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High-Temperature Oxidation of Zircaloy-4 (Zr-1.5Sn) in Steam, Oxygen, Nitrogen and Mixed Atmospheres

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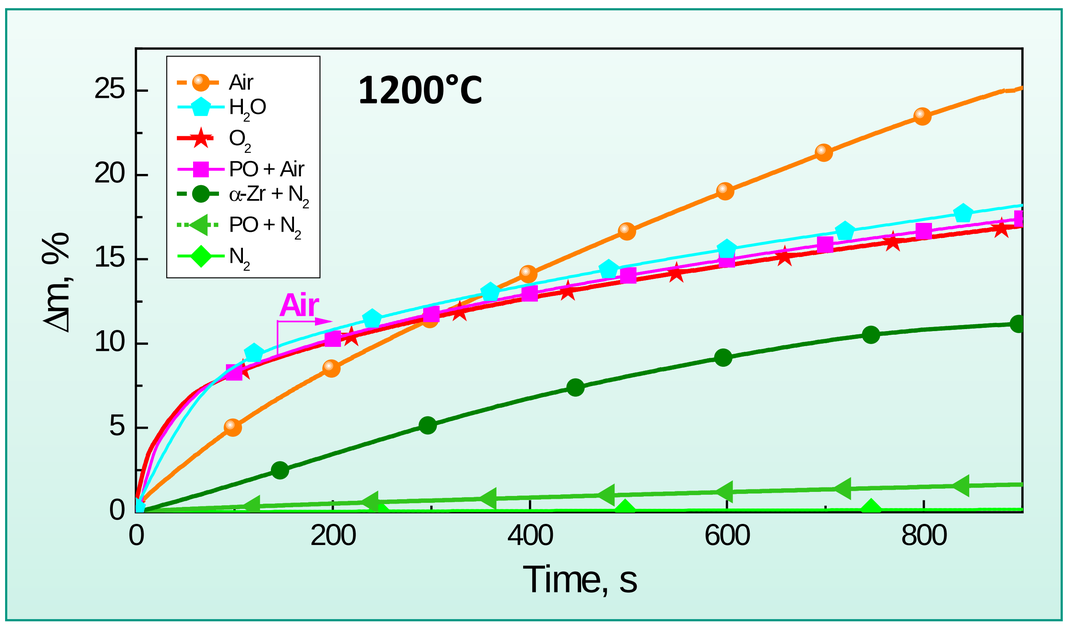
Introduction

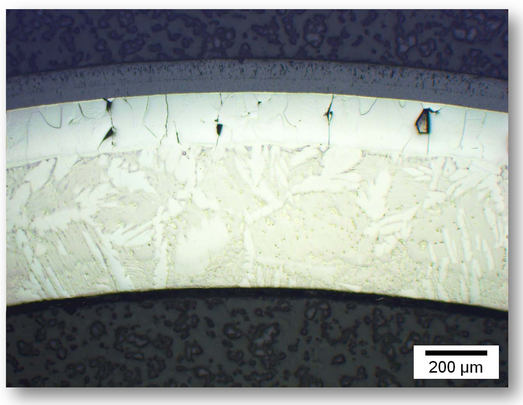
- Zirconium alloys are used as cladding materials in nuclear reactors due to their excellent neutron, mechanical and corrosion properties at operational conditions. During loss of coolant and severe accidents the claddings are exposed to high temperatures. Enhanced oxidation causes mechanical degradation of the cladding and is connected with release of hydrogen and heat.
- Steam is the prototypic atmosphere during nuclear accidents; but air and nitrogen ingress scenarios are discussed as well. Nitrogen is used for inertization of reactor containments and for pressurization of emergency cooling water systems.

Reaction of Zry-4 in	Kinetic rate law	Rel. reaction rate
N_2	parabolic	1
N_2 after pre-oxidation in O_2	linear	10
N_2 with oxygen-stabilized α-Zr(O)	linear	70
O_2, H_2O	parabolic	100
Air after pre-oxidation in O_2	parabolic	100
Air	linear	150

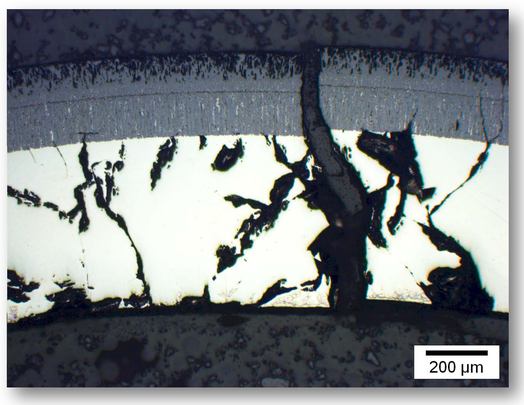
Rate laws and relative reaction rates for oxidation of Zircaloy-4 in various atmospheres (at 1200°C)



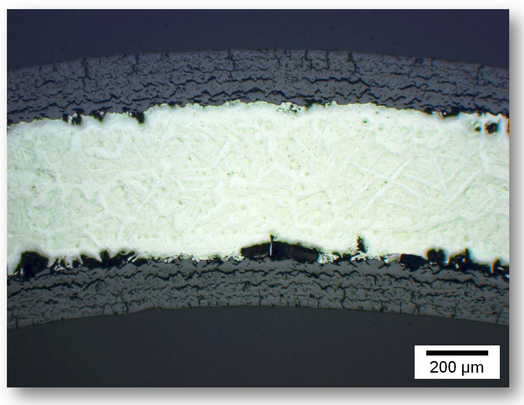
Mass gain during reaction of Zircaloy-4 with various atmospheres



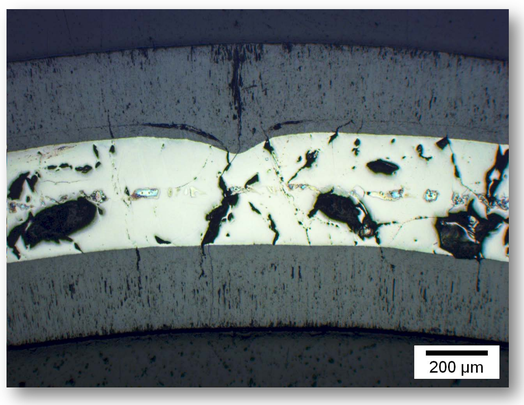
20min, 1200°C, steam: protective oxide, oxygen-stab. α-Zr(O), ductile β-Zr



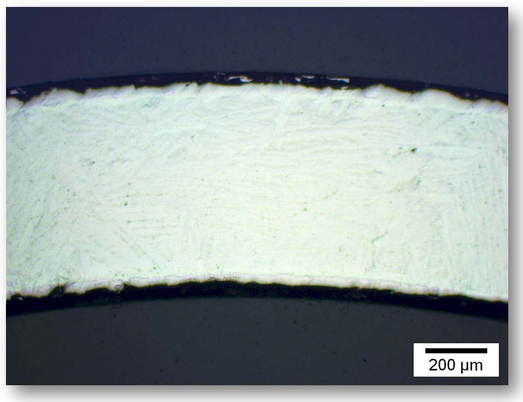
3min, 1600°C, steam: protective oxide with met. precipitates, brittle α-Zr(O)



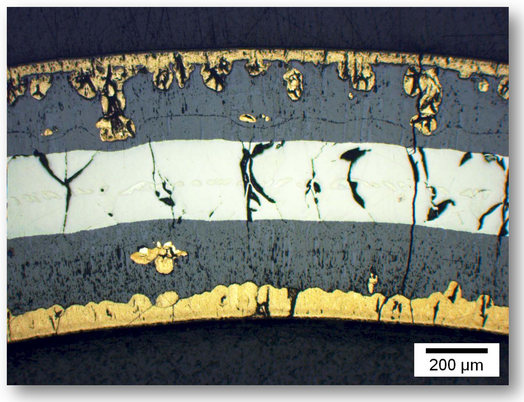
1.5h, 980°C, steam: breakaway oxide, ca. 20 at% hydrogen in metal phase (β)



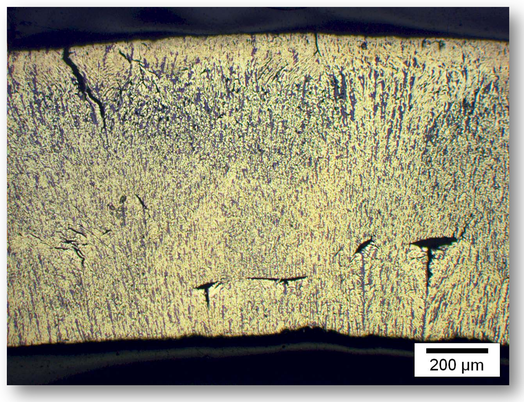
90min, 1200°C, oxygen: protective oxide with self-healed crack, brittle α-Zr(O)



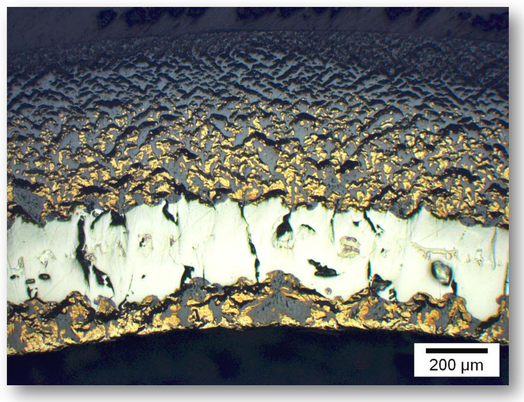
3h, 1200°C, nitrogen: only slightly affected surface (α-Zr(N))



10min O_2, then 50min N_2, 1200°C: external ZrN formation during O_2 starvation



α-Zr(O), 1h N_2, 1200°C: ZrN/ZrO_2 mixture, complete reaction after 1000s



15min, 1200°C, air: very porous oxide with nitride near metal-oxide boundary

- Complex oxidation behavior of zirconium alloys in various atmospheres relevant during severe nuclear accidents
- Transition to breakaway oxidation in steam, oxygen, and air at temperatures below 1100°C
- Strong effect of nitrogen on degradation of zirconium cladding alloys