

**Statement: Nitrogen diffuses rapidly through iron whereas chromium does not.**

**Answer:** In order to prove that this statement is partially correct, mechanisms of diffusion for nitrogen and chromium will in a first place be described and then alternative ways that could change the usual diffusion rate in these materials are going to be analysed.

Diffusion is the migration of atoms from a region of high concentration to a region of low concentration. There are two main different ways to diffuse in the bulk of a crystal: interstitial diffusion and vacancy diffusion.

Interstitial diffusion is considered first. As shown in the figure 1<sup>1</sup>, for any possible crystal material, there is always space between atoms of the lattice.

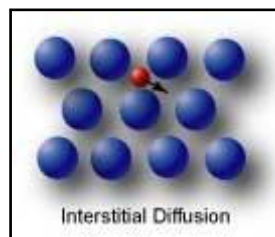


Figure 1: interstitial diffusion

In order to move, atoms have to get a certain amount of energy and also have to fit into the interstitial sites. As a consequence, depending of the size of the atoms diffusing in the material considered, diffusion through the interstices is possible. Furthermore, because of their exceptionally small value of normalized activation energy ( $Q/RT_M$ ), atoms which usually diffuse interstitially through crystals can do it very quickly.

This is what happens for the diffusion of Nitrogen in ferrite for instance. The small nitrogen atoms ( $65 \text{ pm}$ )<sup>2</sup> fit very well in the interstitial sites of the BCC crystal structure ferrite and their normalized activation energy is very low: atoms can move easily. That explains why nitrogen diffuses rapidly through iron.

On the contrary, compared to nitrogen atoms, the chromium atoms are much bigger: more than twice the size ( $140 \text{ pm}$ )<sup>3</sup>. As a consequence they do not fit anymore in the interstitial sites of iron and are forced to diffuse by the second mechanism: through vacancies as shown in figure 2<sup>1</sup>.

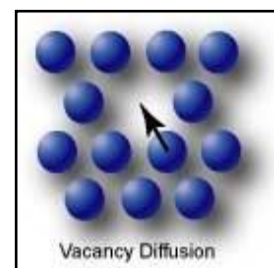


Figure 2: Vacancy diffusion

<sup>1</sup> <http://www.ndt-ed.org/EducationResources/CommunityCollege/Materials/Structure/diffusion.htm>, viewed 11 Nov 2008.

<sup>2</sup> <http://en.wikipedia.org/wiki/Nitrogen>, viewed 11 Nov 2008.

<sup>3</sup> <http://en.wikipedia.org/wiki/Chromium>, viewed 11 Nov 2008.

Obviously this mechanism is much slower than the first one detailed in this question because an atom willing to diffuse has to wait for a vacancy or a missing atom in the crystal structure close to him. Also, the bigger the number of vacancies in the material is, the faster the diffusion is. But still, this way of diffusing remains slower than the diffusion through interstices. It explains why generally chromium doesn't diffuse quickly through ion.

Another way of diffusing through a material, and which only makes this statement partially correct, exists. Indeed sometime, what is called grain boundary diffusion can occur. The gap between grains of a microstructure can sometimes be two atoms wide. As a consequence, the diffusion rate inside theses boundaries can be as much as  $10^6$  greater than in the bulk.<sup>4</sup>

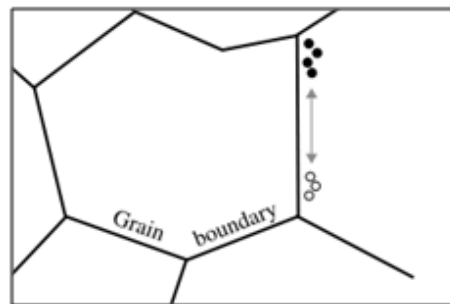


Figure 3: Grain boundary diffusion

It is interesting in our study to know if chromium could use this way of diffusion through ion. The answer is yes probably. If grains size of ion are small enough (typically by varying the cooling rate of the material while manufactured), and as a consequence the number of the boundaries increased to a certain amount, this mechanism would have an important contribution on the global diffusion rate. Considering this, yes chromium could diffuse also quickly into ion.

As a conclusion it has been proved that the statement is partially correct. Indeed because of the interstitial and vacancy diffusion mechanisms, nitrogen generally diffuses rapidly through ion whereas chromium does not. But grain boundary diffusion could also in particular cases have a significant contribution.

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<sup>4</sup> Ashby, M. F., Jones D. R., (2005), *Engineering Materials 1*, Butterworth Heinemann, p. 296

**Statement:** Thermosetting polymers are cross-linked and so do not show a glass transition temperature in the same way as either thermoplastics or elastomers.

**Answer:** The statement is partially right.

To properly answer this question it is important in a first place to describe what a cross-linked polymer is, and then explain the difference between thermosets, thermoplastics and elastomers. In the end, the influence of the cross-linking on the glass temperature will be shown.

All the kinds of polymers mentioned just above are made of very long molecules with a covalent bonding between their carbon atoms. When only secondary chemical bonds exist between these chains, like Van der Waals and hydrogen ones, the material is called a thermoplastic. Also, when heat is applied to the material, secondary bonds melt and chains are free to slip.

On the contrary, cross-linked chains are one of the characteristic properties of thermosetting polymer. These types of bonds are much stronger because they can be either covalent or ionic. They can be made chemically by mixing resin and a hardener agent which react together when heated; or by irradiation of a thermoplastic (figure4)<sup>5</sup>. The resulting polymer is called a thermoset and is usually described as a network material.

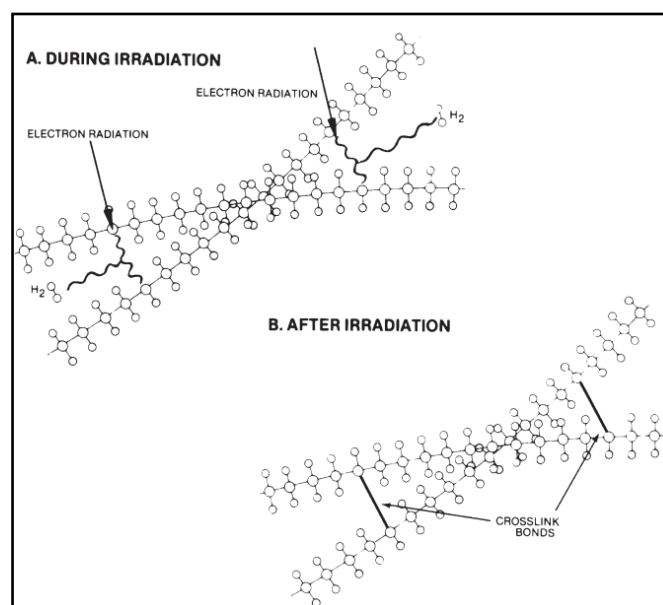


Figure4: Irradiation cross-linking

The third type of polymer exists: the elastomers. Considering the cross-linking property, they can be described as a mix between a thermoset and a thermoplastic. Indeed, they are cross-linked but they have very few of these bonds: only one every hundred or more monomer units<sup>6</sup>.

Now that the description of every material is done, the influence of that kind of bonding on the glass temperature is going to be discussed.

<sup>5</sup> [www.r-scc.com/PDF/Tech-electronics.pdf](http://www.r-scc.com/PDF/Tech-electronics.pdf), viewed Nov 11 2008

<sup>6</sup> Ashby, M. F., Jones D. R., (2005), *Engineering Materials 2*, Butterworth Heinemann, p. 269

When a polymer is heated, it passes through different mechanical states. For a thermoplastic we can easily separate three of them: plastic, viscoelastic, and viscous (at high temperatures). The glass temperature,  $T_g$ , is the temperature at which secondary bonds start to melt. As it has been said before thermoplastics do not have any covalent cross-linking between their chains, and above  $T_g$ , without their secondary bonds, they are likely to slip on each other: the polymer is in his viscoelastic state. If the temperature continue rising, all the Van der Waals and hydrogen bonds melt and the material quickly become liquid.

If the elastomers are now considered: above  $T_g$  their long carbon chains are still linked to each other by strong covalent cross-links which do not melt like secondary bonds. But as it has been explained before, the number of cross-links is very small and as a consequence chains still linked to each other are capable of elastics extensions of 300% or more<sup>7</sup>. The structure of the material cannot be destroyed but the mobility is not completely forbidden.

On the contrary, molecules in thermosetting polymers are not capable of any mobility. Indeed if a large amount of unit on the polymer chain is cross-linked to another chain, the covalent bonds form a very hard 3D network. Also, if the secondary bonds are melted above  $T_g$ , molecules under stress simply cannot move because of the too large number of covalent bonding.

As a conclusion, it has just been proven that this statement is just wrong on small details. It is true that all thermosets are cross-linked polymers. But, as we said before, elastomers have also some of their chains linked but with a very low the density of these bonds. Second, every material has a glass temperature where its secondary bonds start to melt; but the mechanical comportment beyond this point is just different depending on the material. Indeed, if the polymer is highly cross linked like for thermoplastic, nothing happens above  $T_g$  (and before decomposition). If it is an elastomer, the material is going to have a long rubbery state above  $T_g$  and if it is a thermoplastic, it will quickly become liquid above  $T_g$ .

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<sup>7</sup> Ashby, M. F., Jones D. R., (2005), *Engineering Materials 2*, Butterworth Heinemann, p. 269

**Statement:** At low temperatures, metals have a high tendency to oxidise but the rate of oxidation is slow whereas the reverse is true at higher temperatures.

**Answer:** The statement is partially correct. In order to critically discuss this statement, mechanisms of dry oxidation for metals is going to be analysed.

Oxidation of a metal is possible in earth's atmosphere because it contains oxygen. However, not every material react the same way to this aggression and their tendency to oxidise is function of different parameters. Considering a metal M, the process of oxide formation is an electrochemical one and can be described by the following reactions.



Like in any other chemical reaction, the mechanism itself is driven by the energy actually needed for the reaction. As a consequence, as it is clear here, if the energy is negative, a metal in contact with earth's atmosphere will oxidize and if the energy is positive it will not. As a general rule, at 273 K energies of formation of metals oxides are negative and as a consequence metals have indeed tendency to oxidise under normal circumstances. This statement is just wrong for gold which is the only metal completely resistant to oxidation at all temperature and which can therefore be found in its native form in nature.<sup>8</sup>

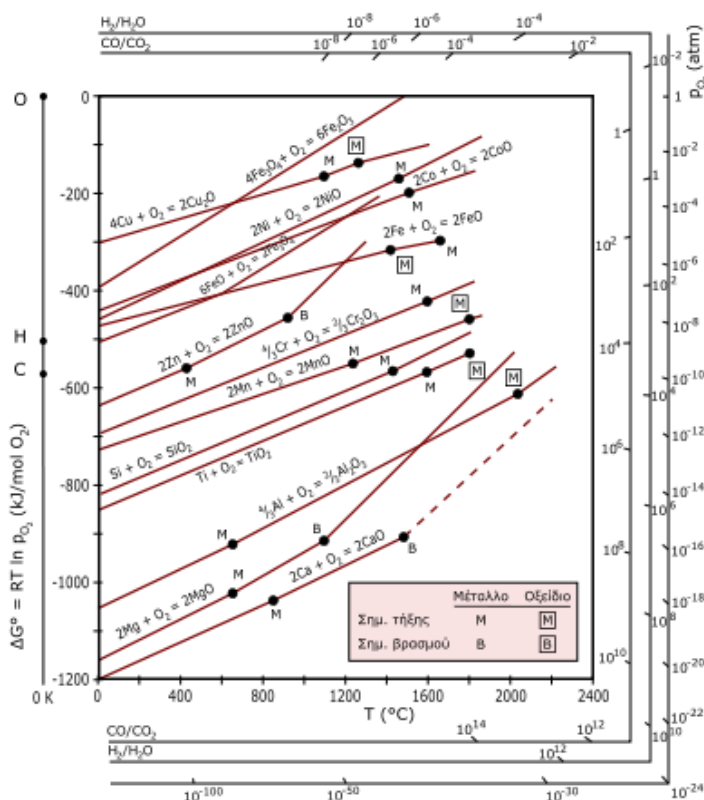


Figure 5: Ellingham Diagram

Furthermore, this tendency to oxidise can be quantified. Indeed, in metallurgy, Ellingham diagrams are used as a source of information concerning the oxidation of a metal under particular conditions. As figure 5<sup>9</sup> shows, this diagram plots the energy of formation of oxides versus the temperature.

The important thing to notice on that diagram is that if any metal is considered, as the temperature goes down, its energy of oxidation becomes more negative. As a consequence, as the temperature goes down metals have a higher tendency to oxidise; and as it has been said before, this rule does not apply only for gold.

<sup>8</sup> Ashby, M. F., Jones D. R., (2005), *Engineering Materials 1*, Butterworth Heinemann, p. 328

<sup>9</sup> <http://commons.wikimedia.org/wiki/Image:Ellingham-diagram-greek.svg>, viewed 11 Nov 2008

Moreover, the rate of oxidation is not driven by the energy of oxidation. For instance, Al which energy of formation equals  $-1045 \text{ kJ mol}^{-1}$  at  $0.7T_M$  oxidise very slowly whereas W which energy of formation equals  $-510 \text{ kJ mol}^{-1}$  at  $0.7T_M$  oxidise very fast<sup>10</sup>. Mechanisms are far more complex. There are in fact two types of oxidation over time:

The first one is the linear oxidation which can be described by the following equation where  $k_L$  is a kinetic constant:

$$\Delta_M = k_L t$$

The second one is the parabolic oxidation which is described by the following equation:

$$(\Delta_M)^2 = k_p t$$

( $\Delta_M$  is the weigh increase, showing that oxygen atoms are added in the material and as a consequence showing that the material becomes oxidised.)

In fact, the oxidation type a metal follows strictly depends on how its oxide film behaves. For instance, as a material becomes oxidised, its oxide film grows and can sometime act like a barrier for the new atoms of oxygen. As a consequence it becomes more and more difficult for them to reach the metal and the oxidation rate goes down following a parabolic behaviour type. It also happens that the oxide film formed is too brittle and cracks quickly under stress. The metal is no longer protected and the oxidation rate remains constant over time.

But still, even if these two different behaviours exist, temperature dependency remains the same. Indeed, as it is show figure 6<sup>11</sup>, both kinetics constants  $k_L$  and  $k_p$  increase exponentially with temperature following the Arrhenius's law:

$$k_L = A_L \times e^{-Q_L/RT} \quad \text{and} \quad k_p = A_p \times e^{-Q_p/RT} \quad \text{where } A_L, A_p, Q_L, Q_p \text{ and } R \text{ are constants.}$$

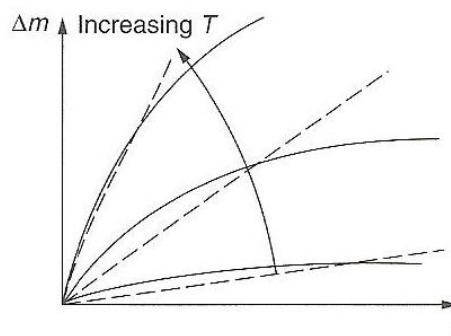


Figure 6: Oxidation time increase with temperature according to Arrhenius's law

Therefore, every metal which has a tendency to oxidise will have its oxidation rate increased as the temperature goes up.

As a conclusion, considering all that has been said in these two pages, the statement was indeed correct except on one tiny thing: it is not true only for gold which is the only metal resistant to oxidation.

<sup>10</sup> Ashby, M. F., Jones D. R., (2005), *Engineering Materials 1*, Butterworth Heinemann, p. 332

<sup>11</sup> Ashby, M. F., Jones D. R., (2005), *Engineering Materials 1*, Butterworth Heinemann, p. 331

**Statement:** A phase diagram is the sole source needed to fully describe the microstructure in a slow cooled binary alloy.

**Answer:** The Statement is almost true.

To prove it, we are going to extract all the information we can get by looking at a random binary alloy phase diagram. Before starting it is important to remember that everything that is going to be said here is by considering that slow cooled means: cooled slowly enough to be at equilibrium. Otherwise, the statement would have been wrong. But the last part of the question will give more detailed about this.

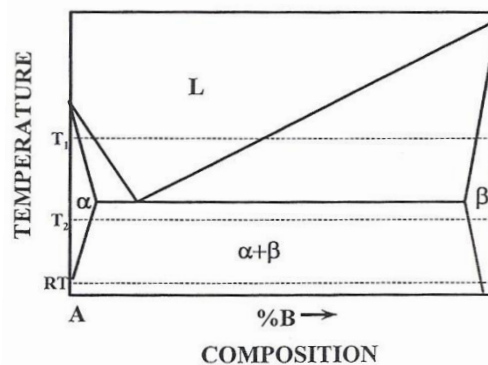


Figure 7: AB phase diagram

The AB phase diagram given in the assessment package is considered. The overall B composition for the whole alloy will always be 50%. Starting from single phase liquid to two solid phases at room temperature, here is everything which can possibly be extracted from this diagram:

1. From very high temperature to liquidus temperature the alloy is a single phase liquid.
2. At  $T_{\text{liquidus}}$  first B crystals start to grow. Their composition is approximately 95% of B
3. As the temperature decrease, more and more  $\beta$  crystals are formed. At  $T_1$ , the proportion of each phase is approximately: 10% of  $\beta$  crystals and 90% liquid (diagram is not very accurate). The composition of each is respectively 95% of B and around 45% of B. Therefore, a quick calculation shows that it makes 50% of B overall.
4. At  $T_{\text{eutectic}} + \epsilon$  there is still 55% liquid in the material. Its composition is 15% of B. But at  $T_{\text{eutectic}}$  liquid is not stable anymore. The 55% remaining liquid transforms in a 2 solid phase component called eutectic.  
Also, at  $T_{\text{eutectic}}$  there is now 55% of a bi-phase eutectic solid and 45% of  $\beta$  solid. The composition for the eutectic is around 90% of A and 10% of B; and for the  $\beta$  solid, around 95% of B.
5. As the cooling continues nothing really moves. The composition of each phase just slightly changes and so at room temperature it is possible to tell that a 1:1 alloy of elements A and B will be made of 55% eutectic and 45% B. The compositions of each are given in 4.

Therefore, the only thing unpredictable is the size or the shape of the grains. This can only be found out by looking at the specimen with a microscope. However, anyone a little bit used to steels could be able to predict it just by looking at the phase diagram.

As a consequence, it has clearly been shown that at equilibrium, (which means enough time has been given to the material to organise while cooling) it is possible to describe most of the microstructure. To summarise what has been just done, it is proven that the following information can be extracted from a phase diagram:

- The overall composition
- The number of phases
- The composition of each phase
- The proportion of each phase

And as said before, the only thing missing is grain size and shape information.

However we could take this discussion a little bit deeper. Indeed, as it has been underlined at the beginning of this answer, until now it has been considered that “slow cooled” meant “at equilibrium”. But this is not very clearly specified in the question... For instance, slow cooled could also have meant cooled in 1000s instead of  $10^5$ s.

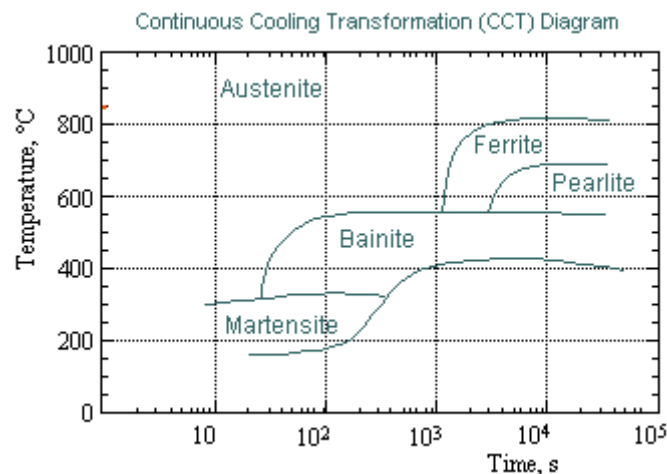


Figure 8: CCT diagram for a 0.4% C, 1.5% Mn, 0.5% Mo steel<sup>12</sup>

As this random CCT diagram shows, the cooling rate has still have influence on the microstructure of the alloy even after  $10^5$ s. Also sometimes on very specific alloys, equilibrium cannot be reached before days. As a consequence, even with a slow cooling rate like said in the statement, the material would still not be at equilibrium and the microstructure could absolutely not be described with a simple phase diagram only. Time-depending curves like on CCT and TTT diagrams would be needed.

Considering all of what have been said in this answer, the statement is partially true but could be also wrong and misinterpreted because of the way it is formulated.

<sup>12</sup> [http://www.matter.org.uk/steelmatter/metallurgy/7\\_1\\_2.html](http://www.matter.org.uk/steelmatter/metallurgy/7_1_2.html), viewed Nov 11 2008.