

FS 2024/25

MSE-422 – Advanced Metallurgy

5-Ni-based alloys

Christian Leinenbach

Ni alloys for high-T applications – introduction

Gas turbines and jet engines



[/www.powergeneration.siemens.de/](http://www.powergeneration.siemens.de/)

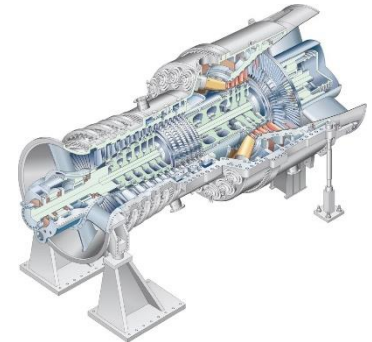


- Jet engines are designed to produce thrust from the direct impulse of exhaust gases
- Light-weight design to save fuel
 - Weight <3t
 - Maximum service T: 1'500°C
 - Thrust/weight ratio: 0.2-0.3
- Designed for frequent start/stop cycles

- Modern gas turbines for power generation are designed to power an electric generator
- Frames, bearings, and blading are of heavier construction than jet engines
 - Total length up to 30 m, weight >440 t
 - Maximum service T: 1'500 °C
 - Power: max 340 MW
- Designed for long-term operation (up to several years)



[/www.airbus.com/](http://www.airbus.com/)

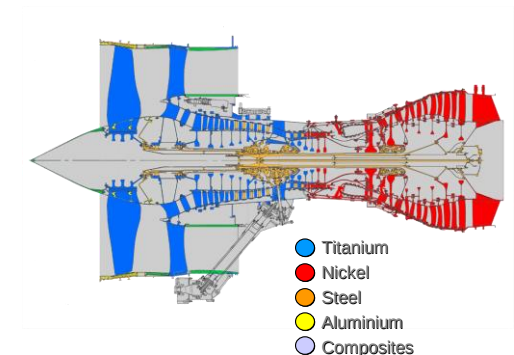
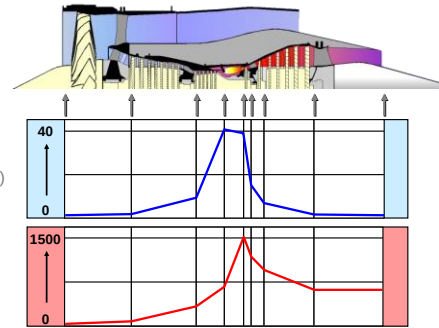
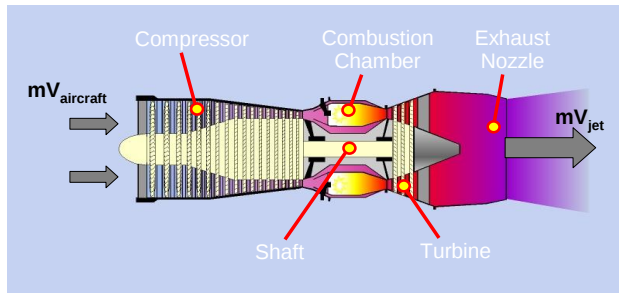


[/www.volvo.com/](http://www.volvo.com/)

Ni alloys for high-T applications – introduction

Design and working principle of a jet engine

- Air is compressed by an arrangement of stator and compressor blades. The conical shape of the support of the compressor blades leads to an increase in pressure and temperature of the air
- The compressed air is then mixed with fuel and ignited in the combustion chamber and the gas is heated to high T (up to 1'500 °C)
- The hot gas flows out through the turbine, leading by the shape of the blades to the rotation of the axis (up to 25'000 rpm)
- The generated torque of the compressor blades is used to compress the air

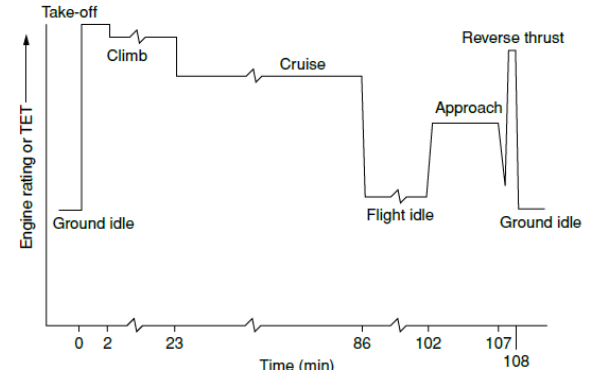


/Cervenka, Rolls Royce, 2000/

Ni alloys for high-T applications – introduction

- Requirements for materials for gas turbines and jet engines
 - Long-term creep resistance at $T > 800^{\circ}\text{C}$ (service intervals 10'000-20'000 h)
 - Resistant against thermo-fatigue (temperature cycles during flight, start-stop cycles)
 - Resistant against high temperature oxidation and gas corrosion
 - Sufficient ductility and fracture toughness even after long-term use

Variation of the turbine entry temperature (TET) during a typical flight cycle of a civil aircraft.



General advantages

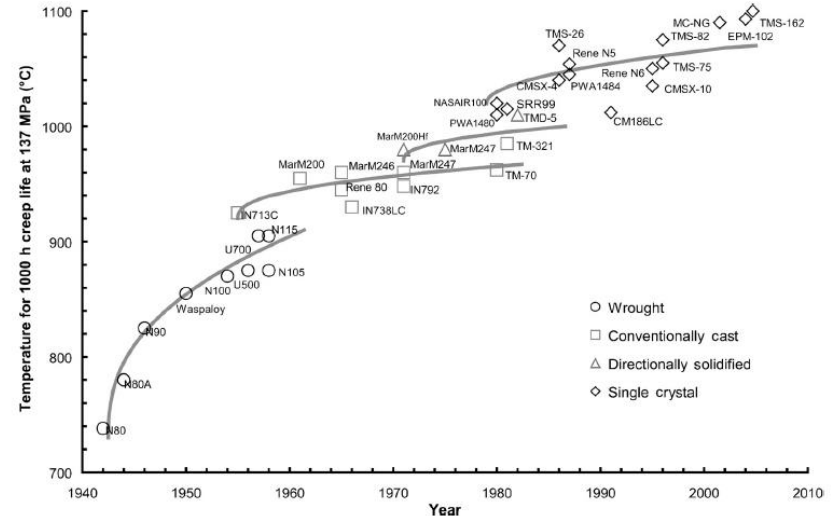
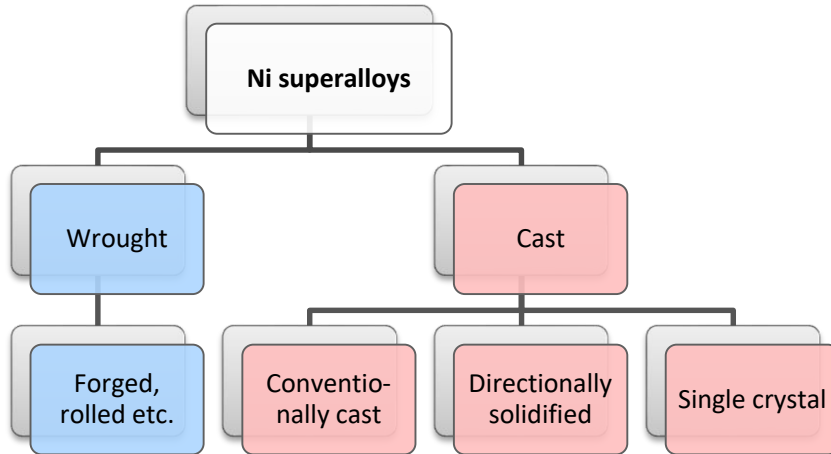
- Ni has an fcc lattice structure with inherently low diffusion coefficients up to the melting point
 - no addition of fcc stabilizing elements like for steels with possible detrimental effects required
- Ni can be alloyed with high amounts of Cr and Al, which form protective layers at the surface
 - Protection against high-T corrosion
- No other metallic base element can be strengthened by alloying for high-T applications like Ni (particle strengthening, ss strengthening)
- Young's modulus (210 GPa) similar to those of Fe and Co, significantly higher than Ti

General disadvantages

- Melting point ($T_m = 1455^\circ\text{C}$) lower than other elements, further decreased by alloying elements
- Operated at high homologous T, which lead to diffusion-controlled processes
 - Long-term operation at $T > 1100^\circ\text{C}$ not possible
- Comparably high CTE and low thermal conductivity
 - Thermo-fatigue critical and very high temperatures and very difficult to control

Classification of Ni alloys

- Ni alloys are primarily distinguished between wrought and cast alloys
- Ni alloys are mainly designated by their trade names and their manufacturers
- Alternative designation: Hastelloy X = NiCr22Fe18Mo → 22 wt.% Cr, 18 wt.% Fe, <1 wt.% Mo

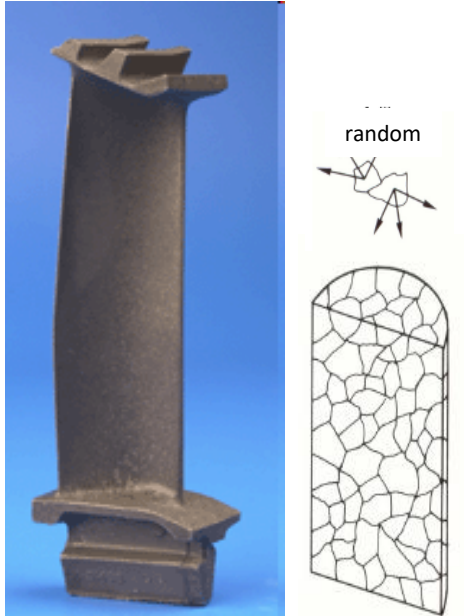


Evolution of the high-temperature capability of the superalloys over a 60 year period since their emergence in the 1940s.

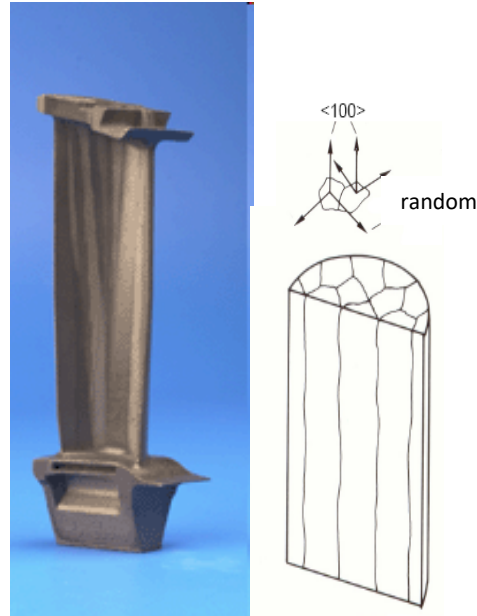
/R.C. Reed, The superalloys – fundamentals and applications, 2006/

Cast Ni superalloys

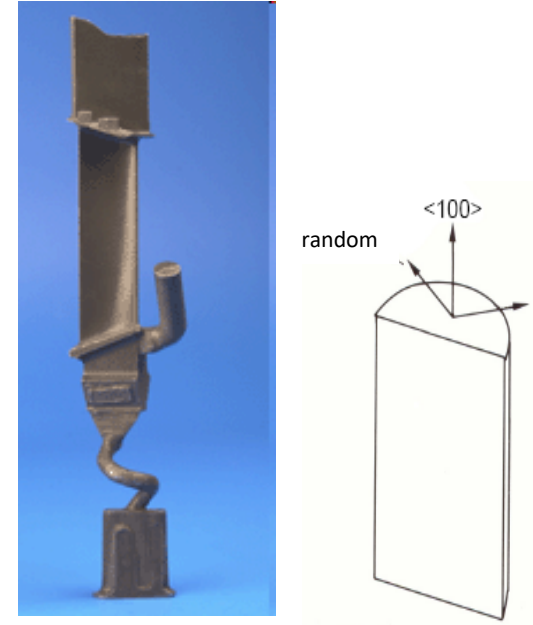
Conventionally cast



Directionally solidified



Single crystal (SX)



Role of main alloying elements in Ni

Element	Effect	Max. wt.%
Fe	+ cheap replacement for Ni - reduces high-T oxidation stability - supports detrimental IM phases	37
Cr	+ Forms Cr-rich protective layer + solid solution strengthener + carbide former - supports detrimental IM phases	30
Co	+ (mild) solid solution strengthener + reduces SFE + reduces solubility of Al and Ti - reduces high-T oxidation stability	20
Mo	+ solid solution strengthener + carbide former + increases E-modulus + reduces diffusion coefficient - supports detrimental IM phases	14

Element	Effect	Max. wt.%
W	Similar to Mo but - increase density - pronounced segregation tendency	4
Nb, Ta, Ti	+ solid solution strengthener + carbide former + increase γ' amount (replace Al) + delay coarsening of γ' (reduction of γ/γ' lattice misfit) - reduces high-T oxidation stability - supports detrimental IM phases	5-12
Al	+ forms γ' -Ni ₃ Al + solid solution strengthener + reduces density + forms stable Al ₂ O ₃ layer at HT	6

Role of main alloying elements in Ni

Element	Effect	Max. wt.%
Si	+ improves high-T oxidation stability - supports detrimental IM phases - reduces solidus temperature	1
C	+ carbide former - reduces solidus temperature	0.2
B	+ stabilizes grain boundaries + boride former - reduces solidus temperature	0.03
Hf, Zr	+ Scavenges S + carbide former +/- can reduce and increase hot cracking during casting + very reactive (mold reactions during casting possible)	0.2-1.5

Element	Effect	Max. wt.%
Re, Ru	+ solid solution strengthener + delay coarsening of γ' (reduction of γ/γ' lattice misfit) - support detrimental IM phases - increase density - very expensive	3-6

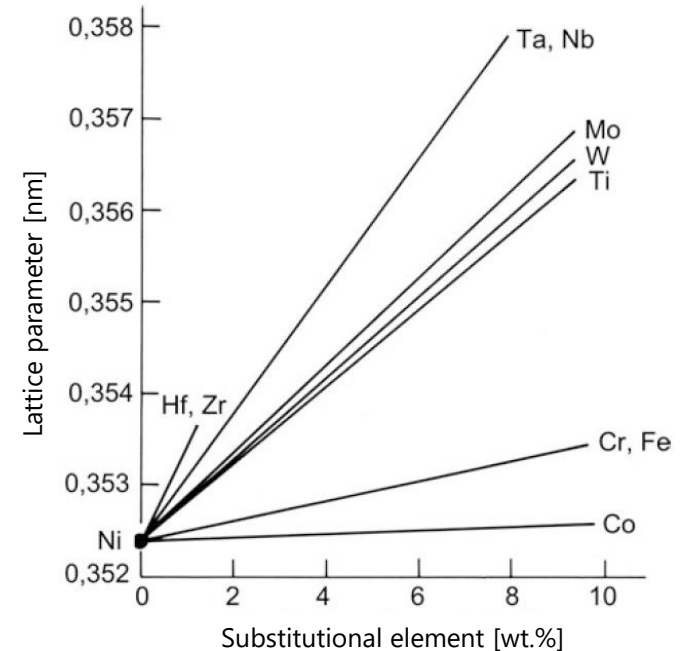
Strengthening mechanisms in Ni alloys

- Solid solution strengthening
- Particle strengthening
 - coherent γ' -Ni₃Al precipitates with fcc superstructure
 - bct γ'' -Ni₃(Nb,Ti) in certain alloys containing Nb
 - carbides (Cr, Mo, W, V, Nb, Ta, Hf, Ti) $\rightarrow$ MC, M₂₃C₆, M₆C, M₇Cr₃ (in wrought alloys)
 - in some alloys oxide dispersion strengthening (ODS) with nm-sized Y₂O₃

Effect of alloying elements in Ni alloys

Solid solution strengthening

- Solid solution strengthening effect depends on size of substitutional atom and solubility in Ni
- The effect of the elements can be ranked
 - weak effect: Fe, Co, Cr,
 - mild effect: V, Ti
 - strong effect: W, Mo, Al, Ta, Nb

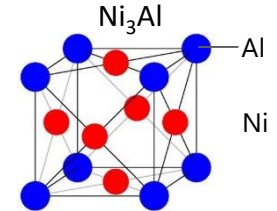
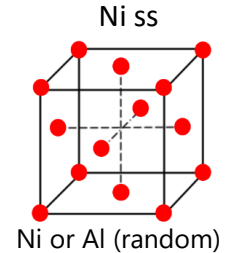
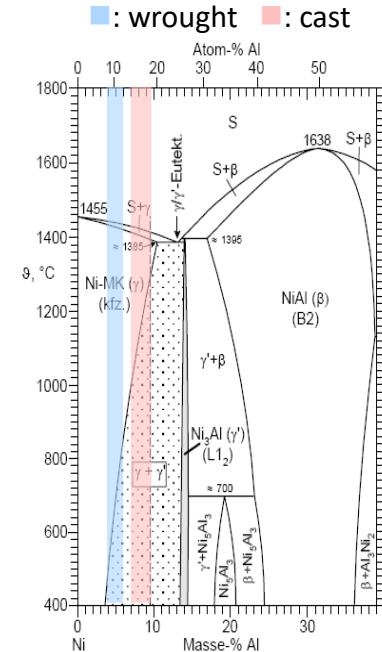


/Maier, Niendorf, Bürgel – Handbuch Hochtemperatur-Werkstofftechnik, 2015/

Effect of alloying elements in Ni alloys

The γ' -Ni₃Al phase

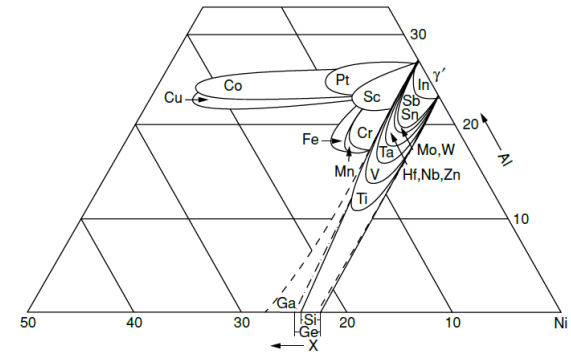
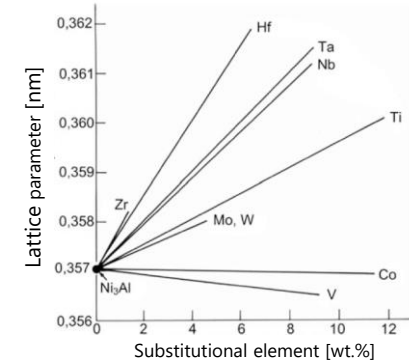
- Pronounced solubility of Al in Ni (max. 20 at.%)
 - Large volume fractions of Ni₃Al in Ni possible (up to 70%)
- Lattice parameter of Ni₃Al (0.357 nm) very similar to lattice parameter of Ni (0.352 nm)
 - Ni₃Al forms coherent precipitates in Ni matrix
- The Ni₃Al phase is stable up to the melting point or dissolution
 - No detrimental phase transformation



Effect of alloying elements in Ni alloys

The γ' -Ni₃Al phase

- Relatively small homogeneity range of Ni₃Al in binary Ni-Al
- Many possibilities for substitution with other elements
 - Main substitute for Ni: Co
 - Main substitutes for Al: Ti, Ta
- The alloying strategy of Ni-based superalloy development has to take into account changes in lattice parameter of both the matrix and the γ' phase to provide coherency with the matrix.

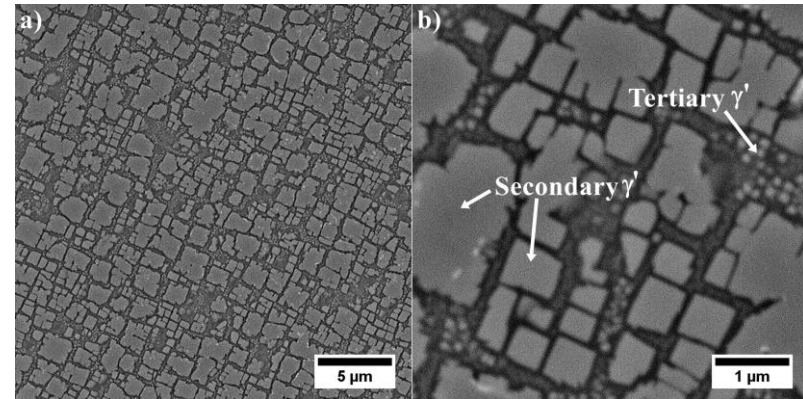
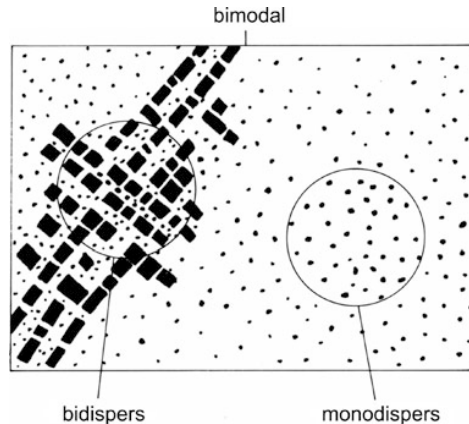


/R.C. Reed, The superalloys – fundamentals and applications, 2006/

Strengthening mechanisms in Ni alloys

The γ' -Ni₃Al phase

- In technical Ni alloys, a bimodal and bi-disperses γ' -Ni₃Al distribution is realized
 - Larger cuboidal γ' grains with narrow, but connected γ channels inbetween
 - Smaller globular γ' grains in the γ channels
- A maximum amount of γ' -Ni₃Al of 60 vol.% is achieved; at higher fractions, the γ -channels are disconnected

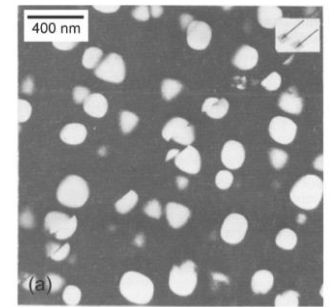
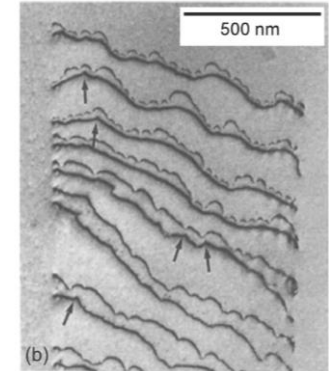
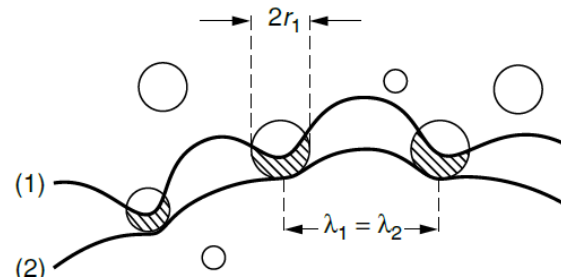
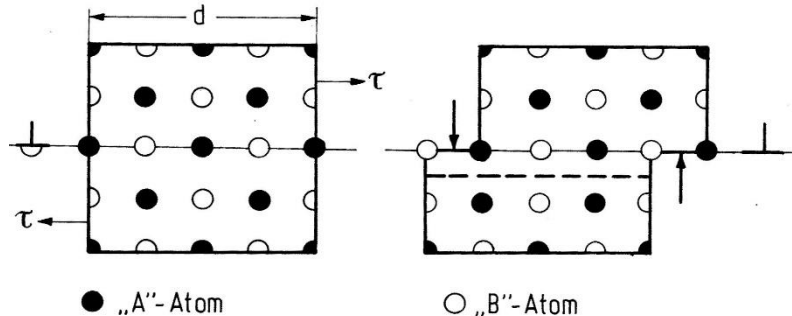


/© Lukas Karge, mlz-garching.de/

Strengthening mechanisms in Ni alloys

The γ' -Ni₃Al phase

- Because of the ordered nature of Ni₃Al, cutting by one single dislocation will create an anti-phase boundary (APB)
→ atoms are in an unfavored configuration
- Dislocations must travel through the γ/γ' structure in pairs, with a second dislocation removing the anti-phase boundary introduced by the first
- The associated anti-phase boundary energy, γ_{APB} , represents a barrier which must be overcome if particle cutting is to occur

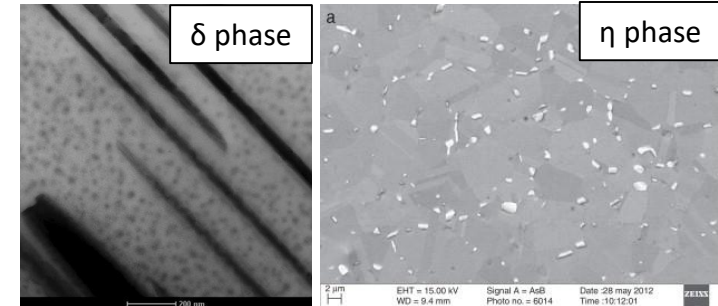
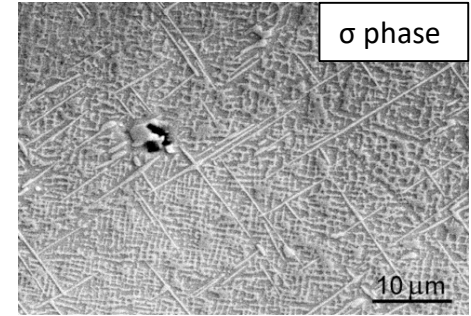


/R.C. Reed, The superalloys – fundamentals and applications, 2006/

Effect of alloying elements in Ni alloys

Undesired IM phases

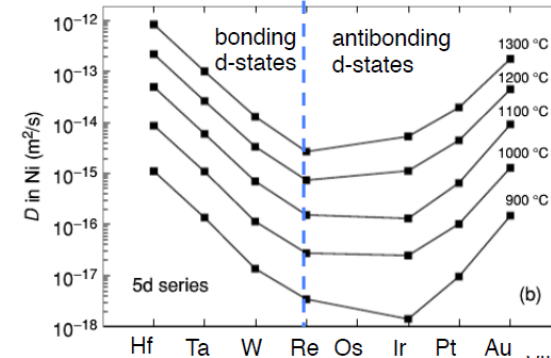
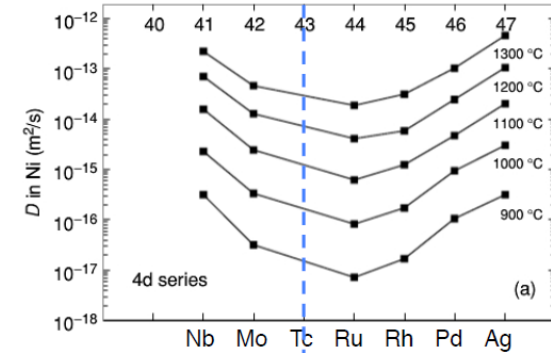
- TCP phases (σ , μ , χ , Laves)
 - They provide incoherent interfaces for rapid diffusion, leading to accelerated coarsening
 - They absorb Cr, Mo, and W from the matrix
→ effect on solid solution strengthening
 - Precipitation on grain boundaries leads to brittleness at low T
- η -phase: Ni_3Ti (hcp) (semi-coherent)
 - precipitates as platelets on the (111) planes of γ matrix.
 - Platelet shape indicates that growth is much easier in direction of high interface energy
- δ -phase: Ni_3Nb (incoherent orthorhombic)
 - The δ -phase is the incoherent, coarsened variant of the – for very small sizes – coherent γ'' Ni_3Nb (D0_{22}).
 - The δ -phase is very similar to θ'' , θ' and θ in Al-Cu alloys.



Effect of alloying elements in Ni alloys

Influence on diffusion properties

- Pronounced effect of 4d and 5d transition metals on the self-diffusion coefficient in Ni-based superalloys.
- Those elements that partition to the γ matrix will present a significant obstacle to γ' coarsening.
- In the latest generation superalloys, Re, Ru and Ir are used as alloying elements; however, Ir is very expensive (~20'000 CHF/kg).
- Ir has the further advantage that it does not promote TCP-phase formation.

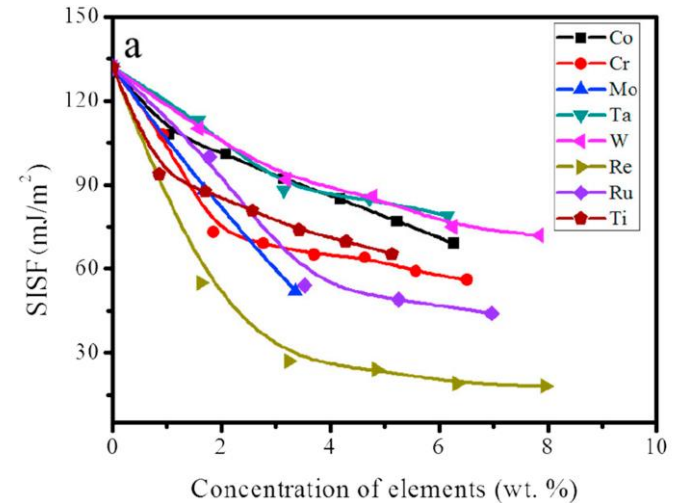


/R.C. Reed, The superalloys – fundamentals and applications, 2006/

Effect of alloying elements in Ni alloys

Influence on stacking fault energies

- The creep rate in Ni decreases with decreasing SFE, approximately to the third power.
- Re, Mo, Ru, Cr have the strongest effect on the SFE, but they promote also the formation of unwanted TCP phases.
- The next best solution is the addition of Co



/W. Yang et al., Vacuum 181 (2020) 109682/

Selected Ni alloys – compositions

Wrought alloys

Alloy	Fe	Cr	Co	Mo	W	Nb	Al	Ti	C	B	Zr	others
Alloy/IN 600; 2.4816; NiCr15Fe	8	15.5					0.2	0.2	0.07	0.003		
Alloy/IN 601; 2.4851; NiCr23Fe	14	23					1.35	0.4	0.1	0.003		1 Mn; 0.5 Si
Hastelloy X NiCr22Fe18Mo	18.5	22	1.5	9	0.6				0.07	0.006		0.5 Mn; 0.5 Si
Haynes 230	1.5	22	2.5	2	1		0.3		0.1			0.5 Mn; 0.4 Si; 0.02 La
Haynes 282		20	10	8.5			1.5	2.1	0.06	0.005		
IN 617; 2.4663; NiCr23Co12Mo		22	12.5	9			1	0.3	0.07			
IN 625; 2.4856; NiCr22Mo9Nb	2.5	21.5		9		3.6	0.2	0.2	0.05			
IN 693	4	29				1	3	0.4	0.05			
IN 718; NiCr19NbMo	18.5	19		3		5.1	0.5	0.95	0.05	0.003		0.007 P
Nimonic 80A; 2.4952; NiCr20TiAl		19.5					1.4	2.3	0.07	0.003	0.06	
Udimet 500; 2.4666; NiCr18CoMo		18	19	4.2			3	3	0.07	0.007	0.05	
Udimet 720		18	14.5	3	1.3		2.5	5	0.03	0.03	0.03	
Waspaloy; 2.4654; NiCr20Co13Mo4Ti3Al		19.5	13.5	4.3			1.3	3	0.04	0.006		0.006 P

Selected Ni alloys – compositions

Conventionally cast alloys

Alloy	Cr	Co	Mo	W	Ta	Nb	Al	Ti	C	B	Zr	others
B 1914	10	10	3				5.5	5.2	0.01	0.1		
G NiCr50; 2 4678	50								0.05			
GTD 111	14	9.5	1.5	3.8	2.8		3	4.9	0.1	0.01		
GTD 222	22.5	19		2	1	0.8	1.2	2.3	0.1	0.008		
IN 100; 2 4674; G NiCo15Cr10AlTiMo	10	15	3				5.5	4.7	0.18	0.015	0.06	1 V
IN 713 LC; 2 4670; G NiCr13Al6MoNb	12		4.5			2	6	0.7	0.05	0.01	0.1	
IN 738 LC	16	8.5	1.7	2.6	1.7	0.9	3	3	0.11	0.01	0.05	
IN 792	12.5	9	1.9	4	4		3.5	3.9	0.08	0.02	0.1	1.4 Hf
IN 939	22.5	19		2	1	1	1.9	3.7	0.15	0.009	0.1	
MAR M 247	8.4	10	0.7	10	3		5.5	1	0.15	0.015	0.05	1.4 Hf
Rene 80	14	9.5	4	4			3	4.8	0.17	0.015	0.03	
Udimet 500; 2 4666	18	19	4				3	3	0.07	0.007	0.05	
Udimet 700	15	17	5.3				4.2	3.3	0.07	0.02		

Selected Ni alloys – compositions

Directionally solidified alloys

Alloy	Cr	Co	Mo	W	Ta	Nb	Al	Ti	C	B	Zr	others
ABB 16	13.2	4.1		1.9	5.1		3.7	5	0.07	0.015	0.016	
ABB 2 DS	12	9		9	5.5		3.5	2.3	0.07	0.015		
ExAl7	12	9	1.8	3.5	4		3.4	3.9	0.08			2.5 Re
GTD 111	14	9.5	1.5	3.8	2.8		3	4.9	0.10	0.01		
IN 6203	22	19		2	1.1	0.8	2.3	3.5	0.15	0.01	0.1	0.75 Hf
IN 792	12.5	9	1.9	4	4		3.5	3.9	0.08	0.02	0.1	1.4 Hf
Rene 80 H	14	9.5	4	4			3	4.8	0.08	0.015	0.02	0.75 Hf
CM 247 LC	8.1	9.2	0.5	9.5	3.2		5.6	0.7	0.07	0.01	0.01	1.4 Hf
MAR M 002	9	10		10	2.5		5.5	1.5	0.15	0.015	0.05	1.5 Hf
MAR M 200	9	10		12		1	5	2	0.1	0.015	0.08	2 Hf
MAR M 247	8.4	10	0.6	10	3		5.5	1	0.15	0.015	0.05	1.4 Hf
Rene 142	6.8	12	1.5	4.9	6.4		6.1		0.12	0.015	0.02	2.8 Re; 1.5 Hf

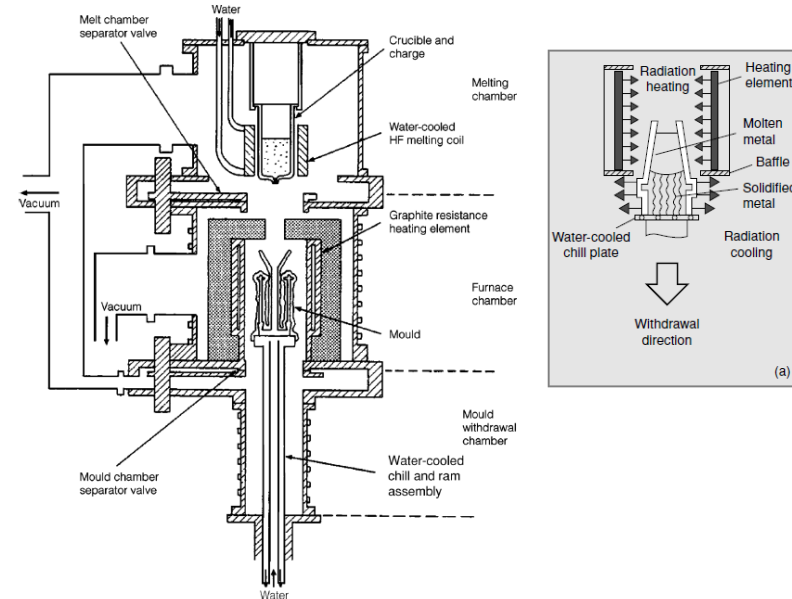
Selected Ni alloys – compositions

Single crystal alloys

Alloy	Cr	Co	Mo	W	Ta	Nb	Al	Ti	Re	C	B	Zr	Hf
CMSX 11B	12.5	7	0.5	5	5	0.1	3.6	4.2					0.04
CMSX 11C	14.9	3	0.4	4.5	5	0.1	3.4	4.2					0.04
PWA 1483	12.2	9	1.9	3.8	5		3.6	4.1		0.07			
CMSX 4	6.5	9	0.6	6	6.5		5.6	1	3				0.1
CMSX 6	10	5	3		2		4.8	4.7			0.03	0.08	
CMSX 10K	2.3	3.3	0.4	5.5	8.4	0.1	5.7	0.3	6.3				0.03
<i>EPM 102</i>	2	16.5	2	6	8.2		5.5		6	0.03	0.00	0.15	0.01 Y; 3 Ru
<i>NASAIR 100</i>	8.5		1.1	10	3.3		5.8	1.2					
<i>PWA 1480</i>	10	5		4	12		5	1.5					
<i>PWA 1484</i>	5	10	2	6	8.7		5.6		3			0.1	
<i>Rene N4</i>	9.75	7.5	1.5	6	4.8	0.5	4.2	3.5		0.05	0.004	0.15	
<i>Rene N5</i>	7	7.5	1.5	5	6.5		6.2		3	0.05	0.004	0.15	0.01 Y
<i>Rene N6</i>	4.2	12.5	1.4	6	7.2		5.75		5.4	0.05	0.004	0.15	0.01 Y
<i>SX 1</i>	4.5	12.5		5.8	7		6		6.3			0.16	

Fabrication of single crystal parts

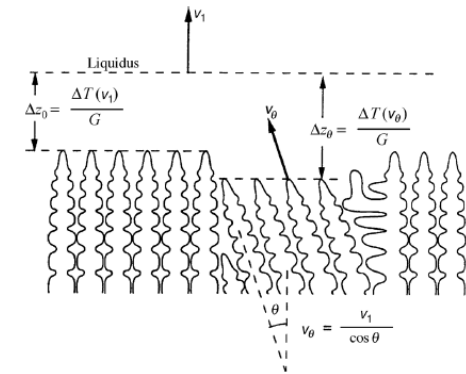
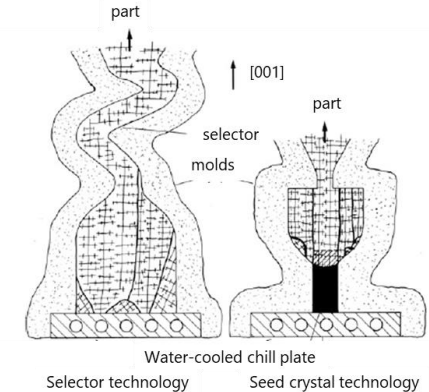
- Single crystalline Ni parts do not contain any grain boundaries and are oriented in $\langle 001 \rangle$ direction
 - No grain boundary sliding at high T
 - Direction with lowest E-modulus
- SX parts (e.g. blades) are produced by casting in vacuum (10^{-8} bar, Bridgman furnace)
 - Directional solidification conditions are ensured by putting the mold on a water-cooled chill plate
 - During casting, the mold is heated to $\sim 1500^{\circ}\text{C}$ (above T_L) to prevent solidification at the walls
 - $[001]$ grain selection occurs before the solidification front enters in the blade mold
 - The mold is slowly withdrawn from the heated zone
 - The standard technique to make the mold is lost wax investment casting



/R.C. Reed, The superalloys – fundamentals and applications, 2006/

Fabrication of single crystal parts

- On the chill plate formation of many randomly oriented grains
- The thermal gradient is set so that columnar dendritic growth occurs ($\sim 4000 \text{ K/m}$)
- The preferred growth direction of crystals during solidification of Ni is $\langle 001 \rangle \rightarrow$ these grains grow fastest $\parallel$ to thermal gradient
- A single $[001]$ is separated with a helical selector or with the seed crystal technology and enters the hot mold
- The dendrites grow at a rate which is controlled by solute diffusion, since the solid phase grows from the liquid with a very different composition from it
 - $\rightarrow$ the local dendrite tip undercooling, ΔT_{tip} , scales monotonically with the velocity, v , of the dendrite, measured along the temperature gradient
- Dendrites misaligned by an angle θ with respect to perfectly aligned ones must grow at a greater undercooling and hence at the rear of the growth front



/Maier, Niendorf, Bürgel – Handbuch Hochtemperatur-Werkstofftechnik, 2015/
/R.C. Reed, The superalloys – fundamentals and applications, 2006/

Fabrication of single crystal parts

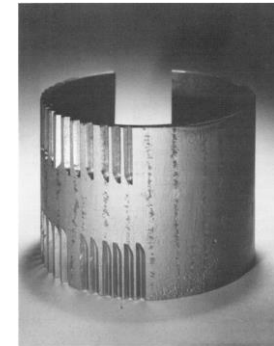
Selected casting defects

Defect	Appearance	Origin
High-angle GBs	Large bi-/poly-crystals in the part	In the case of non-one-dimensional heat flow solidification front is curved and the dendrite stems do not grow parallel; with increasing misorientation, formation of high-angle GBs
Low-angle GBs	Slight angular deviation of dendrite cores	Like high-angle GBs but with small misorientation of dendrites; plastic deformation due to shrinkage constraints
Globular grains	Equiaxed microstructure	Temperature gradient too small and/or withdrawal speed too high
'Freckles'	Small roundish grains parallel to the dendrite cores in the interdendritic areas; enriched in Al, Ti and Ta, depleted in W and Re	Flow of the melt in the interdendritic spaces due to segregation-related density differences; this causes dendrite tips or arms to break off, which lead to new equiaxed grains
'Slivers'	Strip-shaped grains, mainly on the component surface	Reactions of certain alloying elements in the melt with the mold; formation of inclusions that act as nuclei for elongated grains.

Bicrystalline turbine blade



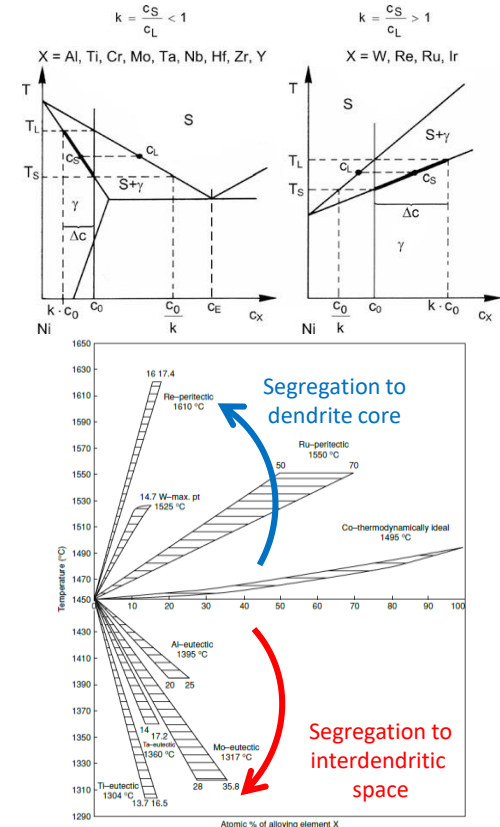
Freckles



/A.F. Giamei, Metall. Trans. 1 (1970) 2183/

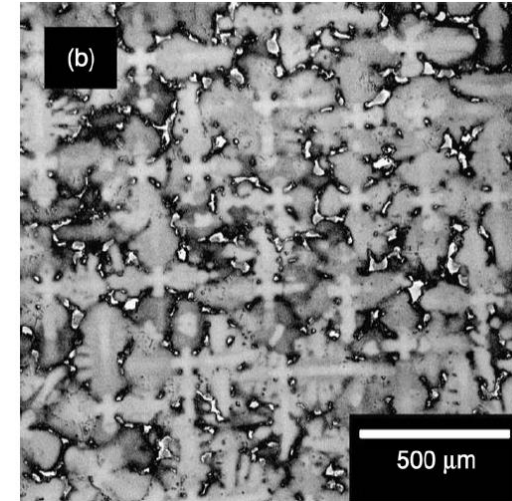
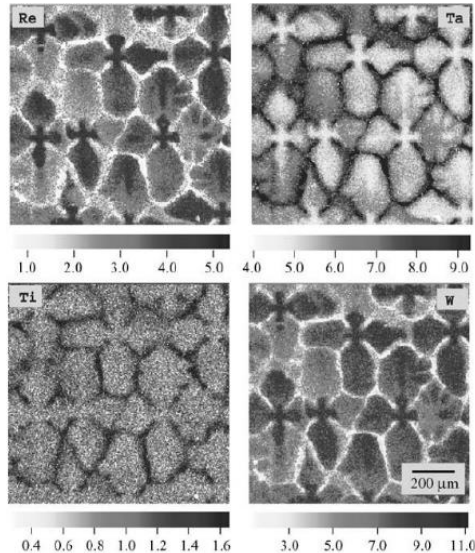
Microsegregation in SX alloys

- Microsegregation occurs because elements have different solubilities in solid and liquid phase, c_S and c_L ; partitioning coefficient is $k = c_S/c_L$
- Since $k \neq 1 \rightarrow$ the composition of the melt changes during solidification
 - $k < 1$: enrichment of element X in the liquid
 - $\rightarrow$ X cannot diffuse quickly enough from the liquid into the solid
 - $\rightarrow$ Large solidification ranges; remaining melt can reach eutectic composition
 - $k > 1$: enrichment of element X in the solid
 - $\rightarrow$ X cannot diffuse quickly enough out of the solid into the liquid
 - $\rightarrow$ The interdendritic regions are depleted of these elements
- The microsegregation depends mainly on
 - The solidification rate
 - The diffusion velocities of the alloying elements
 - The concentration difference Δc of the solid material in the solidification interval



Microsegregation in SX alloys

Partitioning of W and Re to the dendrite core, and Ti and Ta to the interdendritic regions in as-cast CMSX-4 superalloy



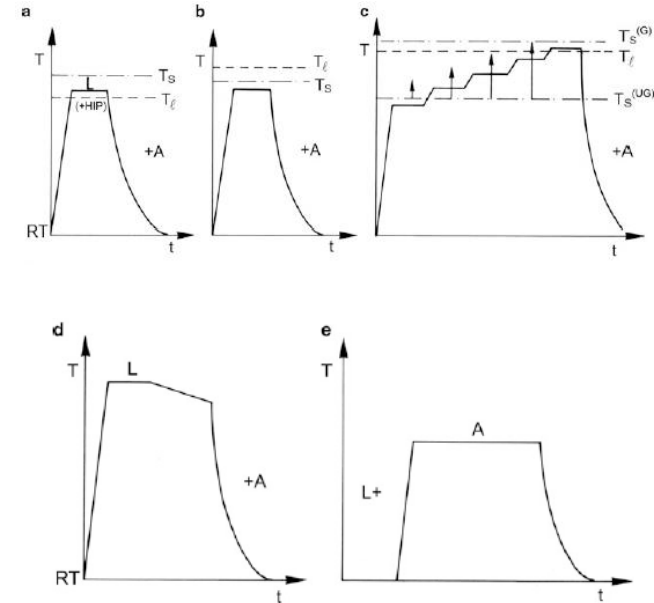
Dendritic microstructure of a single-crystal superalloy in the as-cast state

- The heat treatment of Ni alloys has different functions:
 - to adjust the optimum γ' size, shape and distribution
 - to precipitate hard particles (mostly carbides) on grain boundaries
 - to reduce casting segregation and to distribute the alloying elements as homogeneously as possible; thus to raise the melting temperature towards the equilibrium solidus temperature
 - to reduce or completely dissolve γ/γ' residual eutectic
 - to relieve residual stresses from manufacturing and fabrication
 - to adjust the grain size of wrought materials by recrystallization
 - to selectively change the grain boundary morphology (jagged grain boundaries)
 - to restore the optimum microstructural condition after operation and to eliminate any undesired precipitated phases

Heat treatment of γ' -strengthened Ni alloys

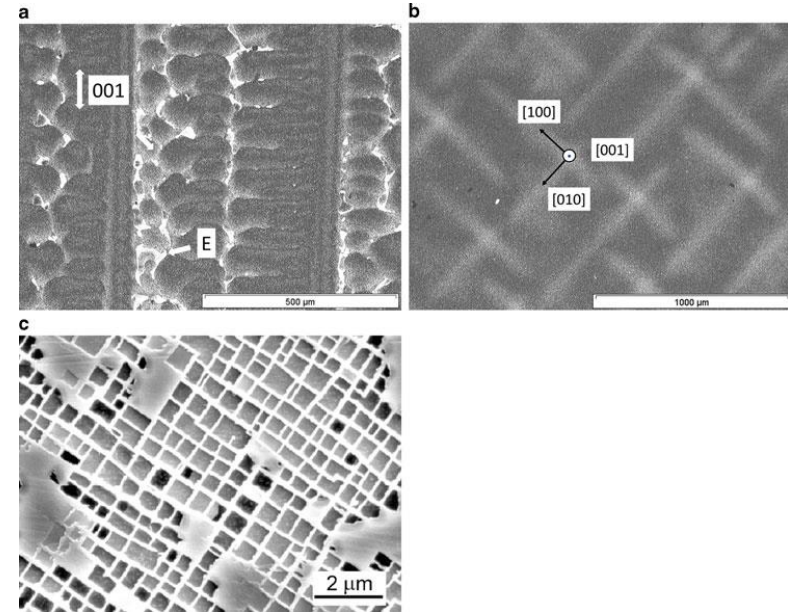
Typical temperature-time profiles

- Schematic temperature/time curves for heat treatments of precipitation hardening alloys (L: solution heat treatment; A: curing; T_l : solution temperature of the precipitates; T_s : solidus temperature).
 - a) Complete solution annealing, possibly simultaneously as a HIP treatment
 - b) Partial solution annealing (in which $T_l > T_s$),
 - c) Multi-stage solution annealing. (T_s^{UG} : out-of-equilibrium solidus temperature; T_s^G : equilibrium solidus temperature),
 - d) Solution annealing with slow cooling to form jagged grain boundaries
 - e) one-step ageing heat treatment



Heat treatment of γ' -strengthened Ni alloys

- Microstructure of the single crystal alloy CMSX-4
 - a) As-cast state with dendritic structure and large γ/γ' eutectic islands (E); longitudinal section with [001] orientation
 - b) After multi-stage solutionizing between 1200 and 1320°C s (transverse section); The dendrite structure is due to not completely removed segregations, mainly of W and Re. The γ/γ' eutectic has disappeared.
 - c) After solutionizing and ageing at 870°C, γ' precipitates (volume fraction approx. 63%)



Mechanical properties of Ni alloys

0.2% yield strength of selected Ni alloys at different temperatures

wrought

Alloy	21°C	540°C	650°C	760°C	870°C
Inconel 600	285	220	205	180	40
Inconel 617	295	200	170	180	195
Inconel 718	1185	1065	1020	740	330
Nimonic 80A	620	530	550	505	260
Udimet 630	1310	1170	1105	860	---
Waspalloy	795	725	690	675	520
René 95	1310	1255	1220	1100	---

cast

Alloy	21°C	540°C	1100°C
IN-713 LC	740	705	---
IN-162	815	795	---
MAR-M-432	1070	910	---
Nimocast 90	520	420	---
CMSX2	1135	1245	1105
PWA-1480	895	905	495

Mechanical properties of Ni alloys

<001> texture/orientation strengthening

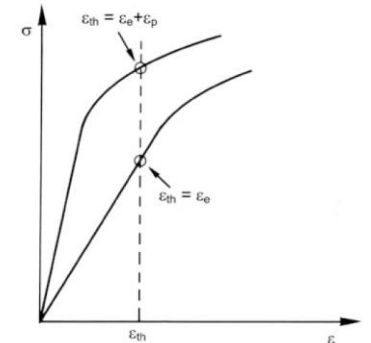
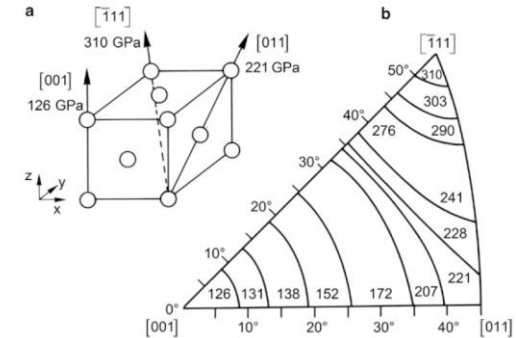
- In a heated constrained part or in a locally heated volume element of a part under loading in z-direction, the strain is

$$\varepsilon_z = \varepsilon_{therm} + \varepsilon_{mech} = \alpha_{CTE} \cdot \Delta T + \frac{\sigma_z}{E} = 0$$

- The resulting stress can thus be calculated as

$$\sigma_z = -E \cdot \varepsilon_{therm} = -E \cdot \alpha_{CTE} \cdot \Delta T$$

- For $E \approx 200 \text{ GPa}$ and $\alpha \approx 15 \times 10^{-6} \text{ 1/K}$ $\rightarrow \Delta\sigma_z = 3 \text{ MPa/K}$
 - For isotropic (polycrystal) Ni, the resulting stresses can exceed the yield strength of the materials
 - In a fcc single crystal, the E-modulus is anisotropic with the lowest value in <001> direction
- the same load leads to significantly lower stresses

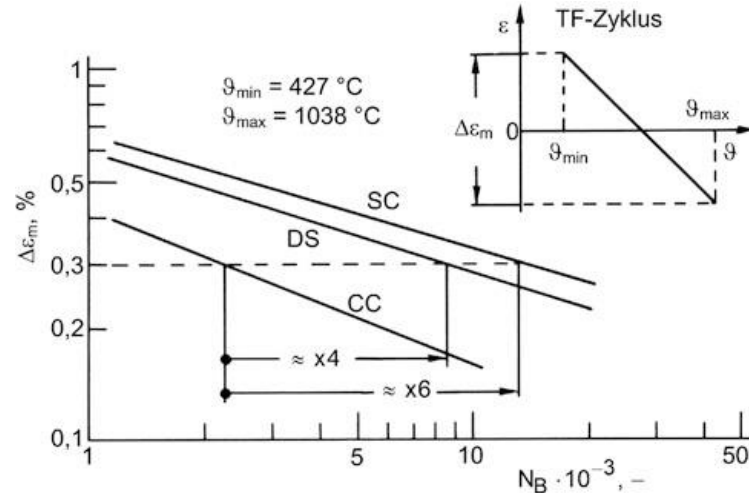


/Maier, Niendorf, Bürgel – Handbuch Hochtemperatur-Werkstofftechnik, 2015/

Mechanical properties of Ni alloys

Thermal fatigue behaviour

- Comparison of material properties under TMF loading between a conventionally cast (CC) superalloy, a directionally solidified superalloy (DS) with grains in $\langle 100 \rangle$ -orientation and a $\langle 100 \rangle$ -oriented single crystal (SC) superalloy.
- The stress direction for the DS and SC alloys is in the $\langle 100 \rangle$ direction of the grains
- $\langle 001 \rangle$ -oriented samples show a significantly longer lifetime at a give strain amplitude



Mechanical properties of Ni alloys

High-T performance of wrought Ni alloys

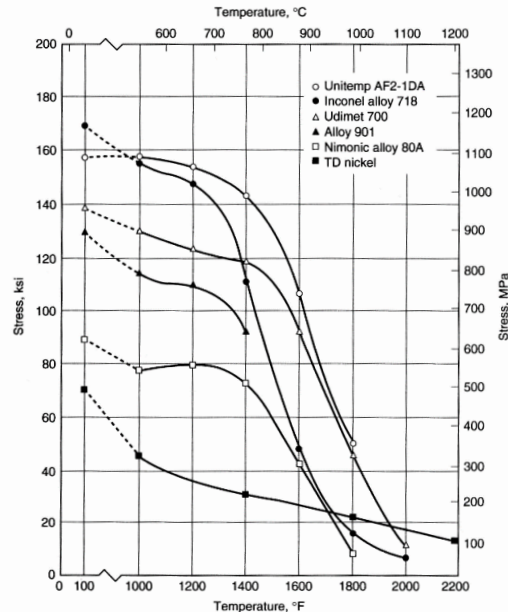


Fig. 15 Effect of temperature on the 0.2% offset yield strength of Inconel 718 and competing alloys. Product form: bar stock. Source: Ref 13

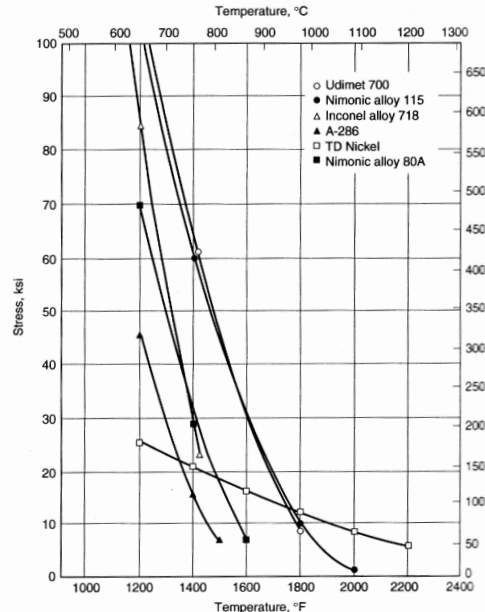


Fig. 16 1000 h stress-rupture strength of Inconel 718 and competing alloys. Product form: bar stock. Source: Ref 13

Mechanical properties of Ni alloys

Anomalous yielding effect in γ' -alloys

- For many superalloys the yield stress increases with increasing temperature (typically until temperatures of about 800°C)
- This is explained by the thermally activated cross slip of screw super dislocations from $\{111\}$ to $\{001\}$ planes in the Ni channels,
- The dislocations are less mobile on the $\{111\}$ planes, preventing the motion of the remaining parts of the dislocations
- With increasing temperature, more cross-slip occurs, so dislocation motion is more hindered and yield strength increases

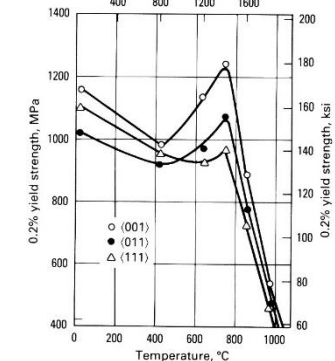
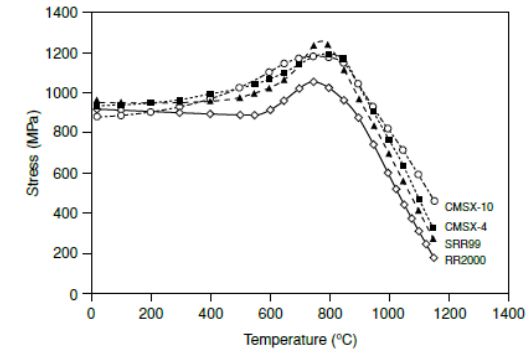
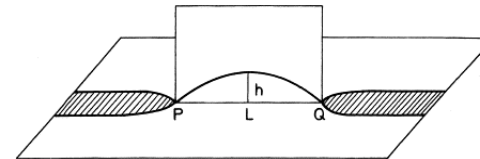
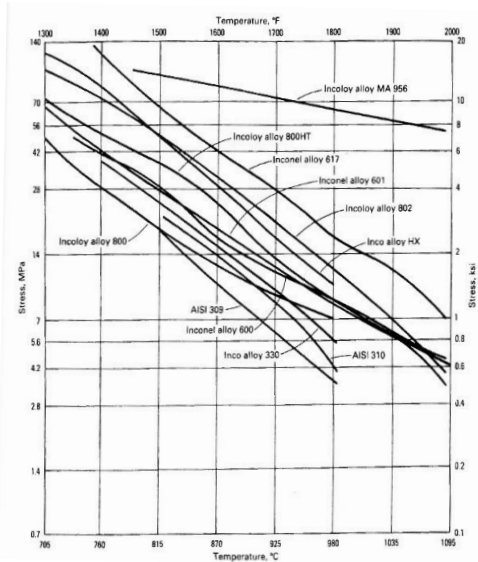


Fig. 8 Yield strength of single-crystal PWA 1480 alloy as a function of temperature and orientation. Source: Ref 15

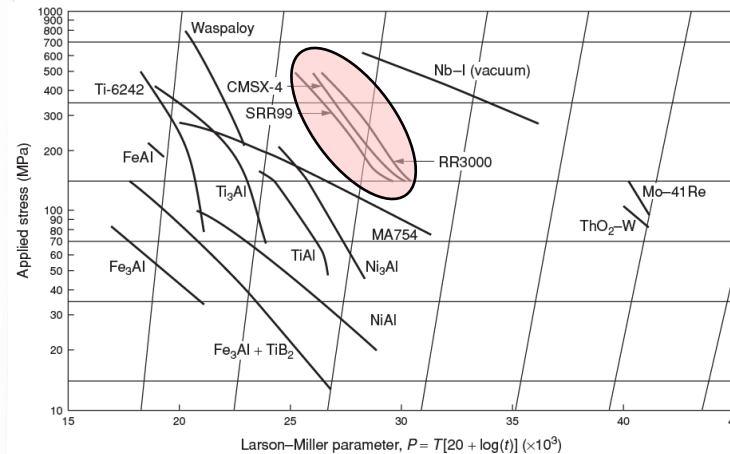
Mechanical properties of Ni alloys

Creep performance of γ' -strengthened alloys

10'000h rupture strength of wrought Ni alloys and stainless steels

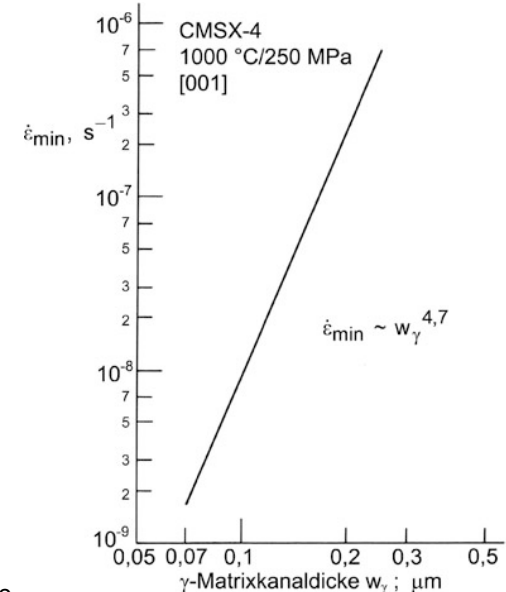


Larson–Miller parameter, P , for a number of high-temperature materials



- The horizontal and near-vertical lines have spacings equivalent to a factor of 2 change in creep life and 200°C temperature capability
- the materials with the best high-temperature performance lie towards the top right of the diagram.

Minimum creep rate as function of matrix channel thickness



/ASM Metals Handbook, Ni and Ni alloys, 1998/

/R.C. Reed, The superalloys – fundamentals and applications, 2006/

/Maier, Niendorf, Bürgel – Handbuch
Hochtemperatur-Werkstofftechnik, 2015/

Mechanical properties of Ni alloys

Accelerated creep testing – Larson-Miller approach

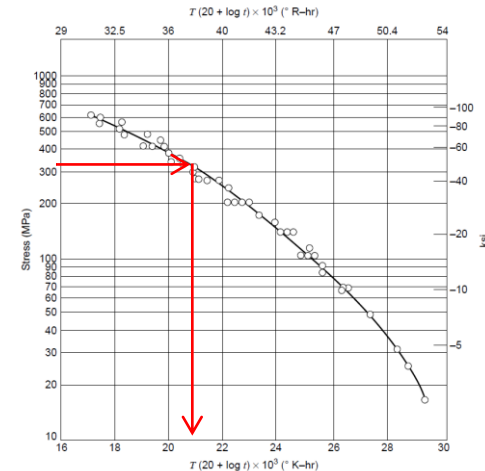
- Creep rupture tests at higher temperatures, comparable stress

- Shorter time periods

- Data extrapolation

Larson-Miller parameter $LMP = T(C + \log(t))$:

For a specific stress the time to rupture is defined
(depending on the temperature)



Mechanical properties of Ni alloys

Accelerated creep testing – Larson-Miller approach

- The service life of turbine blade is on the order of years. A commonly used extrapolation procedure employs the Larson–Miller parameter, defined as: $LMP = T(C + \log(t))$

- **Derive the Larson-Miller relation:**

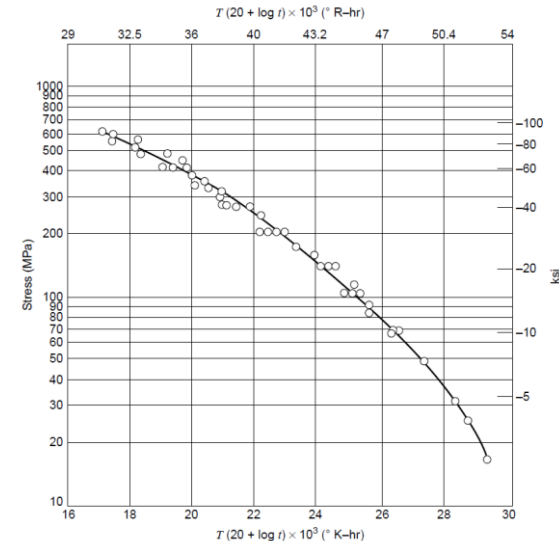
- $\dot{\epsilon} = Ae^{-\frac{\Delta H}{RT}} \rightarrow \frac{\Delta H}{R} = T(\ln(A) - \ln(\dot{\epsilon}))$

- $\frac{1}{t} = A'e^{-\frac{\Delta H}{RT}}$

- $\frac{\Delta H}{RT} = (\ln(A') + \ln(t)) = (2.303\log(A') + 2.303\log(t))$

- $\frac{\Delta H}{R \cdot 2.303} = T(\log(A') + \log(t))$

$$\underbrace{\hspace{1.5cm}}_{LMP} \quad \underbrace{\hspace{1.5cm}}_{C \sim 20}$$



Mechanical properties of Ni alloys

Creep performance of SX Ni alloys

- The creep performance could be significantly improved with the optimization of the SX Ni alloys

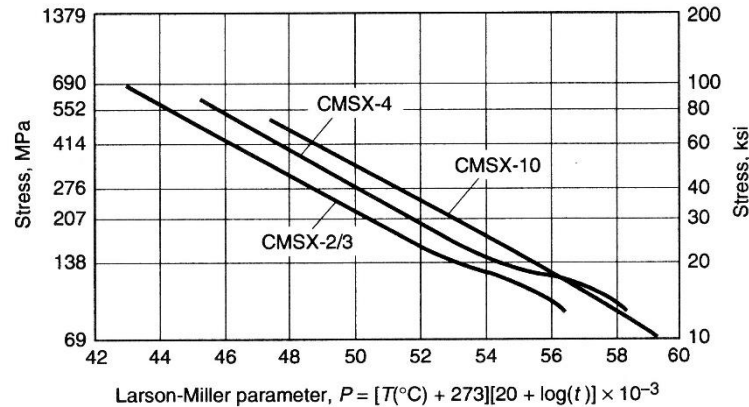


Fig. 19 Average Larson-Miller stress rupture of CMSX-10 vs. that of CMSX-4 and CMSX-2/3. Source: Ref 34

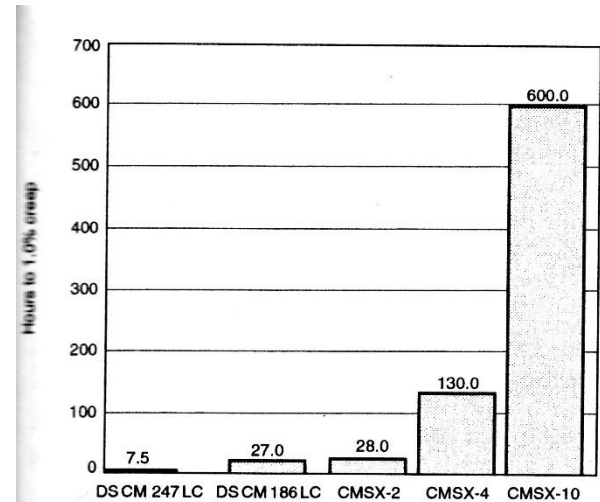


Fig. 21 Average 1.0% creep strengths at 982 °C/248 MPa (1800 °F/36 ksi) test condition for CMSX-10, CMSX-4, CMSX-2, DS CM 186 LC, and DS CM 247 LC. Source: Ref 34

/ASM Metals Handbook, Ni and Ni alloys, 1998/

Microstructural changes in Ni alloys

Coarsening of γ' -Ni₃Al

- During service at elevated temperatures for long durations coarsening of the γ' phase
- This can have detrimental effects on the strength of the alloy
- In Ni alloys with lower γ' fractions the growth follows the Wagner-Lifshitz-Slyozov model:

$$d_T^3 - d_{T0}^3 = k \cdot t \text{ with } k = \alpha \cdot \frac{8D \cdot \gamma_{Ph} \cdot c_0 \cdot V_m^2}{R \cdot T}$$

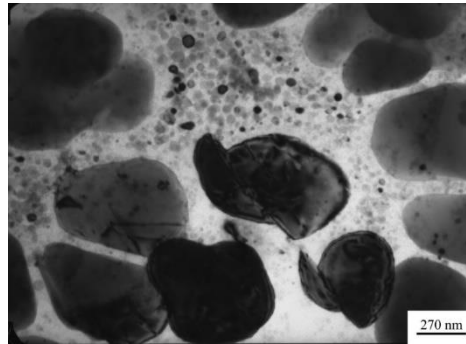
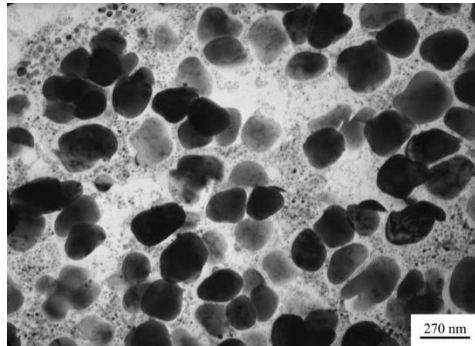
α : constant

D : Diffusion constant of the slowest species

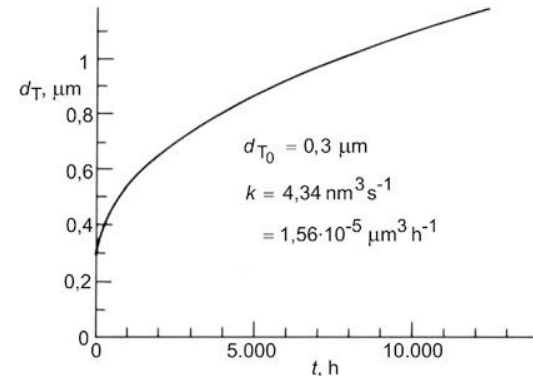
γ_{Ph} : specific interfacial enthalpy matrix/particle

c_0 : saturation conc. of particle-forming element

V_m : molar volume of particles



γ' coarsening in IN738 LC at 920 °C

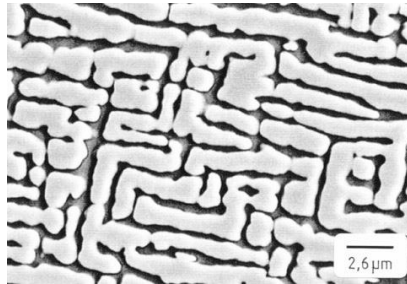
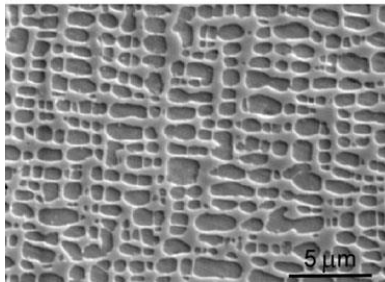


Microstructural changes in Ni alloys

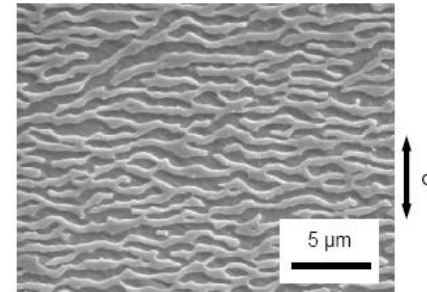
Coarsening of γ' grains in SX alloys under creep load

- In SX alloys with high fractions of γ' and at high T ($> 900^\circ\text{C}$), the coboidal precipitates grow to elongated structures
- At low external stresses, the γ' grains grow in different directions and finally become meander-shaped
- Under external stresses, directional growth of the γ' phase ('rafting')
 - Type N: elongated grains perpendicular to external loading direction
 - Type P: elongated grains parallel to external loading direction

Without or at low external load



175 MPa – type N

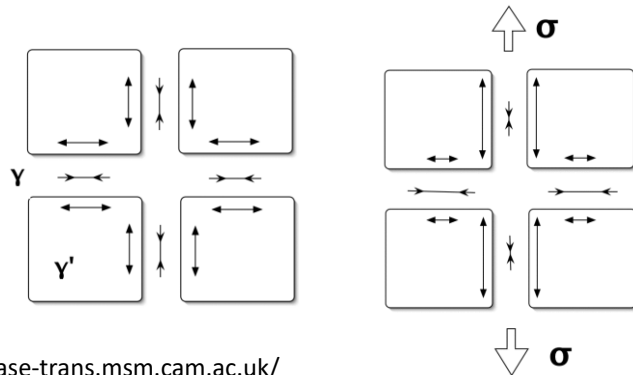


/Maier, Niendorf, Bürgel – Handbuch Hochtemperatur-Werkstofftechnik, 2015/

Microstructural changes in Ni alloys

Coarsening of γ' grains in SX alloys under creep load

- Directional coarsening is caused by the superposition of external load stresses and internal coherence stresses
 - If the γ'/γ lattice mismatch is positive ($a_{\gamma} < a_{\gamma'}$) $\rightarrow$ type P
 - If the γ'/γ lattice mismatch is negative ($a_{\gamma} > a_{\gamma'}$) $\rightarrow$ type N (most frequent case)
- This results in different local stress fields in the γ channels perpendicular and parallel to the loading direction
- These stress differences are the driving force for a directional diffusion; the γ' particles grow in the direction of the lower lattice distortion in the γ channels



- Type N rafting with $a_{\gamma} > a_{\gamma'}$; The γ phase is in compression in the vicinity of the interface with γ' $\rightarrow$ compensating tensile stresses in the γ' .
- The application of a uniaxial tensile stress exaggerates any tensile stress in the vertical direction and reduces those in the horizontal orientation.
- The applied tensile stress reduces the compressive stress in the vertical γ channels and via the Poisson effect, increases those in the horizontal channels.

High-temperature corrosion resistance

- High-temperature corrosion describes the reaction of an alloy with constituents of a gaseous atmosphere (e.g. C, S) at elevated temperatures
- High temperature corrosion properties are characterized by exposing the material to a corrosive atmosphere (e.g. in a combustion chamber) and measuring the weight gain or the depth of attack in the sample as a function of temperature and time

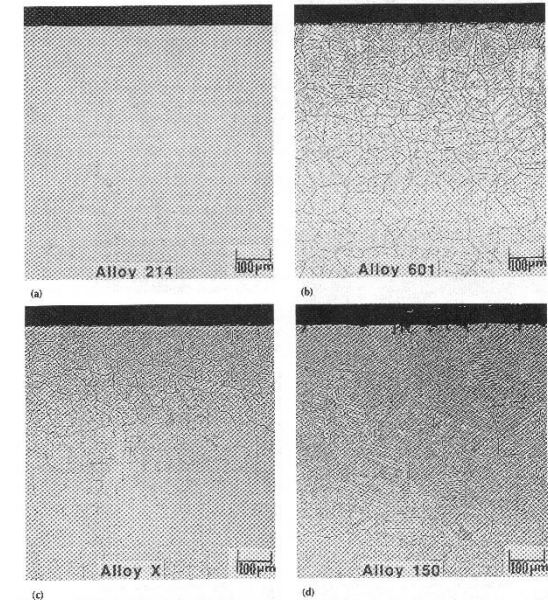
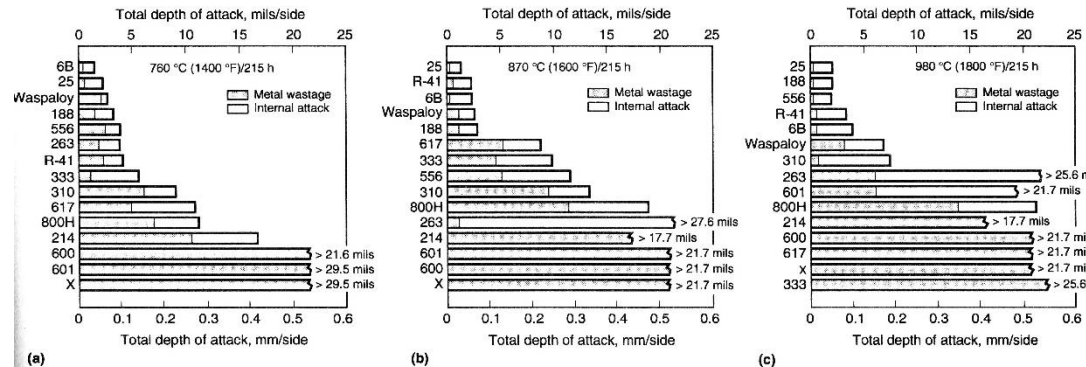


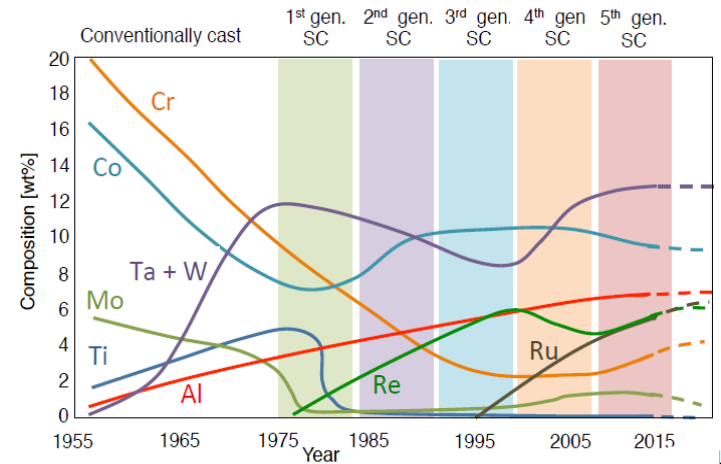
Fig. 18 Corrosion of iron-, nickel-, and cobalt-base alloys after 215 h at (a) 760 °C (1400 °F), (b) 870 °C (1600 °F), and (c) 980 °C (1800 °F) in Ar-5H₂-5CO-1CO₂-0.15H₂S. Source: Ref 38

Main challenges in design of Ni superalloys

- Reaching the optimum amount of $\gamma' \rightarrow \approx 60-70$ vol. pct.
- Stabilizing the γ' phase by reducing the lattice mismatch and hence the interface energy between the matrix γ and the γ' phase reducing the driving force for γ' coarsening. This requires detailed knowledge of the partitioning coefficient, k , of the alloying elements between γ and γ' and their influence on the lattice parameter of both phases. The partitioning coefficient varies with temperature and hence the lattice parameter mismatch may vary with temperature as well.
- Lowering the diffusion coefficient across the matrix to slow down coarsening. Re, Ru and Ir have been found to be particularly powerful for this purpose.
- Preventing formation of unwanted phases, which depends again on the partitioning coefficient between γ matrix and γ' .
- Controlling microsegregation and solidification rate in order to prevent density- and temperature gradient-induced convection in the interdendritic liquid leading to freckles.
- Lowering the stacking fault energy in order to improve the matrix creep resistance.

Evolution of composition of Ni-based superalloys

- Cr has been reduced from over 20% to a few %; Al and Ta take over the role of forming protective oxide scales
- Ta+W have been increased first then reduced to compensate for increasing Re-contents
- Mo and Ti have virtually been eliminated from modern alloys
- Lately Re has been again reduced (and Ta+W increased) as Ru has provided slow diffusion
- Co has been reduced and is now again introduced in order to lower the stacking fault energy.
- The latest developments include Ir additions (after 2005)



/R.C. Reed, The superalloys – fundamentals and applications, 2006/

The need for further alloy optimization

Southwest Airline Flight 1380
March 2018



Fatigue failure of turbine blade
1 person killed

Qantas Flight B734
November 2009



Excessive creep extension of blade, tip
shroud/seal interference and blade rupture

- Difference between wrought and cast Ni alloys (conventional, directional, single crystal)
- Main alloying elements in Ni alloys and their effect on
 - Solid solution strengthening
 - Precipitation strengthening
 - Diffusion properties
 - Stacking fault energies
- The γ' -Ni₃Al phase (structure, composition) and its role for HT-strengthening of Ni alloys
- Fabrication of directionally solidified/single crystal alloys incl. main casting defects
- Role of heat treatments for Ni alloys
- Explain microstructural changes after high-T exposure/heat treatments
- High-T mechanical performance of Ni alloys
 - High-T tensile
 - Creep – Larson-Miller approach
 - Thermo-mechanical

Abbreviations and manufacturers

ABB – Asea Brown Boveri Ltd.

Allvac – ATI Allvac, Allegheny Technologies Comp.

Cabot – Cabot Corp.

CM, CMSX – Cannon-Muskegon Corp.

GTD – General Electric Comp.

Hastelloy – Cabot Corp.

Haynes – Haynes International

Incoloy – International Nickel Comp. (jetzt Special Metals Corp.)

Inconel (IN) – International Nickel Comp. (jetzt Special Metals Corp.)

MAR-M – Martin Marietta Corp.

Nicrofer – Krupp VDM GmbH

Nimonic – International Nickel Comp. (jetzt Special Metals Corp.)

PM – Metallwerk Plansee GmbH

PWA – Pratt & Whitney Aircraft (United Technologies Corp.)

René – General Electric Comp.

RJM – Johnson Matthey & Co Ltd.

SRR – Rolls-Royce Ltd.

Udimet – Special Metals Corp.

Waspaloy – United Technologies Corp.