FS 2025/26

MSE-422 – Advanced Metallurgy

7-Structural Intermetallic Alloys

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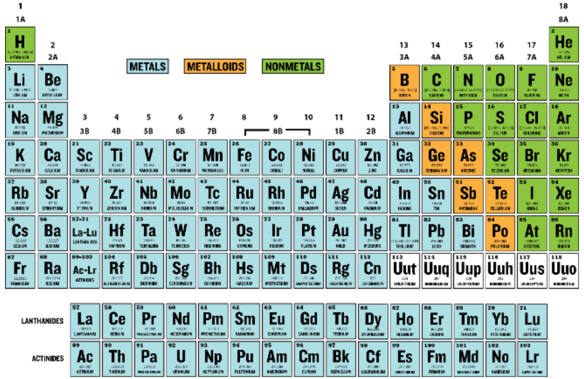
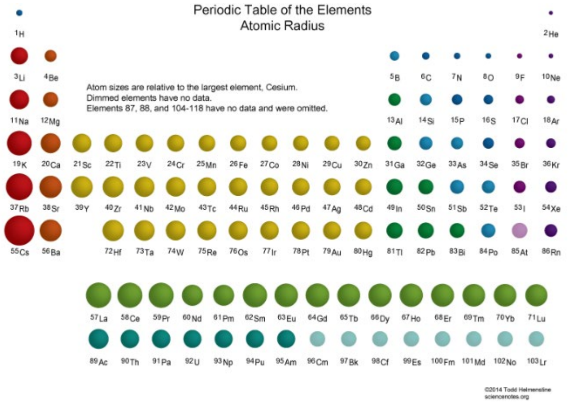
Criteria for the formation of solid solutions

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 intersitial 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.

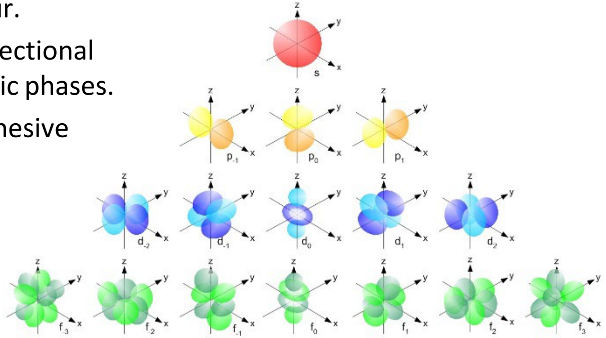




→ If these rules are not fulfilled, then intermetallic compounds will form

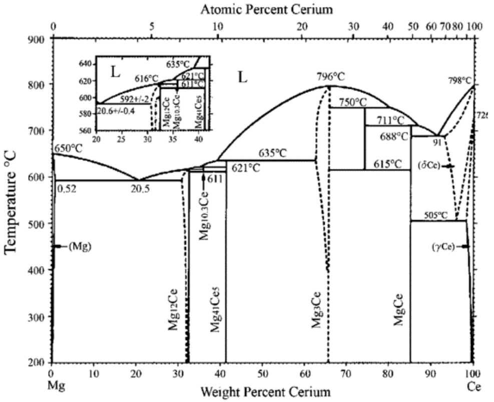
Reminder – basic chemistry concepts

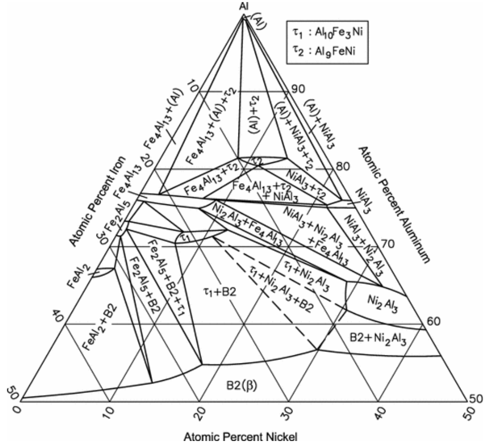
- **Atomic Radius**
  - Effective size of an atom (½ distance between identical neighbours).
  - ↓ across a period, ↑ down a group.
  - Controls solid solubility and lattice distortion.
  - Large size mismatch → favours ordered compound formation (e.g. B2, $L1_2$).
- **Electronegativity**
  - Measure of an atom's tendency to attract bonding electrons.
  - ↑ across a period, ↓ down a group.
  - Difference drives charge transfer and bond polarity.
  - Large $\Delta\chi$ → promotes intermetallic compound formation (Al–Ni, Ti–Al).
- **Valency (Valence)**
  - Number of electrons available for bonding (s + d electrons in metals).
  - Defines electron concentration → key for Hume–Rothery rules.
  - Influences phase stability and electronic structure (Al 3+, Ni ≈ 2, Cu 1).
- **Shell Filling**
  - Distribution of electrons in s, p, d, f orbitals.
  - Determines metallic vs. covalent character, magnetic behaviour.
  - Partially filled d/f shells → directional bonding, complex intermetallic phases.
  - Affects bond strength and cohesive energy.



Some basic facts about intermetallics

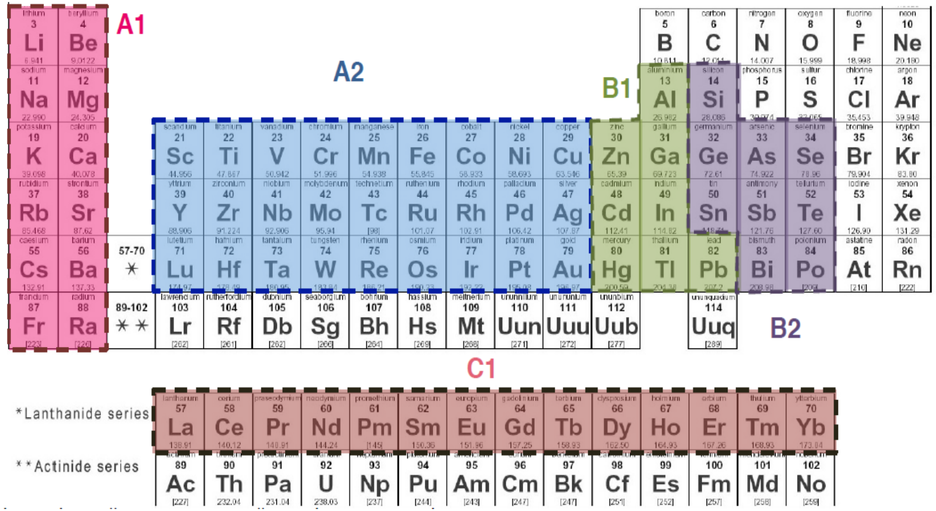
- Intermetallic compound (IMC), also called an intermetallic, or (ordered) intermetallic alloy
- Metallic alloys with ordered lattices formed between two or more metallic elements.
- Over 5000 binary IMCs exist, grouped by characteristics; most are not suitable for structural or functional applications.
- 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.





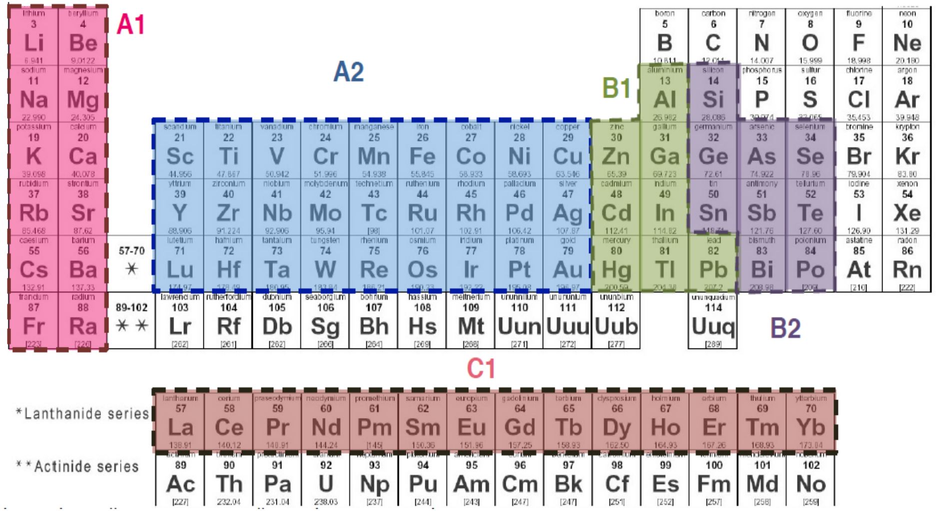
Some basic facts about intermetallics

- 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



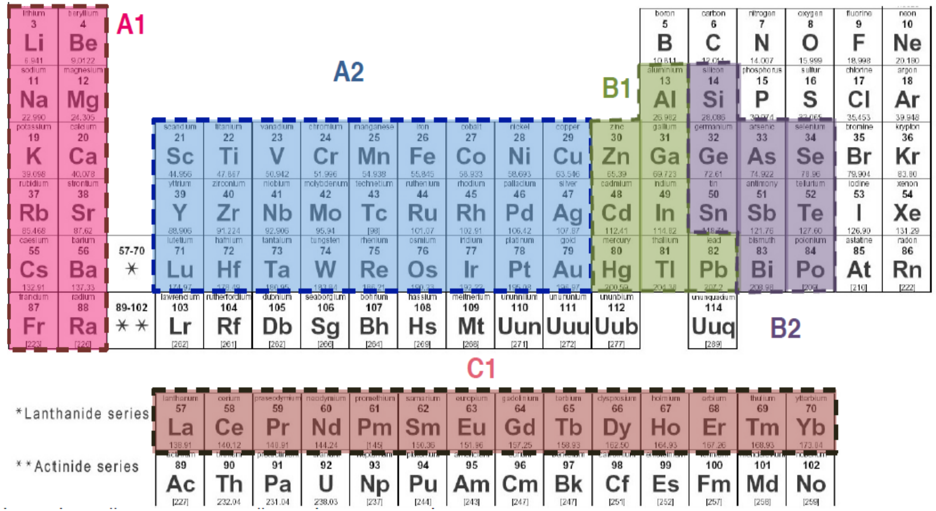
Classes of intermetallics

- 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 (salt-like) Zintl phases



Classes of intermetallics

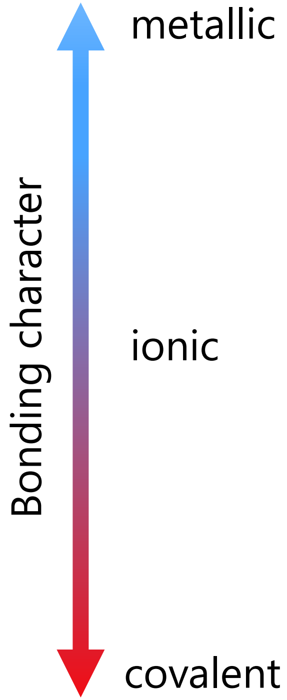
- A2-B1: Valence electron concentration controls intermetallic structures (e.g., Hume-Rothery phases)
- A2-B2: Forms line compounds, often closed-packed with B2 in interstitial sites
- B1-B2: Stoichiometric compounds with covalent bonding, following Grimm-Sommerfeld rule



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.

Classes of intermetallics

- **Solid solutions**
  ↓ *(ordering)*
- **Ordered (superlattice) phases**
  ↓ *(electron concentration control)*
- **Hume–Rothery phases**
  ↓ *(atomic packing density & specific atomic size ratios)*
- **Closed-packed phases & Laves phases (AB_2)**
  ↓ *(increasing ionicity)*
- **CsCl-type (B2)**
  ↓ *(increasing ionicity & covalency)*
- **Zintl phases**
  ↓ *(increasing covalency)*
- **Hägg phases**

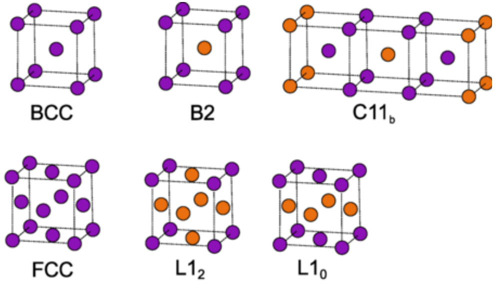


Strukturbericht designation – summary

- Purpose: historical classification system (-1940s, Strukturbericht volumes) used to categorize intermetallic crystal structures based on prototype compounds
- Format: a letter + number (e.g. A1, B2, D0$_3$) identifying structural type families
  - The letter denotes the chemical complexity / crystal class (A: elements, B: binaries, C: ternaries, D/E: more complex systems)
  - The number distinguishes individual structure prototypes within that class
- Today largely replaced by Pearson symbols (e.g. cF4, cI2, tP4) and ICSD prototype notation, but still widely used in metallurgy and alloy design

Some examples

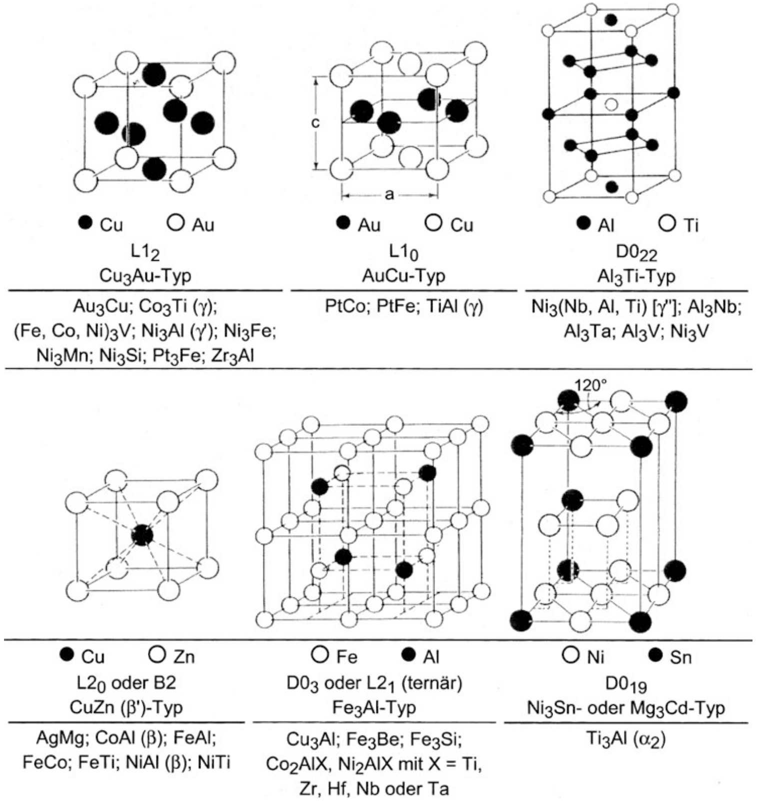
Designation	Prototype	Struktur Type	Space Group
A1	Cu (fcc)	fcc	Fm-3m
A2	W (bcc)	bcc	Im-3m
A3	Mg (hcp)	hcp	P6$_3$/mmc
B1	NaCl	Rocksalt	Fm-3m
B2	CsCl	Ordered bcc	Pm-3m
B3	ZnS	Zincblende	F-43m
D0$_3$	Fe$_3$Al	Ordered bcc (B2×2)	Fm-3m
L1$_0$	AuCu	Tetragonal	P4/mmm
L1$_2$	Cu$_3$Au	fcc-based	Pm-3m



Ordered (Superlattice) Phases

Long-Range Atomic Order in Alloys

- Predominantly type AB or A_3B
- Ordered (superlattice) phases retain the parent metallic lattice (fcc, bcc, hcp) but exhibit long-range atomic order
- The superstructure represents a lattice of one type of atom in the lattice of the other → the atoms occupy fixed lattice sites, i.e. they are not statistically randomly distributed
- 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



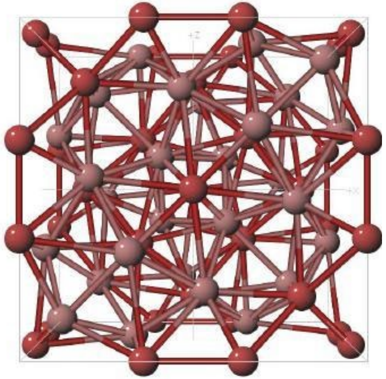
● Cu ○ Au $L1_2$ Cu_3Au-Typ	● Au ○ Cu $L1_0$ AuCu-Typ	● Al ○ Ti $D0_{22}$ Al_3Ti-Typ
Au_3Cu; Co_3Ti (γ); (Fe, Co, Ni)$_3$V; Ni_3Al (γ'); Ni_3Fe; Ni_3Mn; Ni_3Si; Pt_3Fe; Zr_3Al	PtCo; PtFe; TiAl (γ)	Ni_3(Nb, Al, Ti) [γ'']; Al_3Nb; Al_3Ta; Al_3V; Ni_3V
● Cu ○ Zn $L2_0$ oder B2 CuZn (β')-Typ	○ Fe ● Al $D0_3$ oder $L2_1$ (ternär) Fe_3Al-Typ	○ Ni ● Sn $D0_{19}$ Ni_3Sn- oder Mg_3Cd-Typ
AgMg; CoAl (β); FeAl; FeCo; FeTi; NiAl (β); NiTi	Cu_3Al; Fe_3Be; Fe_3Si; Co_2AlX, Ni_2AlX mit X = Ti, Zr, Hf, Nb oder Ta	Ti_3Al (α_2)

The Hume-Rothery phases

- Predominantly metallic bond character
- Close to solid-solution behavior, but stabilized by 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
- 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

Cu_5Zn_8

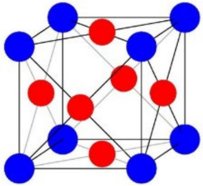


Example: Ni_5Zn_{21} (e=0+21x2=42, a=5+21=26, e/a=42/26=21/13); Cu_5Zn_8

Closed packed phases

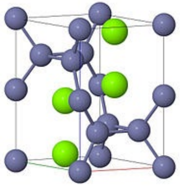
- In metallic systems, increasing atomic packing and size mismatch stabilization lead to close-packed intermetallics — either simple (geometrical) or complex (topological).
- Both arise from the drive toward high coordination and dense atomic packing when solid solutions or simple superlattices can no longer accommodate compositional or electronic imbalance.

- Geometrically closed packed (GCP)
  - Derived from fcc/hcp lattices (ordered variants of dense metallic structures)
  - Stoichiometry: A_3B or AB_3
  - Bonding: metallic, some directional character (ordering energy).
  - Usually extended homogeneity range
  - Examples: Ni_3Al, Ni_3Fe



Ni_3Al

- Topologically closed packed (TCP)
  - Complex polyhedral frameworks maximizing local coordination.
  - Occur in alloys with large atomic-size or electronic mismatch (often high Cr, Mo, W).
  - Stoichiometry: variable (AB_2, A_3B_5, etc.).
  - Usually extended homogeneity range
  - Bonding: metallic + some covalent character.
  - Examples: Laves phases, e.g. Fe_2Mo, Co_2Ta, $MgZn_{2;}$ σ-phase $(Fe,Ni,Co)_x(Cr,Mo,W)_y$ with x≈y μ-phase $((Fe,Co)_7(Mo,W)_6$

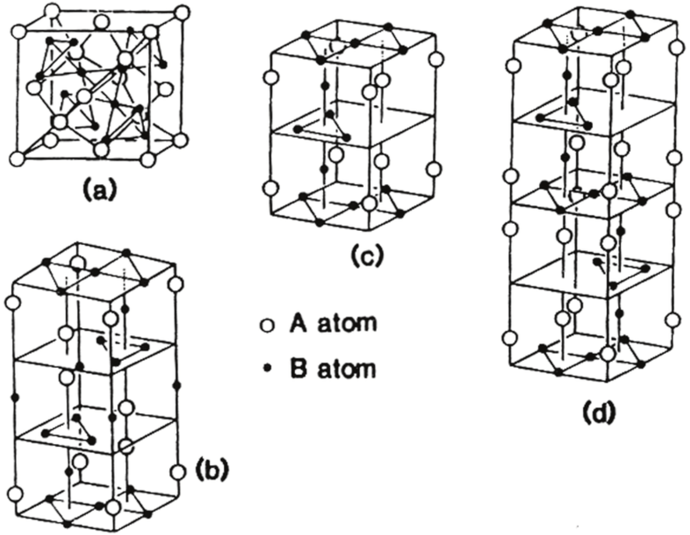


$MgZn_2$

The Laves phases

- Specific subset of TCP 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%
- Can be presented as “an ordered close-packed structure” with specific $r_A/r_B = \sqrt{3/2} = 1.225$ (actual range of variation: 1.05 to 1.68)
- Cubic or hexagonal lattice structure
- Predominantly metallic bonding

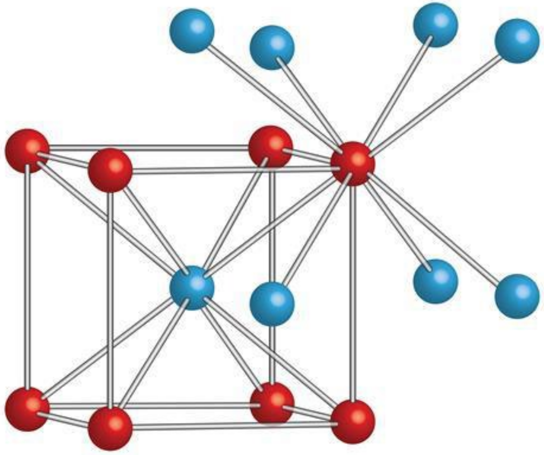
- Examples: Co_2Ti, Cr_2Nb, Cu_2Mg, Fe_2Mo, $MgZn_2$



IMCs with CsCl structure

- Besides metallic bonding strong ionic bonding forces (but still conductive)
- Primitive cubic lattice structure
- AB-type IMCs with the CsCl structure are, after the Laves phases, the second largest class of 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

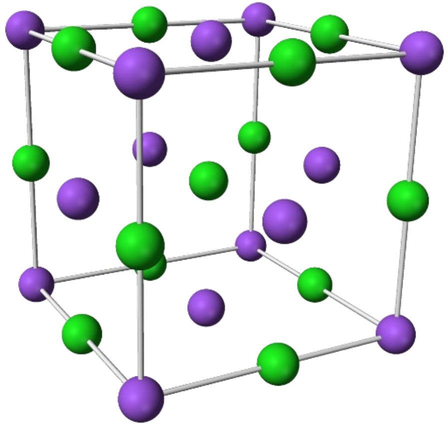
- Examples: CsCl, CuZn, FeAl, NiAl



The Zintl phases

- Predominantly ionic/partly covalent bonding; semiconducting
- Composition corresponds to the chemical valences of the elements
- AB types with NaCl lattice or AB_2 types with CaF_2 lattice.
- Consist of group 1 (alkali metal) or group 2 (alkaline earth) elements and any post-transition metal or metalloid
- No significant homogeneity ranges, because of fixed valencies
- Because of the line-shaped range in the phase diagram they are called line compounds

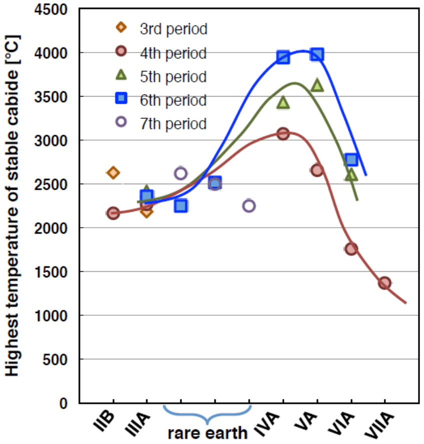
- Examples: Mg_2Si, Mg_2Pb, MgSe



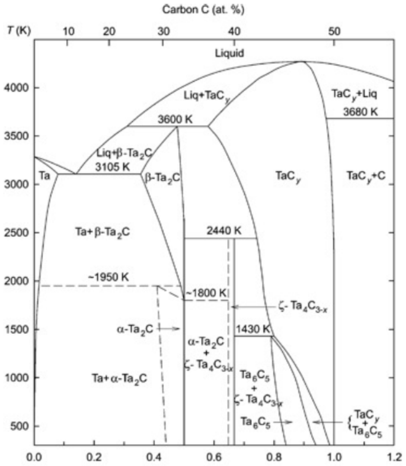
The Hägg phases

- Pronounced covalent bonding character, but still a bit metallic
- Bridge between metallic and ceramic materials
- 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:
- High temperature stability and often high melting point (e.g., TaC at approx. 4000 °C)
- Often high hardness, brittle

- Examples: hydrides, borides, carbides, nitrides, partly also other compounds (Fe_3C, $Cr_{23}C_6$, TiC, TaC, AlN, Cr_2N, TiH_2)



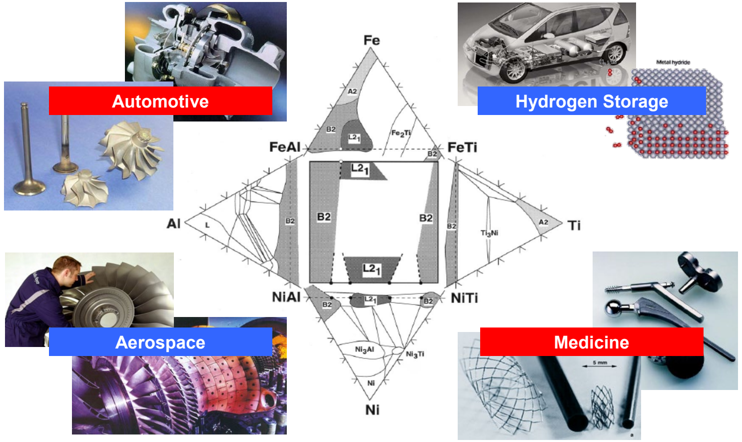
Ta-C



Structural Intermetallic Alloys

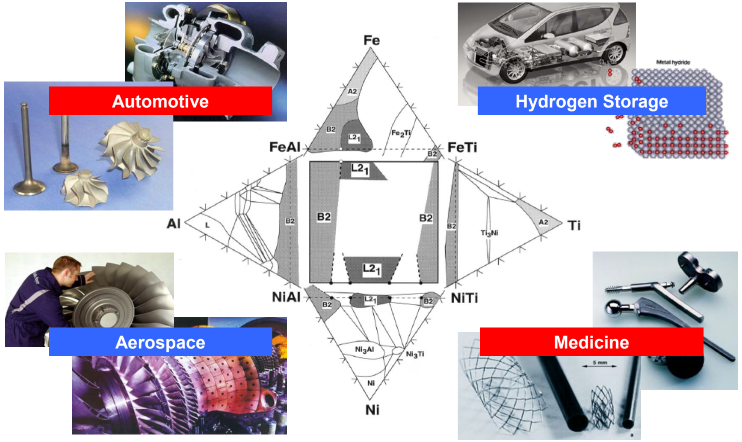
- IMCs have strong bonds with metallic, ionic and some covalent character
- High elastic moduli and Peierls stresses → inherently high strength
- Strong bonding leads to high melting points and low diffusion rates, enhancing HT strength
- Partial metallic bonding reduces brittleness compared to ceramics.

→ IMCs have been of particular interest for HT applications, as a replacement or complement for Ni superalloys



Structural Intermetallic Alloys

- Of the 1000s of known binary and ternary IMCs, only a few are of technical relevance
  - Aluminides for HT structural applications (TiAl/Ti_3Al; NiAl/Ni_3Al; FeAl/Fe_3Al)
  - The shape memory alloy NiTi → not considered here
  - Functional IMCs for superconductors (e.g., Nb_3Sn), catalysts (e.g. Pt_3Ni, PtCo) or hydrogen storage (e.g. TiFe) → not considered here
- Aluminides offer HT stability, good mechanical properties, and low density due to high aluminum content
- Up until now, commercial applications for these IMCs remain limited



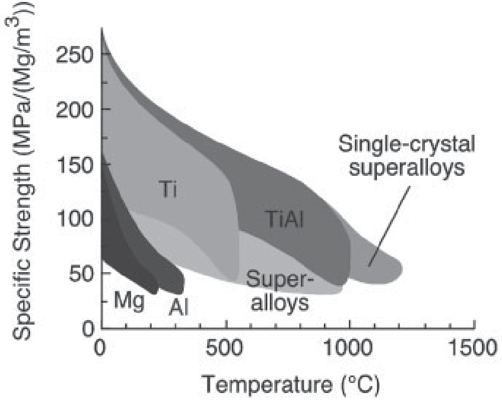
Structural Intermetallic Alloys

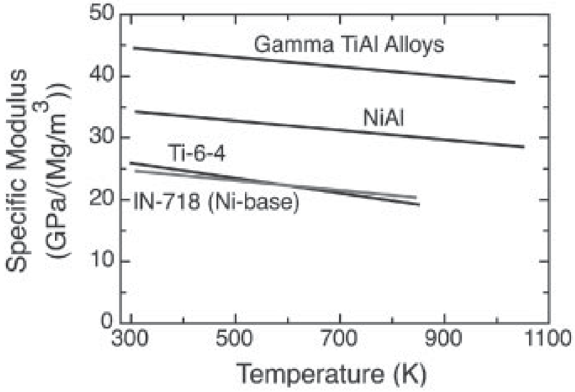
General disadvantages and challenges

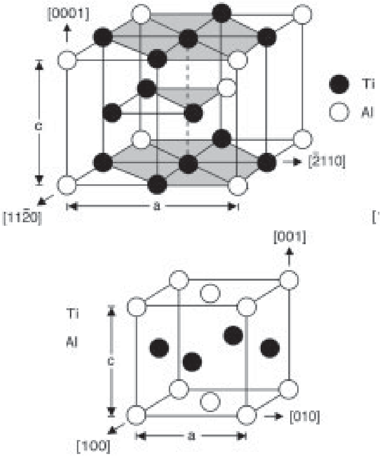
- Intrinsic (atomic-scale) limitations
  - Strong, partly covalent bonding
    → high Peierls stress, few active slip systems
  - Results in brittleness, low ductility, and notch sensitivity
  - Planar dislocation glide and pile-ups promote local stress concentration and early cracking
- Microstructural weaknesses
  - Weak grain boundaries with low cohesive strength and impurity sensitivity (O, N, H)
  - Limited grain refinement due to sluggish diffusion
  - Grain-boundary fracture often dominates failure
- Processing and mechanical challenges
  - Low fracture toughness
    → difficult forming, machining, and joining
  - Casting cracks, porosity, and high scrap risk
  - Creep strength often inferior to Ni-superalloys
    → needs solid-solution, dispersion, or duplex strengthening
- Environmental limitations
  - Some IMCs lack long-term oxidation and corrosion resistance
  - Require protective coatings or Al/Si/Cr alloying for surface stability

Titanium aluminides

- Titanium Aluminides (γ-TiAl – CsCl structure; α_2-Ti_3Al - Laves) have been studied for >40 years
- Properties:
  - low density, high specific strength, and specific modulus
  - low diffusivity and excellent oxidation resistance due to high Al content
- Applications: suitable for use up to 800°C, competing with Ni-based alloys





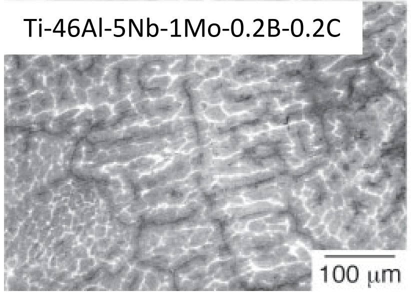


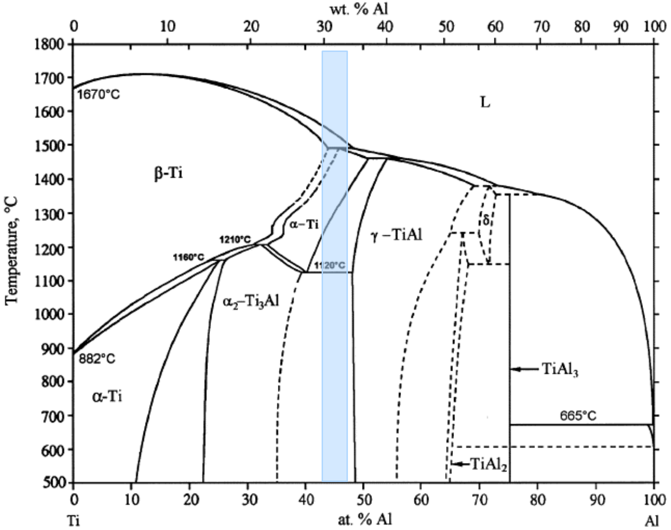
/F. Appel et al., Gamma Titanium Aluminide Alloys, Wiley 2011/

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
  - β-Ti solidifiers
  - hypo/hyper-peritectic with β-Ti or α-Ti as the primary phase
- Upon further cooling to RT transformation into a two-phase α_2/γ microstructure
- Efficient microstructure refinement: addition of B

IMC	lattice	T_{oc} [°C]	T_m [°C]	ρ [g/cm³]	E [GPa]
Ti_3Al	$D0_{19}$ (hcp)	1250	---	4.2	145
TiAl	$L1_0$ (tetr.)	1460	1460	3.91	176


Ti-46Al-5Nb-1Mo-0.2B-0.2C



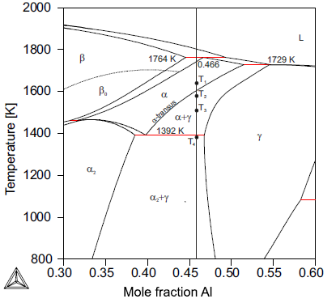
/F. Appel et al., Gamma Titanium Aluminide Alloys, Wiley 2011/

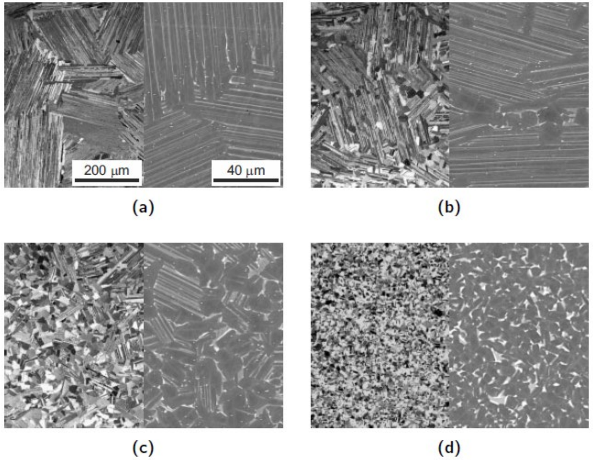
Titanium aluminides

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 α transus at T_2)
  - c) Bimodal/duplex (increased amount of γ after HT at T_3)
  - d) Near-γ (HT below eutectoid temperature at T_4)

a) fully lamellar microstructure,
(b) nearly lamellar microstructure,
(c) a duplex microstructure and
(d) near γ plates.





C. Kenel, PhD thesis Empa and ETHZ, 2016/

Titanium aluminides

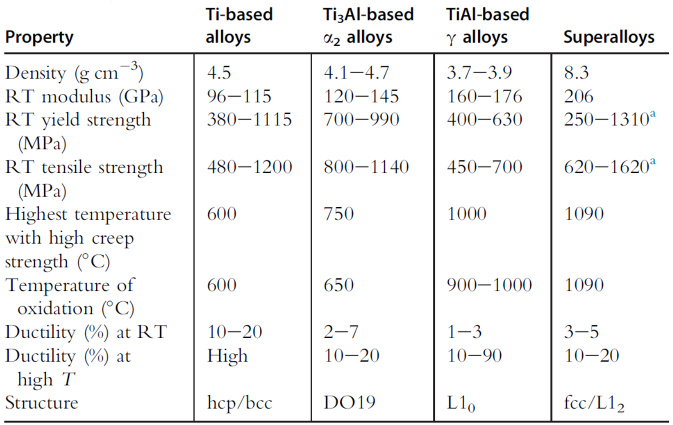
Strengthening mechanisms

- 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

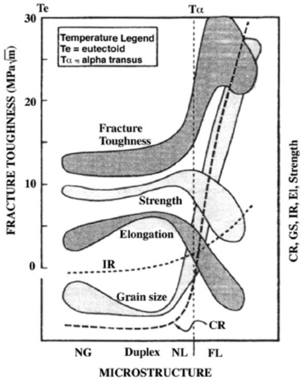
Mechanical properties

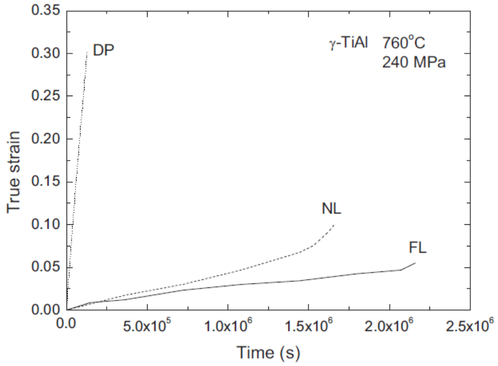
- The properties of modern TiAl alloys are depending on the phase fraction of the γ and the α_2 phase as well as on the microstructure (i.e. the thermal treatment)
- The high-T strength and creep resistance can be improved by increased amounts of α_2
- γ-TiAl exhibits a ductile-to-brittle transition at ~830°C



Property	Ti-based alloys	Ti_3Al-based α_2 alloys	TiAl-based γ alloys	Superalloys
Density ($g\ cm^{-3}$)	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[a]
RT tensile strength (MPa)	480—1200	800—1140	450—700	620—1620[a]
Highest temperature with high creep strength (°C)	600	750	1000	1090
Temperature of oxidation (°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	$L1_0$	fcc/$L1_2$

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

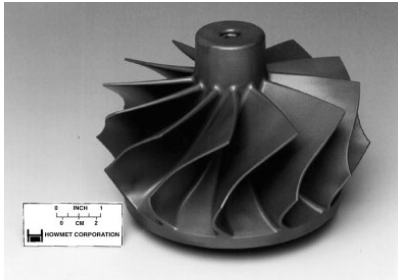




Titanium aluminides

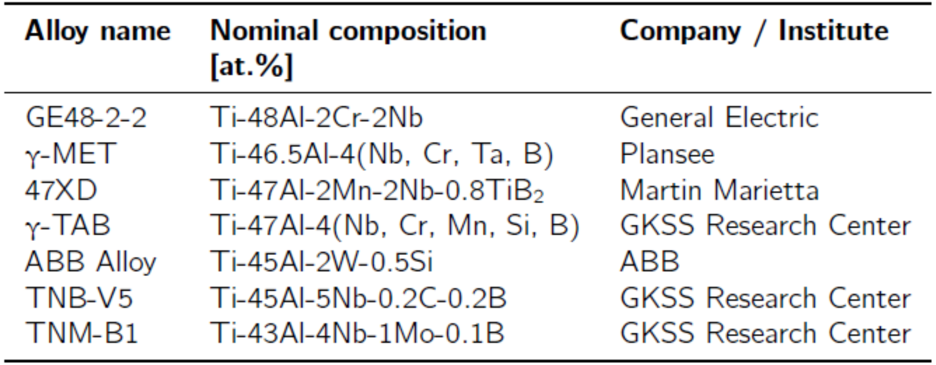
Applications

- 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



Turbo charger parts

Selected state-of-the art TiAl alloys



Alloy name	Nominal composition [at.%]	Company / Institute
GE48-2-2	Ti-48Al-2Cr-2Nb	General Electric
γ-MET	Ti-46.5Al-4(Nb, Cr, Ta, B)	Plansee
47XD	Ti-47Al-2Mn-2Nb-0.8TiB_2	Martin Marietta
γ-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

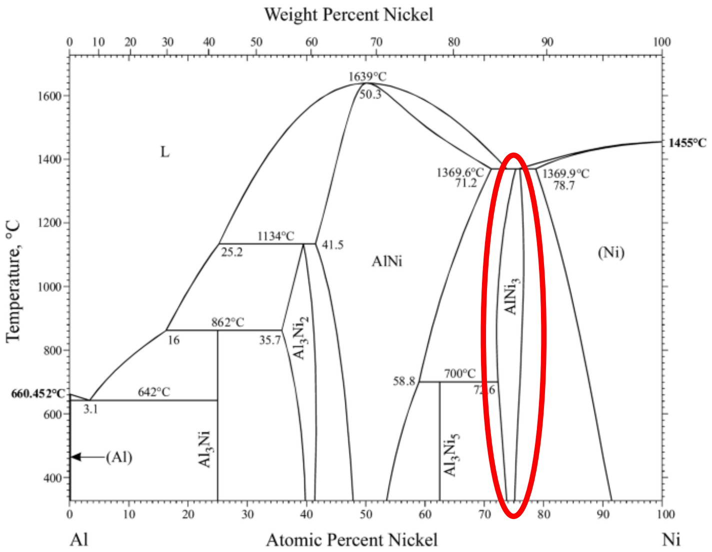
Vanes in aeroengines

Nickel aluminides

Properties of Ni_3Al

- Ni_3Al polycrystals: Brittle due to soft grain boundaries; boron addition can strengthen boundaries.
- Single crystals: Ductile with dislocation glide on {111}/<110> slip systems (von Mises criterion met).
- Oxidation: 13 wt% Al insufficient for dense Al_2O_3 layer at HT; forms NiO with some Al_2O_3.
- Properties: γ-Ni_3Al lacks significant advantages over Ni alloys in physical, mechanical, or corrosion resistance.

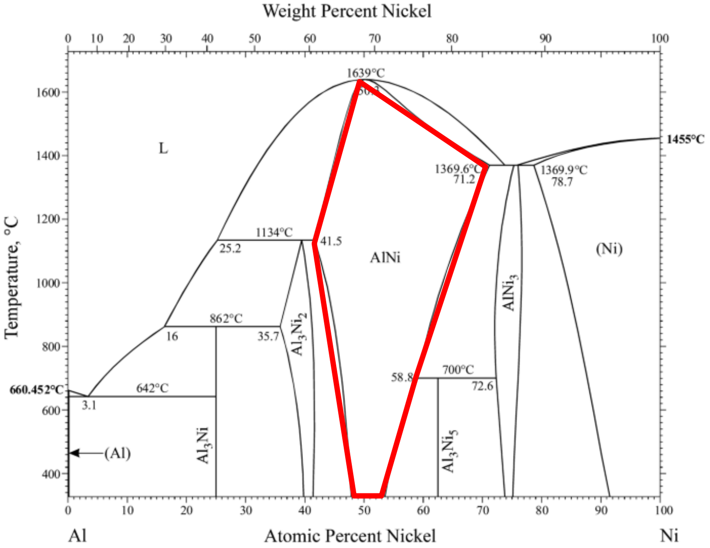
IMC	Crystal structure	T_{oc} [°C]	T_m [°C]	ρ [g/cm³]	E [GPa]
Ni_3Al	$L1_2$ (ordered fcc)	1390	1390	7.5	179



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 Ts) 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.

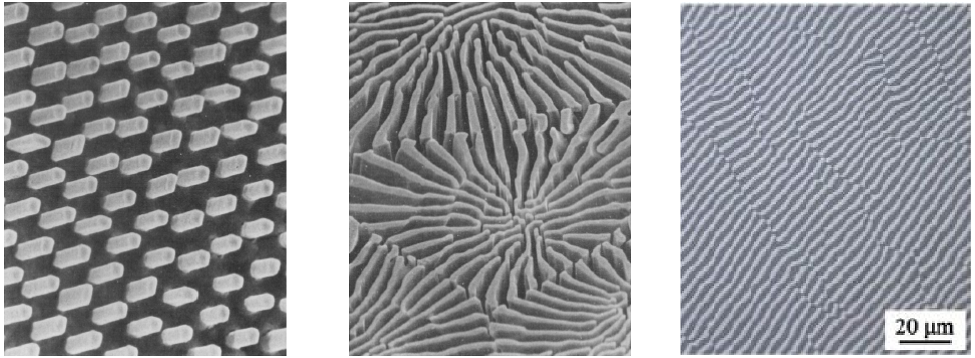


IMC	**Crystal structure**	**T_{oc} [°C]**	**T_m [°C]**	**ρ [g/cm³]**	**E [GPa]**
NiAl	B2 (ordered fcc)	1640	1640	5.86	194

Nickel aluminides

Alloying strategies for improving mechanical properties of NiAl

- Improving NiAl toughness & strength: schieved 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



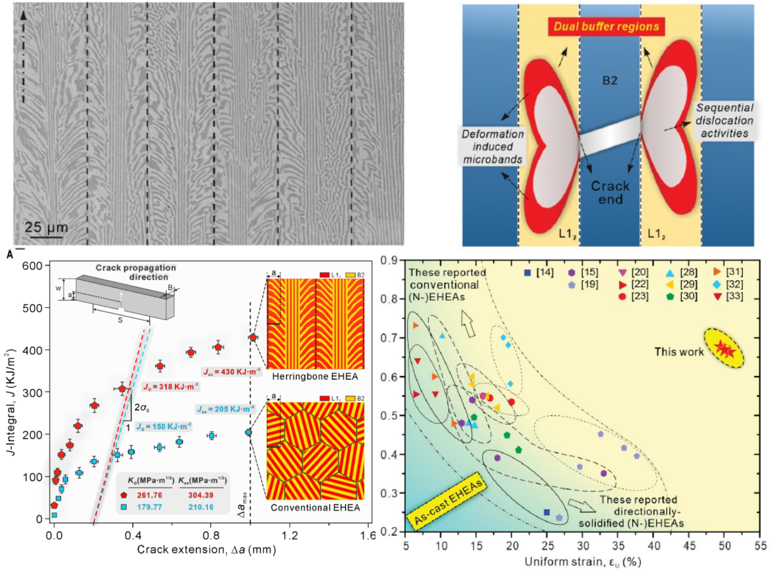
left: NiAl-Cr showing aligned Cr rods in deep-etched NiAl matrix
center: NiAl–Cr(Mo), showing Cr-Mo lamellae in deep-etched NiAl matrix
right: unetched transverse view showing aligned Cr(Mo) lamellae in NiAl matrix

/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

- Example: 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 $L1_2$ (Ni-24Co-27Fe-11Al) phases in lamellar structure.
- Herringbone pattern guides microcrack nucleation in brittle B2 phase, while ductile $L1_2$ phase buffers and prevents crack propagation, delaying failure

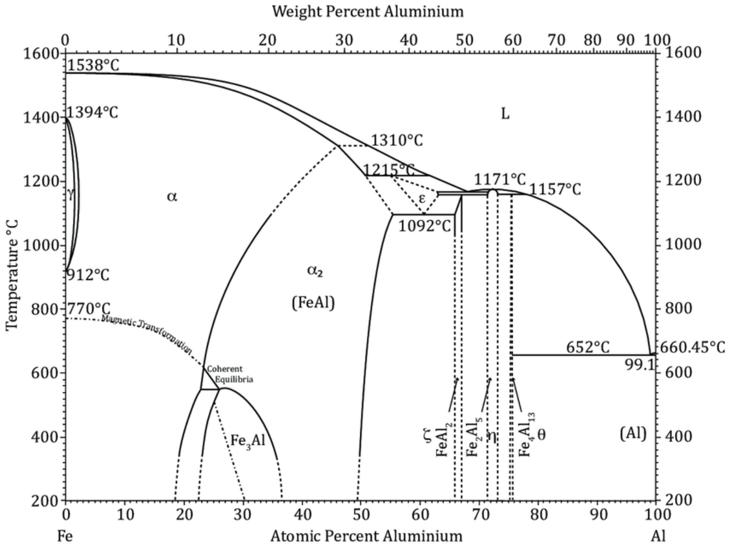


/P.Shi et al., Science. 373 (2021) 912–918/

Iron aluminides

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

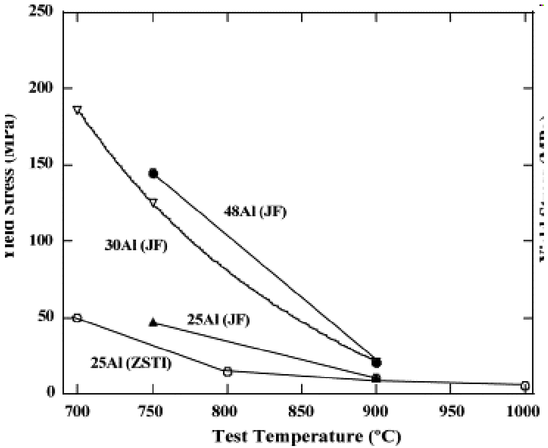
IMC	Crystal structure	T_{oc} [°C]	T_m [°C]	ρ [g/cm³]	E [GPa]
Fe_3Al	$D0_3$ (ordered bcc)	540		6.72	141
	B2 (ordered bcc)	760	1540		
FeAl	B2 (ordered bcc)	1250	1250	5.56	261



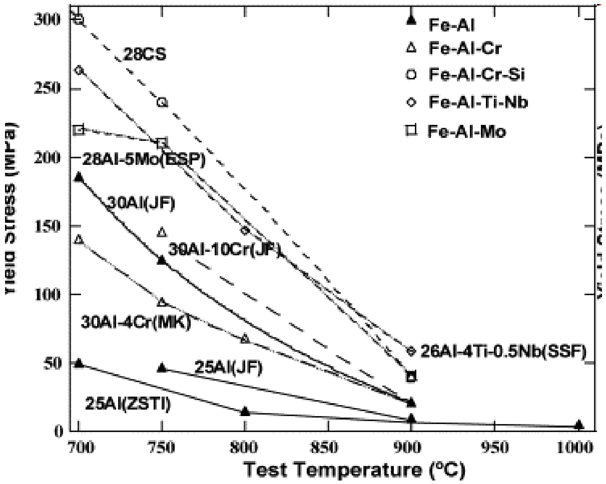
Iron aluminides

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%.



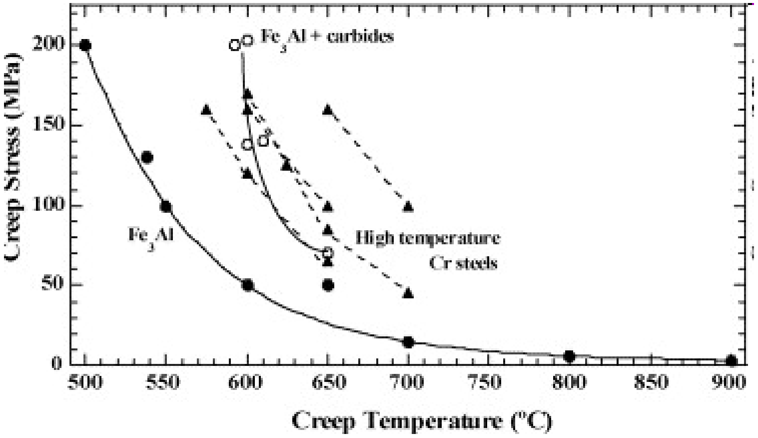
Comparison of flow stresses of high temperature binary Fe–Al alloys and some ternary Fe–Al–X solution alloys.

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

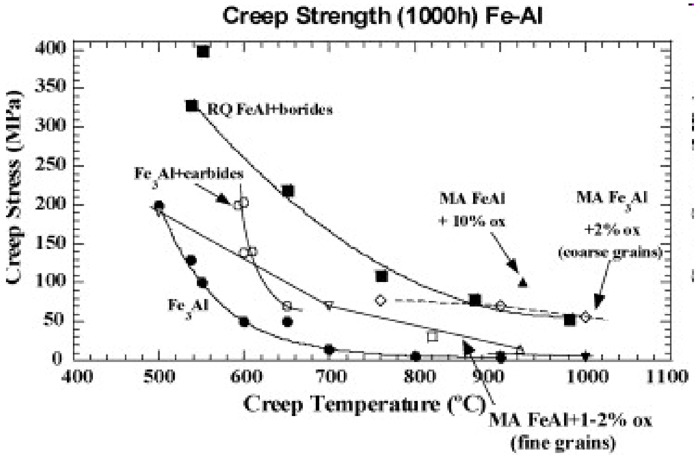
Iron aluminides

Creep behavior

- The creep resistance of Fe_3Al and 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 Fe_3Al, Fe_3Al with carbide additions, and advanced high-temperature steels.



1000 h creep strength of binary Fe_3Al, and various Fe_3Al or 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