Course goal: Define the term ‘Superalloys’ and describe the three main types currently being used. Focus on Ni-base superalloys, understand their complex chemistry, processing and in-service performance.

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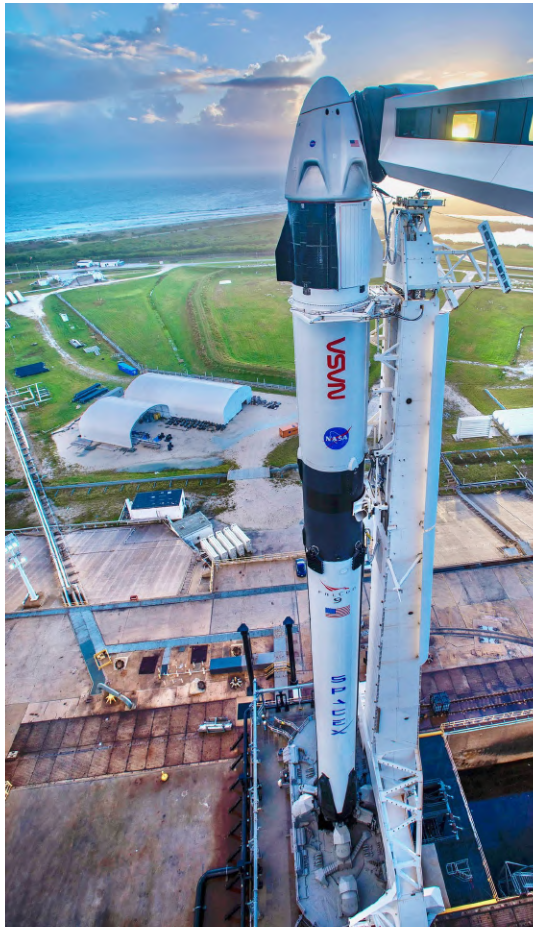


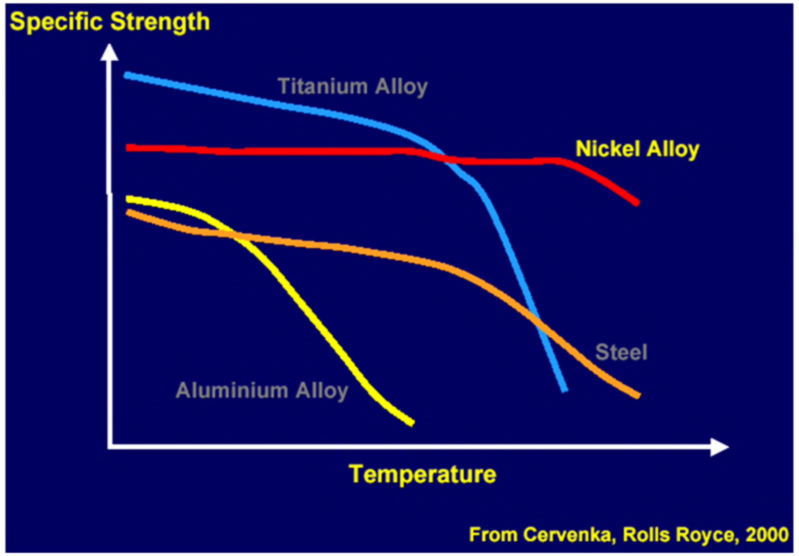
Superalloys have been and will be essential for rocket engines to power space flights.

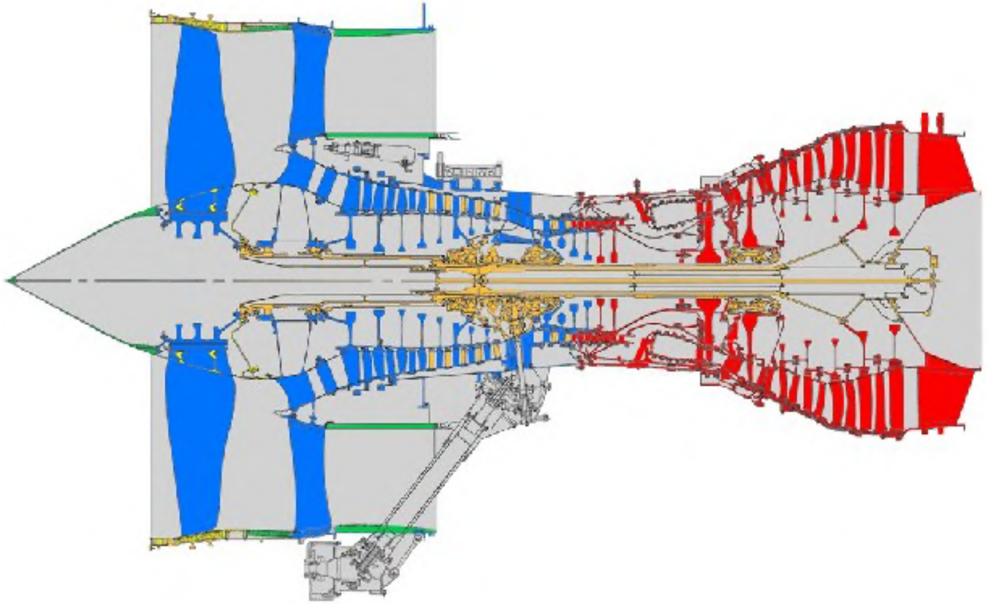
Superalloys

- ***Definition:*** Alloys that exhibit superior strength, temperature capability and environmental survivability as compared to ordinary (moderately alloyed) alloys.

– *For use when stainless and low alloy steels just won't meet performance requirements*

- ***Most important property is maintaining strength at high temperature!***





Fe-Base Superalloys

Properties:

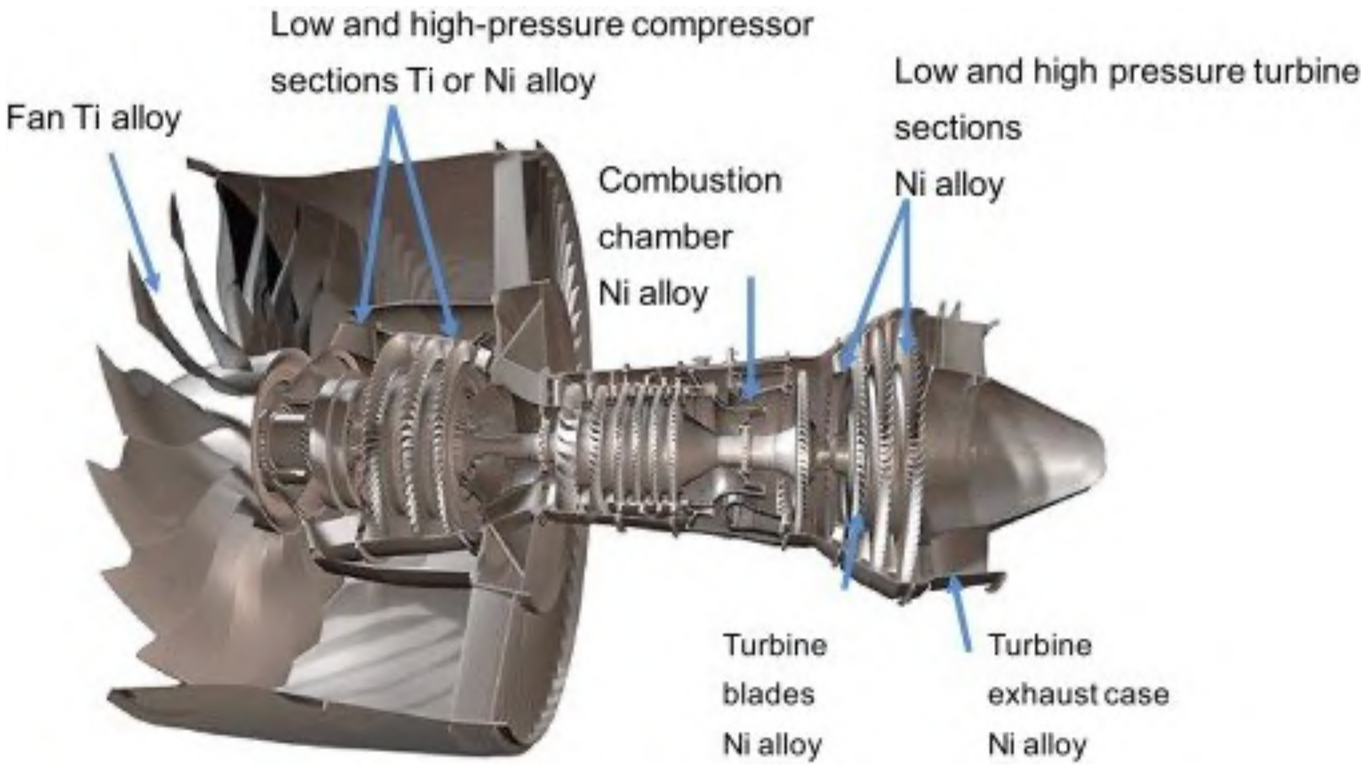
- Least expensive.
- Ni, Cr, etc. enhancements to stainless steel compositions.
- Chromia scale formation to protect against aqueous corrosion and oxidation.
- High RT strength and moderate improvement in elevated temperature strengths.

Uses: steam turbine blades (high Cr), aircraft bearings (high wear application).

Ni-Base Superalloys

Properties:

- Ni-base with significant amounts of Cr, Co, etc., as well as Fe.
- Increased high temperature strength.
- Additions of Al and Ti → creep and thermal fatigue resistance.
- Enhanced corrosion and oxidation (& "Hot Corrosion") resistance.
- *"A highly engineered class of materials"*



Uses: Jet engine *(high temperature parts eg. combuster and turbine)*, chemical and oil and gas industries *(highly corrosive environment eg. pipes, valves)*

Ni-Base Superalloys

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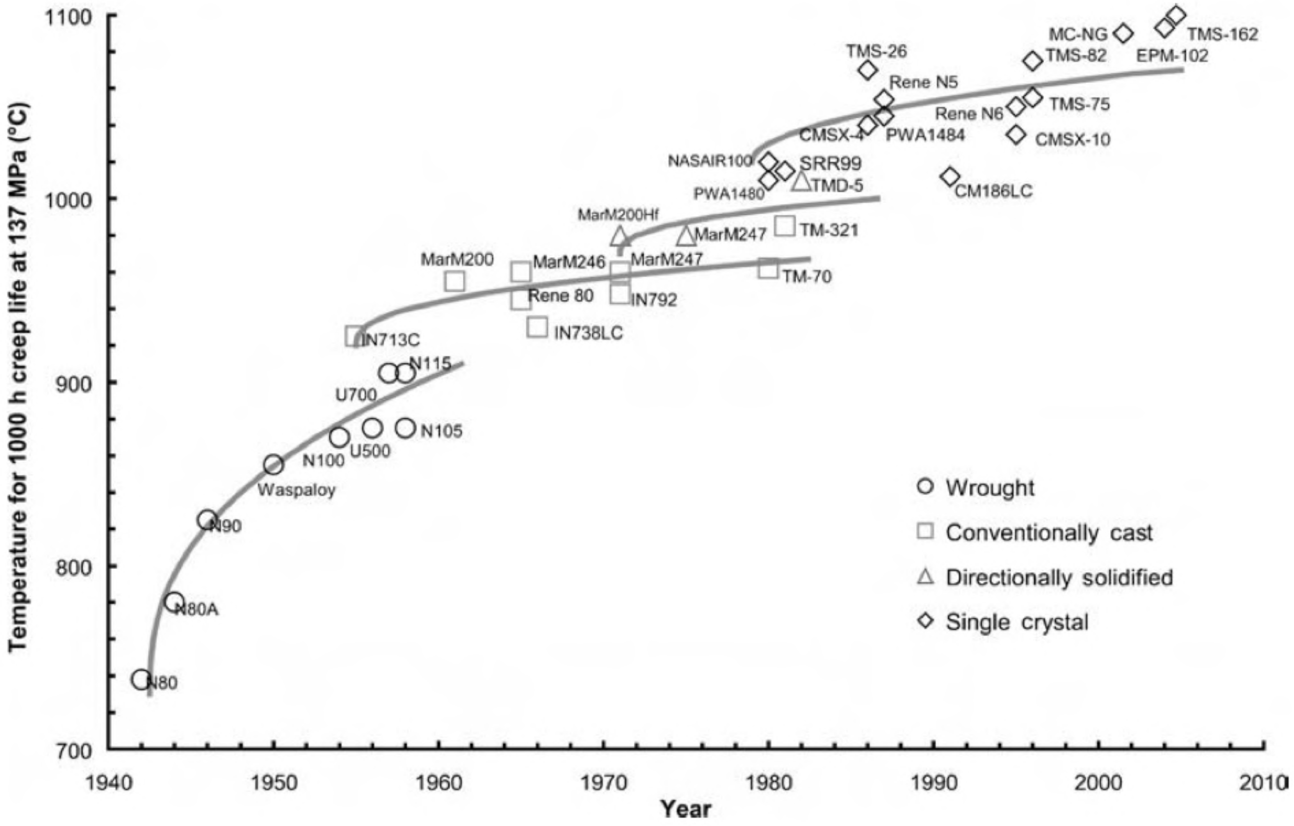


Uses: Jet engine *(high temperature parts eg. combuster and turbine)*, chemical and oil and gas industries *(highly corrosive environment eg. pipes, valves)*

Co-Base Superalloys

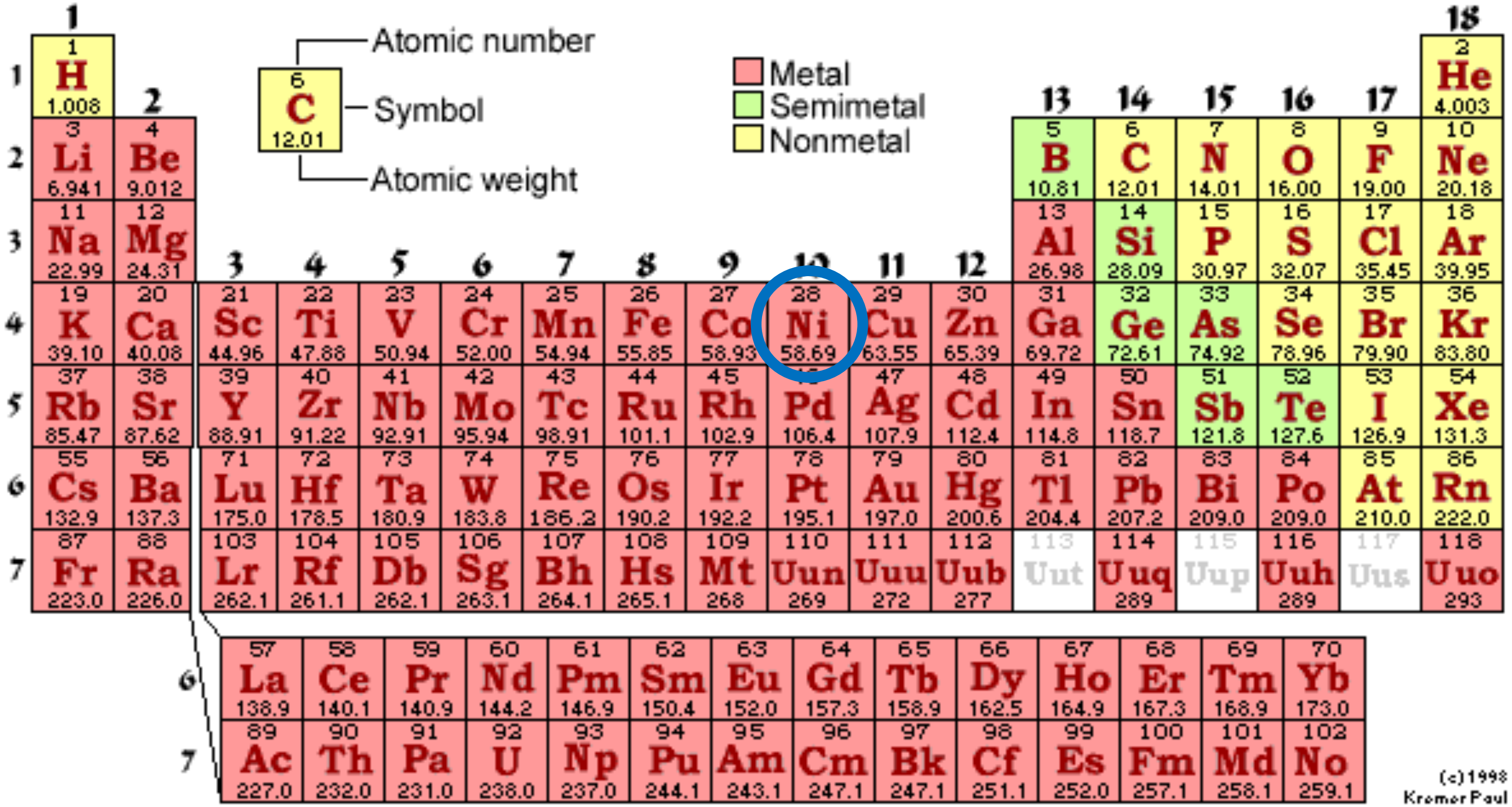
Properties:

- Co-base plus Cr, Ni, C and other elements.
- Hardened by carbide precipitation *(and solid solution hardening).*
- Lower strength but some higher temp. capability.
- Superior oxidation, hot-corrosion resistance, thermal fatigue resistance, weldability.

Uses: Gas turbine blades *(high T, lower stress)*, medical applications, space vehicles, rocket motors.

Ni-base Superalloys

- **Nickel**
- Density: 8900 [kg m^{-3}]
- Melting point: 1455^{o}C
- 5th most abundant element on earth.
- FCC crystal structure



Why Ni-base Superalloys for HT?

- Why Ni-base superalloys for a high temperature material? …

- Let's consider (dimensionless) creep shear strain rate in terms of T/T_m:

$$\bar{\dot{\gamma}} = \frac{\dot{\gamma}\Omega^{2/3}}{D_{T_m}} \propto \Omega^{2/3} \exp\left\{-\frac{Q_v}{RT_m}\left(\frac{T_m}{T} - 1\right)\right\}$$

minimum *maximum* *high T_m*

$\bar{\dot{\gamma}}$ - *dimensionless creep shear strain rate*

$\dot{\gamma}$ - *creep shear strain rate*

Ω – *atomic volume*

D_{T_m} – *diffusivity at melting temperature*

Q_v - *activation energy*

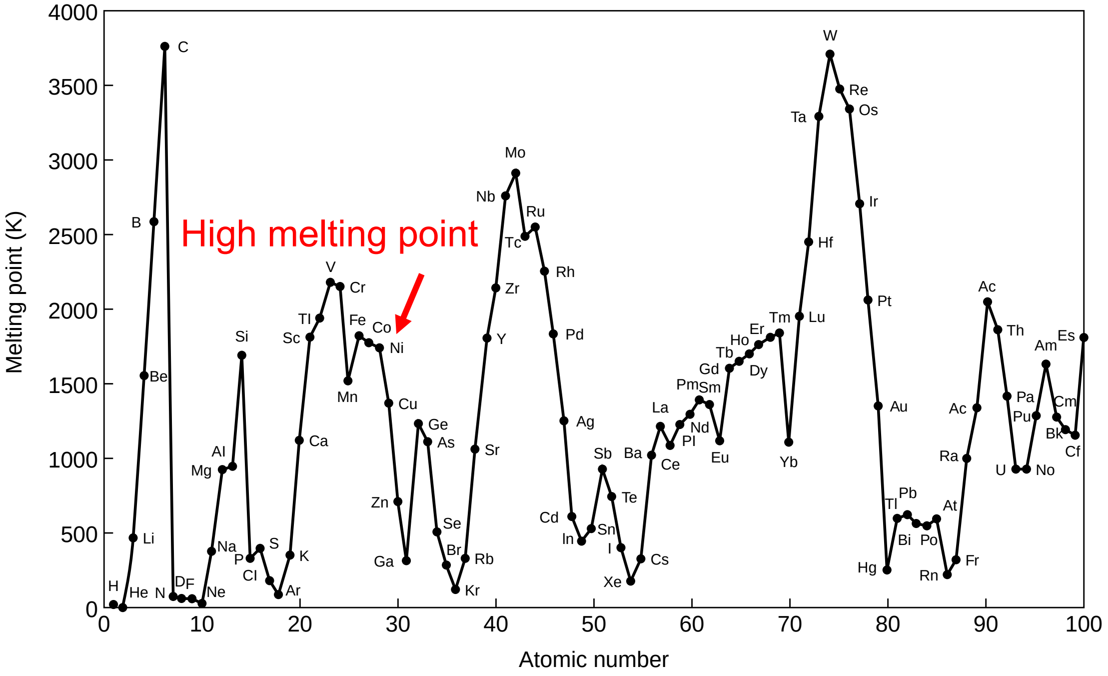
R – *molar gas constant*

T_m– *melting temperature*

T – *temperature*

- *How can we minimise the dimensionless creep shear strain rate?*

Why Ni-base Superalloys for HT?



High melting point

High density, but FCC ductile and tough

BCC

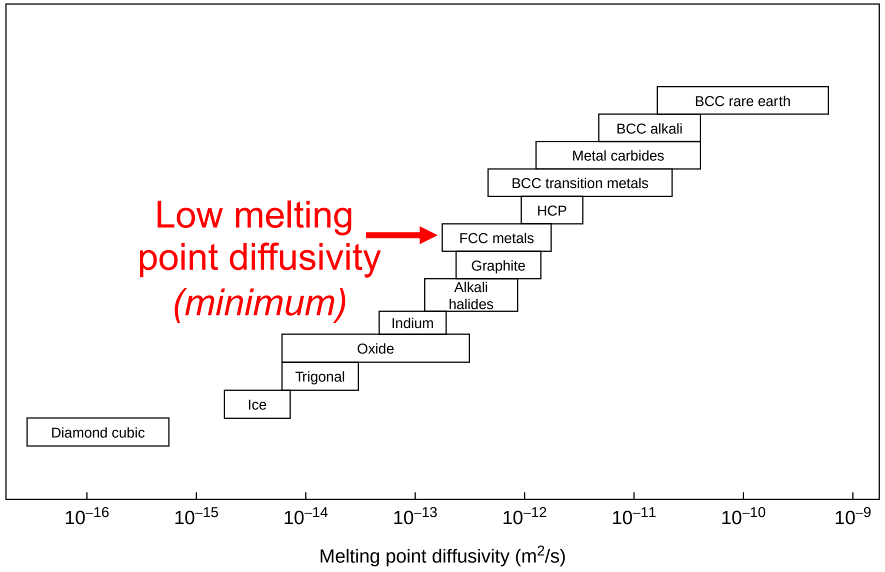
IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB
21 Sc 44.956	22 Ti 47.90	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.9380	26 **Fe** 55.847	27 Co 58.9332	28 **Ni** 58.71	29 **Cu** 63.54	30 Zn 65.37
39 Y 88.905	40 **Zr** 91.22	41 **Nb** 92.906	42 **Mo** 95.94	43 Tc [99]	44 Ru 101.07	45 **Rh** 102.905	46 **Pd** 106.4	47 **Ag** 107.870	48 Cd 112.40
✳ 57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.948	74 **W** 183.85	75 Re 186.2	76 Os 190.2	77 **Ir** 192.2	78 **Pt** 195.09	79 **Au** 196.967	80 **Hg** 200.59

Liquid

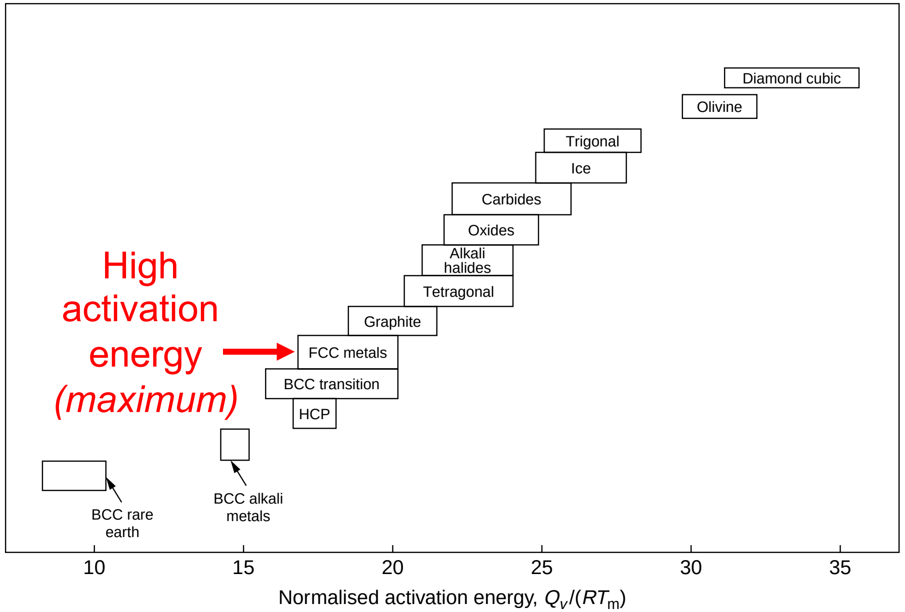
HCP

FCC

PGMs dense and expensive

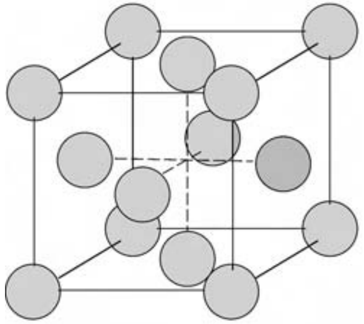


Low melting point diffusivity *(minimum)*



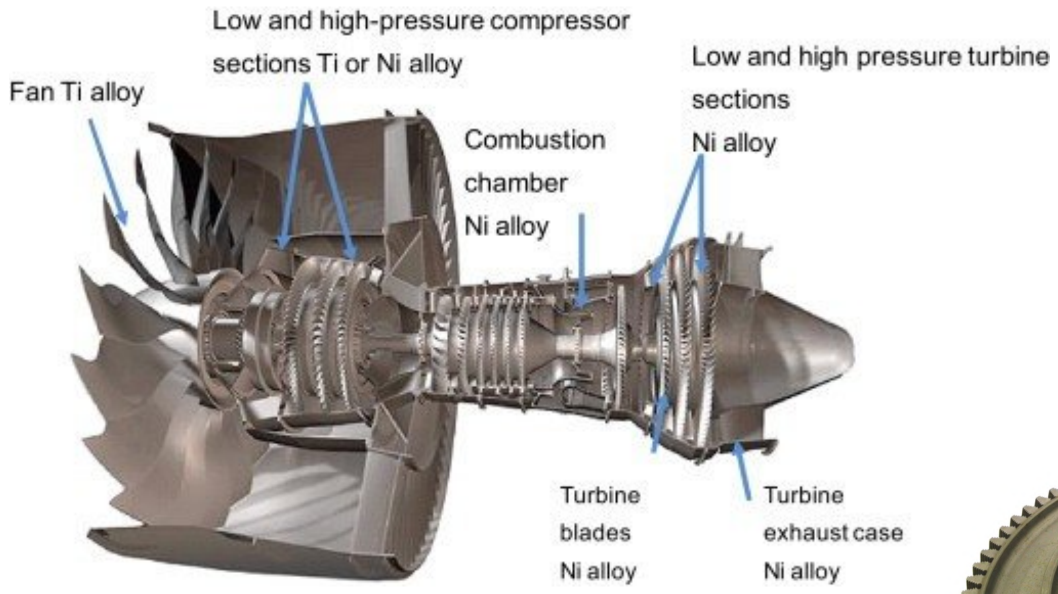
High activation energy *(maximum)*

Stable FCC structure, no phase transformation



Applications of Ni-base Superalloys

High temp. jet engine components



High temp. casings

Land-based gas turbine

Turbine disk –
Hot Isostatically
Pressed component

Single crystal blades

Oil and gas industry *(corrosive environments)*

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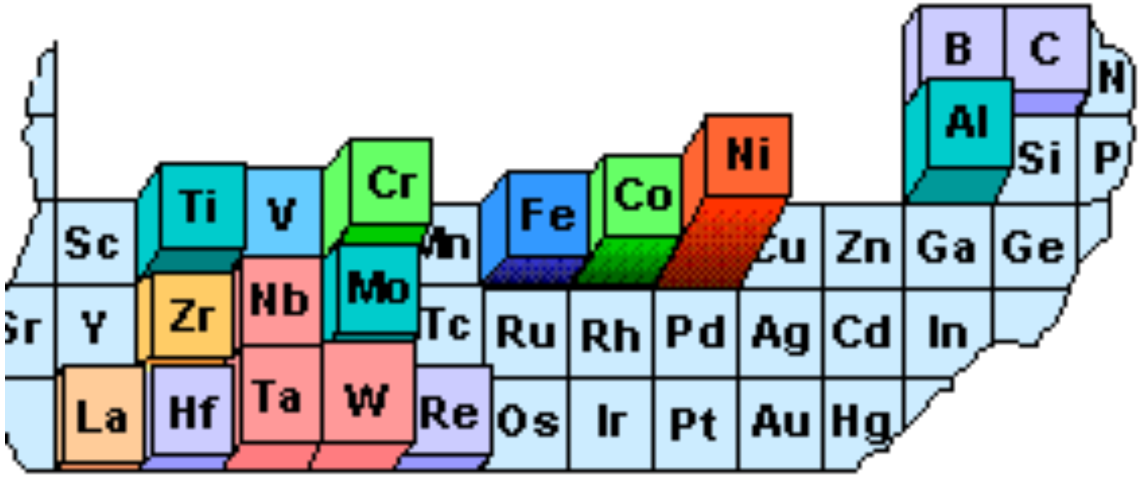


Ni superalloys are highly complex materials.

Superalloy Chemistry

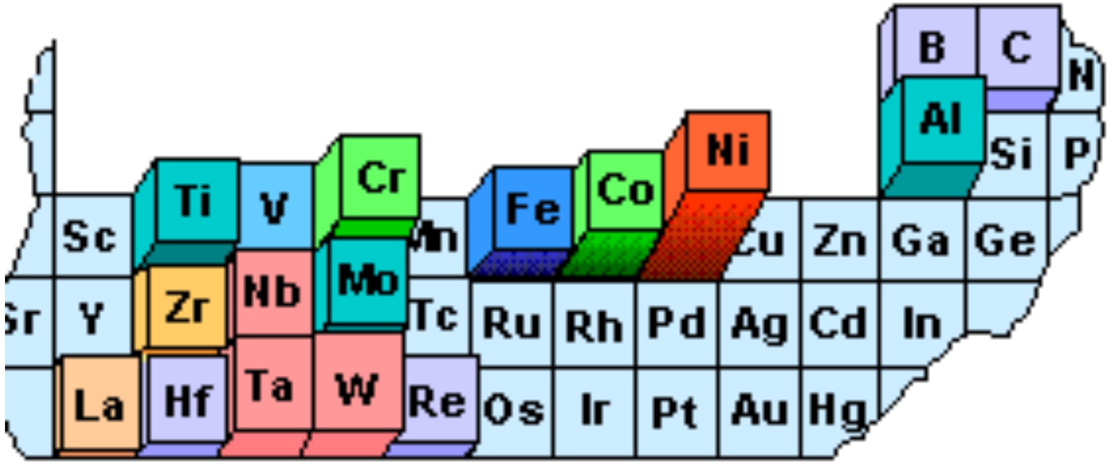
Ni Superalloys;

- Contain at least 50% Ni by weight.
- Many contain more than 10 types of alloying additions, including …

  - *Cr (10% – 20%)*
  - *Co (10% – 20%)*
  - *Al and Ti (up to 8% combined)*
  - *Small amounts of Mo, W, C*
  - *Additional elements…*

Superalloy Chemistry

"Matrix" of Ni plus…

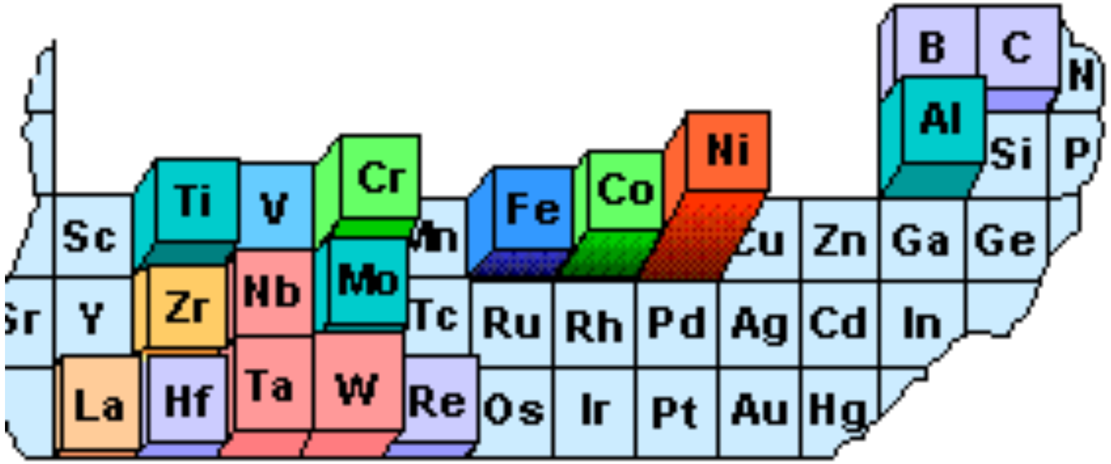


1. **Ni, Co, Fe, Cr, Ru, Mo, Re, W** – *γ (FCC) stabilising, similar atomic radii*
2. **Al, Ti, Nb, Ta** – *γ' (FCC ordered) stabilising, larger atomic radii*
3. **B, C, Zr** – *γ grain boundary, TCP phase, segregators*

- Cr, Mo, W, Nb, Ta can form ***carbides*** with C additions.
- Cr, Mo can form ***borides*** with B additions.

Superalloy Chemistry

"Matrix" of Ni plus…

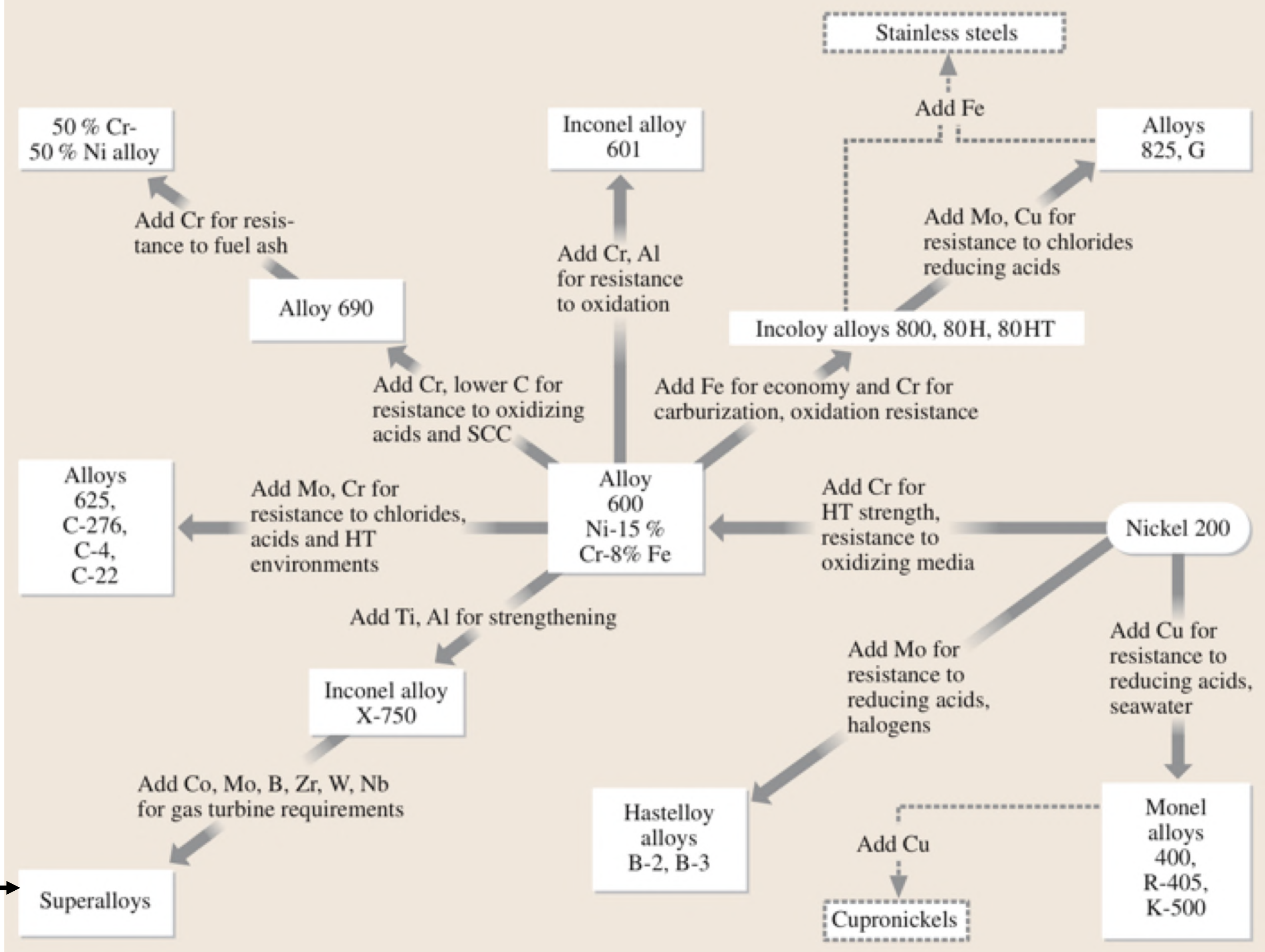


- **Co, Cr, Mo, W, etc.** for Solid Solution Strengthening
- **Al, Ti, Nb, Ta** for Matrix Precipitation Strengthening
- **B, C** for Grain Boundary Precipitation Strengthening
- **Cr, Al** for Oxide Formation (Chromia or Alumina)
- **Cr** for Aqueous Corrosion/SCC Resistance
- **La, Hf, B, Mg** for Grain Boundary Ductility
- **La** for Oxide (and Coating) Adherence
- **Re, Ru, Pt** for Creep Stability

Superalloy Chemistry → Tailor Properties

Mo, Cr for Corrosion Resistance

Ti, Al and Co, Mo, B, Zr, W, Nb for jet engine / gas turbine



Inconel 718
Waspaloy
Udimet 720LI
RR1000
Rene 95

From: W Martienssen and H Warlimont, Handbook of Condensed Matter and Materials, 2005

Cr, Al for Oxidation Resistance

Mo, Cr for Chloride and Acid Resistance

Cr for strength

Mo for Acid Resistance

Cu for Seawater Resistance

Property Development in Ni-base Superalloys

Chemistry

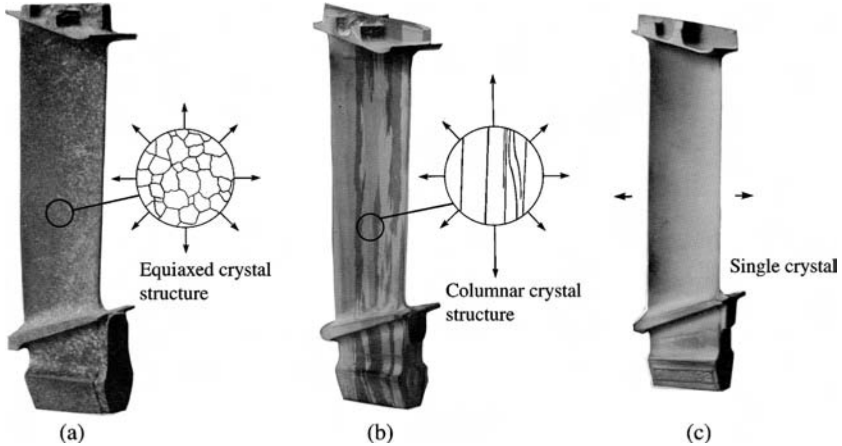
- Develop oxidation/corrosion resistance
- Provide elements for formation of precipitates
- Provide grain boundary strengtheners
- Enhance processability

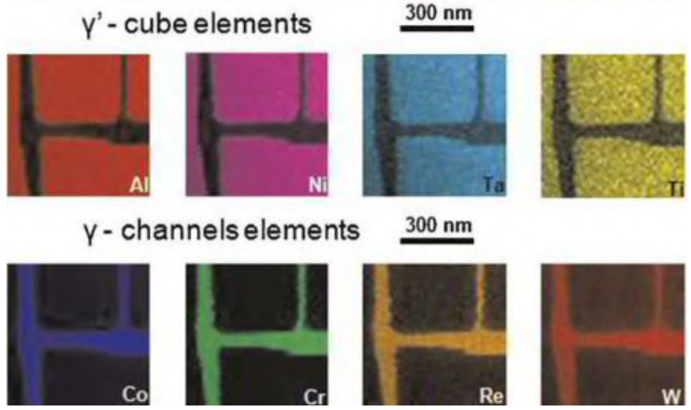
Processing

- Conventional Castings (Polycrystalline)
- Forged Products
- Powder-Metallurgy + Forge
- Directional Casting – Directional Solidification and Single Crystal

Heat Treatment

- Solution Treatment to homogenize chemistry, structure and properties
- Precipitation of matrix strengthening phases
- Precipitation of grain boundary strengthening carbides and boro-carbides
- (Coating treatment integrated with alloy heat treatment)
- Residual stress relaxation





Types of Ni-base Superalloys (1)

Alloy Type	Alloying Element	Key Characteristic	Applications	Examples of Alloys
"Pure Nickel"	Minimal alloying	Magnetic properties	Electronics, Sensors	"Ni-200"
Solid Solution Strengthened	Cr, Fe, Co	Moderate strength to intermediate temperatures, stability of structure & properties	Ducting, diffusers casings	In 625,
Aqueous Corrosion and SCC resistant	Cr	Formation of spinels and chromia corrosion product	Chemical plants, steam systems, Nuclear plants	Alloy 600, alloy 690, (Alloy 800)
Oxidation and Hot Corrosion Resistant	Al (Ti), Cr	Formation of alumina or Chromia scales	Gas turbines, superchargers	In713, In100, Mar-M200, CM247, GTD 191, In738

**Alloys are not named or numbered according to a system.*

Types of Ni-base Superalloys (2)

Alloy Type	Alloying Element	Key Characteristic	Applications	Examples of Alloys
Intermediate Temperature Stress Relaxation Resistant	Al, Ti, Cr, Nb	Formation of small amount of highly stable precipitates – generally lower γ' volume fraction		Alloy 750 Alloy 706, Alloy 617
Elevated Temperature Strength	Al, Ti, Cr, Nb	Forged Precipitation hardened alloys	Turbine disk alloys engine casings, exhausts etc.	Alloys 718, 706, 720
High Temperature Creep Resistant	Al, Ti, Cr, B (C)	Mainly conventionally cast (CC) (but can be forged superalloys), γ-γ' matrix structure, grain boundary "carbide" arrays. High Volume fraction γ' alloys	Hot gas path parts (Blades and Vanes)	In738LC, Mar-M 200, CM247,
Very High Temperature Creep and Fatigue Resistant	Al, Ti, Cr B (C), Hf	Directional solidification (DS) and single crystal (SC) processed, ultimate volume fraction γ'. Elimination or control of Grain Boundaries. (Specialized additions for low angle boundary control)	Hot gas path parts (Blades and Vanes)	PWA 1426, CMSX3 Rene-N5, CMSX-4, PWA1484, CMSX-10

Important Aerospace Superalloys

Alloy		Cr	Co	Mo	W	Ta	Nb	Al	Ti	Fe	C	B	Zr	Re	Hf	Others
ATI 718Plus	wrought	19	9	2.8	1.1		5.6	1.5	0.8	9	0	0.01				
Astroloy	PM	15	17	5.1				4	3.5		0		0			
CMSX2	SX	8	4.6	0.6	7.9	5.8		5.6	0.9							
CMSX4	SX	5.7	11	0.4	5.2	5.6		5.2	0.7					3	0.1	
CMSX6	SX	9.8	5	3		2.1		4.8	4.7							
CMSX10	SX	2	3	0.4	5	8	0.1	5.7	0.2					6	0	
FT750DC	wrought	20			3.5			2.3	2.1	5	0.1	0.01				0.4 Si
Hastelloy X	wrought	22	1.5	9	6					19	0.1					0.5Mn, 0.5Si
Hastelloy S	wrought	16		15				0.2		1	0	0.01				0.02 La
Inconel 600	wrought	16								7.2	0					0.2Mn, 0.2 Si
Inconel 718	wrought	19		3.1			5	0.4	0.9	19	0					0.2Mn, 0.3Si
Inconel 625	Deposited	22	0.1	9			3.5	0.1	0.2	3	0					
MA758	MA/ODS	30			0.5			0.3			0.1					0.6 yttria
MA760	MA/ODS	20			3.4			6		1.2	0.1					1.0 yttria
MA6000	MA/ODS	15			3.9			4.5	2.3	1.5	0.1					1.1 yttria
MAR-M200	cast	9	10		12		1	5	2		0.2	0.02	0.1			
Nimonic 80A	wrought	20	1.1					1.3	2.5			0.06				
Nimonic 105	wrought	15	20	5					1.2	4.5		0.2				
PM1000	MA/ODS	20						0.3	0.5	3						0.6 yttria
Rene N5	SX	7	8	2	5	7		6.2						3	0.2	
Rene N6	SX	4.2	13	1.4	6	7.2		5.8						5	0.2	
Rene 41	wrought	19	11	10				1.5	3.1		0.1	0.05				
RR2000	SX	10	15	3				0.1	4							1 V
RR3000	SX	2.3	3.3	0.4	5.5	8.4		5.8	0.2					6.3	0	
UCSX1	SX	2.3	6	1.5	7	8.4		5.8	0.2					6.3	0	2 Ru
UCSX8	SX	2.3	6	3	6	8.4		5.8	0.2					6.3	0	6Ru
SRR99	SX	8.5	5		9.5	2.8		5.5	2.2							
TMS 63	SX	6.9		7.5		8.4		5.8	0							
TMS75	SX	3	12	2	6	6								5	0.1	
TMS138	SX	3	12	3	6	6								5	0.1	2Ru
TMS162	SX	2.9	5.8	3.9	5.8	5.6		5.8						4.9	0.1	6Ru
Udimet 500	wrought	18	19	4				2.9	2.9		0.1	0.01	0.1			
Udimet 700	wrought	15	19	5.2				4.3	3.5		0.1	0.03				
Waspaloy	wrought	20	14	4.3				1.3	3		0.1	0.01	0.1			

PM = powder metallurgy

SX = single crystal

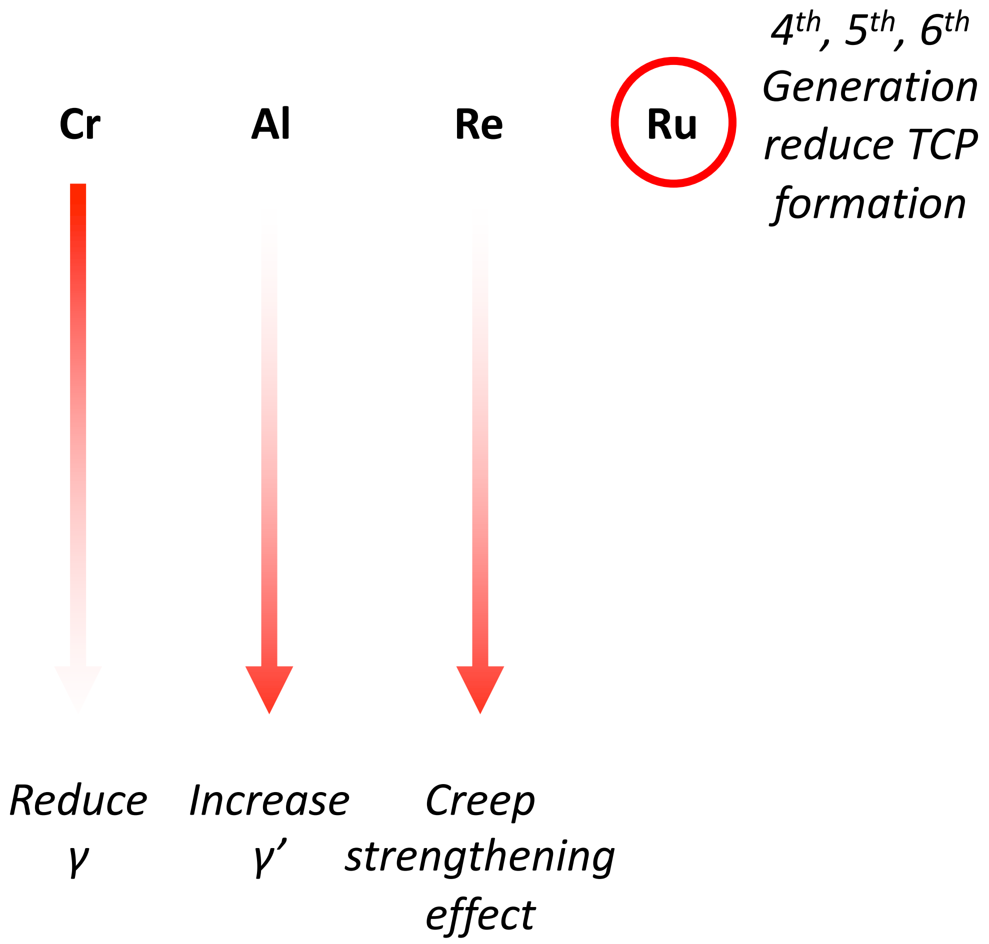
MA = mechanically alloyed

ODS = oxide dispersion strengthened

**Alloys are not named or numbered according to a system.*

Important Single Crystal Superalloys

	Cr	Co	Mo	W	Ta	V	Nb	Al	Ti	Hf	Re
1st Generation											
PWA1480	10	5	0	4	12			5	1.5	0	
Rene N4	9	8	2	6	4		0.5	3.7	4.2	0	
SRR99	8	5	0	10	3			5.5	2.2	0	
RR2000	10	15	3	0	0	1		5.5	4	0	
AM1	8	6	2	6	9			5.2	1.2	0	
AM3	8	6	2	5	4			6	2	0	
CMSX2	8	5	0.6	8	6			5.6	1	0	
CMSX3	8	5	0.6	8	6			5.6	1	0.1	
CMSX6	10	5	3	0	2			4.8	4.7	0.1	
AF56	12	8	2	4	5			3.4	4.2	0	
2nd Generation											
CMSX4	7	9	0.6	6	7			5.6	1	0.1	3
PWA1484	5	10	2	6	9			5.6	0	0.1	3
SC180	5	10	2	5	9			5.2	1	0.1	3
MC2	8	5	2	8	6			5	1.5	0	0
Rene N5	7	8	2	5	7			6.2	0	0.2	3
3rd Generation											
CMSX10	2	3	0.4	5	8			5.7	0.2	0.03	6
Rene N6	4.2	12.5	1.4	6	7.2		0.1	5.75	0	0.15	5.4
TMS75	3	12	2	6	6			6	0	0.1	5
TMS113	2.89	11.9	1.99	5.96	5.96			6.56	0	0.1	5.96



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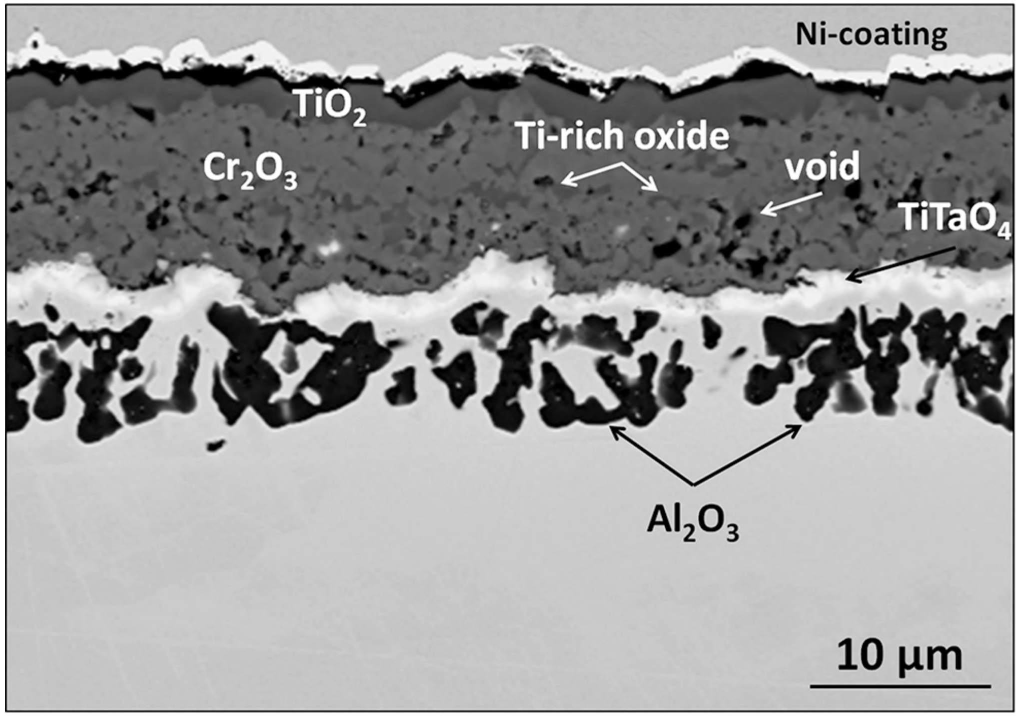
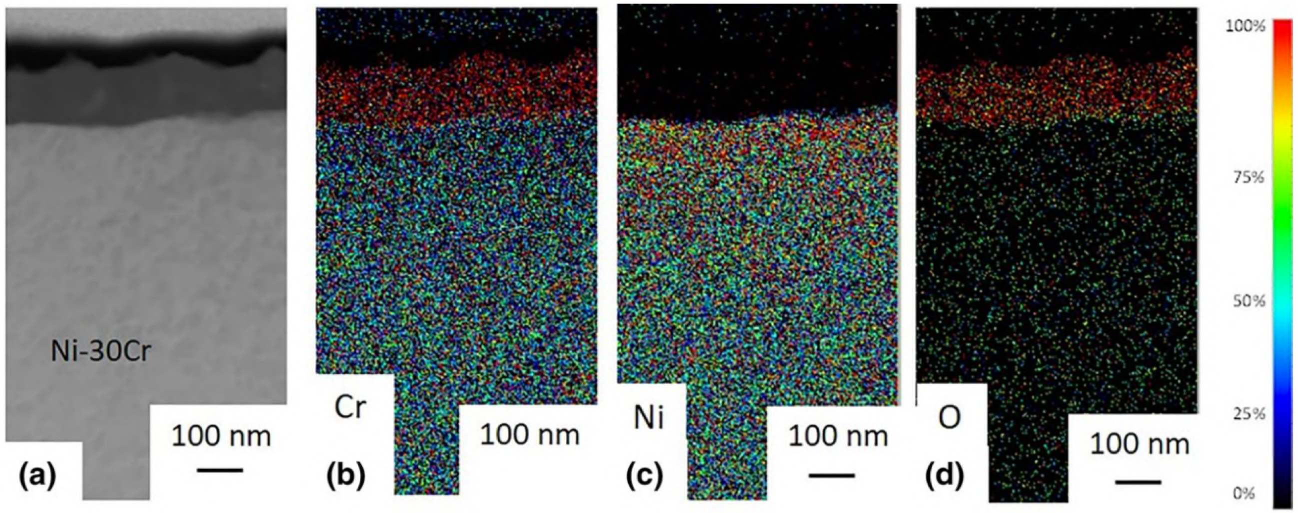


Chromia oxide formation in a Ni superalloy.

Ni-base Superalloys – Aqueous Corrosion

- *Superior resistance to Stainless Steels.*
- Formation of ***Chromia scale.***
- Alloy Ni with ***Cr*** → NiFeCr Spinel → Chromia scale
- May call for other elements to provide strength, etc.
  → change overall composition
- *Potentially use as a clad (via arc deposit) or as a "wallpaper"*



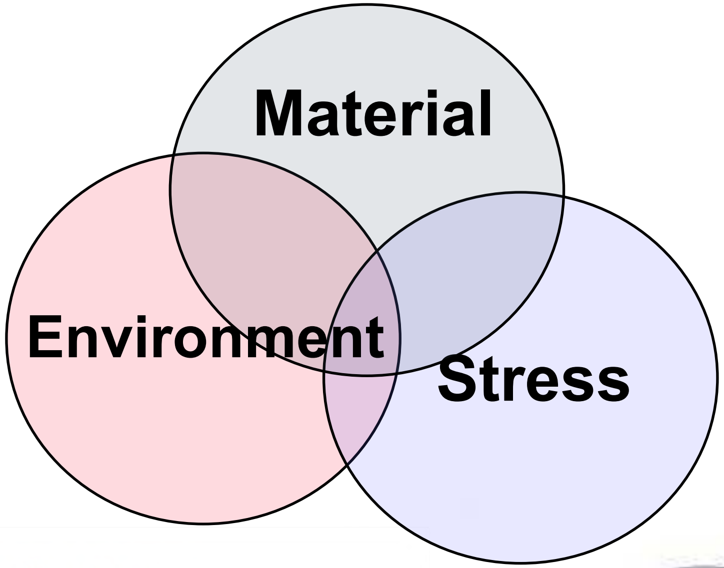
Comparison of the Galvanic Series in Sea Water and the Electromotive Series

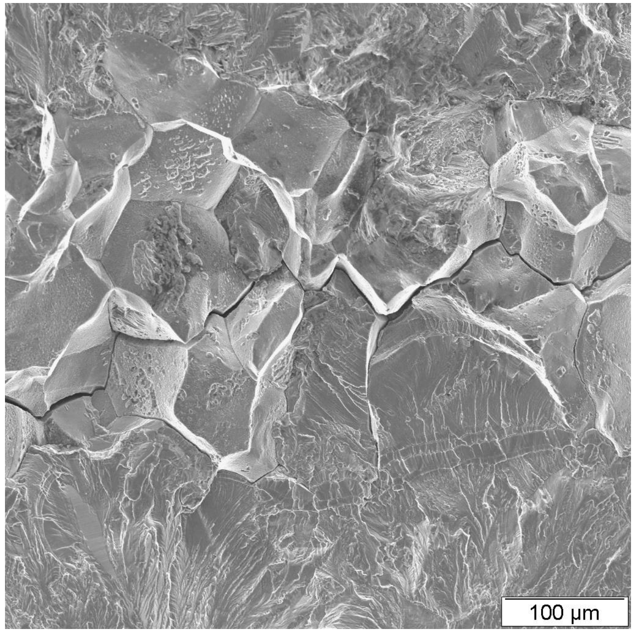
Galvanic series in sea water	Electromotive series†		
Anodic (corroded) end			
Magnesium	Li,	Li^{+}	−3.02 volts
Magnesium alloys	K,	K^{+}	−2.92
Zinc	Na,	Na^{+}	−2.71
Galvanized steel	Mg,	Mg^{++}	−2.34
Aluminum	Al,	Al^{+++}	−1.67
Cadmium	Zn,	Zn^{++}	−0.76
Aluminum alloys	Cr,	Cr^{++}	−0.71
Steel	Fe,	Fe^{++}	−0.44
Wrought iron	Cd,	Cd^{++}	−0.40
Cast iron	Co,	Co^{++}	−0.28
50-50 Solder	Ni,	Ni^{++}	−0.25
18-8 Stainless steel (active)	Sn,	Sn^{++}	−0.14
Lead	Pb,	Pb^{++}	−0.13
Tin	H_2,	H^{+}	0.00 (Reference)
Muntz metal	Bi,	Bi^{+++}	0.23
Nickel	Cu,	Cu^{++}	0.34
Yellow brass	Hg,	Hg^{++}	0.80
Red brass	Ag,	Ag^{+}	0.80
Copper	Pt,	Pt^{++}	1.2
70-30 Cupronickel	Au,	Au^{+}	1.7
18-8 Stainless steel (passive)			
Cathodic (protected) end			

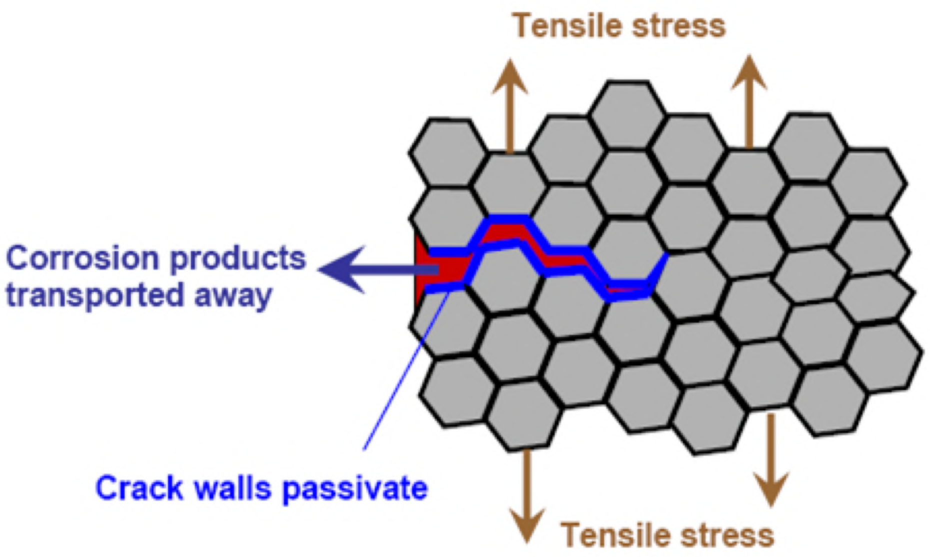
* Adapted from the *Corrosion Handbook*. † Voltages are for oxidation reaction.

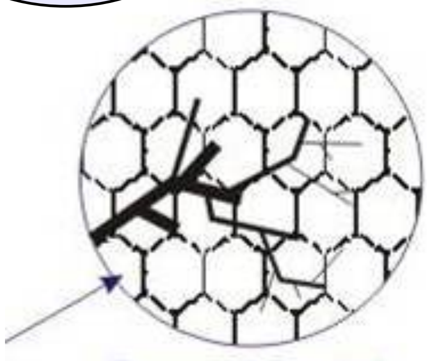
Stress Corrosion Cracking (SCC)

- SCC = *(Delayed)* cracking in the presence of a tensile stress.
- Generally along grain boundaries or specific crystallographic planes
- Ni alloys selected to replace Stainless Steels for better resistance
- Rely on forming adherent Ni/Cr spinel and Chromia scales – *even in tight cracks!*







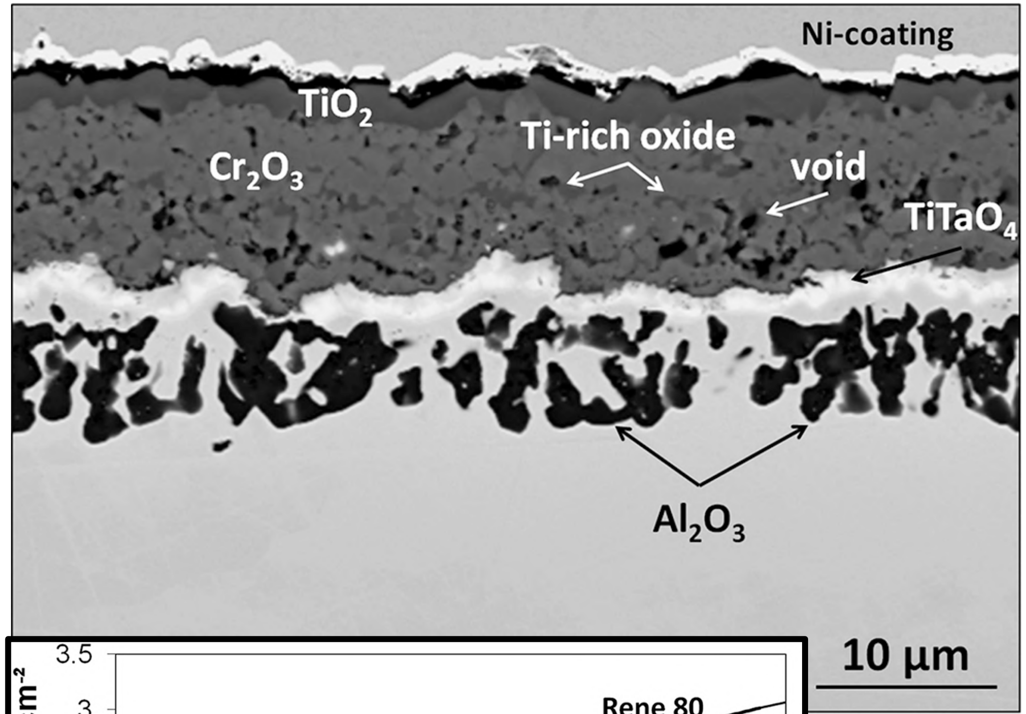


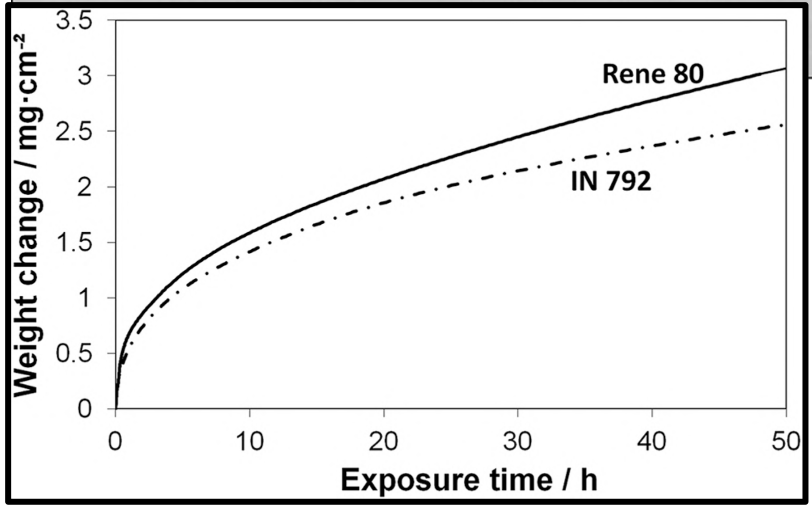
Transgranular breached cracks in the austenitic microstructure (typical of chloride induced SCC)

Ni-base Superalloys – Oxidation

1. Formation of ***Alumina or Chromia*** scales.
2. Compact, crack-free, tightly adherent scales
3. Growth by ionic diffusion (O^{2-} in, or M^{n+} out)
4. Develops parabolic kinetics – with no breakaway.

- ***Alumina*** is a better choice for oxidation protection.
- Which *(Alumina or Chromia)* scale develops depends on chemical activity of the cation species – depends on local chemistry, incl. other elements, and O activity.
- Ti is an aggressive oxide former – but it can have a deleterious effect on the alumina scale.
- ***Chromia starts to evaporate at temperatures above about 1025°C !***

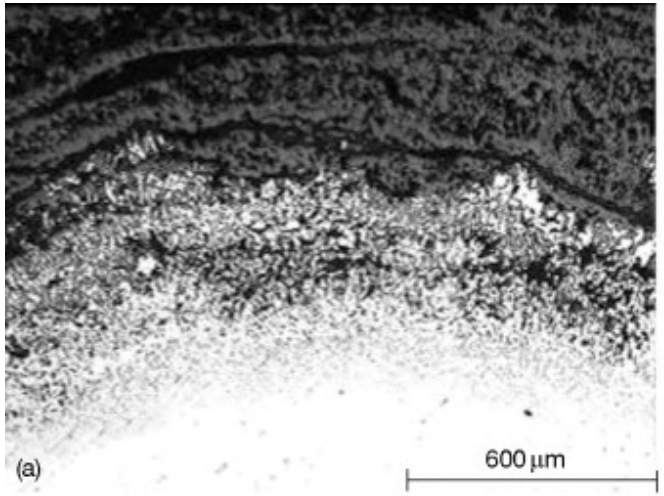




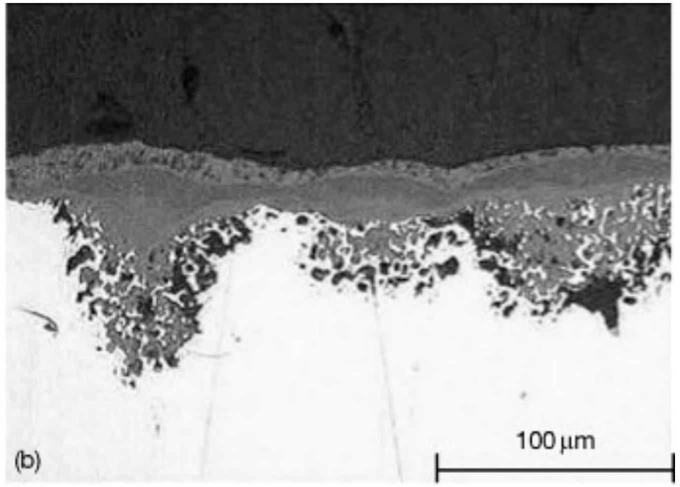
Ni-base Superalloys – Hot Corrosion

- **"Hot Corrosion"** = *Chemically Accelerated oxidation attack*
- Accelerated by presence of S, Na and Cl
- Formation of "sticky sulphates" with e.g W, Mo from alloy
- Problem is Alumina Stability

→ *Utilise Chromia forming alloy*



Type I hot corrosion



Type II hot corrosion

- Type I Hot Corrosion
  - at ***high temperatures***
  - ~ 750°C – 900°C window
  - Macroscopic attack
  - Due to Sulphate (acidic) fluxing of Alumina (amphoteric) oxide

Type II Hot Corrosion

- At ***intermediate temperatures***
- ~ 600°C – 750°C window
- Greatly reduced ductility
- Highly localized at grain boundaries
- Strain rate sensitivity observed

Turbofan Engine Failure

- Thermal cycling and high thermal gradients → thermal fatigue.
- Oxidation and corrosion → tip cracks, develop into v-shaped notches
- Re-welding of blades needed, but this can cause preferential attack and failure.