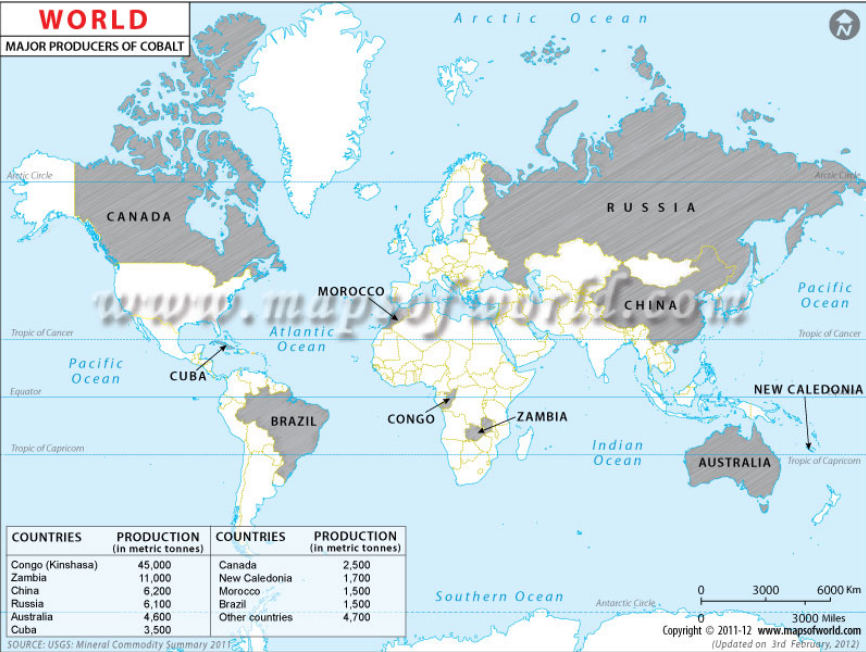


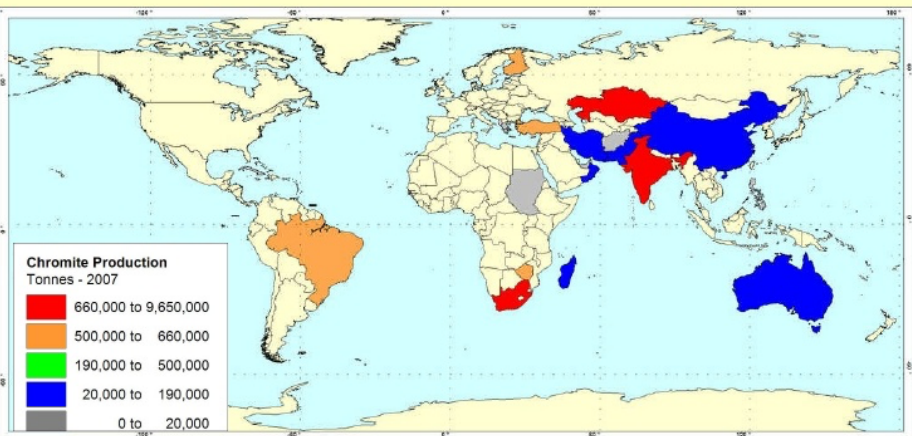
Co, Cr, Ta and Nb has been designated a "strategic aerospace element," because the United States is almost entirely dependent on imports for the consumption of these elements

Three nations, South Africa, Zaire, and the U. S. S. R., account for over half of the world's production of chromium, cobalt, manganese, and platinum group metals.

Disruptions of supply, such as the Canadian nickel strike in 1968 and the rebel interruptions of cobalt production in Zaire in 1978, had a major impact on U.S. industries.



Co



World chromite production

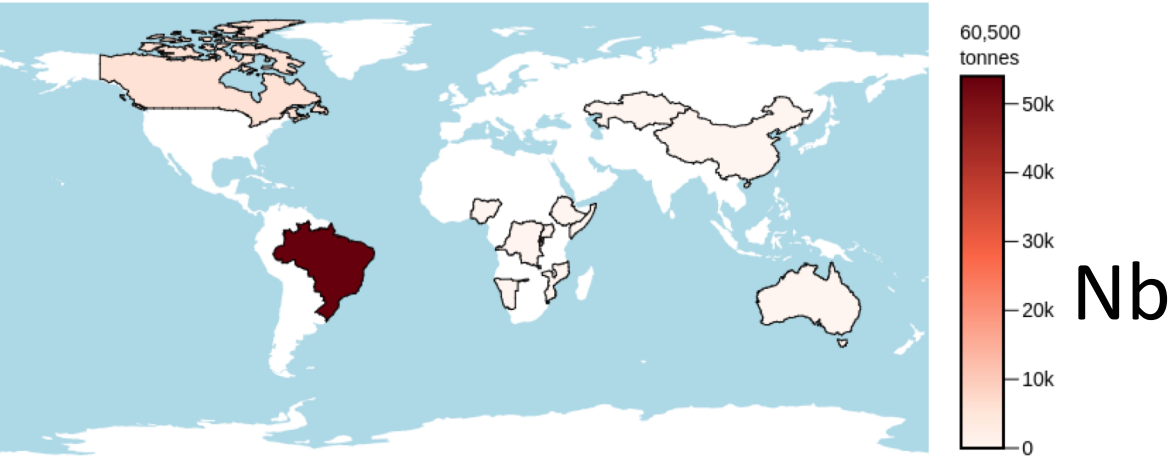
- South Africa, India and Kazakhstan = 78%
- Brazil, Finland, Russia, Zimbabwe and Turkey = 12%
- Canada poised to be the next major producer

Cr

Production concentration of critical raw mineral materials

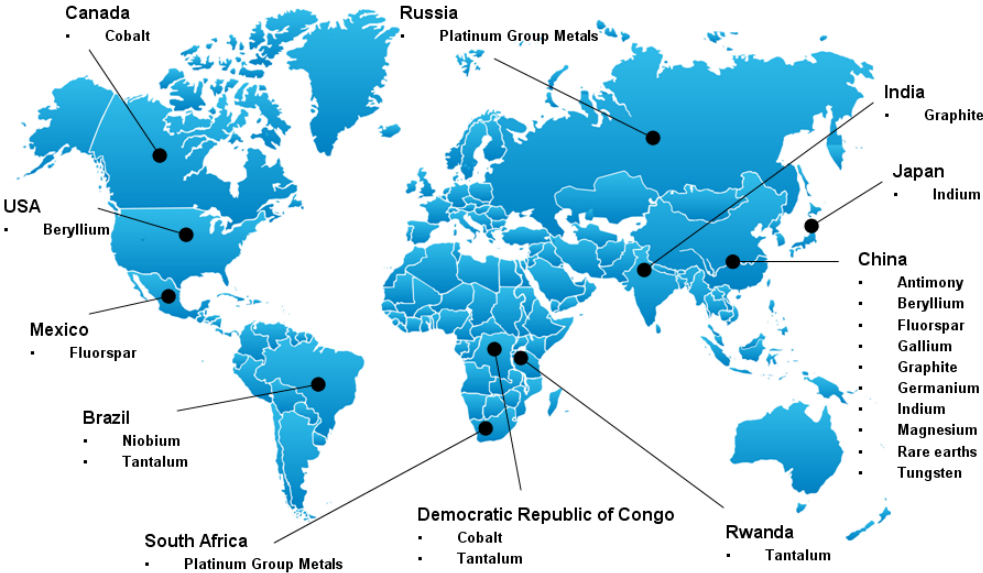
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Niobium Production 2015

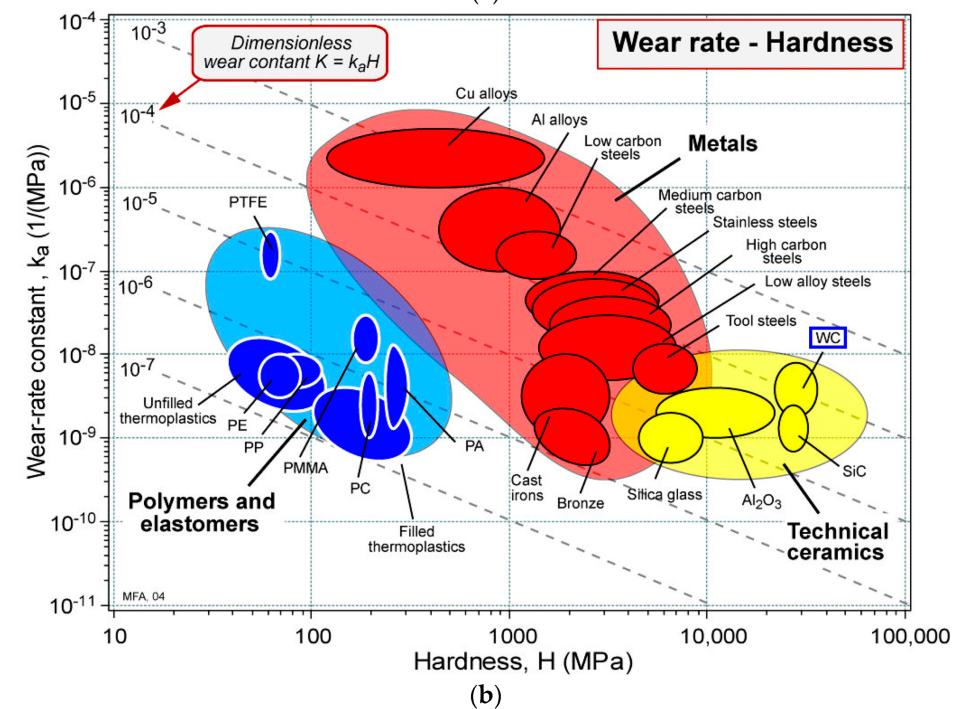
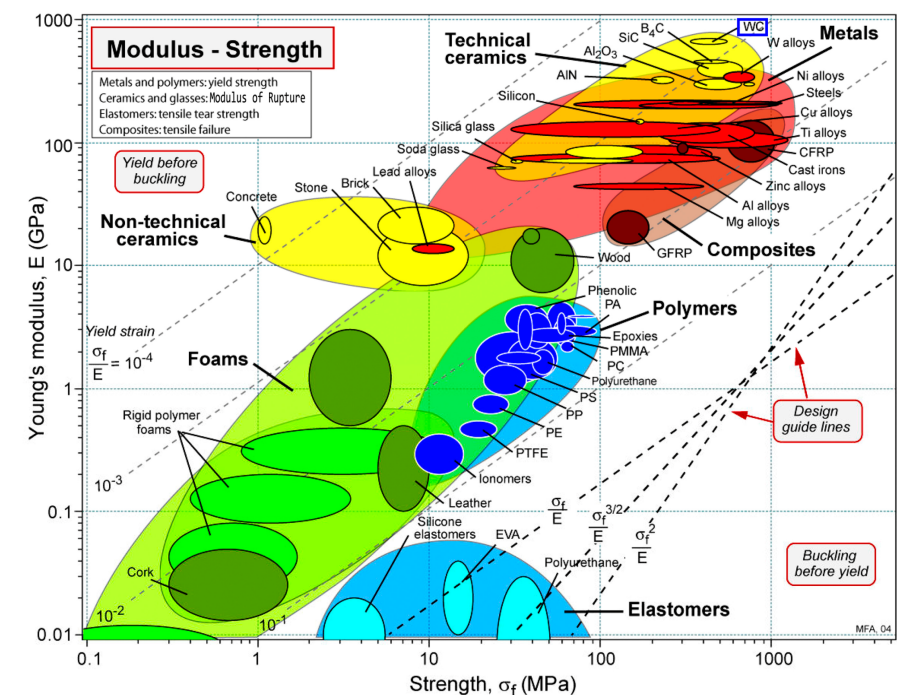
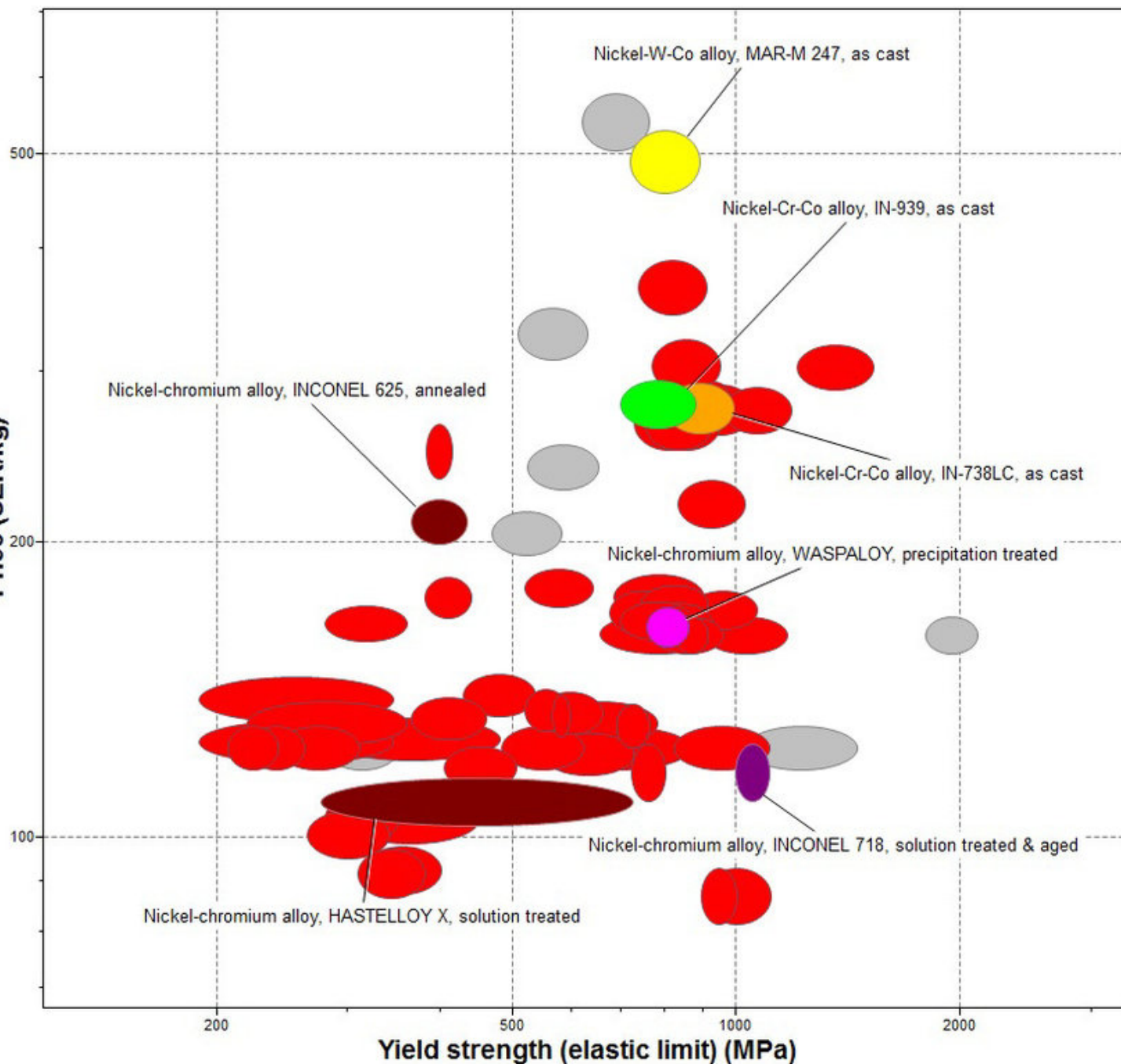


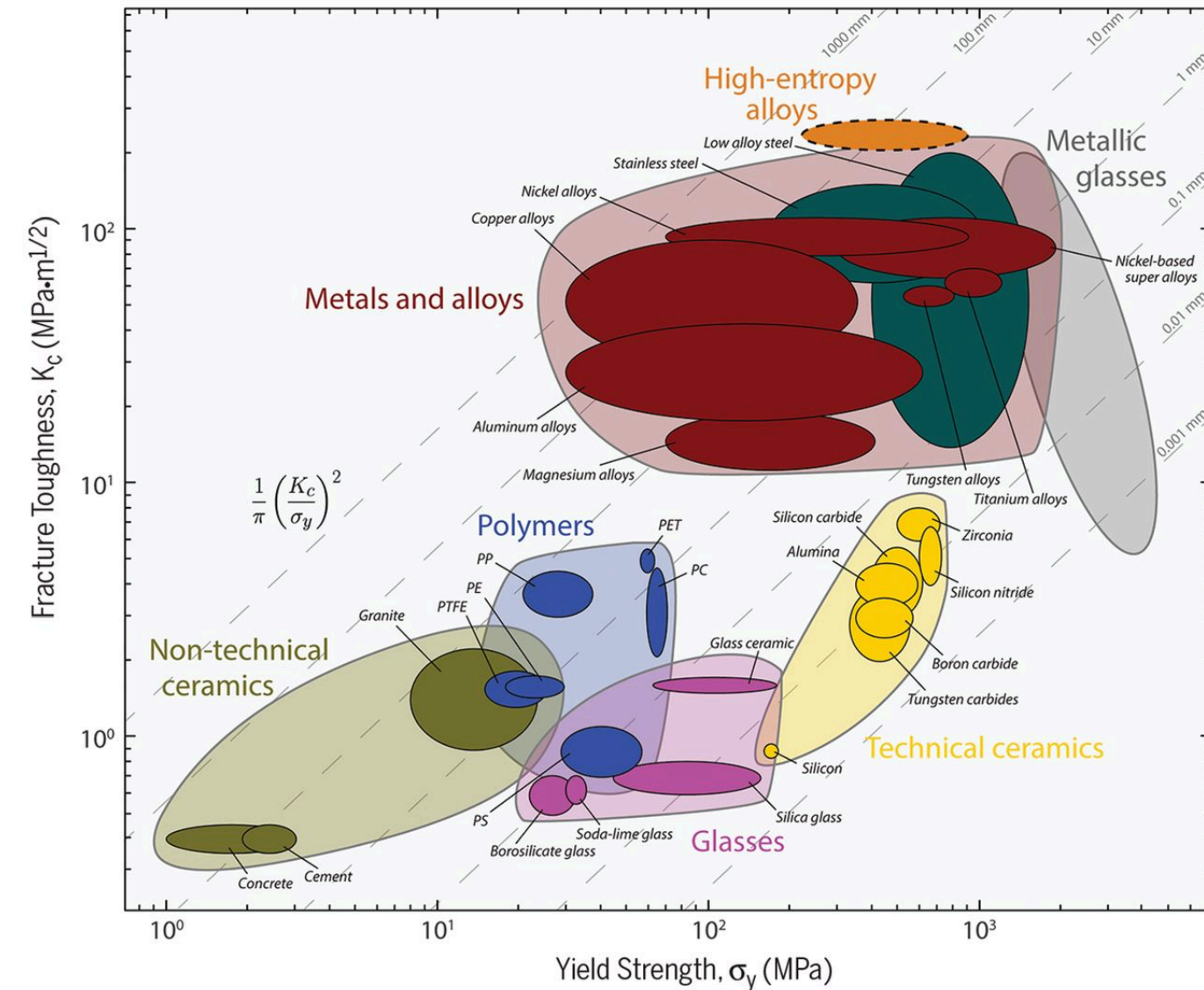
Source: U.S. Geological Survey (USGS)

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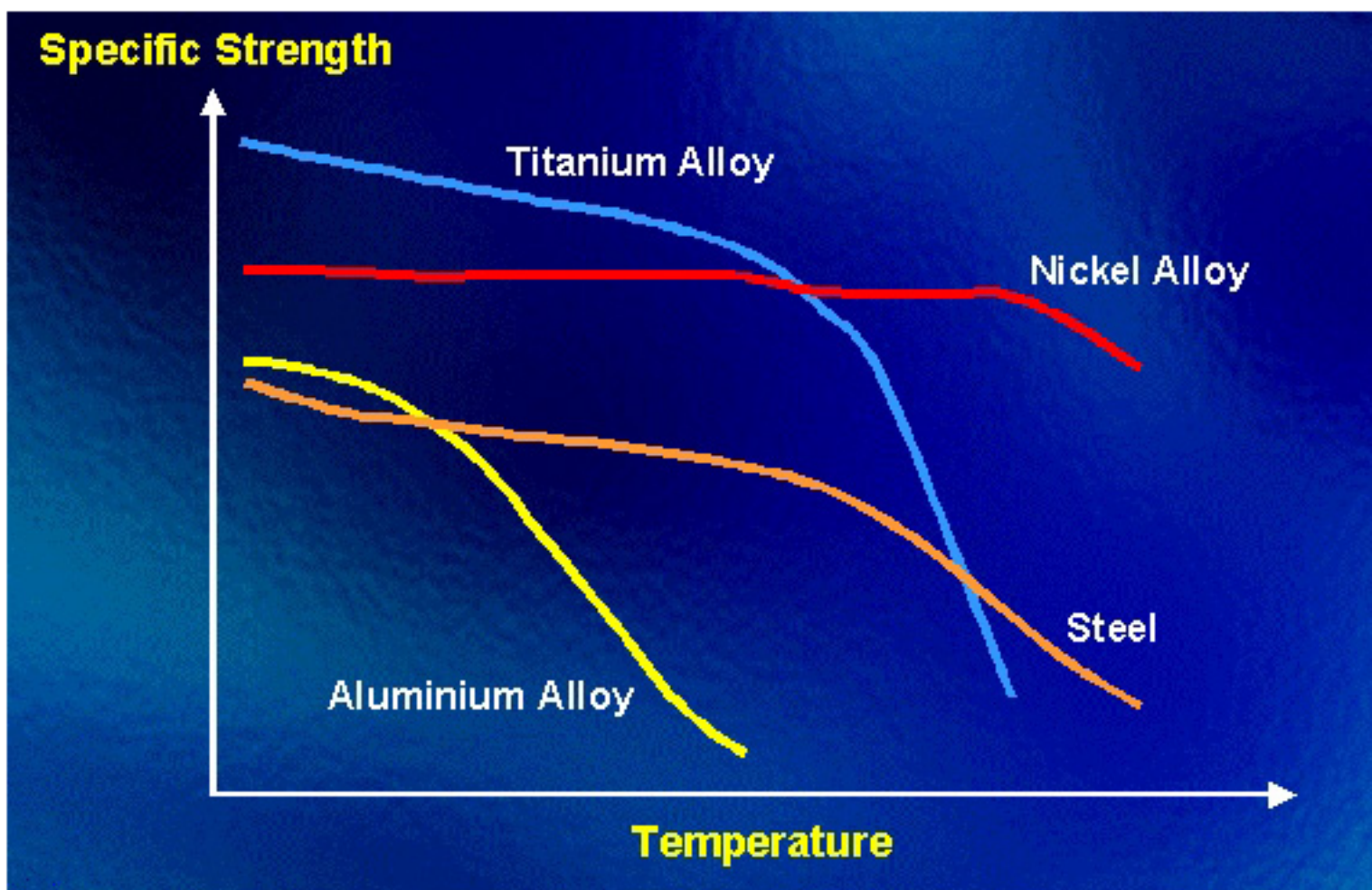


Price (SEK/kg)

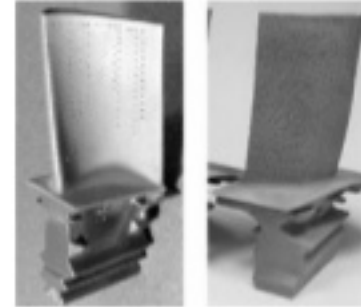
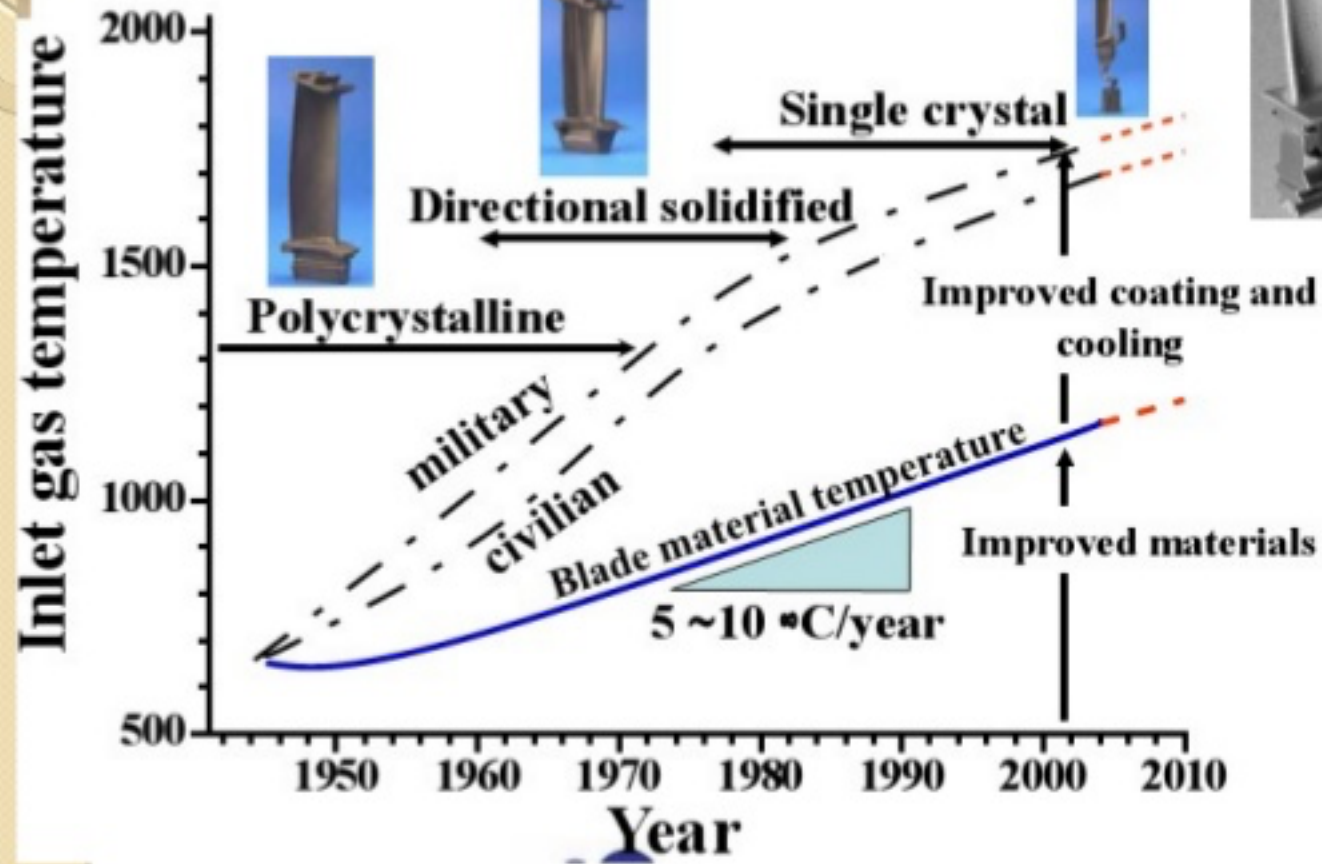


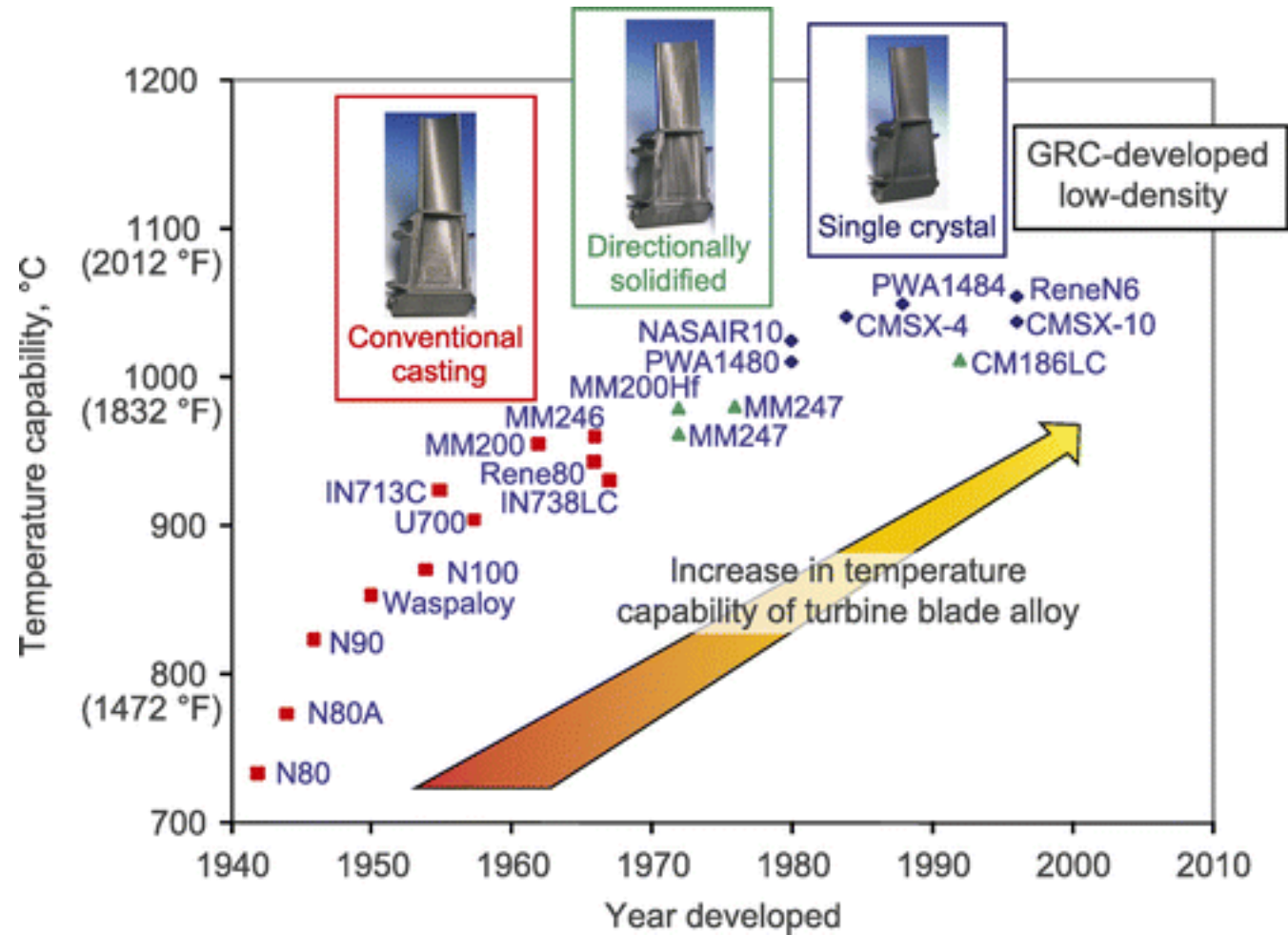


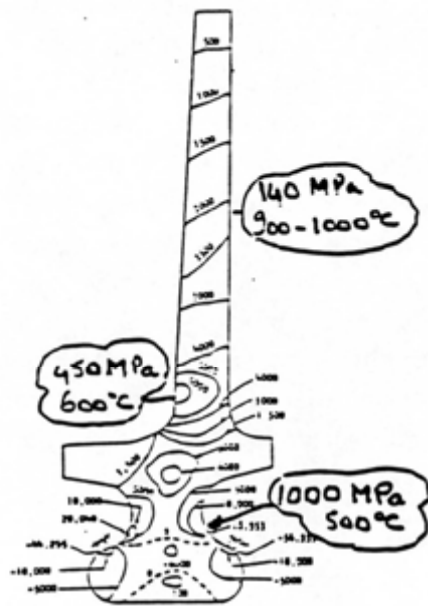
High-entropy alloys (HEAs) are alloys that are formed by mixing equal or relatively large proportions of **(usually) five or more elements**. Elements can be added to iron to improve its properties, thereby creating an iron based alloy, but typically in fairly low proportions, such as the proportions of carbon, manganese, and the like in various steels. The term “high-entropy alloys” was coined because the entropy increase of mixing is substantially higher when there is a larger number of elements in the mix, and their proportions are more nearly equal



NI BASE SUPERALLOY TURBINE BLADE

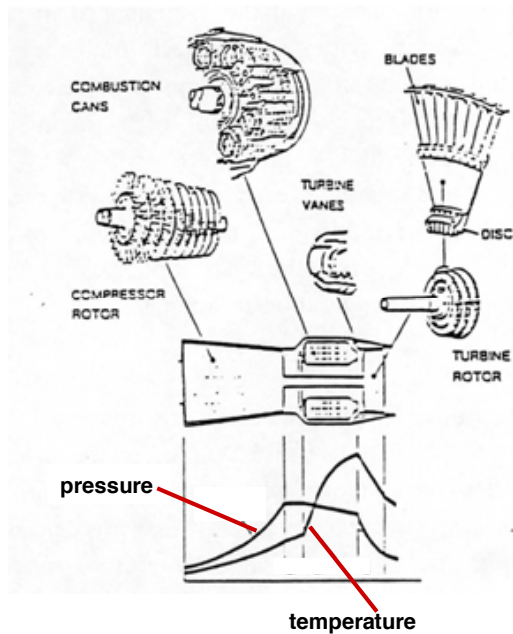






Blade edge,
150 MPa , 650-980°C,
Blade root,
275-550 MPa, 750 °C,

Temperature and stress distribution in a turbine blade.



Principle components of aircraft gas turbine exposed to high loads and temperatures

Aircraft engine

Compressor, Up to 550°C and 550 MPa

Combustion chamber, Weak loaded; gas temp. 1700 °C; under air cooling 1100-1300 °C; main lifetime limiting factors: corrosion and thermal fatigue.

Turbine discs, up to 750 °C, centrifugal force up to 500MPa; a high yield strength and high fatigue strength are required.

Turbine blade, withstand a combination of high stress and high temperature; high yield strength and high creep resistance are required in combination with thermal fatigue resistance and hot corrosion resistance

Further improvements in temperature capability are now being sought, for example for the engines to power the Airbus A380 and the Boeing 787 Dreamliner. Superalloys are being employed increasingly in the land-based turbine systems used for generating electricity, since fuel economy is improved and carbon emissions are reduced by the higher operating conditions so afforded. But new developments in superalloy metallurgy are required for the next generation of ultra-efficient power generation systems. *Over the next 25 years, the world's installed power generation capacity is expected to double*, due to the rapidly growing economies and populations of the developing countries, and because most of the current plant in the developed countries will need to be replaced.

Over the next 25 years, the world's installed power generation capacity is expected to double, due to the rapidly growing economies and populations of the developing countries, and because most of the current plant in the developed countries will need to be replaced. Thus the superalloys have never been more important to the world's prosperity.

$$\eta = \frac{W}{Q_{AB}} = 1 - \frac{T_2 \ln\{V_C / V_D\}}{T_1 \ln\{V_B / V_A\}} = 1 - \frac{T_2}{T_1}$$

In practice, raising T_1 is the more practical option, with the limit for T_1 being the capability of the turbomachinery to withstand the high-temperatures and stresses involved.

What are the desirable characteristics of a high-temperature material?

The first is *an ability to withstand loading at an operating temperature close to its melting point.*

If the operating temperature is denoted T_{oper} and the melting point T_{m} , a criterion based upon the homologous temperature τ defined as $T_{\text{oper}}/T_{\text{m}}$ is sensible; **this should be greater than about 0.6.**

Thus, a superalloy operating at 1000 C in the vicinity of the melting temperature of nickel, 1455 C, working at a τ of $(1000 + 273)/(1455 + 273) \sim 0.75$, is classified as a high-temperature material.

A second characteristic is *a substantial resistance to mechanical degradation over extended periods of time*. For high-temperature applications, a time-dependent, inelastic and irrecoverable deformation known as *creep* must be considered – due to the promotion of thermally activated processes at high τ . Thus, as time increases, creep strain, ϵ_{creep} , is accumulated; for most applications, materials with low rates of creep accumulation, $\dot{\epsilon}_{\text{creep}}$, are desirable

A final characteristic is *tolerance of severe operating environments*. For example, the hot gases generated in a coal-fired electricity-generating turbine are highly corrosive due to the **high sulphur levels** in the charge. Kerosene used for aeroengine fuel tends to be cleaner, but corrosion due to impurities such as **potassium salts** and the ingestion of **sea-water** can occur during operation.

When weight is a consideration, **titanium alloys** are used, but their very poor oxidation resistance restricts their application to temperatures below about 700 C. For some electricity-generating power plant applications which rely upon super-heated steam at 565 C, high-strength creep-resistant **ferritic steels** are preferred on account of their lower cost. However, the latest generation of ultra-supercritical steam-generating coal-fired power stations requires boiler tubing that **can last up to 200 000 hours at 750 C and 100 MPa** – new types of superalloy are being developed for these applications, since ferritic steels cannot be designed to meet these property requirements

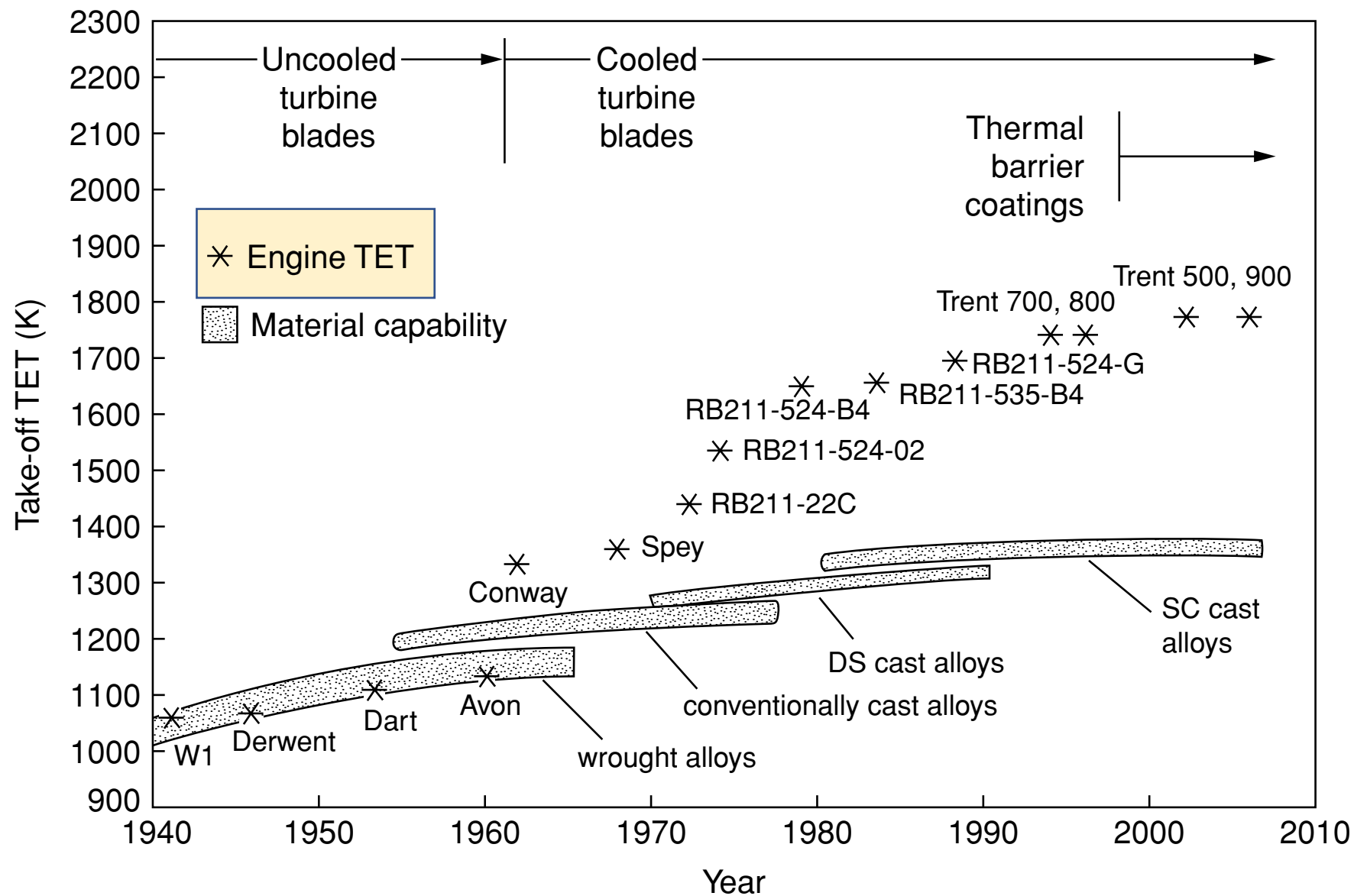
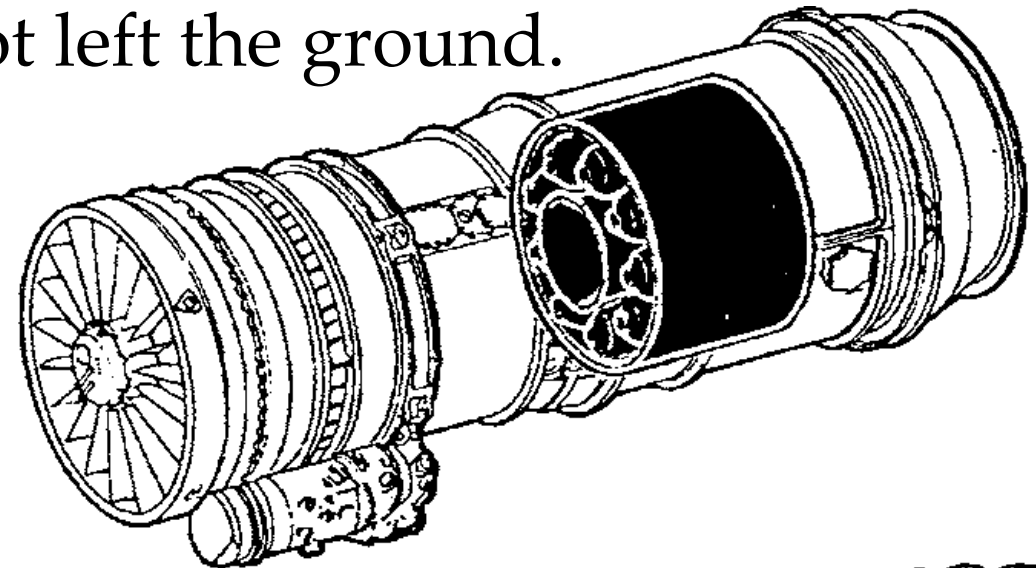
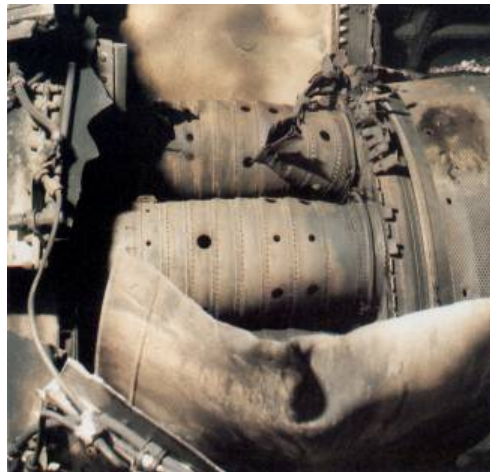


Fig. 1.5. Evolution of the turbine entry temperature (TET) capability of Rolls-Royce's civil aeroengines, from 1940 to the present day. Adapted from ref. [10].

On 22 August 1985, at Manchester Airport in the United Kingdom, a British Airways Boeing 737 carrying 131 passengers and 6 crew suffered an uncontained engine failure during take-off, which was therefore aborted by the crew. Unfortunately, pieces from the port Pratt & Whitney JT8D-15 engine were ejected from the engine – and these punctured a fuel tank causing a catastrophic fire, in which 55 persons on board lost their lives. The aeroplane had not left the ground.



The origin of the failure was a 360° separation of the No 9 combustor can which consisted of 11 pieces of the superalloy Hastelloy X in sheet form, welded together; this allowed hot gases to escape from it and impinge upon the inner surface of the combustion chamber outer case, which ruptured catastrophically during take-off due to localised overheating.

In November 1983, after 3371 cycles, the No 9 can had been inspected and circumferential cracking of 180 mm combined length had been repaired, by fusion welding. Solutioning and weld stress-relief heat treatments had not been applied. It lasted a further 2036 cycles before failure.

Table 1.1. *Evolution of the features of large land-based industrial gas turbines [5]*

Year of introduction	1967	1972	1979	1990 ^a	1998 ^b
Turbine inlet temperature (°C)	900	1010	1120	1260	1425
Pressure ratio	10.5	11	14	14.5	19–23
Exhaust temperature (°C)	427	482	530	582	593
Cooled turbine rows	R1 vane	R1, R2 vane, R1 blade	R1, R2 vane, R1, R2 blade	R1, R2, R3 vane, R1, R2, R3 blade	R1, R2, R3 vane, R1, R2, R3 blade
Power rating, MW	50–60	60–80	70–105	165–240	165–280
Efficiency, simple cycle (%)	29	31	34	36	39
Efficiency, combined cycle (%)	43	46	49	53	58

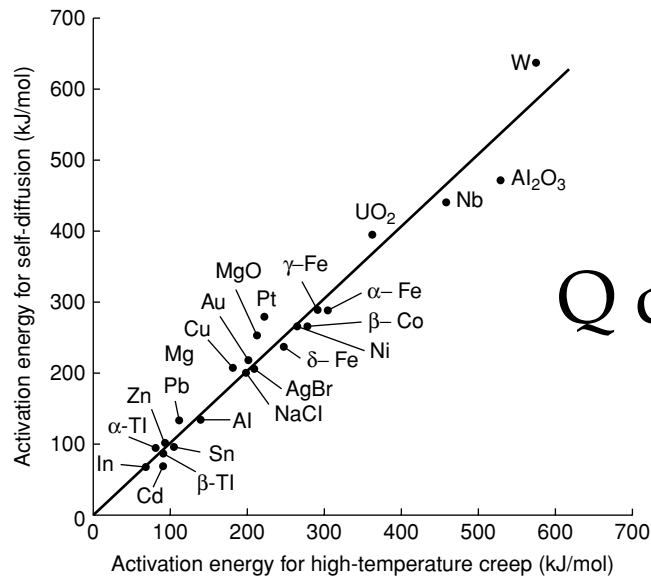
Note: ^a Corresponds approximately to GE 7F, 7A/9F, Westinghouse 501F/701F and Siemens V84.3/94.3 turbines.

^b Corresponds approximately to GE 7H/9H, Westinghouse 501G/701G, Siemens V84.3A/94.3A and ABB GT24/26 turbines.

Larson–Miller approach for the ranking of creep performance

For many materials and under loading conditions which are invariant with time, the creep strain rate, $\dot{\epsilon}_{ss}$, is constant; i.e. it approaches a steady-state. *This implies a balance of creep hardening, for example, due to dislocation multiplication and interaction with obstacles, and creep softening, for example, due to dislocation annihilation and recovery.*

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



Q correlates with the activation energy for self-diffusion,

Fig. 1.15. Correlation between the creep activation energy and the energy for diffusion for several materials. Data taken from ref. [15].

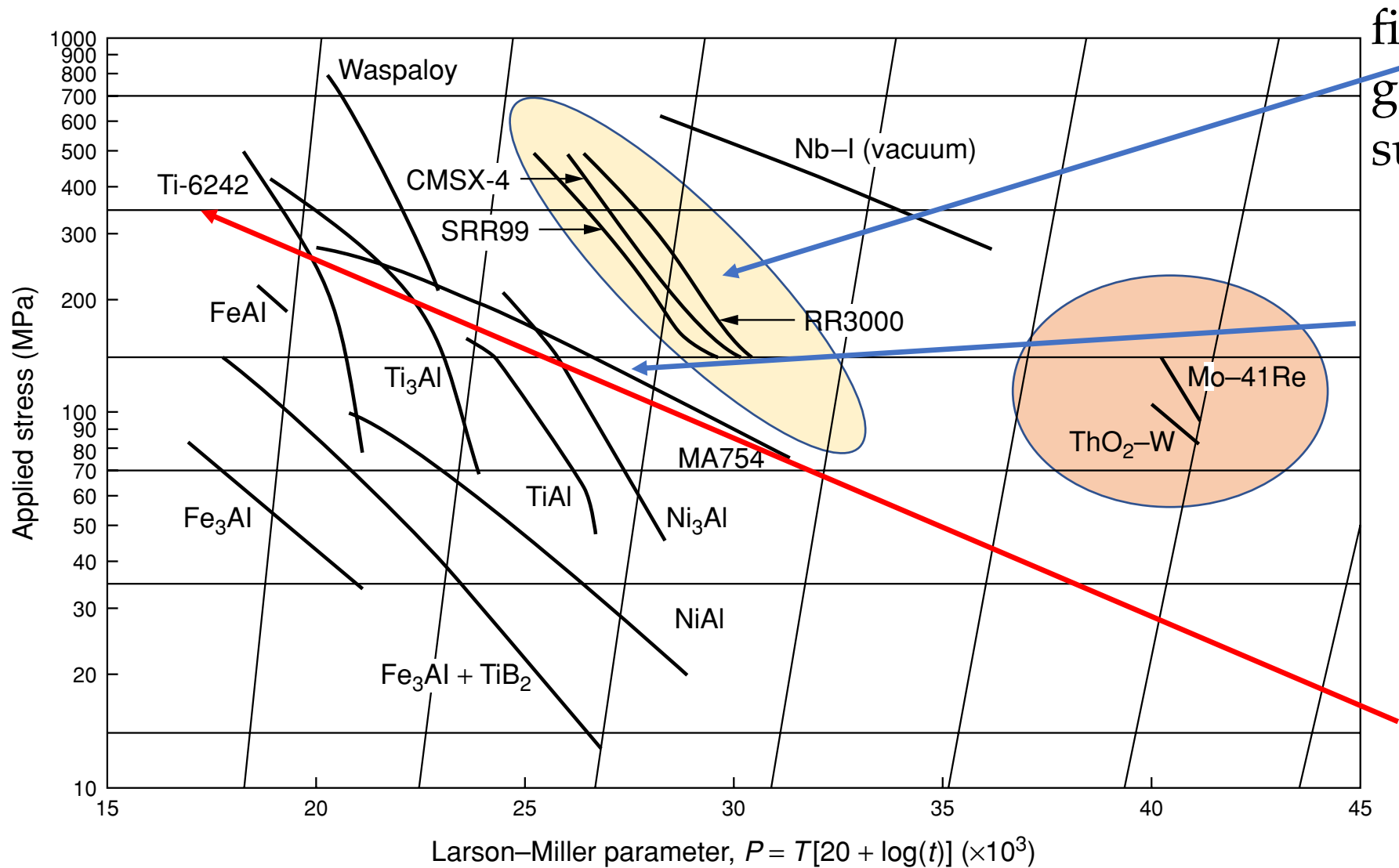
Design against creep usually necessitates a consideration of the *time to rupture*, t_r , which usually satisfies the so-called Monkman–Grant relationship

$$t_r \times \dot{\epsilon}_{ss} = B \quad \text{where } B \text{ is a constant}$$

Then at constant σ one has $\log_{10} t_r - 0.4343 \frac{Q}{RT} = D$ C and D constants

$$T[E + \log_{10} t_r] = P$$

where P is known as the Larson–Miller parameter and E is the Larson–Miller constant; found to vary between 15 and 25 and normally is taken to be 20



first, second and third generation single-crystal superalloys,

oxide-dispersion-strengthened superalloy made by powder metallurgy.

Ti alloy used widely for the compressor sections

it has the highest creep resistance of any of the titanium alloys.

Fig. 1.16. Values of the 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, respectively; the materials which display the best high-temperature performance lie towards the top right of the diagram. Adapted from a graph provided by Dan Miracle.

The **intermetallic** compounds are not bad, particularly if one makes the comparison on a density-corrected basis; it turns out, **however, that their toughness is no match for that displayed by the superalloys.**

titanium alloys behave well, although it has been found that their **oxidation resistance beyond about $\sim 700^{\circ}\text{C}$ is very poor**

Niobium alloys seem attractive, **but their resistance to oxidation is very poor.**

Data indicate that creep rupture lives of the **single-crystal superalloys** have been lengthened from about 250 h at 850 C/500 MPa for a typical first-generation alloy, to about 2500 h for the third-generation alloy. Under more demanding conditions, for example, 1050C/150MPa, rupture life has improved four fold from 250 h to 1000 h. These improvements were won in a period of approximately 15 years between 1980 and 1995, primarily as a consequence of a better appreciation of the physical factors which confer high-temperature strength in these materials.

The first-generation single-crystal superalloys, contain appreciable quantities of the γ' hardening elements Al, Ti and Ta; the grain-boundary-strengthening elements C and B, which were added routinely to the earlier directionally solidified alloys, are no longer present.

Second-generation alloys, are characterised by a 3 wt% concentration of Re, which is increased to about 6 wt% for the third-generation alloys.

Generally speaking, the modern alloys are characterised by significantly lower concentrations of Cr and higher concentrations of Al and Re.

Concentrations of Ti and Mo are now at very modest levels. Since 2000 the fourth-generation single-crystal superalloys, are characterised by additions of ruthenium.

Nickel as a high-temperature material: justification

Under conditions of high-temperature deformation, the creep shear strain rate, $\dot{\gamma}$, of a pure metal such as nickel to be proportional to the volume diffusivity, of activation energy Q_v and pre-exponential term $D_{0,v}$.

$$\dot{\gamma} \propto D_{0,v} \exp \left\{ -\frac{Q_v}{RT} \right\}$$

In order to help in the comparison of different material classes, it is helpful to normalise T by the melting temperature, T_m , and $\dot{\gamma}$ by $DT_m / \Omega^{2/3}$, where DT_m is the diffusivity at the melting temperature and Ω is

the atomic volume

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