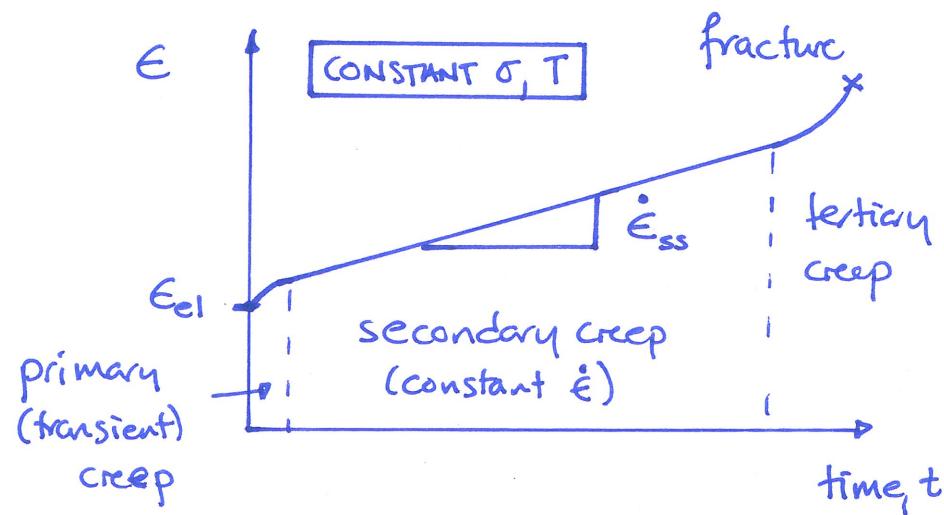


Creep in crystalline metals + ceramics

- for creep to be significant, temperature has to be greater than:
 - most metals : $T > 0.3 T_m$ ($^{\circ}\text{K}$)
 - creep resistant alloys: $T > 0.5 T_m$ ($^{\circ}\text{K}$)
 - ceramics : $T > 0.5 T_m$ ($^{\circ}\text{K}$)
- creep strain depends on stress, temperature

- at $\sigma < \sigma_y$, at high enough temperatures, under constant σ , ϵ increases with time



creep important in high temp. applications

e.g. jet engine turbine blades

power station pipework

hot forming operations
(extrusion, hot rolling)

geology - plate tectonics

- flow of glaciers

Types of creep

- primary creep - produces small strains - we will neglect
- secondary creep - leads to large strains, constant strain rate $\dot{\epsilon}_{ss} = f(\sigma, T)$
 - can be limiting factor in design
 - two types: diffusional flow: $\dot{\epsilon}_{ss} \propto \sigma$
power law creep: $\dot{\epsilon}_{ss} \propto \sigma^n$
- tertiary creep - at sufficiently long time, creep strain rate increases
 \Rightarrow leads to fracture.

Secondary creep: diffusional flow

$$\dot{\epsilon}_{ss} = \dot{\epsilon}_0 \left(\frac{\sigma}{\sigma_0} \right)$$

$\dot{\epsilon}_0, \sigma_0$ material properties

$$\dot{\epsilon}_0 = A \exp(-Q/RT) \quad [\text{Arrhenius law}]$$

Q = activation energy

R = gas constant

T = absolute temperature ($^{\circ}\text{K}$)

A = $1/\text{sec}$

- steady state strain rate linearly dependent on stress, σ
- diffusional flow is important at low stresses + high temperatures

Svante Arrhenius

From Wikipedia, the free encyclopedia

Svante August Arrhenius (19 February 1859 – 2 October 1927) was a Swedish scientist, originally a physicist, but often referred to as a chemist, and one of the founders of the science of physical chemistry. He received the Nobel Prize for Chemistry in 1903 and in 1905 became Director of the Nobel Institute where he remained until his death.^[1] The Arrhenius equation, lunar crater Arrhenius and the Arrhenius Labs at Stockholm University are named after him.



Svante Arrhenius

Contents

- 1 Biography
 - 1.1 Early years
 - 1.2 Middle period
 - 1.3 Later years
 - 1.4 Greenhouse effect
 - 1.5 Racial biology
- 2 See also
- 3 Bibliography
- 4 References
- 5 Further reading
- 6 External links

Biography

Early years

Arrhenius was born on February 19, 1859 at Vik (also spelled Wik or Wijk), near Uppsala, Sweden, the son of Svante Gustav and Carolina Thunberg Arrhenius. His father had been a land surveyor for Uppsala University, moving up to a supervisory position. At the age of three, Arrhenius taught himself to read without the encouragement of his parents, and by watching his father's addition of numbers in his account books, became an arithmetical prodigy. In later life, Arrhenius enjoyed using masses of data to discover mathematical relationships and laws.

| | |
|-------------------|--|
| Doctoral advisor | Per Teodor Cleve, Erik Edlund |
| Doctoral students | Oskar Benjamin Klein |
| Known for | Arrhenius equation Theory of ionic dissociation Acid-base theory |
| Notable awards | Nobel Prize for Chemistry (1903) Franklin Medal (1920) |

At age 8, he entered the local cathedral school, starting in the fifth grade, distinguishing himself in physics and mathematics, and graduating as the youngest and most able student in 1876.

At the University of Uppsala, he was unsatisfied with the chief instructor of physics and the only faculty member who could have supervised him in chemistry, Per Teodor Cleve, so he left to study at the Physical Institute of the Swedish Academy of Sciences in Stockholm under the physicist Erik Edlund in 1881. His work focused on the conductivities of electrolytes. In 1884, based on this work, he submitted a 150-page dissertation on electrolytic conductivity to Uppsala for the doctorate. It did not impress the professors, among whom was Per Teodor Cleve, and he received a fourth class degree, but upon his defence it was reclassified as third class. Later, extensions of this very work would earn him the Nobel Prize in Chemistry.

There were 56 theses put forth in the 1884 dissertation, and most would still be accepted today unchanged or with minor modifications. The most important idea in the dissertation was his explanation of the fact that neither pure salts nor pure water is a conductor, but solutions of salts in water are.

Arrhenius' explanation was that in forming a solution, the salt dissociates into charged particles (to which Michael Faraday had given the name ions many years earlier). Faraday's belief had been that ions were produced in the process of electrolysis; Arrhenius proposed that, even in the absence of an electric current, solutions of salts contained ions. He thus proposed that chemical reactions in solution were reactions between ions.

The dissertation was not very impressive to the professors at Uppsala, but Arrhenius sent it to a number of scientists in Europe who were developing the new science of physical chemistry, such as Rudolf Clausius, Wilhelm Ostwald, and J. H. van 't Hoff. They were far more impressed, and Ostwald even came to Uppsala to persuade Arrhenius to join his research team. Arrhenius declined, however, as he preferred to stay in Sweden for a while (his father was very ill and would die in 1885) and had received an appointment at Uppsala.

In an extension of his ionic theory Arrhenius proposed definitions for acids and bases, in 1884. He believed that acids were substances that produce hydrogen ions in solution and that bases were substances that produce hydroxide ions in solution.

Middle period

Arrhenius next received a travel grant from the Swedish Academy of Sciences, which enabled him to study with Ostwald in Riga (now in Latvia), with Friedrich Kohlrausch in Würzburg, Germany, with Ludwig Boltzmann in Graz, Austria, and with van 't Hoff in Amsterdam.

In 1889 Arrhenius explained the fact that most reactions require added heat energy to proceed by formulating the concept of activation energy, an energy barrier that must be overcome before two molecules will react. The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds.

In 1891 he became a lecturer at the Stockholm University College (*Stockholms Högskola*, now Stockholm University), being promoted to professor of physics (with much opposition) in 1895, and rector in 1896.

Secondary creep : power law creep

$$\dot{\epsilon}_{ss} = \dot{\epsilon}_0 \left(\frac{\sigma}{\sigma_0} \right)^n$$

$\dot{\epsilon}_0, \sigma_0, n$ material properties

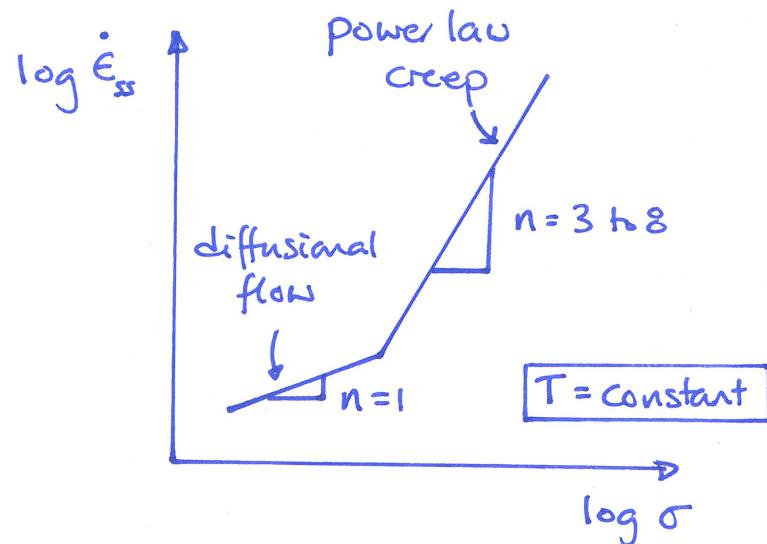
$$\dot{\epsilon}_0 = A \exp(-Q/RT)$$

values of Q different for power law creep + diffusional flow

- steady state strain rate depends non-linearly on stress

- power law creep important at high stress + high temperature

- consider relative magnitude of creep from diffusional flow + power law creep



- at low σ , contribution of diffusional flow to creep can be significant
- at high σ , power law creep dominates creep response

Design for creep

- have to ensure:

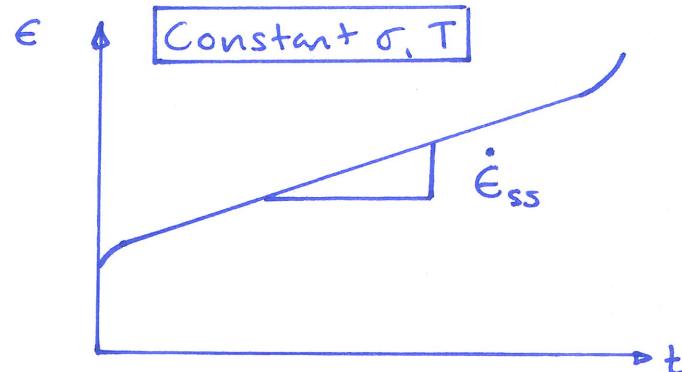
$\epsilon_{cr} < \epsilon_{all}$ (1) total creep strain less than allowable strain for components to fit together

$\epsilon_{all} < \epsilon_f$ (2) creep strain to failure is adequate to cope with allowable strain

$t_d < t_f$ (3) time to failure longer than design life

Measurement of creep parameters

- dead load specimens in a furnace at constant σ & constant Temperature
- measure $\epsilon(t)$



$$\dot{\epsilon}_{ss} = A \exp(-Q/RT) \left(\frac{\sigma}{\sigma_0}\right)^n$$

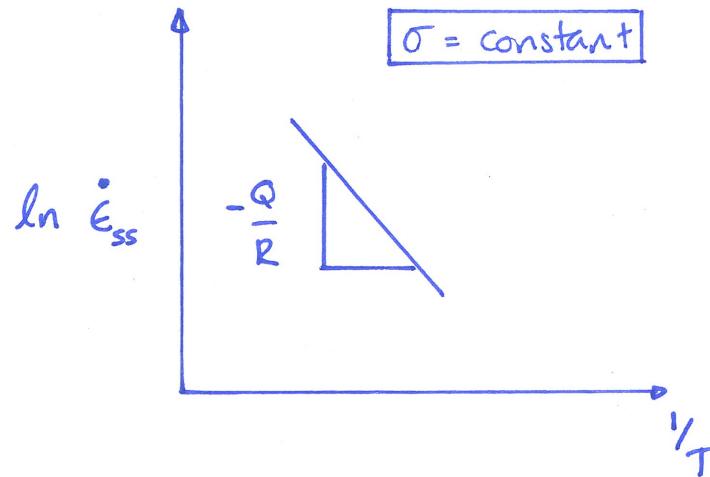
$$A = 1/\text{sec}$$

$$Q = \text{energy/mole}$$

$$R = 8.314 \text{ J}/^\circ\text{K}/\text{mole} (\text{J "K"}^{-1} \text{ mole}^{-1})$$

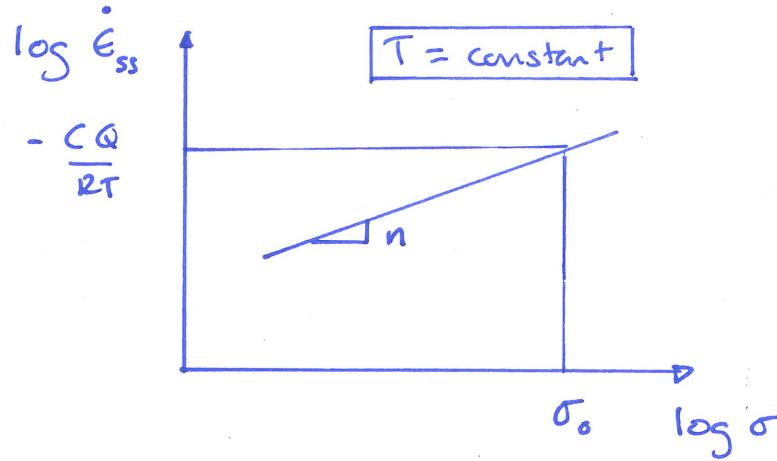
$$T = \text{absolute temperature (}^\circ\text{K)}$$

(a) in one series of tests, hold $\sigma = \text{constant}$ + vary Temperature T



- gives Q , activation energy

(b) in another series of tests, hold temperature = constant & vary σ



$$\text{if } \sigma = \sigma_0 \quad \dot{\epsilon}_{ss} = A \exp(-\frac{Q}{RT})$$

$$\ln \left(\frac{\dot{\epsilon}_{ss}}{A} \right) = - \frac{Q}{RT}$$

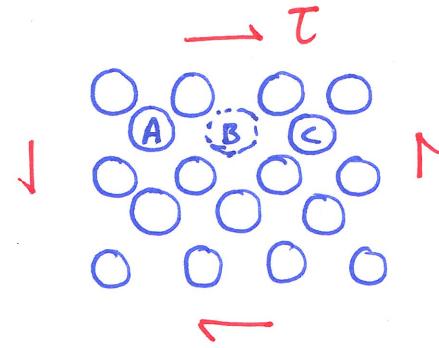
\Rightarrow gives σ_0 , n

(note C on plot because plot is log-log
& eqn is ln)
(base e)

Mechanism of creep: diffusion

- creep in crystalline metals + ceramics caused by diffusion
- different diffusion paths at work in diffusional flow & power law creep
- diffusional flow: bulk diffusion + grain boundary diffusion
- power law creep: dislocation climb

- diffusion can be driven by a mechanical force

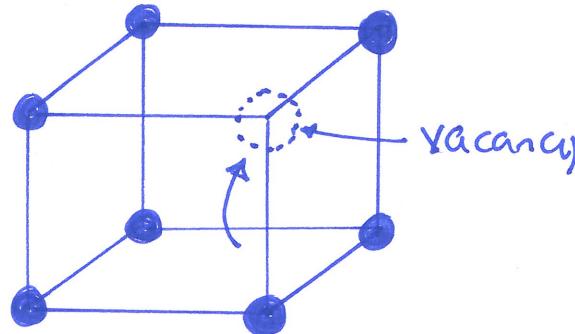


B: vacancy

- if material is unloaded ($\tau = 0$), atoms A and C are equally likely to diffuse into vacancy B
- but if material is loaded ($\tau \neq 0$), it is more likely that A moves into vacancy B than C
- mechanical load biases diffusion in one direction

Mechanisms of creep: diffusional flow

(a) Bulk diffusion

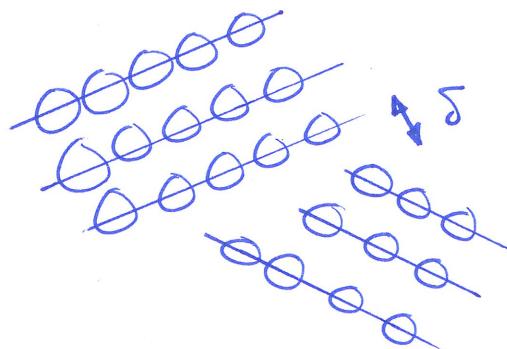


vacancy diffusion

- diffusion to a vacancy site

(b) Grain boundary diffusion

- grain boundary is a region of disorder where differently oriented crystals meet
- more open structure than rest of crystal



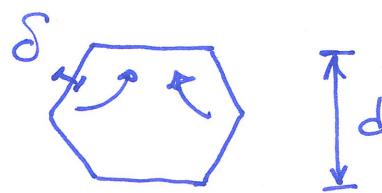
δ = grain boundary width

~ 2 atom diameters

~ 5×10^{-10} m

Grain boundary diffusion

- boundary acts like a high conductivity channel
- contribution to diffusive transport depends on how much grain boundary available, relative to size of grain



d = grain size

δ = grain boundary width

- bulk diffusion occurs across area $\pi(d/2)^2$
- grain boundary diffusion occurs across area $\times \delta d / 2$
(width δ & length $d/2$ into page)
- area for grain boundary diffusion = $\frac{\delta d}{2} / (\frac{d}{2})^2 = \frac{2\delta}{d}$
- diffusion coefficients: $D_v = D_{ov} \exp(-Q_v/RT)$ vacancy (bulk) diffusion
 $D_b = D_{ob} \exp(-Q_b/RT)$ grain boundary diffusion
 $[m^2/s]$

Diffusional flow

$$\dot{E}_{ss} = \frac{42 \sigma \Omega}{kT d^2} (D_v + \frac{\pi \delta}{d} D_b)$$

Ω = atomic volume

k = Boltzmann's constant

T = absolute temp.

d = grain size

δ = grain boundary width

- data give Q_v , D_{av} , Q_b , δD_{ob}
- materials with similar structure + bonding have similar diffusion coeff.
- if data for a particular material is not available, can use archetypal equations for similar structure + bonding.

6.21

TABLE 6.5

DIFFUSIONAL CREEP PARAMETERS

| MATERIAL | η_v (kJ/mole) | D_{av} (m^2/s) | η_B kJ/mole | δD_{ob} (m^3/s) |
|--------------------------------|--------------------|-----------------------|------------------|-----------------------------|
| Titanium Carbide | 740 | 4.4 | 543 | 2×10^{-9} |
| Titanium Carbide | 720 | 1×10^{-1} | 468 | 5×10^{-12} |
| Tungsten | 585 | 5.6×10^{-6} | 385 | 3.3×10^{-13} |
| Silicon | 496 | 9×10^{-1} | (300) | (1×10^{-15}) |
| Titanium Dioxide | 452 | 1.2×10^{-5} | 293 | 2×10^{-15} |
| Tantalum | 413 | 1.2×10^{-5} | (280) | (5.7×10^{-14}) |
| Polybdenum | 405 | 5×10^{-5} | (263) | (5.5×10^{-14}) |
| Obrium | 401 | 1.1×10^{-4} | (263) | (5.0×10^{-14}) |
| Nickel | 308 | 3.6×10^{-5} | (209) | (5×10^{-14}) |
| Ruthenium | 306 | 2.8×10^{-5} | (192) | (5×10^{-15}) |
| Rhenium | 287 | 8.0×10^{-4} | (172) | (1.0×10^{-17}) |
| Monics, Nichromes | 285 | 1.6×10^{-4} | 115 | 3.5×10^{-15} |
| Nickel | 284 | 1.9×10^{-4} | 115 | 3.5×10^{-15} |
| Inainless Steels (304, 316) | 280 | 3.7×10^{-5} | 167 | 2.0×10^{-13} |
| Iron (Austenite) | 270 | 1.8×10^{-5} | 159 | 7.5×10^{-14} |
| Magnesium Oxide | 261 | 2.5×10^{-10} | (230) | (1.3×10^{-15}) |
| Alloy Steels | 251 | 2.0×10^{-4} | 174 | 1.1×10^{-12} |
| Iron, Mild Steel | 251 | 2.0×10^{-4} | 174 | 1.1×10^{-12} |
| Sodium Chloride | 217 | 2.5×10^{-2} | 155 | 6.2×10^{-10} |
| Thallium Fluoride | 214 | 7.4×10^{-3} | - | - |
| Copper (and alloys) | 197 | 2×10^{-5} | 104 | 5×10^{-15} |
| Mercury | 185 | 4.4×10^{-5} | 90 | 4.5×10^{-15} |
| Aluminum (and alloys) | 142 | 1.7×10^{-4} | 84 | 5.0×10^{-14} |
| Magnesium (and alloys) | 135 | 1.0×10^{-4} | 92 | 5.0×10^{-12} |
| Lead | 109 | 1.4×10^{-4} | 66 | 8.0×10^{-14} |
| Neon | 92 | 1.3×10^{-5} | 61 | 1.3×10^{-14} |
| Ne | 59 | 9.1×10^{-4} | (38) | (8.2×10^{-13}) |

6.22

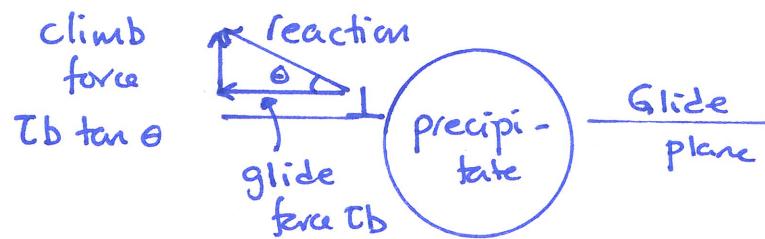
TABLE 6.6

ARCHETYPAL DIFFUSION EQUATIONS

| CLASS OF SOLID | LATTICE DIFFUSION COEFFICIENT m^2/s | BOUNDARY DIFFUSION COEFFICIENT m^3/s |
|------------------------------|--|--|
| METAL CARBIDES | $D = 0.2 \exp - \{24.0 \frac{T_N}{T}\}$ | $\delta D_b = 7 \times 10^{-14} \exp - \{12.6 \frac{T_A}{T}\}$ |
| A.C.C. (1) RARE EARTHS | $D = 1.5 \times 10^{-6} \exp - \{9.1 \frac{T_N}{T}\}$ | $\delta D_b = 1 \times 10^{-11} \exp - \{15.3 \frac{T_A}{T}\}$ |
| S.C.C. (2) ALKALI METALS | $D = 2.5 \times 10^{-5} \exp - \{14.7 \frac{T_N}{T}\}$ | - |
| B.C.C. (3) TRANSITION METALS | $D = 1.6 \times 10^{-4} \exp - \{17.8 \frac{T_H}{T}\}$ | $\delta D_b = 3.4 \times 10^{-13} \exp - \{11.7 \frac{T_M}{T}\}$ |
| H.C.P. METALS | $D = 4.9 \times 10^{-5} \exp - \{17.3 \frac{T_N}{T}\}$ | $\delta D_b = 2.7 \times 10^{-14} \exp - \{10.8 \frac{T_M}{T}\}$ |
| F.C.C. METALS | $D = 5.4 \times 10^{-5} \exp - \{18.4 \frac{T_N}{T}\}$ | $\delta D_b = 9.4 \times 10^{-15} \exp - \{10.0 \frac{T_M}{T}\}$ |
| HEXAGONAL (GRAPHITE) | $D = 2.4 \times 10^{-6} \exp - \{20.0 \frac{T_N}{T}\}$ | - |
| ALKALI HALIDES | $D = 1.7 \times 10^{-3} \exp - \{22.5 \frac{T_N}{T}\}$ | - |
| TETRAHEDRAL (Ia) | $D = 3.2 \times 10^{-6} \exp - \{21.9 \frac{T_N}{T}\}$ | - |
| SIMPLE OXIDES | $D = 5.3 \times 10^{-5} \exp - \{23.4 \frac{T_N}{T}\}$ | $\delta D_b = 4.7 \times 10^{-15} \exp - \{14.7 \frac{T_M}{T}\}$ |
| SILICATES (OLIVINE) | $D = 3.0 \exp - \{31.0 \frac{T_N}{T}\}$ | - |
| TRIGONAL ELEMENTS | $D = 5.5 \times 10^{-3} \exp - \{26.0 \frac{T_N}{T}\}$ | $\delta D_b = 2.7 \times 10^{-14} \exp - \{11.0 \frac{T_M}{T}\}$ |
| ICE | $D = 1 \times 10^{-3} \exp - \{26.3 \frac{T_N}{T}\}$ | - |
| DIAMOND CUBIC ELEMENTS | $D = 6.3 \times 10^{-2} \exp - \{33.9 \frac{T_N}{T}\}$ | - |

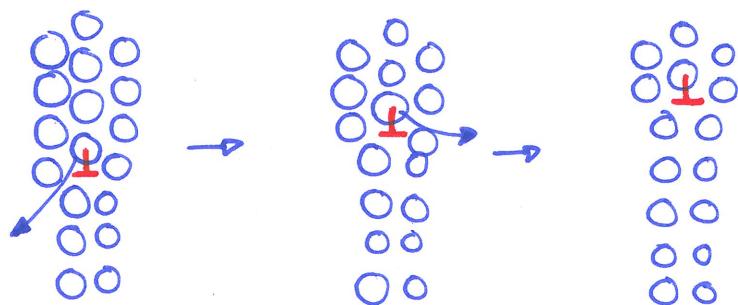
Mechanism of power law creep: dislocation climb

- alloying elements are obstacles to dislocation glide
- diffusion can allow dislocation to "climb" around obstacles + continue glide
- consider dislocation hitting obstacle (e.g. precipitate) at $\sigma < \sigma_y$



- glide force produces reaction on precipitate
- this reaction has a vertical component $T_b \tan \theta$
- tries to push dislocation out of glide plane

- climb force can give rise to diffusion of atoms away from dislocation core
- recall stress field around a dislocation: $\sigma \propto \frac{Gb}{2\pi r} \Rightarrow$ largest stress at core



dislocation climb

- by core diffusion at lower T/T_m
- also can occur by bulk diffusion at higher T/T_m

Power law creep: dislocation climb

- dislocation can "climb" around an obstacle & continue to glide, until it hits the next obstacle; process of climb + glide repeated
 - power law creep data: give Q_c , σ_0 , n
 - rank by activation energy
 - this, for a given temperature, most nearly measures resistance to creep.
-

TABLE 6.4
POWER-LAW CREEP PARAMETERS

| MATERIAL | Q_c kJ/mole | σ_0 MN/m ² | n |
|----------------------------|---------------|------------------------------|------|
| Titanium Carbide | 740 | .015 | 5.0 |
| Zirconium Carbide | 720 | .052 | 5.0 |
| Tungsten | 585 | 0.41 | 4.7 |
| Nimonics | 556 | 3.2 | 7.7 |
| Silicon | 496 | .19 | 5.0 |
| Uranium Dioxide | 452 | 0.89 | 4.0 |
| Tantalum | 413 | 0.34 | 4.2 |
| Molybdenum | 405 | 0.89 | 4.85 |
| Niobium | 401 | 0.11 | 4.4 |
| Vanadium | 308 | 0.62 | 5.0 |
| Chromium | 306 | 0.59 | 4.3 |
| Germanium | 287 | 0.32 | 5.0 |
| Nichromes | 285 | 1.1 | 4.6 |
| Nickel | 284 | 0.5 | 4.6 |
| 316 Stainless Steels | 270 | 33.5 | 7.9 |
| 304 Stainless Steel | 270 | 11.3 | 7.5 |
| γ -Iron (Austenite) | 270 | 1.0 | 4.5 |
| Magnesium Oxide | 261 | 13.2 | 3.3 |
| Low Alloy Steels | 251 | 21.1 | 6.0 |
| α -Iron, Mild Steel | 251 | 1.92 | 6.9 |
| Sodium Chloride | 217 | 0.013 | 3.6 |
| Lithium Fluoride | 214 | 0.6 | 6.6 |
| Copper | 197 | 1.1 | 4.8 |
| Silver | 185 | 1.1 | 4.3 |
| Aluminium | 142 | 0.12 | 4.4 |
| Magnesium | 135 | 0.49 | 5.0 |
| Lead | 109 | 0.08 | 5.0 |
| Zinc | 92 | 1.24 | 4.5 |
| Ice | | | |

Ashby, MF lecture notes

Deformation Mechanism Maps

- Various mechanisms of deformation:

elastic

plastic

- creep - diffusional flow
 - bulk (vacancy) diffusion
 - grain boundary diffusion
- power law creep
 - low temp: core diffusion
 - high temp: bulk diffusion

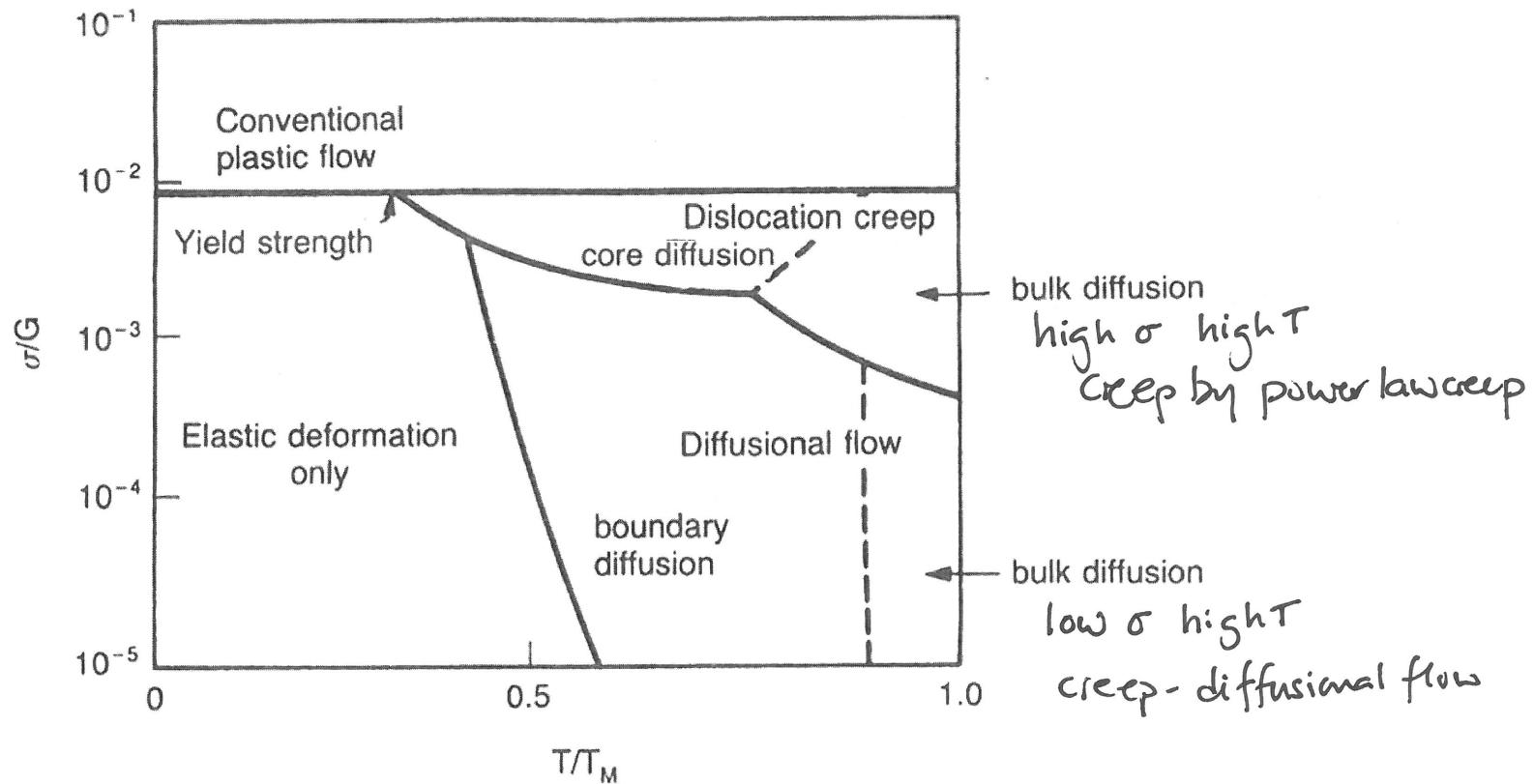
- overall behaviour summarized in deformation mechanism map

- plasticity + creep depend on equivalent stress; plot $\frac{\sigma_s}{G} = \frac{\sigma_e}{\bar{G} G}$ vs $\frac{T}{T_m}$ (homologous temperature)

- see figure, next page
- more detailed map includes $\dot{\gamma}$ contours
- boundaries between two mechanisms correspond to the two mechanisms producing equal strain rate $\dot{\gamma}$
- within one area, one mechanism dominant over all others
- find that materials with similar structure + bonding have similar maps

high σ , low T
plastic

low σ low T
elastic



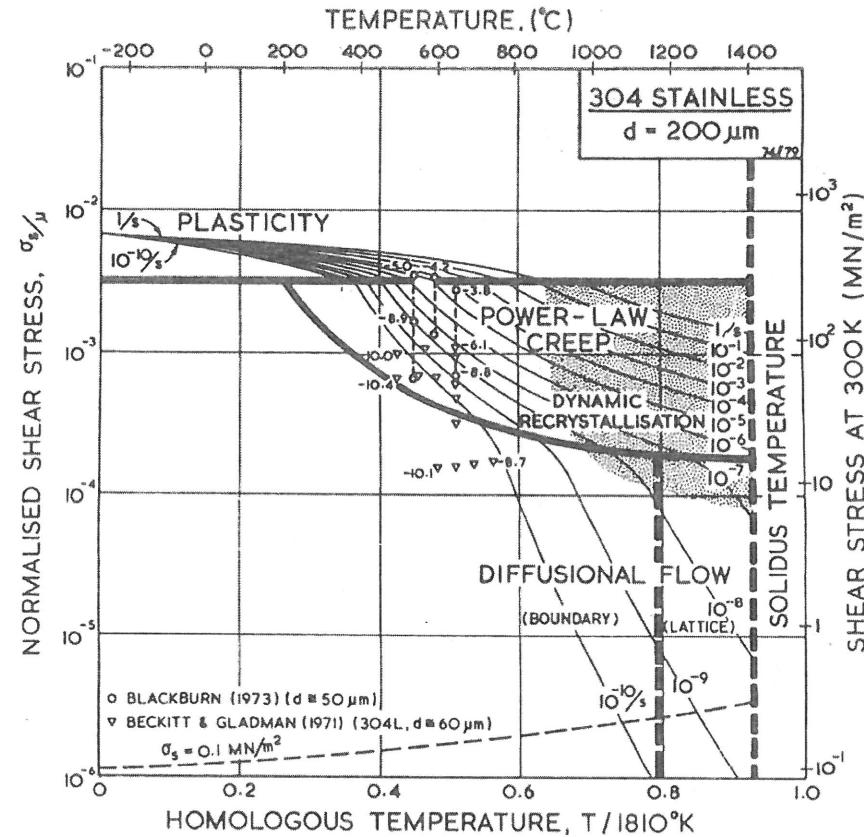
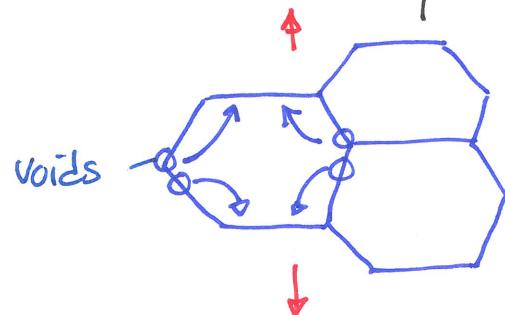


Fig. 8.12. A stress/temperature map for type 304 stainless steel of grain size $200 \mu\text{m}$, showing data.

Frost HJ and Ashby MF (1982) Deformation-Mechanism Maps: The Plasticity and Creep of Metals and Ceramics Pergamon Press.

Creep fracture

- Secondary creep important if design limited by creep strain
- also have to consider creep fracture
- caused by coalescence of voids caused by diffusion



Material leaves inclined boundaries to be deposited on horizontal ones

- empirical relation: Monkman-Grant eq'n (Nick Grant, MIT DMSE)

$$t_f \dot{\epsilon}_{ss}^m = \text{constant} \quad t_f = \text{time to failure}$$

$$\log t_f + m \log \dot{\epsilon}_{ss} = B$$

empirically find $0.77 < m < 0.93$ for many Al, Cu, Ti, Ni, Fe alloys
 $0.48 < B < 1.3$

$$\text{if } m=1 \quad t_f \dot{\epsilon}_{ss} = \text{constant} = \text{strain to failure, } \epsilon_f$$

- can say rupture process related to diffusion

rate of process $\propto A \exp(-Q/RT)$ for constant stress, σ

$$\text{rate} \propto \frac{1}{t_f}$$

$$\therefore \ln \frac{1}{t_f} = \ln A - (Q/RT)$$

or $\frac{Q}{R} = T \underbrace{(\ln A + \ln t_f)}_{\text{Larson-Miller parameter}} = \text{constant}$ (for constant σ)

- Larson - Miller plot next page
- using test data, can plot $T(C + \log t_f)$ for various const. σ
- useful since this allows simulation of long duration tests by increasing temperature.

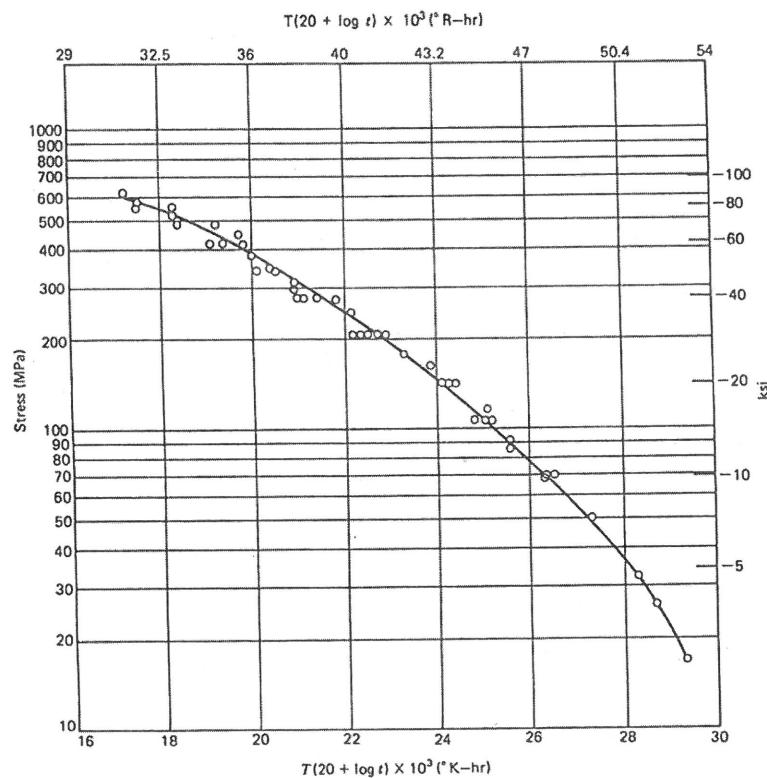


FIGURE 5.25 Larson-Miller plot showing S-590 iron based alloy data presented in Fig. 5.3.

Hertzberg, RW (1996)
Deformation and Fracture
Mechanics of Engineering
Materials. Fourth Edition.
Wiley