

NE 795-014: Advanced Reactor Materials

Fall 2023

Dr. Benjamin Beeler

Housekeeping

- No office hours next week (on travel)
- Presentation info:
 - one presentation modification won out
 - Due date: Nov. 6; presentations on 7th and 9th
 - Slides submitted via moodle
 - 20 minute presentation (hard limit)
 - Examination of topic: background, relevance, latest research, etc.
 - Provide a list of references as a supplementary slide
 - Grade based upon technical content, organization, logic flow, etc.

Last Time

- MOX fuels for SFRs
- MOX restructures into four regions, driven by very high temperatures
 - central void, columnar grains, large equiaxed, as-fab grains
- Pu and actinides migrate toward central pore, U away, due to condensation/evaporation pore migration
- Oxygen also moves down T gradient
- JOG and FCCI are critical phenomena
- High O potential at fuel surface allows for JOG formation (Cs-Mo-O) and for FCCI phases (Cs-Cr-O) to form
- MOX fuels are fabricated with low O content

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
- The main advantages of Na coolant in comparison with Pb are the lower melting temperature, density and dynamic viscosity and the higher thermal and electrical conductivities

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; melting point is 98 C; boiling point is 881 C
- Therefore, sodium is in the liquid phase at FR operating temperatures without pressurization
- For this reason, it is not necessary to adopt the pressurized design employed in light water reactors for SFRs
- Sodium is a great heat transfer medium due to high thermal conductivity, high heat capacity, and large liquid range
- Allows for high power density core and low coolant fraction
- 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

Structural Materials in SFRs

- Austenitic and ferritic/martensitic steels are two key alloy classes for SFR structural materials
- Most research has been done on SS-304 and SS-316, but advanced alloy behavior (T91, ODS steels, etc.) is being studied

Table 1 Structural materials for sodium-cooled fast reactors

	<i>Vessel</i>	<i>Piping</i>	<i>IHX</i>	<i>Steam Generator</i>	
				<i>Evaporator</i>	<i>Superheater</i>
EBR-II	SS-304	SS-304	SS-304	Fe-2.25Cr-1Mo	Fe-2.25Cr-1Mo
Fermi-I	SS-304	SS-304	SS-316	Fe-2.25Cr-1Mo	Fe-2.25Cr-1Mo
FFTF	SS-304	SS-316	SS-304	–	–
BN-600	SS-304	SS-304	SS-304	Fe-2.25Cr-1Mo	SS-304
SPhenix	SS-316L(N)	SS-304L(N)	SS-316L(N)	Alloy 800	
PFR	SS-321	SS-321	SS-316	Fe-2.25Cr-1Mo	SS-316/9Cr-1Mo
PFBR	SS-316	SS-316	SS-316LN	Modified 9Cr-1Mo	

Solubilities and Compatibility

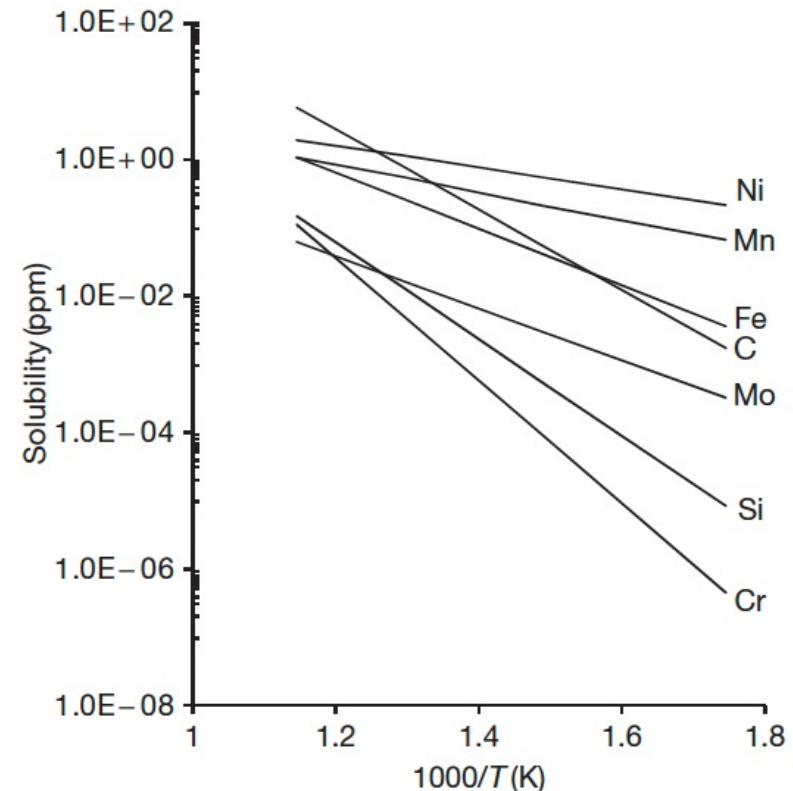
- Among the elements in austenitic stainless steel, the solubility of nickel is greatest
- Therefore, the phase transformation of austenite to ferrite through nickel dissolution is observed on the surface in long-term immersion in sodium

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 is dependent on the solubility in sodium of the elemental composition in the material, temperature, and the rate of solution



$$R_c = K(C_s - C_i)$$

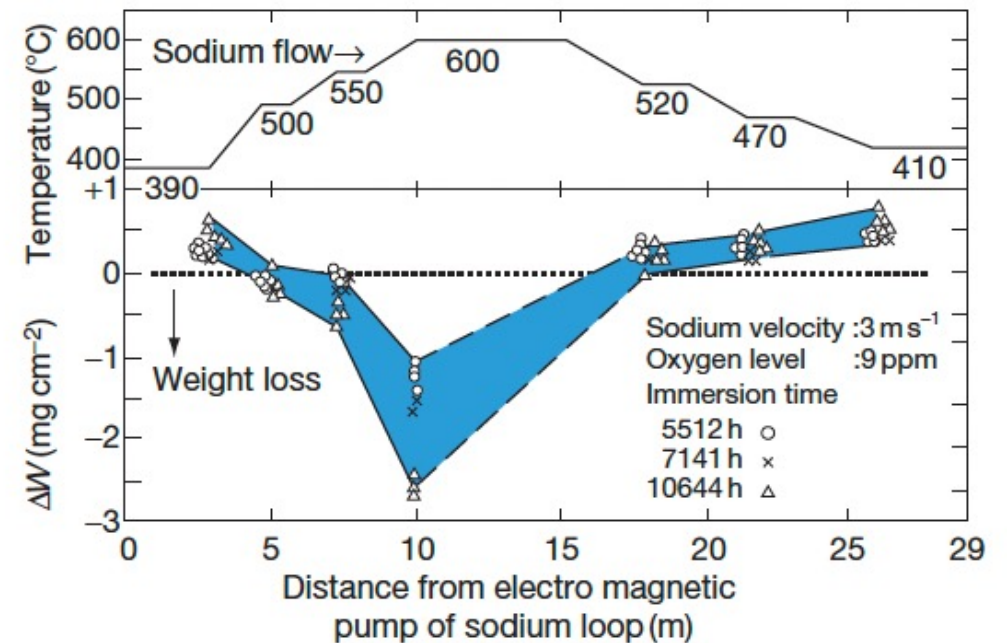
K is the solution rate constant, C_s is the solubility limit in sodium, and C_i is the actual concentration in sodium

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 is 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

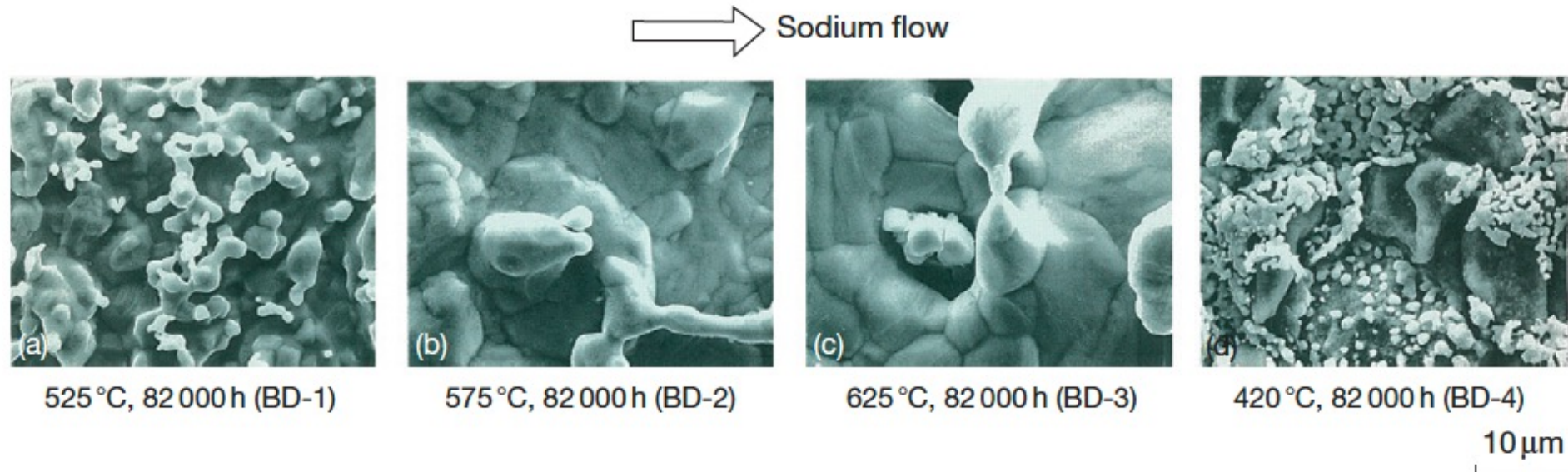
Sodium Corrosion

- 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



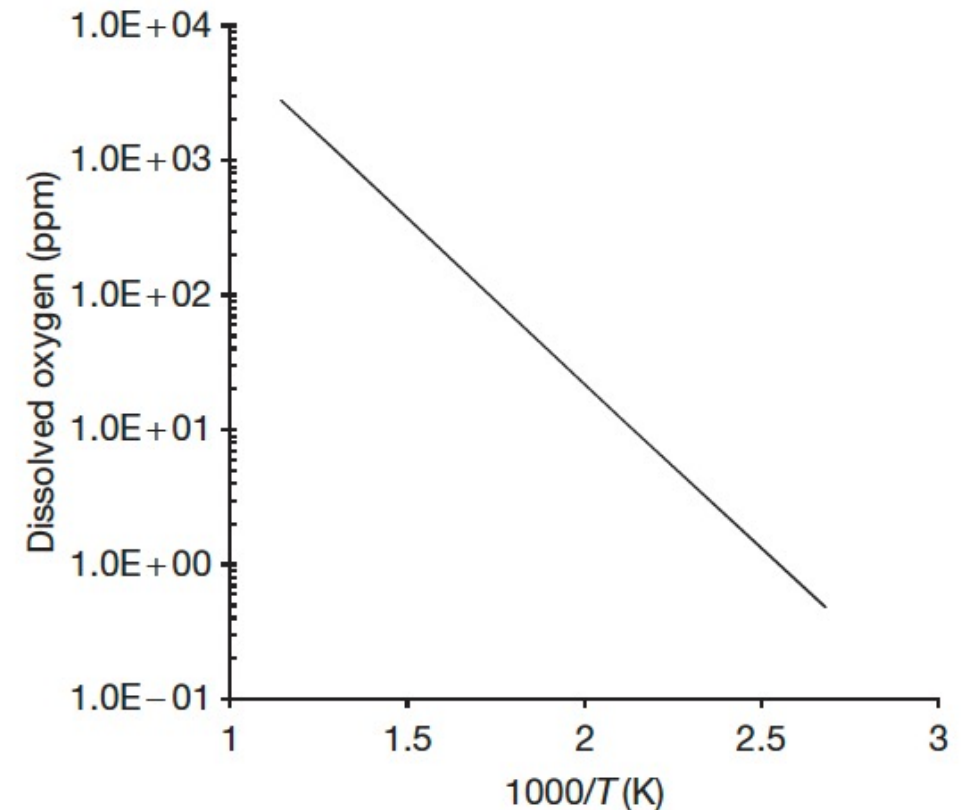
Sodium Corrosion

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



Impurity Sodium Corrosion

- Type II-Corrosion Produced Through Chemical Reaction with the Impurities in Sodium
- The control of impurities in sodium can be achieved by using techniques to deposit the dissolved impurities in sodium
- Impurities such as oxygen, carbon and nitrogen in sodium can have a strong effect on the corrosion rate of a material
- 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



Oxygen Acceleration

- 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.
- The thermodynamically stable oxide in sodium is sodium oxide, Na₂O
- Fe spontaneously reacts with Na₂O above 380°C, forming Na₄FeO₃
- These reactions increase the effective solubility of Cr/Fe in Na

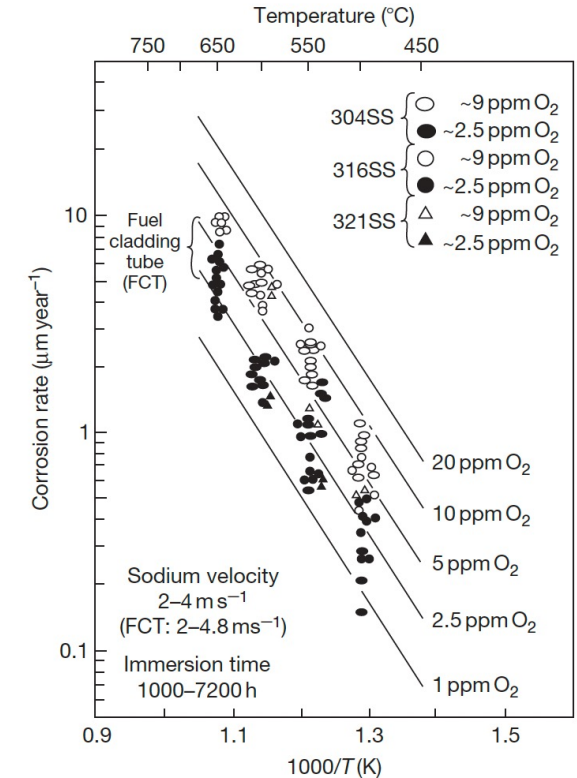
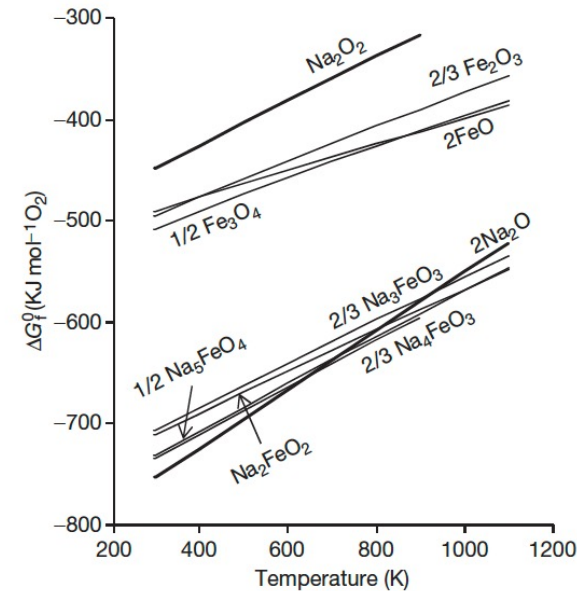
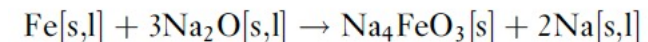
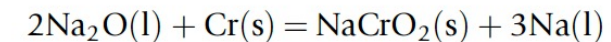
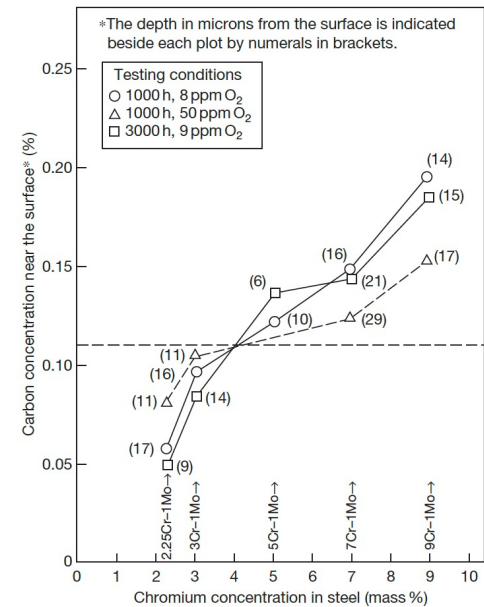
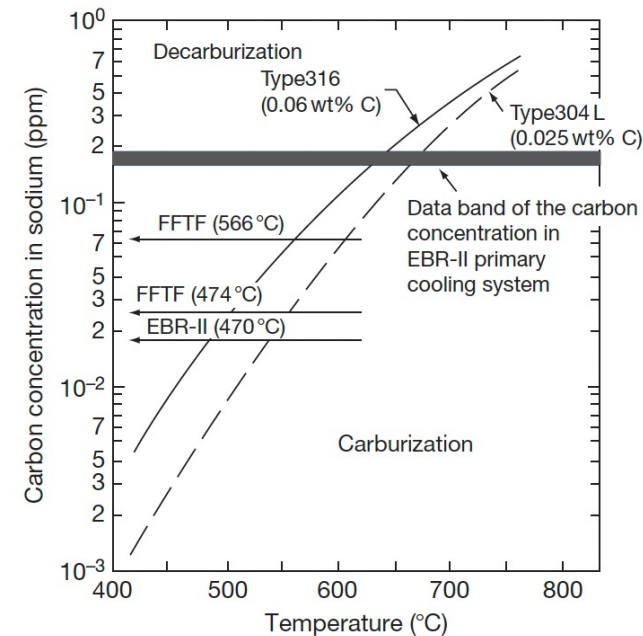


Figure 9 Comparison of corrosion rates of austenitic stainless steels.



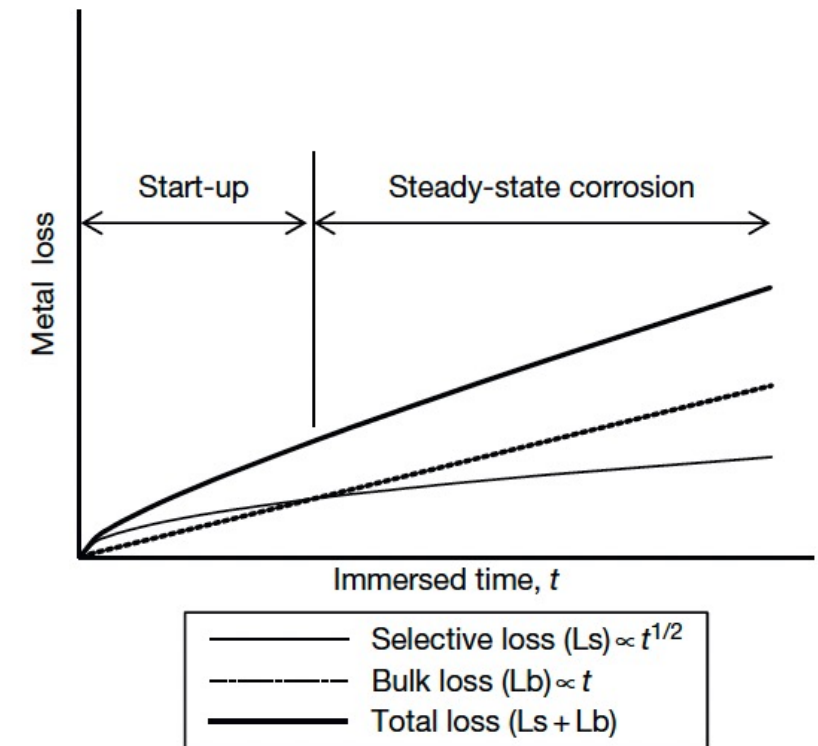
Carbon Effects

- Carbon is an important element in maintaining the superior mechanical strength of steel
- Carbon transfer can occur due to the chemical activity difference resulting from the temperature gradient
- The materials located in the high temperature regions tend to decarburize
- If a system has both austenitic and ferritic steels, carbon transfer can occur due to different chemical activities in these materials; austenitic steels carburize
- High Cr content reduces susceptibility for decarburization, largely through forming Cr-C precipitates



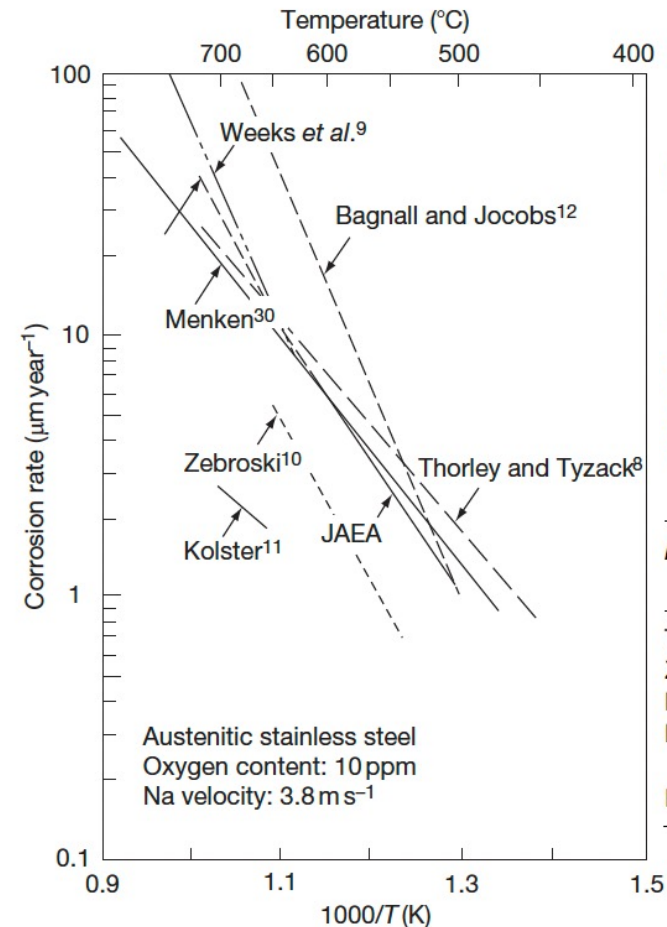
Na Corrosion of Austenitic Steel

- 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 Austenitic Steel

- Corrosion rate follows an Arrhenius function
- The effective 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 $n \sim 1$
- Thus, limiting O₂ in the Na can limit corrosion
- Corrosion rates increase with velocity up to a certain point, then become velocity independent

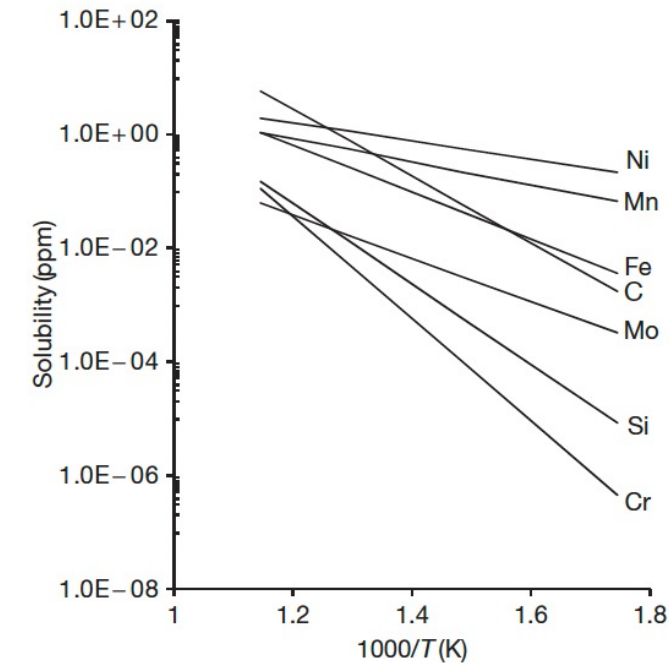
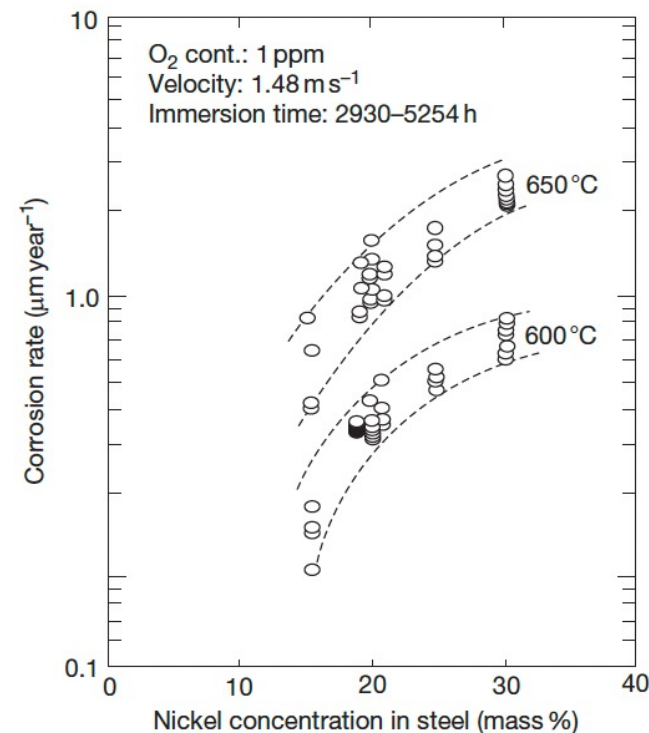


Bibliography	Sodium temperature (°C)	Activation energy (kJ mol ⁻¹)
Thorley	450–725	73.5
Weeks	538–705	108.8
Zebroski	500–700	110.5
Kolster	650–700	114.2
Bagnall	593–723	167.4
Maruyama	500–650	92–109

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 Austenitic 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 Austenitic Steel

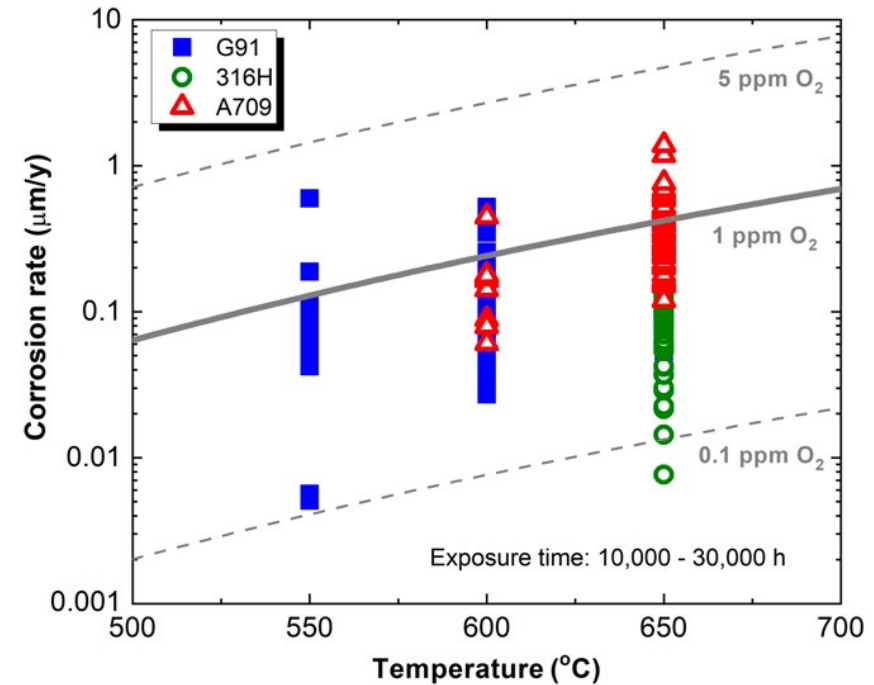
- Corrosion behavior of austenitic stainless steels is well understood over the temperature range of 455–755 C
- It is known that after the initial period of exposure, steady-state corrosion is reached, which governs the long-term corrosion behavior
- Have relationships for corrosion which include flow velocity, oxygen content, and temperature

$$R/\phi = (2.9728 \times 10^8 + 2.9133 \times 10^8 V) \cdot \exp\left(-\frac{18120}{T}\right), \text{ for sodium velocities } < 3 \text{ m/s}$$

$$R/\phi = (1.69805 \times 10^9) \cdot \exp\left(-\frac{18120}{T}\right), \text{ for sodium velocities } > 3 \text{ m/s}$$

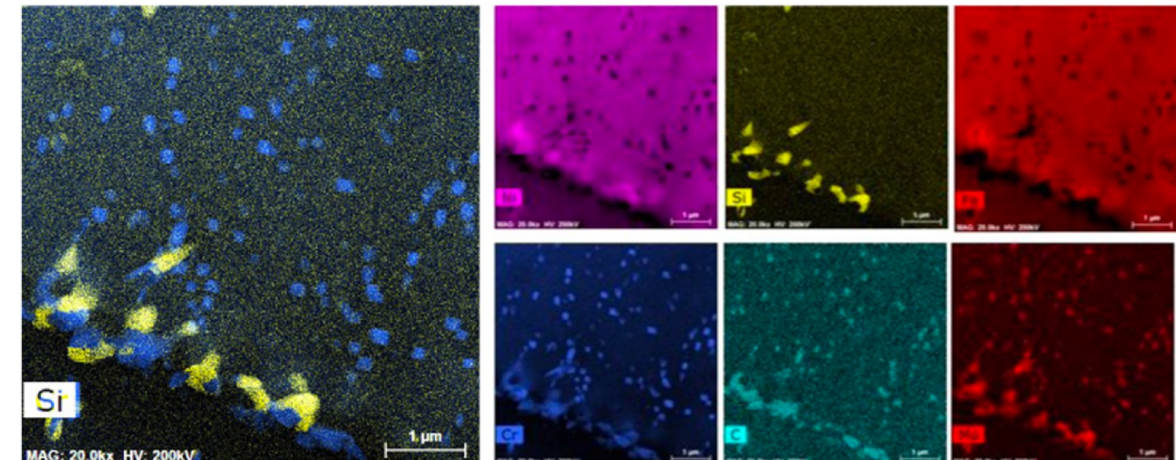
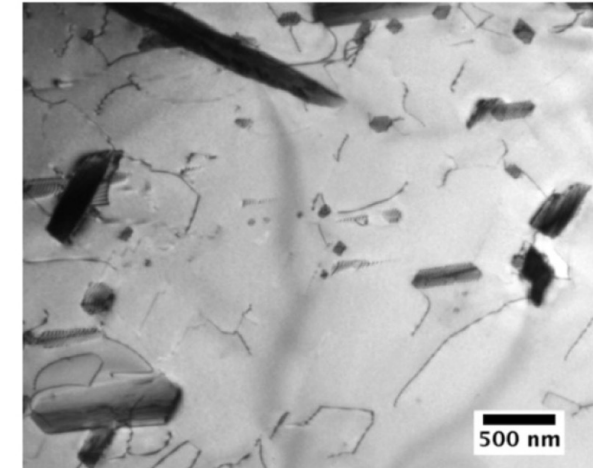
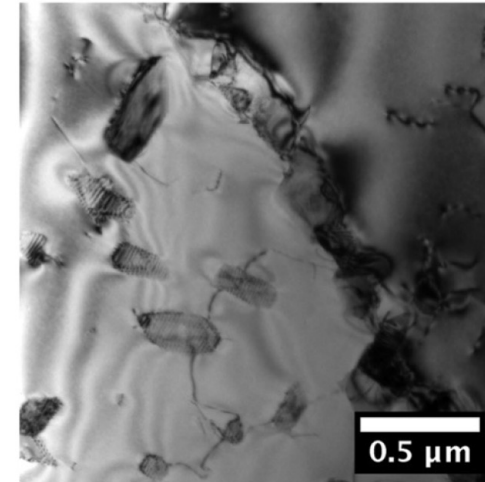
Na Corrosion in Ferritic Steels

- Also sensitive to temperature, oxygen content, and Na flow velocity
- Low-Cr steels show weight loss and decarburization, while high-Cr steels show weight gain and carburization
- Oxygen content tends to increase corrosion rates
- Flow velocity effects taper above 7 m/s, higher than in austenitic steels
- In general, effects of corrosion in F/M steels are similar to austenitic steels, but with different chemical components



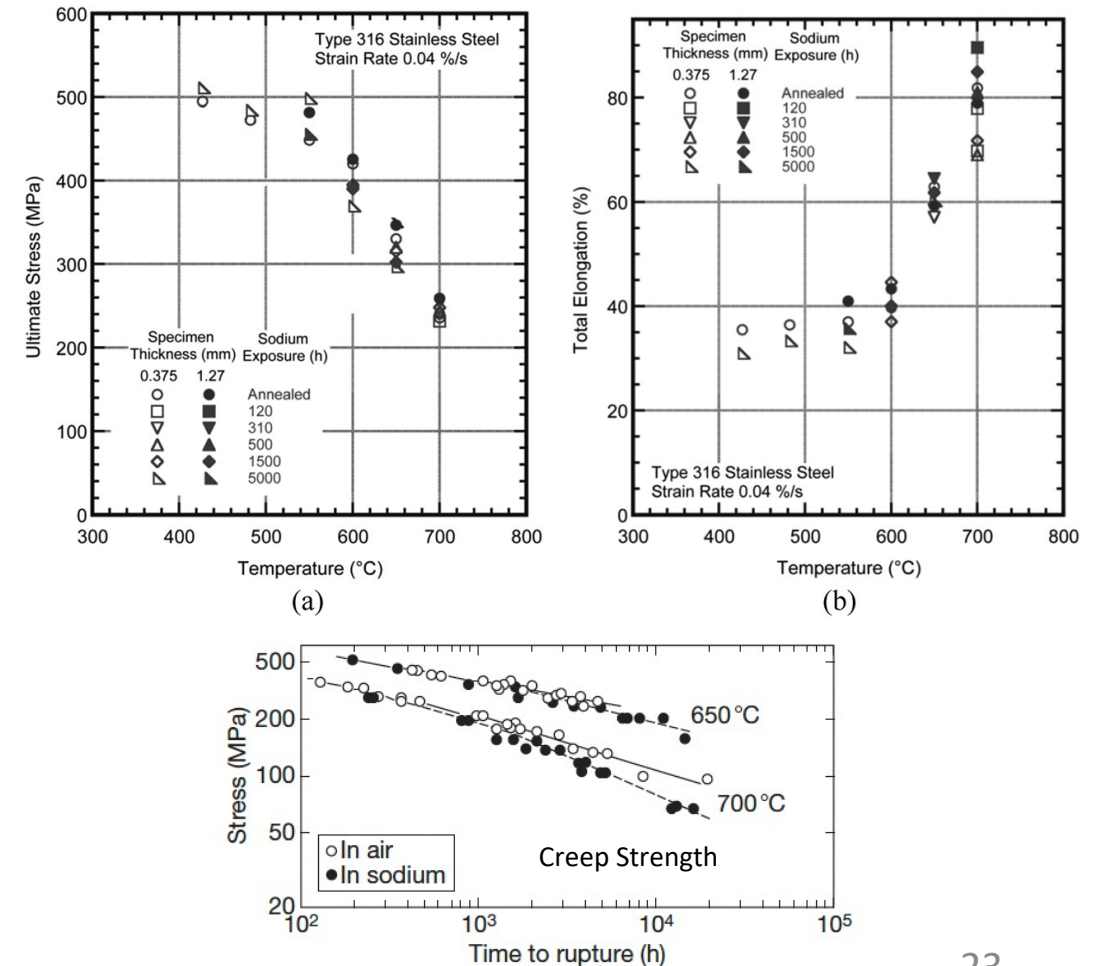
Effects on Microstructure

- Austenitic steels exposed to Na see an increase in the $M_{23}C_6$ carbide precipitates, as well as Laves phases, both intra and intergranularly
- Ferritic martensitic steels exposed to sodium can see a reduction in dislocation density, sub-grain coarsening, carbide coarsening, and precipitation of Laves phases



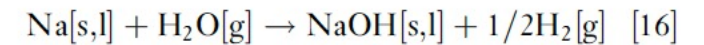
Effects on Mechanical Properties

- 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) oxidation/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
- Minor impacts on tensile strength, elongation, and creep strength for Na vs air
- Slight improvement in creep fatigue in sodium compared to air

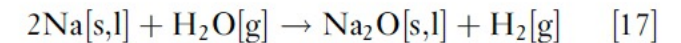


Na-Water/Air Reactions

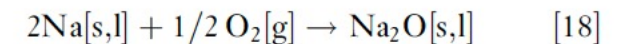
- One of the weak points of the present SFRs is the steam generator
- If the steam generator tube is damaged, high-temperature pressurized steam is blown into the sodium
- The environment around the failed tube is heated to high temperature (potentially up to 1200C) due to exothermic reactions
- When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



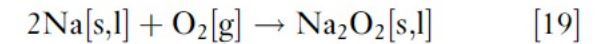
$$\Delta H_{\text{r}298}^0 = -183.8\text{KJmol}^{-1}, \Delta G_{\text{r}298}^0 = -150.9\text{KJmol}^{-1}$$



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



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



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

Summary

- Na is used as a coolant due to high thermal conductivity, high heat capacity, high margin to boiling
- 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
- Temperature gradient mass transfer is of high concern, based upon solubilities of steel elements, and highly impacts Ni
- (De)carburization can occur, but can be limited with high Cr content
- Oxygen accelerates corrosion by increasing effective solubilities
- Sodium modified the microstructure of steels through precipitation, coarsening, etc.
- Mechanical properties and minimally impacted by Na exposure

QUESTIONS?

Concluded SFRs

- Quiz on SFR lectures on October 5 (next Thursday)
- No office hours next Wednesday because I am out of town
- Supplemental office hours will be held at 11am on Tuesday, just in case