

NE 591: Advanced Reactor Materials

Fall 2021

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Last Time

- Pyroprocessing
 - well established method relying on molten salt and anode deposition
- Metallic fuel performance modeling
 - BISON, ALFUS, LIFEMETAL
 - all still currently require extensive assumptions
- MOX intro
 - restructuring, Pu redistribution, Pu agglomerates

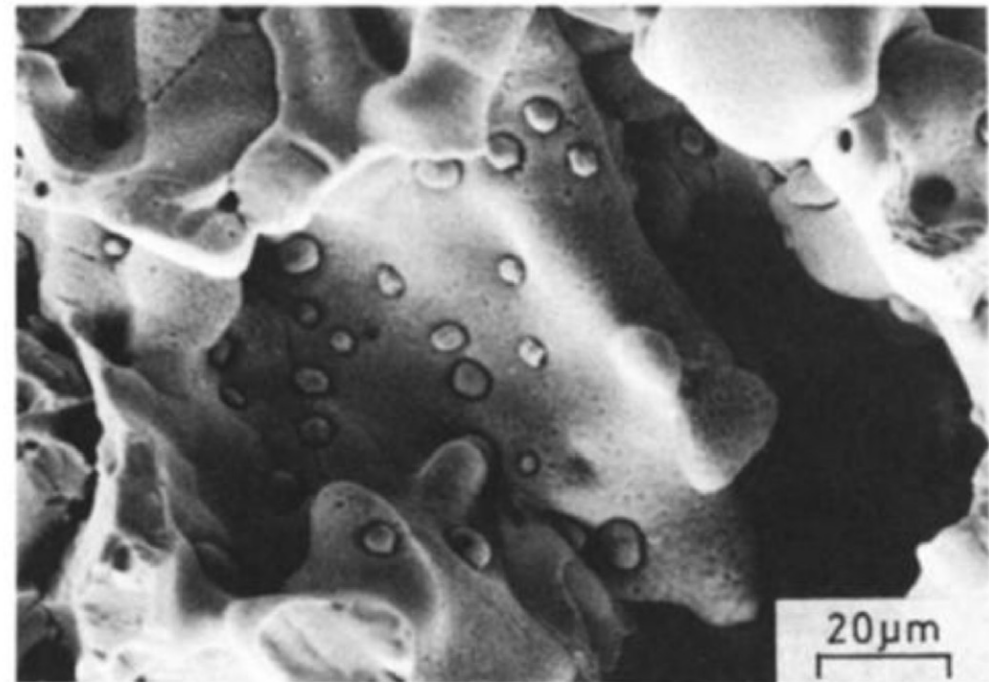
Solid Fission Products

- Fission products in oxide fuels can be grouped into 4/5 categories
- Fission gases and volatile species
- Metallic precipitates
- Oxide precipitates
- Soluble oxides
- LWR fuel vs Pu-containing MOX fuel, we see a higher concentration Ru, Rh, Pd, and a lower concentration of Zr and Mo

Fission Product	Concentration (ppm)		Fission Product	Concentration (ppm)	
	U-235	Pu-239		U-235	Pu-239
Kr	120	60	Sn	32	35
Rb	130	60	Sb	14	14
Sr	260	100	Te	140	170
Y	180	60	In	80	100
Zr	1000	650	Xe	1050	1150
Nb	7	7	Cs	960	950
Mo	890	790	Ba	390	310
Tc	220	210	La	290	260
Ru	480	800	Ce	690	630
Rh	130	230	Pr	340	260
Pd	110	580	Nd	980	870
Ag	8	80	Pm	90	110
Cd	8	35	Sm	140	220
In	1	4	Eu	20	40

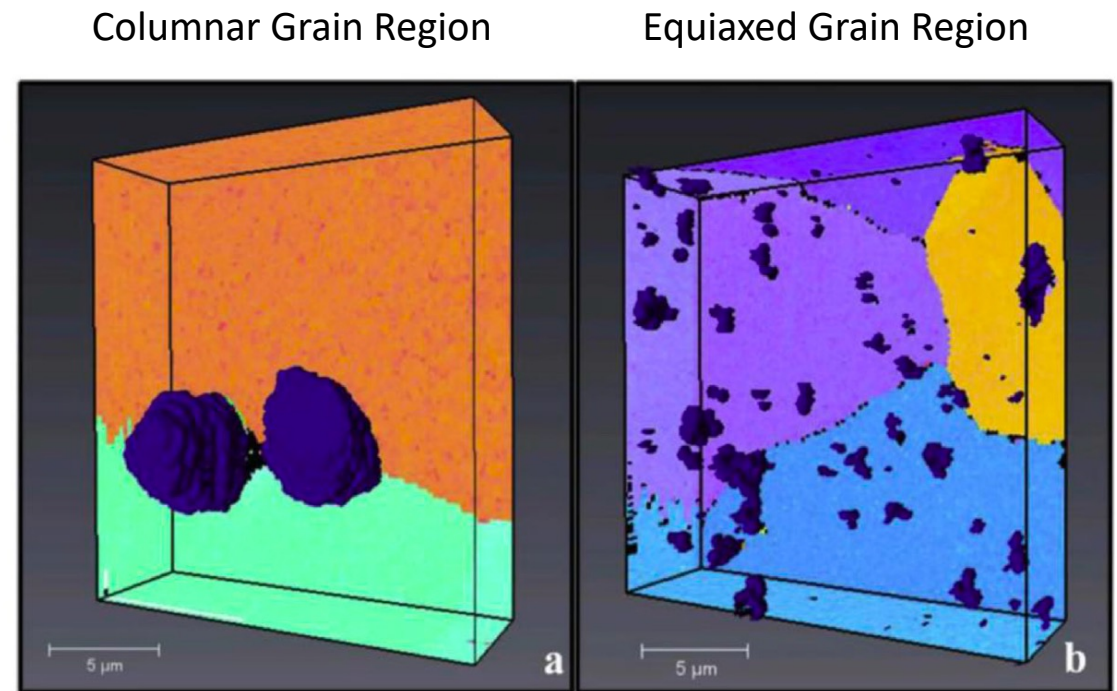
Metallic Inclusions

- Mo, Tc, Ru, Rh, and Pd form prominent phases in irradiated nuclear fuels commonly referred to as “white inclusions,” “noble metal,” or “five-metal” precipitates
- The particles exist as a solid solution taking on the hexagonal close packed (hcp) structure
- The particle size, frequency, and composition exist over a wide range, depending on the burnup and position found within the pellet



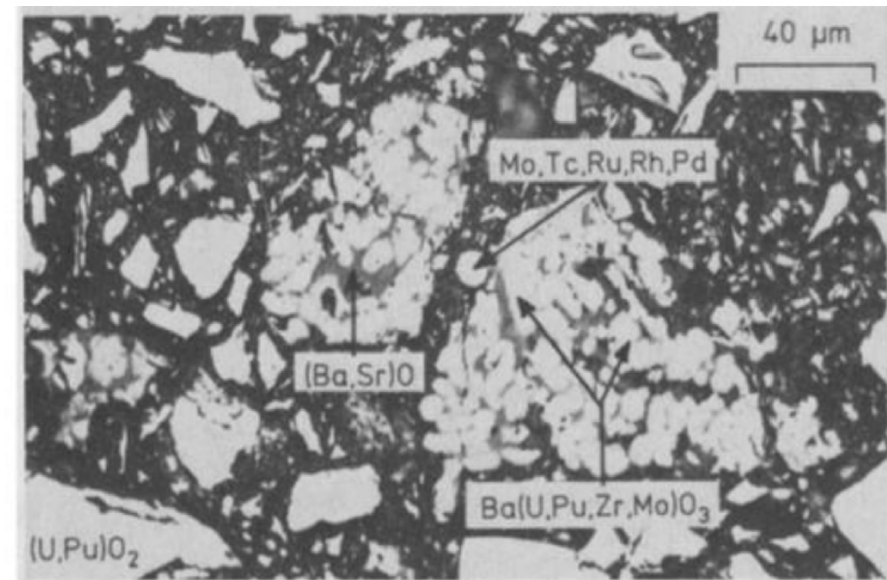
Metallic Inclusions

- In the columnar grain region of the fuel, the particles are commonly 5-10 μm in diameter, collecting primarily on the grain boundaries
- Particles tend to be much smaller (2 μm and below) in the equiaxed and as-sintered regions, but occur more frequently intragranularly
- The particles form as a result of fission product phase agglomeration, as opposed to nucleation and growth process



Oxide Phases

- Oxides containing Sr, Zr, or the rare earth (RE) elements form solid solutions with either UO_2 , PuO_2 , or both at low concentrations
- Barium is only soluble to 1.6 at% in MOX fuels and thus precipitates a separate oxide phase at higher concentrations
- These oxides, commonly referred to as the “grey phase,” form ABO_3 perovskite structures, in which $\text{A}=(\text{Ba}_{1-x-y}, \text{Sr}_x, \text{Cs}_y, x, y \ll 1)$ and $\text{B}=(\text{U}, \text{Pu}, \text{Zr}, \text{Mo}, \text{RE})$
- The particles are primarily Ba rich, followed by Zr, U, Pu, Mo, Sr, and trace amounts of the remaining products
- Due to the sheer number of constituents, the structures are largely unknown
- Grey phase is typically found in the equiaxed or outermost regions of the columnar grains commonly intermixed with other constituent oxides

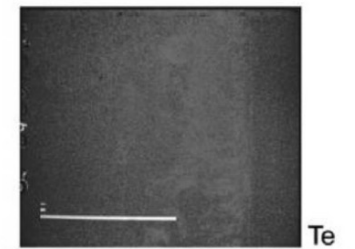
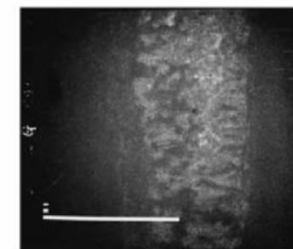
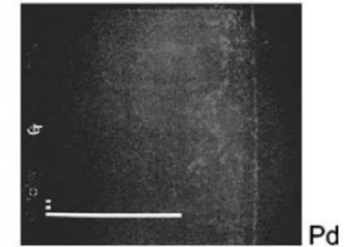
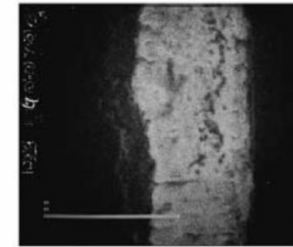
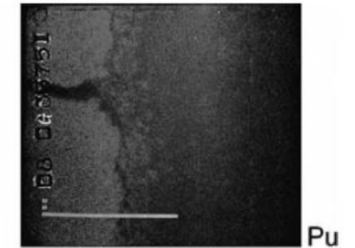
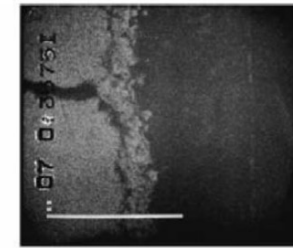
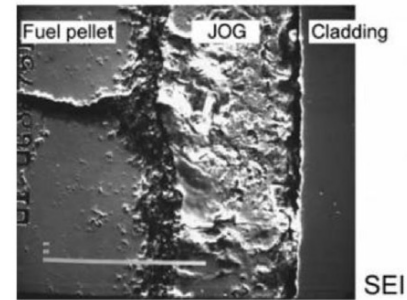


Joint Oxide Gain

- The volatiles class of fission products produced during reactor operation are of particular interest to fuel-cladding interactions
- Cs, Te, and I all evaporate at low operating temperatures and migrate to the coolest part of the fuel assembly where they react with fuel or cladding constituents
- Mo has a tendency to combine with Cs and O to become volatile and migrate toward cooler fuel regions
- This has been termed Joint Oxide Gain (JOG)
- JOG is an oxide buildup formed on the fuel surface between the pellet and cladding
- Primarily Cs_2MoO_4 or $\text{Cs}_2(\text{U}, \text{Pu})\text{O}_4$, the JOG structure is irregular and dense, found in regions where the peak fuel temperature is lowest

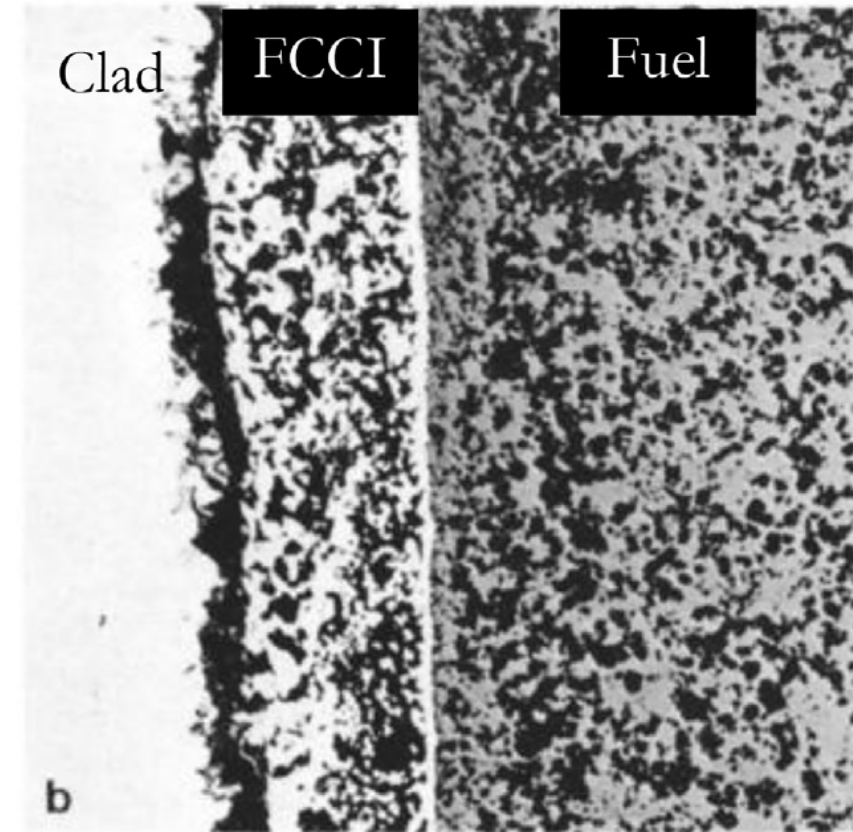
Joint Oxide Gain

- The volatile constituents of the JOG structure evaporate from the fuel pellet at high temperatures and condense to become solid at the cooler top or bottom of the fuel assemblies
- It is believed that the existence of JOG aids in thermal transport of the fuel, as the oxide structures have higher thermal conductivity than a fuel-cladding gap filled with fission gases



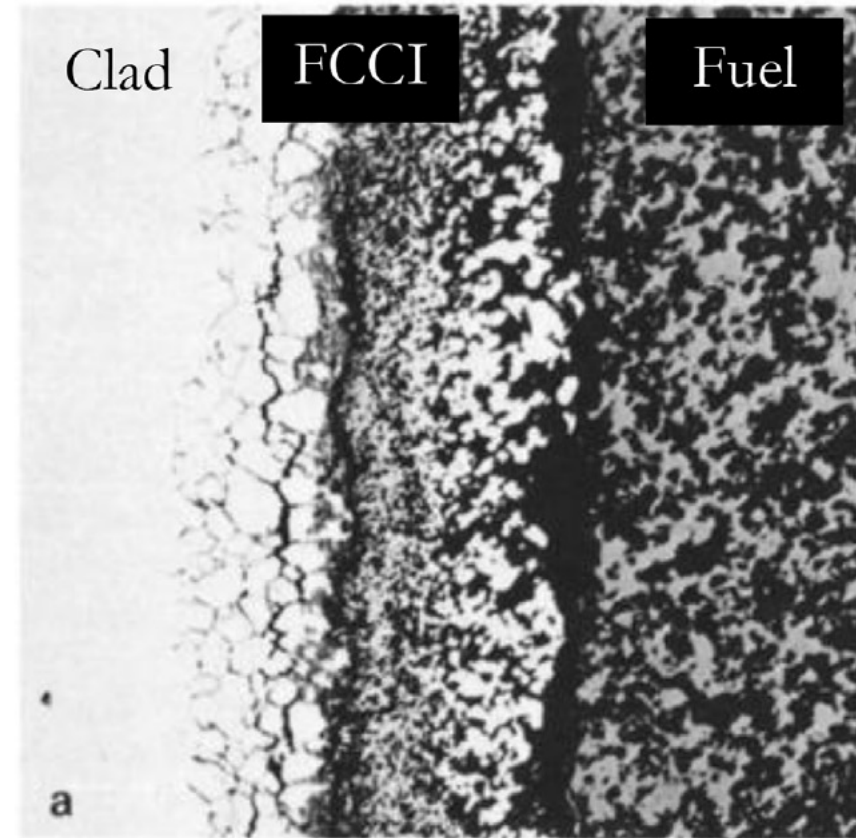
MOX FCCI

- The cladding inner surface temperature of LWR MOX fuels do not reach sufficiently high temperatures under normal operating conditions to initiate detrimental oxidation and chemical attack
- FCCI manifests itself in three primary modes: matrix attack, intergranular attack, or combined, which demonstrates the properties of both matrix and intergranular attack
- Matrix FCCI attack corresponds to the localized oxidation of the cladding material, with primarily oxidation of the Cr in the stainless steel



MOX FCCI

- Intergranular attack modes occur due to the depletion of Cr in grain boundaries due to the formation of Cr_2C_6 carbides allowing penetration of corrosive species
- Oxygen and volatile fission products (Cs, Te, I, etc.) are the primary culprits of FCCI initiation in oxide fuel systems
- In MOX fuels, the oxygen potential of the system is the greatest difference from LWR UO_2
- The preferential formation of noble metals rather than oxide formers leads to an excess of available oxygen in the system



MOX FCCI

- Under normal operation, stainless steel cladding forms a chrome oxide (Cr_2O_3) layer that acts to protect the cladding from corrosion
- Cs is generally unreactive with stainless steel claddings, but reacts with the protective oxide layer to create Cs-chromates (Cs_2CrO_4 or $\text{Cs}_2\text{Cr}_2\text{O}_7$) when excess oxygen is present
- The decay of the protective oxide layer causes deeper penetration of the FCCI into the cladding
- Iodine is primarily bound to Cs in the form of CsI , and can lead to an enhancement in oxidation in hyperstoichiometric fuels
- Tellurium is highly active when combined with Cs to create Cs_2Te , which can dissolve cladding constituents in the presence of high oxygen potential
- The O/M ratio of the fuel before and during irradiation are significant factors, and FCCI can potentially be limited by operating with a hypostoichiometric initial fuel composition

MOX Summary

- Phenomena of interest: Pu redistribution, Pu agglomerates, fission product chemistries, JOG formation, and FCCI
- O/M ratio is one of the most significant factors in determining the nature of actinide redistribution, fission product precipitate chemistries, and FCCI formation
- The effects of fission product precipitates and Pu agglomerates on fuel thermal behavior is highly localized with little discernible influence on the overall fuel burnup behavior

SODIUM COOLANT

Liquid Metal Coolants

- Liquid metals (LM), such as sodium (Na), lead (Pb), and lead–bismuth (Pb–Bi) eutectic, are considered as potential coolants for the fast spectrum nuclear reactors of the next generation

Table 1 Thermophysical parameters of Na, Pb, and Pb–Bi(e) at normal atmospheric pressure and temperature 673.15 K (400 °C)

<i>Parameter</i>	<i>Units</i>	<i>Na</i>	<i>Pb</i>	<i>Pb–Bi(e)</i>
Density	kg m^{-3}	856.0	10 578	10 194
Isobaric volumetric coefficient of thermal expansion	10^{-5} K^{-1}	27.5	12.1	12.7
Adiabatic compressibility	10^{-12} Pa^{-1}	209	29.6	33.5
Isobaric heat capacity	$\text{J mol}^{-1} \text{ K}^{-1}$	29.5	30.4	29.8
Surface tension	10^{-3} N m^{-1}	166	450	395
Saturated vapor pressure	Pa	5.2×10^1	2.8×10^{-5}	3.0×10^{-5}
Dynamic viscosity	10^{-3} Pa s	0.27	2.23	1.51
Electric resistivity	$10^{-8} \Omega \text{ m}$	21.3	98.7	123.2
Thermal conductivity	$\text{W m}^{-1} \text{ K}^{-1}$	72.6	16.6	13.1

Sodium

- Sodium is a solid at room temperature, and the melting and boiling temperatures are 97.82 and 881.4C, respectively.
- Therefore, sodium is in the liquid phase at FR operating temperatures without pressurization
- For this reason, it is not necessary to adopt the proof-pressure design employed in light water reactors for sodium-cooled FRs
- Due to high thermal conductivity and specific heat, sodium can transfer the heat of the reactor core to the power generation system efficiently
- Na has insignificant neutron moderation, making it suitable for the coolant for the FBR
- The weakness of sodium as a coolant is its reactivity with oxygen and/or water

Structural Material Selection for Na

- It is necessary to take the environment into consideration by estimating the mechanical properties and thermal characteristics
- Environments specific to the SFR components include: (a) contact with the coolant, (b) high temperature at which the creep effects must be taken into account, and (c) neutron irradiation
- The dissolution of elements contained in the material, such as iron, chromium, and nickel, in sodium and the reverse phenomenon (deposition) occur on the material surface due to the difference in chemical potential
- The behavior is fundamentally controlled by the solubility of the material elements in sodium and by the diffusion rate of the materials

Solubilities and Compatability

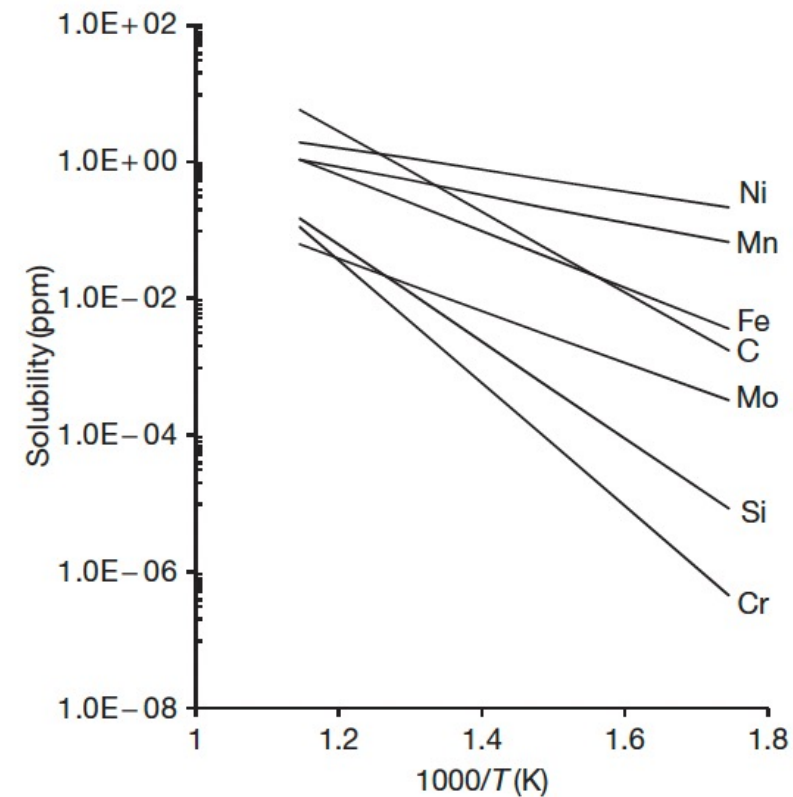
- Among the elements in austenitic stainless steel, the solubility of nickel is greatest
- Therefore, the phase transformation of austenite to ferrite through nickel dissolution is observed on the surface in long-term immersion in sodium

Element	Solubility equation	Temperature range (K)
Cu	$\log S_{\text{wwpm}} = 5.450 - 3055/T \text{ (K)}$	623–773
Ag	$\log S_{\text{wwpm}} = 7.22 - 1479/T \text{ (K)}$	377–806
Au	$S_{\text{wt}\%} = -11 + 0.52 \times (T(K) - 273.15) - 6 \times 10^{-4} \times (T(K) - 273.15)^2$	373–873
Mg	$S_{\text{wt}\%} = -0.1414 + 2.08 \times 10^{-6} \times (T(K) - 273.15) + 1.248 \times 10^{-3} \times (T(K) - 273.15)^2$	
Zn	$S_{\text{wppm}} = 1.4 + 0.057 \times (T(K) - 273.15)$	373–573
Cd	$\log S_{\text{wt}\%} = 3.67 - 1209/T \text{ (K)}$	373–600
Al	$\log S_{\text{wwpm}} = 1.4 + 0.057/T \text{ (K)}$	423–773
Ga	$\log S_{\text{wt}\%} = 1.349 - 1010/T \text{ (K)}$	375–573
In	$\log S_{\text{wt}\%} = 4.48 - 1552/T \text{ (K)}$	373–573
U	$\log S_{\text{wwpm}} = 4.36 - 6010.7/T \text{ (K)}$	560–970
Pu	$\log S_{\text{wwpm}} = 8.398 - 10.950/T \text{ (K)}$	560–970
Sn	$\log S_{\text{wt}\%} = 5.113 - 2299/T \text{ (K)}$	473–673
Pb	$\log S_{\text{wt}\%} = 6.1097 - 2636/T \text{ (K)}$	393–523
Bi	$\log S_{\text{wt}\%} = 2.15 - 2103/T \text{ (K)}$	398–563
	$\log S_{\text{wt}\%} = 5.67 - 4038/T \text{ (K)}$	563–923
Cr	$\log S_{\text{wwpm}} = 9.35 - 9010/T \text{ (K)}$	948–1198
Mo	$\log S_{\text{wwpm}} = 2.738 - 2200/T \text{ (K)}$	500–720
Mn	$\log S_{\text{wwpm}} = 3.640 - 2601/T \text{ (K)}$	550–811
Fe	$\log S_{\text{wwpm}} = 4.720 - 4116/T \text{ (K)}$	658–973
Co	$\log S_{\text{wwpm}} = 0.010 - 1493/T \text{ (K)}$	673–973
Ni	$\log S_{\text{wwpm}} = 2.07 - 1570/T \text{ (K)}$	673–973

Material	Compatible with alkali metal up to (°C)				Factors influencing compatibility
	Li	Na	K	Rb and Cs	
Mg alloys	n.c.	n.c.	300	300	Metal solubility, oxygen exchange
Al alloys	n.c.	350	400	450	Metal solubility
Cu alloys	300	400	400	400	Metal solubility
Ag and its alloys	n.c.	n.c.	n.c.	n.c.	High metal solubility
Au and its alloys	n.c.	n.c.	n.c.	n.c.	High metal solubility
Zn coatings	n.c.	n.c.	n.c.	n.c.	High metal solubility
Pb and its alloys	n.c.	n.c.	n.c.	n.c.	Very high metal solubility
Sn and its alloys	n.c.	n.c.	n.c.	n.c.	Very high metal solubility
Fe	500	700	700	700	Nonmetallic impurities
Low-alloy steels	500	700	700	700	Nonmetallic impurities
Ferritic steels	500	700	700	700	Nonmetallic impurities
High-Cr steels	500	700	700	700	Nonmetallic impurities
Austenitic steels	450	750	750	750	Nonmetallic impurities
Ni alloys	400	600	600	600	Flow velocity
Mo alloys	1000	1000	1000	1000	Nonmetallic impurities
W alloys	1000	1000	1000	1000	Nonmetallic impurities
Ti alloys	700	700	700	700	Nonmetallic impurities
Zr alloys	700	700	700	700	Nonmetallic impurities
V alloys	700	700	700	700	Nonmetallic impurities
Nb alloys	700	700	700	700	Nonmetallic impurities
Ta alloys	700	700	700	700	Nonmetallic impurities
Sintered Al_2O_3	350	500	500	500	Thermomechanical action
Stab. ZrO_2/CaO	350	350	350	350	Intergranular corrosion
Stab. $\text{ThO}_2/\text{Y}_2\text{O}_3$	400	550	550	550	Intergranular corrosion
Glass	n.c.	250	250	250	Chemical reaction
UO_2		750			Excess of oxygen
UC		750			Nonmetallic impurities

Sodium Corrosion

- There are two known mechanisms of sodium corrosion
 - Type I: corrosion produced by the dissolution of alloy elements to sodium
 - Type II: corrosion produced through chemical reaction with the impurities in sodium
- Type I corrosion corrosion is dependent on the solubility in sodium of the elemental composition in the material, temperature, and the rate of solution

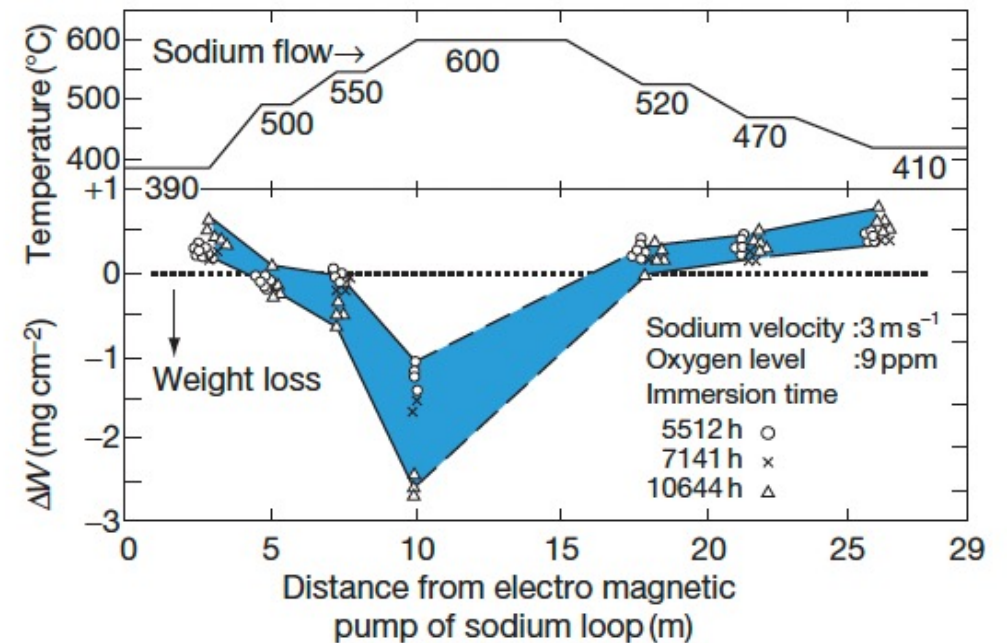


Sodium Corrosion

- The solubility of each of the primary components of stainless steel in sodium at 550 C is less than a few parts per million
- This means that the nominal compatibility of the steels with sodium is excellent
- In the isothermal sodium condition, the corrosion of the steels stops when the dissolved elements reach saturation concentration at the temperature of sodium
- This corrosion behavior called thermal gradient mass transfer under non-isothermal conditions
- In the cooling system, the elements in the materials in the high-temperature section dissolve as a result of the temperature dependency of the solubility of the elements in sodium, and the dissolved elements are deposited on the steel surface in the low-temperature section by the same mechanism

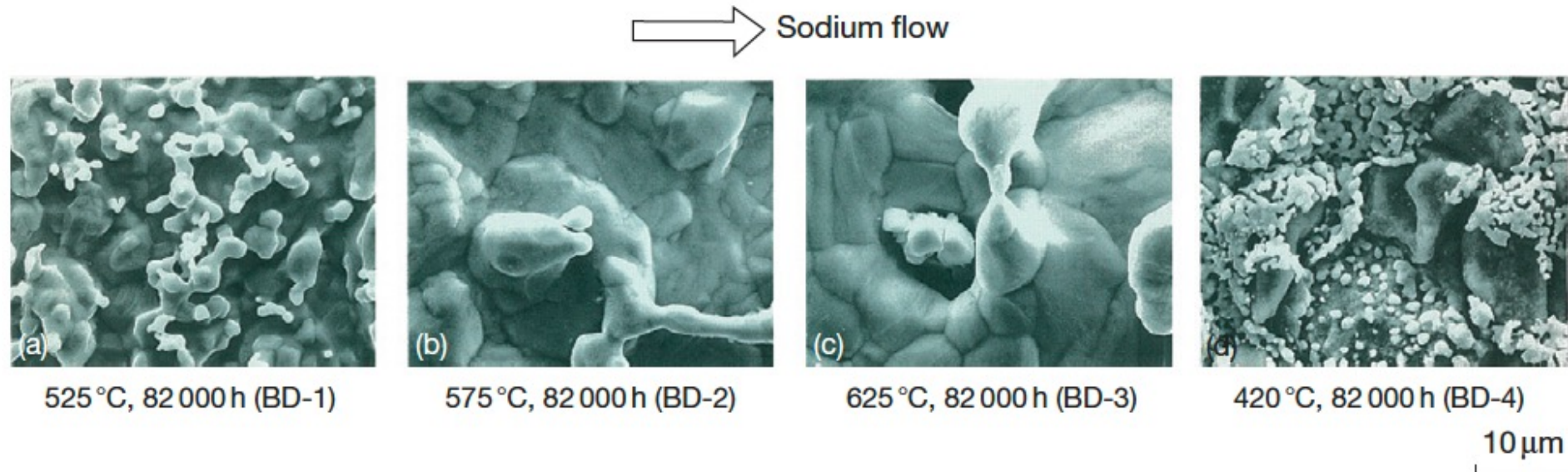
Sodium Corrosion

- The results of thermal gradient mass transfer using a sodium loop made of 316SS
- The weight loss caused by the dissolution of the elements in the steel is measured in the high-temperature section, and the weight gain caused by the deposit of the dissolved elements in sodium is observed in the low-temperature section



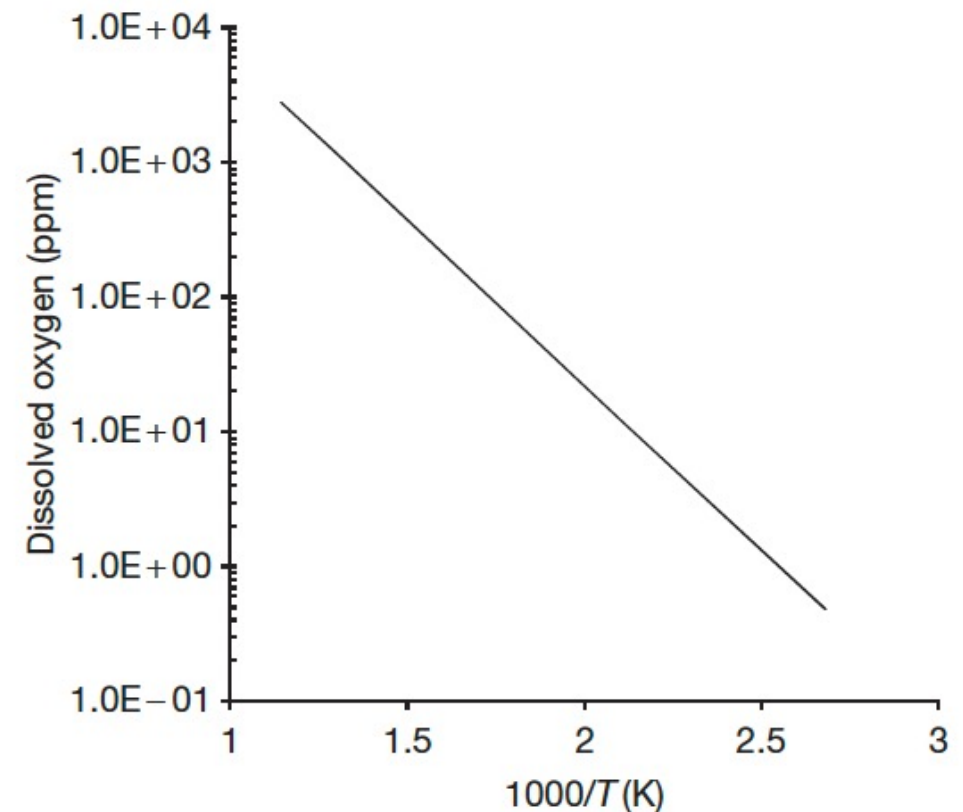
Sodium Corrosion

- Dissolution of the elements in the material is observed in the high-temperature section, and precipitation is observed in the low-temperature section



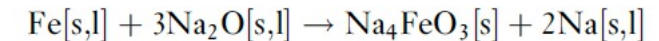
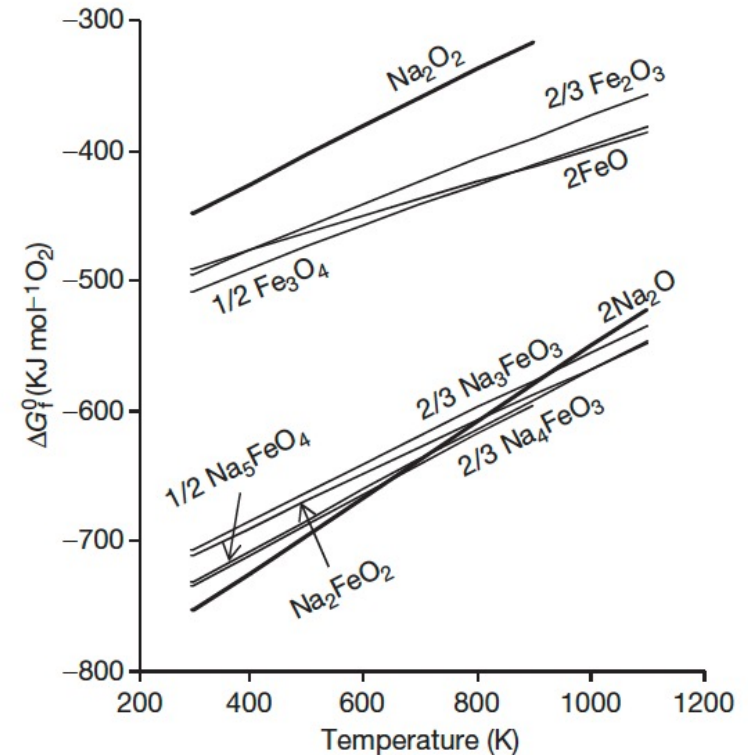
Sodium Corrosion

- Type II-Corrosion Produced Through Chemical Reaction with the Impurities in Sodium
- The most important element in the impurities in sodium is oxygen
- Sodium is the reducing agent, and its affinity to oxygen is very strong
- The solubility of oxygen in sodium is significantly higher than in water
- The introduction of oxygen into sodium may occur during refueling, supplementing of the reactor cover gas, opening of the coolant boundary for maintenance operations, etc.



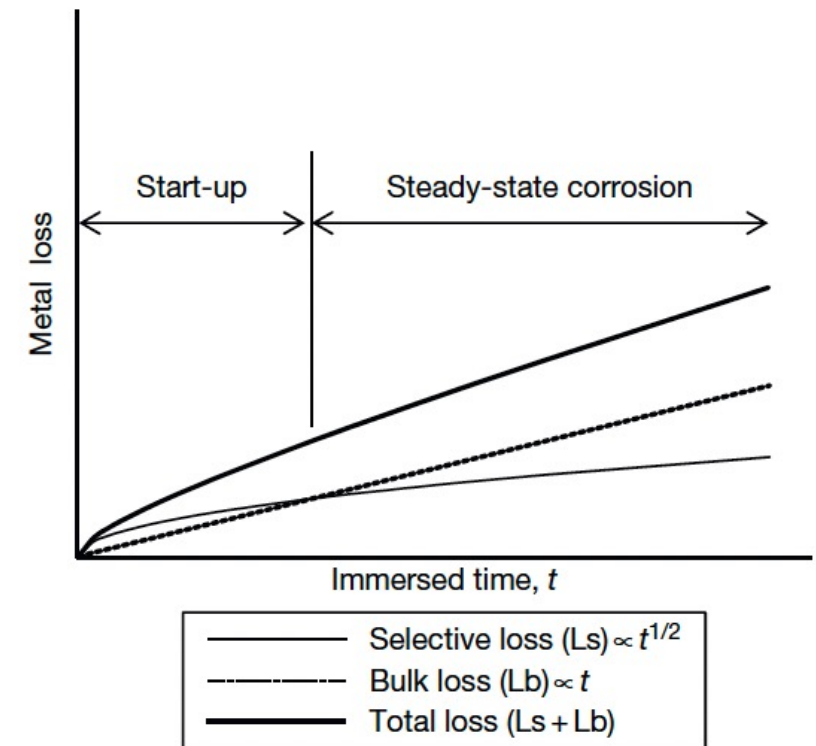
Sodium Corrosion

- These are the paths for contamination through oxides adhering to the components and the impurities in the gas
- The control of impurities in sodium can be achieved by using techniques to deposit the dissolved impurities in sodium
- The thermodynamically stable oxide in sodium is sodium oxide, Na_2O
- Fe spontaneously reacts with Na_2O above 380°C , forming Na_4FeO_3



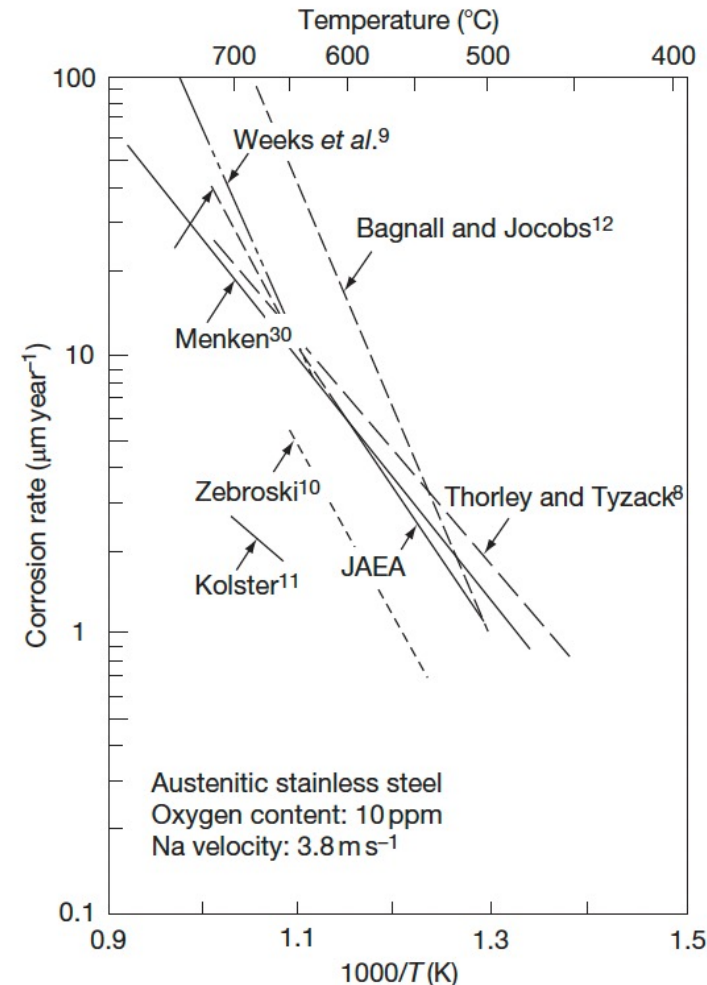
Na Corrosion of Steel

- The important factors which influence the corrosion of the steels in sodium are: (1) immersion time, (2) temperature, (3) dissolved oxygen, (4) sodium velocity, (5) alloy elements, and (6) carburization and decarburization
- Ni and Mn have high Na solubilities and dissolve first in selective (start-up) corrosion, whereas Fe corrodes in general (steady-state) corrosion



Na Corrosion of Steel

- Corrosion rate follows an Arrhenius function
- The activation energy is a function of temperature, and agrees with the activation energy of solubility in Na
- This matches the understanding of corrosion through dissolution processes
- The corrosion rate is proportional to the oxygen concentration to a power n
- Thus, limiting O₂ in the Na can limit corrosion

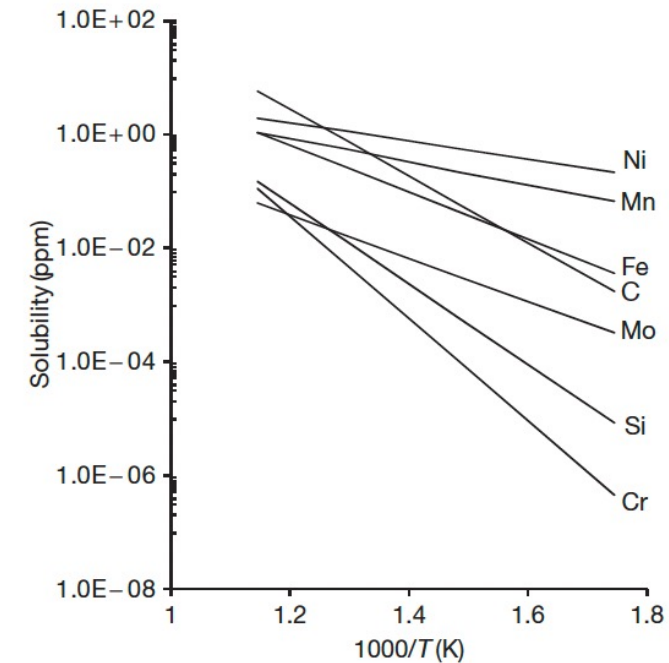
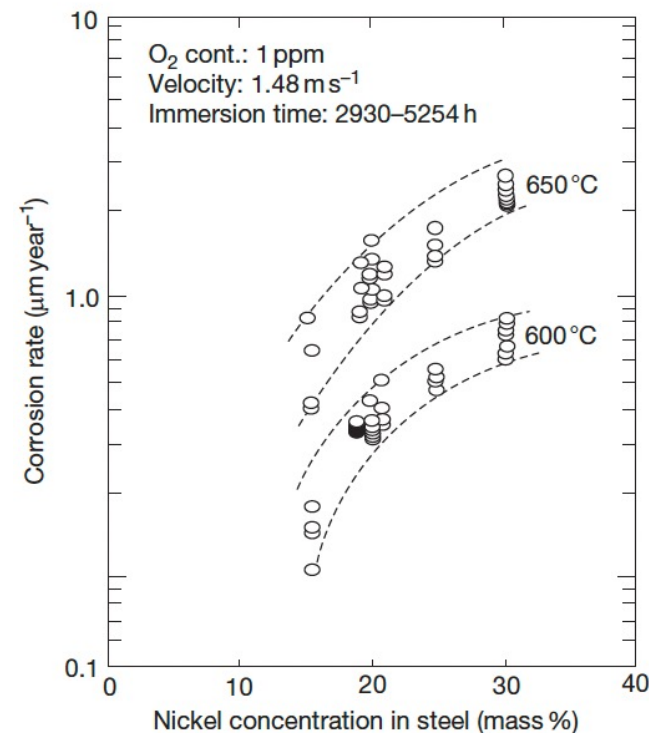


Bibliography	Sodium temperature (°C)	Activation energy (kJ mol ⁻¹)
Thorley	450–725	73.5
Weeks	538–705	108.8
Zebroski	500–700	110.5
Kolster	650–700	114.2
Bagnall	593–723	167.4
Maruyama	500–650	92–109

Bibliography	O ₂ content (ppm)	Coefficient (n)
Thorley	5–100	1.5
Zebroski	12, 50	1, 1.56
Roy	5–30	1.2
Kolster	1–8	0.91
	8–40	>1
Maruyama	2.5–9	0.8

Na Corrosion in Steel

- Because this is a dissolution driven process, the alloying elements are key to corrosion rates
- Ni is especially soluble in Na, and as Ni content increases, corrosion rates increase
- Cr has a much low solubility in Na and is thus preferred as an alloying element for Na-facing components
- Decarburization of steels can also occur due to the temperature-dependent solubility of C in Na



Na Corrosion in Monju

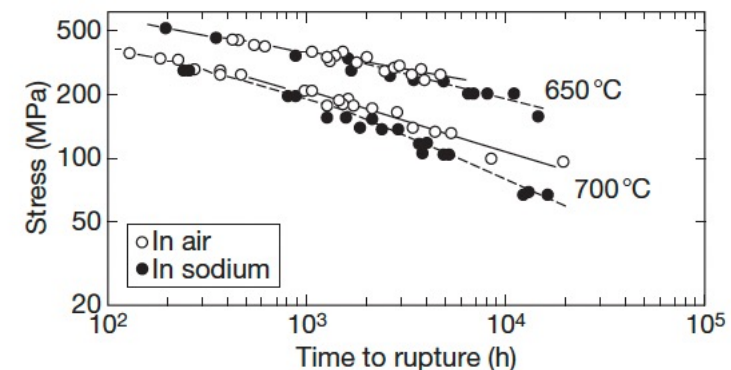
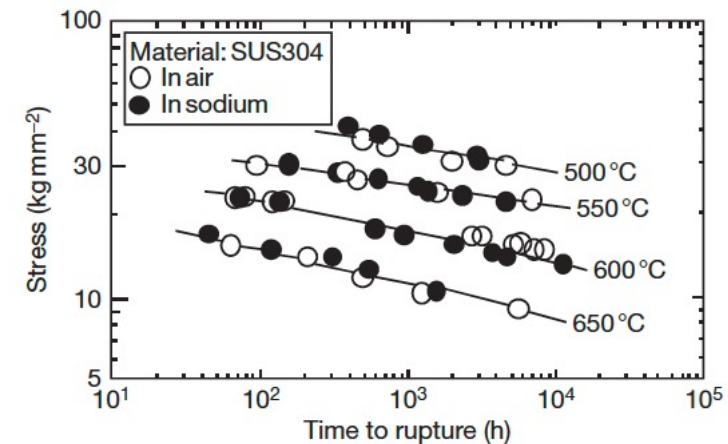
- A corrosion formula was applied for the design and operation of the SFR Monju, where the rate R is in mm/yr
- This equation is valid for structural materials types 304SS, 316SS, 321SS, and 2.25Cr–1Mo steel, and takes into account temperature and dissolved oxygen concentration
- Slightly modified equations were developed for cladding materials

$$\log_{10} R = 0.85 + 1.5\log_{10} C_o - 3.9 \frac{10^3}{T + 273}$$

Sodium Effects on Mechanical Properties

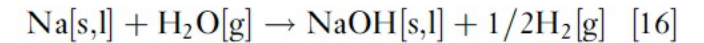
- The effect of sodium on the mechanical strength of steel is determined by three factors: (a) corrosion and mass transfer, (b) decarburization and carburization, and (c) reduction
- Since the cladding tubes are thin components and are exposed to high temperatures, the sodium corrosion affecting the base metal is larger than that of the structural materials

Creep Strength

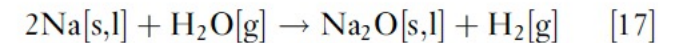


Na-Water/Air Reactions

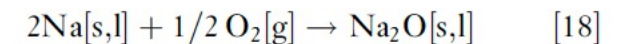
- One of the weak points of the present SFRs is the steam generator
- If the steam generator tube is damaged, high-temperature pressurized steam is blown into the sodium
- The environment around the failed tube is heated to high temperature (potentially up to 1200C) due to exothermic reactions
- When high-temperature sodium is leaked into the atmosphere, it reacts with oxygen, and sodium oxides are formed



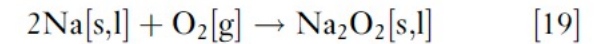
$$\Delta H_{\text{r}298}^0 = -183.8\text{KJmol}^{-1}, \Delta G_{\text{r}298}^0 = -150.9\text{KJmol}^{-1}$$



$$\Delta H_{\text{r}298}^0 = -172.8\text{KJmol}^{-1}, \Delta G_{\text{r}298}^0 = -147.2\text{KJmol}^{-1}$$



$$\Delta H_{\text{r}298}^0 = -414.6\text{KJmol}^{-1}, \Delta G_{\text{r}298}^0 = -147.2\text{KJmol}^{-1}$$



$$\Delta H_{\text{r}298}^0 = -510.9\text{KJmol}^{-1}, \Delta G_{\text{r}298}^0 = -447.5\text{KJmol}^{-1}$$

Summary

- Na has high thermal conductivity, high heat capacity, and can exist as a liquid at operational temperatures and atmospheric pressures
- Na is generally compatible with steels, but corrosion does take place
- Corrosion is a dissolution type process, and weight gain/loss can occur due to temperature gradients producing differing solubilities, and interaction with impurities such as oxygen
- Compared to LWR aqueous corrosion, Na is well behaved, corrosion is fairly slow, and it does not significantly degrade mechanical properties

QUESTIONS?

Concluded SFRs

- Quiz on SFR lectures next Thursday, 9/30