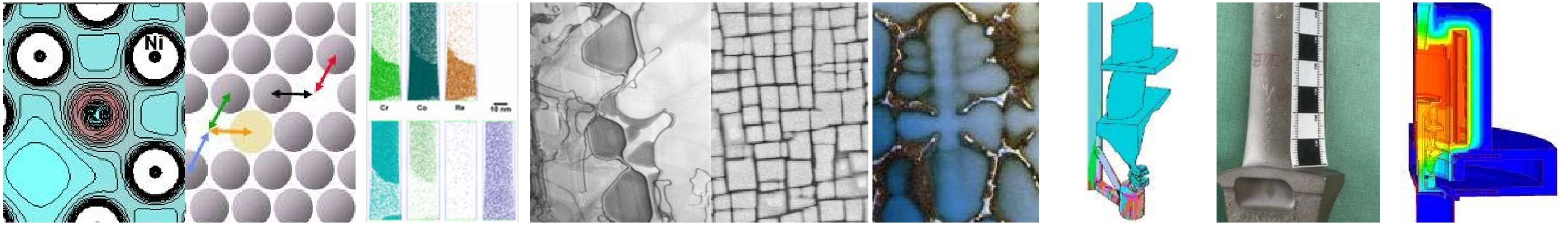

On The Diffusion of Alloying Elements in the Nickel-Base Superalloys

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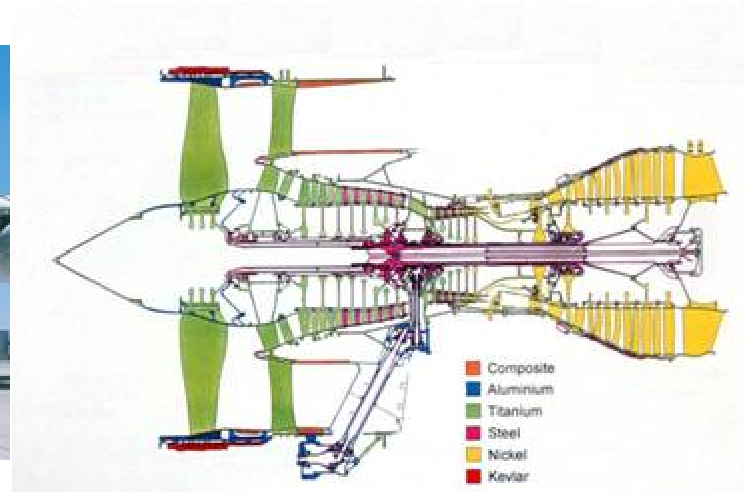
NIST, 12th May 2008


Rolls-Royce
Trent 1000
Spirit of excellence
Trent 1000
the 787 Drea

Motivation for Work in Reed's Group



- **High temperature materials, particularly for turbine applications**
- **Quantification/modelling of physical phenomena**
  - ***design of new alloy systems***
  - ***diffusion, phase transformations, microstructural instabilities***
  - ***improved descriptions of component behaviour, e.g. creep of turbine blade, failure of TBCs***
  - ***manufacturing of critical (life-limiting) parts***
- **Validation by targetted experimentation**
  - ***match tool (TEM, EXAFS, APT, neutron diffractometry) to job***

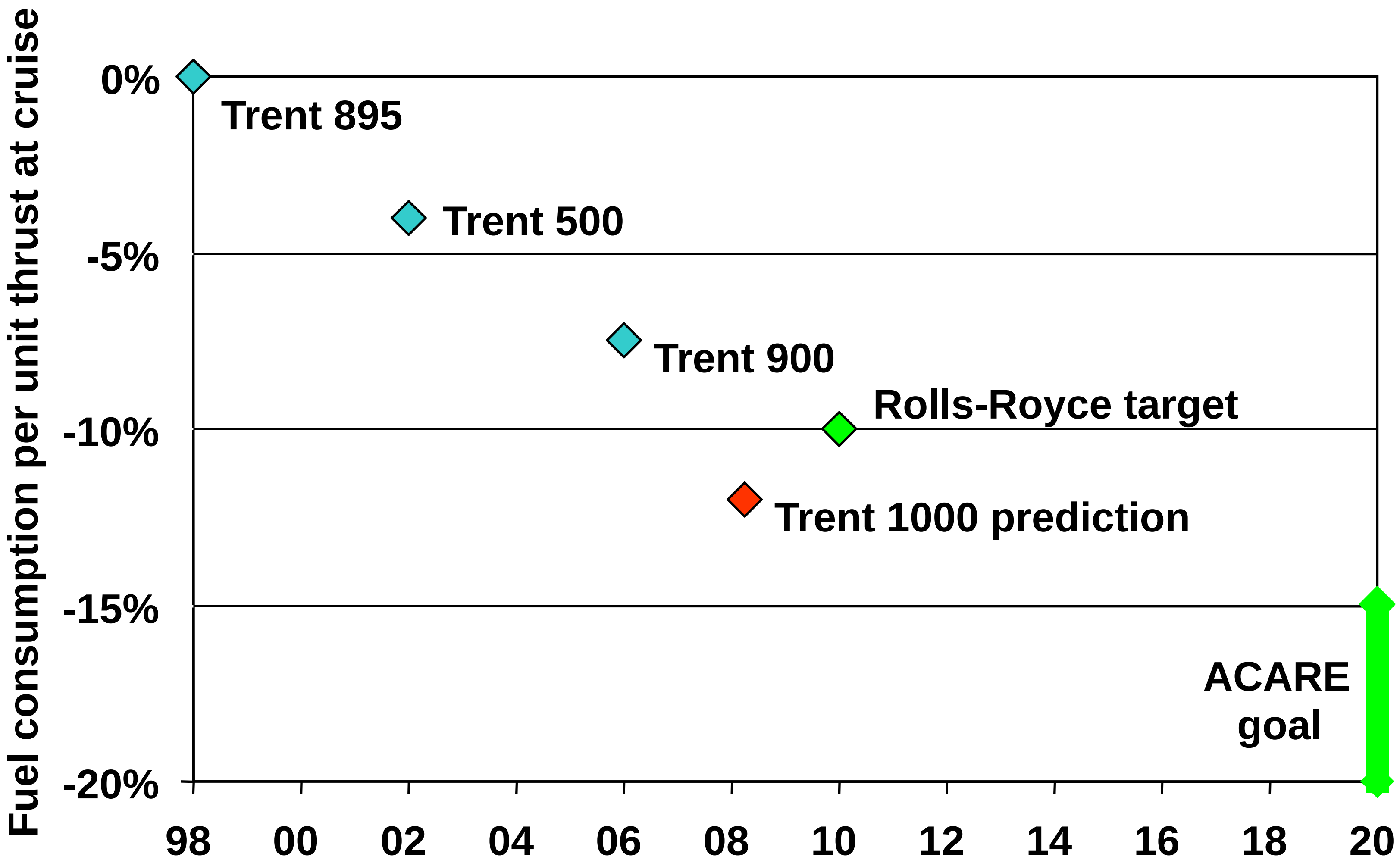
ACARE* Environmental Goals for 2020

- Reduce CO_2 by 50% per passenger kilometre (assuming kerosene remains the main fuel in use)
- Reduce perceived noise to one half of current average levels
- Reduce NO_x emissions by 80%
- Minimise the industry’s impact during manufacture, maintenance, overhaul, repair and disposal

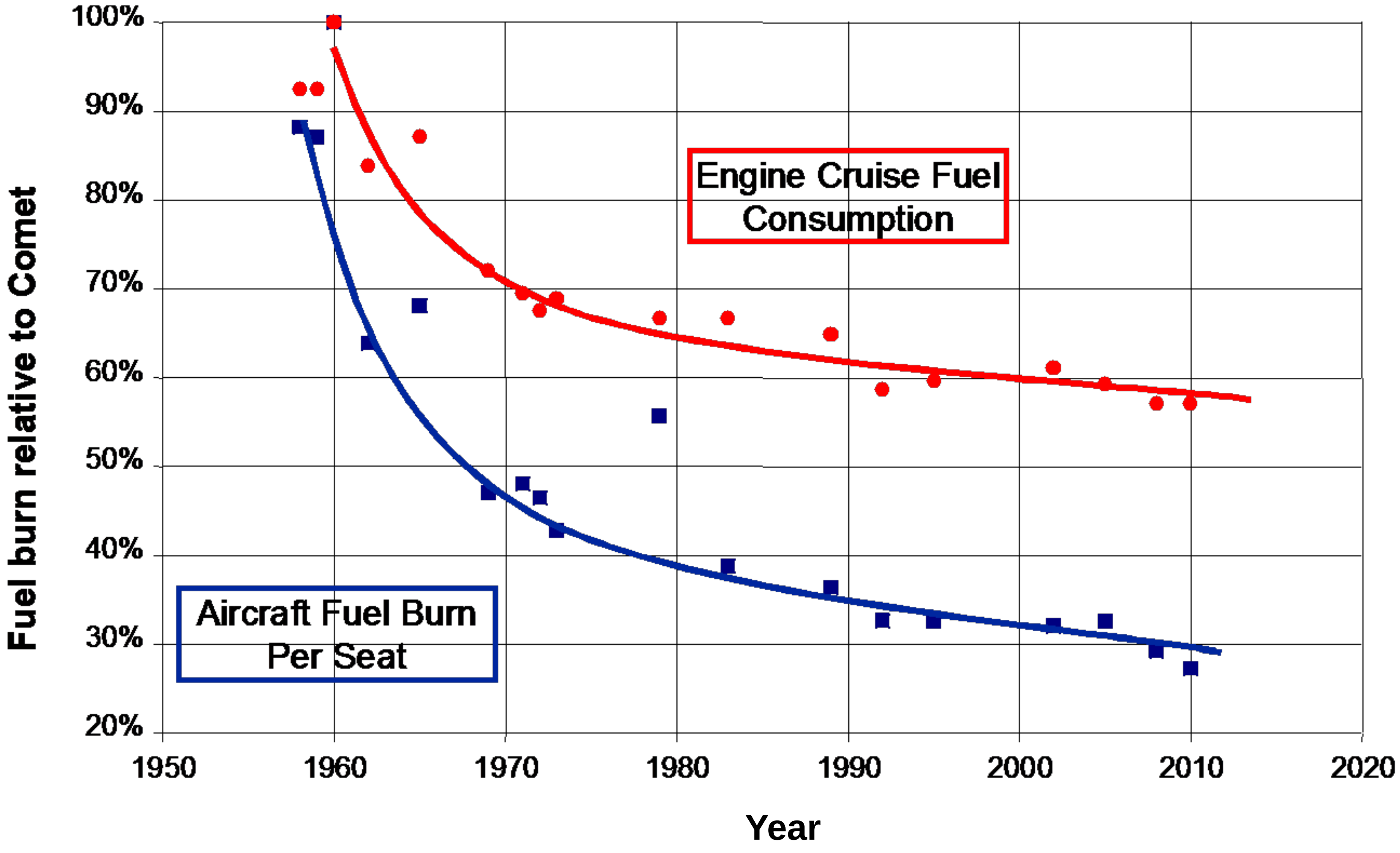
ACARE

*Advisory Council for Aeronautics Research in Europe

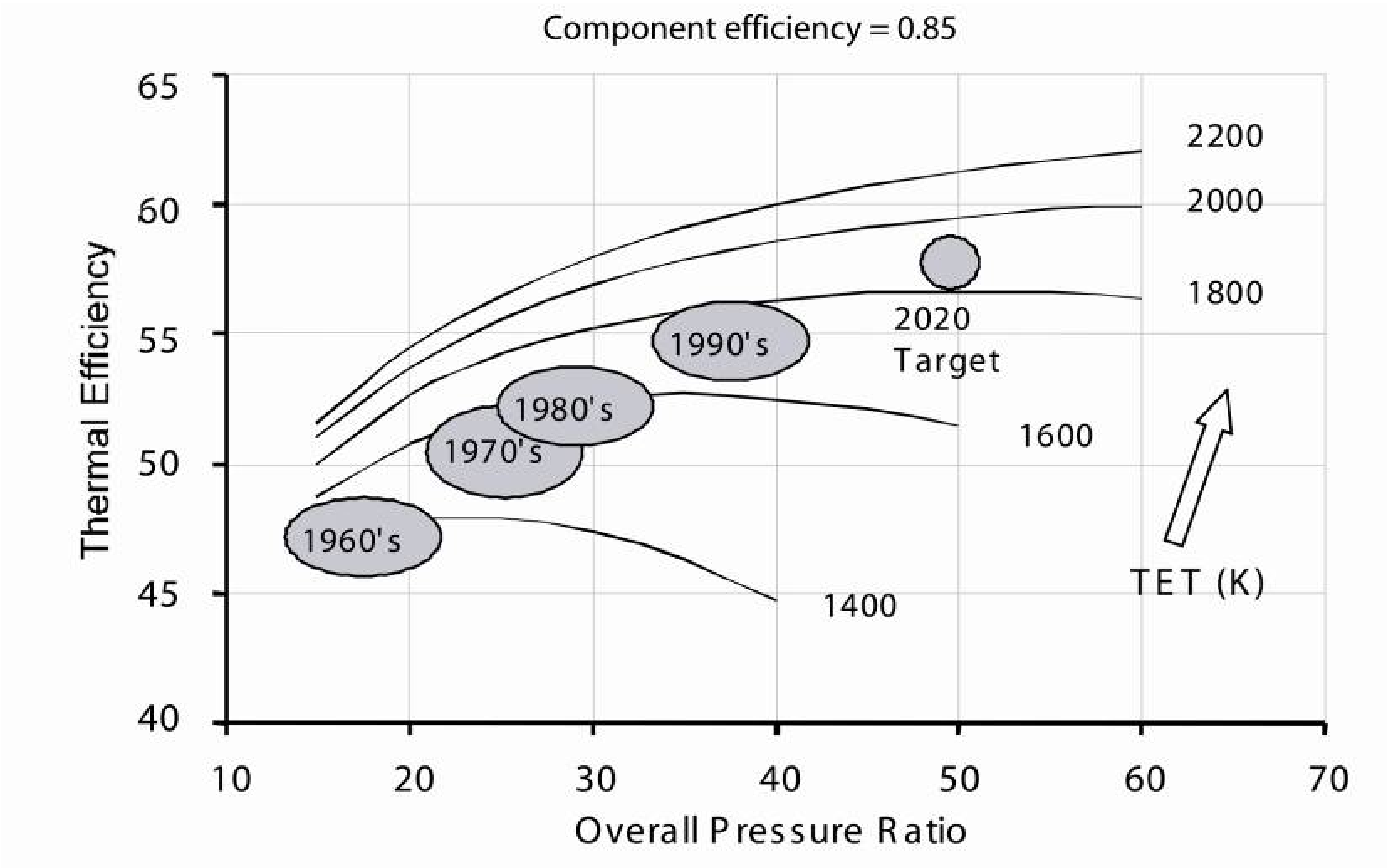
Fuel Consumption (and CO_2) Reduction



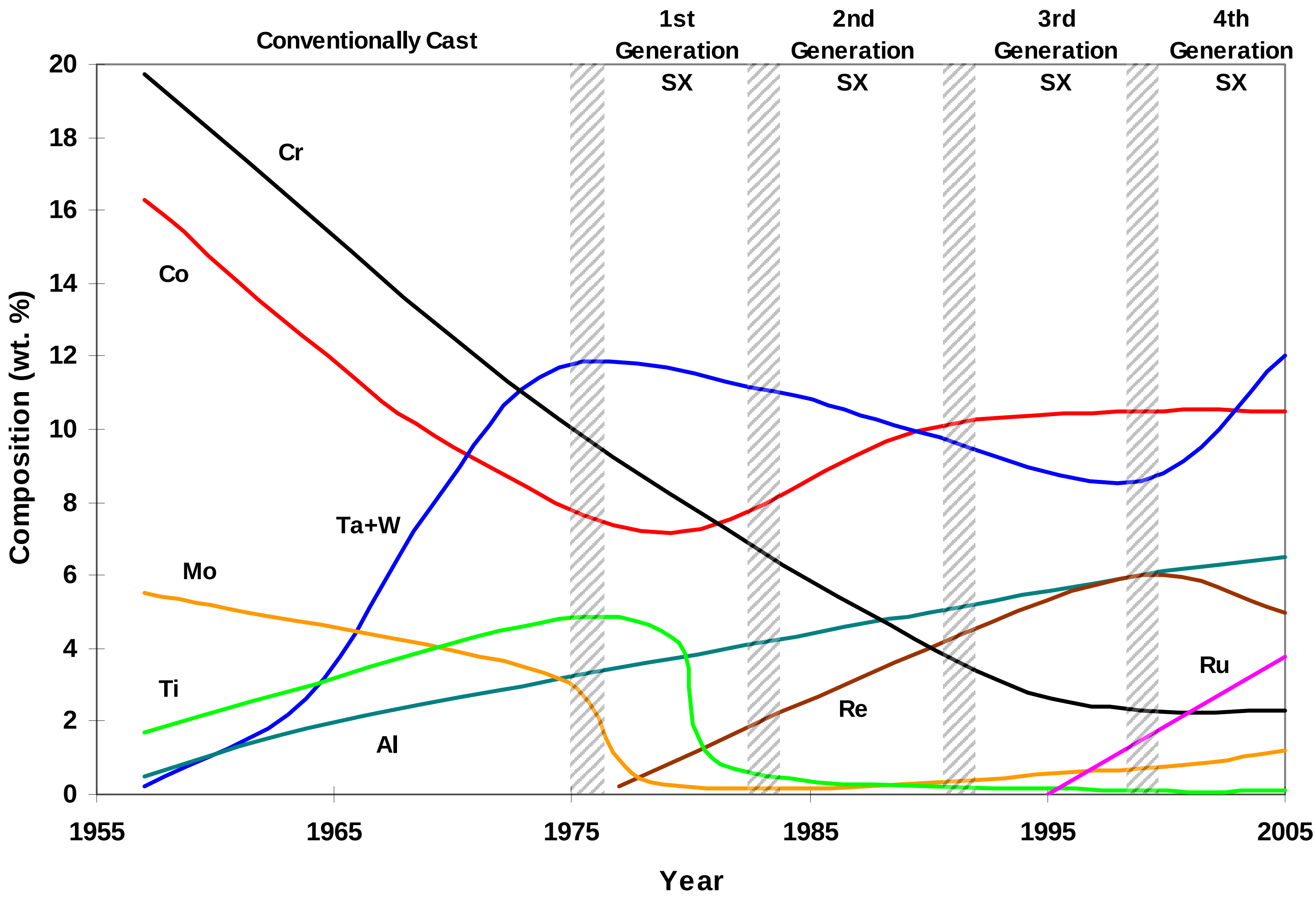
Aircraft Fuel Efficiency – Last 50 Years



2020 Vision for Operating Conditions of Aeroengines



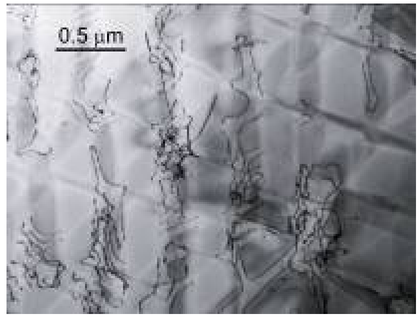
EVOLUTION OF COMPOSITIONS OF CAST TURBINE BLADE AEROFOILS

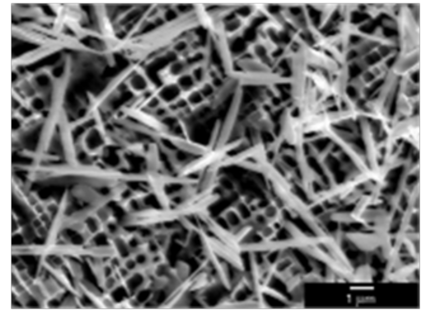


Source: R C Reed, Superalloys: Fundamentals and Applications, Cambridge University Press, 2006

Diffusion is important to superalloy metallurgists..........

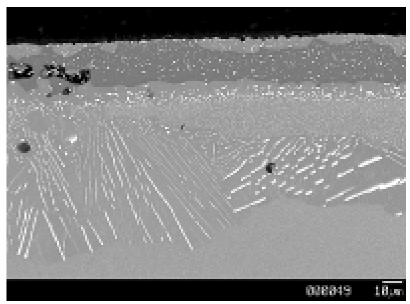
Dislocation creep





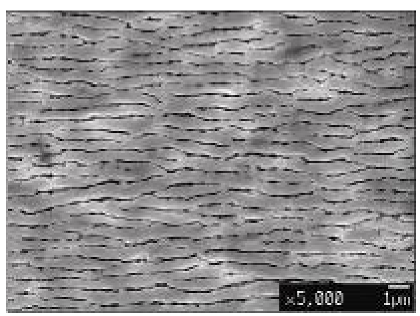
Precipitation of TCP phases

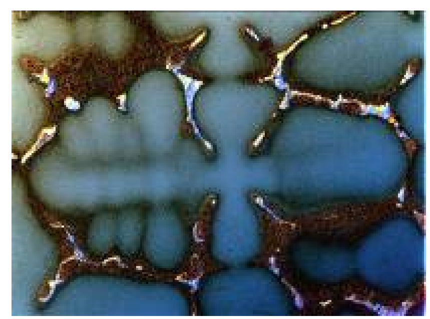
Reaction with coatings



Oxidation

Degradation by the rafting effect

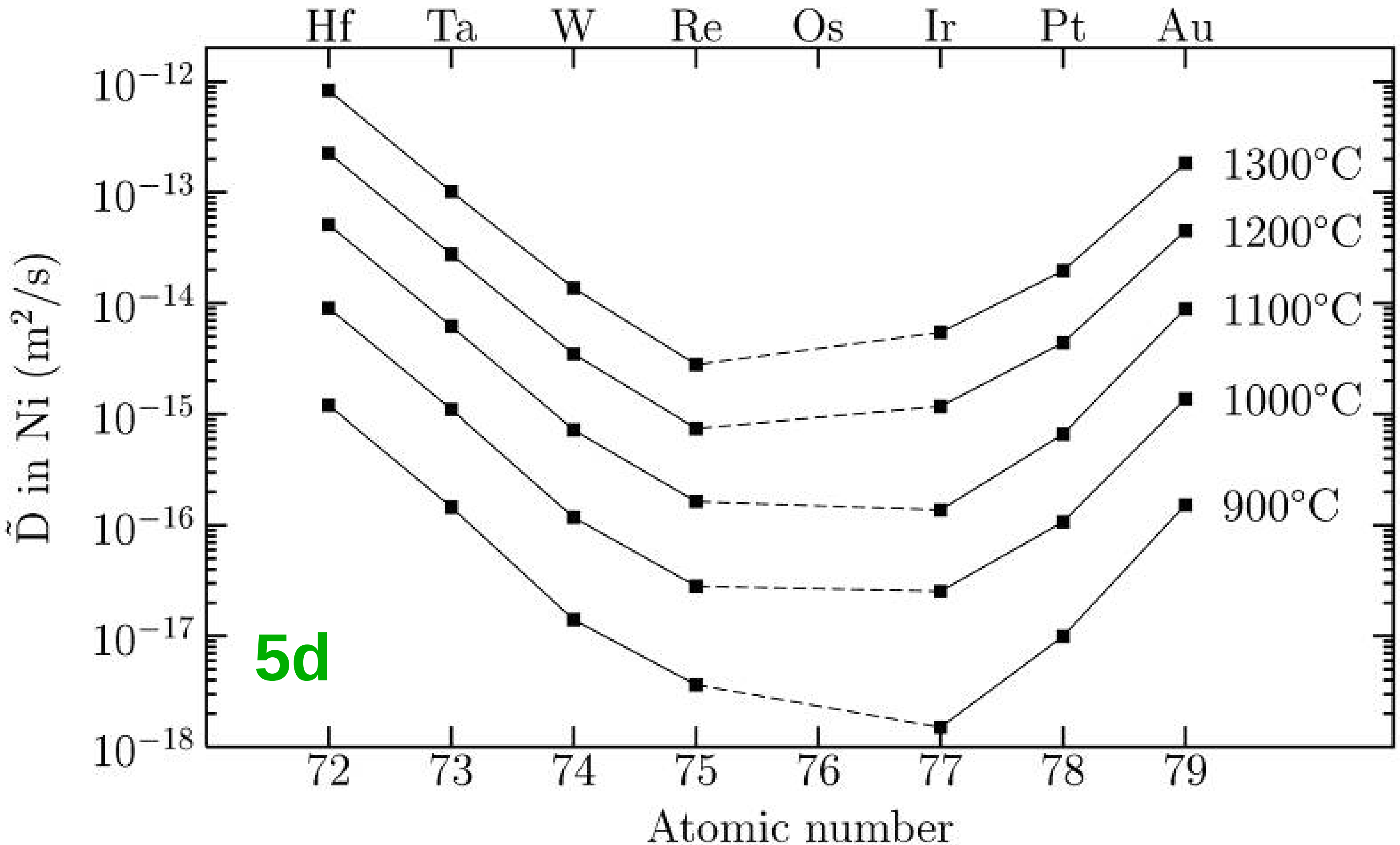




Heat treatment for optimum properties

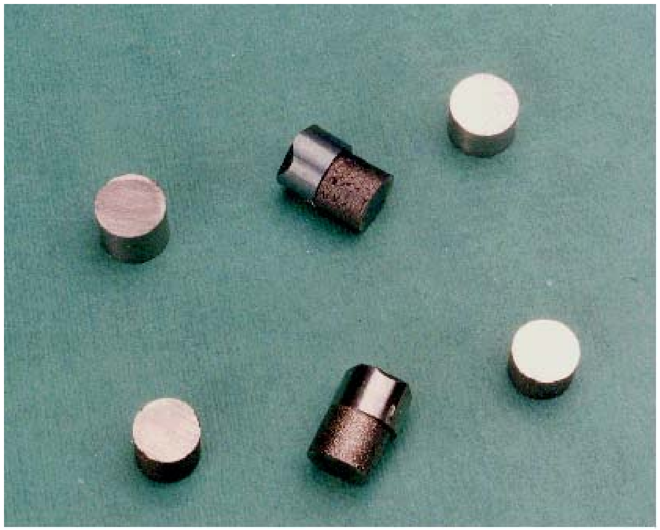
Yet we know very little about the influence of the alloying elements, despite their perceived importance.

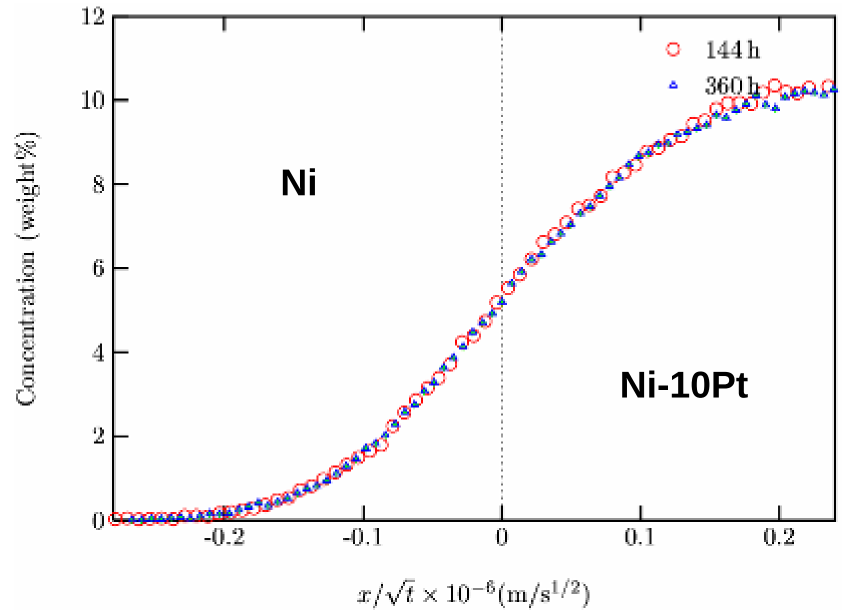
e.g. **diffusion coefficients in γ-nickel**



Karunaratne and Reed, Acta mater, 51, p2905, (2003).

Experiments: Wagner-Sauer-Freise Technique for Interdiffusion Coefficients

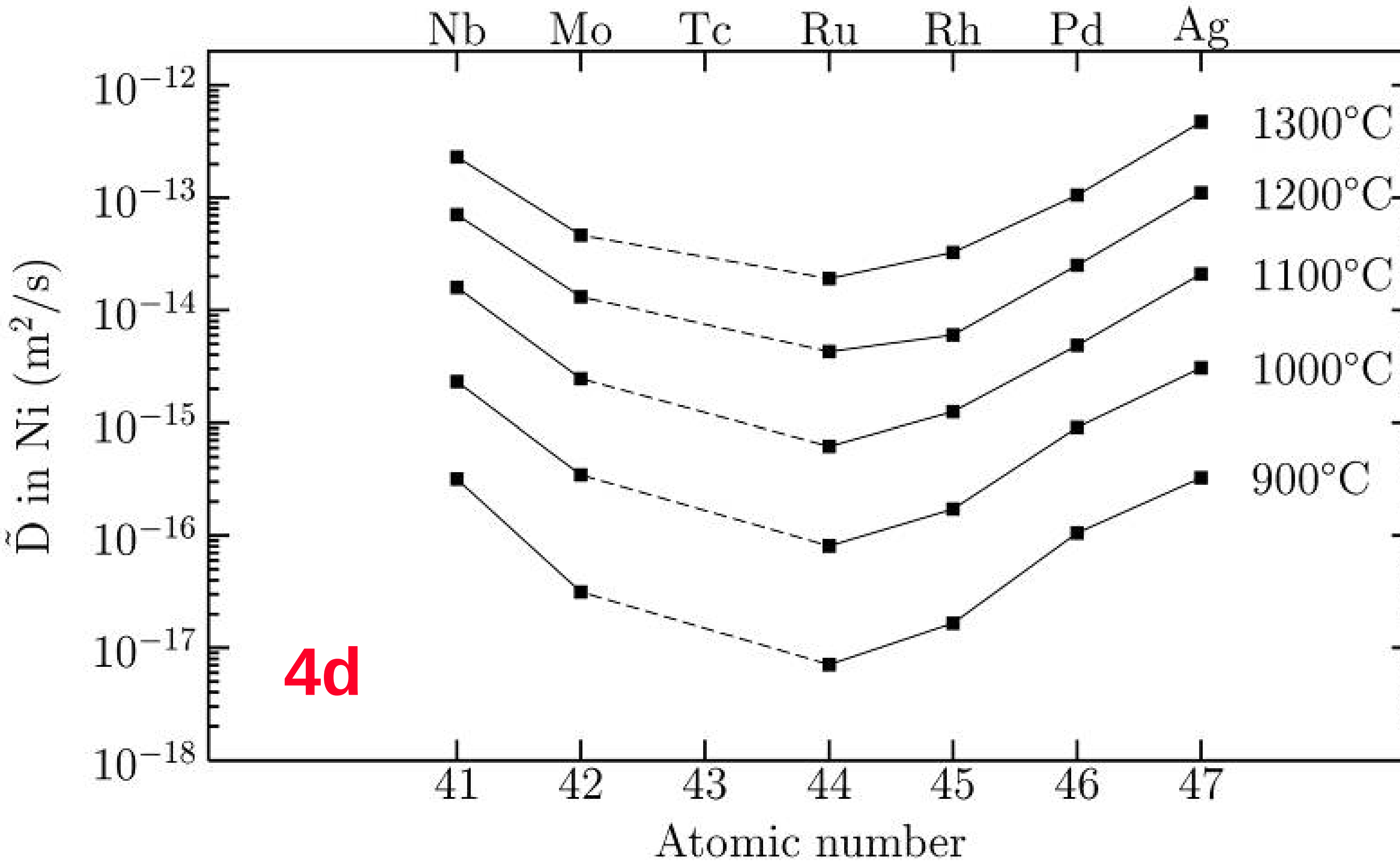




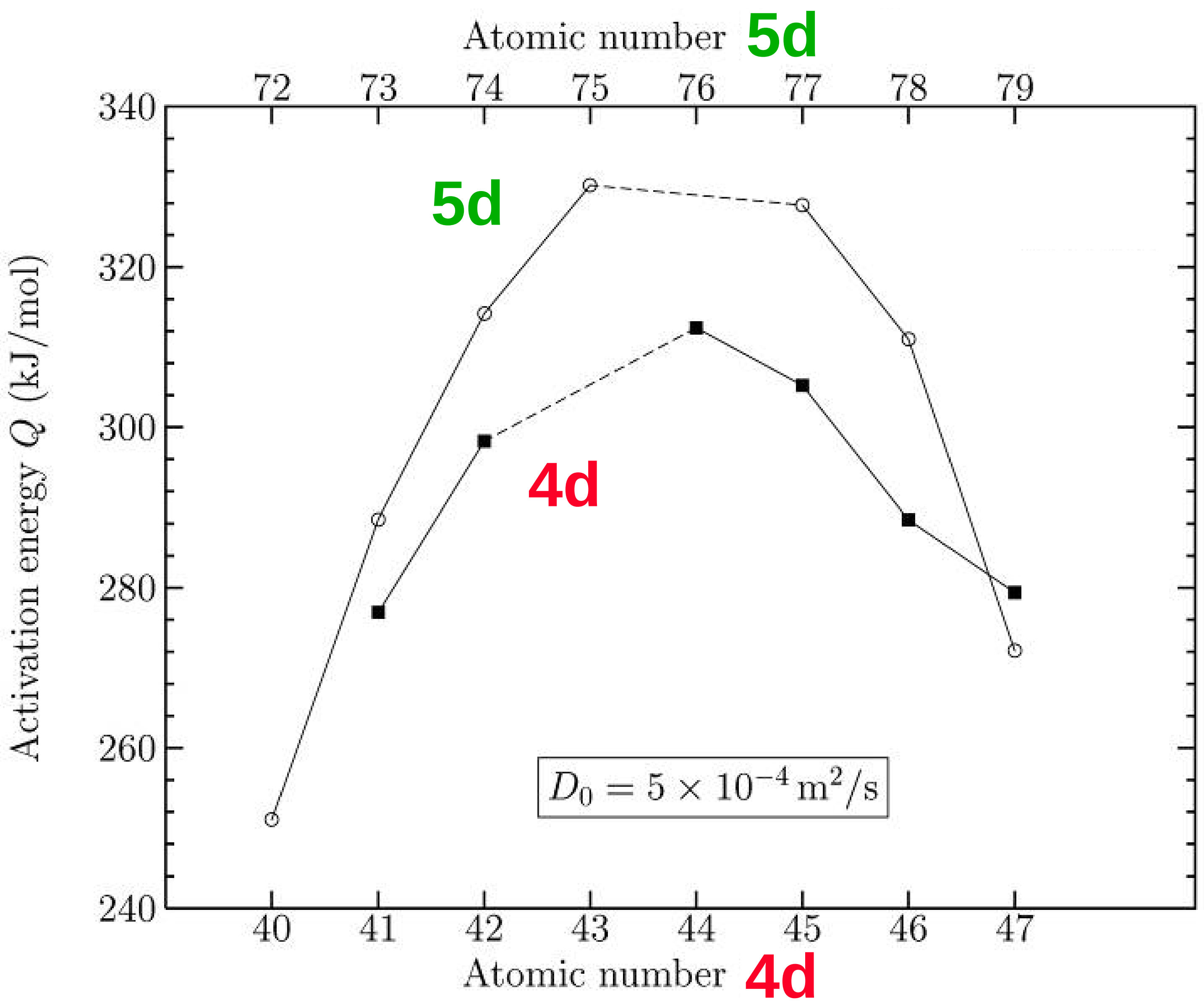
$$\tilde{D} = \frac{1}{2t}\left(\frac{dx}{dY_{\mathrm{Pt}}}\right)_{Y^*_{\mathrm{Pt}}}\left[(1 - Y^*_{\mathrm{Pt}})\int_{-\infty}^{x^*} Y_{\mathrm{Pt}}\,dx + Y^*_{\mathrm{Pt}}\int_{x^*}^{\infty}(1 - Y_{\mathrm{Pt}})\,dx\right]$$

$$Y_{\mathrm{Pt}} = \frac{C_{\mathrm{Pt}} - C^-_{\mathrm{Pt}}}{C^+_{\mathrm{Pt}} - C^-_{\mathrm{Pt}}}$$

Karunaratne and Reed, Acta mater, 51, p2905, (2003).

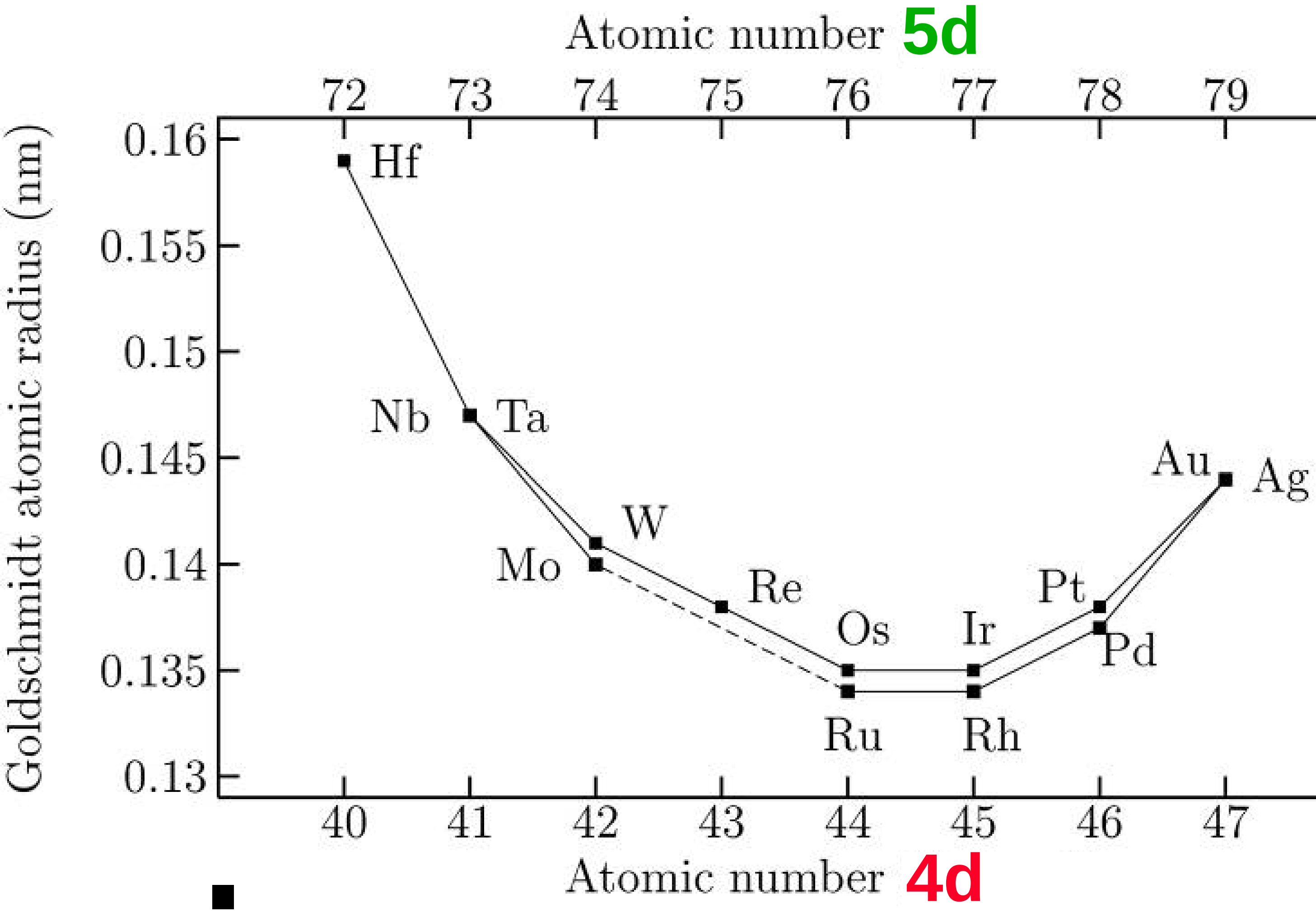


Karunaratne and Reed, Acta mater, 51, p2905, (2003).



Atomic number 5d
72
73
74
75
76
77
78
79
340
320
300
280
260
240
Activation energy Q (kJ/mol)
5d
4d
$D_0 = 5 \times 10^{-4}\,\mathrm{m^2/s}$
40
41
42
43
44
45
46
47
Atomic number 4d

LARGER ATOMS DIFFUSE FASTER!



Ni (0.125nm)

The Need for Quantitative Electron Theory

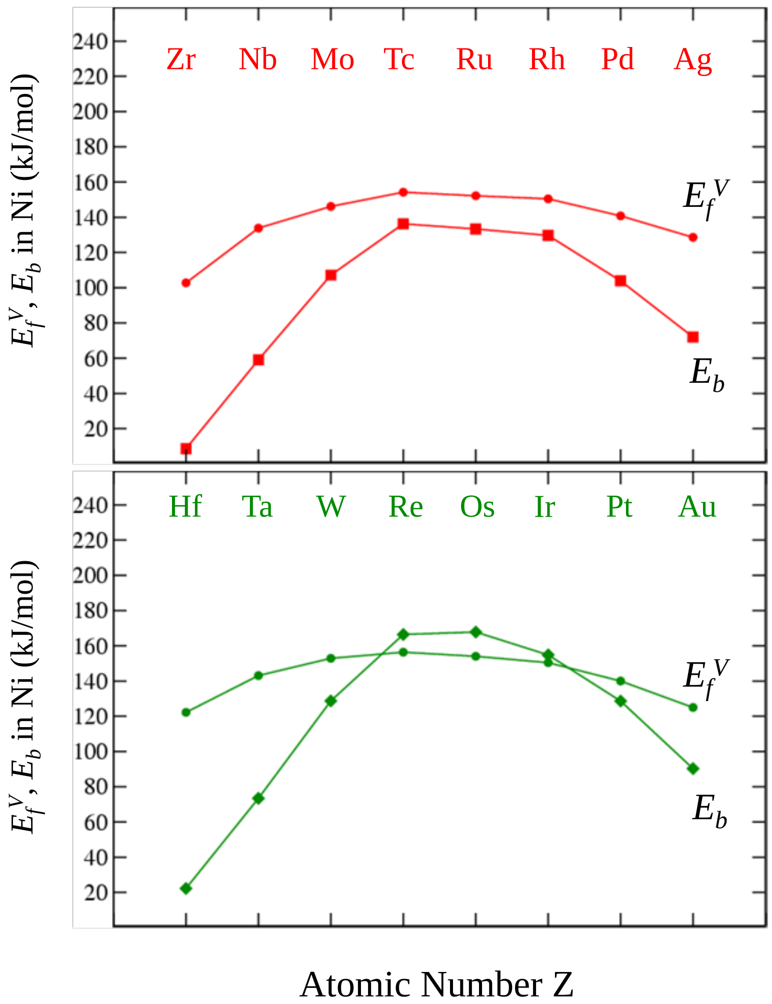
1 The experiments indicate that elements such as Re diffuse very slowly in Ni.

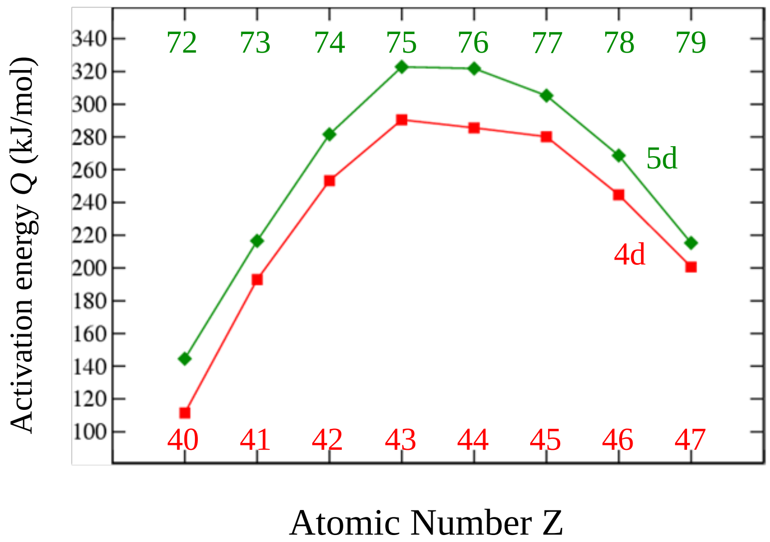
2 Nevertheless, some unanswered questions:

- Why does a small atomic misfit (*e.g.* Re) give a small D?
- Do large atoms (*e.g.* Hf) possess a vacancy cloud?
- What should be the physical interpretation of the correlation between D and atomic number?
- Why do 5d elements diffuse more slowly than 4d ones?
- What about 3d elements, some of which are magnetic?

3 There is a need for quantitative modelling – using statistical mechanics and electron theory – to rationalise these effects.

Predictions for the 4d and 5d Solutes



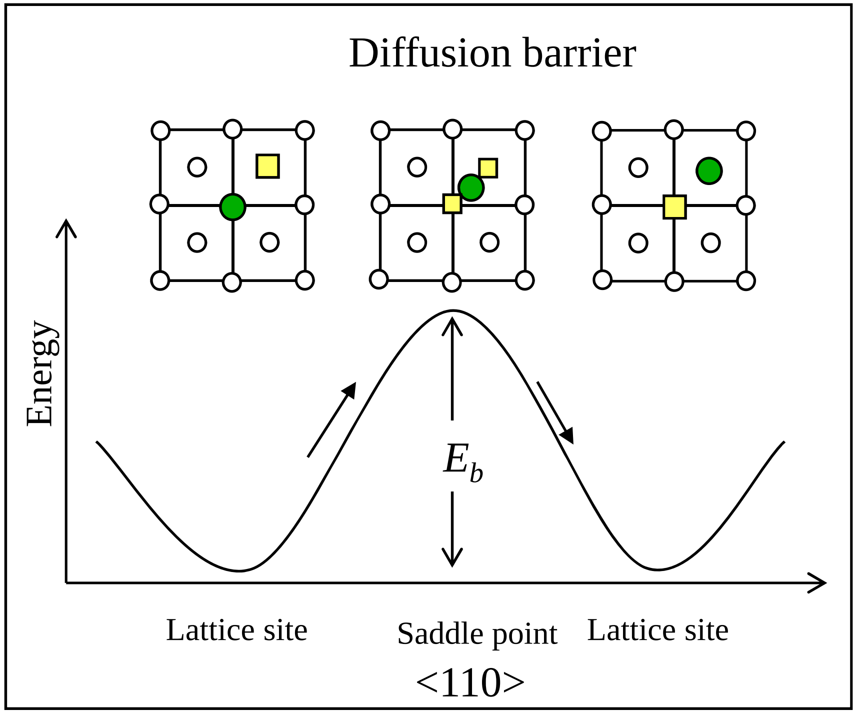


Janotti, Krcmar, Fu and Reed, PRL, 92, 085901, (2004).

-variation of the barrier energy appears to be the most important effect

-activation energy for 5d solutes larger than for 4d

SOLUTE SIZE EFFECT IS UNIMPORTANT!



Contraction of Ni-X bond distance when X at saddle point:

6.8% (0.17Å) Hf

6.2% (0.15Å) Re

5.6% (0.14Å) Au

Janotti, Krcmar, Fu and Reed, PRL, 92, 085901, (2004).

Vacancy-Assisted Diffusion in Nickel Alloys

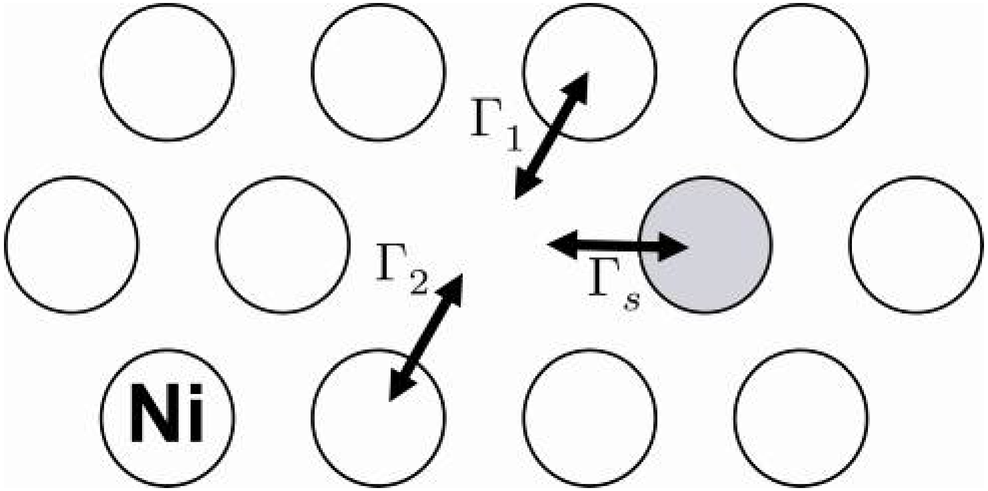
$$\Gamma = \nu_o \exp\left\{-\frac{E_b}{kT}\right\}$$

$$D = f a_o^2 \Gamma p_v$$

$$p_v = C_o \exp\left\{-\frac{E_f^V}{kT}\right\}$$

$$D = f a_o^2 \nu_o \exp\left\{-\frac{E_b}{kT}\right\} \times C_o \exp\left\{-\frac{E_f^V}{kT}\right\}$$

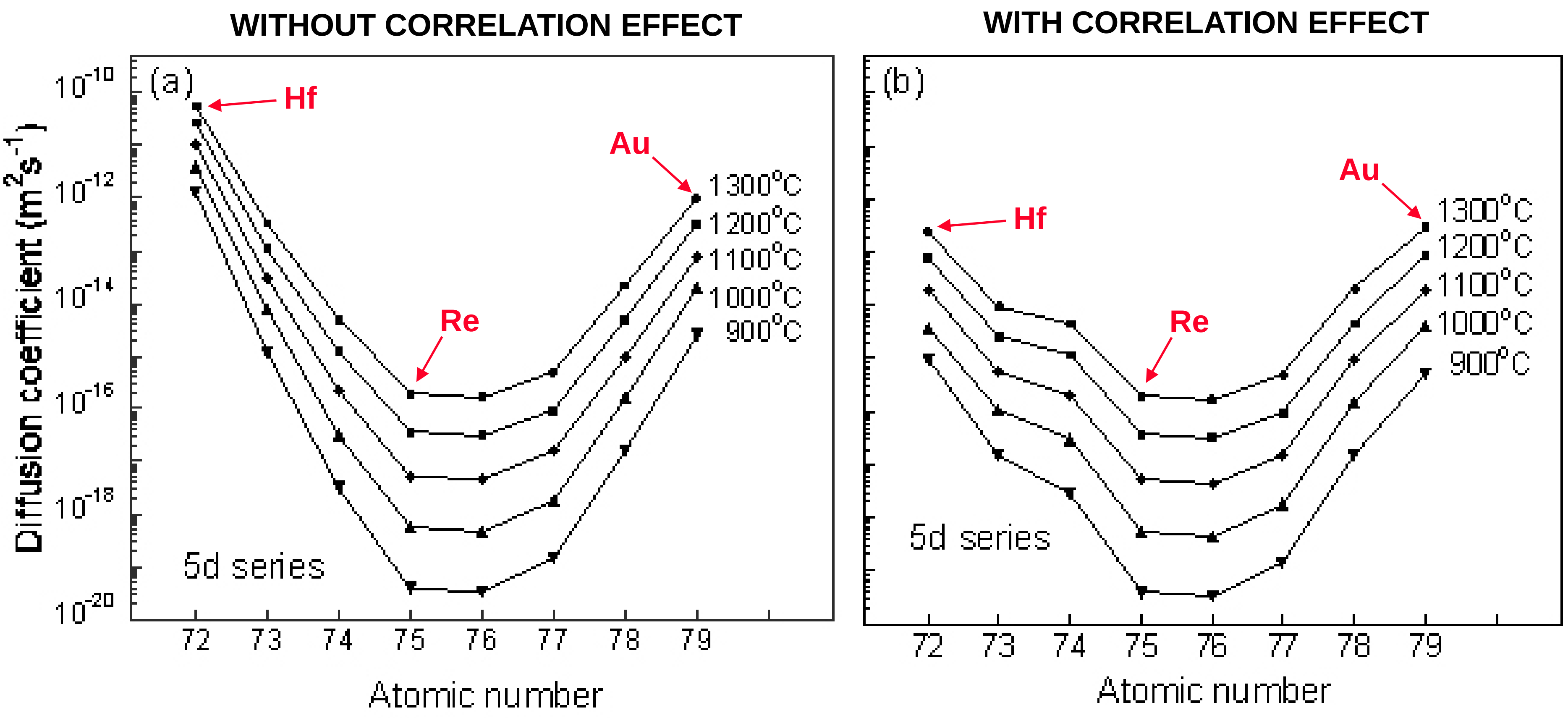
The Correlation Factor in Vacancy-Assisted Diffusion



$$f = \frac{2\Gamma_1 + 7\Gamma_2}{2\Gamma_s + 2\Gamma_1 + 7\Gamma_2}$$

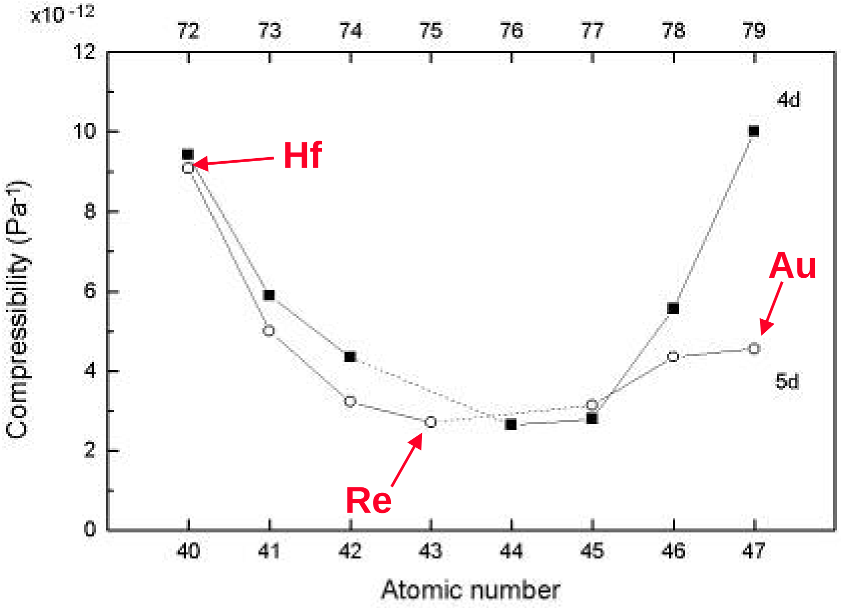
- unity when rate of solute/vacancy exchange is very small
- tends to zero as rate of solute/vacancy exchange -> infinity

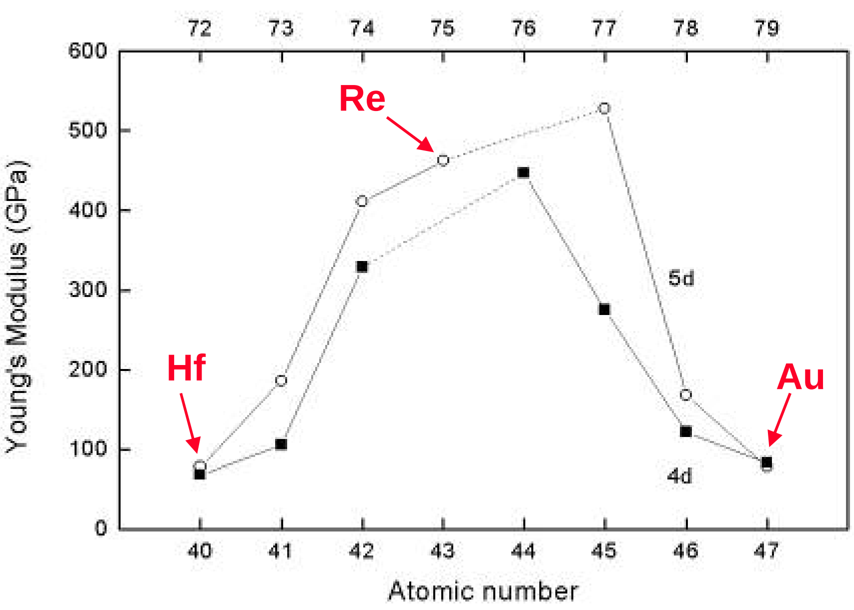
Predictions of Diffusion Coefficients for 5d Solutes



-correlation effects are unimportant for elements from centre of d-block.
-diffusion of Re occurs just as fast as Re/Va exchanges occur.
-within about an order of magnitude of experimental data.

Correlation With Continuum Elastic Behaviour

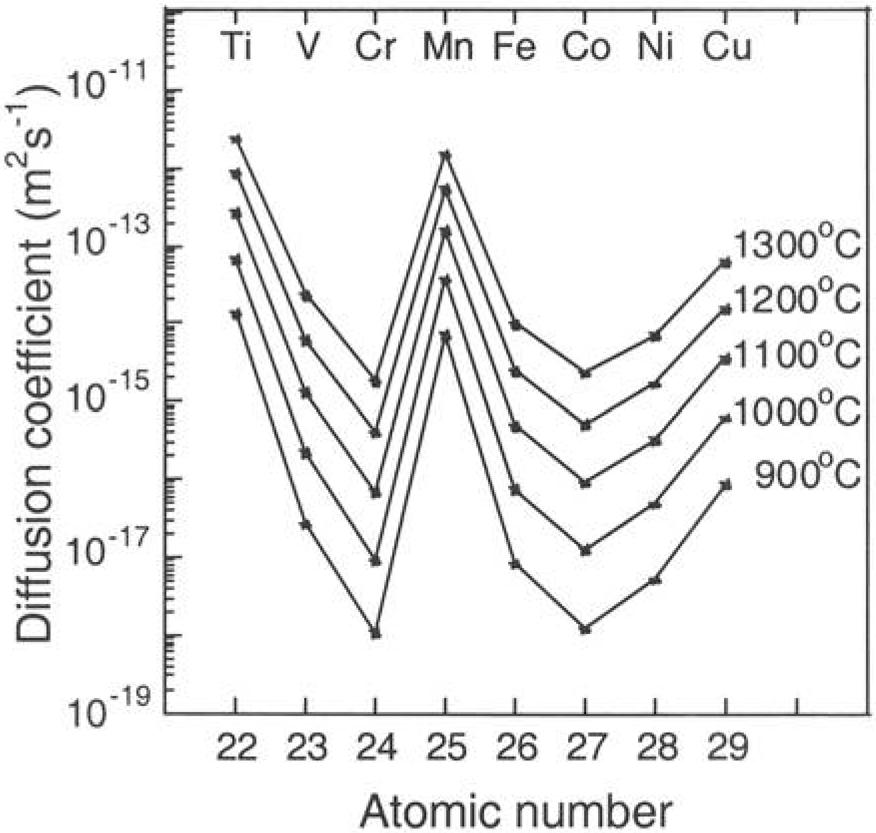




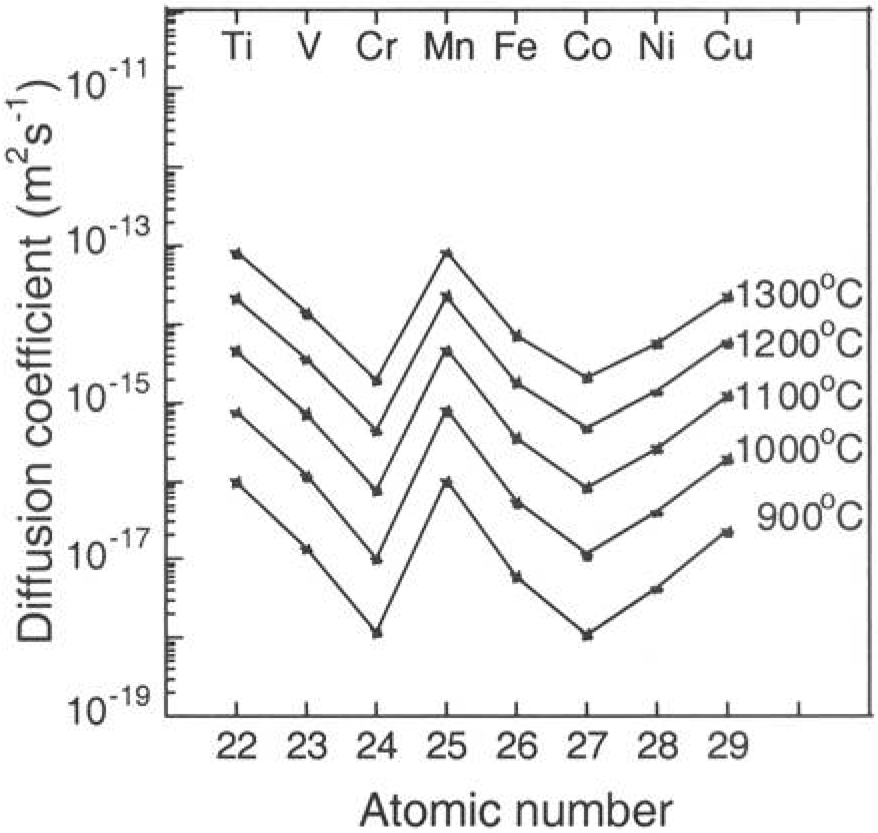
This supports the view that bonding characteristics control diffusion.

Predictions for the 3d Solutes

WITHOUT CORRELATION EFFECT

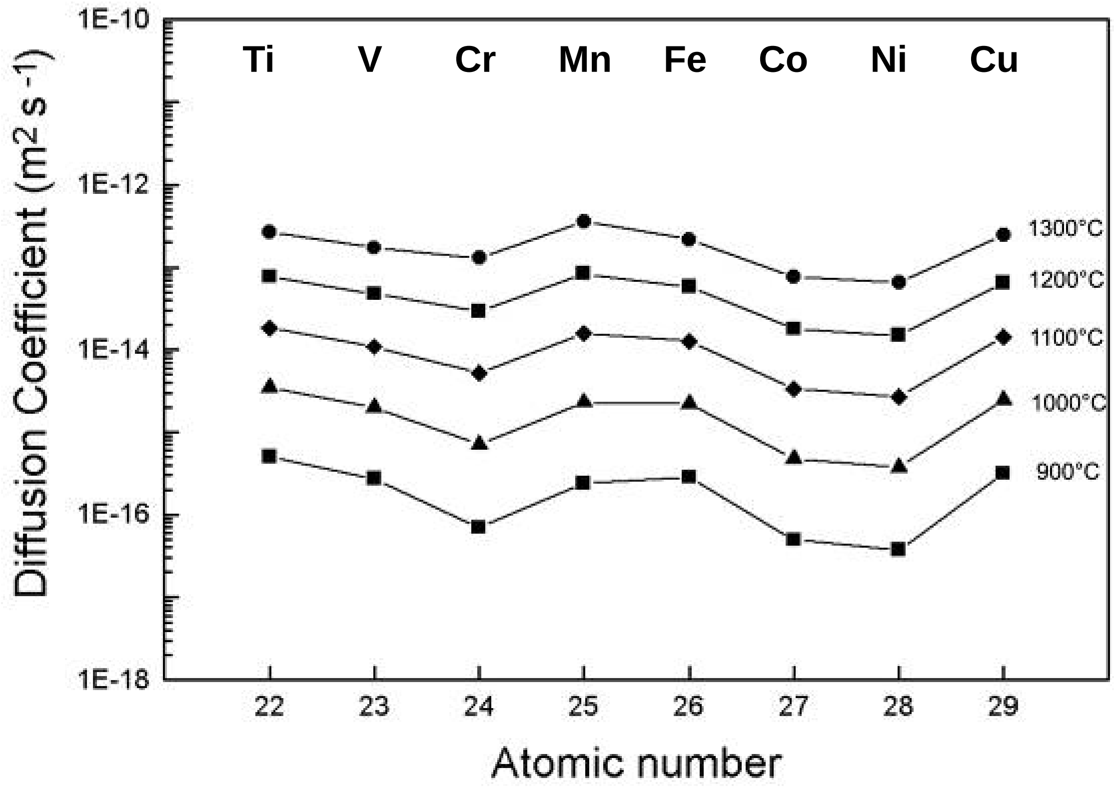


WITH CORRELATION EFFECT



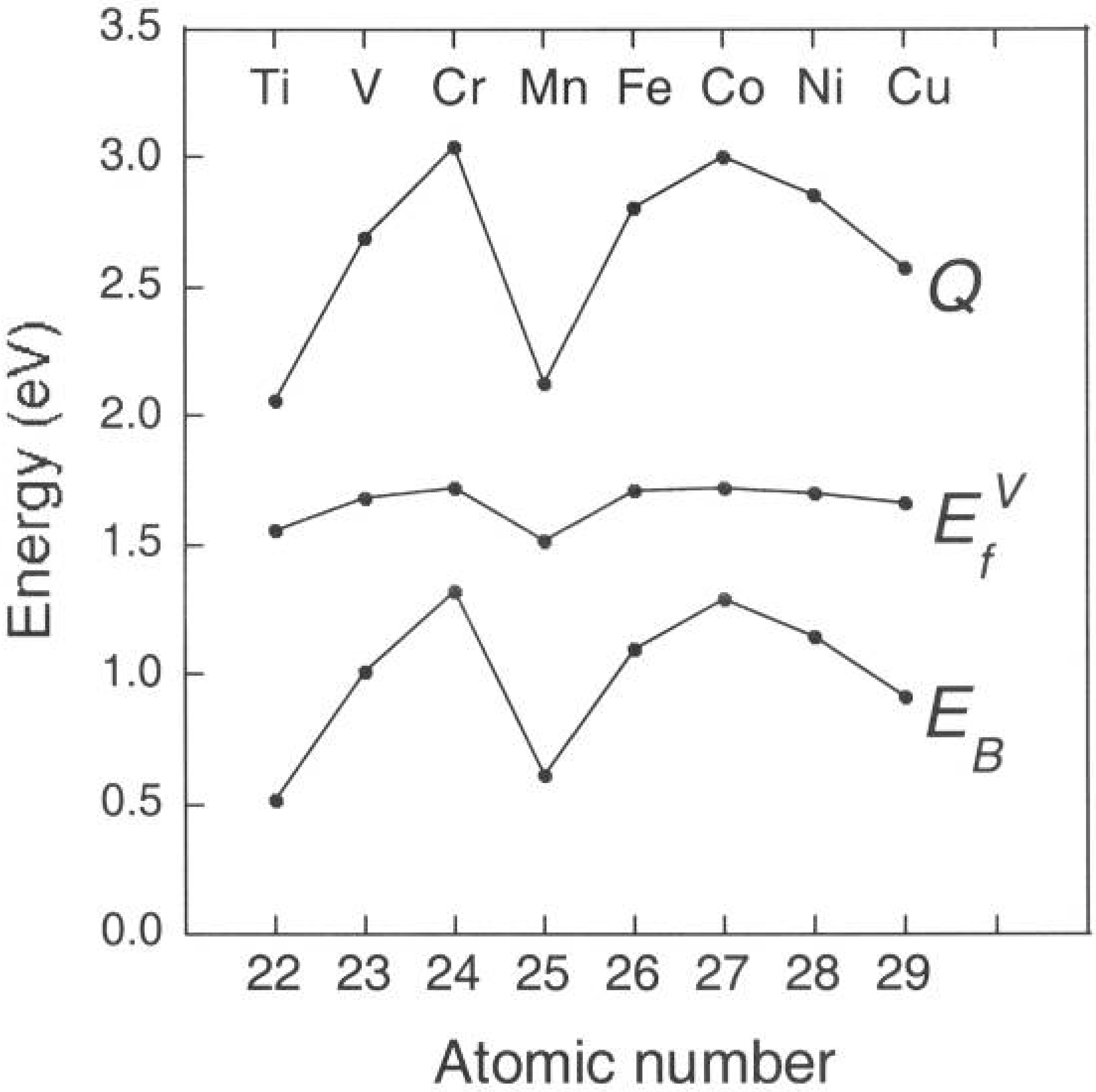
Krcmar, Fu, Janotti and Reed, Acta mater, 53, p2369, (2005).

Experimental Results for the 3d Solutes



Trends correct: but variation of predicted values across d-block about 1 order of magnitude too great

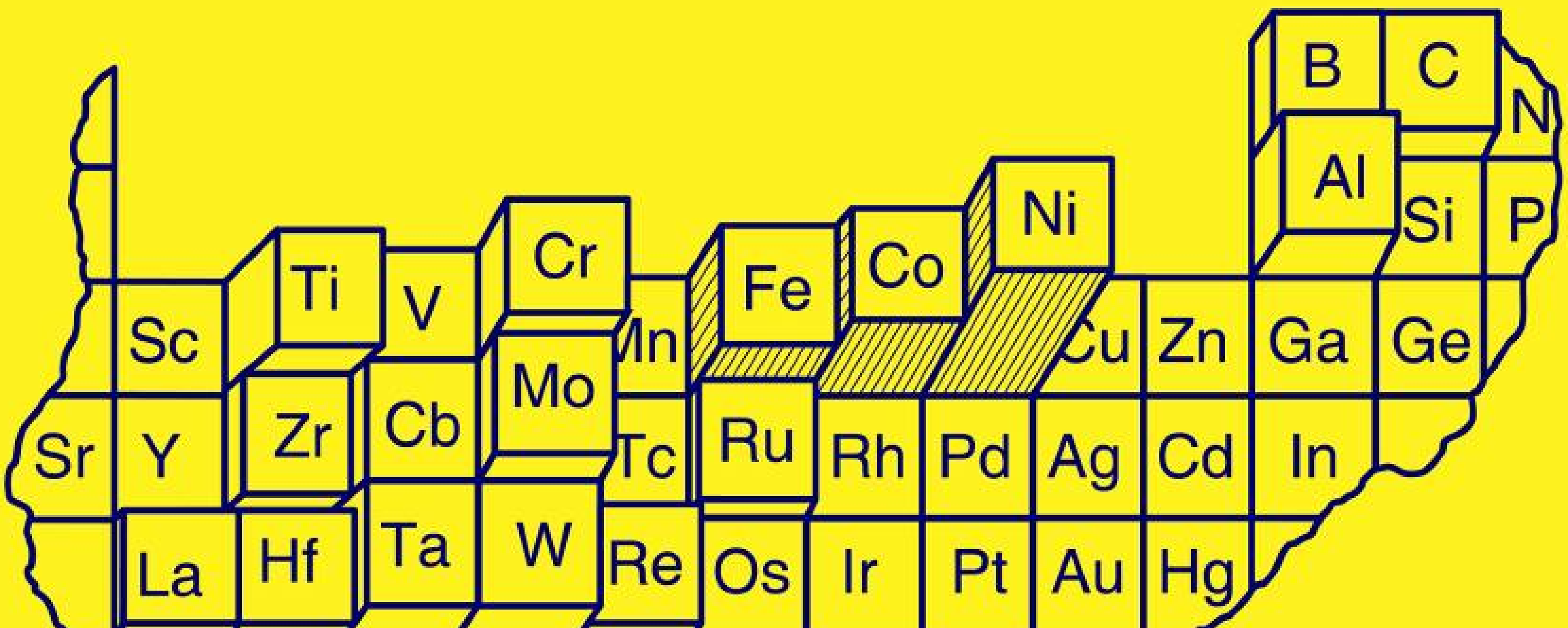
Predictions for the 3d Solutes



Summary & Conclusions

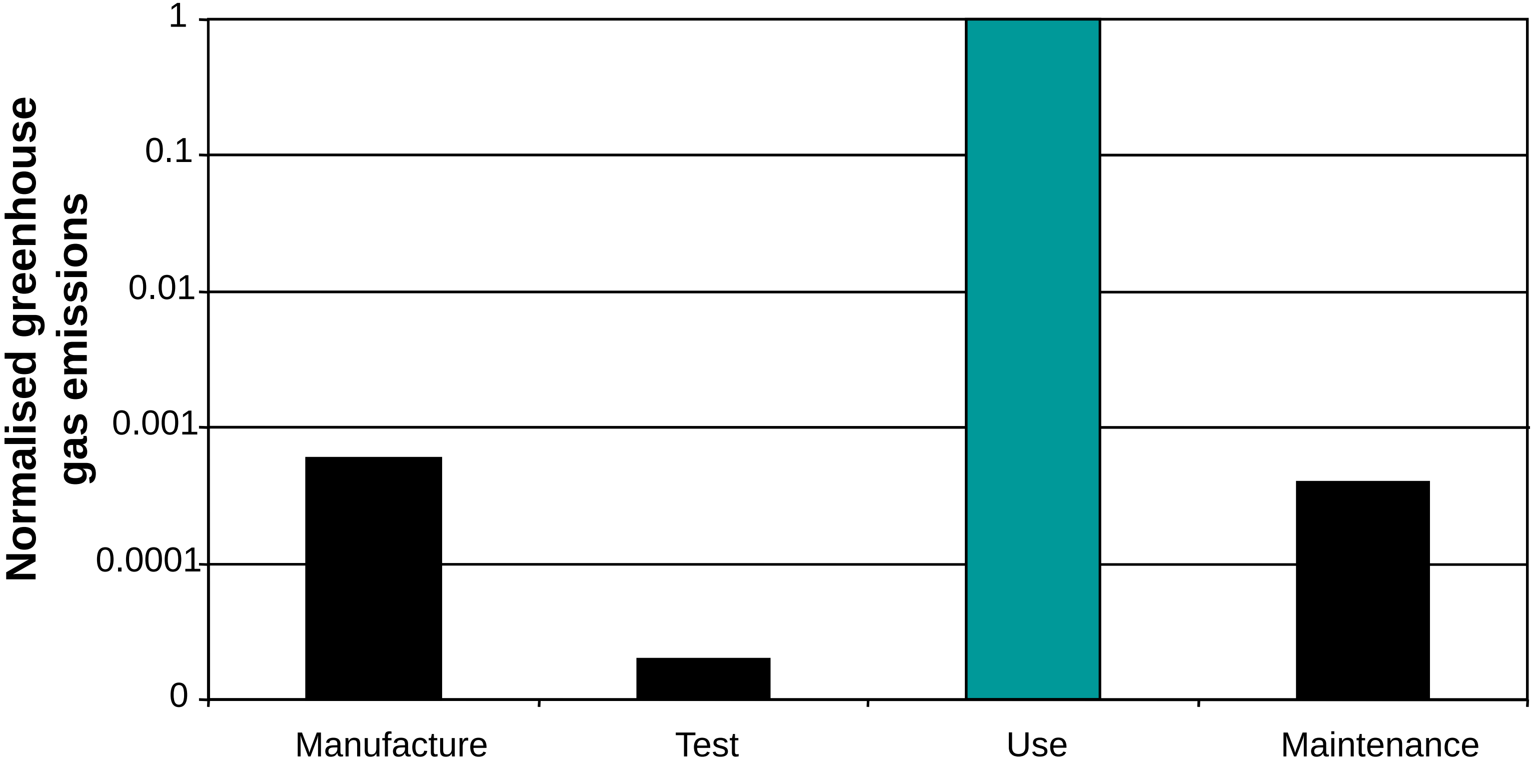
1. **Concerning the diffusion of transition metals in Ni, larger atoms diffuse faster!**
2. **This is due to variations in the solute-solvent bonding characteristics.**
3. **Differences in the diffusion coefficient are caused mainly by variations in the barrier energy:**
   – **Re-Va exchange: 170 kJ/mol Hf-Va exchange: 40 kJ/mol**
4. **Bonding (electronic) effects dominate: solute size effects are relatively unimportant.**
5. **It seems probable that these effects explain why elements such as Re improve the high temperature properties, *e.g.* in creep.**
6. **It should be checked whether the existing CALPHAD kinetic databases reproduce these results.**

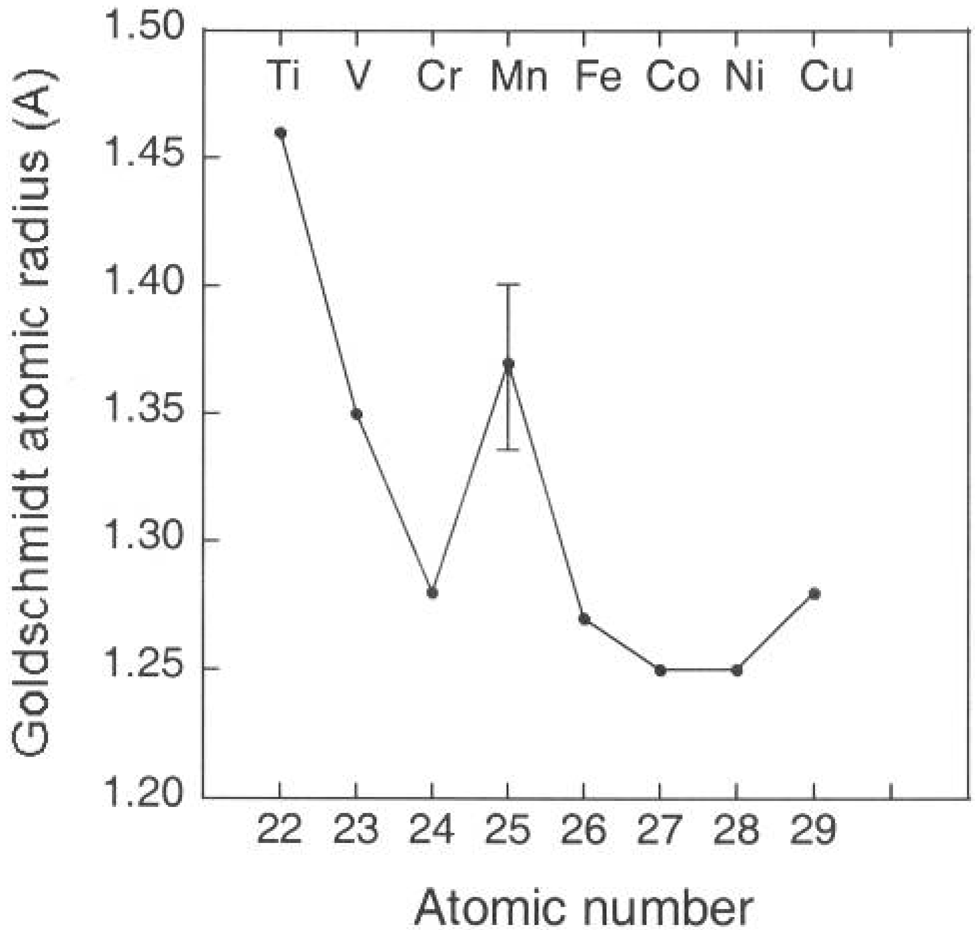
SUPERALLOYS 2008



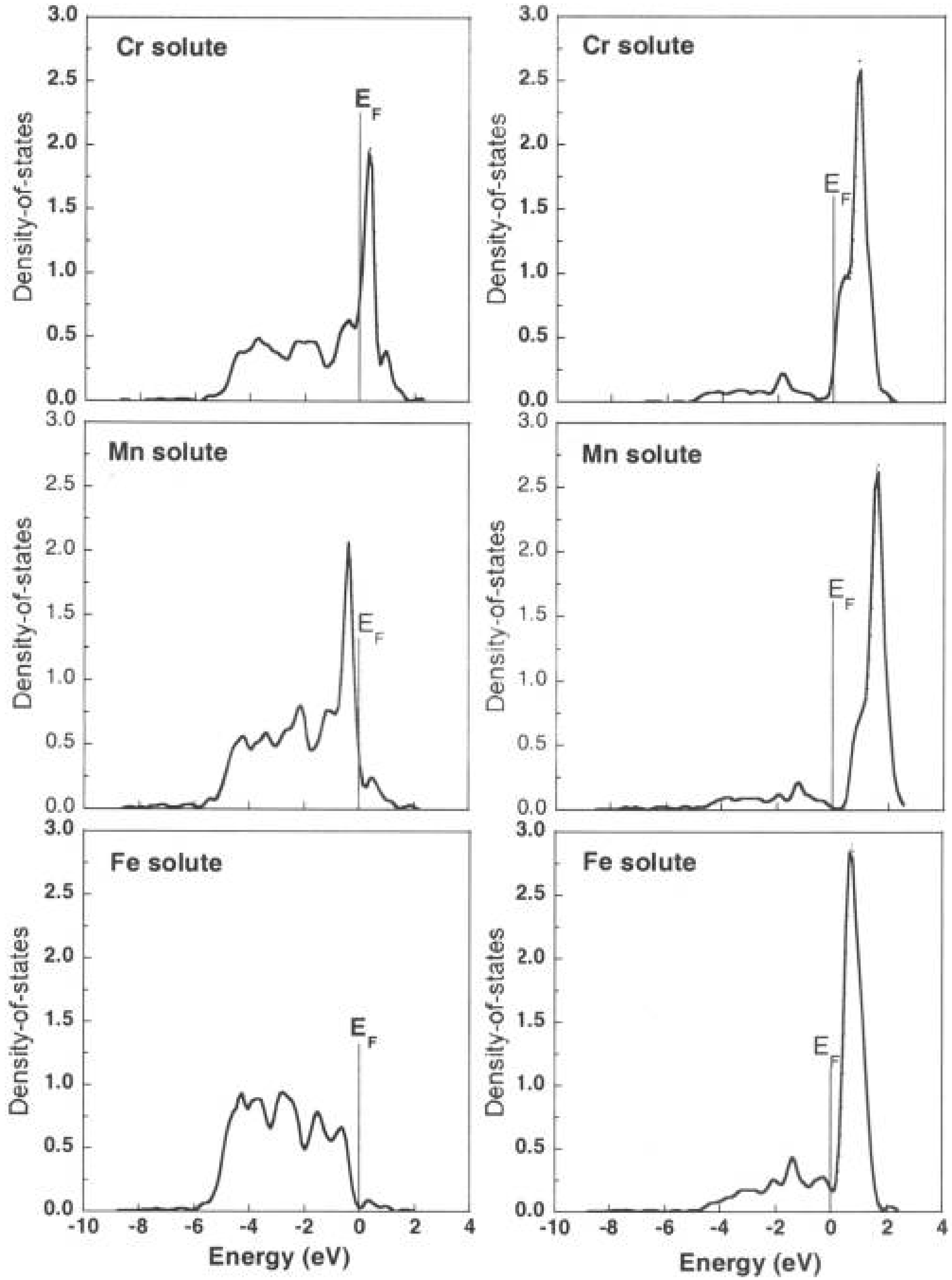
Life Cycle Analysis – The Aeroengine

99.9% of the greenhouse gas emissions associated with an aero engine occur during the ‘in service’ life cycle phase





Goldschmidt atomic radius (A)
1.50
1.45
1.40
1.35
1.30
1.25
1.20
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
22
23
24
25
26
27
28
29
Atomic number



Cr solute
Mn solute
Fe solute
E_F
Density-of-states
Energy (eV)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-10
-8
-6
-4
-2
0
2
4