

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

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

- Uses helium gas as primary coolant
- Operating temperature ~ 750°C to 950°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)







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	Со	Мо	Al	С	Mn	Si	S	Ti	Cu	В	Р	V	Ν	Nb
304/304H	Bal	8.0-	18.0-		-		0.04-	2.0 max	0.75	0.03		_	_	0.045	-	0.10	-
		10.5	20.0				0.08/0.10		max	max				max		max	
316/316H	Bal	10.0-	16.0-	-	2.0-3.0	-	0.04-	2.0 max/	0.75	0.03	-		-	0.045		0.10	
		14.0	18.0				0.08/0.10	0.04-0.10	max	max		-		max	-	max	-
800H	39.5	30.0-	19.0-			0.15-	0.05-0.10	-			0.15-		-			-	-
	min	35.0	23.0	-	-	0.60			-	-	0.60	-		-	-		
2.25Cr-1Mo	Bal	-	2.0-2.5	-	0.90-	-	0.07-0.15	0.30-0.60	0.50	0.025	-	-	-	0.025			-
					1.1				max	max				max	-	-	
9Cr-1Mo-V	Bal	0.40	0005	-9.5 -	0.85-	0.04	0.08-0.12	0.30-0.60	0.20-	0.010				0.020	0.18-	0.30-	0.06-
		max	8.0-9.5		1.05	max			0.50	max		-	-	max	0.25	0.70	0.10
<mark>61</mark> 7	3.0	44.5	20.0-	20.0- 10.0- 8.0-	0015	0.05.0.15	1.0	1.0	0.015	0.6	0.5	0.006					
	max	min	24.0	15.0	10.0	0.8-1.5	0.05-0.15	1.0 max	max	max	max	max	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

Environmental Effects in Alloys in HTGR Helium



- Helium is inert should not corrode alloys
- However, trace levels (few ppm) impurities of H₂O, CH₄, CO,CO₂, H₂, O₂ 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)

Where do impurities come from?



- Small amounts of H₂O and O₂ in the He entering the core
- O₂ reacts with hot graphite to form CO
- Some H₂O reacts with the hot graphite to form CO and H₂
- CO₂ degassing from graphite converts to CO
- Corrosion reactions with alloys may also produce H₂ and CO
- CH₄ can come from leakages of oils
- Radiolytic reaction of H₂ with graphite can lead to CH₄ formation

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

Primary Mechanisms of Corrosion and Impurities Involved



- Oxidation: H₂O and CO
- Carburization: CO and CH₄
- Decarburization: H₂O

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

Primary Mechanisms of Corrosion -Oxidation

bath plating

Cr Oxide

Al Oxide intergrowth



• Oxidation: H₂O and CO

 $2/3Cr + H_2O = 1/3 Cr_2O_3 + H_2$ Possibly protective Cr₂O₃

 $CO + 3Cr = 1/3 Cr_2O_3 + 1/3 Cr_7C_3$ Not be protective due to coformation of Cr_7C_3

Ni from Watts surface laver

> 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 CH₄

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

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

Carburization can lead to lead to loss of ductility and toughness

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



20 µm

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





Primary Mechanisms of Corrosion -Decarburization



Decarburization: H₂O

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

M-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





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



CH₄ injected in helium 900°C for 3000hs, posttensile 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



Partial pressure of oxygen: $log(P(O_2))$

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)





Testing temperatures:

30

Time [min]

-1.5

10

- Formation of a nanocrystalline glaze oxide layer lowers friction and wear
- 650°C 750°C for those involving 800H

1N Load 2N Load

14 850°C - 950°C for 617-on-617 University of Wisconsin – ANL NEUP

5N Load

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





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

Temperature [K]

Concluding Remarks



- Controlling total impurity content in helium to below 10ppm should be targeted*
- Molecular sieves are effective, but they cannot capture CO and H₂; gas flowed over CuO to convert CO to CO₂ and H₂ to H₂O*
- 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

Chemical Reactions in Gas Phase Controlling Carbon Activity and Oxygen Potential



- Carbon activity results from reactions such as:
- $CO + H_2 = [C] + H_2O$ $a_{c} = k (p_{co} \cdot p_{H2})/p_{H20}$ $2CO = [C] + CO_{2}$ $CH_4 = [C] + 2H_2$ $CH_4 + CO = [2C] + H_2O + H_2$ $CO = [C] + 1/2O_2$ Oxygen potential is determined by reactions such as: $pO_2 = [k p_{H2O} / p_{H2})]^2$ $H_2O = 1/2O_2 + H_2$

 $CO_2 = 1/2O_2 + CO$

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