Diffusion

Science

## 5. Diffusion in Iron

Self-Diffusion in Iron

If one plots the **log(D_{SD})**, the *logarithm* of the self-diffusion coefficient versus the *inverse* temperature **1/T** in an Arrhenus plot, a rather straight line results for most basic metals. Here is a link with an example.

- If we do the same thing for iron, we get a surprise:

Self-diffusion data for iron.

Source: Helmut Mehrer, "Diffusion in Solids", Springer, 2007.
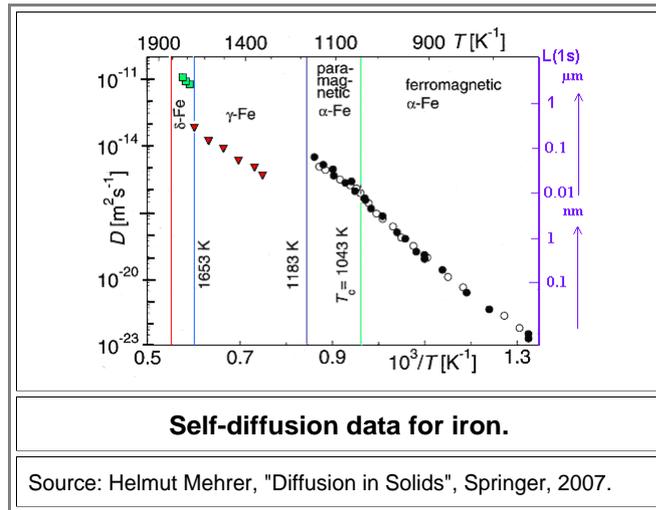
- The violet scale on the right gives the diffusion length **$L = (Dt)^{1/2}$**; sort of the the average **penetration depth** after **1** second in **µm** or **nm**. Multiply with **10** if you want the number for for **100** seconds, with **100** for **10.000** seconds (close to **3** hrs), and so on.

Surprise! *There is no single straight line!* Even the long line marked by the black-white dots is not really straight.
So let's look at the problems we have with diffusion in iron one by one:

- The *first* problem is obvious:
We encounter *one* magnetic and *two* structural phase transitions when we heat up a piece of pure iron. We therefore need to consider diffusion in a grand total of *four* different phases (ferromagnetic α, paramagnetic α, γ, δ), depending on which temperature we pick.
As far as magnetic stuff is touched upon here, refer to the module about magnetism for the basics about iron being magnetic.

- The *second* problem is not so obvious but also clear:
It is impossible, or at least very difficult, to obtain good iron crystals (preferably single crystals) with few defects. Grow a single crystal from an iron melt, and as soon as it undergoes the first phase transformation, all is lost. Same thing at the second transformation. Defects like grain boundaries and dislocations will influence diffusion behavior to some (typically small) extent and we must be aware of this.

- The third problem is not a serious problem but nevertheless worthwhile to mention:
If you look at the phase diagram of carbon steel, you realize that already small amounts of carbon change the phase transition temperatures and the kind of phases you get quit a bit. That is easily remedied, of course, by doing experiments only with high-purity iron - but what then is the relevance of the data for mild (carbon) *steel*?

If we look at the figure, some salient points are readily apparent.
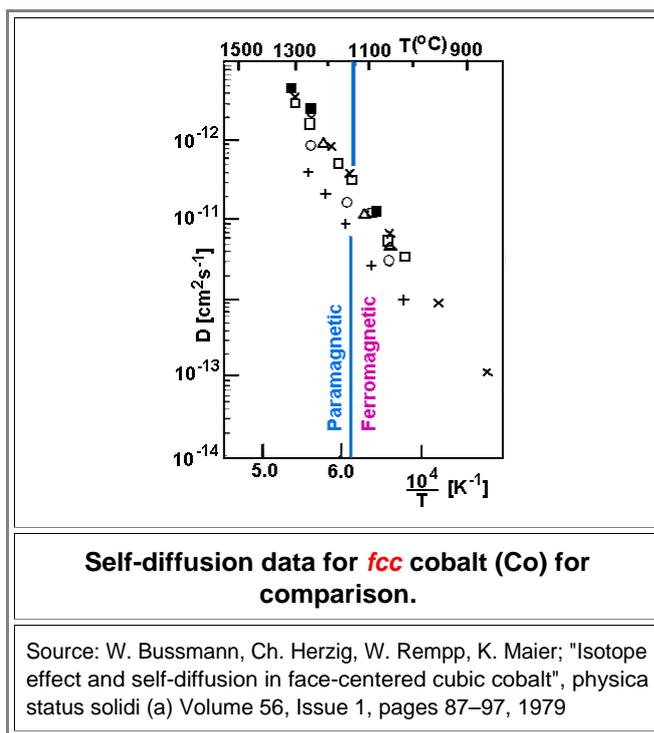
- **1.** The curve in the **bcc** δ-iron region at high temperatures is more or less an extrapolation of the curve for (paramagnetic) ferrite or α-iron. That is what we expect. δ-iron and α-iron are both simple **bcc** crystals, so the diffusion mechanisms including activation energies should be the same.

- **2.** The diffusion coefficient in the **fcc** γ-iron region is substantially smaller than in the other phases. That is as expected. The **fcc** γ phase is a close-packed crystal, where it should be a bit more difficult for the iron atoms or vacancies, respectively, to roam around than in the less densely packed **bcc** lattice.
We also note that there aren't too many data points for the γ phase, in particular at the low-temperature end. That's simply due to the fact that experiments get more difficult at lower temperatures. If atoms / vacancies hardly move not much happens on human time scales and what are you going to measure then?

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3. As soon as the **<u>Curie temperature</u>** is reached, where iron becomes spontaneously ferromagnetic or, in other words, a (second order) phase transition from paramagnetic to ferromagnetic takes place, the data start to deviate substantially from a straight line. That's perhaps not unexpected, but no such effect is found in <u>nickel</u> (Ni) and cobalt (Co; see below), the other two simple metals that also show a magnetic phase transformation.

Self-diffusion data for *fcc* cobalt (Co) for comparison.

Source: W. Bussmann, Ch. Herzig, W. Rempp, K. Maier; "Isotope effect and self-diffusion in face-centered cubic cobalt", physica status solidi (a) Volume 56, Issue 1, pages 87–97, 1979

No influence of the magnetic phase transition on self-diffusion data in cobalt can be seen. In the case of nickel (Ni), it is clear why the magnetic phase transformation does not show up in the <u>data provided</u>: it occurs at a low Curie temperature, below the temperature range used. For cobalt (Co), however, it is not obvious why no effect is seen. Here the Curie temperature is well within the range of the measurements as shown above.
In case you wonder why *fcc* cobalt was used, knowing perhaps that cobalt is *hexagonal* at room temperature: the temperature of the phase transition from the fcc phase to the hexagonal phase occurs at 440 ºC (824 ºF) and is thus outside the temperature range of the measurements.

What's happening? I won't go into details (mostly because I don't know them) but magnetic order in the ferromagnetic phase and vacancy formation / migration interacts in several ways, not easy to calculate. To some extent the effects have opposite signs in the final reckoning (e.g. the formation energy *and* the entropy increases a bit) and thus tend to cancel each other.
Let's look at some numbers now. What follows is a collection of the numbers that I picked up during writing this hyperscript for the formation and migration energy and pre-exponential factors of the vacancy in the various phases of iron. Note that there is always a scatter in the data. First, because measurements are always difficult, and second because the results are influenced by the defect structure, and in particular the content of carbon or other elements.

	α, ferrite paramagn.	α, ferrite ferromagn.	γ, austenite
E_{SD} [eV]	2.57 - 2.68 2.50 2,48	2.91 ± 0.04 3.03	3.03 2,90
$D_{0, SD}$ [m^2/s]	$(6.8 - 12.3) \cdot 10^{-4}$ $2.0 \cdot 10^{-4}$ $1.939 \cdot 10^{-4}$	$6 \cdot 10^{-4}$ $5.40 \cdot 10^{-4}$	$0.89 \cdot 10^{-4}$ $0.356 \cdot 10^{-4}$
$E_{F, V}$ [eV]	1.13 - 1.02	≈ 1.8	
$E_{M, V}$ [eV]	1.5 1.2 - 1.3; 1.24	≈ 1.0	

According to: Heumann , Seeger, Oikawa, Kucera
full references elsewhere in this modules

Sources: Jaroslav Kucera, Karel Stránský: "Diffusion in Iron, Iron Solid Solutions and Steel", Mat. Sci. and Eng. 52, (1982), p. 1 - 38.

Impurity Diffusion in Iron and Steel - Interstitial Mechanism

Going systematically, we need to consider

1. *Interstitial impurity atoms* diffusing by a direct interstitial mechanism: carbon (C), nitrogen (N) and (perhaps) oxygen (O).
2. *Substitutional impurity atoms* diffusing by a vacancy mechanism: the rest.

In case of doubt refresh your memory with this link.

So let's look at the **interstitials first**. Here is an Arrhenius plot for the diffusion coefficients of carbon (C) and nitrogen (N); once more the **diffusion length L** for **1** second is indicated.

Carbon (C) and nitrogen (N) diffusion in iron (Fe).

Source: Werkstoffkunde Stahl, Band 1: Grundlagen; P. 82
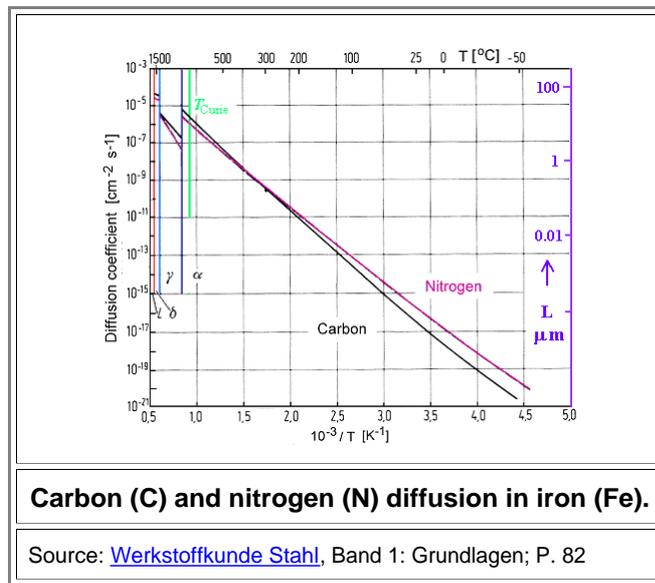
Next, the same kind of diagram from a different source, also including some oxygen data. Figure out yourself if both sets of data are compatible!
The carbon curve is not absolutely straight. That might be due to the magnetic phase transition but personally I don't know if that is the last word on the topic.

More interstitial diffusion in iron

Source: Heumann, Th.; "Diffusion in Metallen", Springer Verlag, 1992
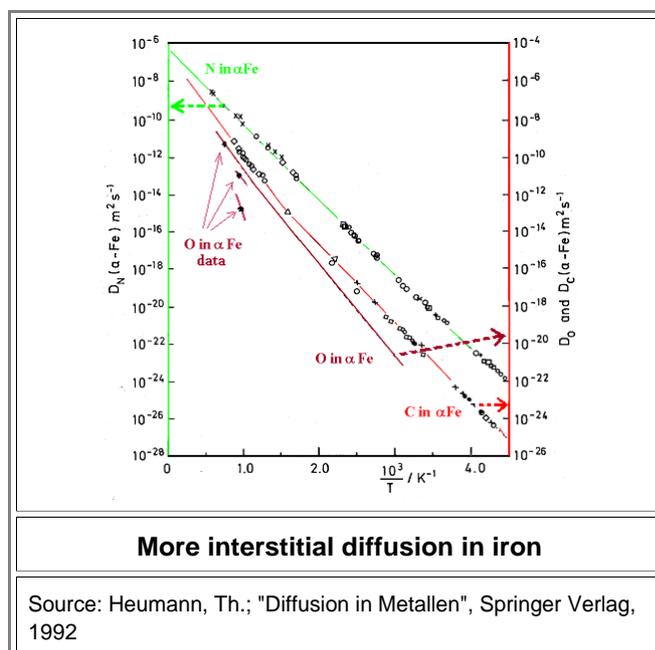
- What we can see is that the diffusion of all three interstitials is roughly the same. At a temperature of **1000 ºC** (1832 ºF) where forging takes place, and at temperatures somewhat below the γ → α transition temperature of 910 ºC (1670 ºF), in pure iron all three interstitial elements can cover distances of several µm in just 1 second.

Now let's look at some numbers for the interstitials:

	C	N	O
E_M [eV]	0.96 0.88	0.8 0.82	0.96 1.0
D_0 [m²/s]	$3.94 \cdot 10^{-7}$ $2.0 \cdot 10^{-6}$	$4.88 \cdot 10^{-7}$ $1.4 \cdot 10^{-6}$	$3.78 \cdot 10^{-7}$
Source: **Heumann, Seeger (ferromagnetic state)**			

- Whichever way one looks at the data, one thing is clear. Any non-uniformity in the interstitial concentration will be "ironed out" during normal forging in a range of several 100 µm or almost millimeter by diffusion.
  Provided that the diffusion of carbon in steel is not completely different from that in iron (it isn't, see below), we have a major insight from this:

> ## Welding layers of hard and soft *carbon* steel will *not* result in a composite blade with hard and soft layers but in a rather uniform medium-hard steel.

- Welding layers of hard and soft *phosphorous* steel, however, is a completely different thing in this respect.

OK - we have *iron* covered, sort of. How about *steel*?
First we need to consider how all these data change if we look at *carbon steel* instead of *iron*. Of course, we need to do this for all possible carbon concentrations and temperatures. Then we need to consider what is going to happen if we alloy the rest of the periodic table one by one. Next, we need to consider the diffusion of carbon and so on if we alloy two elements simultaneously. Since the γ → α transition temperature comes down from 910 ºC (1670 ºF) to 723 ºC (1333 ºF) by adding just 0.025 % of carbon, there is a pronounced influence of the carbon concentration on *diffusion* - even if the diffusion *coefficients* wouldn't change much - since more of the diffusion now happens in the γ phase.

- Yes, it does get boring and labor intensive. The first law of applied science starts to make a lot of sense once more.
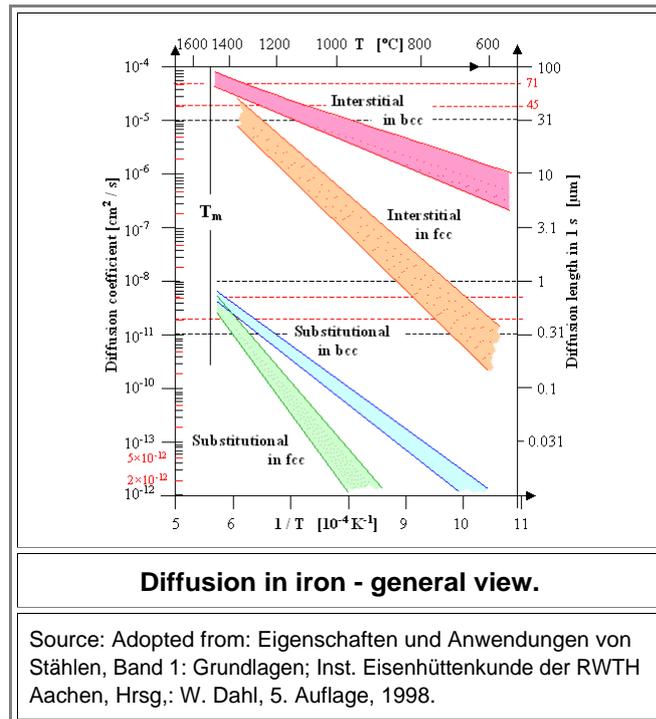
I will not run through the program outlined above in this module, of course. All I will do is to give you a tiny taste treat of what happens to the diffusion of carbon in *carbon steel*.
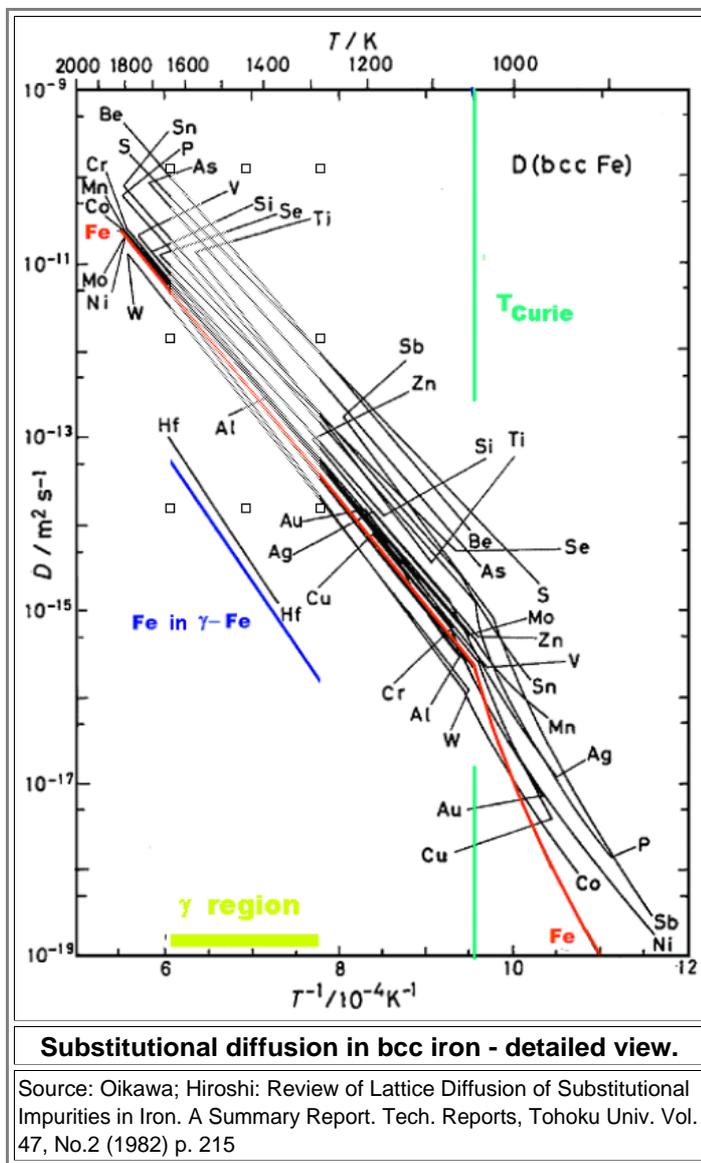

Carbon diffusion in carbon steel

Source: Werkstoffkunde Stahl
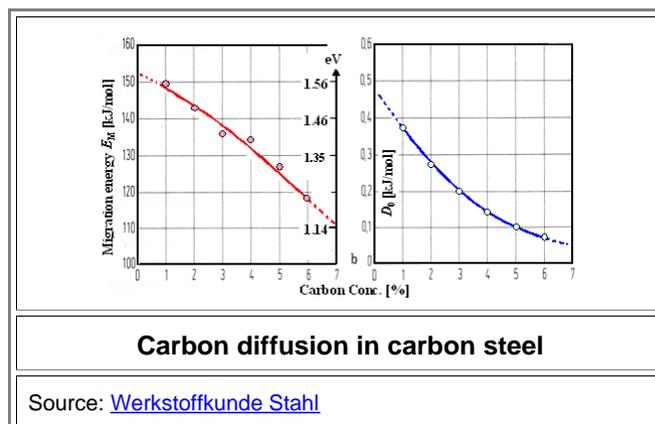
● The figure gives the [migration energy] E_M and [pre-exponential factor] D_0 as a function of carbon concentration for carbon diffusion in *austenite*. All things considered, the **C**-interstitials speed up as the carbon concentration increases, since the decrease in migration energy is more effective than the decrease in D_0.
You figure out if the concentration in the figures above is *weight percent* (likely) or whatever; my source doesn't tell. Out of the kindness of my heart I also gave you the migration energy in an **eV** scale.

Impurity Diffusion in Iron and Steel - Vacancy Mechanism

All that remains to do is to go through the data for the remaining 80 elements or so in *iron*, differentiated for bcc α-iron and fcc γ-iron. Next, the influence of the magnetic phase transition needs to be taken into account. Then we need to consider once more how things change if we look at various kinds of *steel*. If you have a lot of spare time, you are welcome to do this.

● All *I'm* going to do is to show you three figures. Here is the first one. It's kind of very general, just showing the regions where you find diffusion coefficients in α and δ iron:

Diffusion in iron - general view.

Source: Adopted from: Eigenschaften und Anwendungen von Stählen, Band 1: Grundlagen; Inst. Eisenhüttenkunde der RWTH Aachen, Hrsg,: W. Dahl, 5. Auflage, 1998.

● Now let's look at some details:

Substitutional diffusion in bcc iron - detailed view.

Source: Oikawa; Hiroshi: Review of Lattice Diffusion of Substitutional Impurities in Iron. A Summary Report. Tech. Reports, Tohoku Univ. Vol. 47, No.2 (1982) p. 215

● Most values obtain for the δ and α phase. The lines have been extended through the (shaded) γ region (where the values given below obtain) to allow identification of the elements. The curve for self-diffusion of iron in the γ phase is given for comparison.
Now the data for the γ phase:
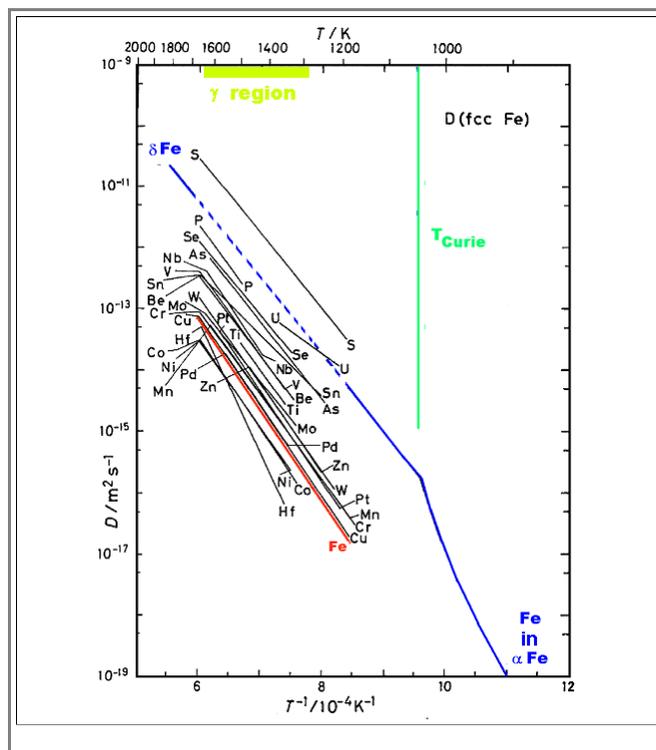
Substitutional diffusion in fcc iron - detailed view.
Source: Oikawa; Hiroshi: Review of Lattice Diffusion of Substitutional Impurities in Iron. A Summary Report. Tech. Reports, Tohoku Univ. Vol. 47, No.2 (1982) p. 215

⬤ The curve for self-diffusion of iron in the α and δ phase is given for comparison onc more.

Nothing more needs to be said. Just assembling all the data was a major piece of work, not to mention getting them. We may assume that diffusion of all these elements in *steel* is somewhat different from the values given here, but not dramatically so. However, if you want to be sure you need to do experiments or (very difficult) calculations.

⬤ A lot of people think that the "complex" financial products that caused all those crises from 2008 - 2012 (and, I fear, beyond) are so complicated that only financial geniuses can understand them. Can you see me smiling? And we haven't even got close to real steel yet.

Conclusion

A lot of work concerning diffusion in iron and steel has been done. A lot of work still needs to be done. Having good numbers is essential for designing *new* kinds of steel.

⬤ The first law of applied science starts to make a lot of sense once more. And there is hope! If you are not too close already to your timely demise, you can rest assured that during your lifetime new *designer* steels with superior properties will appear on the market. And that will happen because we finally *understand* diffusion in steel in ever more detail.

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