a) What is the expected composition of Pb_xTe_y grains (in at.%) measured by EDS in point A on Pb elemental map? (1 pt) *Because the average measured composition of the whole sample was Pb-40at% Te-60at% (Pb_2Te_3), this must be also the composition of the homogenous melt just before its solidification. In attached Pb-Te binary diagram we have to follow the solidification process along a vertical line made at composition 60 at% of Tellurium. As the composition of this melt is hypo-eutectic one should expect during its solidification: i) formation of primary solid grains with composition PbTe (50/50 at%) in the rest of the liquid phase, starting at ~830 ℃. As the cooling and solidification proceeds the composition of liquid phase is gradually changing along the liquidus line towards a higher concentrations of Te, until it reaches the exact eutectic composition (Te-89.1at% / Ge-10.9at%) at the eutectic temperature 410.9 ℃. Under this temperature the last part of the liquid phase solidifies and forms the eutectic, e.g. mixture of PbTe (50/50 at%) and pure Te phases. Point A on Pb elemental map is located inside a primary grain (single phase with one composition) and therefore measured EDS composition should be close to 50at% Pb and 50at% Te (1pt).*

b) What is the expected composition (in at.%) measured by EDS in Area B on Te elemental map? Explain your answer. (2 pt) *Measured composition here should be close to 89.1 at% Te and 10.9 at% Pb (1 pt), expecting to measure the eutectic composition (1 pt), because Area B on Te elemental map is located inside the eutectic area, a mixture of two phases.*

c) Mixture of which two phases is present on the boundaries between grains? (2 pt) *This area contains eutectic of Pb-Te, which according the binary diagram is formed by the mixture of PbTe (50/50 at%) phase and pure Tellurium phase (2 pt).*

d) Which part of the bulk sample started to solidify first, which second and at which temperatures? (3 pt) *Primary grains of PbTe (50 at%/50 at%) phase (1 pt) started to form at ~830 ℃ (1/2 pt) and they gradually grow during cooling until the eutectic temperature (410.9 ℃) is reached. Area in EDS maps between primary grains is the eutectic (1 pt) and solidifies at once when the temperature lowered eutectic temperature 410.9 ℃ (1/2 pt).*

e) Calculate with the lever rule the fractions of different phases present in this Pb_2Te_3 alloy at 600 ℃ and at 200 ℃ (4 pt) *At 600 ℃ with composition of 40at% Pb and 60at% Te we have in equilibrium the PbTe (50/50 at%) solid phase (1/2 pt) and the liquid phase with composition: 22at% Pb and 78at% Te (1/2 pt). From the lever rule the amount of solid phase is: (78-60)/(78-50) = 18/28 = 64.3% (1/2 pt). Similarly the amount of liquid phase is: (60-50)/78-50) = 10/28 = 35.7% (1/2 pt).*
At 200 ℃ the whole sample is solid and contains: (100-60)/(100-50) = 40/50 = 80% (1/2 pt) of PbTe (50/50 at%) phase (1/2 pt) and (60-50)/(100-50) = 10/50 = 20% (1/2 pt) of pure Tellurium phase (1/2 pt).

f) Can you give a potential explanation, why the composition of the bulk does not correspond to the composition of original powder mixture (50/50 at.%) prepared by the researcher? (2 pt) *From the binary diagram one may read that the melting temperature of pure Pb (327.5 ℃) is lower than melting temperature of pure Te (449.6 ℃) (1 pt). These two pure elements represent two starting solid phases, which must be melted before they may form a homogeneous melt. During heating to 950 ℃ liquid Lead evaporates from the melt faster than liquid Tellurium (due to a lower melting temperature) (1pt) and therefore composition of the melt is changed towards a melt richer in Tellurium.*

g) Schematically draw the solidified microstructure, coarsely including the relative fractions of the different phases, in case the measured average composition would have been Pb_3Te_2 (instead of Pb_2Te_3 above). Clearly mark areas of different phases in your sketch with indication of their phase composition. At which temperature was this microstructure completely solidified? (4 pt) *During solidification of the Pb_3Te_2 melt we have to follow vertical solidification line made in binary diagram at 40at% of Te. Solidification starts at ~860 ℃ by formation of primary PbTe (50/50 at%) solid grains dispersed in a liquid phase. As solidification during cooling proceeds the composition of the melt gradually changes towards higher concentrations of Lead, until the composition of pure Lead is reached at 327.5 ℃. Under this temperature the microstructure completely solidifies (1 pt) containing primary grains of PbTe (50/50 at%) and pure Lead (1 pt) on their grain boundaries. Using the lever rule, the pure Lead phase will form (50-40)/50 = 20% fraction of the solidified sample. One possible drawing with a legend follows (2 pt).*
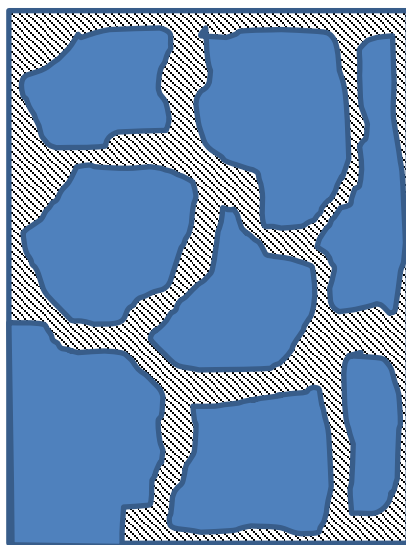
■ *PbTe (50/50 at%)*

▨ *Pb (pure) occupies about 20% of the sketch area*

Exercise 2 (19 points)

A crane lifts with a steel cable with a length of 10 meter its maximum weight of 25000 kg, i.e. 25 tons. Due to the load the cross sectional area of the cable is reduced by 0.12 %. The Poisson ratio of the steel is 0.30 and its Young's modulus is 200 GPa. The steel cable behaves according to linear elasticity, which is also required because of safety. Note that for the calculations below we do not need high precision, i.e. answers with 3 significant number are sufficient.

a) First calculate the strain $\varepsilon_\perp$ acting in the cross sectional area, then calculate the strain $\varepsilon_{//}$ parallel to the length of the cable and calculate the elongation of the cable (preferably in cm). (3 pt) *Let cross sectional area of the original cable was $\frac{1}{4}\pi d^2$. After loading the cross section will be: $\frac{1}{4}\pi(d+\Delta d)^2$. Ratio $\frac{1}{4}\pi(d+\Delta d)^2/\frac{1}{4}\pi d^2$ equals to the relative change of cross sectional area, e.g. 0.9988. Which means: $\frac{\Delta d}{d} = \sqrt{0.9988} - 1 = -0.0006 = \varepsilon_\perp$. Strain perpendicular to the loading direction is -0.0006. Comparing equations for strain in loading direction and direction perpendicular to the loading direction: $\varepsilon_{||} = \frac{\sigma}{E}$ and $\varepsilon_\perp = -v\frac{\sigma}{E}$, one may deduce: $\varepsilon_{||} = \frac{\varepsilon_\perp}{-v} = -\frac{0.0006}{-0.3} = 0.002$. Strain of the cable in loading direction is 0.002, which means that elongation of the 10m long cable in cm is: 10 x 100cm x 0.002 = 2 cm.*

b) Calculate the stress σ in the cable. (1 pt) If you could not answer question a) then assume that the elongation of the cable was 1 *cm*. *To calculate the stress in the cable we may use any of two strains calculated in previous question. Let's use the strain in loading direction: $\varepsilon_{||} = \frac{\sigma}{E}$. Which means: $\sigma = \varepsilon_{||}.E = 0.002 \times 200\ GPa = 400\ MPa$.*

c) Calculate the diameter of the cable. (3 pt) *Using eq. $\sigma = F/A_o$ we may calculate initial cable diameter: $A_o = \frac{F}{\sigma} = \frac{25000\ x\ 9.81\ N}{400\ x10^6\ Pa} = 6.13\ x10^{-4} m^2 = \frac{1}{4}\pi d^2$. Diameter of the cable $d = \sqrt{\frac{6.13\ x\ 10^{-4}m^2}{\frac{\pi}{4}}} = 0.0279\ m = 2.79\ cm.$*

Consider a single crystal of Ni (nickel). It has an fcc (face centered cubic) structure and a critical resolved shear stress of 30 MPa. The load is applied parallel to the $[1\bar{1}1]$ axis. (Explicitly take into account in your answers the overstrike symbol on the middle 1)

d) How many of the total number of slip options of fcc will become active when slip starts to occur in the crystal? Clearly show how you obtain your answer. (4 pt) *The equation for critical resolved shear stress that has to be used is:*
$$\tau_R = \sigma.\cos\phi.\cos\lambda$$
where σ is externally applied stress, ϕ and λ are angles between direction of external stress and i) slip plane normal and ii) slip direction, respectively. In fcc crystal the slip systems are formed by {111} slip planes and $\langle110\rangle$ slip directions. There are four different slip planes in fcc structure: $(111), (\bar{1}11), (1\bar{1}1)$, and $(11\bar{1})$. In each of these slip planes three different slip directions exist. To determine which slip directions exist in each slip plane we will use the equation for angle between two arbitrary vectors $[uvw]$ and $[xyz]$ in Cartesian coordinates:
$$\cos\alpha = \frac{(ux + vy + wz)}{\sqrt{u^2 + v^2 + w^2}\sqrt{x^2 + y^2 + z^2}}$$
where in the numerator the dot product of two vectors is given and in the denominator there is the product of the lengths of the 2 vectors (Pythagoras). In cubic systems the vector [xyz] represents the normal to the plane (xyz). Due to the fact that each of slip direction lies in its corresponding slip plane, the vector of slip direction must be

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perpendicular to the corresponding slip plane normal. For instance slip plane (111) will contain those of 6 possible slip directions $< 110 >$, which are perpendicular to the [111] vector. Using above equation one may conclude that in (111) slip plane the following three slip directions may be active: $[1\bar{1}0]$, $[10\bar{1}]$ and $[01\bar{1}]$ because these three vectors are perpendicular ($\cos \alpha = 0$) to the slip plane normal [111].

    As the external load on the single Ni crystal acts in $[1\bar{1}1]$ direction we may exclude from consideration all slips in $(1\bar{1}1)$ slip plane, because for all these slips: $\cos \lambda = 0$, e.g. there is no shear stress induced in a plane perpendicular to the load direction (1 pt). For the rest of slip systems we may calculate $\cos \phi = \frac{1}{3}$ for (111) slip plane and $\cos \phi = -\frac{1}{3}$ for both $(\bar{1}11)$ and $(11\bar{1})$ slip planes (1 pt). Calculating $\cos \lambda$ for all possible (6) slip directions and the direction of applied stress $[1\bar{1}1]$ we will get: $\cos \lambda = 0$ for [110], [011] and $[10\bar{1}]$ slip directions, $\cos \lambda = \pm \sqrt{\frac{2}{3}}$ for the rest of them: [101], $[1\bar{1}0]$ and $[01\bar{1}]$ (1 pt). From this analysis one may conclude that following slip systems could be potentially active (1 pt):

Plane: (111)　　　　　Directions: $[1\bar{1}0]$ and $[01\bar{1}]$
*　　　　$(11\bar{1})$　　　　　　　　　$[101]$ and $[1\bar{1}0]$*
*　　　　$(\bar{1}11)$　　　　　　　　　$[101]$ and $[01\bar{1}]$.*

e) At which load σ will the atomic planes start to slide (with respect to each other)? Clearly show how you compute your answer. (3 pt) *Substituting into the equation for critical resolved shear stress for slip systems with non-zero values of $\cos \phi$ and $\cos \lambda$ we will get:*

$$30\ MPa = \sigma \cdot \left(\pm \frac{1}{3} \right) \cdot \left(\pm \sqrt{\frac{2}{3}} \right),$$

which means

$$\sigma = \pm 3 \cdot \sqrt{\frac{3}{2}} \cdot 30\ MPa = \pm 110\ MPa \text{ (3 pt)}$$

Particular selection of the slip system will depend on a type of external load (tensile or compression), which is not specified in the question. Atomic planes start to slide when external load reaches 110 MPa.

f) Explain in your own words why in aviation industries the following construction and service rules are very important: a) avoiding sharp changes of the shape; b) regular body material inspections (e.g. also with ultrasound); c) final lifetime. Take into account the most traditional material, operating temperature and characteristic loading conditions. (5 pt) *In aviation industry the safety is very important because dealing with human's life. The most traditional material is Aluminium and its alloys, due to their favourable strength/density ratio (1pt). Taking into account low operating temperatures (~ minus 60 °C) and loading variations (vibrations, taking-offs, landings) one have to consider not only strength but also the fracture toughness and fatigue resistance of applied materials (1pt). Due to the fact, that Al does not show the fatigue limit, it is not possible to design a construction without a danger of fatigue crack propagation and the final brittle fracture. Therefore regular inspections are necessary to check the presence and the size of defects having a potential to growth and finally lead to a catastrophic failure (1pt). Avoiding of sharp changes in the construction shape eliminates the potential of*

Solutions Q3:

a. The energy per unit volume to fracture a material is related to the area under the stress-strain curve. When materials only show a very high tensile strength, but do not show any appreciable strain upon fracture (which typically can occur when straining is only elastic and no plastic deformation can occur), then the area under the stress-strain curve is still very small and it costs little energy to break the material (2 pt).

A material which is nominally loaded at a stress level well below its UTS can still experience, due to stress concentrations, a local stress well above UTS. These stress concentrations are present at the tips of sharp scratches or small defect (like small pre-cracks) inside the materials. Then at these tips cracks must grow due to the high stress. With plastic deformation sharp tips then automatically become blunted and the stress level at the tip goes down and fracture can be stopped. However, when the material (has a very high tensile strength but) does not show plastic deformation, then it is not able to reduce large stress concentrations, sharp crack tips cannot be blunted and the crack will grow catastrophically, even at low nominal stress levels. So, a very high UTS is in this case of very little use. (4 pt)

The above two issues come together in the so-called fracture toughness of the material (energy or stress needed to break a material when a pre-crack is present). This can also be part of above descriptions.

b. When metallic bonding is dominant the electrons are delocalized, i.e. can freely move between the remaining ionic cores and therefore these materials can in general be plastically deformed well. With ionic and covalent bonding the electrons are localized and these materials do not easily allow sliding of atomic planes with respect to each other and are thus, in basic form, hard, brittle and exhibit low fracture toughness. A perfect piece of material can be very strong, but their strength reduce a lot when defects are present. (Max 2 points for this discussion of the effect of bonding).

When role of dislocations is properly integrated in the above descriptions then this is rated positively. That is: dislocations can easily form and slide in metals thereby explaining the plastic deformability of metals and have difficulty to form (because are higher energy defects) in ionic and covalently bonded materials and even when they are present, their mobility is much lower than in metals. This explains why materials with ionic and covalent bonding are hard, brittle and have low fracture toughness.

c. Weight average molecular weight: 0.10x200 + 0.16x400 + 0.21x600 + 0.24x800 + 0.29x1000 = 20+64+126+192 + 290 = 592.

First find number fractions from weight fractions:
$(0.1 + 0.16/2 + 0.21/3 + 0.24/4 + 0.29/5)C = 1$, i.e. $C = 1/0.368$
Now possible to calculate number average molecular weight:
$(0.1 \times 200 + (0.16/2) \times 400 + (0.21/3) \times 600 + (0.24/4) \times 800 + (0.29/5) \times 1000)/0.368 = (20 + 32 + 42 + 48 + 58)/0.368 = 200/0.368 \approx 543.5$

d. Vulcanizations means that the different long molecules in the rubber become cross-linked (In the long molecules still per monomer a double bond remains present after polymerization. These double bonds are reaction sites for bonding with sulfur atoms that can link different molecules together). In a normal state the long molecules are present in the rubber in a disordered curled state. Then upon loading these molecules become stretched, but due to the crosslinks cannot slide with respect to each other. So, when the loading is released, the natural state of the molecules is to curl back. Individual molecules do not curl back to their exact shape as before loading, but the huge numbers of molecules together in the rubber still curl back to about identical shape as before loading. When the rubber is not vulcanized, molecules can slide with respect to each other upon loading and then the rubber deforms permanently by visco-elastic deformation.

Solutions Q4:
a. The best material is the one where the line with slope $E^{1/3}/\rho$ can be shifted most to the upper left corner of the graph. In this case FIR is the best, ALUMINAS is intermediate and STEEL is worst.
b. The best material is the one where the line with slope E/ρ can be shifted most to the upper left corner of the graph. In this case ALUMINAS is best and FIR and STEEL are worse and are about on the same line. STEEL tends to be a bit better than FIR, but the difference is limited.
c. The most efficient shape for resisting bending is a thin-walled hollow rectangle with height perpendicular to the bending axis larger than the width. Exactly the same efficiency can be obtained by a so-called I-profile. The reason is that in these shapes we bring as much as possible material as far as possible from the bending axis (without making the shape too vulnerable to buckling). (2 pts)
The most efficient shape for resisting torsion is a thin-walled hollow tube, because then we bring as much as possible material as far as possible from the rotation axis (without making the shape too vulnerable to wrinkling). (2 pts)
These shapes influence the materials selection, because not all materials can be made as easily (economically) in these shapes. Particularly metals and polymers (particularly thermoplasts) can be easily shaped efficiently, but like wood and ceramics cannot be shaped (and composite materials are intermediate). For lowest weight stiff and strong designs when only solid shaped are compared then wood and CFRP are typically the best materials, much better than the heavy steel. But when steel can be shaped to these thin walled hollow sections then steel becomes again very competitive with wood, even for lowest weight designs. So, the bottom line is that shaping also influence the selection of the most suitable materials. (2 pts)
d. In the first design we can make a thicker plate with a regular pattern of holes in it. The total volume must not increase, i.e. the volume increase by thickening the plate must be compensated by the volume reduction due to the holes. The thickness increase can still

increase the stiffness of the plate since the stiffness relates to the distance to the bending axis squared (whereas the total volume of the plate containing material is unaltered).

The second design we can make a much thinner plate, but put a square pattern of ribs which are can now be relatively high (perpendicular to the plate), because have limited width. So, the solution is to make a plate in the x-y plane where **both in the x and the y direction** instead of a constant thickness D, now a modulation in thickness is used, where generally the thickness is for instance D/2, but periodically ribs on the plate are present that give the plate there locally a thickness of for instance 2D. See an example of a side view of such a plate below, where of course this side view holds for both x- and y-direction. Compared to a plate with uniform thickness weight can be saved, while still the stiffness of the plate increases.

There are more solutions like a thin walled honeycomb structure in-between two thin parallel plates, but with an overall much thicker plate mostly containing empty space within.

Solutions Q5:

a. First it is essential to note that the conductivity is proportional to the product of the number of free charge carriers (e.g. free electrons) and the charge carrier mobility. In metals the number of free charge carriers (electrons) is huge and does not change noticeable with temperature. However, the charge carrier mobility reduces for increasing temperature, because at higher temperature atoms will vibrate more severely and this results in more scattering of electrons and thus lowers their mobility. The effect is that the resistivity of metals increases about linearly with increasing temperature. (2 pts for metals part).

In intrinsic semiconductors the number of free charge carriers (electrons) is zero at zero Kelvin and they are perfect insulators. At higher temperature the probability that electrons can jump over the band gap increases exponentially. The number of free charge carriers, both free electrons and holes, thus also increases exponentially with temperature. Similarly as for metals, the charge carrier mobility reduces for increasing temperature, but this linear decrease is very small compared to the exponential increase in number of charge carriers. The net effect is that the conductivity of semiconductors increases about exponentially with increasing temperature (3 pts for semiconductor part).

b. The big difference between intrinsic semiconductors and well doped n-type semiconductors is that for the latter the electrons do not have to jump over the complete bandgap, but have to jump over a much smaller energy barrier (from a donor level which is already very close to the bottom of the conduction band). Therefore the exponential increase in conductivity in the n-type semiconductor occurs already very fast above zero Kelvin, whereas this increase is much slower in the intrinsic semiconductors. However, already at relatively low temperature, typically say at 100-200 Kelvin all dopant atoms in the n-type semiconductor have donated their free electrons and this source of electrons is thus exhausted. Therefore, for a large temperature range around room temperature the number of free charge carriers for the n-type semiconductor does not change and the temperature dependent behaviour is very similar as for metals. However, the number of free carriers is about 10 million times lower than in the metals and thus the absolute value of the conductivity also orders of magnitude lower.

c. Stays similar, since both materials have the same concentration of hole dopants and when mixing them this concentration is not changed.

d. Decreases dramatically since the number of free electrons and holes are the same, they will compensate (fill) each other such that we kind of end up with the intrinsic semiconductor. At room temperature the conductivity of the intrinsic semiconductor is much lower than if this semiconductor is significantly doped with either n or p-type dopants.

e. Compared to the n-type semiconductor it decreases, but compared to the p-type semiconductor it increases! After mixing with the 4:1 ratio we are left with an n-type semiconductor only having 60% of the free electrons per unit volume as in the original n-type semiconductor. This of course gives a comparable reduction in conductivity at room temperature. However, the mobility of free electrons is typically about four times higher as of holes in semiconductors at room temperature. So, even if the concentration per unit volume of free electrons is reduced to 60% of the number of holes per unit volume then this significantly higher mobility of free electrons compared to holes still lead to a higher conductivity of this mixed semiconductor than the original pure p-type seminconductor.