The reactive element effect of ceria particle dispersion on alumina growth: A model based on microstructural observations

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The oxidation kinetics of alumina-forming metals can be affected by adding a small amount of a reactive (normally rare earth) element oxide \( \text{RE}_x \text{O}_y \) and the segregation of the reactive element \( \text{RE} \) ions to the growing alumina grain boundaries (GBs) has been considered as a responsible reason. However, this interpretation remains a controversial issue as to how \( \text{RE} \) ions are produced by \( \text{RE}_x \text{O}_y \) which is thermodynamically and chemically stable in metals. The question is answered by a model that is based on transmission electron microscopy (TEM) investigation of a CeO\(_2\)-dispersed nickel aluminide oxidized in air at 1100 °C. The CeO\(_2\) dispersion is incorporated into the alumina scale by the inward growth of inner \( \alpha\text{-Al}_2\text{O}_3 \) where it partially dissolves producing tetravalent Ce cations which then transform to trivalent cations by trapping electrons. The trivalent cations segregate to the \( \alpha\text{-Al}_2\text{O}_3 \) GBs and diffuse outward along first the GBs and later the twin boundaries (TBs) in the outer \( \gamma\text{-Al}_2\text{O}_3 \) layer, being precipitated as Ce\(_2\text{O}_3\) particles near surface.

High temperature oxidation, a thermally- and chemically-activated reaction process with an expected increase in severity as the temperature increases, is a key mode of environmental degradation of high temperature structural materials. It normally leads to a loss of their service life. The service life can, however, be highly prolonged if the materials have the ability to develop a scale of thermally grown oxide (TGO) with the merits of compactness, slow growth and thermodynamic stability. The \( \alpha\text{-Al}_2\text{O}_3 \) TGO is such a representative oxide, which can offer excellent resistance to oxidation above 1000 °C. Development and study of oxidation-resistant alumina formers at high temperatures has been attracting great interests for decades. Alumina-forming MCrAl system (\( M = \text{Ni, Fe, Co, or their combinations} \) and nickel aluminides are the well-known oxidation-resistant alloys and coatings. Many reports show that these alumina formers can be further improved in the high temperature oxidation performance by adding small amounts of reactive elements such as yttrium, hafnium, cerium, zirconium, and lanthanum\(^{1-39} \).

The phenomenon that the REs additions improve the oxidation resistance of metals was first found in 1937 by Pfeil\(^{40} \) and is popularly referred to as the "reactive element effects (REEs)". The RE additions into alumina formers are conventionally made by alloying\(^{1,4,5,7,8,12,13,15,18,22,23,25-27,34,35,39} \), ion implantation\(^{38,8,11,15,29,31,35} \) and \( \text{RE}_x \text{O}_y \) dispersions\(^{2,3,6,7,10,14,15,17,18,20,24,26,32,33} \). The REEs on alumina formers have been summarized and reviewed successively by some authors\(^{41-46} \).

One typical REE for alumina formers is that the RE addition tends to decrease their oxidation rates. For example, a decrease in the alumina TGO growth rate has been observed in RE-implanted\(^{8,9,29} \) and RE-alloyed\(^{8,12,15,38} \) \( \beta\text{-NiAl} \). This aspect of REE have been interpreted by two popular models. One is a so-called poisoned interface model (PIM)\(^{47} \), which applies well to interpretation of the REE on growth of the cation-diffusion oxide (e.g. chromia\(^{48} \)) scale. In the PIM, RE atoms are proposed to segregate to the scale/metal interface, pinning the climb of misfit dislocations there required for the scale growth. The other is the grain boundary (GB) segregation model. It indicates that the RE ions which incorporate into the growing alumina normally tend to segregate to the oxide GBs, where they exert the REE through either "site blocking" — blocking the fast diffusion paths for \( \text{Al}^{3+} \), or a "swamping-out" mechanism\(^{49} \), in which the isovalent segregants (e.g. \( \text{Y}^{3+} \)) suppress segregation of other divalent and tetravalent cations (e.g. \( \text{Ca}^{2+} \) and \( \text{Si}^{4+} \)). The aliovalent cation segregation in alumina can enhance the

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GB diffusivity of aluminum cations ($D_{GB}^{Al}$) and oxygen anions ($D_{GB}^{O}$) by increasing the number of anion and cation vacancies. More recently, some investigators attributed the REE on the alumina growth to a modification of the electronic structure of alumina with GB donor and acceptor states to the extent that Al ionization at the interface is decreased$^{30,36}$.

The RE segregation model has been supported by many experimental observations of RE segregation at the alumina GBs by means of TEM in a combination of X-ray energy-dispersive spectroscopy (EDS)$^{3,4,6,7,10,12,15,17,32}$. In addition to the GB segregation, RE has been found to occur as $\text{RE}_6\text{O}_7$ particles on the alumina scale surface$^{15,17}$. On its basis, a dynamic segregation theory (DST) has been proposed, in which the RE segregants at the GBs are not static; they can transport outward along the GBs driven by the oxygen potential (i.e., oxygen chemical activity) gradient across a growing alumina scale and their high affinity for oxygen$^{15}$.

Many literatures$^{15,17,20,24,25,26}$ also reported that addition of the $\text{RE}_6\text{O}_7$ dispersions in an alloy plays a similar role as RE in decreasing the oxidation rate of alumina-forming metals. This effectiveness REE of the $\text{RE}_6\text{O}_7$ on the alumina TGO growth is firstly attributed to the dissolution of $\text{RE}_6\text{O}_7$, which is proposed to occur under the oxygen pressure gradient across the metal-oxide-gas system$^{15,24}$, producing RE atoms to segregate to the oxide/metal interface. However, there has been no experimental evidence for such dissolution (or dissociation) and the latter also appears to have no thermodynamic justification, because $\text{RE}_6\text{O}_7$ (more stable than $\text{Al}_2\text{O}_3$) have a very high thermal stability. The oxygen pressure in the metals, which decreases from the dissociation pressure of $\text{Al}_2\text{O}_3$ at the interface to some low values (depending on the oxygen solubility and diffusivity) at some distance from the interface.

**Figure 1.** Cross-sectional SEM morphology of the nickel aluminide for 30 min oxidation at 1100 °C.

**Figure 2.** (a) Cross-sectional TEM overview of the alumina scale formed for 30 min oxidation at 1100 °C; (b, c) HRTEM images and corresponding SAED patterns of the outer and inner layers, respectively.
interface, is normally not low enough to drive the RE$_O$ dispersions to dissociate and release RE atoms which can segregate to the interface. In view of this, the concerned REE exerted by RE$_O$ appears not be explained fully by DST, although it cannot be explained appropriately by PIM. A much more likelihood that the RE$_O$ dispersions

Figure 3. STEM BF image and EDS mappings of the “A”-framed area in Fig. 2(a).

Figure 4. TEM BF and HRTEM images and corresponding FFT diffractions of the Ce-rich particle as circled in the (a) inner $\alpha$-Al$_2$O$_3$ and (b) outer $\gamma$-Al$_2$O$_3$. 
exert the REE is associated with the dissolution of REO_y dispersions upon incorporation into the alumina scales, as described simply in \textsuperscript{3,6}. This raises a question on how the oxide dispersions enter the alumina TGO.

Recently, an interpretation on the effect of the ceria particle dispersion on the growth process of alumina scale on an alumina-forming aluminide was proposed \textsuperscript{32}. It highlights two points. First, the incorporation of the ceria particles into the alumina TGO results from inward growth of the inner part of the alumina in $\alpha$ phase. Second, the ceria particles do not exhibit the REE until they have been incorporated into the alumina scale, where they may dissolve to some extent to produce the cerium ions that can segregate to the alumina GBs and thus suppress the outward diffusion of Al cations along the short-circuit paths for the TGO growth. However, this interpretation is still lack of sufficient evidences. We further characterized the microstructure of the alumina TGO on the ceria-dispersed aluminide and traced cerium either in its elementary or oxide form from the metal to the TGO. There are new observations: (i) no dissolution of original CeO$_2$ particles in the metal during oxidation, (ii) the identification that the TGO scale is composed of the outward growing $\gamma$-Al$_2$O$_3$ and inward growing $\alpha$-Al$_2$O$_3$ and the CeO$_2$ particles in the metal can be swept over by inward growing $\alpha$-Al$_2$O$_3$, (iii) the detection of cerium ions segregated to the GBs of the inner $\alpha$-Al$_2$O$_3$, and (iv) precipitation of novel Ce$_2$O$_3$ particles along the twin boundaries in the outer $\gamma$-Al$_2$O$_3$. On these bases, we propose a model in the present work, which shows a scenario of a dynamic evolution of the ceria particles in the metal during oxidation. The model is helpful for better understanding of not only the REE on the alumina growth on the ceria-dispersed aluminide but also the concerned REE of the REO_y dispersions in other alumina formers. In addition, it is useful for getting insight into the alumina growth on the metals alloyed with REs, which can be preferentially oxidized into REO_y particles in the metals because the alloyed amounts of REs normally exceed their low solubility limits \textsuperscript{1,3,7,23,25,26,51}.

Results

Ceria dispersion in aluminide before oxidation. The CeO$_2$ particles used, which have a typical CaF$_2$-type crystal structure (space group: Fm3m) with the lattice spacing of $d_{(200)} = 2.7$ Å and $d_{(110)} = 3.1$ Å on a basis of HRTEM investigation and FFT diffraction (see supplementary material 1), are in a size range of 15–30 nm. The particles were co-deposited with Ni, forming a ~35 μm-thick Ni-based composite film, in which the CeO$_2$ particles with the content of 3.5 wt.% are in general uniformly distributed, as viewed previously by using SEM \textsuperscript{37}. After aluminizing, the Ni-CeO$_2$ composite film was converted into a ~43 μm-thick alumina-forming $\delta$-Ni$_2$Al$_3$ \textsuperscript{28}. The CeO$_2$ particles are uniformly dispersed throughout the thickness of the aluminide on a basis of the electron probe microanalysis (EPMA) \textsuperscript{32}. 

![Figure 5. (a) STEM BF image of the aluminide for 30 min oxidation at 1100 °C; (b) an EDS spectrum of an arrowed spot between two close CeO$_2$ particles at the aluminide grain boundary.](image-url)
Ceria dispersion in aluminide and its evolution in alumina scale after oxidation. Figure 1 shows the cross-sectioned aluminide for 30 min oxidation at 1100 °C. The aluminide forms an alumina scale. The inward growth of the alumina, as suggested by the non-planar interface, leads the metal to be either partially (as indicated by 1) or fully (as indicated by 2) enclosed by the oxide. The alumina scale viewed under TEM as seen in Fig. 2(a) displays a double-layered structure. The outer needle-like platelets, which exhibit a high density of lamellar nanotwins with coherent boundaries when tilted to the [110] zone axis, are γ-Al2O3 as identified by HRTEM image and the corresponding SAED pattern in Fig. 2(b). Similar lamellar-twined structure has been observed in deformed fcc γ-grains of a single-phased austenitic steels52 and in Au nanocrystal-seeded Si and Ge nanowires53. This suggests that the growth of γ-Al2O3 platelets is controlled by outward diffusion of aluminum cations along the twin boundaries (TBs) in the [112] orientation. The oxide of the inner layer is α-Al2O3 as unveiled in Fig. 2(c). Between the γ-Al2O3 layer and the α-Al2O3 layer appears a γ- and α-mixed area as seen in Fig. 3. The γ- and α-Al2O3 grains are the smallest in the alumina scale and Ce-rich oxide nanoparticles (see the Ce X-ray mapping) can be sometimes observed. Similar Ce-rich oxide particles occur in the inner α-Al2O3 layer. They are CeO2 as identified in Fig. 4(a), displaying the shape and CaF2-type crystal structure similar to the original CeO2. The outer highly-twined γ-Al2O3 layer is also doped cerium-rich oxide particles, which as circled in the TEM BF image in Fig. 4(b) are seemingly elongated along the twinning orientation, with respect to the particle shape of the original CeO2. The 3.3 Å lattice spacing of both (222) and (222) planes and (Mn0.5Fe0.5)2O3 (space group:Ia3)-similar structure (see HRTEM image and FFT diffraction in Fig. 4(b)) ascertain the particles as new Ce2O3 rather than the original CeO2.

The aluminide has been degraded from δ-Ni2Al3 into β-NiAl due to the aluminum consumption by oxidation, as shown in the inserted SAED pattern in Fig. 5(a). The aluminide contains the nano-dispersions, which have been characterized to be original CeO2. No Ce was acquired around the CeO2 particles by the EDS detector with an incident beam spot size of 1.5 nm. Figure 5(b) shows an EDS result of a specific spot between two close CeO2 particles at the GBs, showing no acquisition of Ce atoms there.

The particles of the CeO2, as inert oxide in the metal, actually act as the immobile markers for the direction of the alumina growth. They occur in the fine-grained γ- and α-mixed area (Fig. 3), suggesting that the area corresponds to the surface zone of the original aluminide. The CeO2 particles in the α-Al2O3 layer arises from the inward growth of the oxide. To further clarify this, the alumina scale formed only for 5 min has been observed. A CeO2 particle which has been swept over by inward growing alumina is clearly seen in Fig. 5. In contrast, the CeO2 particles in the outer γ-Al2O3 layer should be newly precipitated. They can form, suggesting that there exist sufficient Ce cations which can be migrated from the inner α-Al2O3 layer. The larger-sized ions as the Ce cations here doped in the alumina TGOs are easily segregated to and then migrate outward along the GBs. As shown in Fig. 7, the Ce segregation at the α-Al2O3 GBs can be clearly seen by using HADDF-STEM. The HADDF image presents the Ce segregated GBs presents as the lines with a light contrast similar to that of the CeO2 particles (as arrowed in the BF image), because Ce has a higher atomic number than Al. The EDS analysis indicates the GBs containing a mean content of ~0.4 at.% Ce. The Ce at the oxide GBs unlikely originates from its atoms in the aluminide, because the latter have not been acquired in the metal (Fig. 5). It convincingly arises from the segregation of cerium cations, produced by partial dissolution of the CeO2 particles incorporated in the α-Al2O3 layer.
dissolved Ce cations also experience the charge transformation from tetravalent to trivalent in the alumina scale, on a basis of the precipitation of Ce₂O₃ rather than original CeO₂.

In sum, the TEM work presents several observations: (i) the aluminide during oxidation forms an alumina scale being composed of an inner α-Al₂O₃ layer and an outer γ-Al₂O₃ layer; (ii) the CeO₂ dispersions are incorporated into the α-Al₂O₃ layer as the result of its inward growth; (iii) Ce ions segregates to the alumina GBs, and (iv) novel Ce₂O₃ particles are precipitated in the near surface of the γ-Al₂O₃ platelets.

Discussion

The precipitation of new Ce₂O₃ in the outer γ-Al₂O₃ platelets demonstrates a series of evolution of the original CeO₂ particles after they have been incorporated into the growing alumina, including their partial dissolution (since no evidence for such dissolution could be acquired in the aluminide (Fig. 5)), tetravalent-to-trivalent charge transformation and outward migration of the dissolved Ce cations. To unveil the dynamic evolution of the CeO₂ dispersion in the aluminide, a model is schematically illustrated in Fig. 8 based on the TEM observations and interpreted below. The highly-twinned γ-Al₂O₃ grains grow outward quickly on the aluminide at the onset of oxidation, and

**Figure 7.** (a) Magnified STEM BF image of the “B”-framed area in Fig. 2(a); (b) corresponding HADDF image showing the segregation of the element with a lighter contrast at the alumina GBs; (c) EDS analysis identifying the segregated element as Ce.
α-Al2O3 nucleates at the γ/aluminide interface soon after if not simultaneously (Step I). The γ-Al2O3 grains grow into needle-like platelets in the direction preferentially aligned with the [112] twinning orientation; in the meantime, the initially-formed α-Al2O3 grains gradually spread laterally and inward, sweeping over the CeO2 particles in Figure 8. Schematic steps for the evolution of the CeO2 dispersion in the aluminide from being incorporated into inner Al2O3 scale to being precipitated as Ce2O3 in the outer Al2O3 scale.
the aluminate (Step II). \(\alpha\)-\(\text{Al}_2\text{O}_3\) exhibits an n-type behavior with the principal defect of oxygen vacancy \(V^+_O\) or free electron \(e^-'\) (Vink-Kröger’s notation). The \(\text{CeO}_2\) partially dissolves into the \(\alpha\)-\(\text{Al}_2\text{O}_3\) lattice through the reaction

\[
\text{CeO}_2 = \text{Ce}^{2+}_{\text{Al}} + O^+_O + e^- + \frac{1}{2}O_2
\]

where \(\text{Ce}^{2+}_{\text{Al}}\) represents the quaternary-charged \(\text{Ce}\) cations and \(O^+_O\) lattice oxygen. The \(\text{Ce}^{2+}_{\text{Al}}\), in the n-type oxide lattice can then trap an electron and transform to trivalent-charged cation \(\text{Ce}^3_{\text{Al}}\) through the reaction

\[
\text{Ce}^{2+}_{\text{Al}} + e^- = \text{Ce}^3_{\text{Al}}
\]

In combination of Eqs (1) and (2), the \(\text{CeO}_2\) particle dissolution in the alumina lattice can be expressed by

\[
\text{CeO}_2 = \text{Ce}^3_{\text{Al}} + O^+_O + \frac{1}{2}O_2
\]

The reduction of \(\text{CeO}_2\) to \(\text{Ce}_2\text{O}_3\) has been reported in the high temperature sintering of fine \(\text{CeO}_2\) particles.\(^{5,55}\). The \(\text{Ce}^{3+}\) (1.02 Å with the coordination number of 6) is larger than \(\text{Ce}^{2+}\) (0.87 Å with the same coordination number) in the ion size. Larger \(\text{Ce}^{3+}\) in the \(\alpha\)-\(\text{Al}_2\text{O}_3\) grains yields higher lattice misfit microstrain, which drives the trivalent cations to segregate to the \(\alpha\)-\(\text{Al}_2\text{O}_3\) GBs (Step III). Then, the segregated cations migrate from the \(\alpha\)-\(\text{Al}_2\text{O}_3\) layer to the \(\gamma\)-\(\text{Al}_2\text{O}_3\) layer along the GBs in the \(\alpha\)-\(\text{Al}_2\text{O}_3\) and the lamellar TBs in the \(\gamma\)-\(\text{Al}_2\text{O}_3\) platelets, under the driving force of the oxygen potential gradient across the oxide.\(^{5,17}\) \(\gamma\)-\(\text{Al}_2\text{O}_3\) is a p-type oxide with the principal defect of Al vacancy \(V^+_\text{Al}\) and electron hole \(h^+\). The TBs, although they are coherent, contain steps and kinks which can serve as the sinks for vacancy (as having been reported in\(^{57,58}\) like \(V^+_\text{Al}\) here). Steps and kinks in the lamellar TBs in the \(\gamma\)-\(\text{Al}_2\text{O}_3\) can trap \(V^+_\text{Al}\). Once \(\text{Ce}^{3+}_{\text{Al}}\) and \(V^+_\text{Al}\) are both oversaturated there, \(\text{Ce}_2\text{O}_3\) is precipitated (Step IV) through the reaction below:

\[
2\text{Ce}^{3+}_{\text{Al}} + 3O^+_O + 2V^+_\text{Al} + 3V_{\text{GB}}^+ = \text{Ce}_2\text{O}_3
\]

The \(\text{Ce}^{3+}_{\text{Al}}\) cations prefer to diffuse outward along the TBs, causing the \(\text{Ce}_2\text{O}_3\) to be precipitated and elongated in the direction growth of the \(\gamma\)-\(\text{Al}_2\text{O}_3\) platelets (Fig. 4(b)). The precipitates are easily observed in the \(\gamma\)-\(\text{Al}_2\text{O}_3\) layer near the surface, because of higher \(V^+_O\) there which promotes the precipitation reaction.

The oxidation kinetics of alumina formers during 750–1200°C is highly correlated with the diffusion of Al cations and O anions along the alumina GBs.\(^{50}\) A decrease of \(D^O_{\text{Al}}\) by the RE segregations to alumina GBs has been proposed to be the reason why the RE- and REO-doped alumina formers have a lower oxidation rate.\(^{4,6,7,10,12,15,17,32}\) As illustrated in Fig. 8, \(D^O_{\text{Al}}\) in the alumina layer here should be decreased when the Ce segregants outward migrate along the GBs in \(\alpha\)-\(\text{Al}_2\text{O}_3\) layer and the TBs in the \(\gamma\)-\(\text{Al}_2\text{O}_3\) layer.

The model in Fig. 8 strongly suggests that the Ce segregants occur only when the \(\text{CeO}_2\) dispersoids in the aluminate have been swept over by the inward moving alumina/metal interface. In other word, the REE on the alumina growth for the \(\text{CeO}_2\) dispersion in the aluminate is intrinsically pertinent to the incorporation of the oxide particles into the alumina scale by its inward growth. This may be generalized to the REE of the other \(\gamma\)-\(\text{Al}_2\text{O}_3\) on the RE amounts and solubilities in metals, metal compositions and microstructures, alloying and oxidation temperatures.\(^{25,38,51}\) The particles have not been highlighted previously, plausibly because they are sometimes as small in-situ nano-sized particles. Because of a very low solubility limit in metals (e.g., only 0.01 wt % for Y in the FeCrAl alloys), a RE overalloying is hard to avoid. Thus, RE-rich precipitates occur in metals.\(^{1–3,7,25,26,51}\) They can be as nano-sized particles. Because of a very low solubility limit in metals (e.g., only 0.01 wt % for Y in the FeCrAl alloys), a RE overalloying is hard to avoid. Thus, RE-rich precipitates occur in metals.\(^{1–3,7,25,26,51}\) They can be as nano-sized particles.

Method

The \(\text{CeO}_2\) particles with a purity of 99.5%, a commercial product by Alfa Aesar company, were introduced to a nickel aluminate by using a two-step method.\(^{28,37}\) First, the pure Ni samples with dimensions of 15×10×2 mm, after being abraded to a final 800 grit SiC paper, were electrodeposited with a Ni-\(\text{CeO}_2\) composite film from the \(\text{CeO}_2\)-loaded nickel sulfate bath (150 g/l \(\text{NiSO}_4\cdot6\text{H}_2\text{O}\), 120 g/l \(\text{C}_6\text{H}_5\text{Na}_2\text{O}_7\cdot2\text{H}_2\text{O}\), 12 g/l \(\text{NaCl}\), 35 g/l \(\text{H}_2\text{BO}_3\)).
A mechanical agitation was maintained to mitigate the particle agglomeration and sedimentation during electrodeposition, as illustrated by the setup. Second, the samples were aluminized at 620 °C for 5 h using a halide-activated pack-cementation in a powder mixture of Al (particle size: ~75 μm) + 55 wt.% Al₂O₃ (~75 μm) + 5 wt.% NH₄Cl in an Ar (purity: 99.99%) atmosphere. The characteristics of inward growth of the aluminate at the cementation temperature caused the CeO₂ in the electrodeposited film to be trapped, forming a ceria-dispersed nickel aluminate coating on the sample surface. After being ultrasonically cleaned in acetone, the aluminized samples were ready for oxidation.

The samples were not placed into a muffle furnace for oxidation until it was heated up to 1100 °C. The ceria-dispersed nickel aluminate after oxidation were cross-sectioned for the scanning electron microscopy (SEM) investigations, and then ion sliced into thin foils by using techniques detailed elsewhere, with the transparent electrodeposition, as illustrated by the setup. Second, the samples were aluminized at 620 °C for 5 h using a Fe-based yttria-dispersed alloys, J. Electrochem Soc. 131, 923–931 (1984).

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