MSE-422 – Advanced Metallurgy

Exercise 3: Ni alloys

If any questions contact:

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Question 1

The alloys Inconel 738LC (IN-738LC), CMSX-2, and CMSX-4 represent three generations of Ni-based superalloys, widely used for turbine blades in stationary gas turbines. Their chemical compositions (in wt.%) are listed in Table 1. While IN-738LC is a conventionally cast alloy, CMSX-2 and CMSX-4 are first- and second-generation single-crystal superalloys, respectively.

Figure 1 shows the Larson-Miller plots of the three alloys. Consider a turbine blade operating under high-temperature and high-stress conditions.

		Elements (wt.%)											
Alloy	**Generation**	**Ni**	**Cr**	**Co**	**Mo**	**W**	**Re**	**Al**	**Ti**	**Ta**	**Zr**	**B**	**C**
IN-738LC	Conventionally cast	bal.	16	8.5	1.75	2.6	—	3.4	3.5	1.75	0.05	0.01	0.13
CMSX-2	1st generation SX	bal.	8	4.6	0.6	8	—	5.6	1	6	—	—	—
CMSX-4	2nd generation SX	bal.	6.5	9.6	0.6	6.4	3	5.6	1	6.5	—	—	—

Table 1: Chemical composition of Inconel 738LC, CMSX-2 and CMSX-4 (in wt.%)

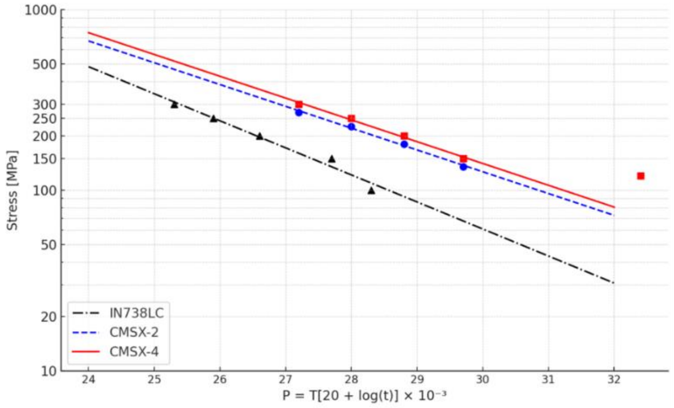
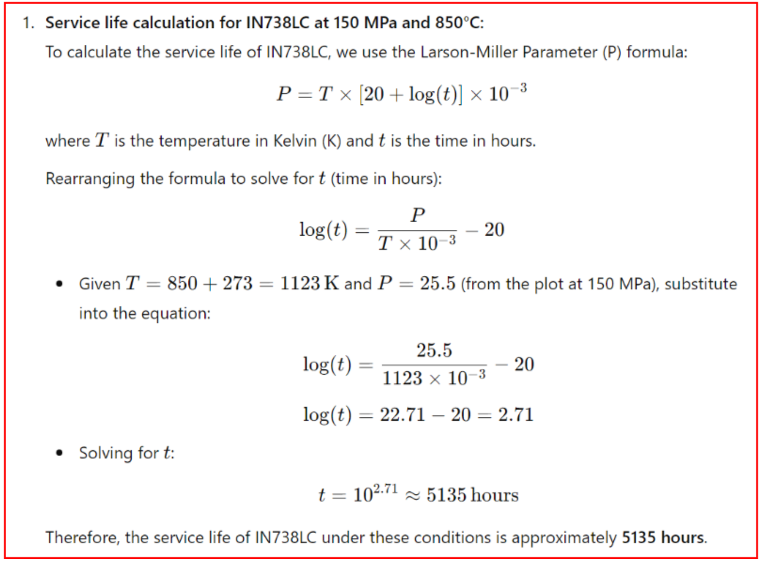


Figure 1. Larson-Miller diagrams of IN738-LC, CMSX-2 and CMSX-4

Question 1

a) Using the provided Larson-Miller plots:

- **Calculate the service life of the turbine blade at a stress of 150 MPa and a temperature of 850°C if it is made from IN738LC**



1. **Service life calculation for IN738LC at 150 MPa and 850°C:**

   To calculate the service life of IN738LC, we use the Larson-Miller Parameter (P) formula:

   $$P = T \times [20 + \log(t)] \times 10^{-3}$$

   where T is the temperature in Kelvin (K) and t is the time in hours.

   Rearranging the formula to solve for t (time in hours):

   $$\log(t) = \frac{P}{T \times 10^{-3}} - 20$$

   - Given $T = 850 + 273 = 1123\,\mathrm{K}$ and $P = 25.5$ (from the plot at 150 MPa), substitute into the equation:

   $$\log(t) = \frac{25.5}{1123 \times 10^{-3}} - 20$$

   $$\log(t) = 22.71 - 20 = 2.71$$

   - Solving for t:

   $$t = 10^{2.71} \approx 5135\ \mathrm{hours}$$

   Therefore, the service life of IN738LC under these conditions is approximately **5135 hours**.

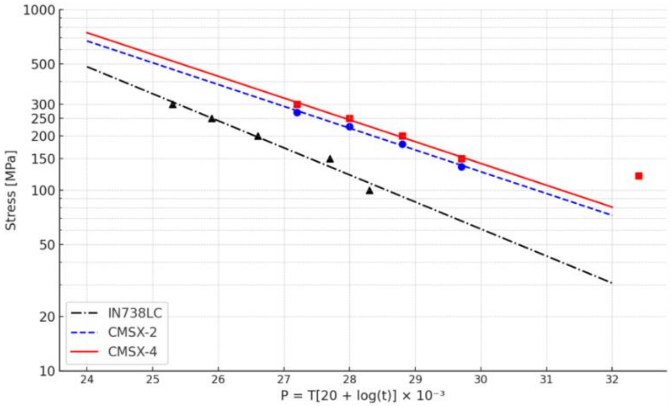
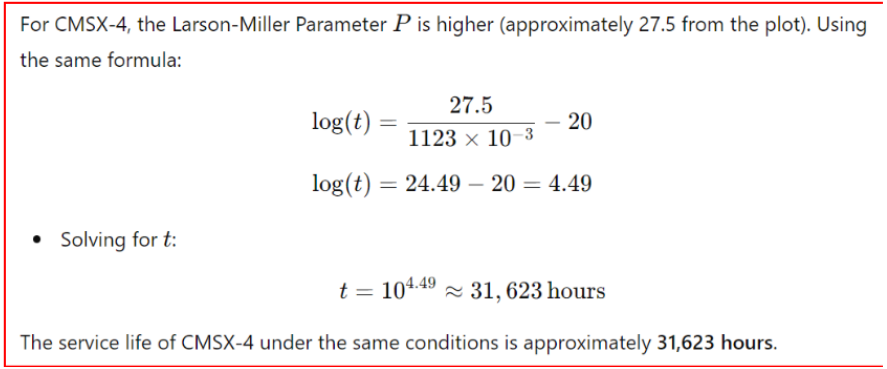


Figure 1. Larson-Miller diagrams of IN738-LC, CMSX-2 and CMSX-4

Question 1

a) Using the provided Larson-Miller plots:
   - Calculate the service life of the turbine blade at a stress of 150 MPa and a temperature of 850°C if it is made from IN738LC
   - **Calculate the gain in service life if the blade is instead made from CMSX-4.**



For CMSX-4, the Larson-Miller Parameter P is higher (approximately 27.5 from the plot). Using the same formula:

$$\log(t) = \frac{27.5}{1123 \times 10^{-3}} - 20$$

$$\log(t) = 24.49 - 20 = 4.49$$

- Solving for t:

$$t = 10^{4.49} \approx 31,623\,\text{hours}$$

The service life of CMSX-4 under the same conditions is approximately **31,623 hours**.

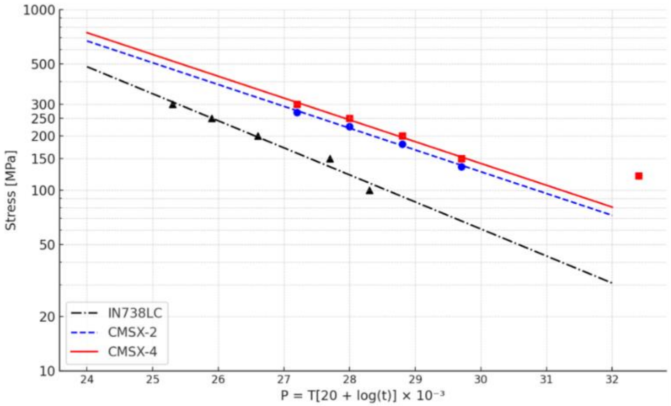


Figure 1. Larson-Miller diagrams of IN738-LC, CMSX-2 and CMSX-4

Question 1

b) What are the primary metallurgical and mechanical reasons for the significant difference in creep life between IN738LC and CMSX-4? Consider the role of alloying elements and microstructure

- CMSX-4 has higher Re and Ta content, improving solid solution strengthening , and stacking fault energy
- CMSX-4's single-crystal structure eliminates grain boundaries, reducing creep deformation mechanisms.

c) Why are Zr, B, and C included in IN-738LC but absent in CMSX-2 and CMSX-4?

- These elements strengthen grain boundaries, necessary in conventionally cast alloys like IN738LC. Single-crystal alloys do not require grain boundary strengthening

d) Considering their chemical compositions, explain the increased creep performance of CMSX-4 in comparison with CMSX-2.

- CMSX-4 contains rhenium, which increases solid solution strengthening, decreases SFE and enhances phase stability at high temperatures.

Question 1 – Additional Information

Mostafaei, A. *et al.* Additive manufacturing of nickel-based superalloys: A state-of-the-art review on process-structure-defect-property relationship. *Progress in Materials Science* **136**, 101108 (2023).

The strengthening mechanism in the Nickel-based superalloys can be attributed to the alloying elements that are selectively included in the austenitic nickel matrix. For instance, Cr, Fe, Co, Mo, W, Hf, Re, and Ru prefer to exhibit in the γ-grain matrix and contribute to the solid solution strengthening of the Nickel-based superalloys; whereas the other elements such Al, Ti, Nb, and Ta tend to partition and form Ni3Al (γ′) or Ni3Nb (γ′′) precipitates with ordered crystal structures (i.e., L12 or D022, respectively). Other examples are the B, C, and Zr elements that have the tendency to segregate in grain boundaries in form of strengthening solute-clusters or precipitates combined with Ti, Ta, Hf, Cr, and Mo. Fig. 1(b) presents the typical alloying elements exist in Nickel base superalloys are illustrated.

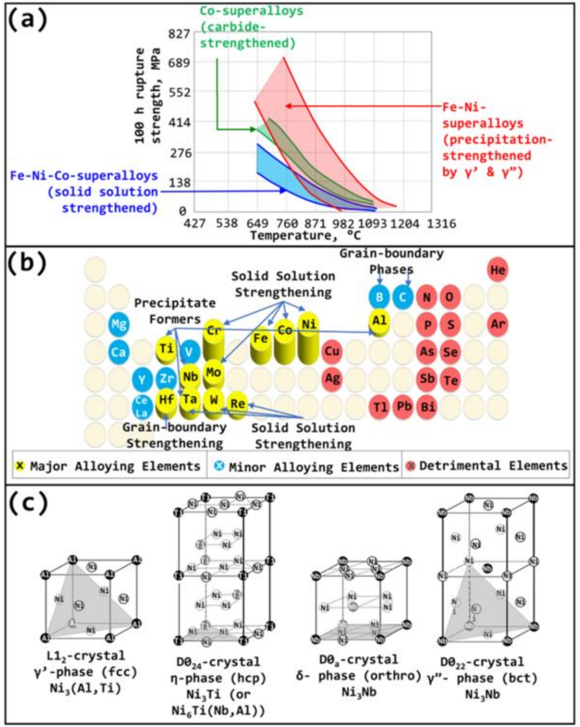


Fig. 1. (a) Typical stress-rupture behavior of three types of superalloy classes, i.e., the iron-nickel-, nickel-, and cobalt-base). Reproduced from [36]. (b) Typical alloying elements exist in the superalloys. Reproduced from [36] (c) Crystal structures of geometrically closed-packed (gcp) phases with ordered crystal structures, i.e., γ′, γ″, δ and η phases found in the microstructure of superalloys. Note that open hollow circle represents Ni atoms, and the solid black circle represents the M atoms (i.e., Al, Ti, and Nb) in compounds; also, a shaded plane shows the closest packed plane in crystal structure. Reproduced from [28].

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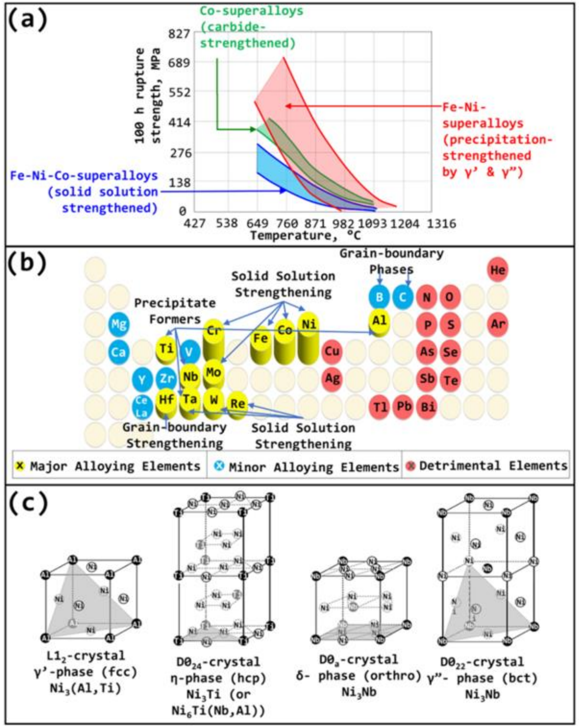
In general, the microstructure of Nickel-based superalloys consists of austenitic (fcc) γ-grain nickel matrix and a range of other secondary phases. Examples are (1) fcc-type carbide phases (i.e., MC, M6C, M23C6, M7C3); (2) the gamma prime (γ′) phase, which is a fcc-type Ni3(Al,Ti) ordered phase; (3) the gamma double prime (γ′′) phase, which is a body-centered tetragonal (bct) type Ni3Nb ordered phase; (4) the eta (η) phase, which is a hexagonal closed pack (hcp)-type Ni3Ti (or Ni6TiAlNb) ordered phase; (5) the delta (δ) phase, which is an orthorhombic Ni3Nb ordered intermetallic compound [27]. The γ′, γ′′ and η phases are also known as the geometrically closed-packed (gcp) phases [26].



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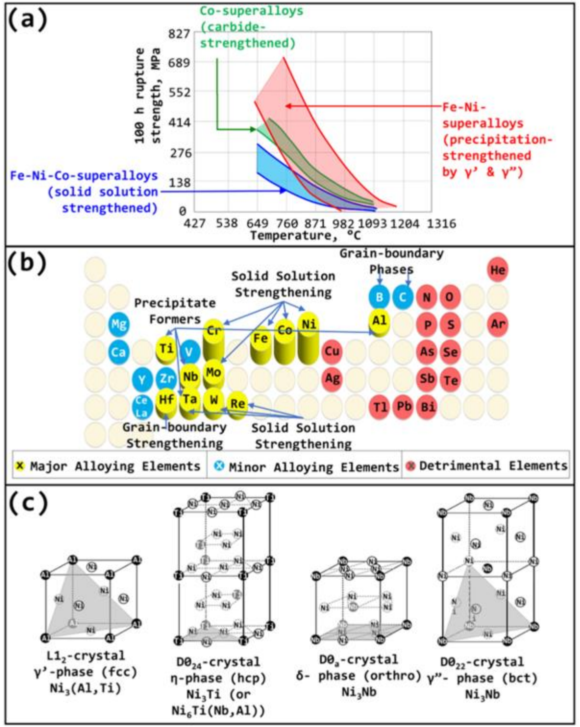
Due to their ordered crystal structure, the γ′, γ′′, δ and η phases play an important strengthening role in the Nickel-based superalloys. This is because they require extra energy to get passed by the dislocations. The ordering increases the antiphase boundary (APB) and stacking fault (SF) energies, which in turn increase the strengthening effect of these phase. The strengthening effect of the ordered phases could be ascribed to the fact that certain elements always occupy specific locations in their crystal structures. For instance, in the ordered (fcc) γ′-phase (i.e., Ni3(Al, Ti)), the Nickel atoms always occupy the face centered positions in the cubic crystal structure while the Ti and Al atoms always occupy the corner positions that are shared with eight other neighboring atoms. In contrast, in the disordered structures, atoms may occupy any given locations and therefore the presence of each atom is identified by a volume or weight fraction within the known unit cell crystal structure [28]. Fig. 1(c) presents the crystal structures of γ′, γ′′, δ and η phases. It is notable that there are other phases in the microstructure of Nickel-based superalloys which are known to have detrimental effect on their mechanical properties. Examples are (1) sigma (σ) phase with a tetragonal crystal structure (i.e., FeCr, FeCrMo, CrFeMoNi, CrCo and CrNiMo); (2) mu (μ) phase with a Rhombohedral crystal structure (i.e., Co2W6 and (Fe, Co)7(Mo, W)6); and (3) Laves phase with a hexagonal crystal structure (i.e., Fe2Nb, Fe2Ti, Fe2Mo, Co2Ta, and Co2Ti). These σ, μ and Laves phases are so known as the topologically close-packed (tcp) phases that mostly likely can form at the interface of γ-matrix and the gcp phases (i.e., γ′, γ′′, δ and η) with an irregularly elongated plate-like or needle-like morphology and less frequently at grain boundary areas [26,29].



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Question 1

e) Figure 2 shows a scanning electron micrograph of heat-treated IN-738LC with the typical γ-γ' microstructure.

- **Explain the terms "primary γ’ " and "secondary γ’ " precipitates in the context of IN-738LC. Discuss their roles in strengthening the alloy and indicate where they can be observed in the micrograph shown in Figure 2.**

- Primary γ': Coarse, provide long-term creep resistance. Visible as larger particles in Figure 2.

- Secondary γ': Finer, strengthen against dislocation motion. Visible as smaller particles.

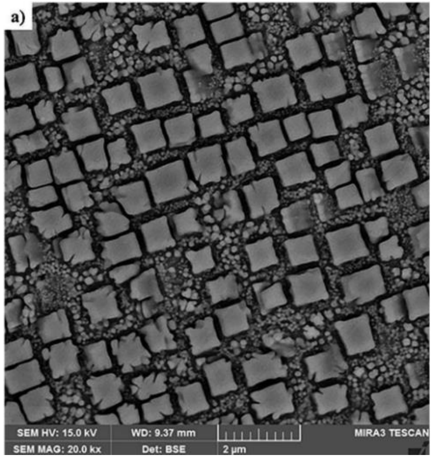

Figure 2. SEM – micrograph of IN-738LC after heat treatment

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- Explain the terms "primary γ'" and "secondary γ'" precipitates in the context of IN-738LC. Discuss their roles in strengthening the alloy and indicate where they can be observed in the micrograph shown in Figure 2.
- **Define the term "antiphase boundary" as it relates to the γ' phase in Ni-based superalloys. Explain how antiphase boundaries contribute to the strengthening mechanisms of these alloys.**

- Antiphase boundaries arise when dislocations cut through ordered γ' precipitates, requiring additional energy, thereby strengthening the alloy.

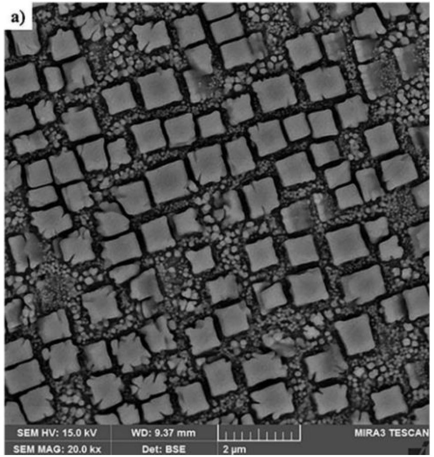
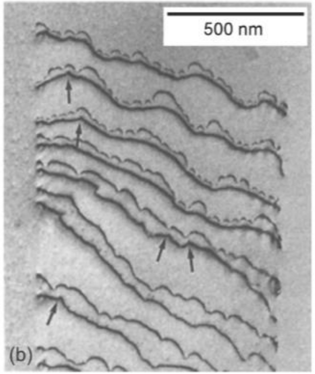


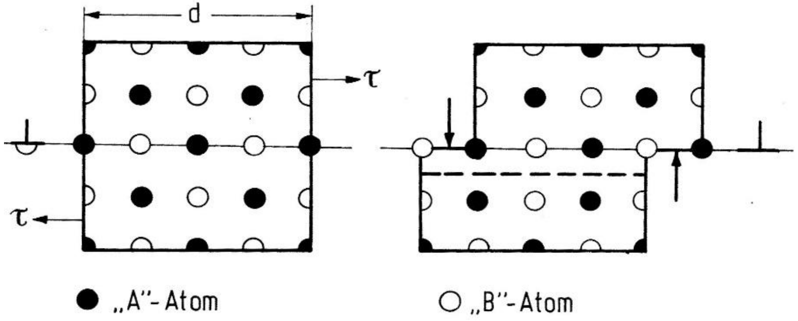
Figure 2. SEM – micrograph of IN-738LC after heat treatment

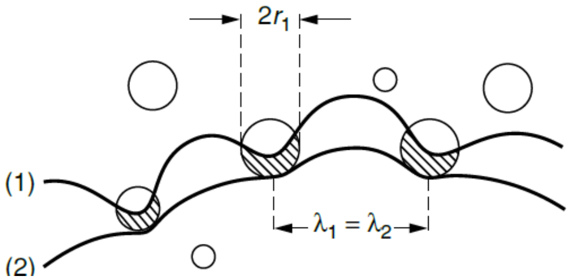
Reminder:Strengthening mechanisms in Ni alloys

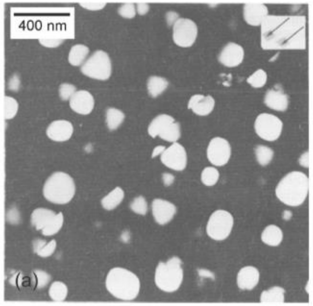
Precipitation strengthening - the γ’-Ni_3Al phase

- Because of the ordered nature of Ni_3Al, cutting by one single dislocation will create an anti-phase boundary (APB)
  → atoms are in an unfavored configuration
- Dislocations must travel through the *γ/γ’* structure in pairs, with a second dislocation removing the anti-phase boundary introduced by the first
- The associated anti-phase boundary energy, γ_{APB}, represents a barrier which must be overcome if particle cutting is to occur







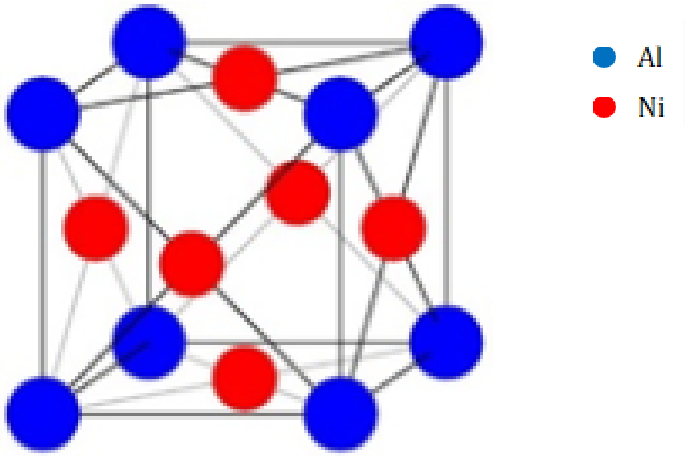


/R.C. Reed, The superalloys – fundamentals and applications, 2006/

Question 2

a)The γ'-phase is important for the high-T performance of Ni superalloys.

- **Sketch the unit cell and give the basic stoichiometry of the γ'-phase.**



Question 2

a)The γ'-phase is important for the high-T performance of Ni superalloys.

- Sketch the unit cell and give the basic stoichiometry of the γ'-phase.
- **What elements are the γ'-phase formers?**

"Al, Ti, Nb, and Ta tend to partition and form Ni3Al (γ′) or Ni3Nb (γ″) precipitates with ordered crystal structures (i.e., L12 or D022, respectively)"

Question 2

a)The γ'-phase is important for the high-T performance of Ni superalloys.

- Sketch the unit cell and give the basic stoichiometry of the γ'-phase.
- What elements are the γ'-phase formers?
- **Explain why the γ'-phase provides an efficient strengthening effect at high-T**

γ'- phase forms coherent precipitates in the Ni matrix, which are stable up to melting point. As γ'-phase has an ordered structure, cutting by one dislocation creates anti-phase boundaries (APB). The associated APB-energy, γAPB, represents a barrier for dislocation movement/particle cutting. Dislocations must travel through the γ/γ’ structure in pairs, with a second dislocation removing the anti-phase boundary introduced by the first

Question 2

b) Explain briefly why high-pressure turbine blades are produced from single crystal Ni-superalloys and not from wrought Ni alloys

Single crystal:

No grain boundaries -> high creep resistance (no grain boundary sliding).

Grain oriented in <001> direction -> direction with lowest E-modulus.

Question 2

c) Why is <001> the preferred growth direction during single crystal fabrication

The <001> direction is the direction with the lowest E-modulus (126GPa)
-> for equal load, the stress is lower.

Question 2

d) Why does the amount of γ' in technical SX-Ni alloys typically not exceed 60 vol%?

Technical Ni alloys are characterized by large cuboidal γ’ grains with connected γ channels containing small globular γ’ grains. For amount of γ’ higher than 60%, the γ-channels become disconnected.

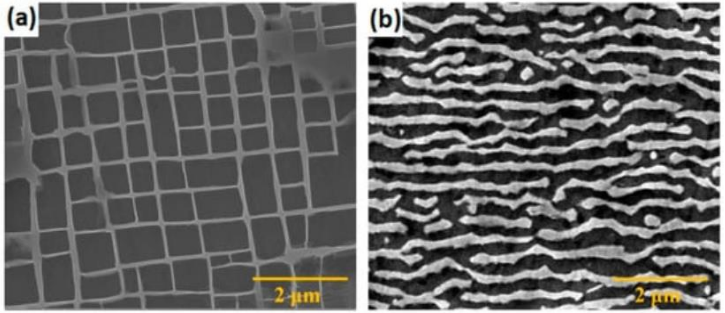
Question 3

You recently joined an Aerospace company as a material expert and you are responsible for the selection, processing and characterization of high-performance Ni and Ti alloys.

a) Your team leader gave you the following scanning electron micrograph (Figure 3), which shows the cross section of a single crystalline turbine blade of the alloy CMSX-4 after 1'000 h of service with a maximum temperature of 950°C in an aero-engine. The alloy has the composition (in wt.%) given in Table 2.

- **Name the phases that can be seen in the micrograph**

γ/γ'



Ni	Cr	Co	Mo	Al	Ti	Ta	Hf	Re
Bal.	6.5	9	0.6	5.6	1.0	6.5	0.1	3.0

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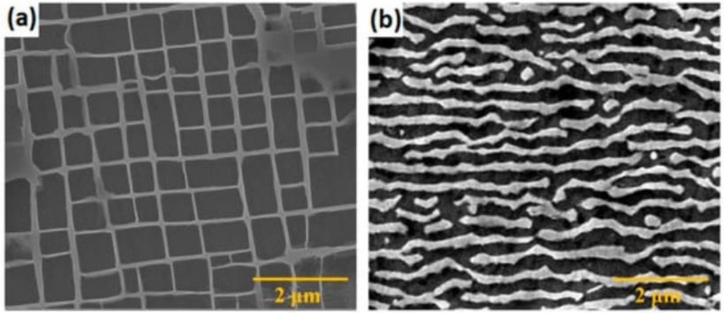
- Name the phases that can be seen in the micrograph
- **Explain the role of the alloying elements Cr and Re.**



Cr: forms Cr-rich protective layer, solid solution strengthener (carbide former, less so in CSMX-4)

Re: solid solution strengthener, delay coarsening of γ' (reduction of γ/γ' lattice misfit)

Ni	Cr	Co	Mo	Al	Ti	Ta	Hf	Re
Bal.	6.5	9	0.6	5.6	1.0	6.5	0.1	3.0

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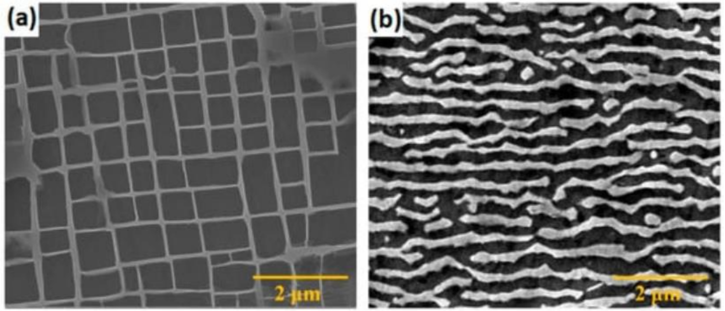
- Name the phases that can be seen in the micrograph
- Explain the role of the alloying elements Cr and Re.
- **Explain the microstructural changes that can be observed between the two micrographs.**

What is the common name for this phenomenon?



Rafting;
Directional coarsening is caused by the superposition of external load stresses and internal coherence stresses
If the γ'/γ lattice mismatch is positive (aγ < aγ') type P , If the γ'/γ lattice mismatch is negative (aγ > aγ') type N (most frequent case)
This results in different local stress fields in the γ channels perpendicular and parallel to the loading direction
These stress differences are the driving force for a directional diffusion; the γ' particles grow in the direction of the lower lattice distortion in the γ channels

Question 3

b) Your team leader shares the results from stress rupture tests performed at different test parameters on Ni-based super alloy used for turbine blades (shown in Figure 4). Consider that LMP = T (ln(t) + c) × 10^{-3} and that the Larson miller parameter constant c is 25.

- **What stress can be applied so that the service life of the alloy at 500°C is 6000 h.**

LMP = 773 (In (6000) + 25)
= 26049 ~ 26000
Log σ = 2.75
σ = 562 MPa

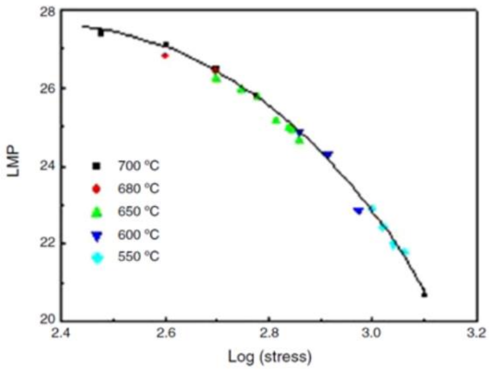


Figure 4. Larson Miller Parameter (LMP) correlation with stress obtained from stress rupture test of Ni-based super alloy

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- What stress can be applied so that the service life of the alloy at 500°C is 6000 h.
- **Additionally, your team leader wishes to have a safety factor of 10% considering the testing uncertainty. What will be your suggested stress for application of the alloy at 500°C is 6000 h?**

Considering the safety factor =
562 x 0.9 = 506 MPa

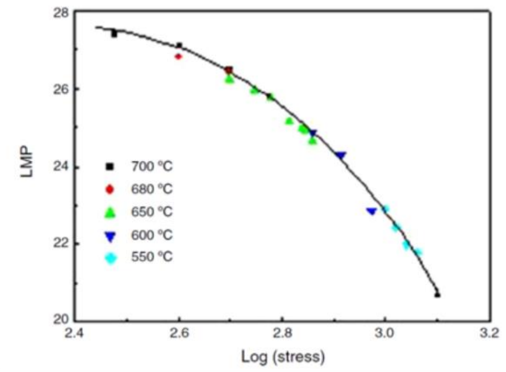


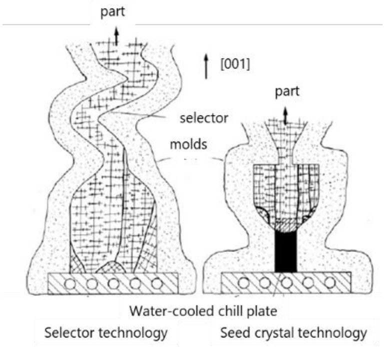
Figure 4. Larson Miller Parameter (LMP) correlation with stress obtained from stress rupture test of Ni-based super alloy

Question 4

Figure 5-a shows a single-crystalline (SX) turbine blade, which was made from the Ni-based superalloy CMSX-4 using the Bridgman furnace process (schematic Figure 5-b). During the casting process, the withdrawal velocity was set to 20 mm/min and the thermal gradient at the solid/liquid interface was set to 2500 K/m.

a) Explain the function of the 'pig-tail' in the lower part of the cast turbine blade.

Pig tail = single crystal selector: only one grain will reach the upper part of the casting mold. Since fcc-Ni grows fastest in (100) direction, a (100) grain will be selected.



/Maier, Niendorf, Bürgel – Handbuch Hochtemperatur-Werkstofftechnik, 2015/

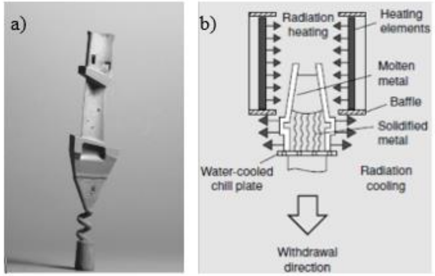


Figure 5: a) Single-crystalline turbine blade; b) schematic of the Bridgman furnace process

Question 4 – Additional Information

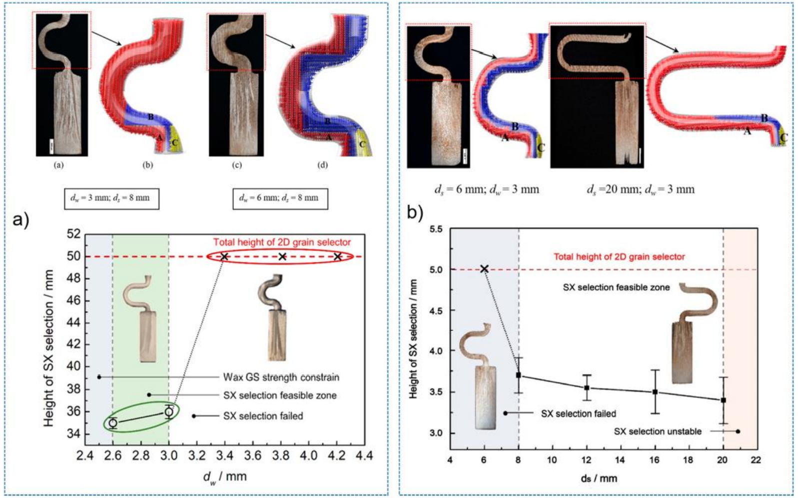


Figure 5. Relationship between the height for SX selection and the wire diameter (dw) of the selector (**a**), and relationship between the height for SX selection and the pitch length (ds) of the selector (**b**).

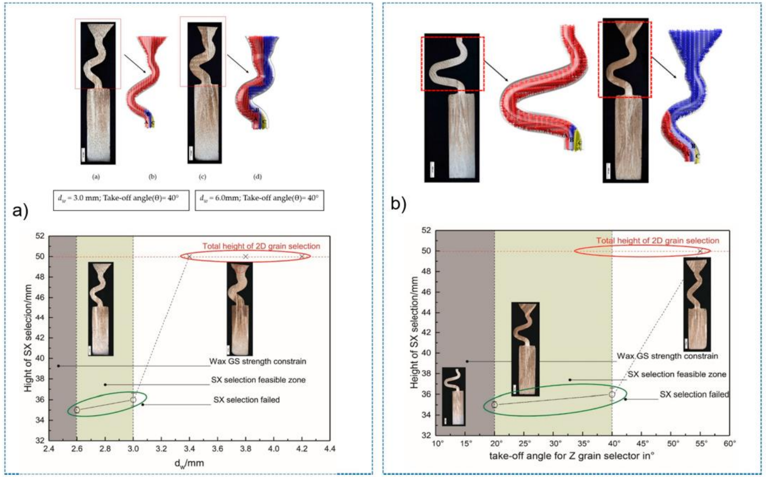


Figure 6. Relationship between the height for SX selection and the wire diameter (dw) of the selector (**a**), and relationship between the height for SX selection and the take-off angle of the selector portion (**b**).

"A Study of Grain Selection in Two-Dimensional (2D) Grain Selectors during the Investment Casting of Single-Crystal Superalloy"

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a) Explain the function of the 'pig-tail' in the lower part of the cast turbine blade.

b)Name and briefly explain two typical casting defects that would occur when increasing the withdrawal velocity to 40 mm/min.

High-angle GBs: if the withdrawal velocity is too high, the heat flow is not uniaxial anymore. The solidification front is curved and dendrites do not grow parallel anymore.

Globular grains: nucleation of grains ahead of solidification front and growth in all directions.

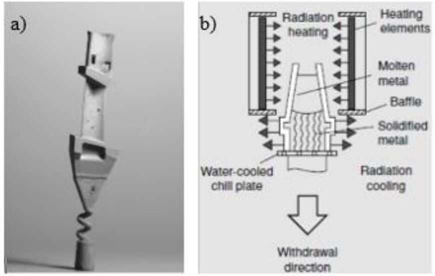

Figure 5: a) Single-crystalline turbine blade; b) schematic of the Bridgman furnace process

Question 4

After casting, components fabricated from single-crystal superalloys undergo a complicated heat treatment designed to remove the microsegregation inherited from the casting process.

c)Explain briefly why microsegregation occurs during casting of Ni superalloys.

Alloying elements have different solubility in solid and liquid phase (C_s and C_L) → partitioning coefficient $k=C_S/C_L$

1.K<1 → enrichment of element x in the liquid

2.K>1 → enrichment of element x in solid

The element x cannot diffuse quickly enough a) from the liquid to solid or b) out of solid into liquid

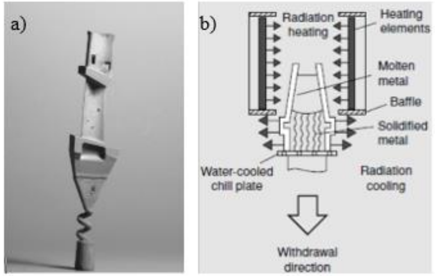

Figure 5: a) Single-crystalline turbine blade; b) schematic of the Bridgman furnace process

Question 4

After casting, components fabricated from single-crystal superalloys undergo a complicated heat treatment designed to remove the microsegregation inherited from the casting process.

c)Explain briefly why microsegregation occurs during casting of Ni superalloys.

d)What would be the implications of not heat-treating the cast components?

Formation of regions with (near) eutectic compositions and low melting point in the interdendritic regions -> risk of liquation cracking upon heating

Non-homogeneous element distribution and variation of physical and mechanical properties in the volume

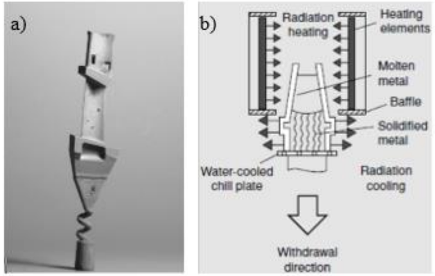

Figure 5: a) Single-crystalline turbine blade; b) schematic of the Bridgman furnace process

Question 4

Creep samples from the single-crystal superalloys TMS-75 and TMS-82+ alloys were cast such that the compositions of the γ and γ'-Ni_3Al phases were on a common tie-line, so that the phase compositions remain invariant. The compositions of the two alloys (in wt.%) are given in *Table 3*. *Figure 6* shows the creep rupture life of the two alloys as a function of the fraction of the γ' phase present at 900°C and at 1100°C.

e) Explain the general shape of the curves, i.e. the first increasing and then again decreasing creep rupture life with increasing γ' phase fraction. Why is the maximum creep resistance not imparted at a 50% fraction of γ' phase?

Increasing amount of γ’ -> increasing particle strengthening effect

Beyond 60 vol% γ-channels (to which dislocation movement is constrained) become disconnected and γ' regions are predominant (creep behavior of γ' intrinsically lower than γ)

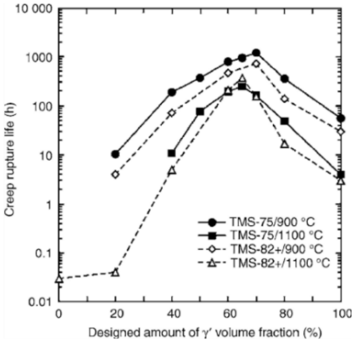

Figure 6: Creep rupture life of TMS-75 and TMS-82+ as a function of the fraction of the γ' phase

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e) Explain the general shape of the curves, i.e. the first increasing and then again decreasing creep rupture life with increasing γ' phase fraction. Why is the maximum creep resistance not imparted at a 50% fraction of γ' phase?

f) Explain the in general higher creep rupture life of the TMS-75 alloy at γ' phase fractions below 60 vol%.

Alloy	Co	Cr	Mo	W	Al	Ti	Ta	Hf	Re	Ni
TMS-82+	7.8	4.9	1.9	8.7	5.3	0.5	6.0	0.1	2.4	Bal.
TMS-75	12.0	3.0	2.0	6.0	6.0	-	6.0	0.1	5	Bal.

TMS-75: higher amount of mainly Co+Re

Co → reduces SFE + solid solution strengthening

Re → pronounced solid solution strengthener + reduction of γ'/ γ-misfit → delayed coarsening of γ'

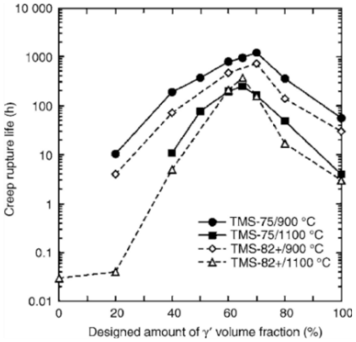


Figure 6: Creep rupture life of TMS-75 and TMS-82+ as a function of the fraction of the γ' phase

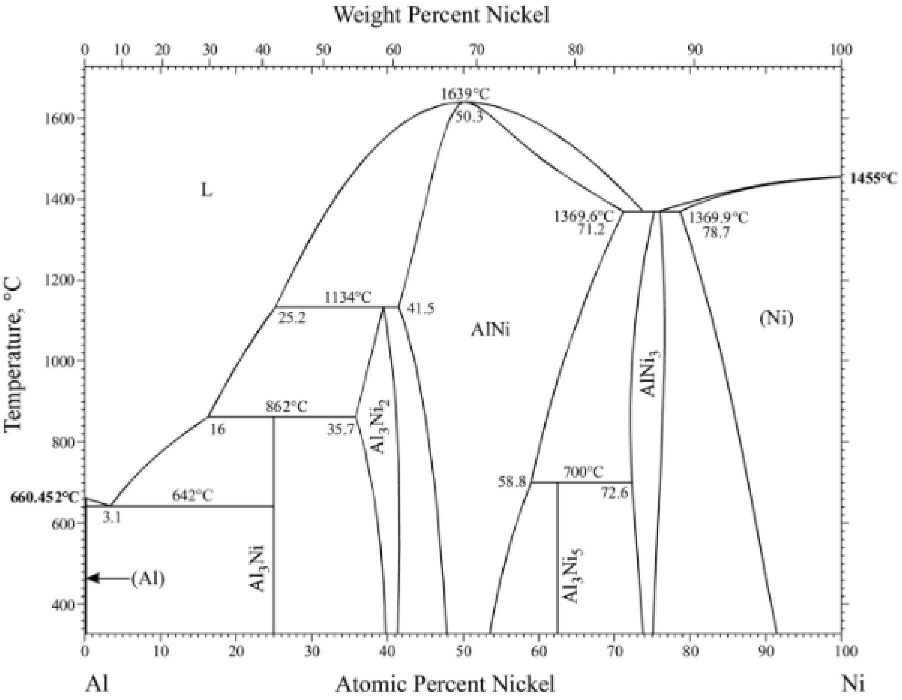
Question 4

g)Give two reasons why alloys with a composition of approximately 50 at.% Ni and 50 at.% Al are of interest as a replacement for Ni superalloys for high-temperature applications such as turbine blades.

Lower density

Higher amount of Al and thus formation of dense Al_2O_3 layer C à protection against HT corrosion

Higher melting point than Ni and Ni-alloys



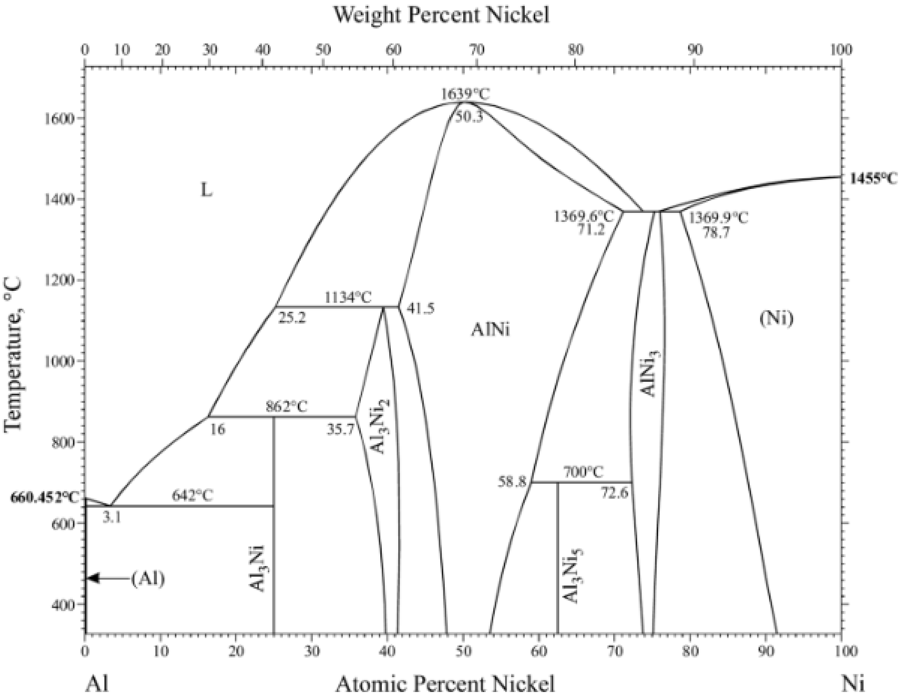
Question 4

h) Is the phase NiAl a Laves phase? Justify your answer.

It is not a Laves-phase

Laves phases are of type A2B or AB2

NiAl is not



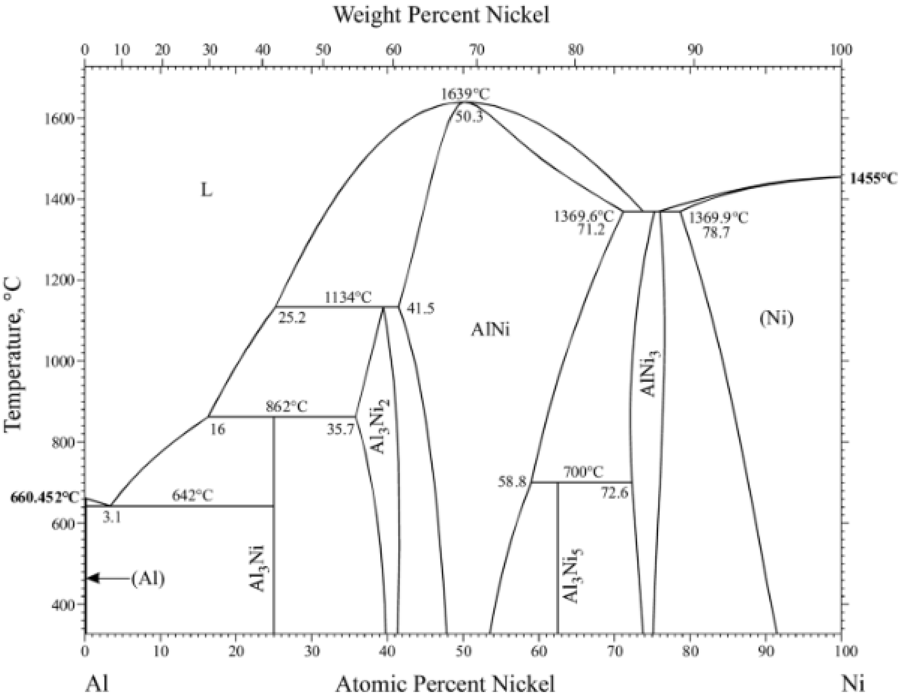
Question 4

i) Explain why pure NiAl exhibits a poor ductility and, as a result, a high notch sensitivity at temperatures below 650°C.

It is a B2 superstructure

High Peierls stresse

Availability of only 3 independent slip systems



Question 4

j)As a result of this low ductility, shape forming of NiAl using e.g. milling or turning is extremely challenging. Name an briefly explain an alternative method that could be used to fabricate parts with more intricate geometries such as turbine blades

Powder metallurgy could be an alternative:

Fabrication of powder via e.g. EIGA

Shape forming

Sintering