

9.4 Phosphorous Steel

9.4.1 Phosphorous Steel - an Orderly Introduction

Why We Need to Look at Phosphorous Steel

Now lets have part of the truth about **Phosphorous** (P) in steel - the rest will follow later. Phosphorous was and still is an undesired element in almost all old and modern steels. Only recently it is used - carefully - as an useful [alloying element](#) in some advanced steels. [Cold shortness](#) is one of the major problems it causes. Phosphorous increases the [DTB transition temperature](#); brittle steel at cold weather results.

But so far I have consistently maintained that phosphorous is supposed to be not *always* harmful like sulfur; it might even be beneficial. So what are its good points?

- Phosphorous can be used to harden steel. So long as it is atomically dissolved it is one of the three outstanding [solution hardeners](#); look at the diagram in the link. What's more, it might protect the steel from corrosion. The uncorroded part of the pattern-welded sword [shown here](#) was phosphorous steel for sure. Phosphorous also changes the [look](#) of your steel. It makes steel brighter or "whiter" and that was of large importance for **pattern welding** techniques, where the pattern should be clearly visible.
- Nevertheless, in the 19th century a lot of time, money and effort went into getting phosphorous out of iron; I'll get to that. Nowadays we rarely employ phosphorous (P) for modern steel - in contrast to sulfur (S)! I've stated that sulfur is *always* bad before, but there are exceptions. It is exactly the "bad" properties of sulfur that are made useful for some special applications; [this link](#) will tell.

So why do I devote a whole sub-chapter to phosphorous steel? Simple:

**Phosphorous steel played a major role
in ancient steelmaking.**

- Moreover, since many European ores tend to contain plenty of phosphorous, dealing with its many effects exercised steelmakers mightily until not so long ago. I will cover that later in some more detail.

Before I get started, one more word to the wise: In the light of more recent insights, it is quite possible that not everything labelled "phosphorous steel" in the past is actually phosphorous (P) steel. It might be steel containing arsenic (As) or an As - P mixture.

It's not so simple to tell the difference without rather modern analytical tools. I will get to that later, too.

The Ancient Iron Pillar in India that Does Not Rust

In Delhi you find a famous 1600-year-old huge **iron pillar** (7 m tall, 6 tons in weight), forged together from many pieces of wrought iron with low carbon content that simply does **not rust**. Its "secret" has recently been unveiled by Indian scientists. The relatively large amounts of

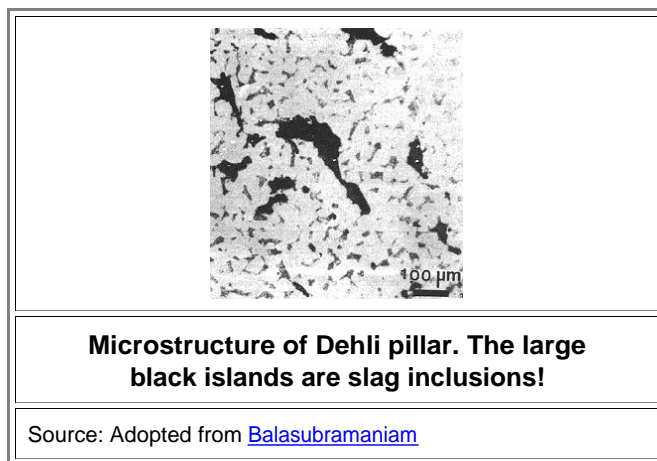
phosphorous in the iron and in **slag particles** within the iron, catalyzed the formation of a special kind of rust, so-called δ -FeOOH ("**Misawite**") plus a layer of crystalline phosphates that together form a stable protective layer on its surface.

This [basic paper](#) from **R. Balasubramaniam** relates the story of the pillar in great detail and goes into great length to describe its microstructure and the history of its investigation. His [second article](#) is shorter and asks if we can learn anything from the old phosphorous-iron? Not surprisingly, his answer is: yes, indeed!

I doubt very much, however, that the international steel community is listening.

- The New Dehli iron pillar, while certainly a work of art and technological cunning, is actually made from a poor kind of steel. Its composition varies and the carbon concentration is generally low. Typically it contains somewhat more phosphorous than carbon. In consequence, it shows the *typical* phosphorous "**ghost structure**" (see below) when a [structural etch](#) is done.

Moreover, it contains *a lot* of slag inclusions. Really - look at the picture below! The large black stuff is slag. I don't want to be a spoil sport, but if a [composite material](#) like this can still be called "steel" is questionable. In any case, a sword made from that material may not have corroded easily but I don't believe you would have been happy with it in a fight.



**Rust proof
1600
years
old iron
pillar in
New
Dehli**

Source:
Wikipedia

- ▶ The Dehli pillar illustrates quite nicely that whenever you attempted to make steel in ancient times, you may have run into phosphorous (P) as one of the major alloying elements in your steel. That was true then, and it still is true now. Part of the reason for this is that the "**bog iron**", used for millennia to make iron and steel in large parts of the world, contained relatively large amounts of phosphorous. Regular ore in large parts of the world is often phosphorous-rich, too. Part of the steel technology of old thus followed the old anglo-saxon proverb "if you can't beat 'em, join 'em", and made and used primarily phosphorous steel or phosphorous-carbon and not "plain" carbon steel.

- You, the smith of old, did not have the faintest idea about phosphorous in your iron, of course. When you made (or more likely bought) a piece of iron / steel, you didn't call it carbon or phosphorous steel. You differentiated the various kinds of iron / steel available in different ways - and we do not know much about that. Perhaps you knew that the "more shiny" steel needed to be treated in a different way.

If you belonged to the smiths who could, for example, make a Roman pattern welded sword of the 3rd century, you must have had a whole bag of tricks up your sleeve, and it is doubtful that we know them all. I have tried to collect some of that in a [science module](#) but we can never be sure of what we missed.

- So you actually made **phosphorous steel swords**. How good they were - I don't know. Many are still around and displayed in museums (not necessarily meaning that the [museum knows](#) that). They may be a bit worse for wear but not as badly corroded as carbon steel swords.

If those phosphorous steel swords would have been an inferior product that got you killed easily, they wouldn't have been on the market for centuries in the good old times.

You will see that phosphorous is just as efficient as carbon and nitrogen (N) for [solid solution hardening](#) of ferrite, just look at [this figure](#) again. Ferrite is the bcc or α phase of iron / steel and that, according to the phase diagram, is what we will have in the iron - phosphorous system for very low phosphorous concentrations at room temperature.

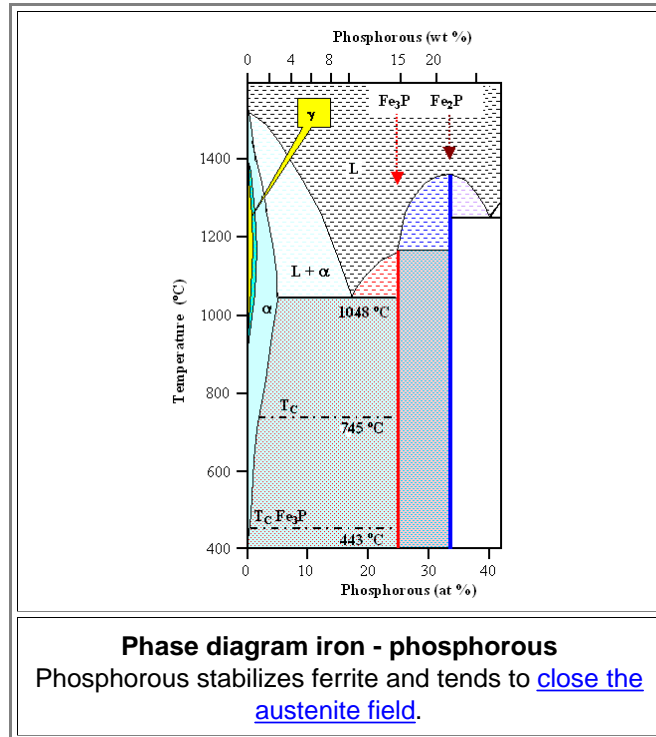
So you actually can harden ferritic iron with a small amount of phosphorous.

- ▶ In what follows I will first give the "science" of phosphorous steel a quick look, and then consider old phosphorous steel a bit. The issue will come up again in the chapters to follow, where I deal with iron / steel making and swords in more detail

The Science of Phosphorous Steel

Let's do a laboratory kind of (thought) experiment and make an ideal **phosphorous** or **P-steel**. R. Balasubramaniam (or rather, I suppose, a grad student) has done exactly that; look it up in the [second article](#) mentioned above. Or maybe don't. If you got so far with this Hyperscript and understood the vital parts of it, you will now go straight to the jugular and tell me: "Give me the iron (Fe) - phosphorous (P) **phase diagram**. Knowing now a bit about hardening mechanism in general, plus having the phase diagram", you are telling me, "will allow me to make some prediction about P-steel. How difficult can it be".

- OK - here goes. Here is the iron - phosphorous phase diagram. If you compare it to the [iron- carbon phase diagram](#) - you probably will get a bit confused. There are some similarities, alright, but especially for the **low phosphorous part** the phase diagram is quite different.

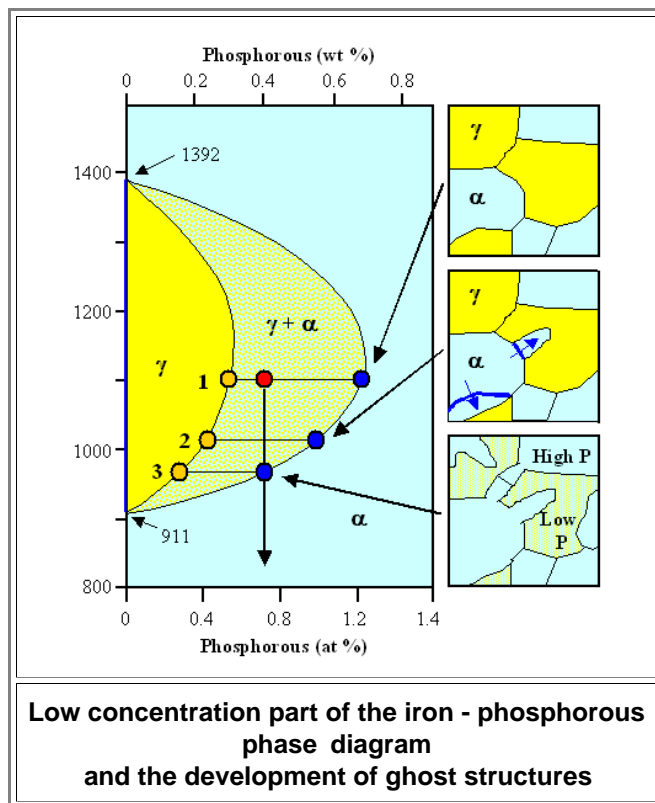


- There is hardly any austenite (the yellow γ phase). That's because phosphorous does what is known as "closing the γ-field"; just like arsenic (As), silicon (Si), aluminium (Al), beryllium (Be), titanium (Ti), vanadium (V), molybdenum (Mo) and chromium (Cr). More to that in the science link.
- Below is an enlargement of the important part of the Fe-P phase diagram. It is actually easy to understand. Just assume that phosphorous hates the γ-phase or austenite so much that it will do everything to avoid it. Ideally there should be *no* γ-phase. On the other hand, pure iron *must* have the fcc γ-phase between 911 °C (1672 °F) and 1392 °C (2538 °F); this is symbolized by the fat dark blue line.

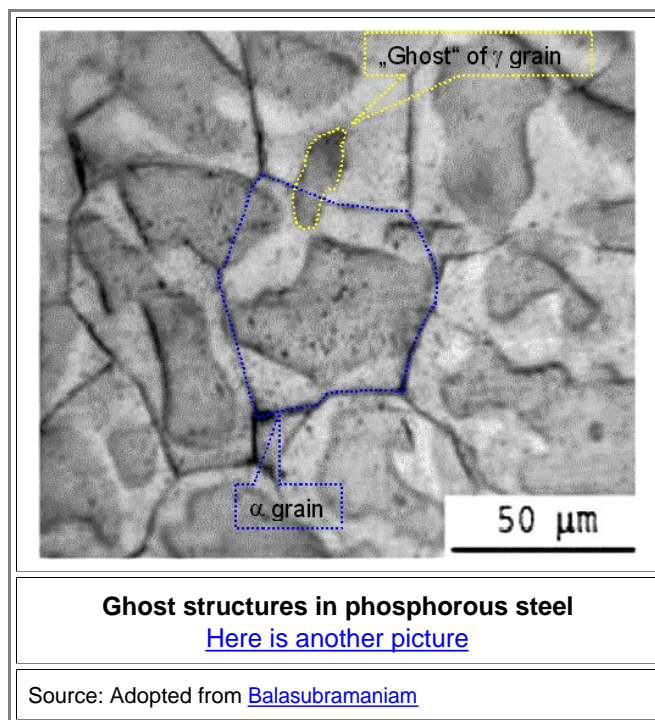
So at compositions close to pure iron the phase diagram as shown below is just the best compromise between totally conflicting demands. By the way; I used different colors for the same phases or phase mixtures in the two phase diagrams shown here. I did that not only because I'm lazy and didn't check what color I used before but also to demonstrate that those colors are completely meaningless. Their only job is to make the pictures prettier and to guide the eye.

[Science Link](#)

**Alloy
science**



Now go ahead and derive the microstructure you are going to see at room temperature, starting with the red [state point](#) I'll give you an hint: Looking at the microstructure at room temperature with some etchant that is sensitive to phosphorous, you will find a "ghost structure". The picture below shows some "ghosts" from the New Delhi pillar. Can you do it? I doubt it. That's why I included a few helpful sketches in the picture above.

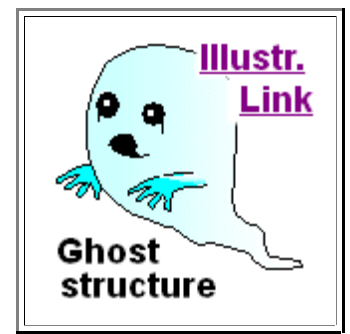


What do we see? We know that we must have ferrite, and the dark lines, as always, are the grain boundaries between the ferrite or α grains. The darker areas are the "ghosts". They become especially well visible if you play with the focus of your microscope a bit. Depending on your focus setting they could also be brighter than the rest. The ghosts in the picture above are actually depressions in the ferrite grains. You thus can focus either on the lower surface within the depressions or the higher surface; both are seen best at some defocus conditions at low magnification. But why should the etchant remove more material in some areas? Because

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The ghosts in the picture above are actually depressions in the ferrite grains. You thus can focus either on the lower surface within the depressions or the higher surface; both are seen best at some defocus conditions at low magnification.

But why should the etchant remove more material in some areas? Because the ghost are phosphorous-*poor* regions, etching a bit faster than the phosphorous-*rich* areas. They are the "memories" of the phosphorous-poor *austenite grains* that formed within the ferrite grains and then disappeared again.



Let's see how that works:

At the temperature where we start in the example above we have coexisting ferrite and austenite grains. If you allow enough time at the starting temperature, the grains will be rather large, with the ferrite grains being phosphorous-rich (about 1.2 %) and the austenite grains being phosphorous-poor (about 0.5 %) as indicated by the necessary splitting of the state point. As soon as we start to cool down, the ferrite grains must grow and the austenite grains shrink. This is easily done, the existing ferrite or α grains will just penetrate into the austenite, as shown in the middle figure. However, the new α parts will be phosphorous-lean since there is normally not enough time for the phosphorous atoms in the "old" α grains to diffuse into the new areas. As soon as we leave the two-phase area around 910 °C (1670 °F), all austenite has turned into ferrite, but it will be phosphorous-poor ferrite!

We have only ferrite now but the former austenite regions will now be phosphorous-poor ferrite embedded into phosphorous-rich ferrite. Since most etchants dissolve phosphorous-poor ferrite a little faster than phosphorous-rich ferrite, the phosphorous-rich regions stand up like mesas on the plane of the phosphorous-poor background. Here are your ghosts!

The link not only gives more details but also points out why phosphorous ghosts are not quite as simple as I make them look here.

But beware! Any alloying element that is an α -stabilizer must have a phase diagram similar to that of iron-phosphorous for low concentrations and thus produce "ghost" austenite.

In either case, if you shall see "ghost" after some defect etching depends on how well the alloying element could equilibrate its concentration during cooling (not all that well, probably) and in particular if your etchant picks up small concentration differences of some element being in there in small average concentrations. That is rather unlikely - except the element in question does similar things as phosphorous and that is probably true for arsenic (As) and maybe antimony (Sb).

It is quite possible (if not very likely) that ancient steels that have been classified as "phosphorous steel" because a ghost structure was seen after etching, actually contain either phosphorous, arsenic, antimony, or a mix of those elements. Research into this is just starting.

What else besides ghost structures might we find in phosphorous steel? **Iron-phosphide precipitates** (Fe_3P), of course. Look at the phase diagram!

Considering that we usually do not have "plain" phosphorous steel but steel with a mix of carbon and phosphorous (plus whatever else might be there), things tend to be even more complicated.

There is no need to delve deeper into this, however.

Knowing the microstructure is nevertheless very important. It gives clues as to the heat treatment and the hardness and ductility of phosphorous steel, and that is no mean feat! Unfortunately the microstructure doesn't tell us much about other interesting properties of phosphorous steel:

- Phosphorous steel is "white", i.e. reflects visible light in a different way than "normal" steel. That is an important property for pattern welded swords since it allows to see the pattern! How that property relates to the structure is something I do not know. I do know, however, that this is a tough nut to crack.
- Phosphorous steel corrodes considerably less than regular (carbon) steel of comparable (medium - low) hardness. Once more a property that is not easy to predict from knowing the microstructure. One might guess that the absence of large cementite particles is helpful but that doesn't lead very far. Just like optical properties, [corrosion relates to surface properties](#) and knowing the bulk structure doesn't help all that much.
- Phosphorous steel has a strong tendency to be "[cold-short](#)"! That is very, very bad! I don't think that anyone could predict the rather extreme influence of phosphorous on the [ductile-to-brittle transition](#) from only knowing the microstructure!

The long and short of all this is: Phosphorous in iron has exercised iron and steel people very much throughout the millennia - and it will keep doing this! It is a kind of thorn in the soft underbelly of iron and steel science that causes permanent pain, reminding us that we are not yet finished with Material Science in general and steel science in particular.

On the other hand it was used a lot. Maybe just out of necessity because you couldn't avoid it but evidence is mounting that our forefathers used the stuff deliberately and possibly even made it on purpose!