OXIDATION OF HIGH-TEMPERATURE ALLOY WIRES FOR HYBRID SEAL APPLICATIONS

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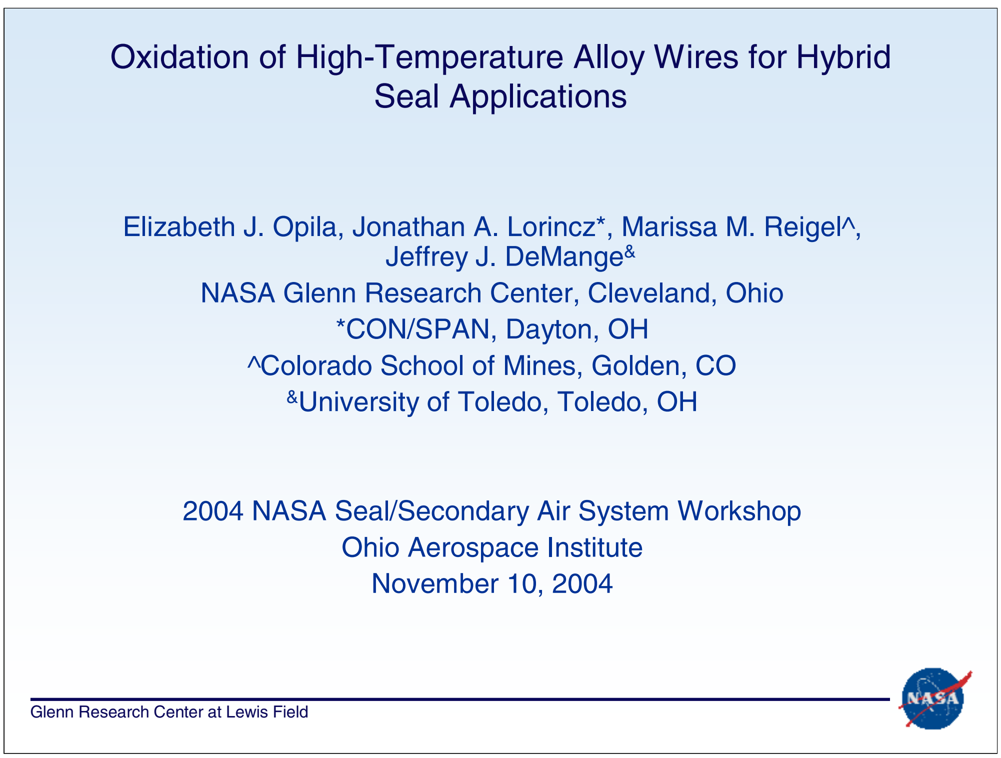
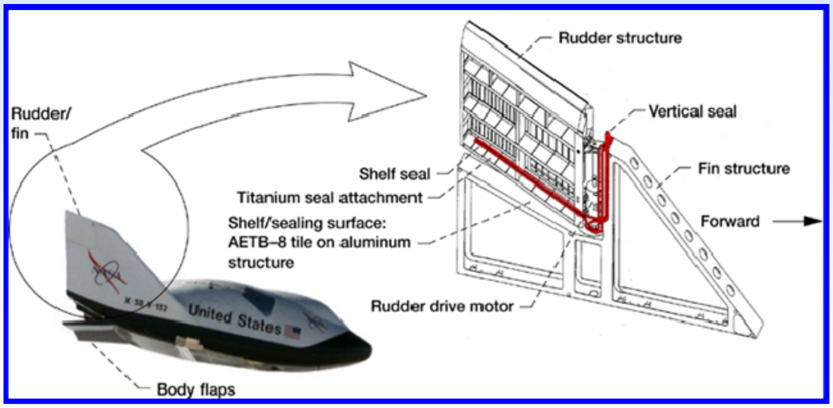


Small diameter wires (150 to 250 μm) of the high-temperature alloys Haynes 188, Haynes 230, Haynes 214, Kanthal A1 and PM2000 were oxidized at 1204 °C in dry oxygen or 50 percent H_2O/50 percent O_2 for 70 hours. The oxidation kinetics were monitored using a thermogravimetric technique. Additional cyclic oxidation exposures were conducted in air for one hour cycles at 1204 °C for times up to 70 hours. Oxide phase composition and morphology of the oxidized wires were determined by x-ray diffraction, field emission scanning electron microscopy, and energy dispersive spectroscopy. The alumina-forming alloys, Kanthal A1 and PM2000, out-performed the chromia-forming alloys under these test conditions. Correlations between oxidation lifetime and wire diameter were considered. PM2000 was recommended as the most promising candidate for advanced hybrid seal applications for space reentry control surface seals or hypersonic propulsion system seals.

Why study oxidation of wires?

Understanding of wire oxidation needed for development of advanced high-temperature seals for future hypersonic and reentry vehicles.



- Structural seal restricts hot gas leakage to underlying low-temperature control actuators
- Wire overwrap needed for wear resistance

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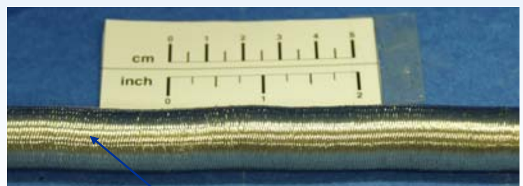
State of the art hybrid seals

- T_{max}=800°C
- Ceramic batting or fiber core (alumina or aluminosilicate)
- Haynes 188 or 230 overwrap/overbraid, 40-125 micron diameter wire



Haynes 230 overbraid

Nextel 312 fibers

Requirements for advanced hybrid seals

- Withstand temperatures up to 1400°C
- Operate without active cooling
- Flexible, resilient, wear resistant
- Airframe control surface seals
  - Reentry environment: reduced pressure air, plasma
  - Reusability of 10 to 100 cycles of 30 minutes each
- Hypersonic propulsion system seals
  - Propulsion environment: high pressure water vapor
  - Reusability of 1000 cycles of 250 sec/cycle (70 hours)

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Objectives of this study

- Characterize isothermal and cyclic oxidation resistance of high-temperature alloy wires
- Guide selection of higher temperature alloys for hybrid seal applications

Alloy wires

Alloy	Composition, wt%	Diameter, µm
Haynes 188	Co base, 22 Cr, 22 Ni, 14 W, Fe< 3, Mn <1.25, 0.5 Si, 0.12 La, trace: C, B	250
Haynes 230	Ni base, 22 Cr, 14 W, Co<5, Fe<3, 2 Mo, 0.5 Mn, 0.4 Si, 0.3 Al, trace: C, La, B	250
Haynes 214	Ni base, 16 Cr, 4.5 Al, 3 Fe, 0.2 Si, trace: Mn, Zr, C, B, Y	250
Kanthal A1	Fe base, 22 Cr, 5.8 Al, Si<0.7, Mn<0.4	250
PM 2000	Fe base, 20 Cr, 5.5 Al, 0.5 Ti, 0.5 Y_2O_3	150

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Haynes 188, and 230 are chromia forming alloys. Haynew 214 is a marginal alumina forming alloy. Kanthal A1 and PM2000 are alumina forming alloys. PM2000 contains the reactive element Y_2O_3 which improves oxide adherence.

Note smaller diameter wire for PM2000.

Experimental Procedure

- Coil 60 cm length of wire
- Oxidation of wires
  - 1204°C (2200°F)
  - 1 atm
  - 70h
  - Three exposure environments
    - Isothermal: O_2 (0.4 cm/sec)
    - Isothermal: 50% H_2O/50% O_2 (4.4 cm/sec)
    - Cyclic: stagnant air, 1h hot, 20 min. cool, 70 cycles
- Weight change of wires
- X-ray diffraction (XRD) analysis
- Field Emission-Scanning Electron Microscopy/Energy Dispersive Spectroscopy (FE-SEM/EDS)

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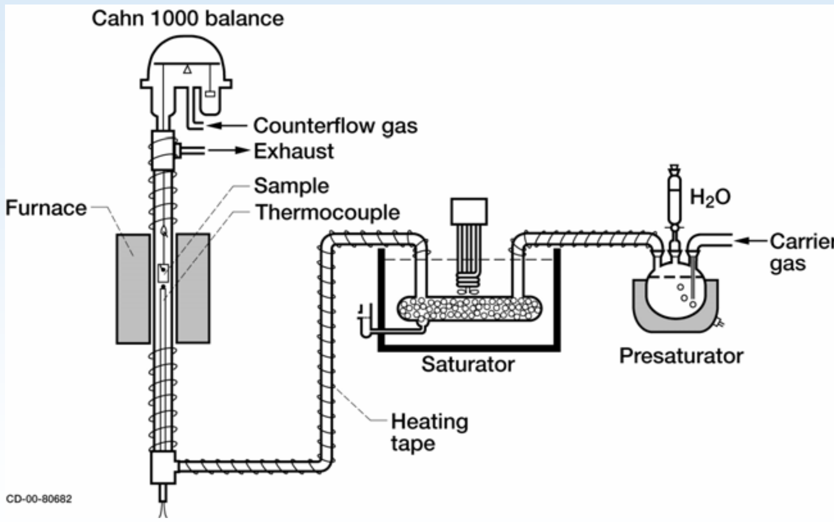
Weight gain indicates oxide formation. Weight loss indicates loss of oxide by spallation or volatilization.

Thermogravimetric Analysis



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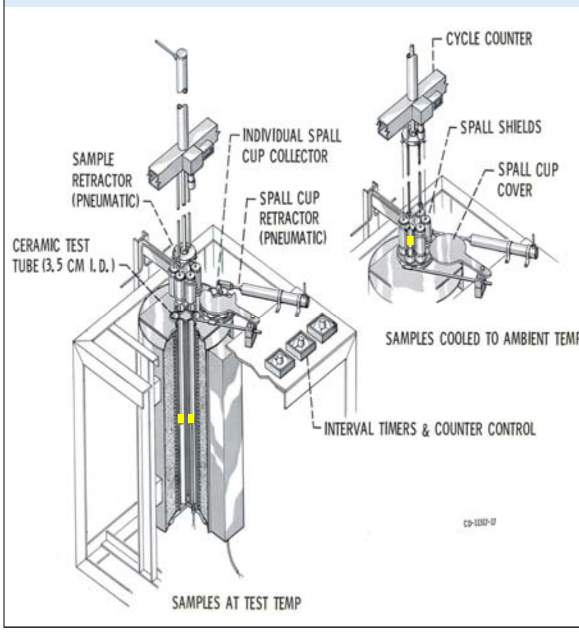
Cyclic Oxidation



One cycle = 1 hour hot, 20 minute cool..

Results for wire oxidation in dry O_2

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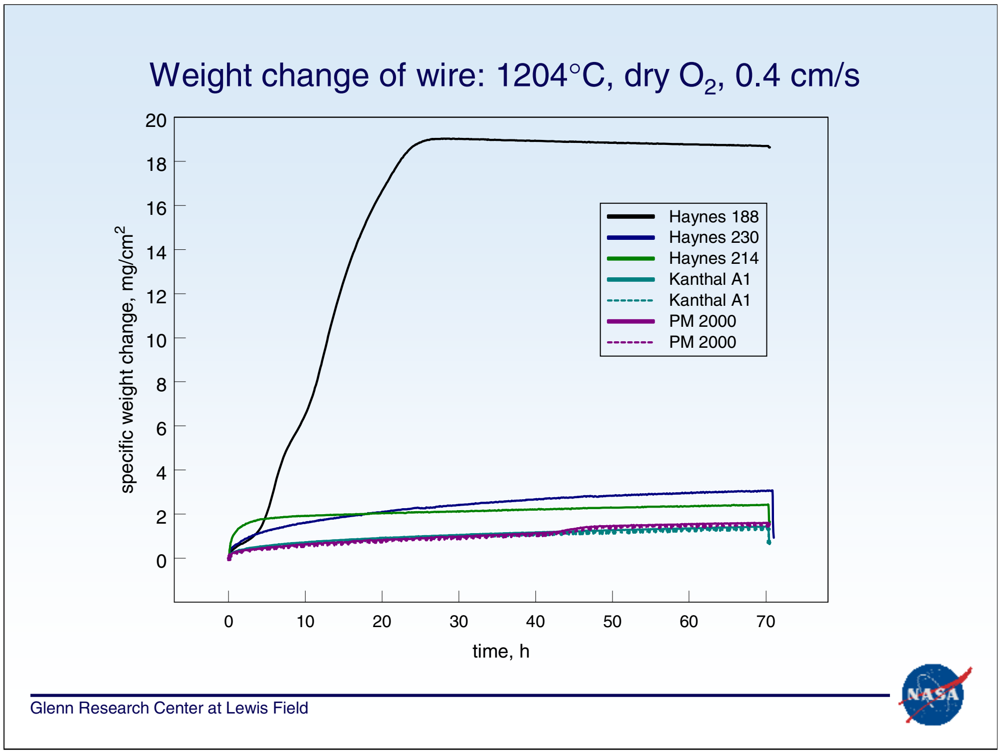
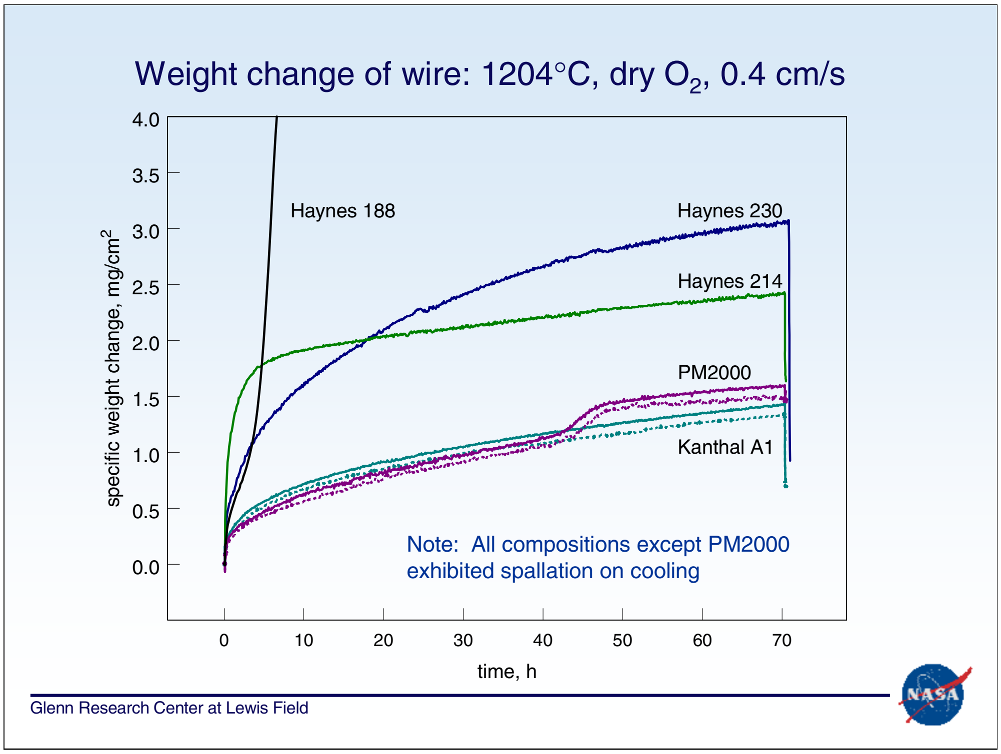


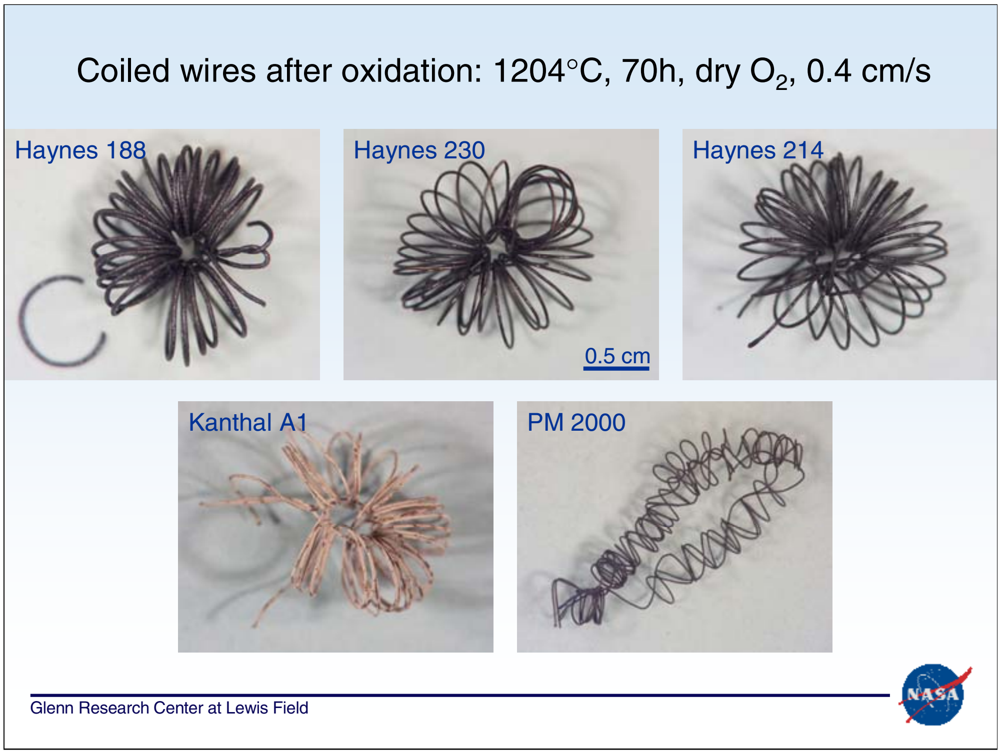
Haynes 188 completely oxidized after about 20 hours.



Haynes 230, PM2000, Kanthal A1 show desired parabolic oxidation kinetics.

Haynes 214 shows protective oxidation after initial transient of fast oxidation.

Bump in PM2000 kinetics at 45h may be due to depletion of alumina and beginning of chromia scale formation.



Haynes 188 brittle. Haynes 230, 214, Kanthal A1 show spallation to bare metal.

X-ray diffraction results for wires: 1204°C, 70h, dry O_2, 0.4 cm/s

Alloy	Major components of alloy, wt%	Oxidation products
Haynes 188	Co base, 22 Cr, 22 Ni, 14 W	$NiWO_4$ $NiCr_2O_4$ NiO
Haynes 230	Ni base, 22 Cr, 14 W	Cr_2O_3 $NiCr_2O_4$ NiO
Haynes 214	Ni base, 16 Cr, 4.5 Al	$NiCr_2O_4$/$NiAl_2O_4$ NiO
Kanthal A1	Fe base, 22 Cr, 5.8 Al	α Al_2O_3
PM 2000	Fe base, 20 Cr, 5.5 Al, 0.5 Y_2O_3	α Al_2O_3

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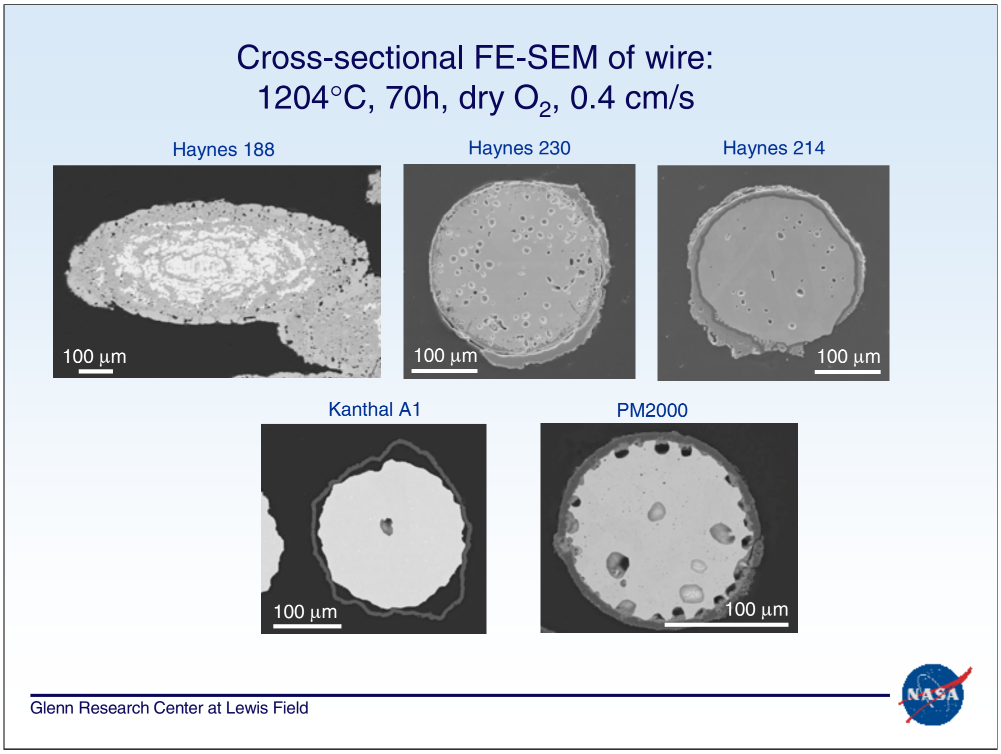
Chromia formation not observed for Haynes 188 after 70h. Note presence of $NiWO_4$ oxide phase.

First three alloys show spinel (AB_2O_4) formation. This is not a protective oxide.



Haynes 188: (Co,Ni)O, CoCr2O4, CoWO4-bright phase. Wire completely consumed.

Haynes 230: Cr2O3

Haynes 214: Al2O3 inner layer, spinel outer layer, NiO blocks on surface

Kanthal A1: Oxide scale completely nonadherent.

Summary of results:
Wire oxidation 1204°C, 70h, dry O_2, 0.4 cm/s

- Haynes 188 completely oxidized
- Haynes 230 formed chromia scale, spalled on cool down
- Haynes 214 formed inner alumina scale, external spinel, NiO, spalled on cool down
- Kanthal A1 formed alumina scale, completely nonadherent after cool down
- PM2000 smaller diameter wire formed an adherent alumina scale, aluminum completely depleted from wire, inner discontinuous layer of chromia, internal void formation

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Results for wire oxidation in 50% H_2O/50% O_2

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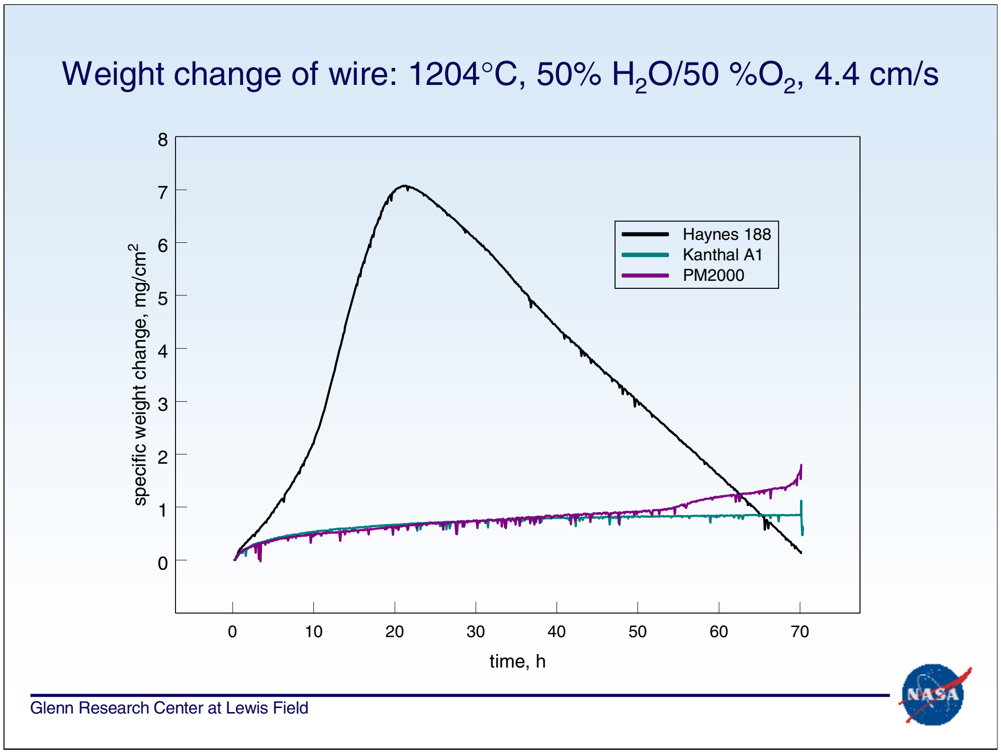
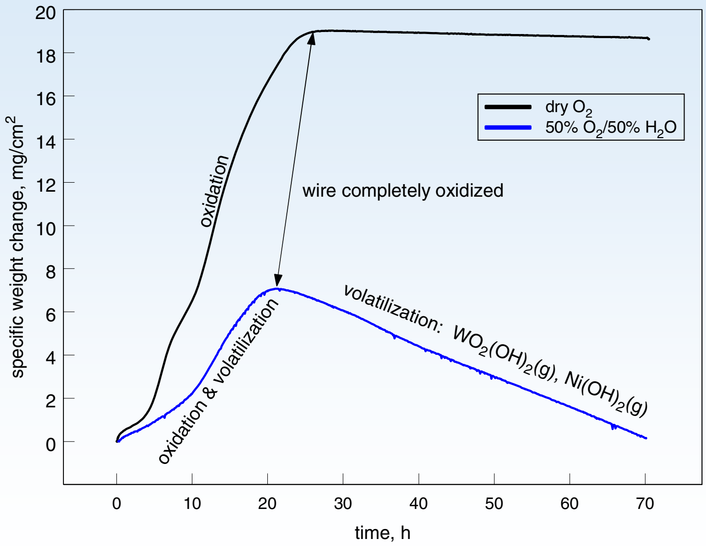


Different weight change behavior for Haynes 188 explained on next slide.

Weight change of Haynes 188 wire: 1204°C



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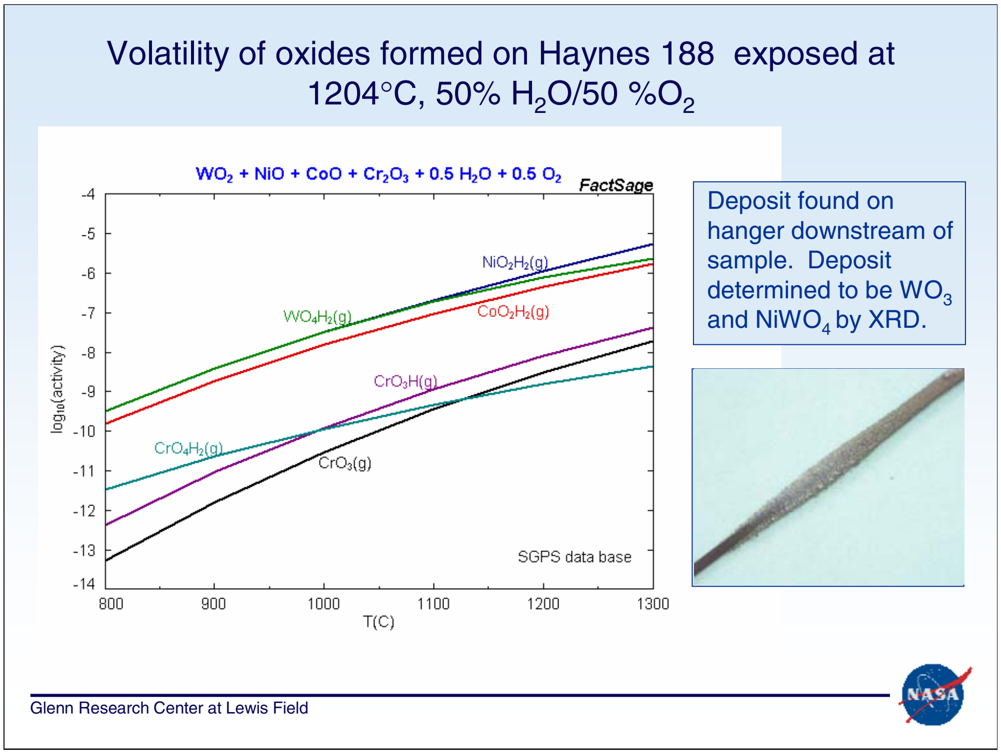
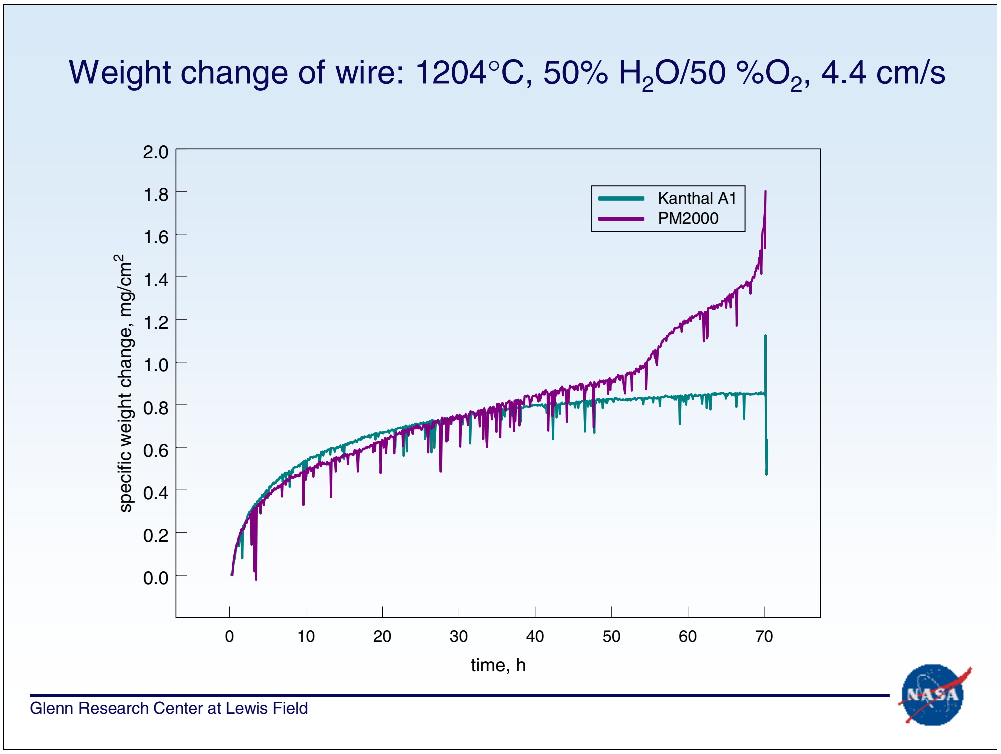
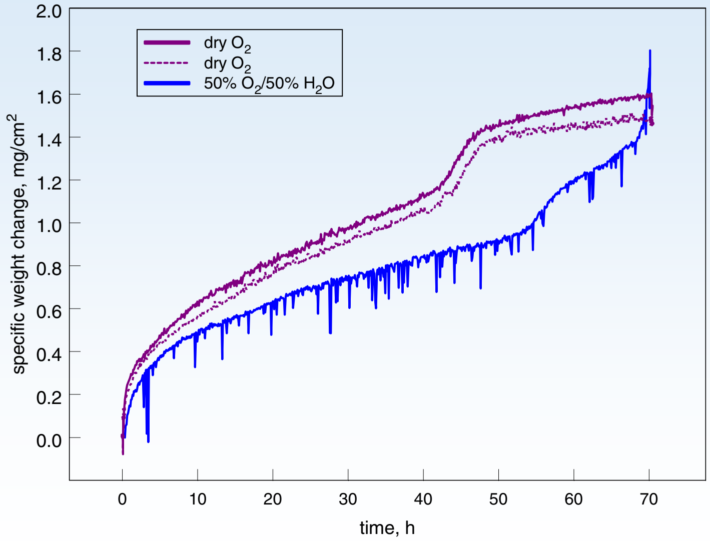


Calculated gas species formed from oxides in water vapor. W is very volatile.



Breakaway oxidation for PM2000 at 68 h.

Weight change of PM2000 wire: 1204°C



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Correlation between breakaway oxidation and wire diameter

- Breakaway oxidation occurs when aluminum is depleted to low level: protective oxide scale formation no longer possible
- Aluminum depletion depends on ratio of wire volume to surface area.
  - Extrapolating time to breakaway for PM2000 at 1204°C in 50% H_2O for other wire diameters.

$$W_m \propto \frac{V}{A} = r \quad W_m \propto \sqrt{t}$$

$$\frac{t_a}{t_b} = \frac{r_a^2}{r_b^2}$$

  W_m = weight of metal consumed during oxidation, V = wire volume, A = wire surface area, r = wire radius, t = oxidation time
  - Experimentally determined time to breakaway for 150 μm dia wire is 68h.
  - Predict time to breakaway for 250 μm dia wire is 189h for comparison to other alloy wires of 250 μm dia.
  - Predict time to breakaway for 40 μm dia wire at 5h for finest diameter wire proposed for use in seal applications.

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X-ray diffraction results for wires: 1204°C, 70h, 50% H_2O/50% O_2, 4.4 cm/s

Alloy	Major components of alloy, wt%	Oxidation products
Haynes 188	Co base, 22 Cr, 22 Ni, 14 W	NiO $NiCr_2O_4$
Kanthal A1	Fe base, 22 Cr, 5.8 Al	α Al_2O_3
PM 2000	Fe base, 20 Cr, 5.5 Al, 0.5 Y_2O_3	$(Fe,Cr)_2O_3$

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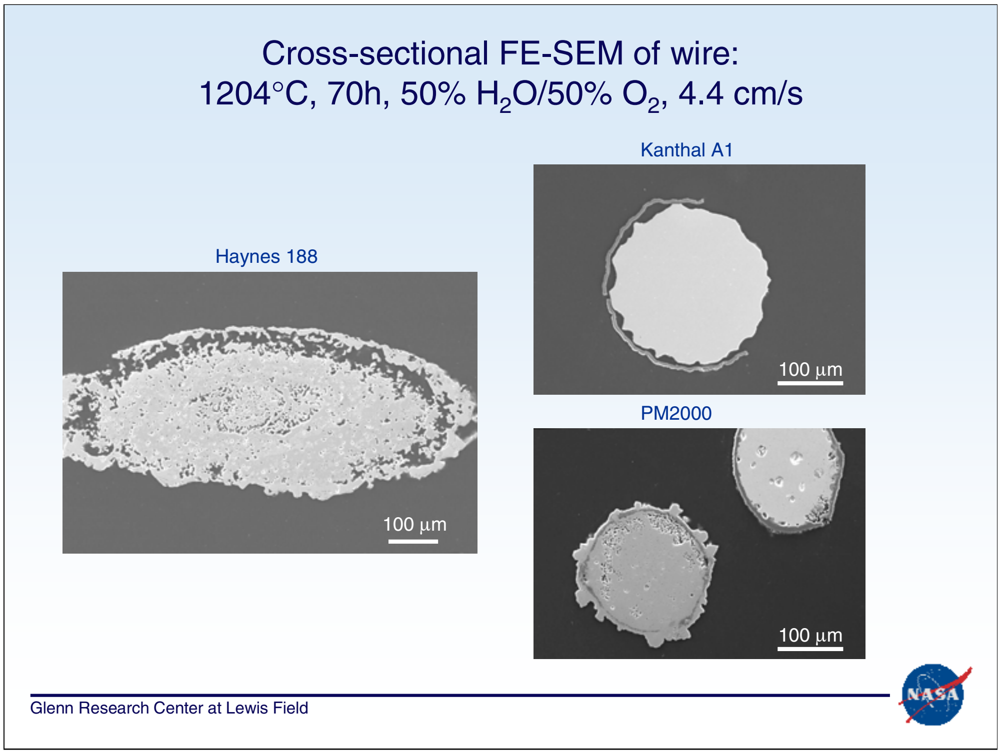
No W containing phase found on Haynes 188. W is completely volatilized.

Al2O3 not found on PM2000 after 70h in this environment in contrast to results in dry O2.



Porosity in Haynes 188 where $NiWO_4$ found after exposure in dry O2.

Oxide scale not adherent on Kanthal A1.

Adjacent cross-sections of PM2000 show one completely oxidized, the other metallic with nearly protective scale still intact.

Summary of results: Wire oxidation, 1204°C, 70h, 50% H_2O/50% O_2, 4.4 cm/s

- Haynes 188 completely oxidized, all W volatilized leaving porosity.
- Kanthal A1 formed alumina scale, completely nonadherent, much of scale spalled.
- PM2000 smaller diameter wire experienced breakaway oxidation. Portions of wire completely oxidized, show remainder of alumina scale. Portions of wire show protective alumina scale.
- Time to breakaway oxidation expected to vary with the square of the wire diameter.

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Cyclic Oxidation Results

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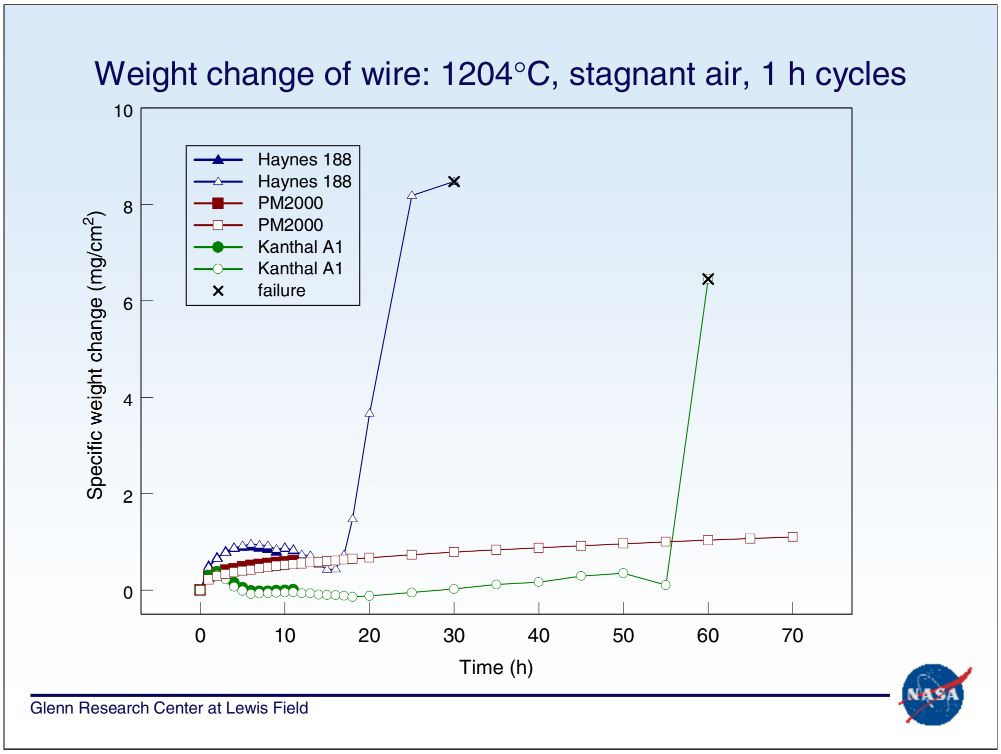

Haynes 188 weight change similar to isothermal exposures in that oxidation is about complete at 20h.

PM2000 showing parabolic oxidation to 60+ hours.

Kanthal A1 shows weight loss and spallation after third cycle. Breakaway oxidation at 55h.

X-ray diffraction results for wires: 1204°C, 1h cycles, stagnant air

Alloy	Major components of alloy, wt%	Time to failure, h	Oxidation products
Haynes 188	Co base, 22 Cr, 22 Ni, 14 W	30	(Ni,Co)O (Ni,Co)Cr_2O_4
Kanthal A1	Fe base, 22 Cr, 5.8 Al	60	Fe_2O_3
PM 2000	Fe base, 20 Cr, 5.5 Al, 0.5 Y_2O_3	>70	tbd

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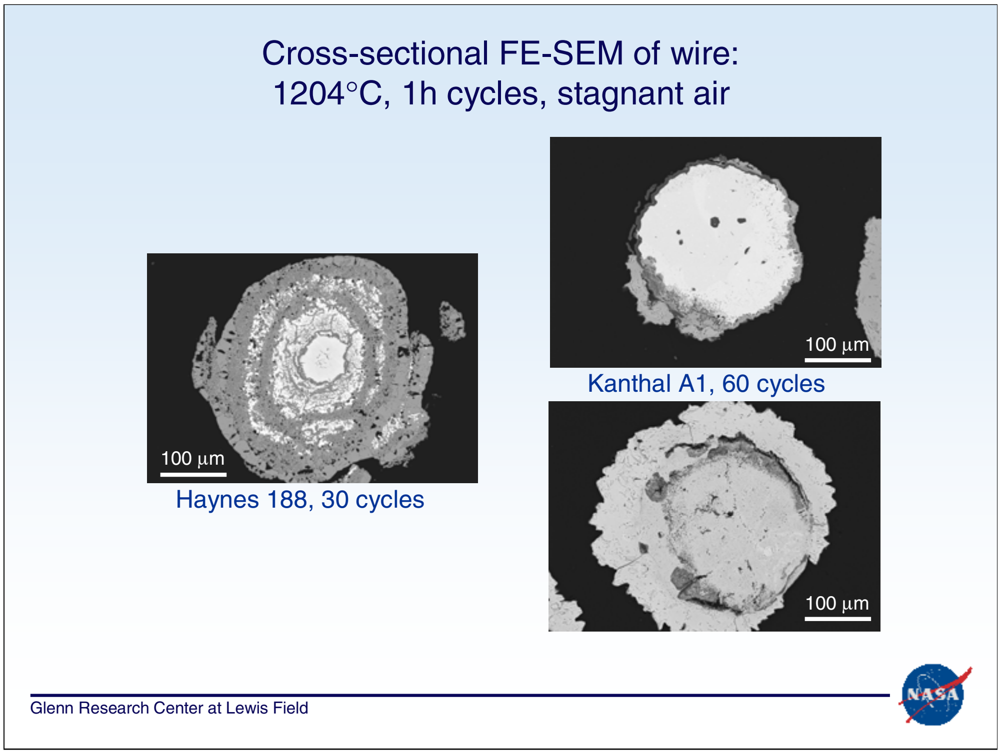
Non protective Fe2O3 found for Kanthal A1.



Haynes 188 shows core of wire still present after 30 cycles.

Kanthal A1 has some cross-sections just beginning non-protective oxide formation (top) and others completely oxidized (bottom). The original wire diameter of Kanthal A1 is marked by darker phases (alumina and chromia) in lower right micrograph.

Summary of results: Wire oxidation, 1204°C, 1h cycles, stagnant air

- Haynes 188 had similar failure time as in isothermal testing.
- Kanthal A1 failed earlier in cyclic oxidation testing. Weight loss and oxide spallation detected as early as third temperature cycle. Breakaway oxidation occurred after 55 cycles.
- PM2000 showed parabolic oxidation kinetics throughout 70h cyclic test. No evidence of spallation.

Conclusions

- Alumina-forming alloys with reactive element additions perform best at 1204°C under all test conditions: O_2, H_2O, temperature cycling
  - Slow growing oxide
  - Alumina is the most stable protective oxide scale in water vapor
  - Adherent scales
- Small diameter wires have limited oxidation lifetimes.
  - Limited reservoir of aluminum for protective scale formation
  - Smaller diameter wires more prone to spallation: increased stress in oxide due to larger radius of curvature
- Oxidation lifetimes can be predicted based on the wire diameter and rate of aluminum loss.
- From these results PM2000 is recommended as the best candidate for further development in advanced hybrid seal applications.

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