therefore, there appears to a correlation between the influence of REs on DOS and the oxide growth rate.



Figure 21. DOS plots of (a) undoped $\Sigma 3GB$, (b) $\Sigma 3GB$ doped with Y, (c) $\Sigma 3GB$ doped with Zr, (d) $\Sigma 3GB$ doped with Hf, (e) $\Sigma 3GB$ doped with Hf and Y, and (f) $\Sigma 3GB$ doped with Zr and Y. The dotted line indicates the Fermi energy.

The DOS plots of the pristine and doped $\Sigma 13$ GB are exhibited in Figure 22. The impact of different REs on the DOS can be seen through comparing the DOS of the undoped GB [Figure 22(a)] and the GBs with dopants [Figure 22 (b)-(f)]. Contrary to the $\Sigma 3$ GB, the insertion of REs does not cause any shift of energy states in the $\Sigma 13$ GB. One possible cause of this discrepancy is the different RE-O bond lengths in these two GBs as summarized in Table 3. Since the RE-O

distances are shorter in the Σ 3 GB, the electron transfer is facilitated compared to the Σ 13 GB. As seen on Figure 22, Y introduces impurity states in the band gap near the bottom of the conduction band at ~ 4eV, but this element brought little modification to the overall DOS of the GB. Zr and Hf each also give rise to new energy states at ~1 eV, and their respective total number of states between 0 and -5 eV reduce slightly. For both cases of co-doping, the dopant effects on the electronic structures are similar. New impurity levels were introduced between the Fermi level and the conduction band, but the band structure remained to be almost identical to the undoped GB. The new energy states in the RE-doped GBs arise from the hybridization of the d-state of the REs and the p-state of the coordinating O atoms, as illustrated by the overlapping of the peaks of RE and O at energy levels above the Fermi level. The doping of REs also leads to longer RE-O separations compared to Al-O bonds in the undoped GB, as shown in Table 3. Therefore, these new impurity states can also be attributed to the different bonding environment caused by the REs.

The influences of REs on DOS near the $\Sigma 13$ GB differ from the effects of the same REs on the DOS of the $\Sigma 3$ GB. This difference might be attributed to the different electronic structure of the undoped GBs. In the pristine $\Sigma 13$ GB, its number of available DOS in the valence band is lower than that in the undoped $\Sigma 3$ GB, meaning that the former GB intrinsically possesses lower electron transfer rates. Moreover, the $\Sigma 13$ GB has a higher degree of structural disorder compared to the $\Sigma 3$ GB, as the former has a GB energy of 2.45 eV/m² while the latter has a GB energy of 0.26 eV/m². As a result, it is energetically harder for electron transfer to take place in the $\Sigma 13$ GB, which explains the difference in DOS between the two GBs. Therefore, the discrepancy of the DOS in different GBs also implies that the RE effects also depend on the atomic structure of the GB.



Figure 22. DOS plots of (a) undoped $\Sigma 13GB$, (b) $\Sigma 13GB$ doped with Y, (c) $\Sigma 13GB$ doped with Zr, (d) $\Sigma 13GB$ doped with Hf, (e) $\Sigma 13GB$ doped with Hf and Zr, and (f) $\Sigma 13GB$ doped with Zr and Y.

4.2.2 ELF

ELF provides insights into distribution of electrons and thereby chemical bonding. Therefore, ELF calculation was performed for all the GB models to examine the influence of REs on bonding in both Σ 3 and Σ 13 GBs. The value of ELF ranges from 0 to 1, with ELF=1 indicating perfect localization and ELF = 0.5 indicating electron gas [82]. The 2D projection of ELF of both GBs cut through the Al atoms. Figure 23 displays the images of cross section of ELF around the Σ 3 GB region with and without RE dopants. The electron localization is labeled with the corresponding atoms - Al and O in black, and REs in red. In Figure 23 (a), electron density is localized on the oxygen atoms that are closer to the outermost surface in an undoped GB, which is consistent with findings from literature [96]. In Figure 23 (b), it is shown that there is a higher localization of electron around Y compared to the Al in the same position in the undoped GB, implying the formation of ionic Y-O bonds. In Figure 23 (c)-(d), one can see that Zr and Hf induced delocalization of electron near the dopant compared to the undoped GB. The transfer of charges from both REs to the nearby O atoms likely have caused the downward shift of the DOS of these GBs, as shown in Figure 21 (c)-(d). In Figure 23 (e)-(f), it is illustrated that Y increased the electron localization around a neighboring O atom significantly in both co-doped GBs, as indicated by the larger red contour on the O atom compared to the undoped GB. This phenomenon indicates the transfer of electrons from Y to the neighboring O atom, causing the downward shift of DOS as seen in Figure 21 (e)-(f).



Figure 23. Cross section of the ELF of (a) pristine $\Sigma 3GB$, (b) $\Sigma 3GB$ doped with Y, (c) $\Sigma 3GB$ doped with Zr, (d) $\Sigma 3GB$ doped with Hf, (e) $\Sigma 3GB$ doped with Hf and Y, and (f) $\Sigma 3GB$ doped with Zr and Y.

The cross section of ELF around the $\Sigma 13$ GB region is exhibited in Figure 24. These images show that the addition of REs in this GB resulted in little change in the localization of electrons around the dopants compared to the $\Sigma 3$ GB. This difference can be attributed to the longer distances of RE-O in the $\Sigma 13$ GBs compare to the $\Sigma 3$ GBs, so the electrons are more delocalized in the former GB. Like the $\Sigma 3$ GB, there is a high level of electron localization on oxygen atoms, as displayed in Figure 24 (a). The high value of ELF around O atoms and low value around Al atoms in this GB indicate the formation of ionic bonds between these atoms. In the cases with single dopant, as seen in Figure 24 (b)-(d), the REs caused little change to the electron localization. For both co-doped scenarios, the addition of two REs results in slight delocalization of electron of the O atoms near the dopants, as demonstrated in Figure 24 (e)-(f). Overall, REs did not induce significant change to the electron localization in the $\Sigma 13$ GB, which is consistent with the DOS of the same GB.



Figure 24. Cross section of the ELF of (a) pristine $\Sigma 13GB$, (b) $\Sigma 13GB$ doped with Y, (c) $\Sigma 13GB$ doped with Zr, (d) $\Sigma 13GB$ doped with Hf, (e) $\Sigma 13GB$ doped with Hf and Zr, and (f) $\Sigma 13GB$ doped with Zr and Y.

4.3 Segregation of Vacancies to α-Al₂O₃ GBs

The formation and growth of α -Al₂O₃ hinges on the GB diffusion of Al and O ions [33]. Since the GB transport of both ions involves their vacancies, the influence of REs on Al and O vacancies in GBs might be an indicator of the RE impact on GB transport of Al and O ions. This subchapter focuses on the segregation of aluminum and oxygen vacancies in GBs. In α -Al₂O₃ crystal, the formation energy of the Schottky defects (substitutional O vacancies) is lower than that of the O-Frenkel pair between an oxygen vacancy and an oxygen interstitial [97]. As a result, the formation of substitutional O vacancies is more thermodynamically favorable. The segregation of these vacancies at GBs gives implication on the electronic conductivity and the GB transport of Al and O, which are related to the growth of scale. Therefore, the influence of RE substitutional defects on the segregation of vacancies at GBs was investigated, which is estimated by their segregation energies. Charged vacancies, V_0^{2+} and V_{Al}^{3-} , were considered. These charge states are the most stable for the respective vacancies in α -Al₂O₃ [98].

In the undoped Σ 3 GB, the segregation of $V_0^{2^+}$ and $V_{Al}^{3^-}$ in eight O sites and eight Al sites near the GB plane, respectively, was examined. The mean segregation energies of $V_0^{2^+}$ and $V_{Al}^{3^-}$ are -1.33 eV and -0.52 eV, respectively, as illustrated in Figure 25. The error bars indicate confidence intervals of 95%. The negative values of the mean segregation energies signify that it is thermodynamically favorable for both $V_0^{2^+}$ and $V_{Al}^{3^-}$ segregate at the Σ 3 GB. The concentration of $V_0^{2^+}$ is higher as it has a lower mean segregation energy.

The mean segregation energies of $V_0^{2^+}$ in eight O sites and $V_{AI}^{3^-}$ in eight Al sites near the GB plane in the undoped $\Sigma 13$ GB were estimated. The calculated results are shown in Figure 25, in which the error bars specify confidence intervals of 95%. The mean segregation energies of $V_0^{2^+}$ and $V_{AI}^{3^-}$ are -0.93 eV and -2.75 eV, respectively. Since both values are negative, it is energetically favorable for both types of vacancies to segregate to this GB. Compared to the undoped $\Sigma 3$ GB, the mean segregation energy of $V_0^{2^+}$ is increased, while that of $V_{AI}^{3^-}$ is decreased. As a result, unlike in the undoped $\Sigma 3$ GB, the GB segregation is more favorable for $V_{AI}^{3^-}$ than $V_0^{2^+}$ is in the undoped $\Sigma 13$ GB. This finding is supported by a study of Takahashi et al., who revealed the formation energy of $V_0^{2^+}$ is higher than $V_{AI}^{3^-}$ in the same $\Sigma 13$ GB, indicating that it is easier for $V_{AI}^{3^-}$ to form in this GB [99]. The authors suggested that the defect energetics depend on the lattice distortions in the GB. The differences of vacancy segregation and formation in these two GBs implies that the diffusivity of oxygen and aluminum varies in different GBs. Indeed, Nakagawa et

al. have discovered that the diffusivities of oxygen in several different α -Al₂O₃ GBs ranges from 7.5E-8 m³/s to 4.0E-2 m³/s, illustrating that the GB characters play an important role in GB diffusivity of oxygen [44]. Since the GB energy of the Σ 13 GB (2.45 eV/m²) is significantly higher than that of the Σ 3 GB (0.26 eV/m²) and both GBs have different structures, the discrepancy of vacancy segregation in these two GBs is reasonable.



Figure 25. Mean segregation energy of $V_0^{2^+}$ and $V_{Al}^{3^-}$ vacancies in the undoped $\Sigma 3$ GB (solid filled) and the undoped $\Sigma 13$ GB (pattern filled).

4.3.1 GB Segregation of Vo²⁺

Figure 26 demonstrates the mean segregation energies of $V_0^{2^+}$ at the undoped Σ 3 GB and the same GB doped with different REs. These segregation energies were calculated for four coordinated oxygen sites neighboring the RE substitutional dopants. The error bars in the graph represent the 95% confidence level. This graph shows that Y slightly decreased the mean segregation energy of the vacancy, meaning that this element enhances the segregation of $V_0^{2^+}$ and its GB diffusion. On the contrary, both Hf and Zr raised the mean segregation energy of the

same vacancy to positive values, illustrating the beneficial RE effect induced by these dopants on reducing segregation of V_0^{2+} . These findings have a correlation with the effectiveness of these REs on reducing growth of Al₂O₃. Li et al. reported that Hf and Zr are significantly more effective in suppressing scale growth than Y [53]. In other studies, it was also shown that Hf is more powerful than Y in hindering growth of Al₂O₃ [15], [56]. One possible cause behind the effect of these REs is the electrostatic repulsion between the dopants and the nearby V_0^{2+} . A negative charge is generated by substituting Al with Y, while Hf and Zr induced positive charges in the system. Consequently, the repulsion between the positively charged Hf or Zr and V_0^{2+} renders the segregation of this vacancy energetically unfavorable. In contrast, the negatively charged Y enhances the segregation of V_0^{2+} due to electrostatic attraction. Similar influence of REs has also been reported in a study on two Σ 7 GBs, in which the segregation energy of V₀²⁺ is increased due to the addition of Hf and Zr, while Y had little impact on it [18]. The authors attributed these results to the repulsion between the charged REs and the V_0^{2+} . Hence, the electrostatic interactions between the REs and the Vo²⁺ play a factor in the segregation of this vacancy regardless of the GB structure.

Moreover, the electronic structure of the doped GB also sheds light on the RE effect on the segregation of V_0^{2+} . Figure 21 (c)-(d) show that both Zr and Hf caused the peaks of the DOS to shift to lower energy levels. As the valence band in the DOS shifts further away from the Fermi level, the availability of charge carriers (holes) is diminished. Therefore, the diffusion of V_0^{2+} is impeded. On the other hand, since the segregation of Y to the GB introduces impurity states at around 5 eV in the conduction band (Figure 21 (b)), these new states might act as electron carriers and enhance electronic conductivity in this material. This mechanism is also in agreement with the decreased segregation energy of V_0^{2+} caused by Y. It is also possible that the effect of these REs

stems from the strength of the RE-O bonds: in Al₂O₃, Hf-O and Zr-O are stronger bonds than Y-O [100]. However, more study is required to assess the significance of RE-O bond strength on the RE effect compared to other factors. By analyzing the impact of the three individual REs on the electronic structure and the segregation energy of V_0^{2+} of the Σ 3 GB, a correlation between them is revealed. Since the growth of aluminum oxide involves diffusion of oxygen, which hinges on diffusion and segregation of oxygen vacancies, it is evident that Hf, Y, and Zr impose their impact on the scale growth through altering the electronic properties of the GB.

The impact of co-doping of two REs in the Σ 3 GB on the segregation of V₀²⁺ is also illustrated in Figure 26. Both co-doping scenarios increase the segregation energy of V_0^{2+} substantially, indicating that the segregation of this vacancy is hindered by co-doping Hf-Y and Zr-Y. Similarly, it has also been observed in experiments that both Zr-Y and Hf-Y are effective in suppressing scale growth [15], [16]. Hence, there appears to be a correlation between the segregation of V_0^{2+} and the growth of α -Al₂O₃. Particularly, one can see that by adding Hf or Zr to the GB that already contains Y, both Hf and Zr offset the enhancement of the segregation of V_0^{2+} caused by Y. This influence is likely caused by a combination of electrostatic force and change of electronic structure, similar to the Σ 3 GB doped with individual REs that are discussed above. There is repulsion between the positively charged Hf or Zr and Vo²⁺, making the segregation of vacancy less thermodynamically favorable. Moreover, both Hf-Y and Zr-Y cause a shift of the states to lower energy levels in the DOS, as shown in Figure 21 (e)-(f). Therefore, both Hf and Zr have the more dominant impact on the DOS while being co-doped with Y. Due to the shift of the energy states, the concentration of holes is reduced, resulting in a slower diffusion of V_0^{2+} . This result is in good agreement with literature, as it has been reported that Hf has a more important role than Y in reducing the rate of Al₂O₃ growth [15]. Furthermore, the possible Y-O ionic bond shown in ELF

plots in Figure 23 (e)-(f) might also contribute to reducing segregation and diffusion of $V_0^{2^+}$. Since the Y-O bond is strong, it takes more energy for GB transport of $V_0^{2^+}$ to occur. A similar assessment on the impact of Y-O ionic bonds has been made in another computational study on Y-doped $\Sigma 13$ GB [61], which reaffirms that besides electrostatic force and electronic structure, RE-O bond strength also affects the GB segregation and formation of $V_0^{2^+}$ in Al₂O₃.

For the $\Sigma 13$ GB, Figure 26 summarizes the influence of REs on the mean segregation energies of Vo²⁺ at four sites near the dopants with confidence intervals of 95%. In this GB, the mean segregation energy of Vo²⁺ remains negative after the addition of REs, meaning that it is still thermodynamically favorable for this vacancy to segregate to the $\Sigma 13$ GB. This energetically advantageous segregation can be attributed to the large space in this GB and its elevated interfacial energy. Compared to the undoped GB, Hf, Zr, and Zr-Y increased the mean segregation energy by less than 1 eV, indicating modest impediment to the segregation of Vo²⁺ caused by REs. These REs hinder the segregation of V_0^{2+} in both the $\Sigma 3$ and $\Sigma 13$ GBs, so the causes behind their impact on segregation energetics are likely the same. The electrostatic repulsion between these positively charged REs and V_0^{2+} can have an adverse effect on the GB transport of this vacancy. Moreover, the reduction in energy states in the valence band below the Fermi level, as exhibited in Figure 22 (c)-(e), causes decreased concentration of charged carriers, thereby also impeding the segregation of V_0^{2+} . For the Zr-Y pair, the effect of Zr is more dominant than Y, just like in the Σ 3 GB. On the other hand, Y and Zr-Hf further decreased the segregation energy of V_0^{2+} , indicating the enhancement on the segregation of this vacancy caused by these REs. This effect of Y can be attributed to (1) its electrostatic attraction with the positively charged vacancy, and (2) its new energy states at around 3 eV near the conduction band in the DOS Figure 22 (b), which increase the concentration of electrons and thereby the electronic conductivity in the GB. However, Zr-Hf decrease the mean segregation energy of $V_0^{2^+}$, contrasting with the effect of doping Zr or Hf separately. This anomaly is likely the result of interaction between these two REs, as Hf is located at Al site #1 and Zr is at Al site #2. The interaction of these dopants might alter the charge distribution around the surrounding area and attract $V_0^{2^+}$, making its segregation more energetically beneficial. However, whether there is an interaction between Zr and Hf cannot be proven by the existing data in this thesis. Further study will be required to investigate their interaction in order to clarify the relationship between it and their co-doping effect. He et al. also claimed that the interaction between RE ions is an important factor behind the co-doping effect, but the authors were not able to provide more details about such interaction either [16].



Figure 26. Segregation energy of oxygen vacancies at undoped and doped Σ 3 and Σ 13 GBs.

4.3.2 GB Segregation of V_{Al}³⁻

The impact of different REs on the segregation of V_{AI}^{3-} in the $\Sigma 3$ GB are summarized by their mean segregation energies, as shown in Figure 27. The segregation energies in RE-doped GBs were calculated based on four Al sites the RE substitutional dopants. The error bars in the graph constitute the 95% confidence level. It is shown that Hf, Y, and Zr all remarkably hamper the segregation of this vacancy. In contrast, Hf-Y and Zr-Y further enhance it. These results suggest that the causes behind the impact of these REs on the segregation of V_{AI}^{3-} are different than how

the same REs affect the segregation of $V_0^{2^+}$. For instance, Hf and Zr diminish the segregation of $V_0^{2^+}$ due to repulsion of the same charge. But these positively charged REs also reduce the segregation of $V_{AI}^{3^-}$, meaning that the electrostatic repulsion does not have significant contribution to the segregation of $V_{AI}^{3^-}$. Moreover, Hf-Y and Zr-Y both decrease the segregation energy of $V_{AI}^{3^-}$, which is the opposite effect compared to doping those REs separately. This effect is also contradictory to the synergistic effect of reducing $V_0^{2^+}$ segregation imposed by these co-dopants. The influence of the DOS on $V_{AI}^{3^-}$ is also unclear. Hf, Zr, Hf-Y, and Zr-Y all cause a shift of the DOS, as shown in Figure 21 (c)-(f). However, these REs have different influences on the segregation of $V_{AI}^{3^-}$. All in all, there is not a clear relationship between the electronic properties of the $\Sigma 3$ GB and the RE effect on segregation energetics of $V_{AI}^{3^-}$ based on the data in this study.

As for V_{AI}^{3-} in the $\Sigma 13$ GB, the mean segregation energies of this vacancy at four Al sites near the REs are shown in Figure 27. The confidence level of these values is 95%. Y and Zr-Y increase the mean segregation energy of V_{AI}^{3-} , meaning that they make the segregation of vacancy less energetically advantageous. On the other hand, Hf, Zr, and Zr-Hf instigate reduction of the mean segregation energy, signifying that these REs favor the segregation of V_{AI}^{3-} in the $\Sigma 13$ GB. Just like the $\Sigma 3$ GB, the influence of REs on the segregation of V_{AI}^{3-} in the $\Sigma 13$ GB mainly constitutes of factors other than electronic properties. Zr and Hf might attract V_{AI}^{3-} due to their positive charges and decrease its segregation energy, while Y can repulse V_{AI}^{3-} and cause its segregation to be more difficult, as illustrated in Figure 27. On the other hand, Zr-Hf decrease the mean segregation energies of both V_0^{2+} (Figure 26) and V_{AI}^{3-} (Figure 27) in this GB, and Zr-Y cause an increase in the mean segregation energies of both vacancies in the $\Sigma 13$ GB (Figure 26: V_0^{2+} in $\Sigma 13$ GB; Figure 27: V_{AI}^{3-} in $\Sigma 13$ GB). The impact of these co-dopants hints that the effect of these two REs depend more on the GB atomic structure and other factors, rather than electronic characteristics of the GB.



Figure 27. Segregation energy of aluminum vacancies at undoped and doped Σ 3 and Σ 13 GBs.

There have been few studies on aluminum transport in α -Al₂O₃ than oxygen transport, and there is not yet a comprehensive understanding of the influence exerted by REs on aluminum and aluminum vacancy at α -Al₂O₃ GBs. However, some hints of the mechanisms of the RE effect on aluminum diffusion and vacancy segregation can still be extracted from literature. At the Σ 13 GB, it was discovered that the formation energy of V_{Al}³⁻ is related to the structural distortion caused by RE dopants [99]. Moreover, the addition of REs in α -Al₂O₃ can lower the migration energy barrier of diffusion of V_{Al}³⁻, so the kinetics also play a role in the GB transport of V_{Al}³⁻. Therefore, understanding the segregation of V_{Al}³⁻ in α -Al₂O₃ GBs also requires investigation of the mechanical and kinetic effects induced by the REs, which is beyond the scope of this thesis.

5 Conclusion

5.1 Summary of Research

To further understandings of the mechanisms behind the "RE effect" on the growth of α -Al₂O₃, *ab initio* calculations have been carried out using DFT in this work. The main objective of this thesis is to investigate the influence of several REs on the electronic structure and the segregation of vacancies at two representative α -Al₂O₃ GBs.

Based on the segregation energies of REs and the binding energies between the co-dopants, five Σ 3 GB models and five Σ 13 GB models with singly- and co-doped REs were selected for further investigation since they are energetically stable. The electronic structures of these GB models were then inspected. At the Σ 3 GB, the DOS was shifted to lower energy levels by Hf, Zr, Hf-Y, and Zr-Y, which also gave rise to some mid-gap states. While Y only induced marginal changes to the number of states near the conduction band. The electron localization characterized by ELF suggest electron transfer and hybridization of states likely caused those changes in DOS. At the Σ 13 GB, its available states below the Fermi level were slightly reduced by Hf, Zr, Zr-Y, and Zr-Hf, while Y imposed similar changes as it did to the DOS of the Σ 3 GB. The ELF plots show these changes in the DOS can be rationalized by the decreased localization of electrons. The impact of REs on the segregation of V_0^{2+} and V_{Al}^{3-} was also evaluated according to the segregation energies of these vacancies. In the Σ 3 GBs, the addition of Hf, Zr, Hf-Y, and Zr-Y significantly increased the segregation energy of V_0^{2+} , while Y slightly decreased it. In the $\Sigma 13$ GBs, the addition of Hf, Zr, and Zr-Y significantly increased the segregation energy of Vo²⁺, while Y and Zr-Hf slightly decreased it. The lack of synergetic effect of Zr-Hf is attributed to their interactions.

These changes are related to the changes brought by these REs to the DOS at the GB. In both co-doping pairs, Hf and Zr are the more dominant REs than Y. By comparing the segregation energies of V_0^{2+} computed in this work to experimental results of GB diffusivity of oxygen and growth of Al₂O₃, one can see that the GB segregation of V_0^{2+} is well correlated with the scale growth. Therefore, it is evident that the impact of REs on the electronic properties of the GB plays an important role to their influence on GB segregation and transport of V_0^{2+} and oxygen, as well as on the growth of oxide, regardless of the GB. On other hand, the mechanisms behind the influence of REs on the segregation of V_{Al}^{3-} are more complex. Based on the findings in the current work, there is not enough evidence to provide a comprehensive understanding of the "RE effect" on the segregation of V_{Al}^{3-} , nor the relationship between the segregation of this vacancy to the oxide growth. Accordingly, a more extensive study on segregation of V_{Al}^{3-} will be required to examine how it is affected by the REs.

The result in this work confirms that the influence of REs on the electronic structure of the GB plays a role on the growth of α -Al₂O₃ through altering GB segregation of V₀²⁺. Therefore, the electronic structure should be considered in future studies on the "RE effect". Furthermore, by comparing the results from both GBs, it is also noticeable that the GB characteristics also contribute to the "RE effect". Moreover, the synergy between the co-dopants depends on their interactions, which also reveals the complexity of the mechanism behind the suppression of growth of Al₂O₃ caused by the REs. Therefore, the mechanisms behind the "RE effect" are most likely a combination of several competing factors, and the dominant mechanism might vary with the species of the RE as well as the GB.
5.2 Suggested Topics for Future Work

Although the results from this work provide some insights into the mechanisms through which Hf, Y, Zr and their co-doping pairs reduce the growth rate of α -Al₂O₃, there remain many aspects left to be explored in order to gain more thorough knowledge about the mechanisms behind the "RE effect. In this thesis, only the co-doping of Hf, Y, and Zr were investigated. As mentioned previously, a synergistic "RE effect" have been illustrated by many co-doped pairs, such as Hf-Zr [15], La-Y [14], and Pt-Dy [13]. However, the mechanism behind the synergy of co-doping has rarely been investigated, and computational studies on this topic are lacking. Therefore, more computational studies should be carried out to look into the mechanism behind the synergy imposed by the known co-doped RE pairs that are not covered in this study. Furthermore, since the concentration of REs varies within the TGO [45], the correlation between the concentration of RE and their impact on the oxide growth requires a systematic investigation. Such a study has been carried out on Y, which revealed that a 87.5% monolayer coverage of Y at the GB plane imposed a significantly greater influence on the DOS compared to a single Y substitutional defect [18]. However, studies on the impact of concentration of other RE species are still missing, so more work will be required to address this topic. In addition, this thesis only covers the thermodynamics aspect behind the RE effect. In practice, the kinetics is also an important factor for clarifying how the REs affect the growth of scale through altering diffusion of ions and vacancies. Currently, the understanding on the relationship between the kinetics and the RE effect is limited. Studies focusing on the diffusion barriers of oxygen and aluminum vacancies in α-Al₂O₃ with the presence of REs have been performed, but only the bulk structure of α -Al₂O₃ was investigated [65], [98]. Therefore, there should be effort dedicated to exploring the influence of REs on the kinetics with a focus on the GB areas of α -Al₂O₃ in the future.

To continue the work of this thesis, the first step can be conducting a study on the impact of REs on the diffusion barriers of oxygen vacancies at the GBs using the same computational models employed in this project. Next, this project can be further expanded to cover more co-doped pairs and doping of REs at different concentrations.

Appendices

GB	Al site	Eseg of Zr (eV)	Eseg of Y (eV)	E _{seg} of Hf (eV)
$\Sigma3(10\overline{1}0)$	1	-0.123	-0.099	-0.027
	2	-0.707	-0.628	-0.707
	3	-0.130	-0.102	-0.027
	4	-0.706	-0.631	-0.706
	5	-0.221	0.093	-0.237
	6	-0.200	-0.246	-0.142
	7	-0.224	0.091	-0.240
	8	-0.198	-0.250	-0.142
	9	-0.215	0.096	-0.232
	10	-0.159	-0.253	-0.141
	11	-0.213	0.101	-0.231
	12	-0.210	-0.262	-0.147
Σ13(10 <u>1</u> 4)	1	-1.832	-1.762	-1.461
	2	-0.225	-0.579	-0.294
	3	-1.670	-1.776	-1.680
	4	-0.332	-1.116	-0.522
	5	-1.345	-1.278	-1.277
	6	-1.075	-1.216	-0.909
	7	-0.626	-1.294	-1.116
	8	-0.599	-1.767	-0.510

Table S1. Segregation energy of RE dopants at different substitutional aluminum sites at Σ 3 GB and Σ 13 GB.

6 References

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