

# Corrosion of Iron and Steel

## Advanced

I can't bring myself to write a long treatise to this topic. It is too painful and too complicated. I have also covered parts of this elsewhere so let's keep it short. I'm just going to ask (and answer) a few basic questions.

### 1. Iron and Steel rusts. Why?

The answer, for simplicities sake first for *pure* iron only, is simple: Iron rusts, meaning it oxidizes because iron atoms like to be surrounded by oxygen atoms (or sulfur atoms or...) far more than to be surrounded by brethren iron atoms. Being oxidized is closer to nirvana than being pure. That's why we find only iron ore and not the pure metal in nature.

● Good answer, perfectly correct but not satisfactory. If you don't see why, look at my next question

### 2. Why does aluminum, silicon, and many other pure elemental crystal *not* rust or corrode?

Now we are at the heart of the problem. The answer above applies to all these elements just as well as to iron - but they do not corrode! At least far slower than iron.

● Once more we have the two essential ingredients to Materials Science and Engineering in a nutshell:

1. *Equilibrium thermodynamics* ("nirvana seeking theory") tells us what some material wants to be, what goal it has in life. Iron and aluminum, silicon, and so on most certainly want to be oxidized if there is oxygen around at ambient temperature and normal pressure. No doubt about this.
2. *Kinetics* tells us how far it is to the goal, how long it will take to get there. You can take this literally. If something is to change, atoms need to move some distance, and that takes some time, on occasion about forever.

● The answer to the question then is: Silicon, aluminum, and many other materials actually do oxidize. The oxide layer formed on the surface of these materials, however, has two [important properties](#):

1. It prevents oxygen and about everything else to reach the material - oxide interface. If no more oxygen can reach the silicon, aluminum, and so on, no more oxidation can occur.
2. If that extremely thin (typically a few nm at best) and therefore invisible layer is damaged, e.g. because it is scratched or fractured, it immediately heals itself again.

Somewhat simplified, iron rusts because its oxide layer does not have the first property - but *not* the second! The second condition is crucial. A simple protective layer without self-healing capacity can be made by painting some lacquer or something on the material. We do that a lot, of course, but you know how much good that does on the long run. Especially on a sword blade.

The next question is obvious now:

### 3. Why is an iron-oxide layer *not* self-healing, in contrast to silicon or aluminum oxide layers?

That is a tough one. In fact, the quality of iron oxide layers as rust protectors vary quite a bit. If one makes the right oxide carefully, it does protect, or to use the proper word, **passivate** the surface nicely. The process of "bluing" does just that. The right oxide is [magnetite](#) ( $\text{Fe}_3\text{O}_4$ ), the black oxide of iron. [Haematite](#) ( $\text{Fe}_2\text{O}_3$ ), the red oxide, is bad. It reacts with water to some kind of hydroxide (like  $\text{FeO}(\text{OH})$ ) and that causes a large volume change with unavoidable cracking, blistering and flaking off that doesn't stop as long as there is some iron to consume. You have seen that. It's called rusting.

● If you like, the root of all that evil comes from the deplorable fact that there are several iron oxides and hydroxides that can form in a normal oxygen-rich and humid atmosphere. They compete with each other and transform into each other, depending on conditions, ripping apart the protective layer whenever that happens. In contrast, silicon produces only extremely tough and stable silicon dioxide ( $\text{SiO}_2$ ) and aluminum is quite happy with its very hard and very stable only oxide ( $\text{Al}_2\text{O}_3$ ), the stuff for making [gemstones](#).

But let's go on:



#### 4. Actually, pure iron doesn't even rust all that much - in contrast to **carbon steel**. Why?

Easy in principle. Not so easy if you look a details. The easy part is that as soon as you "look" (with a microscope) at the surface of carbon steel, you see (slightly oxidized) ferrite and cementite. [Here](#) are pictures to that.

The cementite cannot be covered with an oxide. If you could oxidize it, the gas  $\text{CO}_2$  would be produced and no solid layer. At the edges where iron and its oxide meets the cementite, mechanical and "chemical" stress is produced that offers points of attack for oxygen and water molecules from the air.

- The difficult part comes in when we consider that corrosion is part of electrochemistry. As soon as two materials or phases have direct contact **and** some contact to a liquid, you have a battery with a built-in voltage that can drive chemical processes otherwise not observed. Steel, any steel, by definition is a composite of at least two phases, typically many more. Some electrochemistry is bound to happen in a humid environment and corrosion is rather the rule than the exception.

#### 5. How come, then that we have something like stainless steel that doesn't rust?

The answer to that has two parts.

The first and easy one concerns stainless steel. A typical [stainless steel](#) needs to have enough chromium alloyed to it (at least 11 %) to enable the formation of a closed chromium oxide layer on the surface. Since chromium oxide ( $\text{Cr}_2\text{O}_3$ ) meet both requirements from above, the steel surface is now passivated and resists corrosion attacks.

The second and more difficult part to the answer concerns [Corten steel](#). That's a special steel with weird alloy elements that manages to produce a stable and rather thick oxide. It's so thick that the steel actually looks very rusty. But rusting does not continue after the initial formation of the oxide.

#### 6. Anything else one should know about iron and steel corrosion?

You must answer that yourself. Going beyond what I have given you is best done by reading good books, possibly preceded by a few years of studying the necessary basics in chemistry, materials science, and physics.