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THE OXIDATION OF AlN IN DRY AND WET OXYGEN

Elizabeth Opila
Cleveland State University
Cleveland, OH 44115

Nathan Jacobson
NASA Lewis Research Center
Cleveland, OH 44135

Donald Humphrey
NYMA, Inc.
Brookpark, OH 44142

Tetsuo Yoshio
Okayama University
Okayama, JAPAN

Kohei Oda
Yonago National College of Technology
Yonago-shi, JAPAN

The oxidation kinetics of AlN containing 3.5 wt% Y_2O_3 were studied by thermogravimetric analysis in dry oxygen and 10% H_2O /balance oxygen at temperatures between 1000 and 1200°C for times between 48 and 100 h. The oxidation kinetics for AlN in dry oxygen were parabolic and of approximately the same magnitude and temperature dependence as other alumina forming materials. In this case, diffusion of oxygen and/or aluminum through the alumina scale is the rate limiting mechanism. The oxidation kinetics for AlN in wet oxygen were nearly linear and much more rapid than rates observed in dry oxygen. Numerous micropores were observed in the alumina formed on AlN in wet oxygen. These pores provide a fast path for oxygen transport. The linear kinetics observed in this case suggest that the interface reaction rate of AlN with wet oxygen is the oxidation rate limiting step.

INTRODUCTION

AlN has been proposed for use as a high temperature structural material due to its good thermal properties, including good thermal conductivity, low thermal expansion, and good thermal shock resistance. AlN forms alumina scales in high temperature oxidizing environments. If the rate of alumina formation is low, as it is for other alumina forming materials, AlN would be an ideal candidate for high temperature structural applications. However, the oxidation rate of AlN is often reported to be higher than that of other alumina forming materials. In this paper the oxidation kinetics of AlN were determined in both dry and wet oxygen and compared to the oxidation kinetics of NiAl. The possible rate limiting mechanisms for oxidation of AlN in both environments are discussed.

The literature on the oxidation of AlN has many contradictory results. Only those studies conducted with dense AlN are reviewed here. Parabolic oxidation rates were

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N.S. Jacobson	5160	NASA LeRC	(216) 433-5498	106-1	110
D.L. Humphrey	5160	C	(216) 433-5521	106-1	108
T. Yoshio		O			
K. Oda		O			

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RESULTS AND DISCUSSION

Dry Oxygen

The weight change kinetics for AlN oxidation in dry oxygen is shown in Figure 1. It can be seen that the kinetics follow a parabolic rate law (with the exception of one experiment at 1000°C). The parabolic rate constants calculated from these results are shown in Figure 2 and compared to those for NiAl_{0.25} (wt. fraction) (8). The magnitude of the rate constants are within an order of magnitude of those determined for alumina formation on NiAl. In addition, the activation energy for oxidation from this study for AlN, 322 ± 113 kJ/mol (90% confidence), is statistically the same as that for NiAl, 293 kJ/mol. Both of these results indicate that the alumina formation rate limiting mechanism is the same for both materials. While there remains some discussion, it is generally believed that at long times the oxidation rate of NiAl is controlled by outward transport of aluminum and inward transport of oxygen along short-circuit paths such as grain boundaries (9).

Wet Oxygen

The weight change kinetics for AlN in 10% H₂O/balance oxygen are shown in Figure 3. In this case the oxidation kinetics approximate a linear law. Since the oxidation mechanisms in dry and wet oxygen differ, it is difficult to compare oxidation rates under these two conditions. As a result, the oxide thicknesses formed after a given time are compared in Table 1. The oxide thickness of two samples, measured using SEM, are also shown in Table 1 for comparison. It is clear from these results that water vapor has a dramatic effect on the oxidation rate of AlN. This difference in oxidation rates in dry and wet oxygen is not observed for NiAl, as shown in Figure 4 (10). Possible mechanisms for water vapor-enhanced oxidation rates of AlN are now discussed.

Table 1. Calculated oxide thickness based on linear weight change or parabolic rate constant

Conditions	Wet oxygen ("linear")	Dry oxygen (parabolic)
1000°C, 100 h	13 μm	2 μm
1100°C, 96 h	105 (100±11)*	6
1200°C, 48 h	347 (367±48)*	16

*measured using SEM

The first possible explanation for enhanced oxidation rates is that different phases of alumina are formed in each environment. Oxygen transport is expected to vary in different alumina phases. Possible phases include amorphous alumina, θ-alumina, α-alumina, or aluminum oxynitride. XRD showed α-alumina, minor amounts of Al₂Y₄O₉, and very minor amounts of Y₃Al₅O₁₂ for samples oxidized in dry and wet oxygen. In

observed for AlN in dry O₂ at temperatures of 900 and 1000°C (1). The growth rates were compared to self-diffusion rates through alumina and found to be much higher, but oxidation rates were not compared to other alumina forming materials.

Oxidation studies conducted in air generally show linear kinetics at temperatures less than 1200-1300°C (2,3). At higher temperatures oxidation kinetics are parabolic. Studies conducted in controlled amounts of water vapor find linear oxidation kinetics for AlN, with oxidation rates increasing with water vapor content (4-6). Again at high temperatures (~1250 to 1400°C), parabolic kinetics are observed. Oxidation rates in air or wet oxygen are all enhanced over those rates observed in dry oxygen. The enhanced oxidation rates are primarily attributed to micro-pore formation (2,4-6), although other effects such as cracks in the scale (5) or substitution of nitrogen on the oxygen sublattice (7) may play a role. The parabolic rates observed at higher temperatures have been attributed to a change in transport mechanism due to sintering of micro-pores (2,4,5).

Several questions remain unanswered by these studies. Under what conditions are linear or parabolic oxidation kinetics observed for AlN? What is responsible for this change in kinetics? How do oxidation rates of AlN in both dry and wet oxygen compare to those of other alumina-forming materials? Why does enhanced oxidation of AlN occur in wet oxygen when this does not happen for other alumina-formers? These questions will be discussed herein.

EXPERIMENTAL PROCEDURE

AlN containing 3.5 wt% Y₂O₃ (Tokuyama Soda Company) was used for this study. No impurities >5 ppm were detected in this material. Coupons of dimensions 4 x 0.4 x 0.3 cm and a surface area of about 6 cm² were cleaned in detergent, DI H₂O, acetone and alcohol prior to oxidation. Samples were suspended from a Cahn 1000 microbalance using a sapphire hanger. Isothermal exposures were conducted at 1000, 1100, and 1200°C for times between 48 and 100 h. Gases consisting of dry oxygen (dried with Mg(ClO₄)₂) or 10% H₂O/balance oxygen were supplied to an alumina furnace tube at a rate of 100 sccm. Weight change versus time was acquired digitally. After oxidation, X-Ray Diffraction Analysis (XRD) and Nuclear Magnetic Resonance Analysis (NMR) were conducted to determine the oxide phases present. Scanning Electron Microscopy (SEM), Field Emission Gun-SEM (FEG-SEM), and Transmission Electron Microscopy (TEM) with Electron Dispersive Spectroscopy (EDS) were used to characterize the oxide morphology and composition.

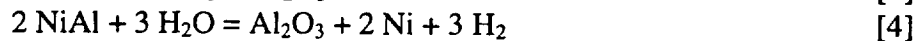
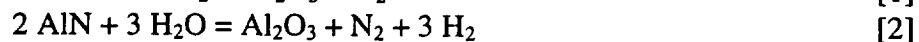
separate experiments using AlN powder partially oxidized in air for four hours at 1000°C, NMR showed no evidence of aluminum oxynitride to a sensitivity of about 5%. The α -alumina phase formed by oxidation of AlN is the same as that formed on NiAl (with additional discrete particles of aluminum-yttrium oxides). Thus, the increased oxidation rates can not be due to the formation of different oxide phases.

Another possibility is that the point defect concentration is increased by some mechanism such as $2\text{N}_\text{O}' + \text{V}_\text{O}^{\bullet\bullet}$ (7) or $\text{OH}_\text{O}^\bullet + \text{O}_\text{i}''$ (11). Increasing the number of defects would increase the rate of oxidation. This, however, does not explain the linear kinetics observed for AlN in wet oxygen.

Finally, the enhanced oxidation rates may be explained by formation of short circuit transport paths such as cracks or pores. A few cracks were observed in the oxide scales formed on AlN in wet oxygen in this study. The cracks may have formed on cooling due to the thermal expansion mismatch between AlN and alumina and the higher stresses generated in the thicker scales formed in wet oxygen. Cracks were not observed in the oxide formed on AlN in dry oxygen.

Micropores were observed in the alumina scales formed on AlN in both wet and dry oxygen, as shown in Figures 5 and 6. A few pores were observed in alumina formed on AlN in dry O_2 ; however, both the number and size of pores found in alumina formed on AlN in wet O_2 were dramatically higher. In addition, the number and size of micropores increased with temperature for alumina formed at 1000 to 1200°C in wet oxygen.

It is possible that these pores form primarily due to the generation of gaseous products during the oxidation of AlN in wet oxygen. Consider the following oxidation reactions:



Reactions 1,3, and 4 are observed to occur by parabolic kinetics and little or no porosity is observed in the oxide (8-10). Reaction 2 is observed to occur by linear kinetics with significant microporosity. The following mechanism is proposed to explain the experimental observations for AlN oxidation in wet oxygen. The generation of both N_2 and H_2 is necessary for significant pore formation. The number of pores generated in reaction 2 is sufficient to form a short circuit path for transport of oxidant to the AlN/oxide interface. The rate of transport is sufficiently rapid in this case so that oxidation is no longer limited by transport, but by the reaction of AlN with the wet oxygen. Linear oxidation kinetics are observed. At temperatures higher than those of this study (>1200°C), sintering of the pores would be expected. This would explain the return

to parabolic kinetics observed in other studies at high temperatures under otherwise similar conditions.

SUMMARY AND CONCLUSIONS

In summary, alumina formation on AlN in dry oxygen at temperatures between 1000 and 1200°C is parabolic with time, within an order of magnitude of rates reported for NiAl, and with the same temperature dependence as NiAl. By analogy with NiAl, it is concluded that oxidation rates are limited by transport of aluminum and/or oxygen through the alumina scale on short circuit paths such as grain boundaries. Oxide growth on AlN in 10% H₂O/balance O₂ at temperatures between 1000 and 1200°C is nearly linear with time and at rates much more rapid than those observed in dry oxygen. This behavior differs from that of NiAl under otherwise identical conditions. Large numbers of micropores are observed in the scale formed on AlN in wet oxygen. These micropores have been attributed to the generation of N₂ and H₂ gaseous oxidation products. The micropores provide a fast path for oxygen transport to the AlN/scale interface. The linear oxidation kinetics suggest that the interface reaction of AlN with wet oxygen is the rate limiting step.

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REFERENCES

1. S. Jones and W. D. Scott, *Adv. in Ceramics*, **26**, 151 (1989).
2. A. Bellosi, E. Landi and A. Tampieri, *J. Mater Res.*, **8** [3] 565 (1993).
3. D. Robinson and R. Dieckmann, *J. Mater. Sci.*, **29**, 1949 (1994).
4. T. Sato, K. Haryu, T. Endo and M. Shimada, *J. Mater. Sci.*, **22**, 2277 (1987).
5. H. -E. Kim and A.J. Moorhead, *J. Am. Ceram. Soc.*, **77** [4] 1037 (1994).
6. Y. Kuromitsu, H. Yoshida, S. Ohno, H. Masuda, H. Takabe and K. Morinaga, *J. Cer. Soc. Jap., Int. Ed.*, **100**, 70 (1992).
7. D. A. Robinson, G. Yin and R. Dieckmann, *J. Mater. Sci.*, **29**, 2389 (1994).
8. F. S. Pettit, *Trans. Met. Soc. AIME*, **239**, 1296 (1967).
9. R. Prescott, D. F. Mitchell and M. J. Graham, in *Microscopy of Oxidation 2*, S.B. Newcomb and M.J. Bennett, Editors, p. 455, Institute of Materials, London (1993).
10. unpublished work, J. A. Nesbitt
11. T. Norby, *Adv. in Ceramics*, **23**, 107 (1987).

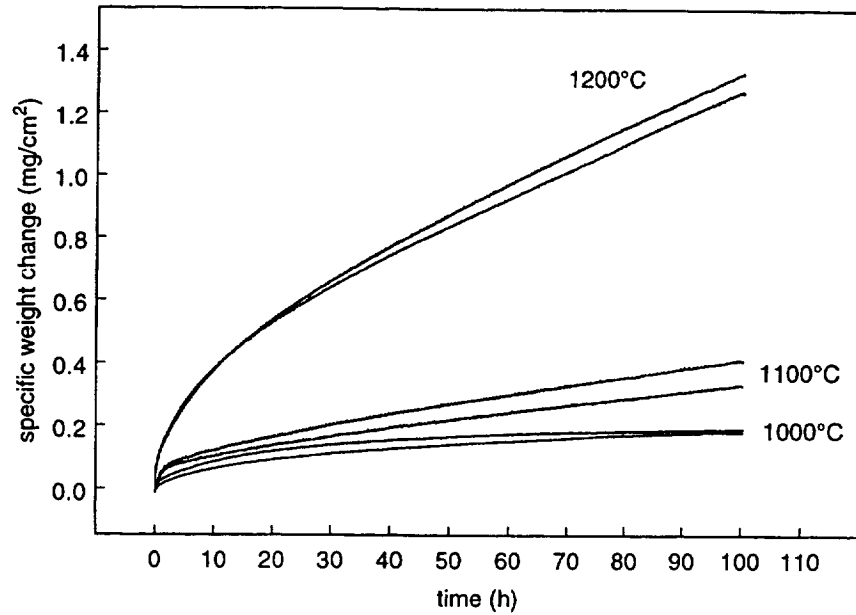


Figure 1. Weight change kinetics for AlN oxidized in dry oxygen.

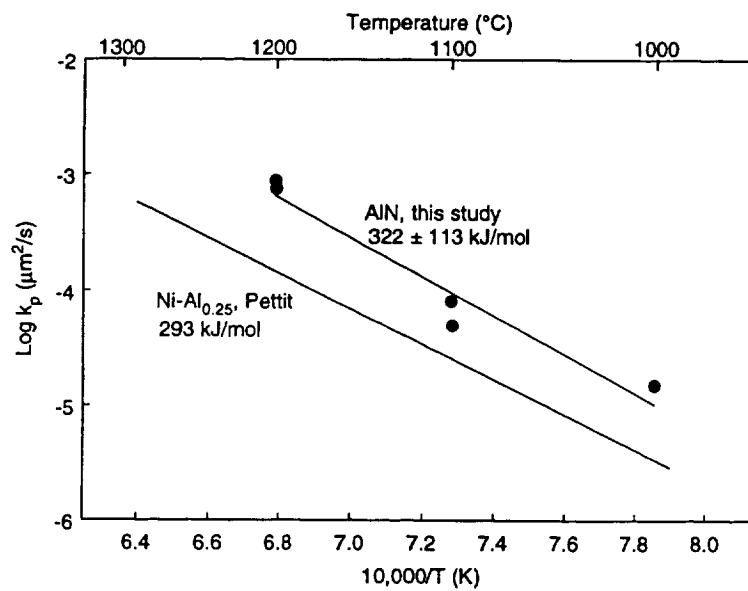


Figure 2. Comparison of parabolic oxidation rates as a function of temperature for AlN and NiAl (10) in dry oxygen.

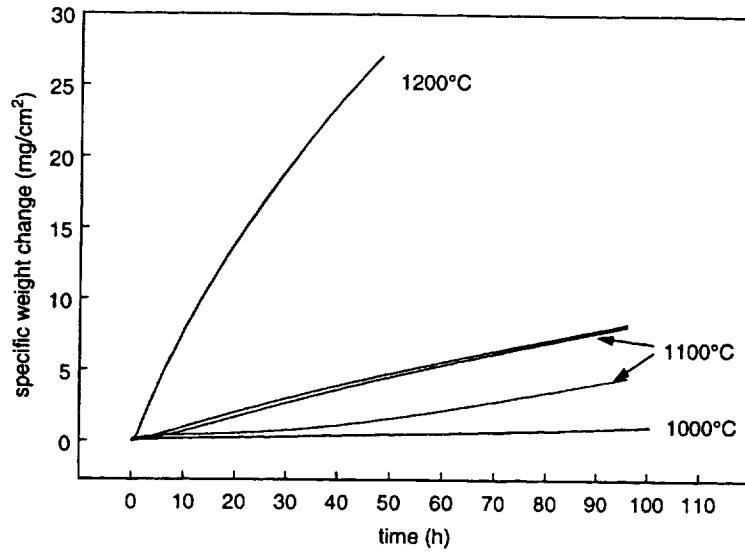


Figure 3. Weight change kinetics for AlN oxidized in wet oxygen.

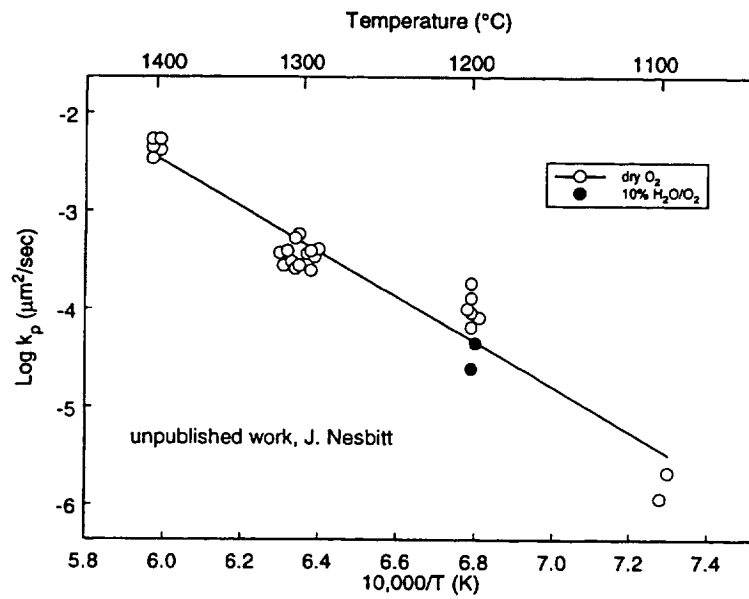


Figure 4. Parabolic oxidation rates as a function of temperature for NiAl in dry and wet oxygen.

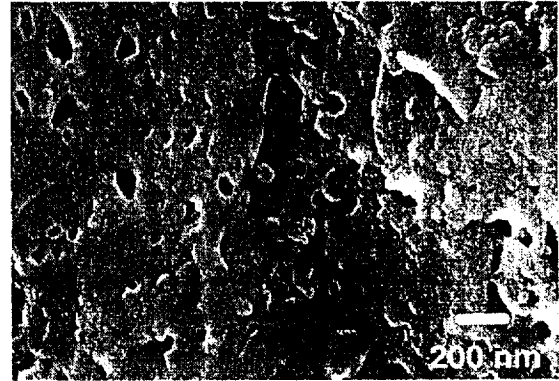
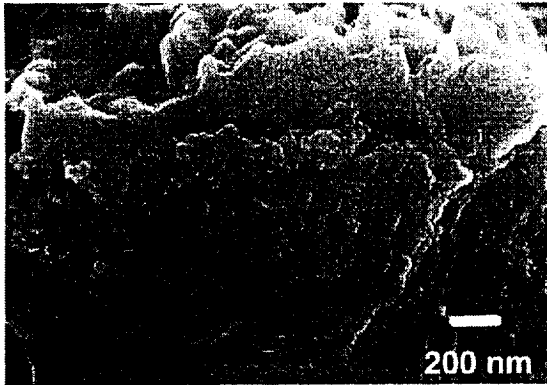


Figure 5. Fracture cross-section of oxide grown on AlN at 1000°C for 100h in dry oxygen (left) and wet oxygen (right).

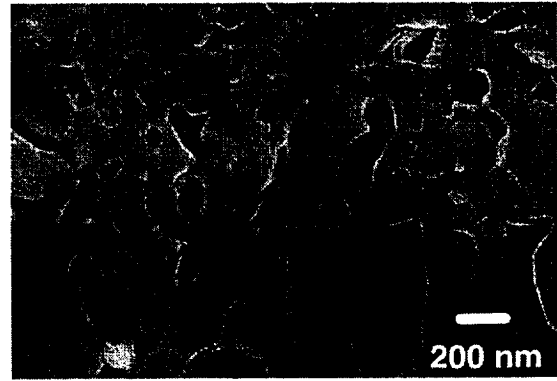


Figure 6. Fracture cross-section of oxide grown on AlN at 1200°C for 100h in dry oxygen (left) and for 48h in wet oxygen (right).

