

## 9.3 High Alloy steels

### 9.3.1 Stainless Steel

#### The Steel Corrosion Problem

Now let's improve a particularly undesirable property that all the steels we have "made" so far possess to a smaller or larger extent: they **rust** (apparent exceptions, like the [pillar in New Delhi](#), prove the rule).

- Rusting means that the iron reacts with the oxygen from the air (helped by water) to form all kinds of iron oxides and hydroxides, subsumed under the generic name **rust**.

There is no good reason why it shouldn't do that. The iron-oxygen bond is far preferable to the iron-iron bond as far as the second law is concerned, and iron, just like aluminum (Al), titanium (Ti), chromium (Cr), nickel (Ni), silicon (Si) and so on, has very good reasons to oxidize as much and as fast as it can.

Let's be clear about that: In an oxide containing atmosphere all metals - except the noble ones - need to be fully oxidized if they want to achieve nirvana.

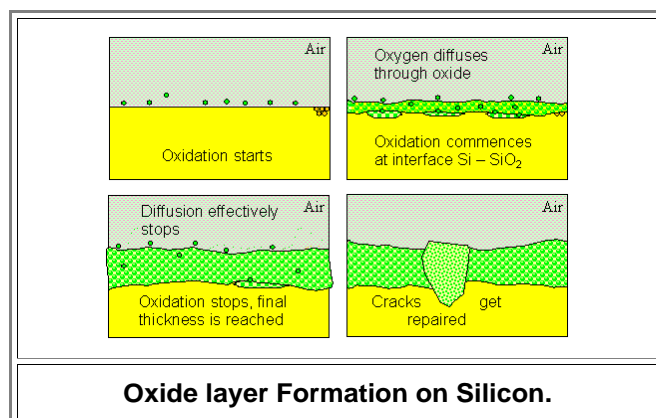
However, from the materials named above only iron visibly rusts or corrodes, to use the polite name, while aluminum, titanium, chromium, nickel, silicon and so on tend to be rather stable at room temperature. They don't seem to corrode much. How come?

Well, **all** these (pure) elements are actually very happy to react with oxygen, indeed. In doing so they form an **oxide layer** on the surface. We now have to basic possibilities:

- The oxide layer is "dense" and after it reached a certain thickness protects the material beneath it from direct contact with whatever is on the surface of the oxide - including the oxygen! Even better, if the layer gets damaged, e.g. by scratching, it heals itself quickly and forms a closed layer once more.
- The oxide layer is not "dense" - you may call it "porous" then. It does allow all kinds of stuff to reach the surface of the metal and commit atrocities there. If damaged, it may not heal but allow other reactions to take place.

- The first case by necessity contains the miraculous property that the growing oxide film stops its own growth as soon as it has reached a thickness that does not allow more oxygen to make it to the metal. That doesn't take much. Silicon (Si), for example, grows a very thin layer of (amorphous)  $\text{SiO}_2$ , otherwise known as quartz, rather fast in air. Quartz ware, as you might know, is used in pretty much all of chemistry because the material reacts with almost nothing and is impenetrable to most everything. That's why a silicon dioxide ( $\text{SiO}_2$ ) layer with a thickness of **only** 2 nm (or about 8 atomic layers) is already perfectly capable to stop further oxidation of silicon around room temperature "forever".

Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) does about the same for aluminum (Al), and so on. Below is a schematic picture that shows what happens.



- The picture would be much the same for most metals. It is important to realize that the oxidation happens at the interface metal - oxide and that means that oxygen atoms must **diffuse** through the oxide that has already formed to the interface oxide - metal, where the oxidation takes place. Since oxidation is the first step in corrosion, we learn an important fact right here:

**Advanced  
Module**

**Corrosion**

## Corrosion is a surface or interface property!

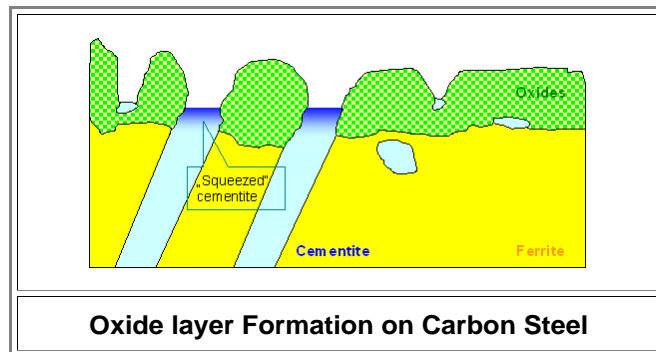
The chemical reactions leading to corrosion must take place at the surface, or more precisely the metal / oxide interface as defined above. The properties of the interface / surface layers determine what happens. Of course, the surface structure of some crystal is determined to some degree by the bulk structure but just knowing the bulk structure will not be sufficient to predict the corrosion behavior

Since diffusion at room temperature is typically slow, it will be effectively zero for oxide layers just a few nm thick. In the case of silicon, the "native" oxide it carries around at room temperature is typically 2 nm thick. If you increase the temperature to, say 1000 °C (1832 °F), you get thicknesses up to a 1 μm if you keep going for a few days. Layers just a few nm thin are invisible to the eye, and that's why all these oxide protected metals (including silicon) look just as silvery-gray as the "naked" metal (that few people outside science have ever seen). There are also metals where the oxide layer eventually grows so thick that you see it - take "green" copper, for example. In contrast to iron and particularly carbon steel, the oxide layers immediately formed upon contact to oxygen for well- *passivated* metals, as we call the effect, are uniform and dense. After they have formed to a sufficient thickness, they simply prevent oxygen from reaching the metal and thus stop further oxidation. If they are damaged, new oxide forms faster than anything else, effectively repairing the protective layer.

Iron, and in particular steel, doesn't passivate by just sitting in air. This is a bit peculiar - most metals, if you think about, appear to passivate. Well - no! We just never think much about all those metals and alloys that don't. All [Alkali](#) and many [earth alkali](#) metals (e.g. Li, Na, K, Rb, Cs, Ca, Sr, Ba) won't last long in air (or, worse, water). We just never think about those elements because they we never use them as "metals".

Why does the "oxide passivation" *not* work in this case? There is no simple *general* answer. There are steels, after all, where it does work - so-called "[weathering steels](#)" for example.

There is, however, a simple *specific* answer for carbon steels! In these steels you have largish cementite phases. We don't know (yet) if that oxidizes and, if it does so, what kind of oxide it will form. Carbon (di)oxide? That's a gas! In any case, the oxide layer forming on the ferrite simply cannot cover the cementite too. There is simply no closed oxide layer on carbon steel and at the "edges" all kinds of bad things can now happen. An outline of that is shown below.



Above larger cementite parts no oxide can form. The oxide to the left and right, since it expands when formed, "squeezes" the cementite, meaning that there is a lot of stress and strain in the surface near layers now. Smaller cementite particles will disturb the oxidation locally; they also may become embedded in the oxide formed, possibly causing cracks. Add to this that there are several kinds of iron oxides and hydroxides (in contrast to aluminum, and silicon, for example), and that not all oxides are insulators (like silicon and aluminum oxide) but semiconductors that may participate in "electrochemical" corrosion, you get a first idea why carbon steel readily rusts while wrought iron does not.

Moreover, do you also get a first idea of what to do about preventing rusting? I hope so.

In summary: Many metals (and other elements), while reacting strongly with oxygen (O), tend to form thin *passivating* oxide layers that protects the metal surface from further oxidation. Their oxides, we say, are efficient *diffusion barriers* at room temperature, disallowing diffusion of the oxide (and anything else) to the metal. We are back to our old *adage*:

**If the atoms can't move, nothing can happen.**

Not so with iron or plain carbon steel. There are many possible iron oxides (more to corrosion of steel in [this link](#)) but a dense layer with diffusion barrier properties does not easily form and your blade will corrode if you don't give it extensive care.

Let's face an uncomfortable truth: there is no such thing as a corrosion resistant plain carbon steel. It just can't be. If you want corrosion resistant or stain-proof steel, you must do one or all of the following:

- Avoid large non-oxidizing phases of all kinds, in particular lamellar cementite.
- Establish conditions where a closed oxide layer can be formed.
- Supply chemical "incentives" to make that oxide "good" oxide that is closed, dense and able to do "self-repair".

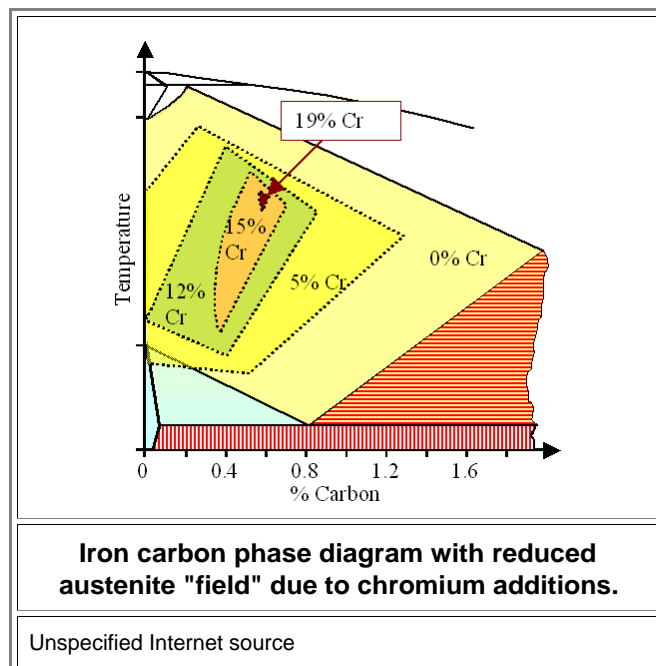
That is quite a list. What comes to mind now is certainly "**stainless steel**". However, there is no such thing as "a" stainless steel; it's rather a large family of [high alloy steels](#). Let's give that type of steel a first cursory look; more in [this link](#)

### Stainless Steel

The major trick to make "stainless" steel, meaning steel that does not rust, is to make sure that its surface is always covered with a dense layer of essentially chromium oxide ( $\text{Cr}_2\text{O}_3$ ), a good diffusion barrier for oxygen, that will protect the steel from further attack by the oxygen.

- Plating a layer of pure chromium on your steel will do that, too. However, you cannot do anything to your product after the plating because any damage to the thin Cr layer will induce localized corrosion of the steel underneath.
  - Alternatively, you can include that much chromium (Cr) into your steel that there is always a sufficient number of chromium atoms at the surface to induce a closed layer of mainly chromium oxide. ( $\text{Cr}_2\text{O}_3$ ). It's not as much as you might guess, all you need is more than 11 % (a number that can actually be [calculated](#)); up to 25 % or so are used in practice. Interestingly, this mix - just iron and chromium, no carbon - [stays bcc at almost all temperatures](#). Hardly any austenite is formed when heating up. That also means that there is no strong hardening upon quenching because there is no phase transformation, martensite formation, and so on.
- A bit of carbon, 0.6 % or so, changes that. There will be some austenite and thus the possibility of (case) hardening by quenching and martensite formation. What we get then is a simple but good ferritic "stainless" steel for ball bearings, kitchen knives or surgical instruments.

The kind of composite phase diagram below illustrates that.



- What the figure shows is how the region of stable austenite (yellowish colors) decreases with increasing chromium concentration. Chromium, in other words, is a [ferrite stabilizer](#). Above 12 % chromium austenite does not exist any more for low carbon concentrations. If you go to 0.5 % carbon, you will still have austenite; only the transition temperatures are somewhat changed. More to that in the science link.

This opens a whole new bag of tricks that can we explore by adding substantial amounts of other element to achieve certain parameters.



● The possibilities are humongous but I will only mention one more member of the high-alloy family: [austenitic \(stainless\) steel](#). Add some 10 % of nickel and 1 % or so of manganese, and the transformation temperature from austenite to ferrite comes [way down](#) from its customary 770 °C (1418 °F). It gets low enough so it doesn't take place at all anymore. You now have steel with an fcc lattice with the remarkable property that it is **not magnetic**.

Austenitic steels are not only rustproof and non-magnetic, they can also be made to be relatively hard. Since they are [fcc crystals](#), they do not suffer much from the dreaded [ductile-to-brittle \(DTB\) transition](#) and thus are great for low-temperature applications. They are typically more ductile than comparable plain carbon steel and thus are easy to work with because they can be pressed or drawn. They also have better aging properties but are more difficult to machine.

● You will find a lot of austenitic steel around you. Your kitchen sink will almost certainly consist of austenitic steel but also the inside of your electron microscope, and many of the pipes in your nuclear power plant.

▶ By the way, I know that a lot of you guys out there hate stainless steel knives on the ground that they cannot be kept sharp. I will address this topic later.