What does this analysis reveal? If one assumes for the moment that the combination $Q_v/(RT_m)$ is approximately the same for the different materials under consideration for this application, then for the best high-temperature performance (implying a small value of γ) it is necessary to work at a low homologous temperature T/T_m ; this emphasises the importance of materials which melt at high temperatures.

Alternatively, if one accepts the need to work at a particular T/T_m , for example, $T = 0.8T_m$, then crystal classes which display the *maximum* $Q_v/(RT)$ and *minimum* $DT_m/\Omega^{2/3}$ are the ones which will display the best properties.



Fig. 1.19. Variation of the melting temperatures of the elements with atomic number.

IIIB	IVB	VB	VIB	VIIB	4	– VIIIB –		IB	IIB
21	22	23	24	25	26	27	28	29	30
Sc	Ti	v	Cr	Mn	Fe	Со	Ni	Cu	Zn
44.956	47.90	50.942	51.996	54.9380	55.847	58.9332	58.71	63.54	65.37
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd
88.905	91.22	92.906	95.94	[99]	101.07	102.905	106.4	107.870	112.40
米 57	72	73	74	75	76	77	78	79	80
La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg 🗸
138.91	178.49	180.948	183.85	186.2	,190.2	192.2	195.09	196.967	200.59

the face-centered cubic (FCC) metals lie towards the far east of the period (groups VIII and 1B), hexagonally close-packed (HCP) metals are at the centre (group VIIB) and the bodycentered cubic (BCC) metals are at the far west (groups VB, VIB). Clearly, if one prefers for this application an FCC metal on the grounds that it will be ductile and tough, then the number of available metals is limited

BCC

In fact, it turns out that if one widens the search to include materials of different crystal classes, considering oxides and carbide ceramic systems for example, then there is quite a spread in the normalised activation energies, $Q_v/(RT_m)$, and the melting point diffusivity, DT_m .

The FCC metals display very high and low values, respectively, and these are considerably better than for the BCC and the HCP metals, at $Q_v/(RT_m) = 18.4$ (compare 17.3 for HCP metals and 17.8 for the BCC metals) and $DT_m = 5 \times 10^{-13} \text{ m}^2/\text{s}$ (compare $\sim 2 \times 10^{-12}$ m²/s for HCP and $10^{-12} - 10^{-11}$ m²/s for the BCC transition metals). Other observations support these conclusions. For example, the BCC \rightarrow FCC and BCC \rightarrow HCP transformations in Fe and Ti, respectively, cause a 100-fold reduction in the measured diffusivity.

First, nickel displays the FCC crystal structure and is thus both *tough* **and** *ductile,* due to a considerable cohesive energy arising from the bonding provided by the outer d electrons.

Nickel is stable in the FCC form from room temperature to its melting point, so that there are no phase transformations to cause expansions and contractions which might complicate its use for high-temperature components. Other metals in the transition metal series which display this crystal structure, i.e. the platinum group metals (PGMs), are dense and very expensive.

Second, low rates of thermally activated creep require low rates of diffusion – as suggested by the correlation between the activation energies for self-diffusion and creep in the pure metals. **Diffusion rates for FCC metals such as Ni are low**; hence, considerable microstructural stability is imparted at elevated temperatures.

Finally, consider other elements which possess different crystal structures. Of the HCP metals, only **Co** displays an acceptable density and cost; **Re and Ru** are PGMs and are therefore expensive; **Os** has an oxide which is poisonous; and **Tc** is radioactive.

Co-based superalloys are, in fact, used for high-temperature applications; however, they tend to be more expensive than the nickel-based superalloys. The BCC metals such as Cr are prone to brittleness, and there is a ductile/brittle transition which means that the toughness decreases significantly with decreasing temperature.



the number of alloying elements is often greater than ten and consequently, if judged in this way, the superalloys are amongst the most complex of materials engineered by man.

Fig. 2.2. Categories of elements important to the constitution of the nickel-based superalloys, and their relative positions in the periodic table. Adapted from ref. [1].

Most of the alloying elements are taken from the **d** block of transition metals. Unsurprisingly, the behaviour of each alloying element and its influence on the phase stability depends strongly upon its position within the periodic table A first class of elements includes Ni, Co, Fe, Cr, Ru, Mo, Re and W; these prefer to partition to the austenitic γ and thereby stabilise it. These elements have atomic radii not very different from that of nickel. A second group of elements, Al, Ti, Nb and Ta, have greater atomic radii and these promote the formation of ordered phases such as the compound Ni₃(Al, Ta, Ti), known as γ' . **B**, **C** and **Zr** constitute a third class that tend to segregate to the grain boundaries of the γ phase, on account of their atomic sizes, which are very different from that of Ni. Carbide and boride phases can also be promoted. Cr, Mo, W, Nb, Ta and Ti are particularly strong carbide formers; Cr and Mo promote the formation of borides

The microstructure of a typical superalloy consists therefore of different phases:

The gamma phase, denoted γ . This exhibits the FCC structure, and in nearly all cases it forms a continuous, matrix phase in which the other phases reside. It contains significant concentrations of elements such as Co, Cr, Mo, Ru and Re, where these are present, since these prefer to reside in this phase.

The gamma prime precipitate, denoted γ' . This forms as a precipitate phase, which is often **coherent** with the γ -matrix, and rich in elements such as Al, Ti and Ta. In nickel–iron superalloys and those rich in Nb, a related ordered phase, γ'' , is preferred instead of γ'

Carbides and borides.C, often present at concentrations up to 0.2wt%, combines with reactive elements such as Ti, Ta and Hf to form MC carbides. During processing or service, these can decompose to other species, such as $M_{23}C_6$ and M_6C , which prefer to reside on the γ -grain boundaries, and which are rich in Cr, Mo and W. B can combine with elements such as Cr or Mo to form borides which reside on the γ -grain boundaries

Other phases can be found in certain superalloys, particularly in the service-aged condition, for example, the topologically close-packed (TCP) phases μ , σ , Laves, etc. *However, the compositions of the superalloys are chosen to avoid, rather than to promote, the formation of these compounds*.





Topologically close pack (TCP) phases, also known as **Frank-Kasper (FK) phases**, are one of the largest groups of intermetallic compounds, known for their complex crystallographic structure and physical properties.

In each of the three classes of Laves phase, if the two types of atoms were perfect spheres with a size ratio of $\sqrt{3}/2 = 1,225$, the structure would be topologically **tetrahedrally close-packed**. At this size ratio, the structure has an overall packing volume density of 0.710. Compounds found in Laves phases typically have an atomic size ratio between 1.05 and 1.67. Analogues of Laves phases can be formed by the self-assembly of a colloidal dispersion of two sizes of sphere

The FCC phase

$$\Delta G_{\text{Ni}}^{\text{BCC} \to \text{FCC}} = G_{\text{Ni}}^{\text{FCC}} - G_{\text{Ni}}^{\text{BCC}} = 750 \times (-10) = -7500 \,\text{J/mo}$$



Fig. 2.4. Variation of the liquid and BCC lattice stabilities of Ni, with respect to the FCC form.



Fig. 2.5. Estimates of the enthalpies and entropies of transformation necessary to convert one mole of transition metal from the (a) FCC to HCP and (b) BCC to HCP forms [5]. The symbols α , ζ and β refer to the FCC, HCP and BCC phases, respectively. In (a), the FCC form is preferred for positive and negative values of the enthalpy and entropy changes, respectively; in (b), the BCC form is preferred for positive and negative values of the enthalpy and entropy changes, respectively. Estimates for the magnetic elements Mn and Fe cannot be made with this simplistic method.

The gamma prime phase

The binary Ni–Al system exhibits a number of solid phases other than the FCC one, as the phase diagram confirms. These possess the following characteristics:(i) a significant degree of directional, covalent bonding such that precise stoichiometric relationships exist between the number of Ni and Al atoms in each unit cell, and

(ii) crystal structures in which Ni–Al rather than Ni–Ni or Al–Al bonds are preferred. Thus a strong degree of chemical order is displayed, and consequently these phases are therefore referred to as *ordered* to distinguish them from the *disordered* solutions based on the FCC or BCC crystal structures.
(iii) The chemical formulae are Ni₃Al, NiAl, Ni₂Al₃, NiAl₃ and Ni₂Al₉.



the enthalpies of formation at 25 C are plotted against the enthalpy of mixing of the FCC phase

The data in Figure indicate that the ordering energy for Ni₃Al with respect to the FCC phase is about 3 kJ/mol

Fig. 2.10. Variation of the enthalpy of formation, $\Delta H_{\rm f}$, for the various intermetallic compounds in the binary Ni–Al system [8]. The broken line corresponds to the enthalpy of mixing of the disordered FCC phase, with respect to the pure Ni and Al constituents.

the gamma prime (γ') phase, Ni₃Al, displays the primitive cubic, L1₂, crystal structure, with Al atoms at the cube corners and Ni atoms at the centres of the faces. It is notable that each Ni atom has four Al and eight Ni as nearest neighbours, but that each Al atom is co-ordinated by twelve Ni atoms – thus Ni and Al have distinct site occupances.





Elements such as **Co and Pt** promote γ' phase fields which are parallel to the Ni–X axis on the ternary section, implying a Al fraction constant and providing confirmation that substitution for Ni on the first of the two sublattices is preferred. Ni Elements such as **Ti and Ta** promote fields

Fig. 2.12. Superimposed ternary phase diagrams Ni–Al–X [9], illustrating the great effect of X on the extent of the γ' phase field. parallel to the Al–X axis, and thus they

replace Al on the second sublattice

The behaviour of the element X in this regard depends rather strongly on its size relative to Ni and Al. The lattice parameter, *a*, of γ' at room temperature is **0.3570** nm, which is equivalent to the Al–Al distance; this is only ~ 1.5% larger than the lattice parameter of pure Ni, which is 0.3517 nm. The Ni–Al distance is $a/\sqrt{2}$, or 0.2524 nm. Thus substitution for Al is favoured by large elements such as Ta and Ti, whereas smaller atoms such as Co substitute for Ni.

Does the γ' remain ordered until the melting temperature is reached? For many years this question remained unanswered, **but it is now known that the ordering temperature of Ni₃Al is roughly equivalent to its melting temperature of about 1375°C**, although it does depend strongly upon the degree of stoichiometry and the concentrations of any impurities (es. Fe)

Binary Ni–Al alloys of composition consistent with a two-phase γ/γ' microstructure exhibit γ' precipitates which are **often cuboidal in form.**

The lattice parameters of the disordered γ and ordered γ' phases are very similar,

The properties of the superalloys are found to depend critically on the coherency of

the γ / γ' interface. This is favoured by small values of the lattice misfit, δ , defined

according to
$$\delta = 2 \times \left[\frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma'} + a_{\gamma}} \right]$$

the lattice parameter of the γ phase shows the greater sensitivity to solute additions.

The lattice misfit, δ , then depends on two factors:

(i) the partitioning of solutes i between γ and γ ' and

(ii) the corresponding influence of the solutes i on the lattice parameters consistent with Vegard's law.



$$a_{{
m A}_{(1-x)}{
m B}_x} = (1-x) a_{
m A} + x a_{
m B}$$

Variation of the Vegard coefficients with position in the transition metal series: (a) for the disordered FCC phase, γ and (b) for the ordered Ni₃Al phase, γ' .

В



It was shown that the morphological development occurs in the sequence spheres, cubes, arrays of cubes and eventually solid-state dendrites as coarsening is promoted by ageing

the γ' precipitate sizes at which significant departure from the spherical shape was observed were found in turn to be 0.3-0.7µm. This suggests that when the magnitude of the misfit is small, the γ' particles must grow to a larger size before the cuboidal form is found.



The gamma double prime phase

In **Ni-Fe superalloys**, which contain quantities of **Nb**, the primary strengthening precipitate is not γ' but instead a **body-centred tetragonal** (BCT) ordered compound; with a composition which can be represented approximately by **Ni**₃**Nb**.



Nickel–iron alloys which are strengthened by γ'' are susceptible to the formation of an orthorhombic δ phase in the overaged condition. This is invariably incoherent with γ , and therefore does not confer strength even when present in significant quantities. It forms in the temperature range 650 to 980C, but the characteristics of its formation depend strongly upon temperature. Below 700 C, nucleation of δ is observed at γ -grain boundaries and growth occurs at the expense of γ'' . In the range 700 C to 885 C, formation of δ is accompanied by rapid coarsening of γ'' ; beyond the solvus temperature of 885 C γ'' is no longer stable. At temperatures between 840 C and 950 C, the plates of δ form rapidly in times less than 24 h. The δ solvus temperature is ~ 1000 C.

TCP phases

Additions of some refractory elements, such as **Re and W**, have played a key role in improving the high temperature properties of this class of material. **TCP phases are** principally composed of the elements Ni, Cr, Co, Mo, W, Re, and unfortunately this list contains the elements which are most effective at solution strengthening. Thus the formation of TCP phases depletes the surrounding matrix of refractory solidsolution strengthening elements, and reduces their solid strengthening effect. In addition, the precipitation of TCP phases during prolonged exposure at high temperatures is frequently associated with the formation of voids which may potentially act as initiation sites for fracture. As these brittle intermetallic TCP phases precipitate, they can initiate or accelerate crack propagation, leading to toughness reduction.

TCP phases

Excessive quantities of **Cr**, **Mo**, **W** and **Re** promote the precipitation of intermetallic phases which are rich in these elements



The resulting phases have a number of distinct characteristics:

(i) a high and uniform packing density of atoms,

(ii) a degree of non-metallic, directional bonding and

(iii) complex crystal structures,

This last fact gives rise to the name topologically close-packed, or TCP, phases.

TCP could also be translated as tetrahedrally closed packed, i.e. without octahedral interstices. 3D-periodic structures can only be realised by large unit cells and these do not contain "nice" glide planes. Moreover, the Burgers vectors are longer.

Generally speaking, the TCP phases have chemical formulae AxBy, where A and B are transition metals, (A = Mn, Cr, W, Mo, Tc B = Re, Co, B.

The μ phase is based on the ideal stoichiometry A_6B_7 and has a rhombohedral cell containing 13 atoms; examples include W_6Co_7 and Mo_6Co_7 .

The σ phase is based upon the stoichiometry A_2B and has a tetragonal cell containing 30 atoms; examples include Cr_2Ru , $Cr_{61}Co_{39}$ and $Re_{67}Mo_{33}$.

The **P** phase, for example, $Cr_{18}Mo_{42}Ni_{40}$ is primitive orthorhombic, containing 56 atoms per cell.

the **R** phase, for example, $Fe_{52}Mn_{16}Mo_{32}$, has a rhombohedral cell containing 53 atoms.

The addition of the platinum group metal ruthenium (Ru) suppress the formation of TCP phases improving the high-temperature creep resistance

Carbide and boride phases

MC, M₆C, M₂₃C₆, M₇C₃ and M₃B₂,

where M stands for a metal atom such as Cr, Mo, Ti, Ta or Hf.

In many superalloys the MC carbide, which is usually rich in **Ti**, **Ta** and **Hf** since these are strong carbide formers, precipitates at high temperatures from the liquid phase. Consequently, the carbide is often found in interdendritic regions and no distinct orientation relationship with the matrix is displayed.

Carbides such as M23C6 form at lower temperatures – around 750 C – during protracted periods of service exposure, particularly in alloys which are rich in Cr. Their formation has been attributed to the breakdown of the MC carbides, via reactions of the type $MC + \gamma \rightarrow M_{23}C_6 + \gamma'$

The role of carbides and borides has proved controversial, but it is now accepted that the high-temperature creep properties of the superalloys are improved in many circumstances if carbon and boron are present. Thus, C and B are often referred to as grain-boundary strengtheners.

Temperature dependence of strengthening in the superalloys

The nickel alloys exhibit a remarkable characteristic: the yield stress, does not decrease strongly with increasing temperature, as is the case for most other alloy systems. In fact, for many superalloys the yield stress <u>increases</u> with increasing temperature, typically until temperatures of about 800 C are reached.



Fig. 2.52. Data for the yield stress of alloys in the binary Ni–Al system as a function of composition and temperature. Adapted from ref. [53].



Fig. 2.53. Variation with temperature of the yield stress of the Mar-M200 alloy in single-crystal form, and a monolithic Ni₃Al alloy of composition equivalent to the γ' particles in it. In both cases, testing was along (100). Adapted from ref. [54].