

Water Vapor-Enhanced Diffusion in Alumina

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Experimental results indicate effective faster diffusion of oxygen in polycrystalline alumina when exposed to water vapor at high temperatures. α -Al₂O₃ containing Ni metal particles was exposed to dry air or humid environments at 1300°C for up to 20 h. Oxidation of Ni in α -Al₂O₃ to form NiAl₂O₄ was used to determine oxygen diffusion depth from the surface. The apparent kinetic rate constant for oxygen diffusion in the presence of water vapor was 79% higher compared with that in a dry atmosphere at 1300°C (1.4×10^{-13} m²/s for 0.2 atm $P_{\text{H}_2\text{O}}$ versus 7.9×10^{-14} m²/s for dry air). (OH)[−] ions are smaller and more polarizable than O^{2−}, which would be expected to lead to faster diffusion. This effect may impact sintering, creep, corrosion, oxidation, and the performance of thermal barrier coatings (TBC).

I. Introduction

THE controlling mechanism in many ceramic processes is grain-boundary diffusion, which in alumina is greatly diminished in the presence of certain cations, e.g., reducing creep rates¹ or slowing thermal barrier coatings (TBC) bond coat oxidation.² One might wonder if there are anion impurities or the equivalent which actually enhance grain-boundary diffusion; (OH)[−], which can be up to 20% smaller than O^{2−},³ comes naturally to mind. Oxide surfaces easily adsorb water, forming superficial (OH)[−] and grain boundaries are also expected to do so. Numerous reports exist of accelerated reaction kinetics, more rapid coarsening/grain growth, and faster sintering/densification for ceramic oxides in the presence of high-temperature water vapor.^{4–8}

Herein, we offer an experiment to test if water vapor effects grain-boundary diffusion of oxygen in a technologically relevant ceramic, viz. α -Al₂O₃. Alumina, used for many high-temperature structural applications, is also produced as a thermally grown oxide (TGO) upon metallic bond coats for TBC on Ni-based turbine blades. Most experiments on α -Al₂O₃ show oxygen is the slower diffusing ion compared with aluminum.⁹ In this experiment, Ni-particles are embedded in a dense α -Al₂O₃ matrix^{10–12} and subsequently exposed to an oxidizing environment. The oxidation of Ni via formation of NiAl₂O₄ is measured in dry and humid oxidizing environments at elevated temperatures, and correlated with oxygen diffusion values.

II. Experimental Procedure

High-purity α -alumina powder (Baikowski Inter. Corp., Charlotte, NC) and nickel oxide powder (Alfa Aesar, Ward Hill, MA) were milled, dried, sieved, then heated at 700°C

for 5 h in 4% H₂-Ar at a flow rate of 50 cm³/min to reduce NiO to 0.5 vol% elemental Ni. Cylindrical specimens were cold isostatic pressed at 380 MPa and sintered at 1500°C for 3 h in a reducing environment of 4% H₂-Ar. Density was measured by Archimedes method. Sintered samples were polished to a 0.1 μ m finish. Oxidation at 1300°C was conducted for 5, 10, 15, or 20 h. Ultrapure zero grade dry air was used for dry oxidation, whereas bubbling dry air through a water bath created water vapor, with a flow rate for both of 50 cm³/min. By adjusting the temperature of the water bath, the water vapor partial pressure was varied from 0.2 atm $P_{\text{H}_2\text{O}}$ to 0.83 atm $P_{\text{H}_2\text{O}}$.

X-ray diffraction (XRD) analysis with a SmartLab X-ray Diffractometer (Rigaku, Tokyo, Japan) used CuK α radiation and scans steps of 0.05° from 20° to 90°. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was performed on a Magellan 400 (FEI, Eindhoven, The Netherlands). Grain size was measured using ImageJ (NIH, Bethesda, MD). Backscatter electron imaging was used to differentiate between nickel aluminate spinel (NiAl₂O₄) and unreacted Ni and to measure the oxidation depth x . To obtain an average depth of oxidation for each sample, at least 1 mm parallel to the surface was imaged and measured in increments of 100 μ m along the surface with a depth of 150 μ m.

III. Results and Discussion

While α -Al₂O₃ and NiO are the only phases in the initial powder, Ni is formed and NiO peaks disappear after reduction (Fig. 1). The sintered compacts retain Ni metal, but subsequent oxidation forms NiAl₂O₄ [Fig. 1(d)] in regions near the surface probed by XRD. Interplanar d-spacings for α -Al₂O₃ do not change, indicating limited solid solubility of Ni in bulk alumina.¹³

The density of the sintered α -Al₂O₃/0.5 vol% Ni was 97%–98% theoretical density (4.07 g/cm³). The average alumina grain size is 1.2 ± 0.5 μ m. Before oxidation, there is a reasonably homogeneous distribution of submicrometer Ni-particles throughout the α -Al₂O₃, typically located at the grain boundaries, [Figs. 2(a) and (b)].

Figure 3 compares oxidation depths in dry and humid environments. The difference in oxygen chemical potential between the surface and the interior drives oxygen inward oxidizing the Ni, producing NiAl₂O₄. The depth of Ni-spinel formation measures the oxygen grain-boundary diffusion. When water vapor is present, there is a significant increase in oxidation depth for Ni-spinel formation for the same time and temperature (Fig. 3). For example, after 5 h at 1300°C, the oxidation depth is 43% greater for humid oxidation (0.2 atm $P_{\text{H}_2\text{O}}$) versus dry air.

A depleted zone between the Ni and NiAl₂O₄ zones [Fig. 3(a)] was often observed and these regions had a lower overall Ni concentration determined by EDS, whereas oxidized regions with spinel formation had higher concentrations of Ni than in the bulk. The depletion zone is irregular and more obvious in dry air samples. The presence of this

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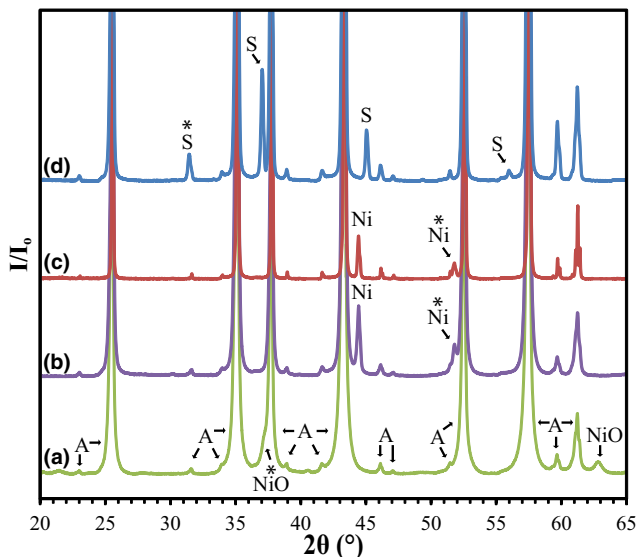


Fig. 1. XRD pattern of (a) milled $\text{Al}_2\text{O}_3 + \text{NiO}$ powder before reduction, (b) $\text{Al}_2\text{O}_3 + 0.5 \text{ vol\% Ni}$ powder after reduction, (c) sintered $\text{Al}_2\text{O}_3 + 0.5 \text{ vol\% Ni}$ sample, and (d) a sample exposed to dry oxidation for 20 h at 1573 K. (A = Al_2O_3 , S = NiAl_2O_4 spinel and * signifies an overlap with Al_2O_3).

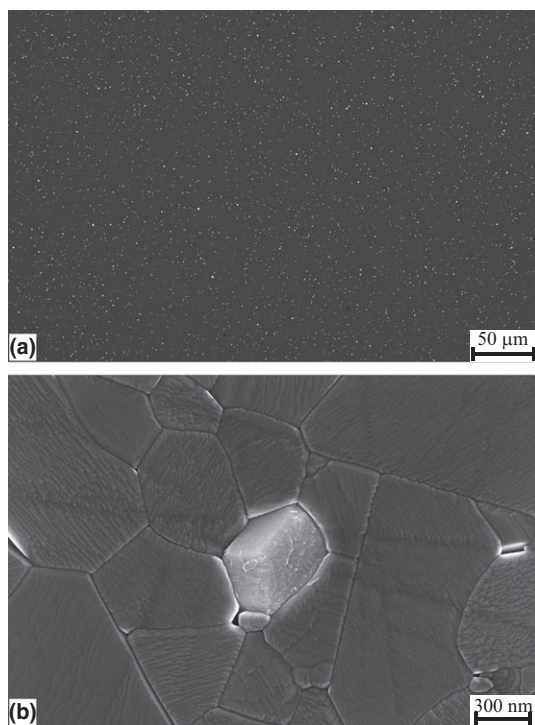


Fig. 2. SEM (a) backscattered electron image at low magnification showing random distribution of Ni-particles and (b) secondary electron image showing a Ni particle in Al_2O_3 .

depleted zone implies faster outward diffusion of Ni than inward diffusion of oxygen, as also documented by researchers studying Ni diffusion through TGO alumina in TBCs.¹⁴

The square of the average oxidation depth is plotted against annealing time in Fig. 4. The depth of oxidation is an averaged value between the end depth for formation of NiAl_2O_4 particles and the beginning depth for residual unoxidized Ni-particles. A parabolic rate law is used to model the diffusion-controlled reaction processes to form spinel to determine oxidation kinetics. The kinetic rate constants are calculated by determining the slope of each line. The rate

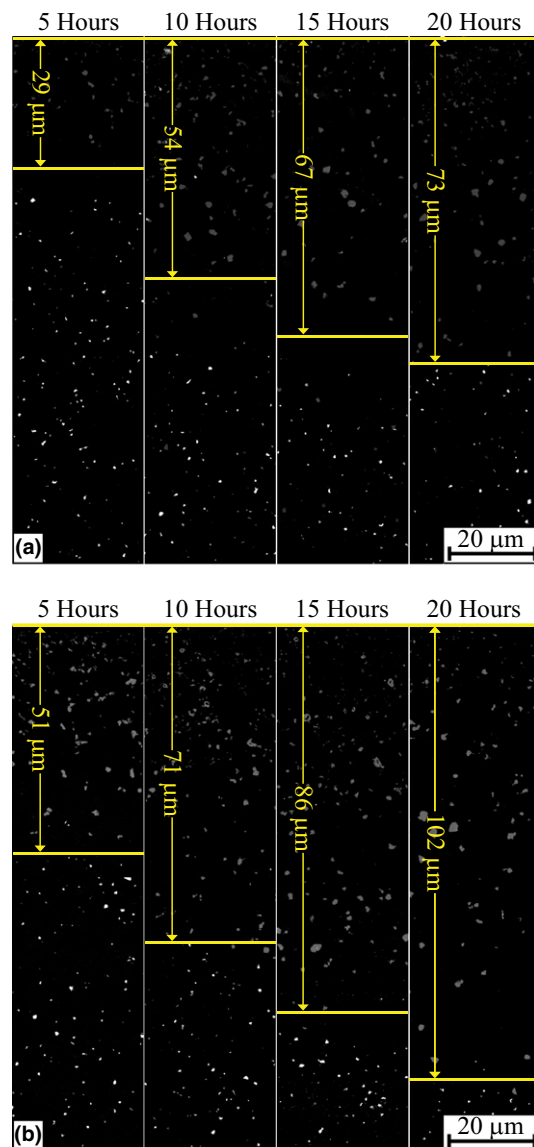


Fig. 3. Average depth of oxidation x from top free surface for the time lengths of 5, 10, 15, and 20 h at 1300°C under (a) dry and (b) humid (0.2 atm $P_{\text{H}_2\text{O}}$) atmospheres.

constant for dry oxidation at 1300°C was $k_{\text{dry}} = 7.93 \times 10^{-14} \text{ m}^2/\text{s}$, within 8% of the value reported previously at that temperature for oxidation of Ni in alumina forming spinel in air.¹² The rate constant for each level of humidity was $k_{0.2 \text{ atm } P_{\text{H}_2\text{O}}} = 1.42 \times 10^{-13} \text{ m}^2/\text{s}$ and $k_{0.83 \text{ atm } P_{\text{H}_2\text{O}}} = 1.46 \times 10^{-13} \text{ m}^2/\text{s}$. The negligible difference in oxidation depth for 0.2 atm $P_{\text{H}_2\text{O}}$ and 0.83 atm $P_{\text{H}_2\text{O}}$ suggests that 0.2 atm $P_{\text{H}_2\text{O}}$ is close to the saturation point for incorporation of hydroxyl ions. Such saturation has also been observed for TBC lifetime reduction in humid environments.¹⁴ The rate constant at 1300°C for humid oxidation is 79% higher than dry oxidation. The presence of water vapor significantly accelerates inward oxygen diffusion and subsequent oxidation of the Ni-particles forming Ni-spinel.

The enhanced oxygen mobility likely can be attributed to the smaller size and lower valence of the hydroxyl ion; perhaps slightly counterintuitive is that the size of an O^{2-} anion in an oxide lattice shrinks by ~20% when a proton is within it [forming $(\text{OH})^-$]. The repulsions in the p -electron cloud of the oxygen ion are decreased due to the embedded proton.¹⁵ In addition, the hydroxyl ion can be more easily polarized,¹⁶ resulting in an ion that could more easily squeeze through interstitial sites. A simplistic, albeit straightforward, consequence

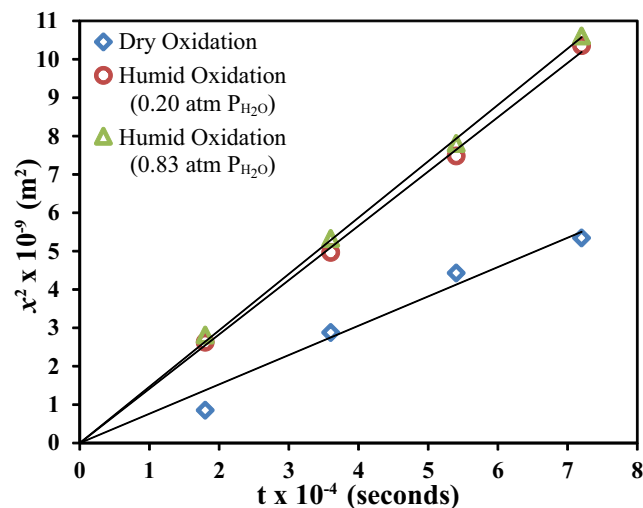


Fig. 4. Square of the average oxidation depth versus annealing time for dry oxidation and humid oxidation at 0.2 atm $P_{\text{H}_2\text{O}}$ and 0.83 atm $P_{\text{H}_2\text{O}}$ environments at 1573 K. (Trend line fitted using least squares regression.)

would be that oxygen ions with associated protons (forming hydroxyl ions) can diffuse more readily due to their smaller size, decreased charge, and flexible shape. Surface diffusion of hydroxyl ions is known to be significantly faster than oxygen ion diffusion for alumina,¹⁷ so it should come as no surprise that the same would be true for hydroxyl ions diffusing along grain boundaries. $(\text{OH})^-$ is not likely to enter the bulk alumina lattice due to valence imbalance, whereas grain boundaries are more accommodating.

Protons are strongly bonded within oxygen anions in alumina,¹⁸ so coupled diffusion as hydroxide is reasonable. Proton hopping from oxygen to oxygen ion occurs and quantum tunneling is also known.¹⁹ This would increase oxygen transport via proton-assisted accelerated diffusion of one mobile oxygen ion and then another. Each time a proton hops and forms a bond within an oxygen ion, the anion becomes smaller, diffusing more easily. Enhanced diffusion of hydroxide ions has also been proposed as a reason for faster oxidation of metals that form oxide scales in the presence of water vapor at high temperatures.²⁰ During the oxidation of metals, researchers have suggested that water vapor can easily be incorporated into oxide films as $(\text{OH})^-$ with faster diffusion via proton hopping and an increase in cation vacancies.²¹

There are several caveats to this simple interpretation. Eutectic liquid films formed by impurities can enhance diffusion at grain boundaries. It is conceivable that $(\text{OH})^-$ could produce thin liquid films at grain boundaries by the interaction with impurities already present. It is also known that high-temperature water vapor may remove diffusion-inhibiting anion impurities (such as Cl^-)²² from grain boundaries. The impurity anion concentration is not known. $(\text{OH})^-$ additionally provides a charge compensating mechanism for the presence of Ni^{2+} replacing Al^{3+} in the grain boundaries as nickel diffuses outward. Charge compensation will affect diffusion values for nickel, the focus of a future study.

This result of accelerated diffusion in the presence of water vapor at high temperatures has significance for alumina films and coatings (especially TBC), as this predicts enhanced penetration of oxygen under such conditions. This effect may also be related to the enhancement of creep rates in alumina in the presence of water vapor.^{23,24} More extensive studies are in progress, including with a range of temperatures to determine activation energies, a range of grain sizes, and the deuterium effect.

IV. Conclusions

The incorporation of hydroxyl groups from water vapor at high temperatures appears to enhance grain-boundary oxygen diffusion in aluminum oxide, as evidenced by oxidation of marker Ni metal particles in $\alpha\text{-Al}_2\text{O}_3$ to form NiAl_2O_4 . This result certainly anticipates that other diffusional phenomena relating to $(\text{OH})^-$ incorporation, such as sintering, creep, and corrosion, will be affected.

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References

- J. Cho, C. M. Wang, H. M. Chan, J. M. Rickman, and M. P. Harmer, "Role of Segregating Dopants on the Improved Creep Resistance of Aluminum Oxide," *Acta Mater.*, **47** [15–16] 4197–207 (1999).
- J. A. Nychka and D. R. Clarke, "Quantification of Aluminum Outward Diffusion during Oxidation of FeCrAl Alloys," *Oxid. Met.*, **63** [5–6] 325–52 (2005).
- R. D. Shannon, "Revised Effective Ionic-Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Crystallogr. A*, **32** [Sep1] 751–67 (1976).
- P. J. Anderson and P. L. Morgan, "Effects of Water Vapour on Sintering of MgO ," *T. Faraday Soc.*, **60**[4975] 930–7 (1964).
- R. O. Petersen and I. B. Cutler, "Effects of Water Vapor on Initial Sintering of Calcia," *J. Am. Ceram. Soc.*, **51**[1] 21–2 (1968).
- R. B. Bagwell and G. L. Messing, "Effect of Seeding and Water Vapor on the Nucleation and Growth of $\alpha\text{-Al}_2\text{O}_3$ from $\gamma\text{-Al}_2\text{O}_3$," *J. Am. Ceram. Soc.*, **82** [4] 825–32 (1999).
- T. Kozawa, K. Yanagisawa, and Y. Suzuki, "Water Vapor-Assisted Solid-State Reaction for the Synthesis of Nanocrystalline BaZrO_3 Powder," *J. Ceram. Soc. Jpn.*, **121** [1411] 308–12 (2013).
- J. Barbier Jr. and D. Duprez, "Steam Effects in 3-Way Catalysis," *Appl. Catal. B*, **4** [2–3] 105–40 (1994).
- A. H. Heuer, "Oxygen and Aluminum Diffusion in $\alpha\text{-Al}_2\text{O}_3$: How Much Do We Really Understand?" *J. Eur. Ceram. Soc.*, **28** [7] 1495–507 (2008).
- M. Nanko, N. D. Thuy, K. Matsumaru, and K. Ishizaki, "High Temperature Oxidation of Al_2O_3 -Based Composites with Ni Particle Dispersion," *J. Ceram. Proc. Res.*, **3** [3] 132–5 (2002).
- T. C. Wang, R. Z. Chen, and W. H. Tuan, "Oxidation Resistance of Ni-Toughened Al_2O_3 ," *J. Eur. Ceram. Soc.*, **23** [6] 927–34 (2003).
- H. K. Cheng, S. J. Dillon, H. S. Caram, J. M. Rickman, H. M. Chan, and M. P. Harmer, "The Effect of Yttrium on Oxygen Grain-Boundary Transport in Polycrystalline Alumina Measured Using Ni Marker Particles," *J. Am. Ceram. Soc.*, **91** [6] 2002–8 (2008).
- F. A. Elrefaie and W. W. Smeltzer, "Phase-Equilibria in the Subsolidus Region of the $\text{NiO-}\alpha\text{-Al}_2\text{O}_3$ System Between 1000 and 1920°C," *Oxid. Met.*, **15** [56] 495–500 (1981).
- J. A. Haynes, K. A. Unocic, and B. A. Pint, "Effect of Water Vapor on the 1100°C Oxidation Behavior of Plasma-Sprayed TBCs with HVOF NiCo-CrAlX Bond Coatings," *Surf. Coat. Technol.*, **215** [0] 39–45 (2013).
- T. Norby, "Proton Conduction in Oxides," *Solid State Ionics*, **40-1**, 857–62 (1990).
- R. D. Shannon and R. X. Fischer, "Empirical Electronic Polarizabilities in Oxides, Hydroxides, Oxyfluorides, and Oxychlorides," *Phys. Rev. B*, **73**[23] 235111 (2006).
- M. Pijolat, M. Dauzat, and M. Soustelle, "Influence of Water-Vapor and Additives on the Surface-Area Stability of $\gamma\text{-Al}_2\text{O}_3$," *Solid State Ionics*, **50** [1–2] 31–9 (1992).
- A. K. Kronenberg, J. Castaing, T. E. Mitchell, and S. H. Kirby, "Hydrogen Defects in $\alpha\text{-Al}_2\text{O}_3$ and Water Weakening of Sapphire and Alumina Ceramics Between 600 and 1000°C -I. Infrared Characterization of Defects," *Acta Mater.*, **48** [7] 1481–94 (2000).
- T. Norby and Y. Larring, "Concentration and Transport of Protons in Oxides," *Curr. Opin. Solid State Mater.*, **2** [5] 593–9 (1997).
- S. Basu, N. Obando, A. Gowdy, I. Karaman, and M. Radovic, "Long-Term Oxidation of Ti_2AlC in Air and Water Vapor at 1000–1300°C Temperature Range," *J. Electrochem. Soc.*, **159** [5] S9–S9 (2012).
- S. R. J. Saunders, M. Monteiro, and F. Rizzo, "The Oxidation Behaviour of Metals and Alloys at High Temperatures in Atmospheres Containing Water Vapour: A Review," *Prog. Mater. Sci.*, **53** [5] 775–837 (2008).
- S. Balcon, S. Mary, C. Kappenstein, and E. Gengembre, "Monopropellant Decomposition Catalysts II. Sintering Studies on $\text{Ir/Al}_2\text{O}_3$ Catalysts, Influence of Chloride Anions," *Appl. Catal. A*, **196** [2] 179–90 (2000).
- J. Castaing, A. K. Kronenberg, S. H. Kirby, and T. E. Mitchell, "Hydrogen Defects in $\alpha\text{-Al}_2\text{O}_3$ and Water Weakening of Sapphire and Alumina Ceramics Between 600 and 1000°C -II. Mechanical Properties," *Acta Mater.*, **48** [7] 1495–504 (2000).
- C. J. Armani, M. B. Ruggles-Wrenn, G. E. Fair, and R. S. Hay, "Creep of Nextel (TM) 610 Fiber at 1100°C in Air and in Steam," *Int. J. Appl. Ceram. Technol.*, **10** [2] 276–84 (2013).