

Homework #9A

solution outlines

Averill, Chapter 12

28. Covalent solids, such as the diamond form of carbon, have discrete, directional bonds. Application of a shearing force to the crystalline lattice requires many bonds in the plane parallel to the force to break without the opportunity to reform. Metals, on the other hand, are composed of atoms that are bonded to many nearest neighbors (12 in the case of hcp or ccp lattices), through the delocalization of bonding electrons. The ductility of metals (their ability to be drawn into wires) arises from the ability of the bonding electron density to deform to accommodate reorientation of the atoms to new lattice sites.
29. Work hardening increases the strength of a metal by forming a network of dislocations within the lattice that pin each other, preventing their migration in response to applied external forces. Due to this network of dislocations, the metal becomes less malleable, less ductile, and more brittle.
30. Work-hardened metals and covalent solids crack under applied stresses because of their inability to reorient atoms with respect to their nearest neighbors. In the case of work-hardened metals, this results from the pinning of dislocations. In covalent solids such as diamond, the discrete and directional nature of the covalent bonds hinders the local shifting of large blocks of atoms.
31. To improve the ductility of a metal, impurity atoms of similar size should be used. These will substitute for atoms on lattice sites without greatly disrupting the atomic packing and will therefore be less likely to hinder atomic reorientation during shaping of the sample. Atoms much smaller in size may act as interstitial impurities, while much larger atoms may aggregate due to their inability to substitute on lattice sites. Both defects will reduce the ability of the planes of metal atoms to move past each other. Impurity atoms that can form polar covalent bonds will decrease

ductility as a result of their directional bonding with neighboring metal atoms, again hindering reorientation of the metal atoms during the shaping process.

- 32.** Substitutional impurities are more effective at tuning the properties of a material when used in high concentrations because they typically have similar atomic properties as the host, often neighboring them on the periodic table. Interstitial impurities tend to have very different chemical properties than the host atoms, such as size and electronegativity, possibly leading to polar covalent bonding with neighboring host atoms. This disruption of the lattice has a larger effect on its physical properties, even at low concentrations.
- 33.** Since O^{2-} and F^{-} are both very similar in size, substitution is possible without disruption of the ionic packing. The difference in charge, however, requires the formation of a vacancy on another F^{-} site to maintain charge neutrality.
- 34.** To induce oxide vacancies in an ionic crystal, metal cations with less positive charge could be substituted for similarly sized cations in the lattice. For example, the replacement of Ti^{4+} with Mn^{2+} requires the formation of one vacancy on an O^{2-} lattice site to maintain charge neutrality.
- 35.** Many nonstoichiometric compounds contain transition metal ions that can exist in multiple oxidation states. Cations in different oxidation states require different numbers of anions to balance the total charge of the lattice, allowing the formation of point defects. For example, reduction (gain of electrons) of a cation in a lattice requires the formation of a vacancy on one of the anion sites to maintain charge neutrality.
- 36.** To induce oxide vacancies in an ionic crystal, metal cations with less positive charge should be substituted for similarly sized cations in the lattice. The substitution results in a net negative charge on the lattice, which must be compensated by removal of anions.

- 83.** Substitutional impurities have similar radii to the atoms (or ions) they replace. Since K^+ is much larger than Na^+ , it is unlikely to be a substitutional impurity.
- 84.** Interstitial impurities have much smaller radii than the atoms of the solid. Boron is the only possible interstitial impurity.
- 86.** Zirconium(IV) oxide and yttrium(III) oxide both contain cations in their highest oxidation states. Further, these cations are similar in size, so Y^{3+} should substitute for Zr^{4+} in the ZrO_2 lattice. For every two Zr^{4+} that are replaced, the total charge of the lattice changes by -2 , which is equal to the charge of an oxide ion. Therefore, one oxide vacancy will be formed for every two Y^{3+} that are added. Using the molar mass of Y_2O_3 , the number of moles of Y^{3+} is $2 \times (0.35 \text{ g}) \div (225.8 \text{ g/mol}) = 3.1 \times 10^{-3}$ mol. Therefore, the number of oxide vacancies formed will be 1.55×10^{-3} mol if all the Y^{3+} is incorporated.

To find the percentage of vacancies that are formed, the total number of oxide sites that should be present in the final Zr/Y oxide lattice must be determined. In the absence of vacancies, the final material would have a stoichiometry of MO_2 , meaning there should be two O^{2-} for every metal cation. The total number of cations is equal to the number of moles of Y^{3+} ($= 3.1 \times 10^{-3}$ mol) plus the number of moles of Zr^{4+} :

$$(25.0 \text{ g}) / (123.2 \text{ g/mol}) = 0.203 \text{ mol}$$

The total number of moles of cations is therefore 0.206 mol. Since there are two oxide sites for every cation, the number of oxide sites is $2 \times (0.206 \text{ mol}) = 0.412 \text{ mol}$. However, as discussed above, 1.55×10^{-3} mol of vacancies will be formed to balance the charge. The percentage of vacancies formed is therefore $(1.55 \times 10^{-3} \text{ mol}) \div (0.412 \text{ mol}) = 0.38\%$.

- 87.** To induce oxide vacancies, which causes a decrease in the total negative charge of the anion sublattice, the total positive charge of the cation sublattice must be decreased. This is accomplished by substituting a cation with a lower charge for Ca^{2+} . Although K^+ is considerably bigger than Ca^{2+} and may not fit well into the Ca^{2+} sites of the crystal structure, it is the only candidate for substitution. Substitution of F^- for O^{2-} would replace some of the oxides, but not create oxide vacancies; in fact, by the same rationale above this would result in Ca^{2+} vacancies.

$$1. \quad (i) f_v = A \exp -\frac{\Delta H_v}{k_B T} = 1.1 \exp -\frac{1.03 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-22} \times (20 + 273)} = 2.19 \times 10^{-18}$$

$$(ii) f_v = A \exp -\frac{\Delta H_v}{k_B T} = 1.1 \exp -\frac{1.03 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-22} \times (20 + 1085)} = 1.67 \times 10^{-4}$$

number of copper sites / unit volume (also known as *site density*) given by ratio of $N_{Av} / V_{molar} \therefore \text{site density} = 6.02 \times 10^{23} / 7.11 \text{ cm}^3 = 8.47 \times 10^{22}$

\therefore vacancy density = $f_v \times \text{site density}$

$$(i) \text{ vacancy density at } 20^\circ\text{C} = 1.85 \times 10^5 \text{ cm}^{-3}$$

$$(ii) \text{ vacancy density at } 1085^\circ\text{C} = 1.41 \times 10^{19} \text{ cm}^{-3}$$

NOTE: the ratio of $f_v(1085^\circ\text{C}) / f_v(20^\circ\text{C}) = 7.62 \times 10^{13} !!!$

2. All we need to know is the temperature dependence of the vacancy density:

$$\frac{n_v}{N} = A e^{-\frac{\Delta H_v}{RT}} \quad \text{where } T \text{ is in Kelvins and the m.p. of Ir is } 2446^\circ\text{C}$$

$$3.091 \times 10^{-5} = A e^{-\Delta H_v / RT_1}, \quad \text{where } T_1 = 1234^\circ\text{C} = 1507 \text{ K}$$

$$5.26 \times 10^{-3} = A e^{-\Delta H_v / RT_2}, \quad \text{where } T_2 = 2446^\circ\text{C} = 2719 \text{ K}$$

Taking the ratio:

$$\frac{5.26 \times 10^{-3}}{3.091 \times 10^{-5}} = \frac{A e^{-\Delta H_v / RT_1}}{A e^{-\Delta H_v / RT_2}} = e^{\frac{\Delta H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad \therefore \ln 170.2 = -\frac{\Delta H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\therefore \Delta H_v = -\frac{R \times \ln 170.2}{\frac{1}{1507} - \frac{1}{2719}} = -\frac{8.314 \times \ln 170.2}{\frac{1}{1507} - \frac{1}{2719}} = 1.44 \times 10^5 \text{ J/mole vac}$$

$$\therefore \Delta H_v = \frac{1.44 \times 10^5}{6.02 \times 10^{23}} = 2.40 \times 10^{-19} \text{ J/vac} = 1.5 \text{ eV/vac}$$

3.(a) We need to know the temperature dependence of the vacancy density:

$$\frac{1}{10^4} = A e^{-\frac{\Delta H_v}{kT_1}} \quad \text{and} \quad \frac{1}{10^3} = A e^{-\frac{\Delta H_v}{kT_x}}$$

$$\text{From the ratio: } \frac{\frac{1}{10^4}}{\frac{1}{10^3}} = \frac{10^3}{10^4} = \frac{A e^{-\Delta H_v / kT_1}}{A e^{-\Delta H_v / kT_x}} \quad \text{we get } -\ln 10 = -\frac{\Delta H_v}{k} \left(\frac{1}{T_1} - \frac{1}{T_x} \right)$$

$$\therefore \left(\frac{1}{T_1} - \frac{1}{T_x} \right) = \frac{k \ln 10}{\Delta H_v}$$

$$\frac{1}{T_x} = \frac{1}{T_1} - \frac{k \ln 10}{\Delta H_v} = \frac{1}{1073} - \frac{1.38 \times 10^{-23} \times \ln 10}{2 \times 1.6 \times 10^{-19}} = 8.33 \times 10^{-4}$$

$$T_x = 1200 \text{ K} = 928^\circ\text{C}$$

(b) repeat the calculation following the method given above but with $\Delta H_v = 1.0 \text{ eV}$ to find that $T_x = 1364 \text{ K} = 1091^\circ\text{C}$

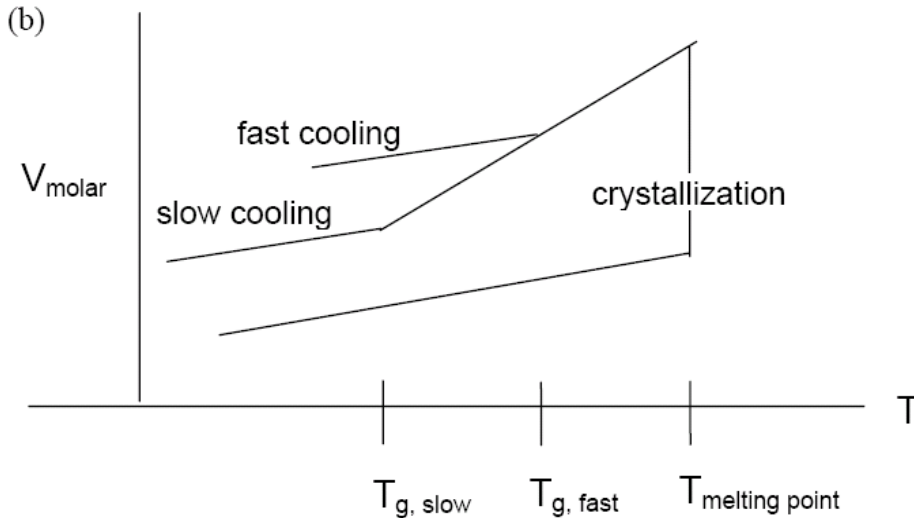
NOTE: the change in ΔH_v from 2.0 eV to 1.0 eV resulted in a change from 128 K to 291 K in ΔT .

4.

Defect	Type	Improved Materials Properties	Adversely Affected Materials Properties	Visible Signs of Defect
Point Defect	Vacancy f(T)	- diffusivity - color centers - ionic conductivity	- electron mobility - carrier lifetime	-empty lattice position
Point Defect	Substitutional	- conductivity (dopant) - strength (hardness) - characteristic T (like T_M)	- conductivity (impurities) - ductility - characteristic T	-foreign atom occupying lattice position.
Point Defect	Interstitial	- strength - characteristic T - electrical properties	- ductility - characteristic T - electrical properties	-atom occupies non lattice position.
Line Defect	Dislocation	- ductility (malleability) - strength (at high dislocation density)	- strength - yield stress - optical properties - lasing action	-extra half-plane of atoms.
Planar Defect	Grain Boundaries	- strength	- creep resistance - electrical properties - magnetic properties	-disruption of ordered crystal structure at interface of misaligned crystal grains.

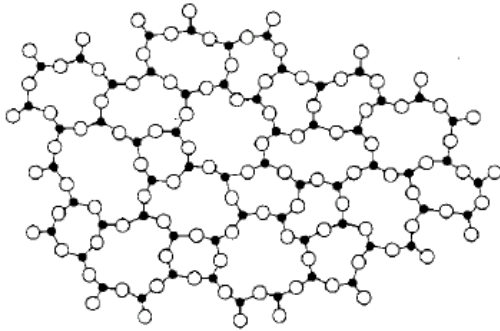
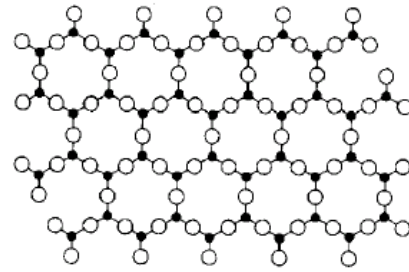
5. Indium has a FCC structure so slip occurs along the densest packed planes (planes with the highest planar density) which is the $\{111\}$ family of planes. Along (111) slip occurs along the densest packed directions, which are: $[110]$, $[1\bar{1}0]$, $[01\bar{1}]$, $[0\bar{1}1]$, $[10\bar{1}]$, and $[\bar{1}01]$.

6. (a) formers: SiO_2 , P_2O_5 , B_2O_3 , GeO_2
 modifiers: CaO , MgO , Na_2O ...
 intermediates: Al_2O_3 , TiO_2 , ZnO



- (c) - how extreme the change is in atomic arrangement required upon transforming liquid into solid, i.e., complexities of both structures.
 - cooling rate/viscosity
7. Al will not form a stable glass because atomic scale (re)ordering into an FCC structure requires only atomic jumps of short distance and thus small amounts of activation energy (available to some extent already at low temperatures). Ordering of Se (transition of Se from glassy to crystalline state) is impeded by the complexity of unit species on lattice sites (Se_8 rings) and by inadvertent chain growth ($\text{Se}_8 - \text{Se}_{20}$). These result in steadily increasing viscosity (with decreasing temperature) and, thus, in decreasing probability of stabilizing an ordered atomic structure.
8. (a) The simplest way to differentiate a glass from a crystal is exposure to x-rays. In glass we encounter only scattering; in crystalline material X-rays can give rise to diffraction.
 (b) We can also heat up the substances. Glass will soften gradually; a crystalline material will likely melt at one particular temperature, or a solid and liquid phase will coexist over a temperature range.
 (c) Under tensile stress a crystalline material will deform plastically, while the glass will fracture in a brittle mode.

9. (a)

amorphous B_2O_3 crystalline B_2O_3

- (b) Na_2O is a modifier. It dissociates to form Na^+ cations and O^{2-} anions. The oxide anions attack the bridging -O- oxygens in the borate network thereby disrupting it. The resulting smaller borate units are able to move more easily than the antecedent larger units. This is manifest in the lower value of viscosity for the modified melt.
- (c) Increase. As high cooling rates there is not enough time for the melt constituents to rearrange themselves before the temperature has fallen to the point at which the existing structure is rendered immobile.
- (d) 1. Ion exchange. Immerse the glass in a molten salt containing alkali cations that are larger than those present in the glass. The concentration gradient in such cations will drive them to diffuse into the glass where they will substitute for smaller ions. This results in the generation of compressive stress in the surface and raises the level of stress needed to break the glass
2. Tempering. Subject the glass to surface cooling by air jet. This results in differential cooling rates: the surface region is cooling at a higher rate than the interior. If you look at a plot of V vs. T , the final volume of the fast-cooled surface layer will be greater than that of the slow-cooled interior. This results in the generation of compressive stress in the surface and raised the level of stress needed to break the glass.
- (e) Covalent bonds. Tightly bound electrons. High band gap energy, ~ 5 eV. No dopants that introduce donor or acceptor levels 2 – 3 eV from the valence band or the conduction band, e.g., the Hope diamond.