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" Fundamentals of Thermodynamic Modelling of Materials "

November 15-19, 2010
INSTN – CEA Saclay, France

PROFESSOR & TOPIC

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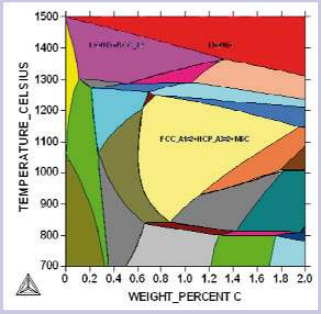
Birmingham University, UK



Application of CT for superalloys

[01002]

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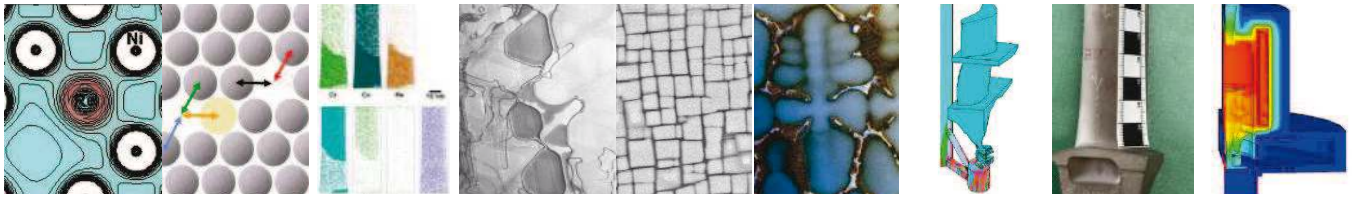


An Alloy Design Approach for Single Crystal Superalloys

Roger C Reed, Atsushi Sato, T Tao and Nils Warnken
Dept of Metallurgy and Materials/Interdisciplinary Research Centre
University of Birmingham, UK

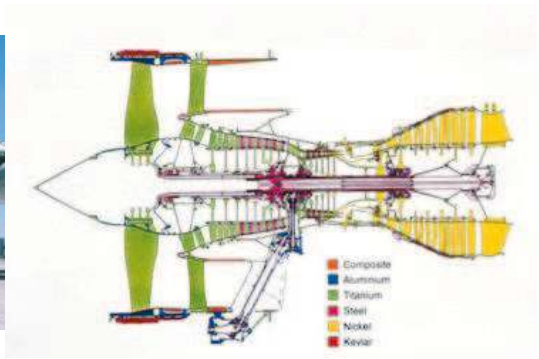
15th November 2010

significantly based upon:
R C Reed, T Tao and N Warnken, Acta mater., 57 (2009) pp5898-5913
A Sato and R C Reed, Acta mater., accepted.

UNIVERSITY OF BIRMINGHAM

Interdisciplinary Research Centre

Technical Focus in Reed's Group: High Temperature Materials



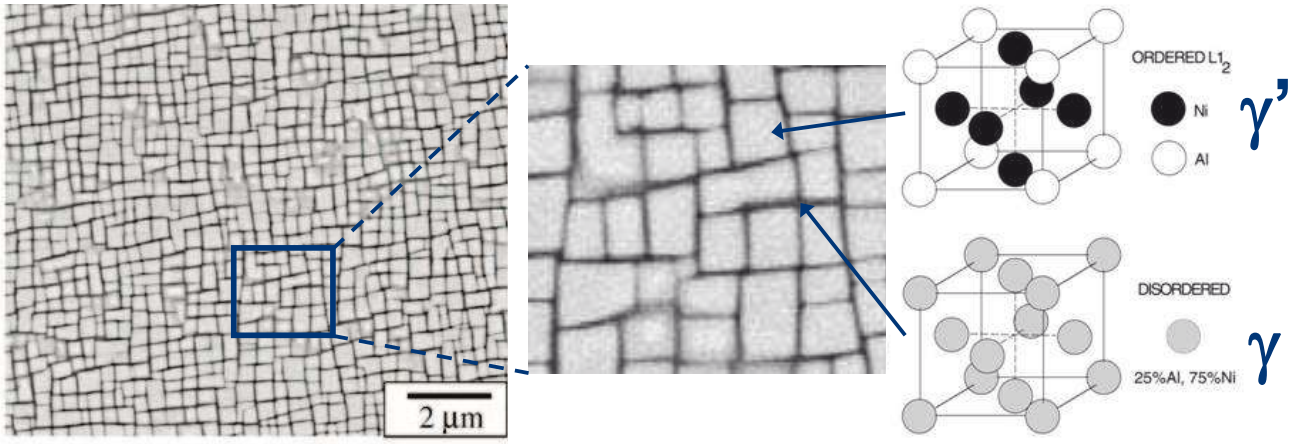
- **Quantification and modelling of factors controlling composition-dependence of key properties of high temperature materials:**
  - ***Mechanical performance, e.g. creep and fatigue.***
  - ***Microstructural stability, e.g. rafting, resistance to TCP precipitation.***
  - ***Environmental resistance, e.g. to oxidation, TBC adherence.***
  - ***Manufacturing, e.g. prediction of processing, including defect formation.***
- **Integration of modelling methods to enable intelligent design of new alloy systems and processes by simulation-driven approaches.**

Can computational modelling be used to design better alloys?

Overview of Presentation

- Introduction
- Design of Alloys-By-Design Method
- Demonstration of Alloys-By-Design Procedure
- Case Study: Design of a Single Crystal Superalloy for Industrial Gas Turbine Application
- Summary and Conclusions

Microstructure and Compositions of Nickel-Based Superalloys



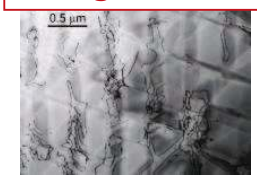
Alloy	Cr	Co	Mo	W	Al	Ti	Ta	Re	Ru	Hf	C	B	Ni
CMSX-4	6.5	9.6	0.6	6.4	5.6	1.0	6.5	3.0	–	0.1	–	–	Bal
CMSX-10	2.0	3.0	0.4	5.0	5.7	0.2	8.0	6.0	–	0.03	–	–	Bal
MX4	2.0	16.5	2.0	6.0	5.55	–	8.25	5.95	3.0	0.15	0.03	–	Bal
PWA1484	5.0	10.0	2.0	6.0	5.6	–	9.0	3.0	–	0.1	–	–	Bal
Rene N5	7.0	8.0	2.0	5.0	6.2	–	7.0	3.0	–	0.2	–	–	Bal
Rene N6	4.2	12.5	1.4	6.0	5.75	–	7.2	5.4	–	0.15	0.05	0.004	Bal

- 10 alloying elements: concentration to within 1 wt% (range 0 to 10 wt%) yields 10^{10} possible alloys!

Conclude: one cannot hope to find optimal composition(s) without analysis and modelling.

What Makes a Good Single Crystal Superalloy? The Design Requirements

Design Constraints



Resistance to creep

Oxidation resistance

Castability e.g. freckling

Density

£, $, €

Cost

Phase constitution, gamma prime γ' fraction, lattice misfit, stability of TCP phases, Al_2O_3 scale kinetics, diffusion coefficients, solid/liquid partitioning, buoyancy of interdendritic liquid, elemental densities, cost/lb…….

???

Composition – Microstructure – Property relationships

Bulk Chemistry

Ni

Cr

Co

Al

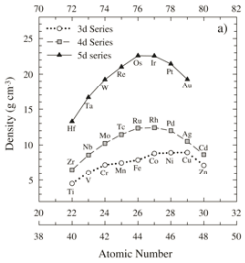
Re

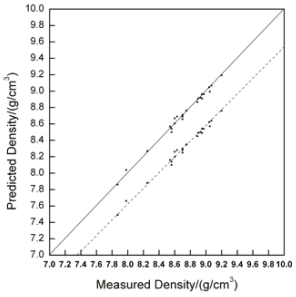
Ru

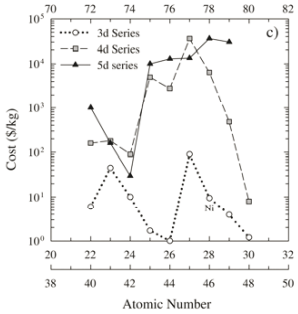
W

Ta

Alloy Design Concept – Single Crystal Superalloys





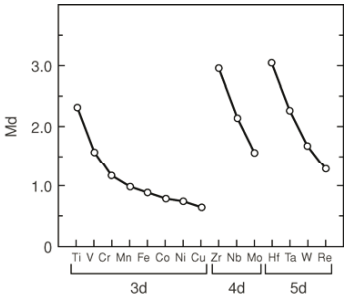


$$M_{creep} = \sum_i x_i / \tilde{D}_i$$

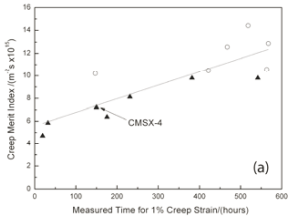
DENSITY | COST

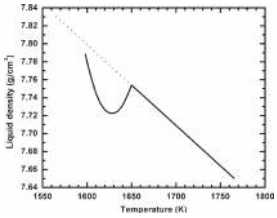
CREEP RESISTANCE | MICROSTRUCTURAL STABILITY

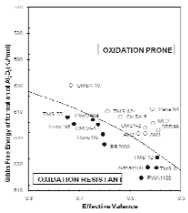
PROCESSING: CASTABILITY | OXIDATION RESISTANCE



$$\overline{M_d} = \sum_i \overline{x}_i M_{di}$$

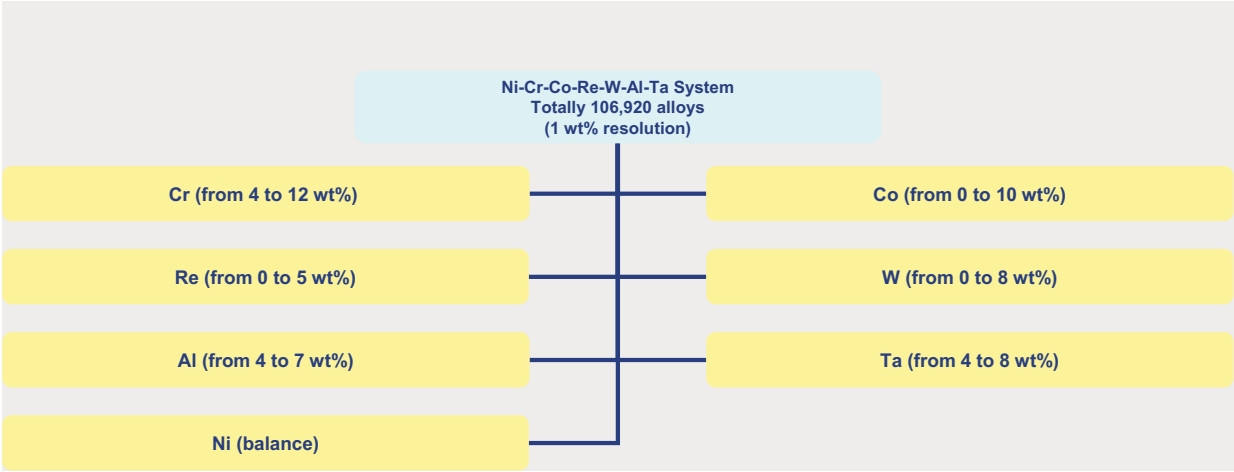






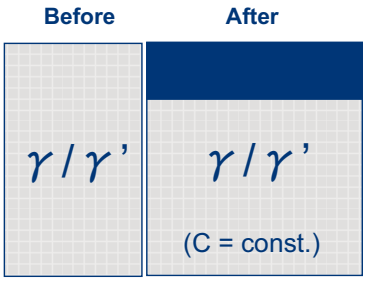
- quantitative composition/property relationships are needed.

The Alloy-By-Design Concept



- Choose an alloy design space in which to work: composition limits and an appropriate resolution, e.g. 0.1wt%, 0.5wt%, 1.0wt%.
- For each composition, calculate merit indices for creep, oxidation, castability, cost, density, etc
- Eliminate compositions which have undesirable microstructural characteristics: incorrect phase balance, misfit too large, unstable with respect to TCP formation etc.
- Apply systematically the design limits which are acceptable, eliminating compositions from the dataset as they are shown to be unsatisfactory.
- Once final dataset has been chosen, search for compositions which display the optimal properties or optimal combination of them.

Model for Oxidation Resistance



$$\left(\frac{4}{3}\right)\mathrm{Al\ (in\ superalloy)} + \mathrm{O_2(gas)} \rightarrow \left(\frac{2}{3}\right)\mathrm{Al_2O_3\ (solid)}$$

$$k_t = -\frac{\sigma_t (t_a + t_c) t_{el}}{z_c^2 z_a^2 e^2} \boxed{\Delta G_f}$$

Nernst-Einstein relation…

$$\frac{c_o z_a^2 e^2}{kT} D_O$$

when n-type..

$$0 \quad 1$$

$$-\frac{\sigma_t (t_a + t_c) t_{el}}{z_c^2 z_a^2 e^2}$$

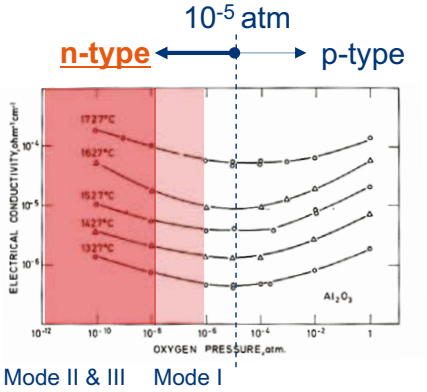
$$\Delta G_f = \Delta G_0 + RT \ln \left(\frac{a_{\mathrm{Al_2O_3}}^{2/3}}{a_{\mathrm{Al}}^{4/3} P_{\mathrm{O_2}}} \right)$$

1

$0.2193 \times T$ -1127.3137 (kJ/mol)

0.23

thermodynamical calculation



For example.. $\left(\frac{V_{\ddot{O}}}{c_o}\right) D_{V_{\ddot{O}}}$

$$= -\frac{c_o D_{O_i}}{z_c^2 kT} = \underbrace{\left(-\frac{(D_{V_{\dot{O}}} \text{ or } D_{V_{\ddot{O}}})}{z_c^2 kT} \right)}_{\text{const. at const. } T} \left[V_{\dot{O}} \text{ or } V_{\ddot{O}} \right] \propto \Delta e' = \boxed{\sum_{n=i} (z_i - z_{\mathrm{Al}}) c_i}$$

~Oxidation rate~
1. *f* (ΔG_f)
2. *f* (impurities factor)

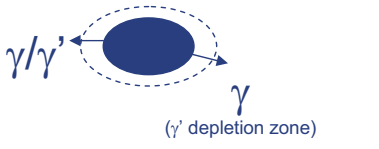
Knacke O, et al. Thermochemical properties of Inoganic substances,1991.
Kofstad P. Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides.1983.

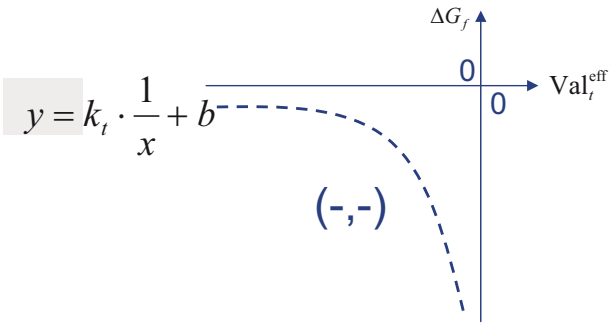
Models for Oxidation Resistance: Concept of Oxidation Diagram

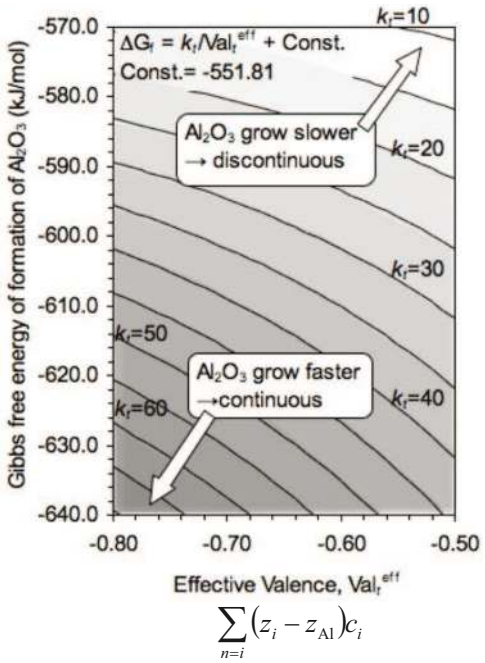
Oxidation rate of Al_2O_3 k_t proposed;

$$k_t \propto \left[\sum_{n=i} (z_i - z_{\mathrm{Al}}) c_i \right] \cdot \Delta G_f$$

x- axis y- axis





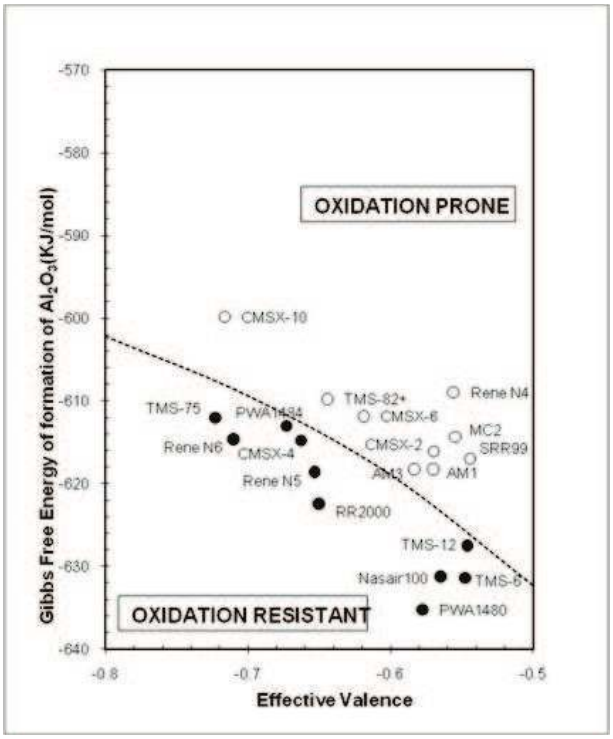


A Sato and R C Reed, Acta mater, accepted for publication.

Models for Oxidation Resistance: Merit Index $M_{oxidation}$

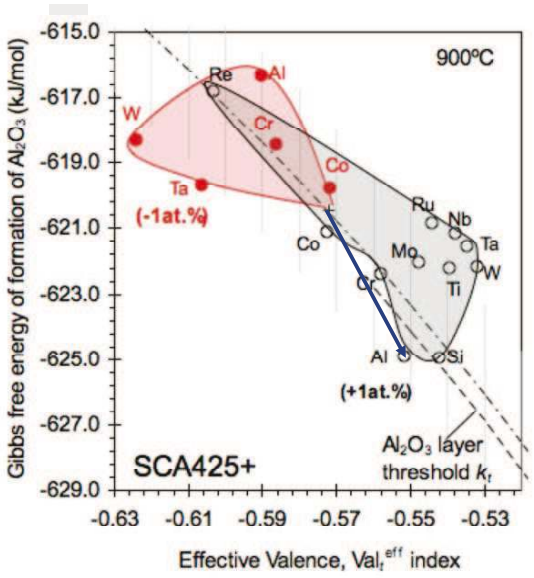
- **Definition of Oxidation Merit Index**
  Since the Al_2O_3 formation depends on both ΔG_f and Val_t^{eff} predictions, 'oxidation diagrams' can be developed. An example is given opposite.

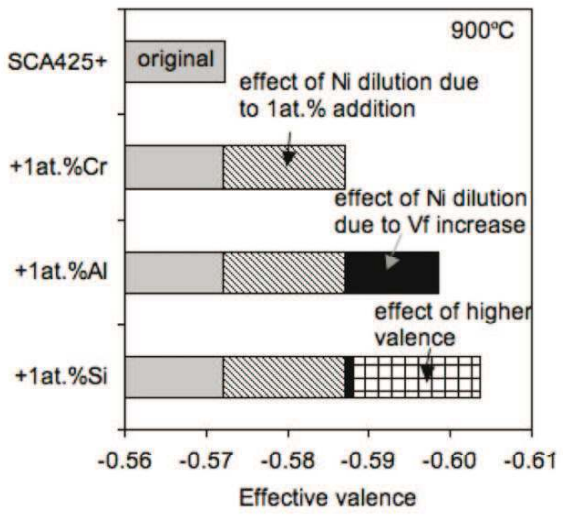
  Alloys with perfect Al_2O_3 layer are expected to lie towards the bottom of the diagrams while those towards the top right are unlikely to form a good Al_2O_3 layer. Furthermore, based on the oxidation diagram, an oxidation merit index $M_{oxidation}$ is introduced which is defined as the distance between the plotted point and the dashed line in the oxidation diagram.



A Sato and R C Reed, Acta mater, accepted for publication.

Applications of Merit Index $M_{oxidation}$





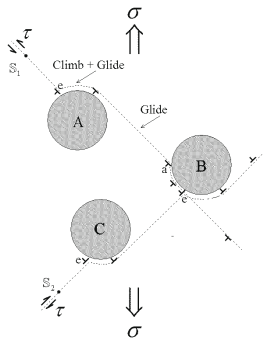
~For Al_2O_3 formation~

Beneficial:	Al and Si
Neutral:	Cr, Co and Re
Detrimental:	Mo, W, Ti, Ta, Nb and Ru

Si addition is as good as Al addition because of
(1) similar thermodynamical effect and
(2) smaller increase of Vf

Model for Dependence of Creep Deformation on Composition in SX Superalloys

- Assume only a fraction of the total mobile dislocation network is gliding at any given time
- Assume gliding dislocations supplied by thermal activation of climbing dislocations, then



$$\dot{\varepsilon} = 2M^{-1}\,\rho_m\,\phi_p\left(1-\phi_p\right)\left(\sqrt{\pi/4\phi_p}-1\right)c_{j,0}D_{v,0}\,e^{-Q_{d/j}/RT}\sinh\left(\frac{(\sigma-\sigma_k)b^2\,\lambda_p}{MkT}\right)$$

Mobile dislocation density

Back stress

Creep strain rate

γ′ volume fraction

diffusivity of jogs

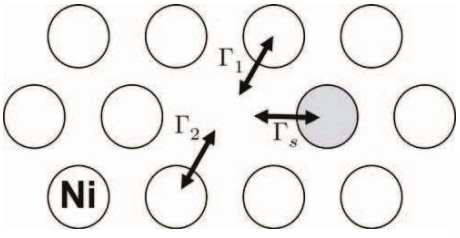
Particle spacing

after B.F.Dyson,
Materials Science and Technology, (2009).

- Suppose 'microstructural architecture' (γ' phase fractions, morphologies, initial dislocation density) is constant; then

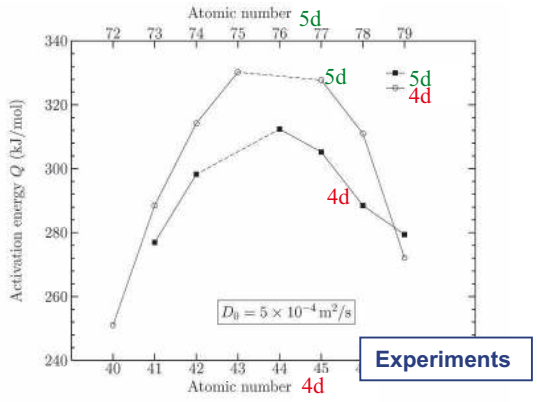
Composition dependence of creep deformation rate depends largely upon the diffusivity term.

Activation Energies for Vacancy-Assisted Diffusion of Solutes in Nickel

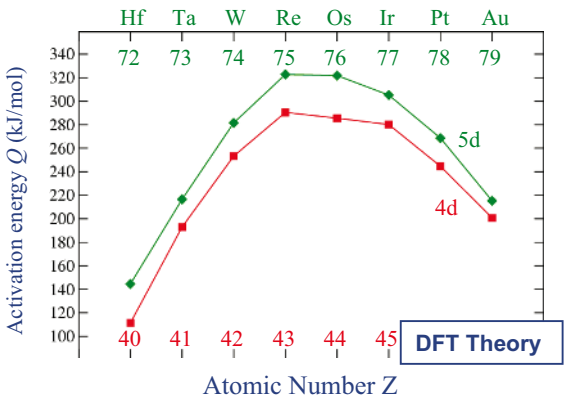


$$D = f a_o^2 \Gamma p_v \qquad \Gamma = \nu_o \exp\left\{-\frac{E_b}{kT}\right\} \qquad p_v = C_o \exp\left\{-\frac{E_f^V}{kT}\right\}$$

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



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

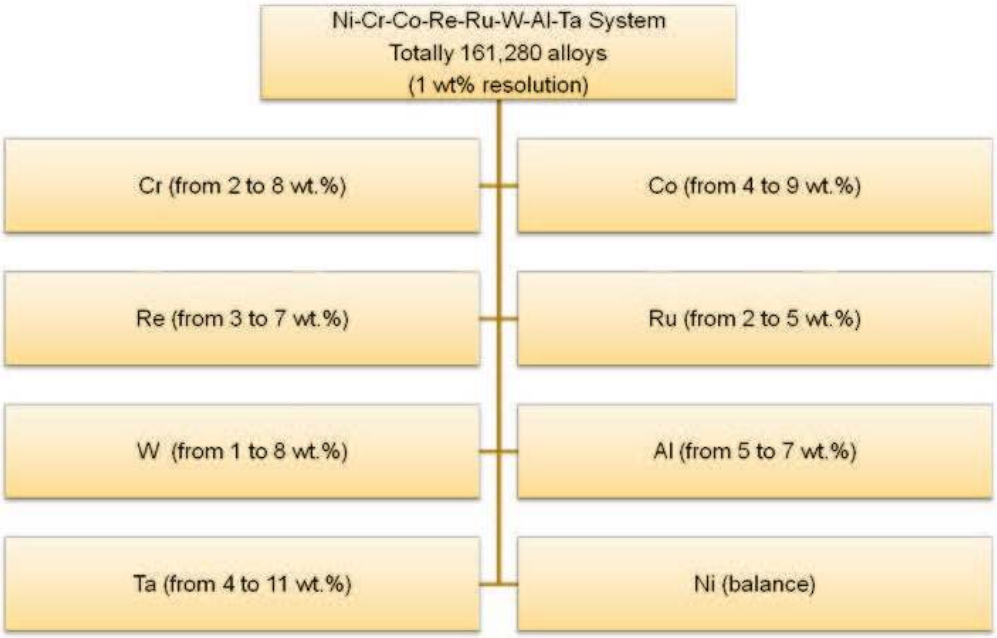


Janotti, Krcmar, Fu and Reed, PRL, 92, 085901, (2004).

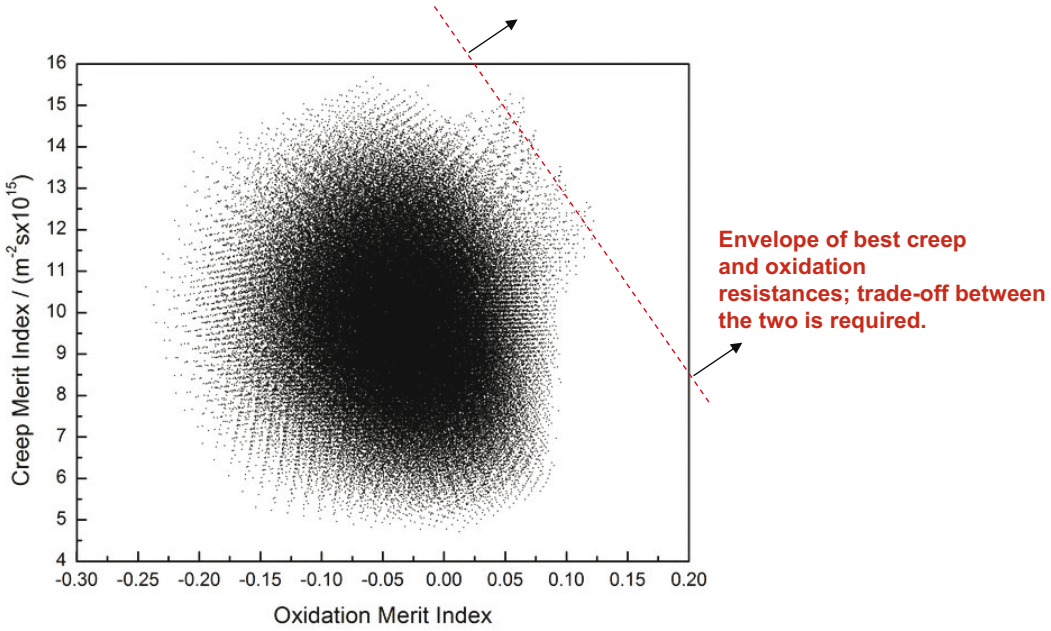
-activation energy for 5d solutes larger than for 4d
-variation of the vacancy/solute barrier energy with atomic no dominates composition dependence

Design Study

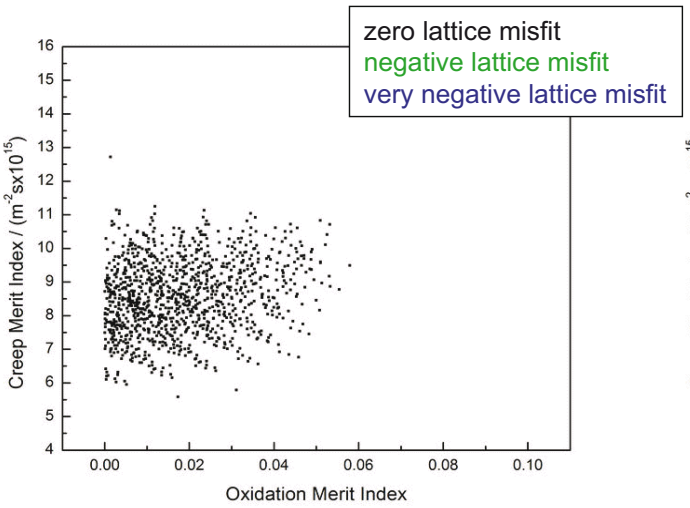
Oxidation Resistant, Creep Resistant Re, Ru-Containing Alloy at Lowest Possible Density and Acceptable Cost



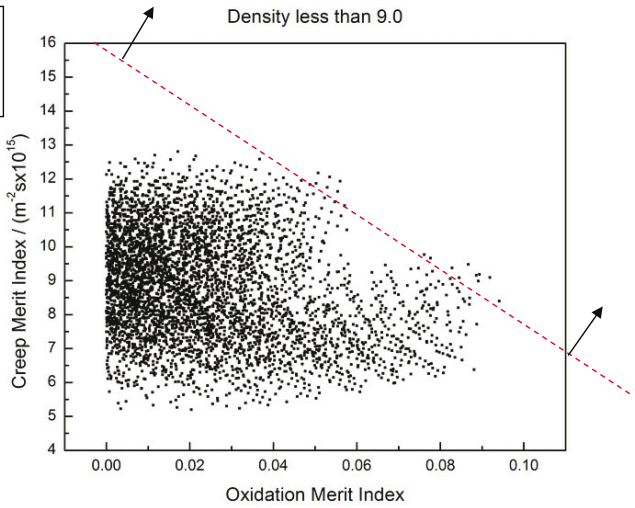
Elimination of Alloys with Oxidation Merit Index of Wrong Sign



Demonstration of the Application of Filters for Lattice Misfit and Density

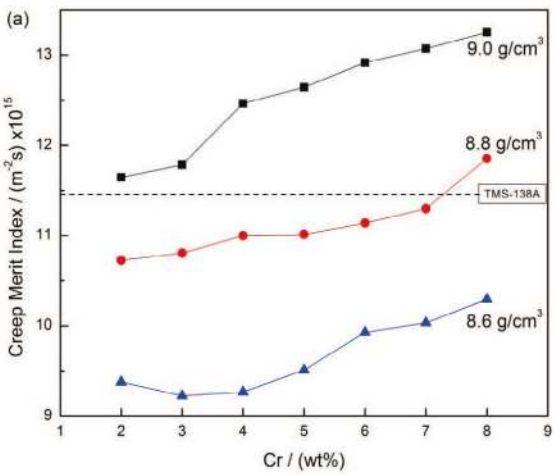


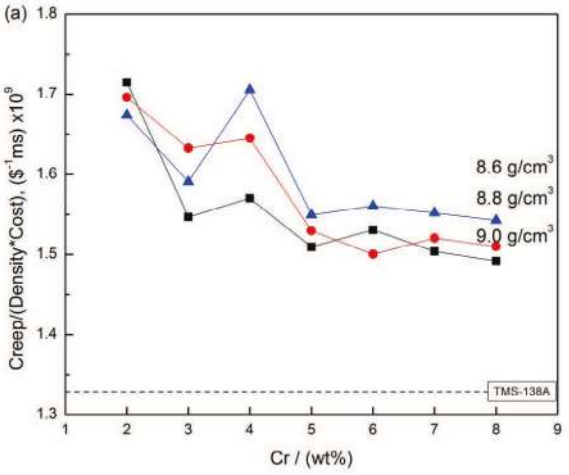
Need somewhat negative misfit to get the best predicted creep resistance.



As density criterion is made more strict, predicted creep resistance is impaired.

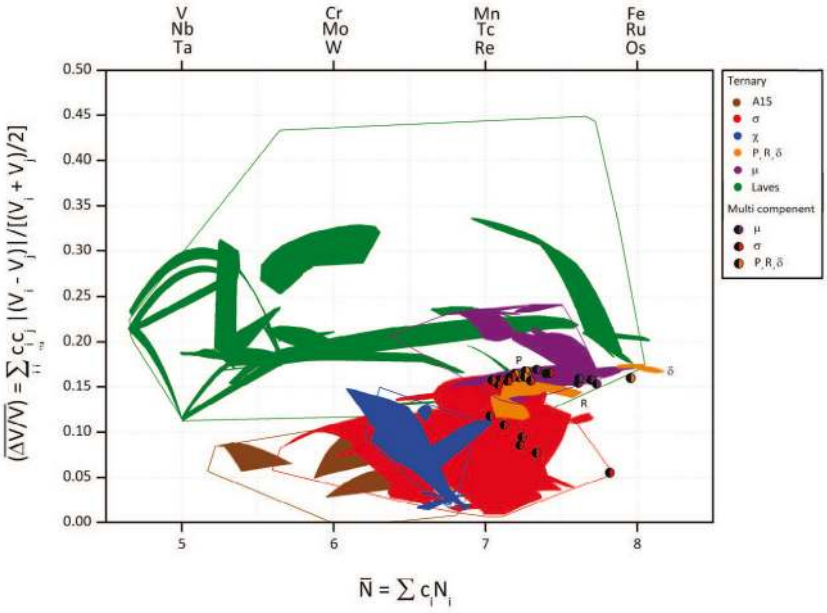
Results for the selected alloys





- (a) Variation of maximum predicted Creep Merit Index as a function of Cr content for different density ranges.
- (a) Variation of maximum predicted ratio of Creep Merit Index/(Density*Cost) as a function of Cr content for different density ranges.

Structure Map for TCPs – Seiser/Pettifor (Oxford)



$$\bar{N} = \sum c_i N_i$$

$$\overline{\Delta V/V} = \sum c_i c_j \frac{|V_i - V_j|}{(V_i + V_j)/2}$$

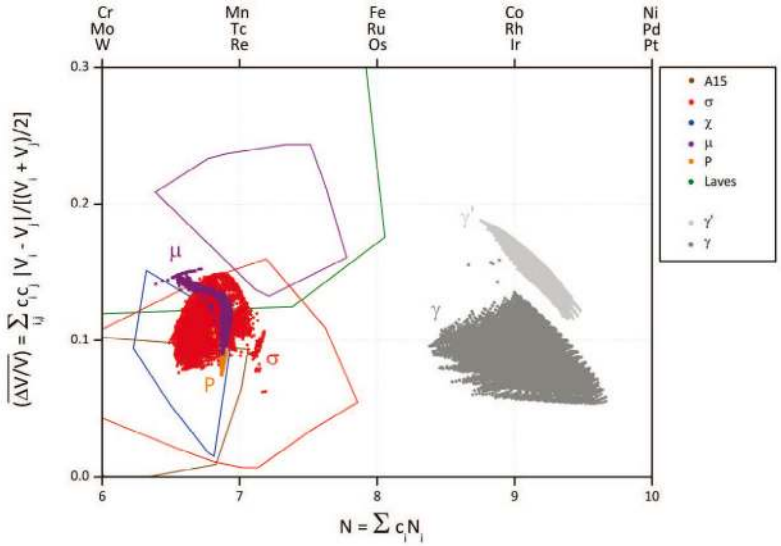
Experimental data from
C M F Rae et al Acta Mat. (2001)
RR2071 – RR2077 2nd generation
11 component alloys containing
~ 1 at. % (3 wt.%) Re with

$7 < \bar{N} < 7.5$
$0.15 < \overline{\Delta V/V} < 0.17$

B Seiser and D G Pettifor, Acta mater, submitted.

Fall in σ / μ overlap region

Test of CALPHAD Against Pettifor Structure Map

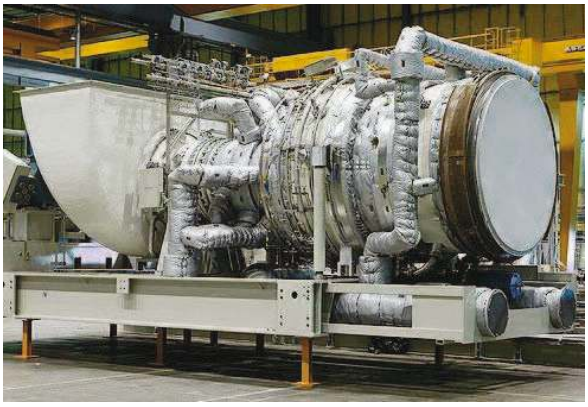


CALPHAD predicts σ in expected domain but μ and P in wrong domains. Supports Zhao and Henry's recent observation that μ and P poorly described because reliable thermodynamic information lacking in CALPHAD database

Strong evidence that existing CALPHAD thermodynamic database needs modification.

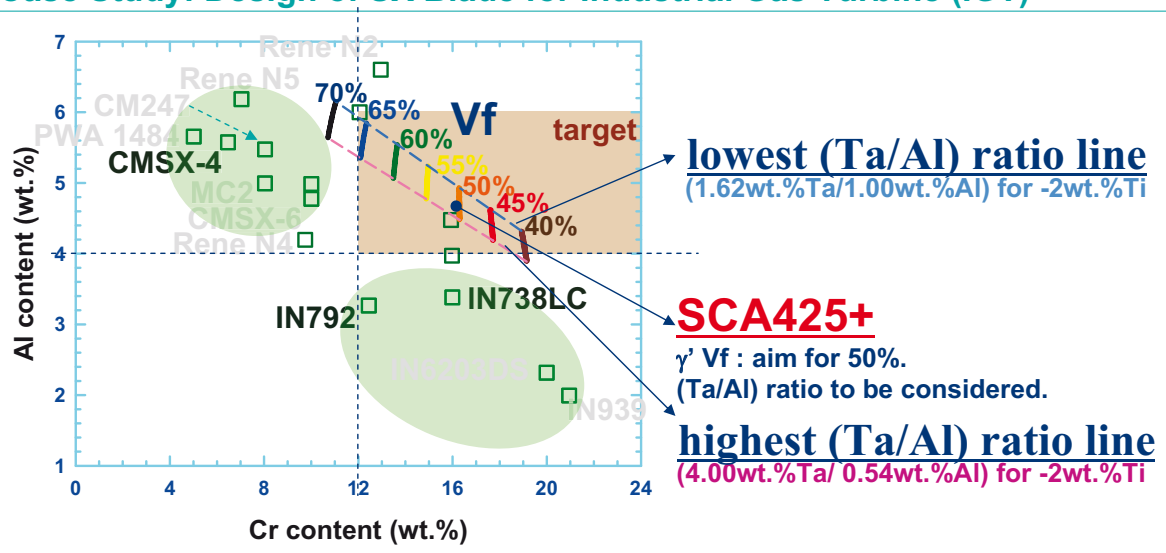
Case Study: Design of SX Blade for Industrial Gas Turbine (IGT)

- Cr > 12 wt.% for corrosion resistance
- Creep performance to match IN792
- Oxidation to match CMSX-4
- Density < 8.5 g/cm^3
- Cost low, via Re elimination
- Processing: into SX form without freckling
- Misfit low, for phase stability
- V_f of γ' : around 50% at 900ºC for a good combination of creep, fatigue and microstructual stability
- Long-term microstructual stability and resistance to TCP precipitation
- Wide heat treatment window for processing



SIEMENS SGT-800
- Output: 47MW
- Efficiency: 37.5%
- Compressor pressure ratio: 19:1
- Rotation speed: 6600 rpm

Case Study: Design of SX Blade for Industrial Gas Turbine (IGT)



	Co	Cr	Mo	W	Al	Ta	Ti	Hf	Re	Other
IN738LC	8.5	16	1.7	2.6	3.4	1.7	3.4	-	-	0.01B 0.1Zr 0.05C
SCA425+	5	15.5	1	4	**4.55**	**8**	**-**	0.1	-	200ppmCe

	Co	Cr	Mo	W	Al	Ta	Ti	Hf	Re	Other
IN792	9	12.5	1.8	4.2	3.5	4.2	4.2	-	-	Mechanical target
CMSX-4	9.5	6.5	0.6	6.5	5.65	6.5	1	4.2	3	Oxidation target

Case Study: Design of First Row Blade for Industrial Gas Turbine (IGT)

Alloy No.	1	2	3	4	5	6	7
γ′ %	40	45	50	55	60	65	70
Ni	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Al	4.04	4.34	4.64	4.94	5.23	5.53	5.82
Cr	19.05	17.66	16.27	14.89	13.52	12.16	10.80
Co	5.61	5.33	5.05	4.78	4.50	4.23	3.96
Mo	1.16	1.09	1.01	0.94	0.87	0.80	0.73
Ta	6.53	7.28	8.03	8.78	9.52	10.25	10.98
W	4.11	4.06	4.01	3.96	3.91	3.87	3.82
Liquidus (°C)	1360	1358	1356	1354	1352	1350	1349
γ-solidus (°C)	1312	1310	1308	1307	1306	1305	1304
γ′-solvus (°C)	1120	1145	1172	1199	1227	1257	1289
HT window (°C)	192	165	136	108	79	48	15

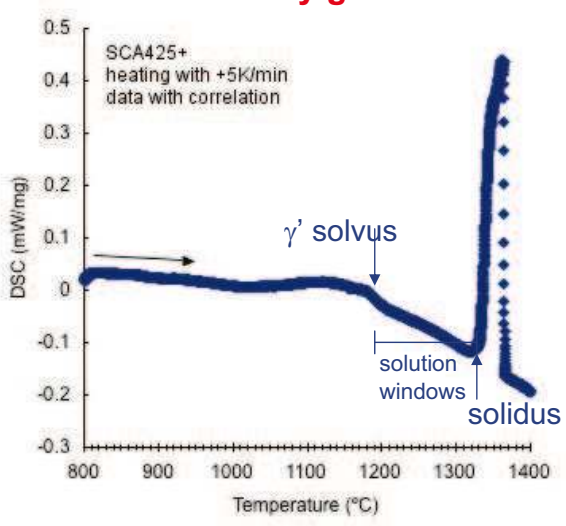
* All concentration in wt.%

Processing of SCA425+

Castability:

>50 SX cast bars in total
92% acceptable single crystal
: no freckling observed
79% are less than 10º from <001>

Very good castability



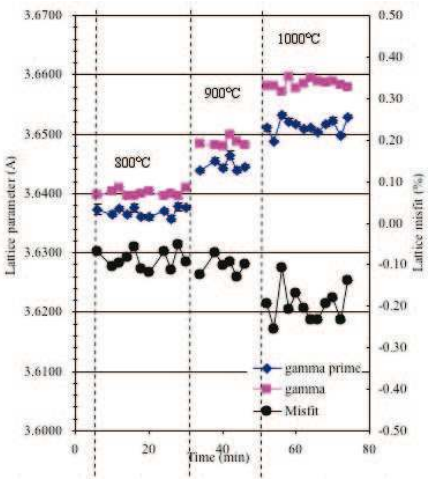
Heat treatment window (DSC)

Solvus (ºC)	Solidus (ºC)	Liquidus (ºC)	HT window (ºC)
1196	1318	1364	122

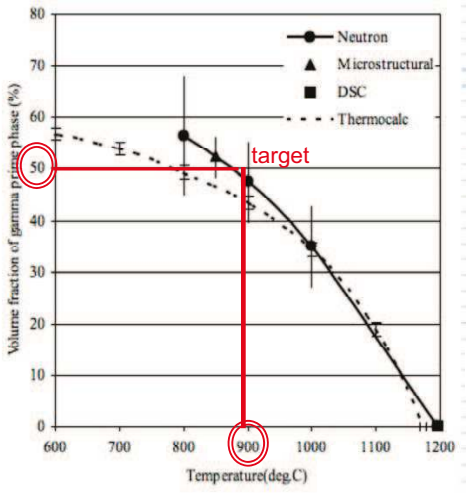
Wide enough – solutioning possible

Misfit/Stability

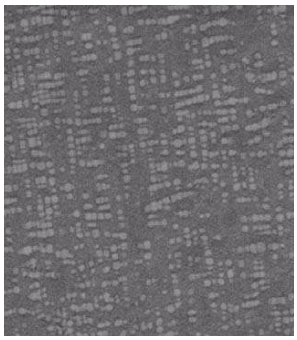
Lattice Misfit
neutron diffraction



Vf of γ'



Stability

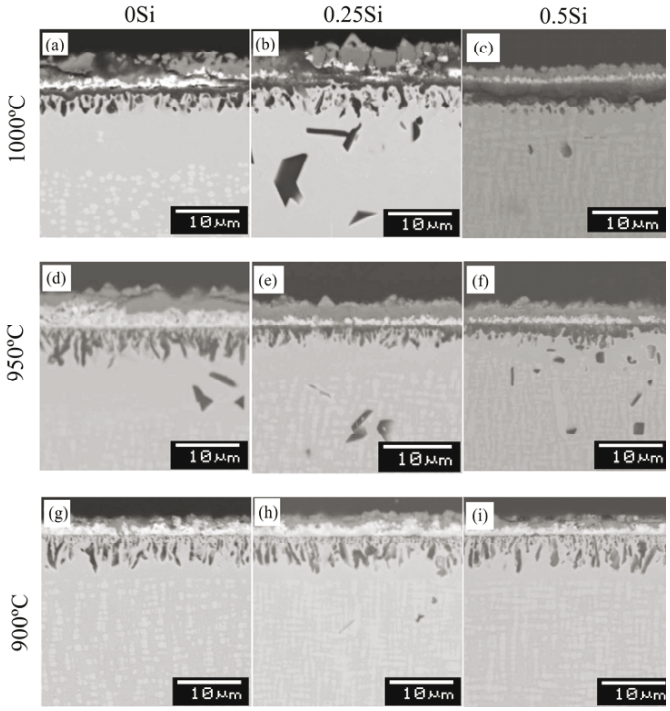


average lattice misfit δ
800ºC : -0.09±0.03%
900ºC : -0.10±0.03%
1000ºC : -0.20±0.07%
->Low enough

Good agreement with CALPHAD calculation

No TCP phases after creep test at 850ºC/275MPa for 858hrs

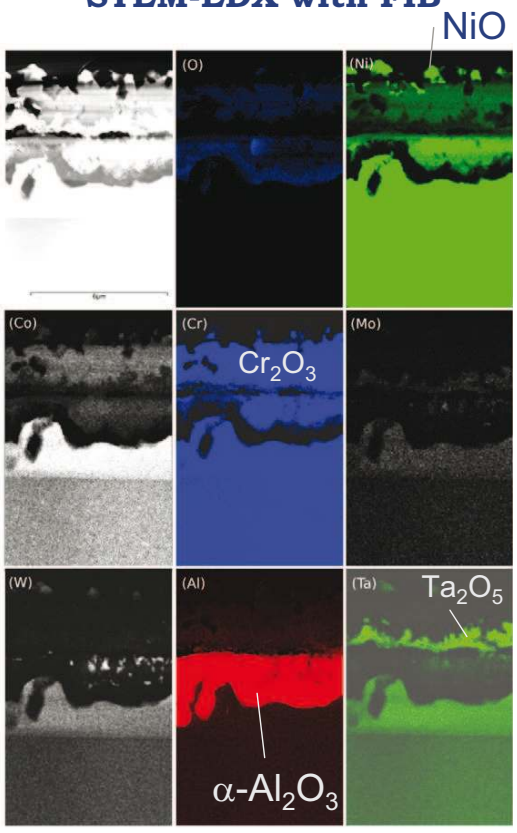
Morphologies of Oxide Scale on SCA425+



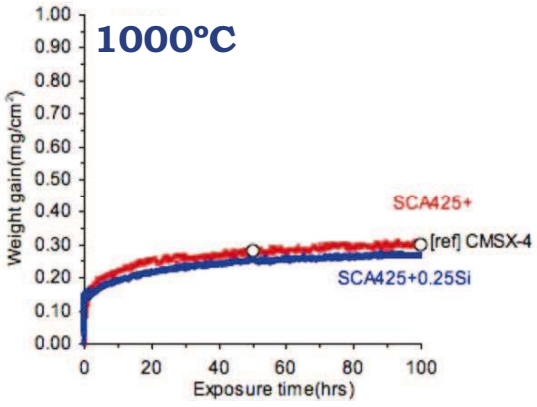
Al2O3 is continuous:

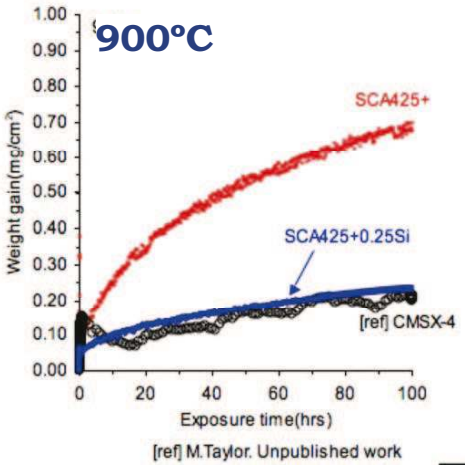
(i) at higher temperature
(ii) with greater Si

STEM-EDX with FIB



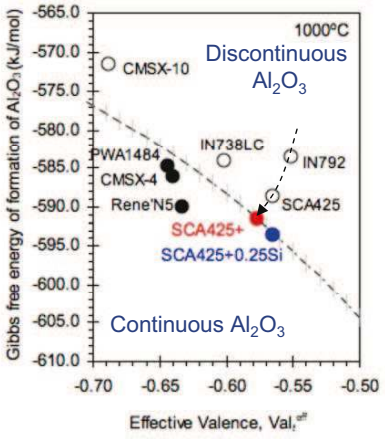
Oxidation (vs CMSX-4)

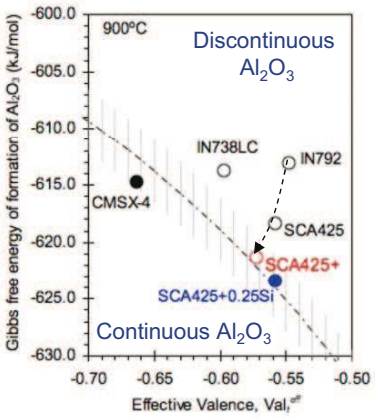




[ref] M.Taylor. Unpublished work

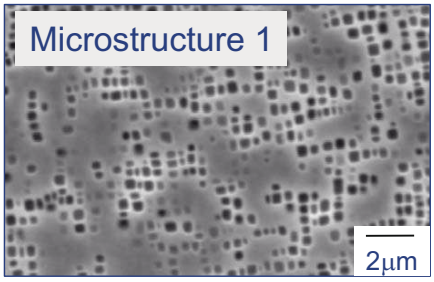
Calculation



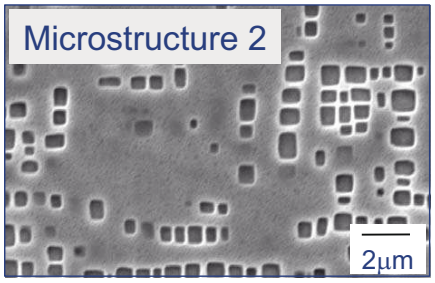


- **Comparable with CMSX-4 at 1000ºC.**
- **Comparable with CMSX-4 when Si is doped at 900ºC.**
- **Good agreement between the experiment & modelling**

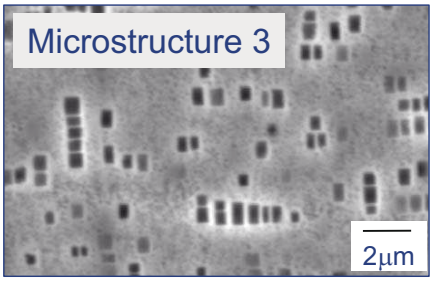
Microstructure of SCA425+



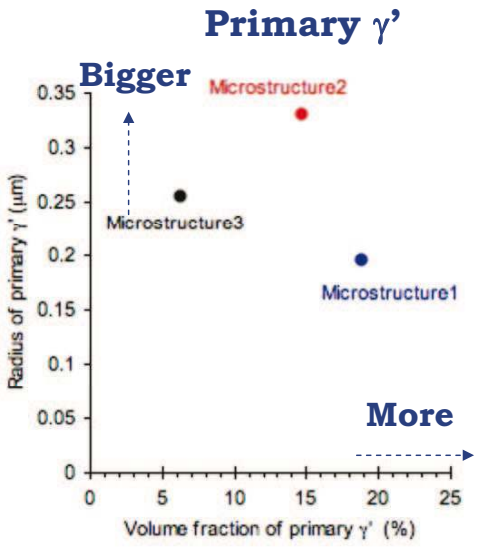
- Primary ageing : **1100ºC 6hrs**
- Uniform microstructure similar to CMSX-4



- Primary ageing : **1120ºC 24hrs**
- Bimodal microstructure similar to IN792



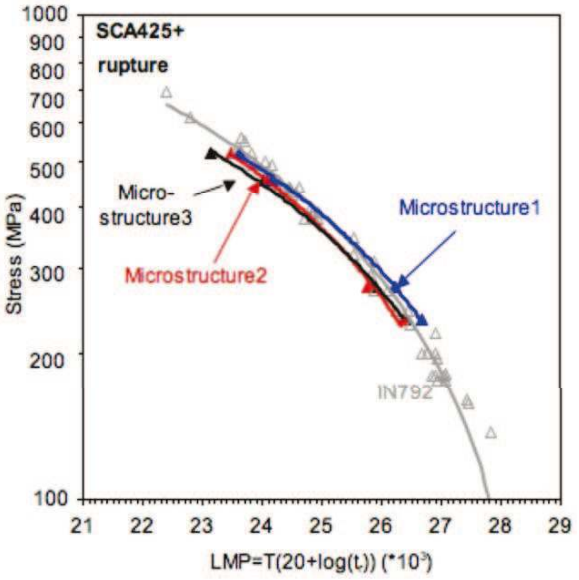
- Primary ageing : **1160ºC 4hrs**
- Bimodal but smaller primary γ' than microstructure2



Solvus temperature is 1196 deg C

Creep (vs IN792) and Thermal mechanical fatigue (vs CMSX-4)

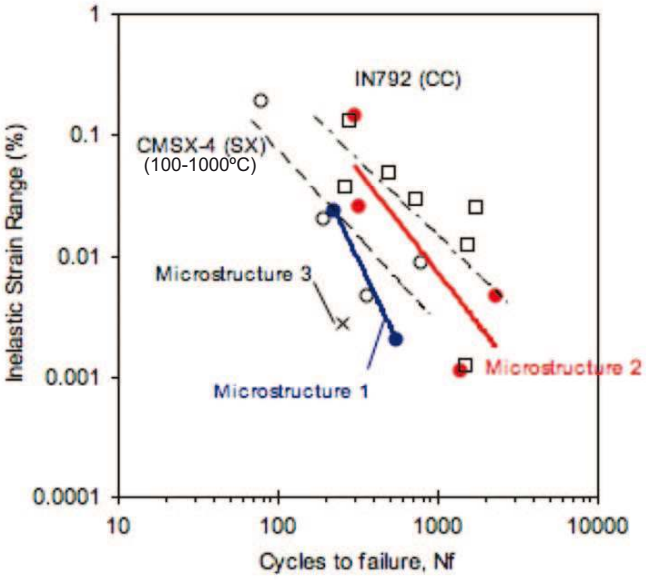
Creep



Microstructure1 (uniform) performs best.

TMF

OP 100-950°C Hold: 5 mins



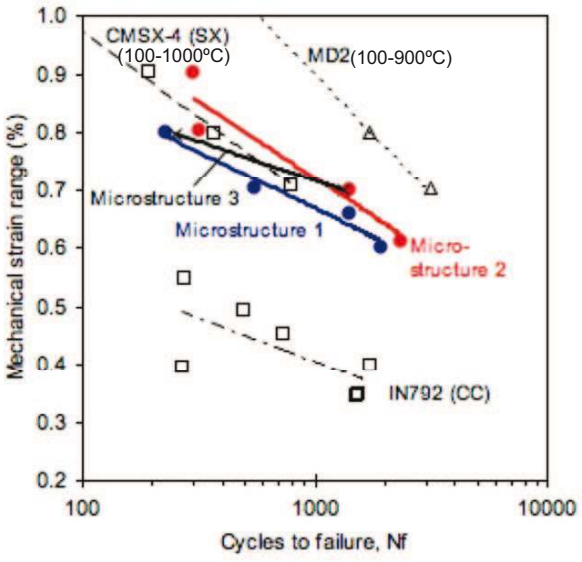
TMF properties do NOT correlate with creep properties.

TMF∝ size and amount of primary γ'

TMF properties of SCA425+ (v.s. CMSX-4)

TMF

OP 100-950°C Hold: 5 mins



TMF properties do NOT correlate with creep properties.

TMF∝ size and amount of primary γ'

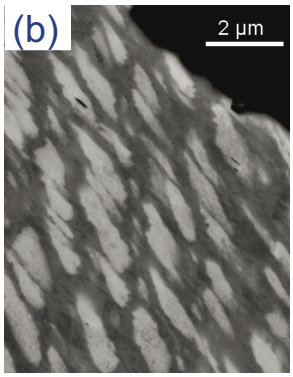


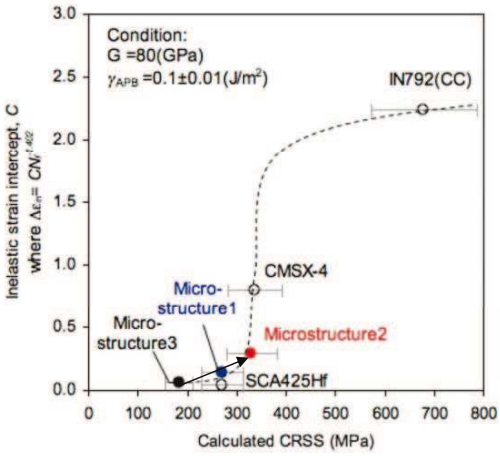
Fig.b Microstructure2 after TMF

Plastic deformation from the **shearing of γ'** has larger effect than that of creep relaxation.

CRSS (weakly coupled):

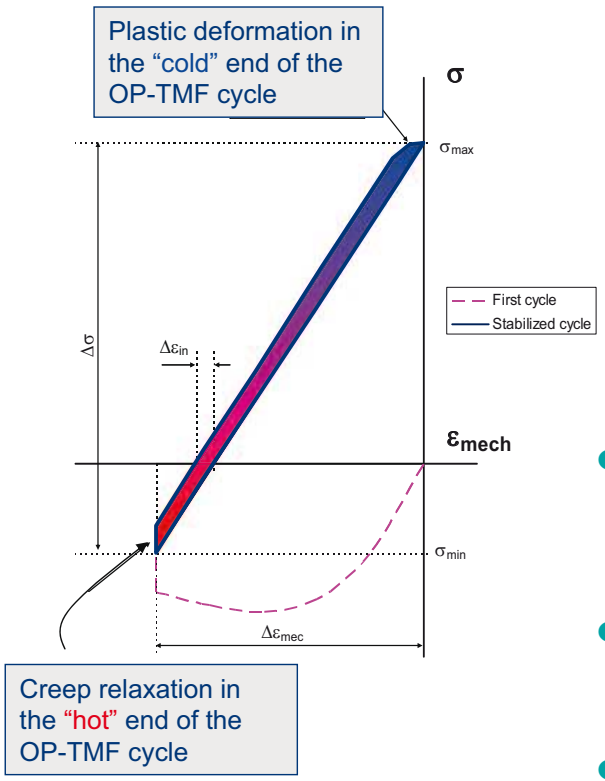
$$\tau_c \propto \sqrt{r \cdot f}$$

Radius of γ' volume fraction of γ'



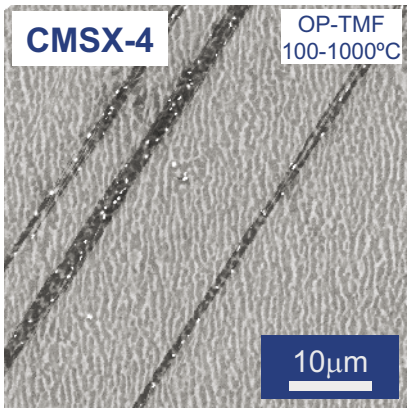
Inelastic strain range is the function of CRSS

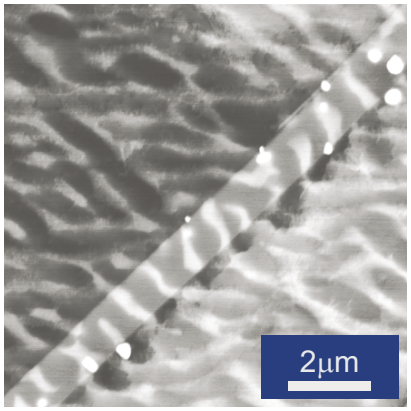
Background to TMF Testing



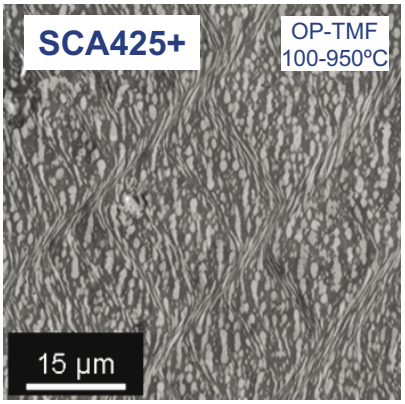
- For hot components, the high stresses will normally relax during service, since most critical locations tends to be strain controlled rather then stress controlled.
- This means that high stresses will occur during shut down and the 'damage temperature' might actually be the lowest temperature
- However, there is a strong interaction between the deformation at high and low temperature

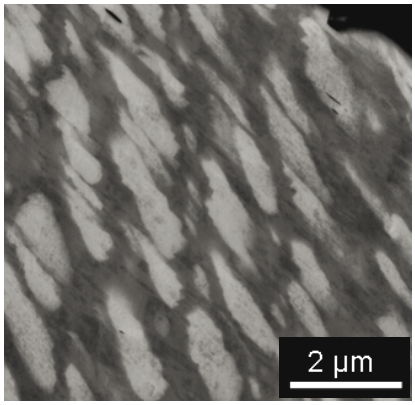
Different fracture modes in TMF





twinning + strain-induced TCP precipitation

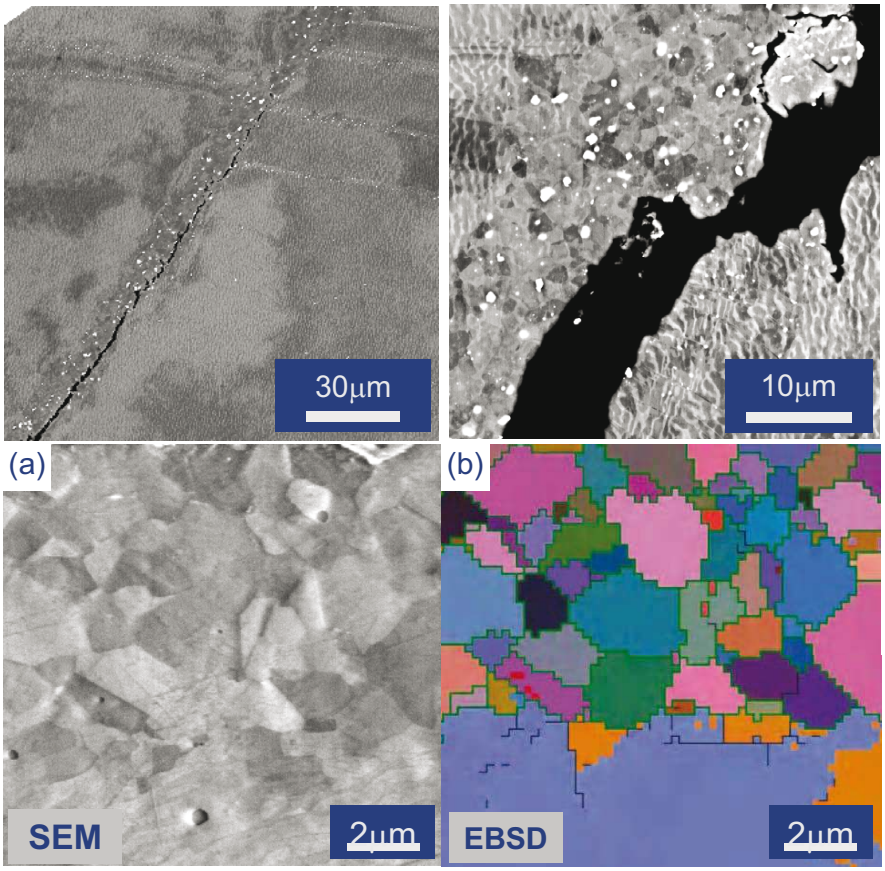




Slip-band

J.J. Moverare, S. Johansson and R.C. Reed, `Deformation and Damage Mechanisms during TMF of a Single Crystal Superalloy', Acta mater., 57, 2266, (2009).

Recrystallisation in CMSX-4 during OP-TMF



J.J. Moverare, S. Johansson and R.C. Reed, `Deformation and Damage Mechanisms during TMF of a Single Crystal Superalloy', Acta mater., 57, 2266, (2009).

Summary and Conclusions

- An Alloys-By-Design approach has been proposed; application of it allows compositions of single crystal superalloys to be identified using modelling methods.
- First order estimates of important characteristics (creep resistance, oxidation resistance, castability…..) are made for alloys in a chosen compositional space. From it are eliminated those compositions which do not satisfy design constraints.
- The methods are being applied to design various new alloy systems against minimum property targets, *e.g.*
  - An oxidation resistant Re-free (low cost) castable alloy for industrial gas turbine applications.
  - An oxidation resistant Re and Ru containing alloy, meeting specified creep life at (i) minimum density, (ii) minimum cost.
- Any success depends upon accuracy of underlying sub-models and databases (*e.g.* CALPHAD); these need to be further improved.
- Still many challenges: *e.g.* corrosion, thermal-mechanical fatigue for which quantitative models are still needed.

Acknowledgements

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