Corrosion Effects in Materials in High Temperature Gas-Cooled Reactor (HTGR) Environments

Kumar Sridharan
Department of Engineering Physics
Department of Materials Science & Engineering
University of Wisconsin, Madison

e-mail: kumar.sridharan@wisc.edu

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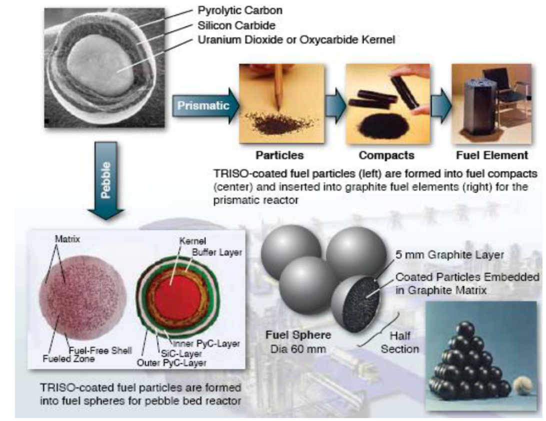
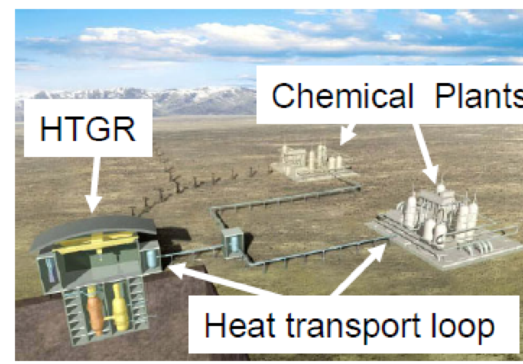
High-Temperature Gas-Cooled Reactor (HTGR) - Background

- Uses helium gas as primary coolant
- Operating temperature ~ 750^{o}C to 950^{o}C
- Graphite moderator
- TRISO fuel particles in pebble bed or prismatic configuration
- Byproduct heat for, e.g., chemical plants, hydrogen production, desalination
- Five decades of building and operating experience (Dragon, UK; Ft. St. Vrain, US; AVR, Germany)





HTGR – ASME Code Certified Materials

ASME Section III Division 5 Framework for Nuclear Components (Part II) allows for the use of only the following six alloys

Material	Fe	Ni	Cr	Co	Mo	Al	C	Mn	Si	S	Ti	Cu	B	P	V	N	Nb
304/304H	Bal	8.0-10.5	18.0-20.0		-	-	0.04-0.08/0.10	2.0 max	0.75 max	0.03 max	-	-	-	0.045 max	-	0.10 max	-
316/316H	Bal	10.0-14.0	16.0-18.0	-	2.0-3.0	-	0.04-0.08/0.10	2.0 max/ 0.04-0.10	0.75 max	0.03 max	-	-	-	0.045 max	-	0.10 max	-
800H	39.5 min	30.0-35.0	19.0-23.0	-	-	0.15-0.60	0.05-0.10	-	-	-	0.15-0.60	-	-	-	-	-	-
2.25Cr-1Mo	Bal	-	2.0-2.5	-	0.90-1.1	-	0.07-0.15	0.30-0.60	0.50 max	0.025 max	-	-	-	0.025 max	-	-	-
9Cr-1Mo-V	Bal	0.40 max	8.0-9.5	-	0.85-1.05	0.04 max	0.08-0.12	0.30-0.60	0.20-0.50	0.010 max	-	-	-	0.020 max	0.18-0.25	0.30-0.70	0.06-0.10
617	3.0 max	44.5 min	20.0-24.0	10.0-15.0	8.0-10.0	0.8-1.5	0.05-0.15	1.0 max	1.0 max	0.015 max	0.6 max	0.5 max	0.006 max	-	-	-	-

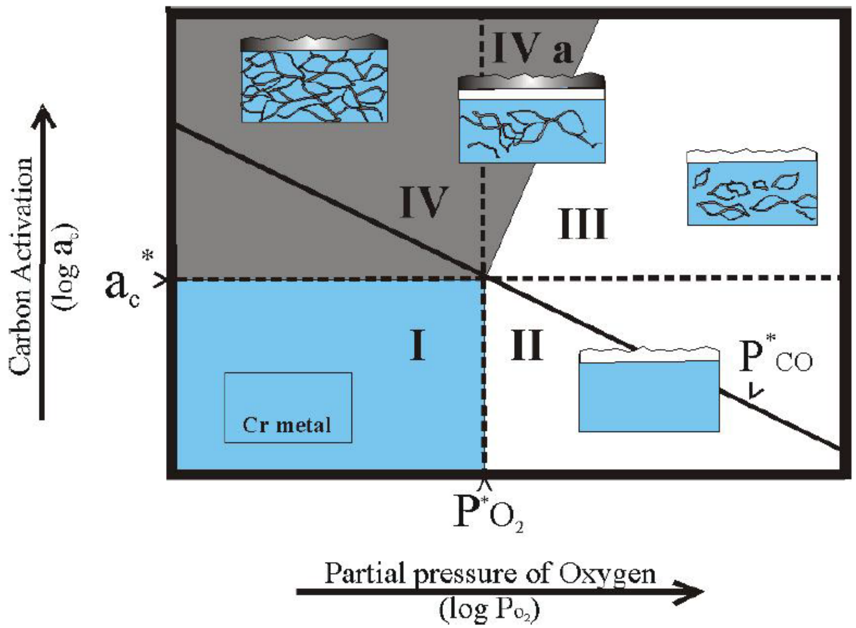
- **Alloy 800H codified for use up to 750°C for 300,000 hours**
- **Alloy 617's code case just completed for operation up to 954°C for 100,000 hours**

Dr. Richard Wright, INL

Environmental Effects in Alloys in HTGR Helium

- Helium is inert - should not corrode alloys
- However, trace levels (few ppm) impurities of H_2O, CH_4, CO,CO_2, H_2, O_2 in helium can induce corrosion in alloys
- Effect of impurities in helium on corrosion of structural alloys studied since the 1970s
- Ground-breaking papers in the 1980s (and subsequently) that provide useful guidance for the path forward

Impurity Regimes of Corrosion in HTGR Helium



- Zone 1: Reducing environment (may be decarburization)
- Zone II: Strongly oxidizing
- Zone III: Stable oxide and stable internal carbides in the alloy (most desirable)
- Zone IV: Strongly carburizing
- Zone IVa: Carburizing and oxidizing (mixed phases)

- **ppm levels of impurity shifts can alter the corrosion mechanism**
- **Cr is the most important participant in the corrosion reactions (present in 19% to 24% in 800H and 617)**

Dr. Richard Wright, INL, INL/EXT-06-11494

Where do impurities come from?

- Small amounts of H_2O and O_2 in the He entering the core
- O_2 reacts with hot graphite to form CO
- Some H_2O reacts with the hot graphite to form CO and H_2
- CO_2 degassing from graphite converts to CO
- Corrosion reactions with alloys may also produce H_2 and CO
- CH_4 can come from leakages of oils
- Radiolytic reaction of H_2 with graphite can lead to CH_4 formation

L. Graham, UK and K. Natesan et al, ANL, NUREG/CR-6824

Primary Mechanisms of Corrosion and Impurities Involved

- **Oxidation: H_2O and CO**
- **Carburization: CO and CH_4**
- **Decarburization: H_2O**

Need to form a thin, dense, adherent, thermodynamically and mechanically stable oxide layer which prevents further oxidation, and acts as a barrier for carburization and decarburization

K. Brenner and L. Graham, UK, 1984

Primary Mechanisms of Corrosion - Oxidation

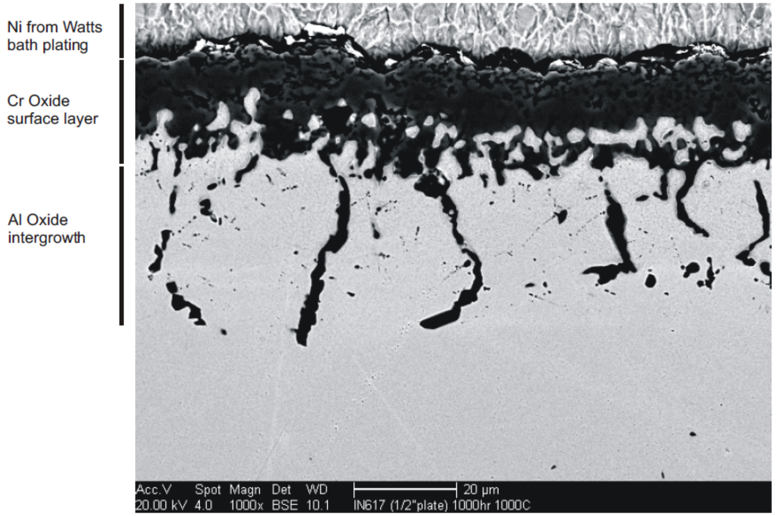
- **Oxidation: H_2O and CO**

$$2/3Cr + H_2O = 1/3\ Cr_2O_3 + H_2$$

Possibly protective Cr_2O_3

$$CO + 3Cr = 1/3\ Cr_2O_3 + 1/3\ Cr_7C_3$$

Not be protective due to co-formation of Cr_7C_3



Alloy 617 exposed to oxidizing conditions (1000°C/1000 hours); internal oxidation due to Al

Micrograph Dr. Richard Wright, INL, INL/EXT-06-11494

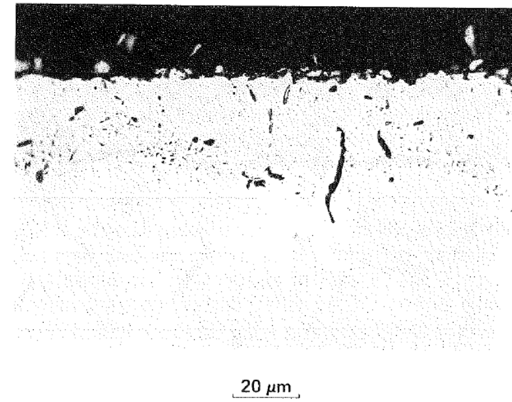
Primary Mechanisms of Corrosion - Carburization

- **Carburization: CO and CH_4**

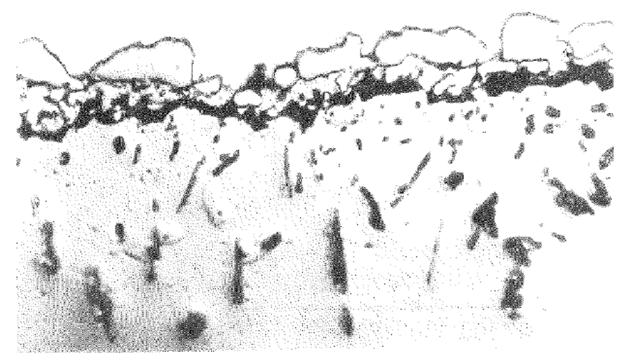
$$7/3Cr + CH_4 = + 1/7\ Cr_7C_3 + 2H_2$$

$$CO + 3Cr = 1/3\ Cr_2O_3 + 1/3\ Cr_7C_3$$

Carburization can lead to lead to loss of ductility and toughness



Carburized layer in Alloy 800H -2500 hrs, 1000°C (*H. Inouye, ORNL, 1983*)



Mixed carbide/oxide layer in Alloy 617 -10,000 hrs, 900°C (*Brenner, Germany, 1983*)

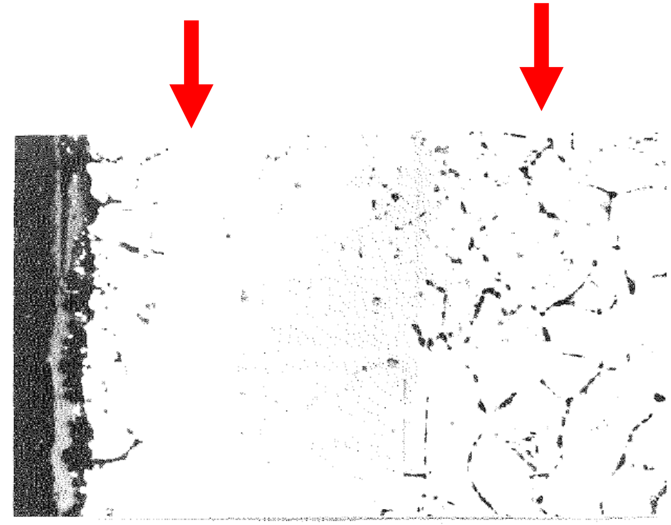
Primary Mechanisms of Corrosion - Decarburization

- **Decarburization: H_2O**

Strengthening carbide phases in alloy (typically $M_{23}C_6$ and M_6C) can get decarburized

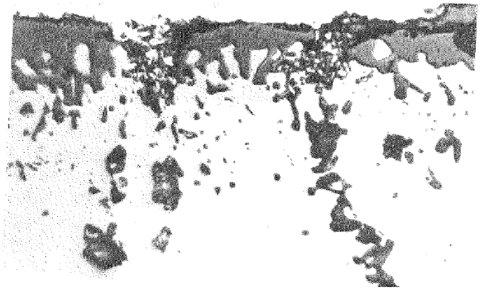
$$M\text{-}carbide + H_2O = M + CO + H_2$$

Decarburization leads to loss of creep-rupture strength

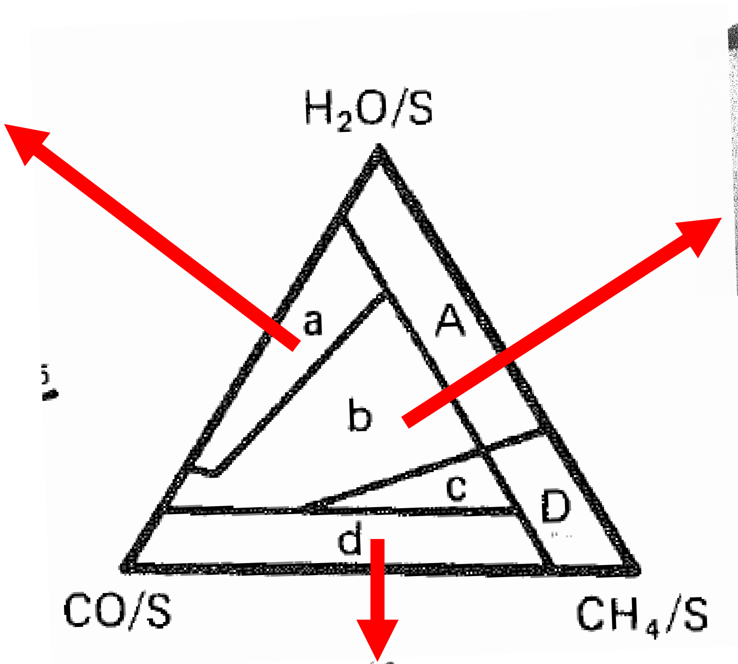


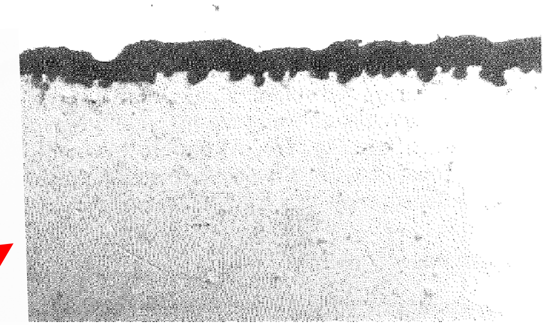
Alloy 800H subjected to decarburizing environment 870°C, 2500hrs (*Cappelaere, France, 1984*)

Conceptual Ternary Environmental Attack (TEA) Diagram



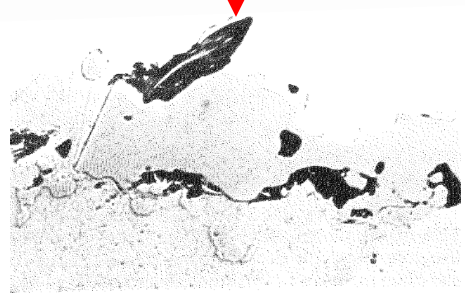
Decarburizing





Protective Oxide

Regimes of corrosion in various regimes of the three most significant impurity species

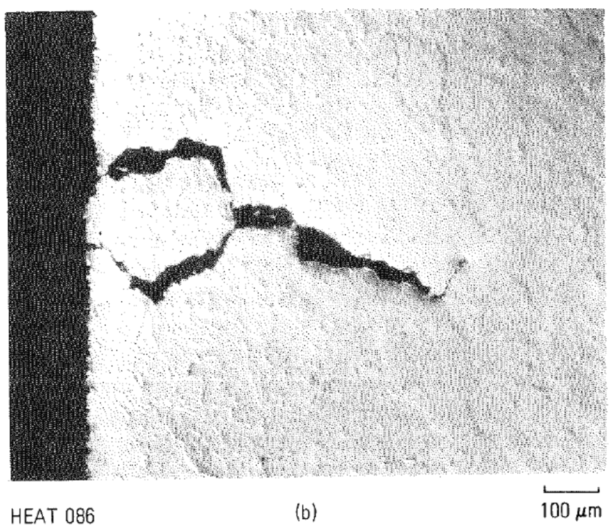


Carburizing

Work on Nimonic alloys (Ni-based, similar to Alloy 617) K. G. Brenner, UK

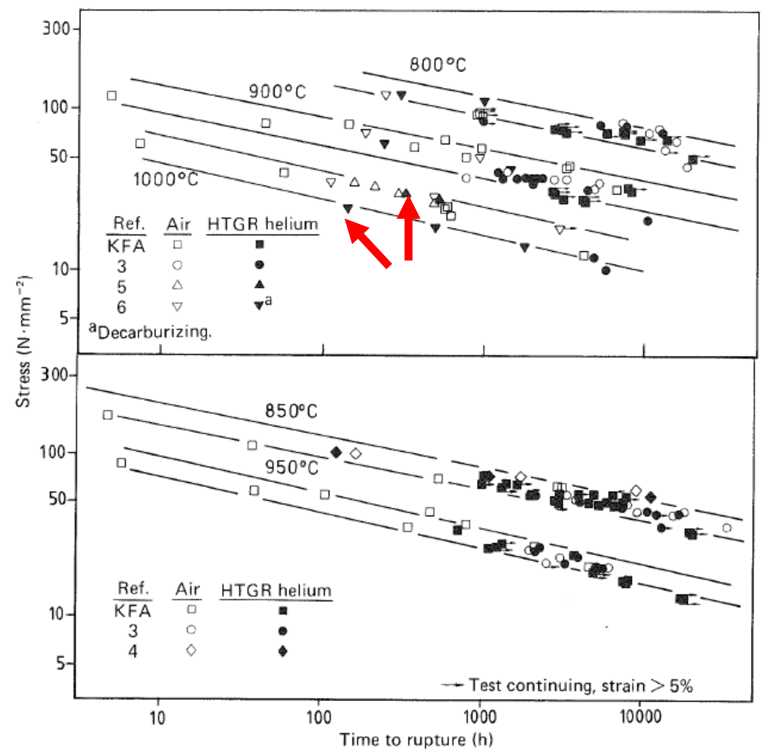
Consequences of Corrosion - Mechanical Properties

- **No instances of mechanical failures due to corrosion in HTGRs; most experimental studies performed by using accelerated carburization or decarburization conditions**



CH_4 injected in helium 900°C for 3000hs, post-tensile test cracks (*Li, US*)

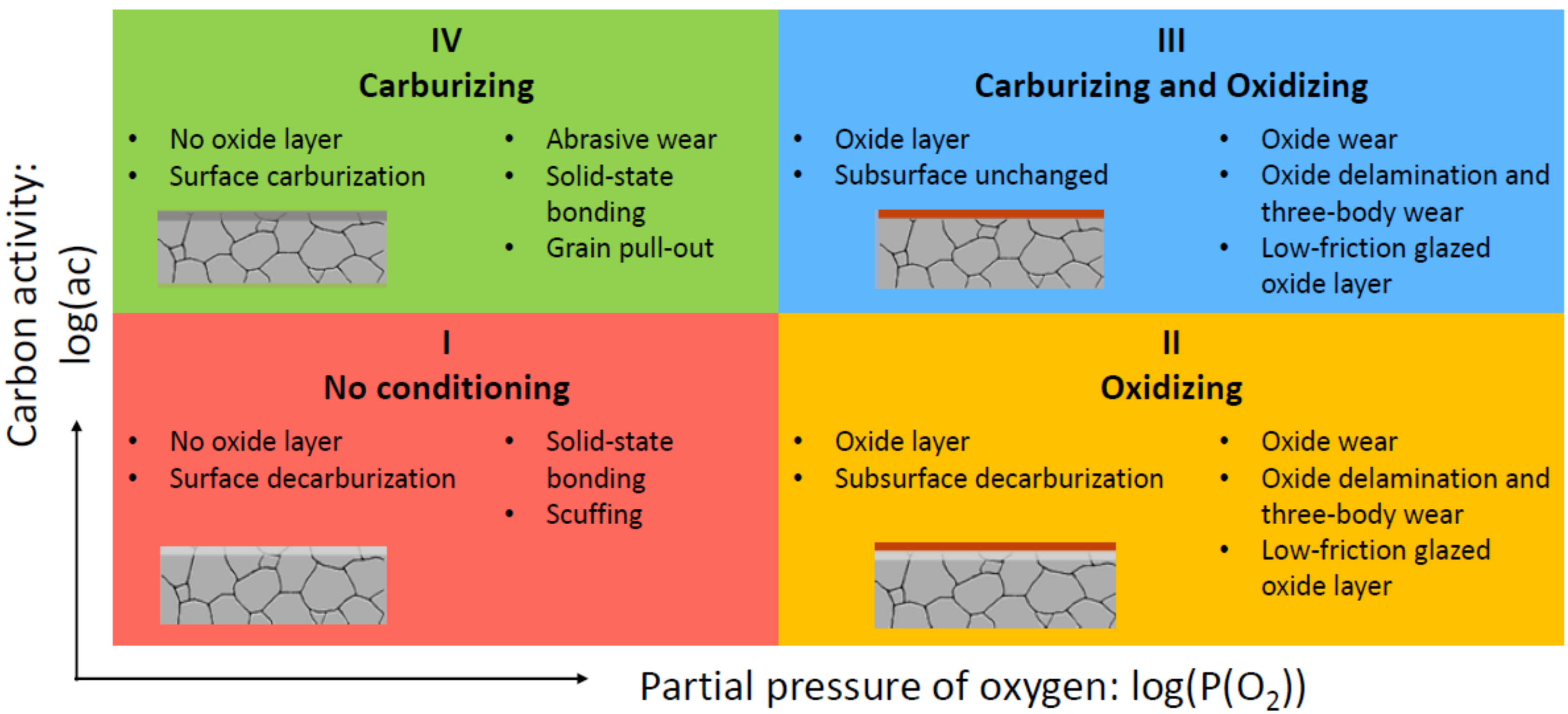
Cracks initiate in carburized layer (SCC could also be a possibility)



Creep-rupture tests (617); carburization has no effect but decarburization does at 1000°C (*Ennis, Germany*)

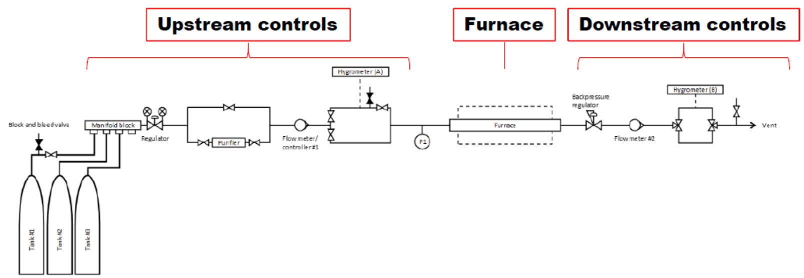
Consequences of Corrosion – Wear Behavior (NEUP – University of Wisconsin)

Wear and friction behavior between rubbing components (e.g, valves) can vary dramatically between the various corrosion regimes

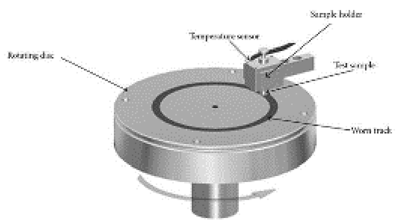


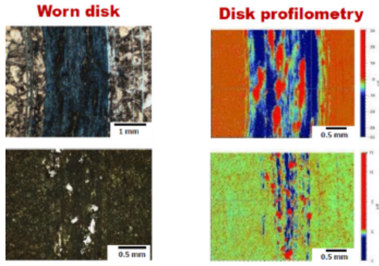
K. Sridharan PI, University of Wisconsin NEUP; D. Singh ANL (collaborator); Dr. Sam Sham TPOC

Consequences of Corrosion – Wear Behavior: Alloys 800H and 617 (NEUP – University of Wisconsin)



Once through He flow loop (impurity control at ppm level, UW



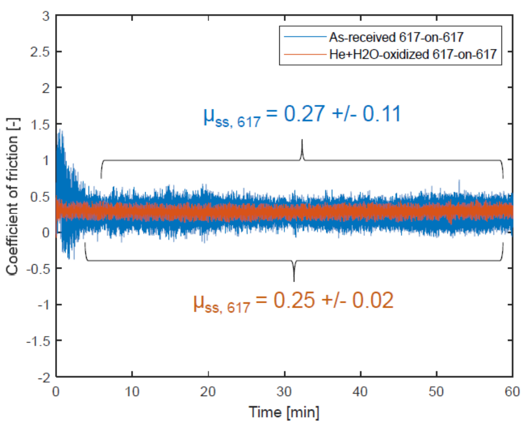


800H

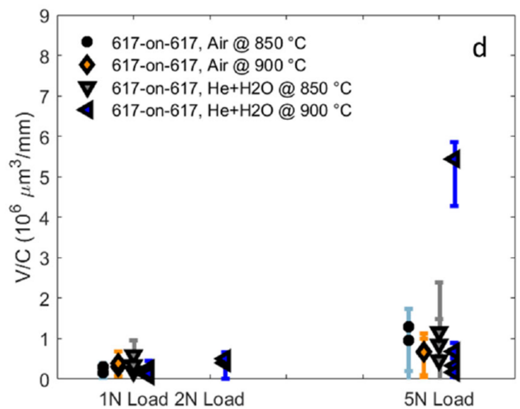
617

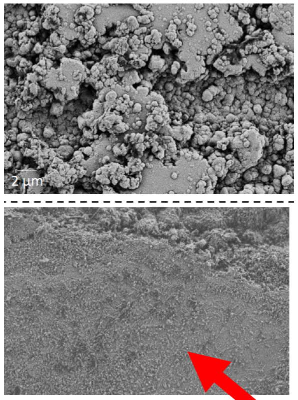
High temperature pin-on-disk wear test (ANL)

Friction measurements



Wear volume measurements





Formation of a nanocrystalline glaze oxide layer lowers friction and wear

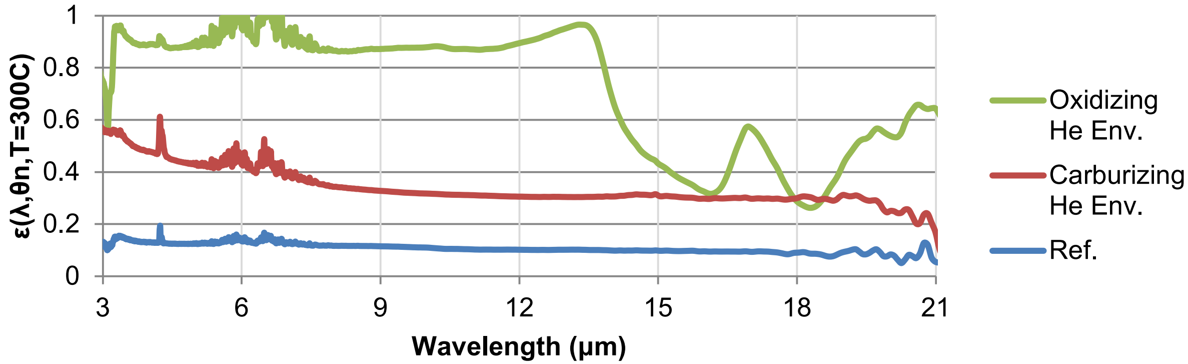
Testing temperatures:

- **650°C - 750°C for those involving 800H**
- **850°C - 950°C for 617-on-617**

University of Wisconsin – ANL NEUP

Consequences of Corrosion & Environmental Effects – Emissivity Changes (NEUP – U. Wisconsin/U. Missouri)

In-617 in 1000ºC He for 500 hours (samples from INL helium loop, Dr. Wright)

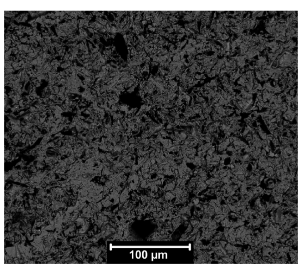


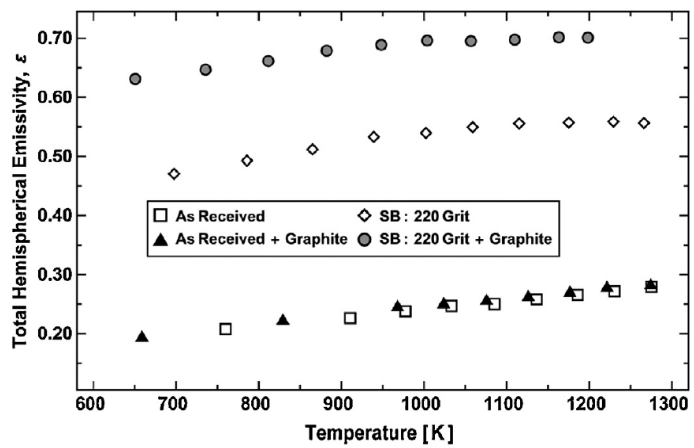
Radiation heat transfer(Q) important in HTGR

$Q = K.\varepsilon T^4$

Stefan-Boltzmann equation, ε is emissivity and T is temperature

Graphite deposition on metallic surfaces can change emissivity





University of Wisconsin - University of Missouri NEUPs; Dr. Sam Sham TPOC

Concluding Remarks

- Controlling total impurity content in helium to below 10ppm should be targeted*
- Molecular sieves are effective, but they cannot capture CO and H_2; gas flowed over CuO to convert CO to CO_2 and H_2 to H_2O*
- Back streaming of oils must be minimized*
- Graphite in HTGR core plays a dominant role in corrosion*
- Effect of flow-velocity and system pressure should be considered in corrosion prediction
- Data mining and analysis of the large amount of literature on HTGR-He corrosion of 800H and 617 will be very valuable
- Since the alloy composition cannot be altered, surface modification approaches to promote passive oxide layer formation (*making corrosion immune to the regime*) is an attractive option

Dr. Richard Wright, INL, INL/EXT-06-11494

Chemical Reactions in Gas Phase Controlling Carbon Activity and Oxygen Potential

- Carbon activity results from reactions such as:

$CO + H_2 = [C] + H_2O$ $a_c = k\,(p_{CO} \cdot p_{H2})/p_{H2O}$

$2CO = [C] + CO_2$

$CH_4 = [C] + 2H_2$

$CH_4 + CO = [2C] + H_2O + H_2$

$CO = [C] + 1/2O_2$

- Oxygen potential is determined by reactions such as:

$H_2O = 1/2O_2 + H_2$ $pO_2 = [k\,p_{H2O}\,/\,p_{H2})]^2$

$CO_2 = 1/2O_2 + CO$

K. Natesan et al, ANL, NUREG/CR-6824