

FS 2024/25

# MSE-422 – Advanced Metallurgy

## 8-Structural Intermetallic Alloys

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# Criteria for the formation of solid solutions

## The Hume-Rothery rules

### ■ H-R-rules for substitutional solid solutions

- 1) The atomic radius of the solute and solvent atoms must differ by no more than 15%
- 2) The crystal structures of solute and solvent must be similar
- 3) Complete solubility occurs when the solvent and solute have the same valency
- 4) The solute and solvent should have similar electronegativity

### ■ H-R-rules for interstitial solid solutions

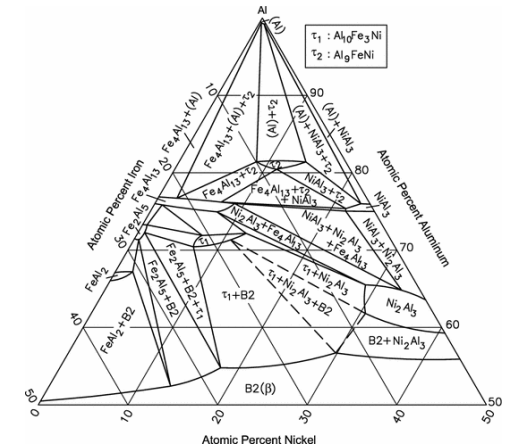
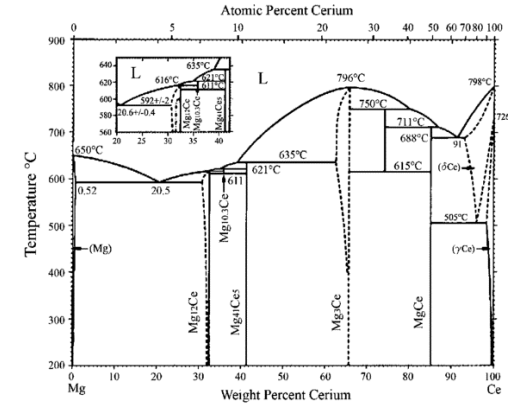
- 1) Solute atoms should have a smaller radius than 59% of the radius of solvent atoms
- 2) The solute and solvent should have similar electronegativity
- 3) Valency factor: two elements should have the same valence.

1																		2	
1A																		8A	
1																		2	
H 1.00794 HYDROGEN																		He 4.002602 HELIUM	
2																		18	
2A																		18	
3																		10	
Li 6.941 LITHIUM																		Ne 20.1797 NEON	
4																		10	
Be 9.012182 BERYLLIUM																		Ne 20.1797 NEON	
		METALS																	
		METALLOIDS																	
		NONMETALS																	
11																		18	
Na 22.98976928 SODIUM																		Ar 39.948 ARGON	
12																		18	
Mg 24.304 MAGNESIUM																		Ar 39.948 ARGON	
13																		18	
Al 26.9815385 ALUMINUM																		Ar 39.948 ARGON	
14																		18	
Si 28.08558 SILICON																		Ar 39.948 ARGON	
15																		18	
P 30.973761508 PHOSPHORUS																		Ar 39.948 ARGON	
16																		18	
S 32.06 SULFUR																		Ar 39.948 ARGON	
17																		18	
Cl 35.453 CHLORINE																		Ar 39.948 ARGON	
18																		18	
Ar 39.948 ARGON																		Ar 39.948 ARGON	
19																		18	
K 39.0983 POTASSIUM																		Ar 39.948 ARGON	
20																		18	
Ca 40.078 CALCIUM																		Ar 39.948 ARGON	
21																		18	
Sc 44.955912 SCANDIUM																		Ar 39.948 ARGON	
22																		18	
Ti 47.88 TITANIUM																		Ar 39.948 ARGON	
23																		18	
V 50.9415 VANADIUM																		Ar 39.948 ARGON	
24																		18	
Cr 51.9961 CHROMIUM																		Ar 39.948 ARGON	
25																		18	
Mn 54.938044 MANGANESE																		Ar 39.948 ARGON	
26																		18	
Fe 55.845 IRON																		Ar 39.948 ARGON	
27																		18	
Co 58.933194 COBALT																		Ar 39.948 ARGON	
28																		18	
Ni 58.6934 NICKEL																		Ar 39.948 ARGON	
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Cu 63.546 COPPER																		Ar 39.948 ARGON	
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Zn 65.38 ZINC																		Ar 39.948 ARGON	
31																		18	
Ga 69.723 GALLIUM																		Ar 39.948 ARGON	
32																		18	
Ge 72.64 GERMANIUM																		Ar 39.948 ARGON	
33																		18	
As 74.921595 ARSENIC																		Ar 39.948 ARGON	
34																		18	
Se 78.96 SELENIUM																		Ar 39.948 ARGON	
35																		18	
Br 79.904 BROMINE																		Ar 39.948 ARGON	
36																		18	
Kr 83.80 KRYPTON																		Ar 39.948 ARGON	
37																		18	
Rb 85.4678 RUBIDIUM																		Ar 39.948 ARGON	
38																		18	
Sr 87.62 STRONTIUM																		Ar 39.948 ARGON	
39																		18	
Y 88.90584 YTTRIUM																		Ar 39.948 ARGON	
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Zr 91.224 ZIRCONIUM																		Ar 39.948 ARGON	
41																		18	
Nb 92.90638 NIIOBIUM																		Ar 39.948 ARGON	
42																		18	
Mo 95.94 MOLYBDENUM																		Ar 39.948 ARGON	
43																		18	
Tc 98.90625 TECHNETIUM																		Ar 39.948 ARGON	
44																		18	
Ru 101.07 RHODIUM																		Ar 39.948 ARGON	
45																		18	
Rh 102.90550 RHODIUM																		Ar 39.948 ARGON	
46																		18	
Pd 106.42 PALLADIUM																		Ar 39.948 ARGON	
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Ag 107.8682 SILVER																		Ar 39.948 ARGON	
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Cd 112.411 CADMIUM																		Ar 39.948 ARGON	
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In 114.818 INDIUM																		Ar 39.948 ARGON	
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Sn 118.710 TIN																		Ar 39.948 ARGON	
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Sb 121.757 ANTIMONY																		Ar 39.948 ARGON	
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Te 127.60 TELURUM																		Ar 39.948 ARGON	
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I 126.905 IODINE																		Ar 39.948 ARGON	
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Xe 131.29 XEON																		Ar 39.948 ARGON	
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Cs 132.90545 CESIUM																		Ar 39.948 ARGON	
56																		18	
Ba 137.327 BARIUM																		Ar 39.948 ARGON	
57-71																		18	
La-Lu LANTHANIDES																		Ar 39.948 ARGON	
72																		18	
Hf 178.49 HAFNIUM																		Ar 39.948 ARGON	
73																		18	
Ta 180.94788 TANTALUM																		Ar 39.948 ARGON	
74																		18	
W 183.84 WOLYBIUM																		Ar 39.948 ARGON	
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Re 186.207 RHENIUM																		Ar 39.948 ARGON	
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Os 190.23 OSMIUM																		Ar 39.948 ARGON	
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Ir 192.222 IRIDIUM																		Ar 39.948 ARGON	
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Pt 195.084 PLATINUM																		Ar 39.948 ARGON	
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Au 196.966569 GOLD																		Ar 39.948 ARGON	
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Hg 200.59 MERCURY																		Ar 39.948 ARGON	
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Tl 204.3833 THALLIUM																		Ar 39.948 ARGON	
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Pb 207.2 LEAD																		Ar 39.948 ARGON	
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Bi 208.9804 BISMUTH																		Ar 39.948 ARGON	
84																		18	
Po 209 POLONIUM																		Ar 39.948 ARGON	
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At 210 ASTATINE																		Ar 39.948 ARGON	
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Rn 222 RADON																		Ar 39.948 ARGON	
87																		18	
Fr 223 FRANCIUM																		Ar 39.948 ARGON	
88																		18	
Ra 226 RADIUM																		Ar 39.948 ARGON	
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Rf 261 RUTHERFORDIUM																		Ar 39.948 ARGON	
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Sg 266 SEABORGIUM																		Ar 39.948 ARGON	
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Bh 264 BOHRIUM																		Ar 39.948 ARGON	
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Hs 277 HASSIUM																		Ar 39.948 ARGON	
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Mt 268 MEITNERIUM																		Ar 39.948 ARGON	
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Ds 271 DARMSTADTIUM																		Ar 39.948 ARGON	
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Rg 272 ROENTGENIUM																		Ar 39.948 ARGON	
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Cn 277 COGNACIUM																		Ar 39.948 ARGON	
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Uuq 289 UNUNQUADIUM																		Ar 39.948 ARGON	
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Nd 144.242 NEODYMIUM																		Ar 39.948 ARGON	
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Es 252.08328 EINSTEINIUM																		Ar 39.948 ARGON	
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101																		18	
Md 258.10358 MENDELEVIUM																		Ar 39.948 ARGON	
102																		18	
No 259.10358 NOBELIUM																		Ar 39.948 ARGON	
103																		18	
Lr 262.10358 LAWRENCIUM																		Ar 39.948 ARGON	

→ If these rules are not fulfilled, then intermetallic compounds will form

# Some basic facts about intermetallics

- Intermetallic compound (IMC), also called an intermetallic, or (ordered) intermetallic alloy
- Metallic alloys with ordered lattices formed between two or more metallic elements.
- Over 5000 binary IMCs exist, grouped by characteristics; most are not suitable for structural or functional applications.
- Formed by bonding between two or more metals in specific stoichiometric ratios (e.g.,  $A_xB_y$ ,  $A_xB_yC_z$ ).
- IMC bonds are a mix of metallic, covalent, and ionic character.



# Some basic facts about intermetallics

- Formation of intermetallics is to a large extent a matter of electronegativity, but size ratios do also play a role
- The type of IMC that is formed depends on the position of the elements involved in the PSE
  - The **electropositive metals (typically with large radii)**, A1
  - The **transition metals (with variably filled d-shells)** A2
  - the **elements of early s and p-shell filling** B1
  - the **elements of late s and p-shell filling** (mostly with covalent component), B2,
  - the **Lanthanides (f-shell filling)**, C1.

The periodic table is color-coded to show different regions relevant to intermetallic formation:

- A1 (Pink):** Group 1 (Li, Na, K, Rb, Cs, Fr) and Group 2 (Be, Mg, Ca, Sr, Ba, Ra).
- A2 (Blue):** Transition metals (Groups 3-10).
- B1 (Green):** Groups 11-12 (Cu, Ag, Au, Zn, Cd, Hg, Ni, Pd, Pt, Rh, Ir, Os, Ru, Rh, Pd, Ag, Cu, Zn, Cd, Hg).
- B2 (Purple):** Groups 13-18 (B, C, Si, Ge, Sn, Pb, N, P, As, Sb, Bi, O, S, Se, Te, Po, F, Cl, Br, I, At, Ne, Ar, Kr, Xe, Rn).
- C1 (Yellow):** Lanthanide series (La-Lu) and Actinide series (Ac-Lr).

Below the main table, the Lanthanide and Actinide series are listed:

\* Lanthanide series: La (57), Ce (58), Pr (59), Nd (60), Pm (61), Sm (62), Eu (63), Gd (64), Tb (65), Dy (66), Ho (67), Er (68), Tm (69), Yb (70).

\*\* Actinide series: Ac (89), Th (90), Pa (91), U (92), Np (93), Pu (94), Am (95), Cm (96), Bk (97), Cf (98), Es (99), Fm (100), Md (101), No (102).

# Classes of intermetallics

- A1-A1, A2-A2: Similar electronegativities form solid solutions or Laves phases (if radii differ by ~15-20%); large radius differences lead to immiscibility.
- B2-B2: Forms intermetallics with covalent bonding.
- A1-A2: Significant size difference favors Laves phases.
- A1-B1: Large size and electronegativity differences create Laves phases and cluster compounds.
- A1-B2: High electronegativity difference leads to Zintl phases (salt-like, not intermetallic).

The periodic table is color-coded to show different classes of intermetallics:

- A1 (Pink):** Group 1 and 2 elements (Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba, Fr, Ra).
- A2 (Blue):** Groups 3 through 10 elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Pb, Bi, Po, At, Rn).
- B1 (Green):** Groups 11 and 12 elements (Al, Si, Ga, Ge, In, Sn, Pb, Bi, Po, At, Rn).
- B2 (Purple):** Groups 13 through 16 elements (B, C, N, O, F, Ne, P, S, Se, Br, Kr, As, Te, I, Xe, Sb, Sn, Pb, Bi, Po, At, Rn).
- C1 (Red):** Groups 17 and 18 elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No).

# Classes of intermetallics

- A2-B1: Valence electron concentration controls intermetallic structures (e.g., Hume-Rothery phases).
- A2-B2: Forms line compounds, often closed-packed with B2 in interstitial sites.
- B1-B2: Stoichiometric compounds with covalent bonding, following Grimm-Sommerfeld rule.

**A1**

**A2**

**B1**

**B2**

**C1**

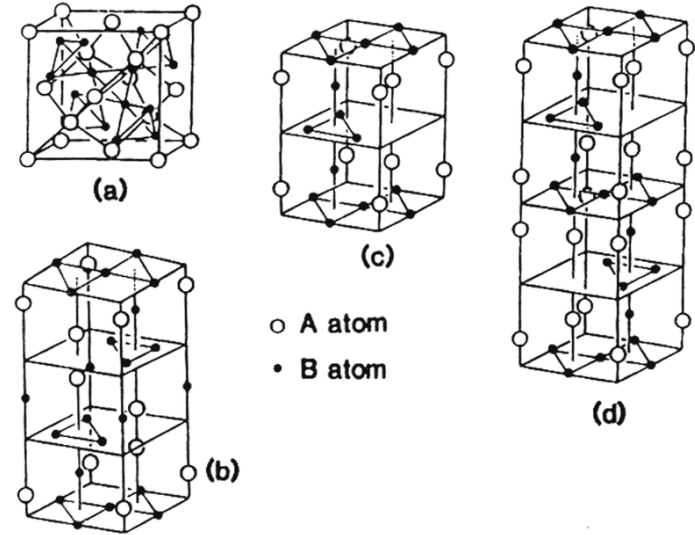
\* Lanthanide series

\*\* Actinide series

G-S rule: main group elements (N-k & N+k) behave similarly to group N elements  
 → example: III-V compounds (GaAs, InP) behave like Si, Ge semiconductors.

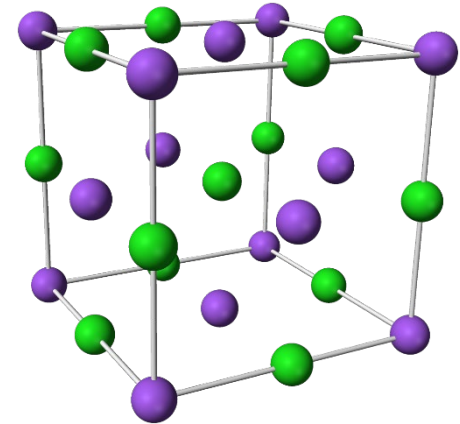
# The Laves phases

- Laves phases are the largest class of IMCs
- Composition ratio  $AB_2$  (not all intermetallic phases with  $AB_2$ -composition are Laves phases, however)
- Very high packing density of atoms, maximum volume filling of 71% with a ratio of  $r_A/r_B = \sqrt{3}/2 = 1.225$  (actual range of variation: 1.05 to 1.68)
- Cubic or hexagonal lattice structure
- Predominantly metallic bonding
- Examples:  $Co_2Ti$ ,  $Cr_2Nb$ ,  $Cu_2Mg$ ,  $Fe_2Mo$ ,  $MgZn_2$



# The Zintl phases

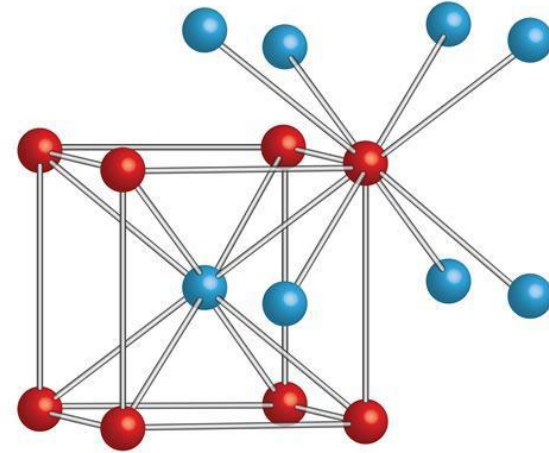
- AB types with NaCl lattice or  $AB_2$  types with  $CaF_2$  lattice.
- They are the product of a reaction between a group 1 (alkali metal) or group 2 (alkaline earth) and any post-transition metal or metalloid
- Composition corresponds to the chemical valences of the elements; Besides metallic bonding strong ionic bonding forces
- No significant homogeneity ranges, because of fixed valencies
- Because of the line-shaped range in the phase diagram they are called line compounds
- Examples:  $Mg_2Si$ ,  $Mg_2Pb$ ,  $MgSe$





# IMCs with CsCl structure

- AB-type IMCs with the CsCl structure are, after the Laves phases, the second largest class of IMCs
- While the ordered AB structures based on a bcc lattice are formed from a disordered solid solution, the CsCl-type IMCs solidify congruently from the melt
- The CsCl structure is typically formed by one element A to the left of group VIA, i.e. Cr, Mo, W and one element B to the right
- Primitive cubic lattice structure
- Predominantly ionic bonding
- Examples: CsCl, CuZn

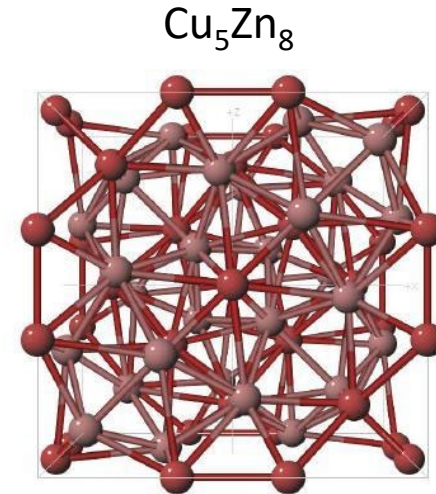


# The Hume-Rothery phases

- H-R phases have a specific valence electron concentration  $e/a$  ( $e$ : number of valence electrons,  $a$ : number of atoms)
- Characteristic values:  $e/a=3/2$ ,  $21/13$ ,  $7/4$
- Predominantly metallic bond character
- Mostly extended homogeneity range

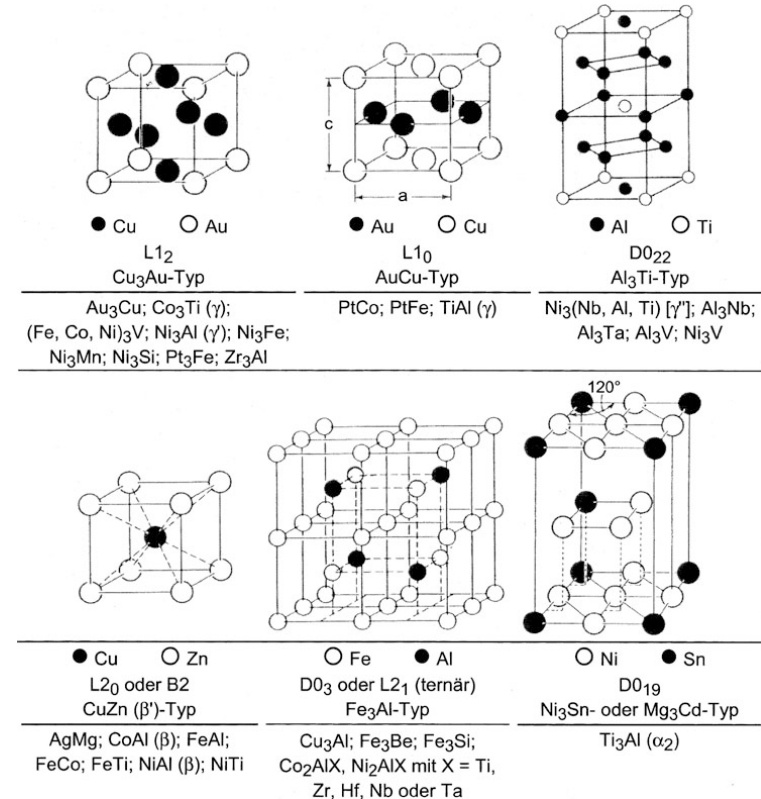
Elements	$e$
Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt	0
Cu, Ag, Au	1
Be, Mg, Zn, Cd	2
Al, Ga, In	3
Si, Ge, Sn, Pb	4
P, As, Sb, Bi	5

Example:  $\text{Ni}_5\text{Zn}_{21}$  ( $e=0+21\times 2=42$ ,  $a=5+21=26$ ,  $e/a=42/26=21/13$ );  $\text{Cu}_5\text{Zn}_8$



# The ordered phases with superstructure

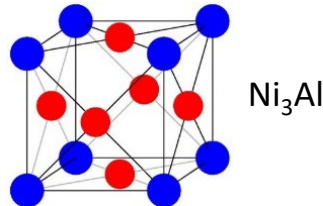
- Predominantly type AB or  $A_3B$
- The atoms occupy fixed lattice sites, i.e. they are not statistically randomly distributed
- The superstructure or long-range order represents a lattice of one type of atom in the lattice of the other
- Usually wider homogeneity range
- Range of existence often limited up to the critical order temperature in the solid state (entropy effect)
- Example: CuZn,  $Ni_3Al$ , NiAl, FeAl



# Closed packed phases

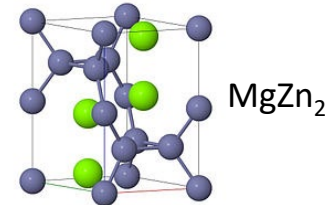
## ■ Geometrically closed packed (GCP)

- $A_3B$  composition with atomic radius relation  $r_A < r_B$
- Ordered crystal structure ( $\rightarrow$  subgroup of the ordered phases)
- Densest sphere packing related to the space filling
- Usually extended homogeneity range
- Examples:  $Ni_3Al$ ,  $Ni_3Fe$



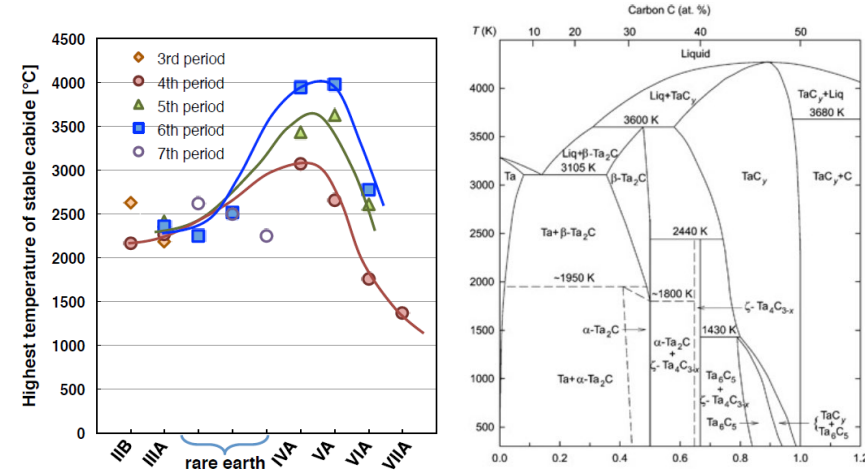
## ■ Topologically closed packed (TCP)

- Densely packed lattice planes with intervening layers of larger atoms (combination of periodic and aperiodic structure)
- Complex crystal structure, very large unit cells
- Usually extended homogeneity range
- Examples:  
All Laves phases, e.g.  $Fe_2Mo$ ,  $Co_2Ta$ ,  $MgZn_2$   
 $\sigma$ -phase  $(Fe,Ni,Co)_x(Cr,Mo,W)_y$  with  $x \approx y$   
 $\mu$ -phase  $((Fe,Co)_7(Mo,W)_6$



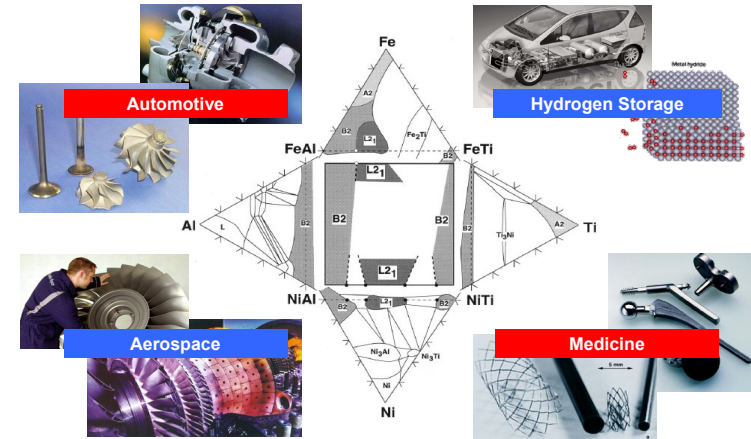
# The Hägg phases

- Compounds of transition metal and non-metal with small covalent radius (H: 0.32 Å, B: 0.82 Å, C: 0.77 Å, N: 0.75 Å); thus: hydrides, borides, carbides, nitrides, partly also other compounds
- High non-metallic bonding fraction (covalent radii decisive); these phases have a strong ceramic character
- High temperature stability and often high melting point (e.g., TaC at approx. 4000 °C)
- Often high hardness
- Examples:  $\text{Fe}_3\text{C}$ ,  $\text{Cr}_{23}\text{C}_6$ , TiC, TaC, AlN,  $\text{Cr}_2\text{N}$ ,  $\text{TiH}_2$



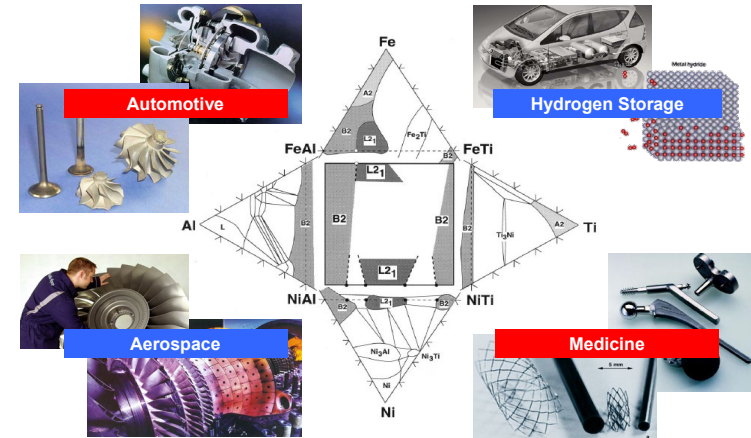
# Structural Intermetallic Alloys

- IMCs have strong bonds with covalent, ionic, and some metallic character
  - High elastic moduli and Peierls stresses give IMCs inherently high strength
  - Strong bonding leads to high melting points and low diffusion rates, enhancing HT strength
  - Partial metallic bonding reduces brittleness compared to ceramics.
- IMCs have been of particular interest for HT applications, as a replacement or complement for Ni superalloys



# Structural Intermetallic Alloys

- Only a few IMCs are of technical relevance
  - Aluminides for HT structural applications ( $\text{TiAl/Ti}_3\text{Al}$ ;  $\text{NiAl/Ni}_3\text{Al}$ ;  $\text{FeAl/Fe}_3\text{Al}$ )
  - The shape memory alloy  $\text{NiTi}$  → not considered here
  - Functional IMCs for superconductors (e.g.,  $\text{Nb}_3\text{Sn}$ ), catalysts (e.g.  $\text{Pt}_3\text{Ni}$ ,  $\text{PtCo}$ ) or hydrogen storage (e.g.  $\text{TiFe}$ ) → not considered here
- Aluminides offer HT stability, good mechanical properties, and low density due to high aluminum content
- Despite ~50 years of research, commercial applications for these IMCs remain limited



# Structural Intermetallic Alloys

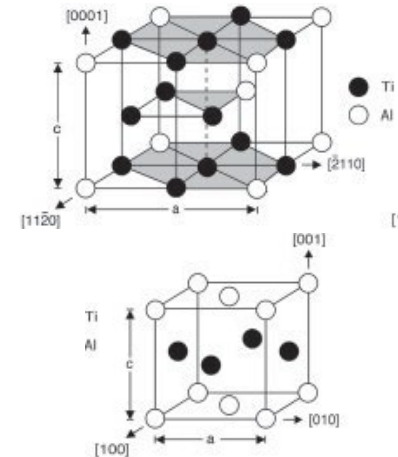
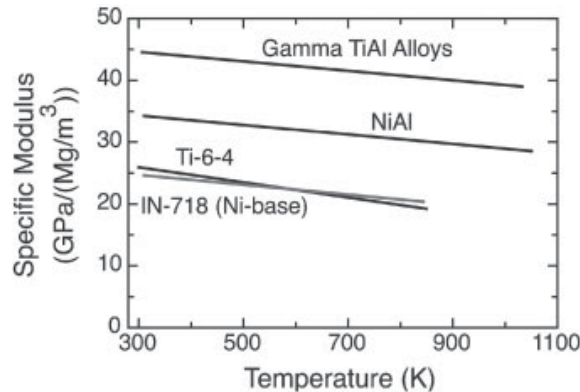
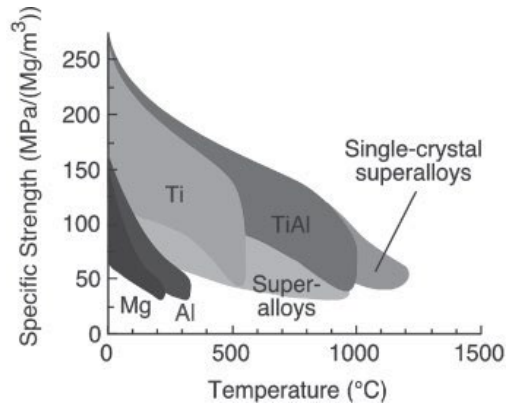
## General disadvantages and challenges

- Creep strength in IMCs is often lower than in superalloys at similar temperatures
  - requires solid solution strengthening, particle strengthening, or biphasing
- Pronounced brittleness
  - Brittle fracture can occur up to  $\sim 0.5$  TS with high notch sensitivity, especially under severe notches
  - Limited number of slip systems and high Peierls stress hinder plasticity, causing stress concentrations and cracking
  - Planar dislocation arrangements and dislocation pile-ups increase local stresses
  - Grain boundary weakness: low separation strength and impurity sensitivity (e.g., oxygen) can weaken grain boundaries
- Brittleness and low fracture toughness make fabrication, machining, and handling challenging, often with high scrap risk
- Some IMCs lack long-term oxidation resistance, requiring compatible coatings for durability



# Titanium aluminides

- Titanium Aluminides ( $\gamma$ -TiAl,  $\alpha_2$ -Ti<sub>3</sub>Al) have been studied for >30 years for their low density, high specific strength, and specific modulus.
- Properties: low diffusivity and excellent oxidation resistance due to high Al content
- Applications: suitable for use up to 800°C, competing with Ni-based alloys

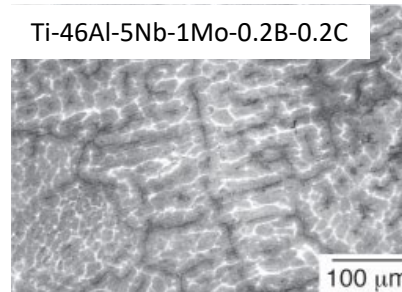


/F. Appel et al., Gamma Titanium Aluminide Alloys, Wiley 2011/

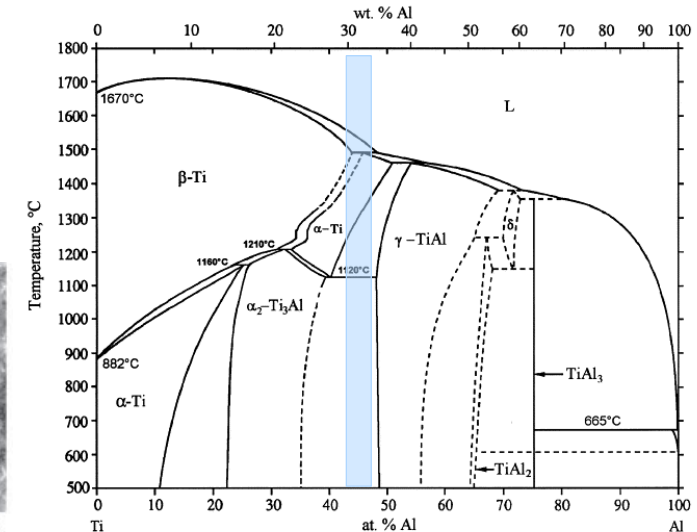
# Titanium aluminides

- Engineering alloys usually have a composition Ti-(45-48Al)-(0.1-10)X (at.%) with X=Cr, Nb, V, Ta, Mo, Zr, W, Si, C, and B
- Depending on composition and cooling rate
  - $\beta$ -Ti solidifiers
  - hypo/hyper-peritectic with  $\beta$ -Ti or  $\alpha$ -Ti as the primary phase
- Upon further cooling to RT transformation into a two-phase  $\alpha_2/\gamma$  microstructure
- Efficient microstructure refinement: addition of B

IMC	lattice	T <sub>oc</sub> [°C]	T <sub>m</sub> [°C]	$\rho$ [g/cm <sup>3</sup> ]	E [GPa]
Ti <sub>3</sub> Al	DO <sub>19</sub> (hcp)	1250	---	4.2	145
TiAl	L1 <sub>0</sub> (tetr.)	1460	1460	3.91	176



/F. Appel et al., Gamma Titanium Aluminide Alloys, Wiley 2011/

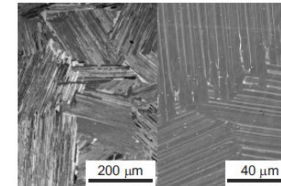
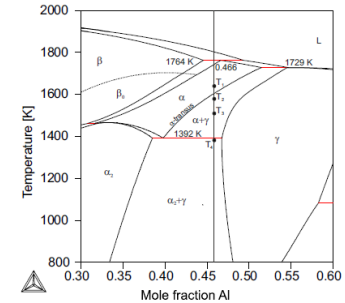


# Titanium aluminides

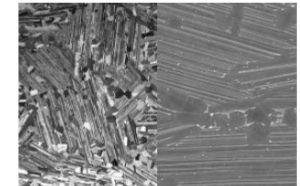
## Microstructures after heat treatment

- TiAl alloys are not directly applied in the as-processed condition but are heat treated
- Thermal treatments lead to microstructures similar to those of Ti alloys
  - a) Lamellar (HT at  $T_1$ , slow cooling)
  - b) Nearly lamellar (HT close to  $\alpha$  transus at  $T_2$ )
  - c) Bimodal/duplex (increased amount of  $\gamma$  after HT at  $T_3$ )
  - d) Near- $\gamma$  (HT below eutectoid temperature at  $T_4$ )

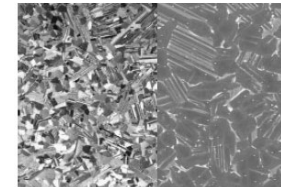
- a) fully lamellar microstructure,  
(b) nearly lamellar microstructure,  
(c) a duplex microstructure and  
(d) near  $\gamma$  plates.



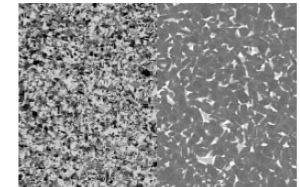
(a)



(b)



(c)



(d)

# Titanium aluminides

## Strengthening mechanisms

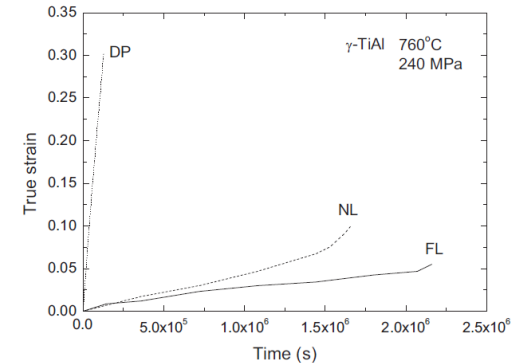
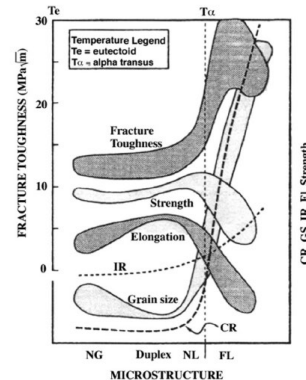
- Solid solution strengthening
  - Alloying with modest levels (<3-5 at.% in total) of Cr, V, Cr, Mn, Mo, Ta, Nb, and Zr provides some potential for solid solution strengthening
- Dislocation strengthening
  - Low effectivity because of the inherent brittleness of Ti aluminides
- Grain boundary strengthening
  - Effect similar to Ti alloys with grain diameter or lamellae width as important parameter
  - Less effective at elevated T
- Particle strengthening
  - Nanometric borides, nitrides, oxides, and silicides may provide precipitation strengthening
  - Coarse precipitates seem to be harmful for ductility

# Titanium aluminides

## Mechanical properties

- The properties of modern TiAl alloys are depending on the phase fraction of the  $\gamma$  and the  $\alpha_2$  phase as well as on the microstructure (i.e. the thermal treatment)
- The high-T strength and creep resistance can be improved by increased amounts of  $\alpha_2$
- $\gamma$ -TiAl exhibits a ductile-to-brittle transition at  $\sim 830^\circ\text{C}$

Property	Ti-based alloys	Ti <sub>3</sub> Al-based $\alpha_2$ alloys	TiAl-based $\gamma$ alloys	Superalloys
Density ( $\text{g cm}^{-3}$ )	4.5	4.1–4.7	3.7–3.9	8.3
RT modulus (GPa)	96–115	120–145	160–176	206
RT yield strength (MPa)	380–1115	700–990	400–630	250–1310 <sup>a</sup>
RT tensile strength (MPa)	480–1200	800–1140	450–700	620–1620 <sup>a</sup>
Highest temperature with high creep strength ( $^\circ\text{C}$ )	600	750	1000	1090
Temperature of oxidation ( $^\circ\text{C}$ )	600	650	900–1000	1090
Ductility (%) at RT	10–20	2–7	1–3	3–5
Ductility (%) at high T	High	10–20	10–90	10–20
Structure	hcp/bcc	DO19	L1 <sub>0</sub>	fcc/L1 <sub>2</sub>



/M.-T. Perez-Prado, M.E. Kassner, Creep of Intermetallics, in: Fundamentals of Creep in Metals and Alloys, Elsevier 2015/

# Titanium aluminides

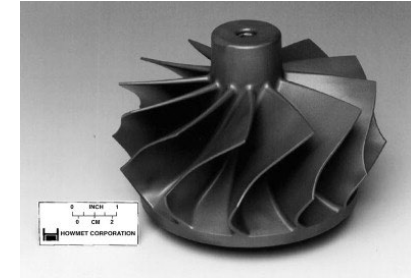
## Applications

- After several decades of research and development, parts fabricated from TiAl alloys have recently been introduced on the market
- Fields of application are turbocharger parts, aeroengine parts

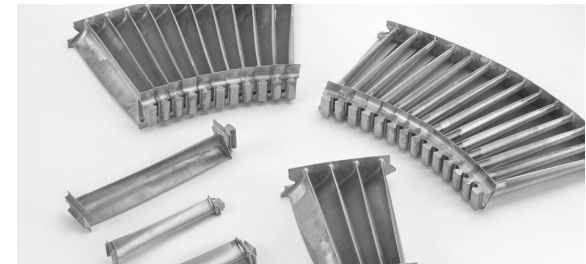
Selected state-of-the art TiAl alloys

Alloy name	Nominal composition [at.%]	Company / Institute
GE48-2-2	Ti-48Al-2Cr-2Nb	General Electric
$\gamma$ -MET	Ti-46.5Al-4(Nb, Cr, Ta, B)	Plansee
47XD	Ti-47Al-2Mn-2Nb-0.8TiB <sub>2</sub>	Martin Marietta
$\gamma$ -TAB	Ti-47Al-4(Nb, Cr, Mn, Si, B)	GKSS Research Center
ABB Alloy	Ti-45Al-2W-0.5Si	ABB
TNB-V5	Ti-45Al-5Nb-0.2C-0.2B	GKSS Research Center
TNM-B1	Ti-43Al-4Nb-1Mo-0.1B	GKSS Research Center

Turbo charger parts



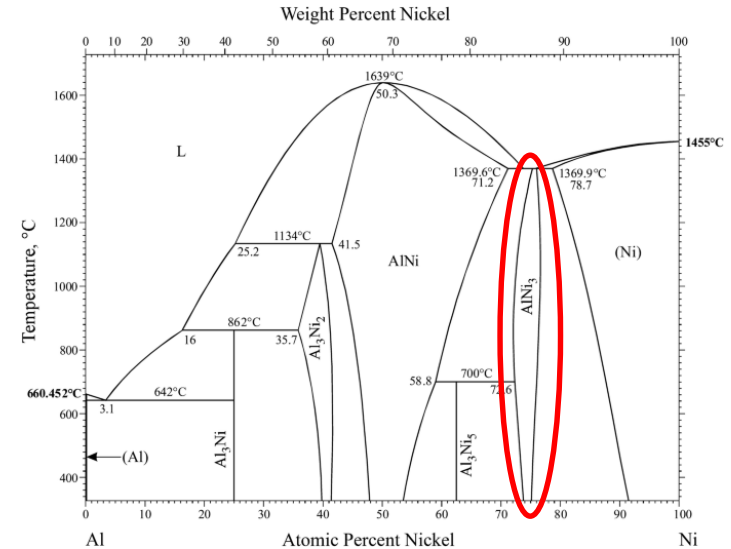
Vanes in aeroengines



# Nickel aluminides

## Properties of $\text{Ni}_3\text{Al}$

- $\text{Ni}_3\text{Al}$  polycrystals: Brittle due to soft grain boundaries; boron addition can strengthen boundaries.
- Single crystals: Ductile with dislocation glide on  $\{111\}/\langle 110 \rangle$  slip systems (von Mises criterion met).
- Oxidation: 13 wt% Al insufficient for dense  $\text{Al}_2\text{O}_3$  layer at HT; forms NiO with some  $\text{Al}_2\text{O}_3$ .
- Properties:  $\gamma\text{-Ni}_3\text{Al}$  lacks significant advantages over Ni alloys in physical, mechanical, or corrosion resistance.

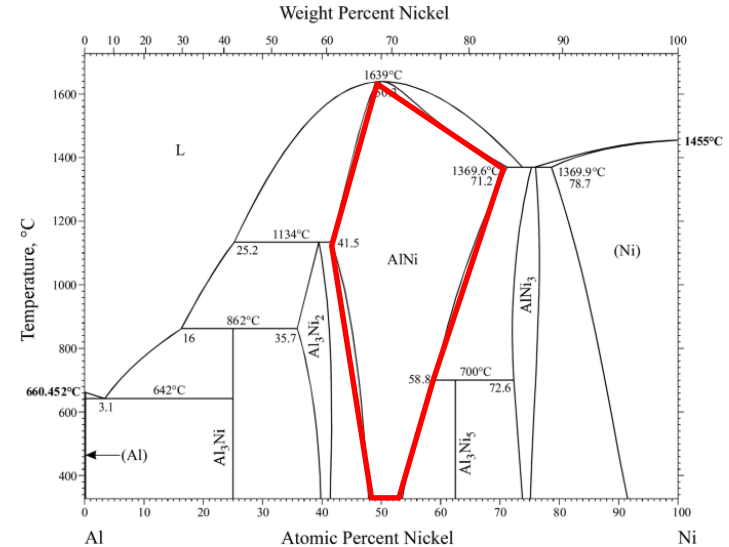


IMC	Crystal structure	T <sub>oc</sub> [°C]	T <sub>m</sub> [°C]	ρ [g/cm <sup>3</sup> ]	E [GPa]
Ni <sub>3</sub> Al	L1 <sub>2</sub> (ordered fcc)	1390	1390	7.5	179

# Nickel aluminides

## Properties of NiAl

- High oxidation resistance due to ~30 wt% Al.
- 25% lower thermal expansion and ~5x higher thermal conductivity than Ni superalloys.
- Brittle up to ~650°C (~0.3-0.5  $T_s$ ) due to high Peierls stress and limited slip systems, resulting in low fracture toughness and high notch sensitivity.
- Limited creep resistance from open B2 lattice structure with high diffusivity.
- Ductile-to-brittle transition in polycrystals affected by composition, grain size, and processing.



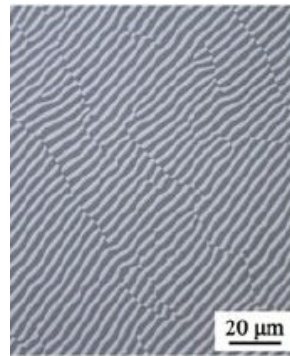
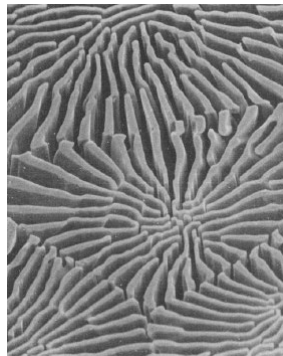
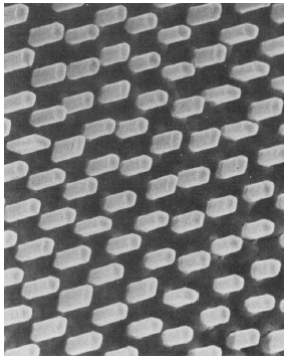
IMC	Crystal structure	$T_{oc}$ [°C]	$T_m$ [°C]	$\rho$ [g/cm <sup>3</sup> ]	E [GPa]
NiAl	B2 (ordered fcc)	1640	1640	5.86	194



# Nickel aluminides

## Alloying strategies for improving mechanical properties of NiAl

- Improving NiAl toughness & strength: achieved by adding a ductile, creep-resistant refractory phase
- Eutectic strategy: NiAl forms eutectics with bcc elements (e.g., Cr, Mo, W, Ta) during solidification
- Promising alloys: directionally solidified NiAl-Cr/Mo with aligned Cr-18Mo lamellae in a NiAl matrix offers fine, creep-resistant structure



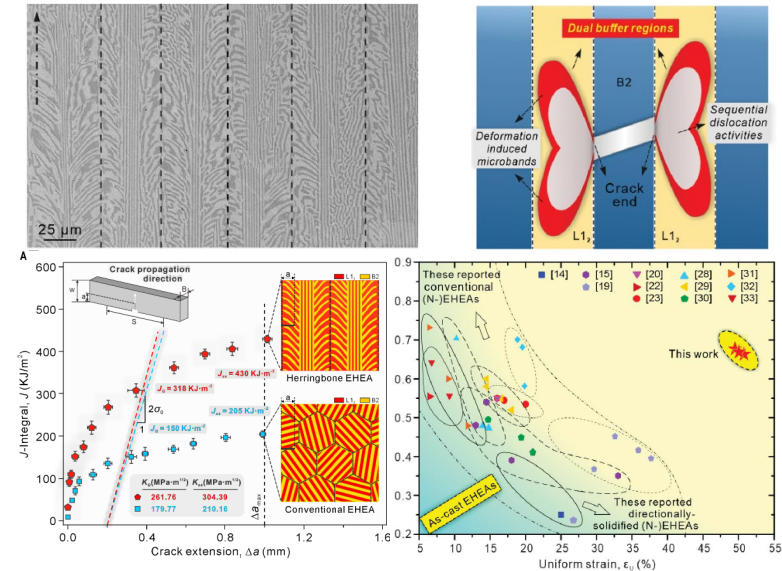
left: NiAl-Cr showing aligned Cr rods in deep-etched NiAl matrix  
center: NiAl-Cr(Mo), showing Cr-Mo lamellae in deep-etched NiAl matrix  
right: unetched transverse view showing aligned Cr(Mo) lamellae in NiAl matrix

/H.E. Cline et al. Metall. Trans. 2 (1971) 189–194/  
/D.R. Johnson et al. Intermetallics. 3 (1995) 99–113/

# Nickel aluminides

## Alloying strategies for improving mechanical properties of NiAl

- Ni-20Co-20Fe-19Al eutectic alloy:
  - recently shown to be crack-tolerant and highly ductile in tension.
- Contains Al-rich B2 (Ni-17Co-17Fe-27Al) and Al-lean L1<sub>2</sub> (Ni-24Co-27Fe-11Al) phases in lamellar structure.
- Herringbone pattern guides microcrack nucleation in brittle B2 phase, while ductile L1<sub>2</sub> phase buffers and prevents crack propagation, delaying failure

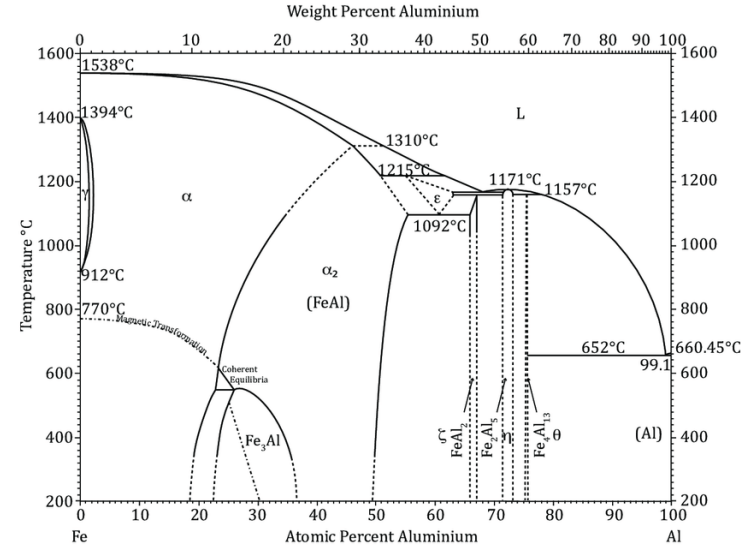


/P.Shi et al., Science. 373 (2021) 912–918/

# Iron aluminides

- Studied as low-cost, low-density alternatives to high-alloy steels.
- Offer good wear resistance, oxidation, and corrosion resistance.

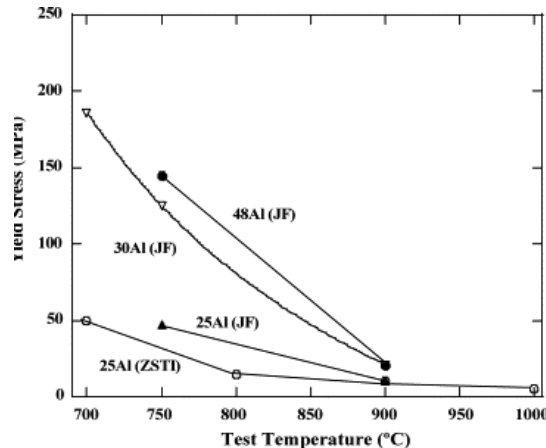
IMC	Crystal structure	T <sub>oc</sub> [°C]	T <sub>m</sub> [°C]	ρ [g/cm <sup>3</sup> ]	E [GPa]
Fe <sub>3</sub> Al	D0 <sub>3</sub> (ordered bcc)	540		6.72	141
	B2 (ordered bcc)	760	1540		
FeAl	B2 (ordered bcc)	1250	1250	5.56	261



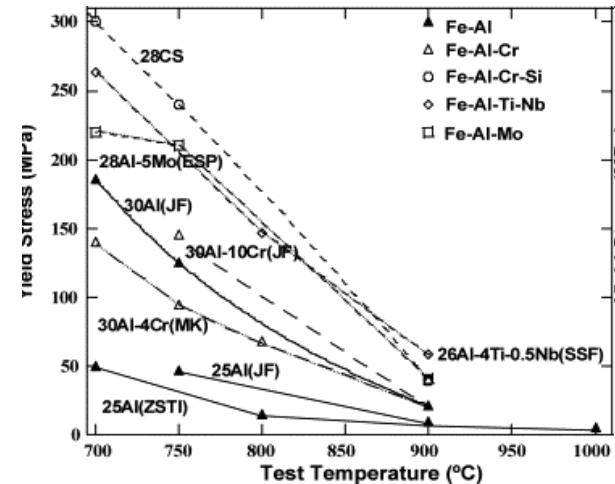
# Iron aluminides

## Mechanical performance

- Additional alloying elements can increase the HT strength



Comparison of flow stress at high temperature in binary Fe–Al alloys with a range of Al contents between 25 and 48%.

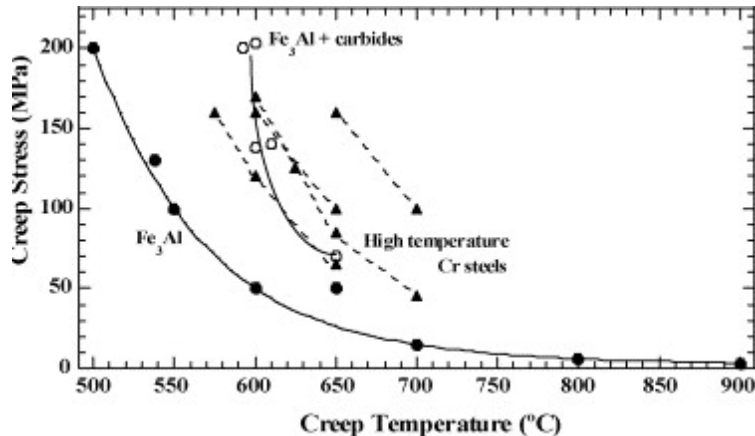


Comparison of flow stresses of high temperature binary Fe–Al alloys and some ternary Fe–Al–X solution alloys.

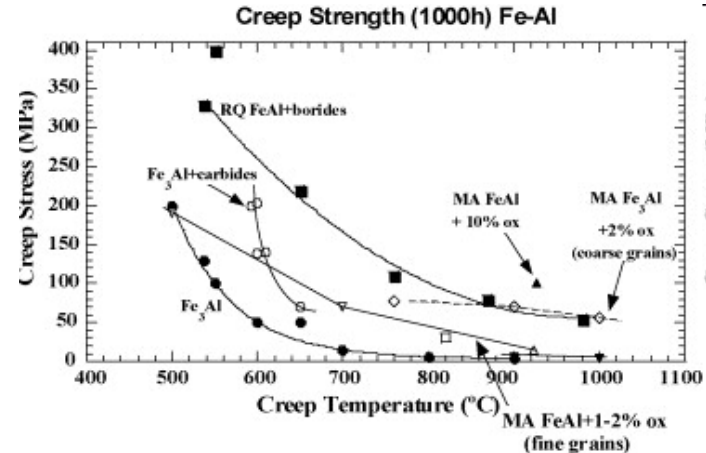
# Iron aluminides

## Creep behavior

- The creep resistance of  $\text{Fe}_3\text{Al}$  and  $\text{FeAl}$  alloys is in general inferior to that of high alloyed steels
- Particle strengthening with carbides, borides or oxides possible



1000 h creep strength of binary  $\text{Fe}_3\text{Al}$ ,  $\text{Fe}_3\text{Al}$  with carbide additions, and advanced high-temperature steels.



1000 h creep strength of binary  $\text{Fe}_3\text{Al}$ , and various  $\text{Fe}_3\text{Al}$  or  $\text{FeAl}$  alloys strengthened with carbides, borides or oxides.

/D.G. Morris et al. Acta Mater, 52(9) (2004) 2827-2836/

# Learning objectives

- Hume-Rothery rules for substitutional/interstitial phases
- The different classes of IM phases and their main characteristics
- Structural intermetallics
  - The advantages/disadvantages of IMCs
  - Fundamental properties of the alloys from the Ti-Al, Ni-Al and Fe-Al systems
  - Potential fields of application