Proton Assisted Diffusion in Oxides (Does Steam Damage Ceramics?)

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Abstract

Ceramics are usually very stable materials but this can change when they are exposed to high temperature steam. This research measures the changes that occur when steam passes over the surface of a ceramic oxide with small inclusions of nickel metal particles. Results show that oxygen enters the ceramic and moves through it more quickly when exposed to humid air than in dry air. At high temperatures this causes significantly faster corrosion (oxidation) of the nickel particles embedded in the ceramic. This accelerated corrosion in the presence of steam can have serious economic consequences. For example, high temperature water vapor may degrade the performance of jet engines that use ceramic coatings to protect metal turbine blades.

Background

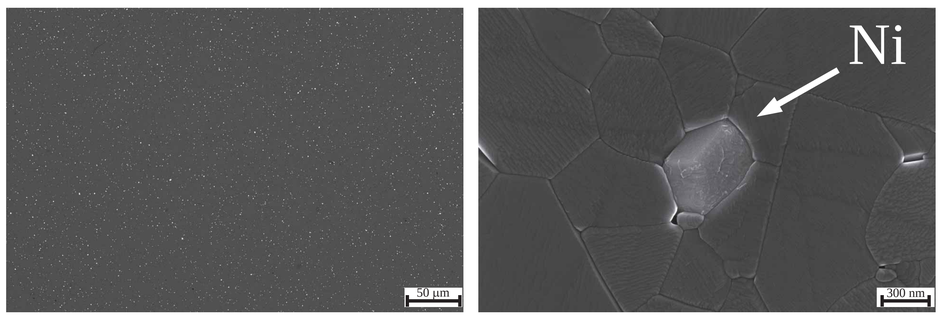
• Steam can cause water vapor to be adsorbed on oxide surfaces and form superficial $(OH)^-$ (an oxygen ion with an associated proton).

• We hypothesize that $(OH)^-$ can diffuse more rapidly than O^{2-} through a ceramic oxide due to the smaller size, decreased charge, and flexible shape (from increased polarizability) of $(OH)^-$ compared to O^{2-}.

Processing & Characterization

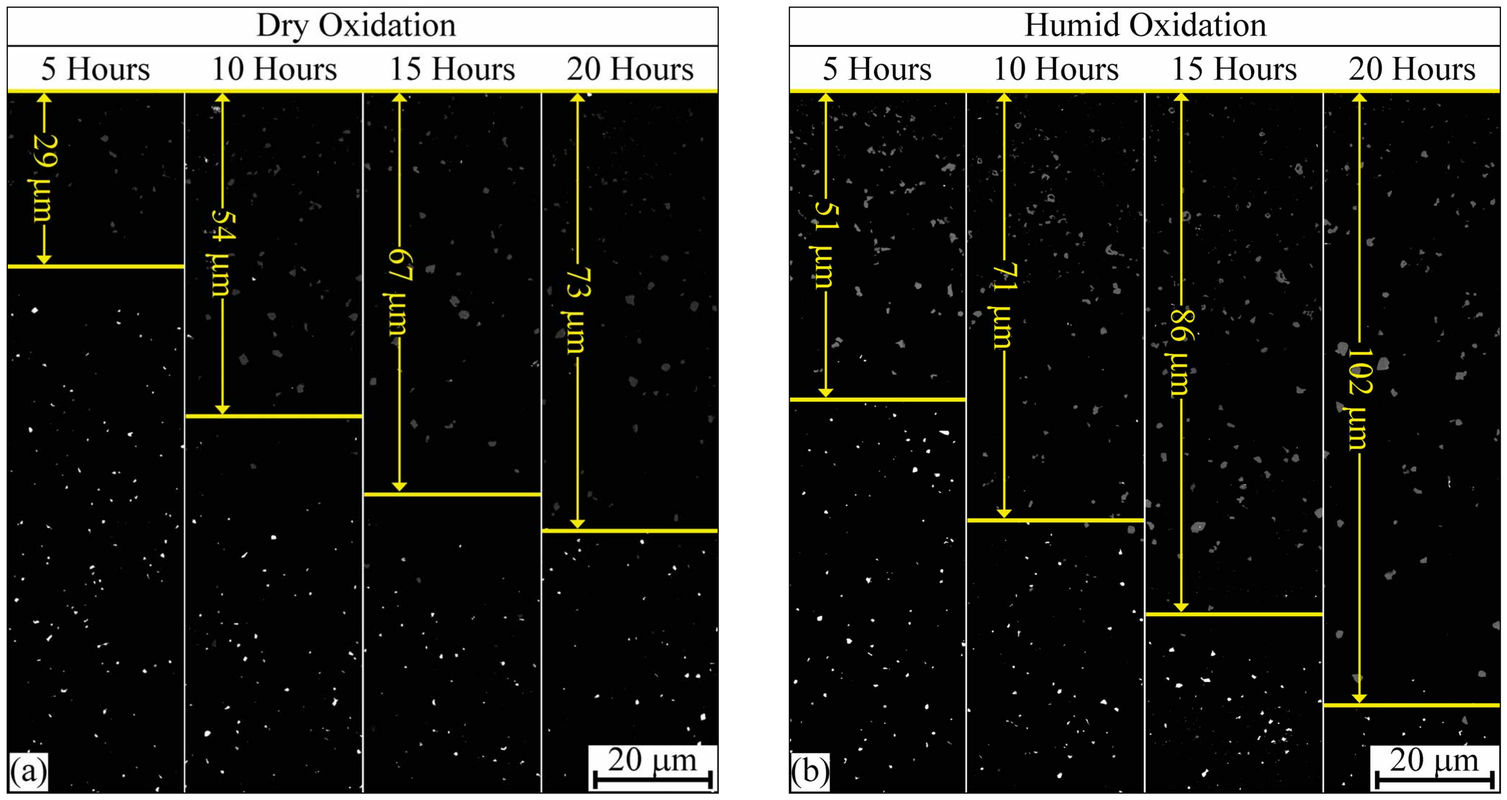
• Compacts of Al_2O_3 and 0.5 vol% Ni were sintered at 1500°C in a reducing environment to 98-99% density.

• Scanning electron microscopy (SEM) shows a homogeneous distribution of Ni particles located at grain boundaries throughout the Al_2O_3 matrix.



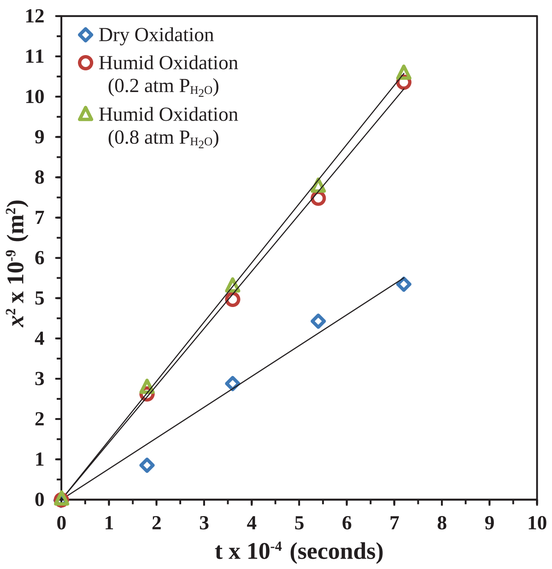
High Temperature Oxidation

Samples were oxidized at 1300°C in dry air or steam for 5-20 hours. Backscattered SEM of cross-sections are presented below. Oxidation of Ni (white particles) results in the formation of $NiAl_2O_4$ (gray particles) near the exposed surface of the Al_2O_3 (black matrix).



Average depth of oxidation in yellow for (a) dry air or (b) steam (humidity = 0.2 atm P_{H_2O}).

Reaction Kinetics



Square of the average oxidation depth versus annealing time. A parabolic rate law is used to model the diffusion controlled reaction processes, with the slope equal to the rate constant.

k_{dry} = 7.9 x 10^{-14} m^2/s
$k_{0.2atm\ PH2O}$ = 1.4 x 10^{-13} m^2/s
$k_{0.8atm\ PH2O}$ = 1.5 x 10^{-13} m^2/s

Conclusions and Future Work

• Results suggest that oxygen diffusion is 80% faster in the presence of high temperature water vapor (steam).

• The hypothesis that this effect is due to faster diffusion of $(OH)^-$ compared to O^{2-} will be tested using deuterium.

• Oxidation experiments at various temperatures will determine activation energies and the minimum temperature that will affect sintering, creep, and corrosion.

• Since ceramic thin films and coatings typically experience stress, additional experiments will tell if stress-assisted diffusion is also significantly accelerated in the presence of high temperature water vapor.

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