

## 9.4.2 Phosphorous Steel - a Chaotic Succession

Originally I planned to call this module "Phosphorous in Ancient Times". After quite some time of looking into the issue, I concluded that the new headline is better. So I won't go smoothly from one point to the next, pointing out how they are all related, that we understand it all, and that my brethren and I are really superior guys who you should send large amounts of money to or at least worship a bit.

I'll just give you a taste treat of what is out there. Since the topic "phosphorous in iron" will come up several times again in various contexts, I will on occasion also give links to one of the modules *ahead*.

Let's start with a quote from [Samantha Rubinson's](#) 2010 thesis, p.280:

- "Phosphoric iron was a commonly used alloy in the Early Medieval Britain. 66% of the artifacts examined in [this study](#) contained significant amounts of phosphorus in their iron alloys. This research found that phosphoric iron was one of the three major iron alloys used in Early Medieval Britain. This result indicates that phosphoric iron was present in much larger quantities than previous studies (McDonnell 1987b, McDonnell 1992, Tylecote and Gilmour 1986) were able to identify. This discrepancy was due to the limitations in identification of the alloy. .... These results indicate that many of the preconceptions of phosphoric iron are invalid."<sup>1)</sup>

Consider this, and in addition that phosphoric steel was nearly always used in the heydays of the pattern-welded sword (300 AD - 800 AD) on the continent. A first *major* question emerges:

**Did our forebears make phosphoric iron *intentionally*?**

Did our forebears *like* to work with the stuff? So far everybody (including me) more or less assumed without much discussion that phosphorous in (old) iron got in there *unintentionally* because phosphorous-bearing iron ore was used in smelting. Samantha Rubinson and others are not so sure anymore. Maybe the old ironmongers added phosphorous-bearing stuff like [bones](#) (containing apatite or calcium phosphate) *intentionally* to what they put into their smelters?

- This questions leads us straight to smelting technologies, the growing awareness that smelting iron is far more tricky than imagined, and that our ancestors could smelt iron and steel in far better ways than imagined not so long ago.

We simply do not know enough about the old "bloomery" techniques used before the advent of the blast furnace - roughly - around 1400. More to that (far more!) in [chapter 10.2](#)

There is second (minor) question hiding in that quote: Who discovered when and where that ancient steel was often phosphoric steel?

- Samantha quotes work of McDonnell, Tylecote and Gilmour from about 1985. I feel certain that there are older sources but don't feel like looking into that right now. That feeling is partially due to the expectation that early researchers stumbling on to phosphoric iron could not possibly have gotten everything right. Getting a grasp on phosphoric iron needs more than seeing some [ghosts](#), interpreted as phosphorous-rich areas, after defect etching. And that "more" was not available until 20 years ago.

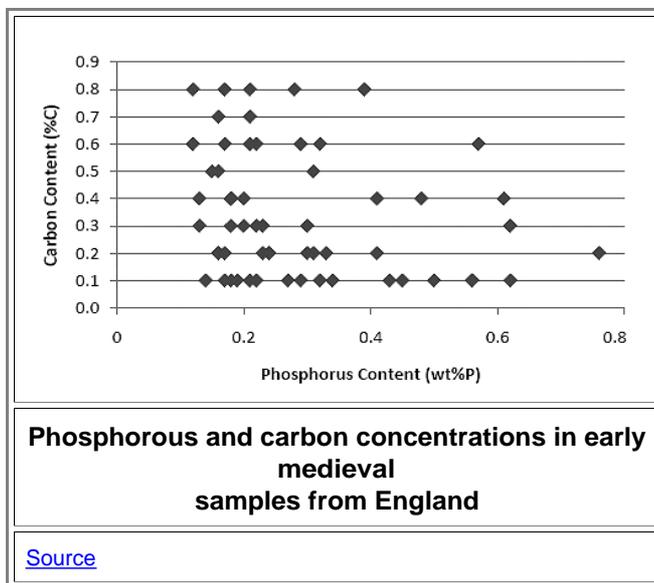
This leads straight to the next point, raised more recently by Samatha Rubinson but also by others:

- Could it be that "ghost structures" or other etching results that were interpreted as caused by phosphorous were actually due to other elements, e.g. arsenic? Or maybe a mixture of elements? The general answer is: Yes, it could be. After that it becomes muddy. While there are indications that there is such a thing as ancient arsenic iron or phosphoric-arsenic iron, it is to early for me to go deeper into this.

Of course, one needs also to consider the negation of the question above: Could it be that there is phosphorous / arsenic / etc. in the steel and *no* [ghost structures](#) are produced?

- Yes, that could be; says Samantha ("In many cases no indicators were present to identify the presence of phosphorus in the ferritic microstructure"). Ghosts are tricky (the British should know) and not always around when they should be. Again, a topic that needs far more research before much more can be said.

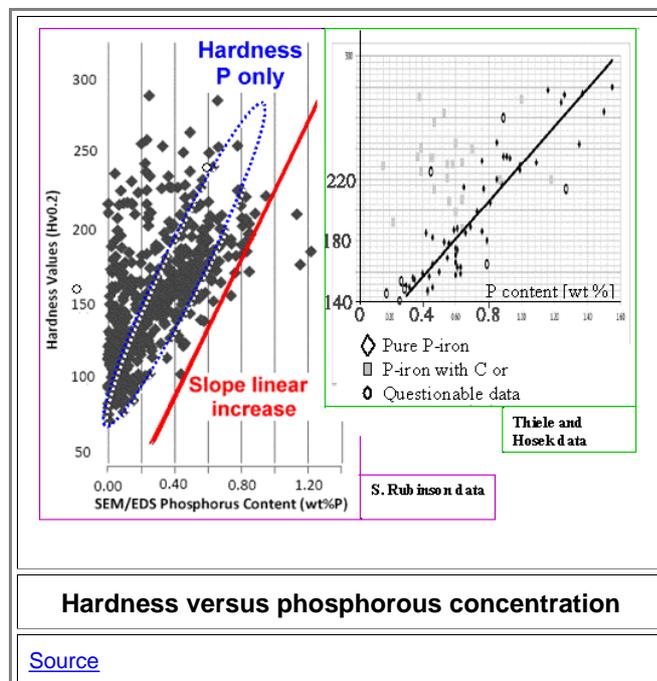
While a steel containing some phosphorous *and* some arsenic can be expected to behave roughly like a steel with only phosphorous at some higher concentration (the sum of both), the same can not be true for a steel that contains phosphorous and some *carbon*. While we do know a few things about P,C- steel, I won't go into that topic except to note that this kind of ternary alloy was rather common, at least as far as studied by Samantha Rubinson. Here is what she found:



There is no particular trend visible; almost everything goes. Note on the side that almost pure carbon steels come with concentrations between 0.1 % and - hypereutectoid (!) 0.9 %.

Now let's look at a few more interesting points:

- There seems to be some consensus that phosphoric iron is **easier to forge** and to work with than carbon steel. It seems to be particularly beneficial to **wire drawing**. That is not only claimed in the link given above but seems to be a kind of diffuse common knowledge. Of course, we will only get to know particulars if experienced smiths do specific and well-designed experiments.
- Phosphoric iron can be **harder** than wrought iron. That is no surprise, we know already that it is one of the three outstanding **solution hardeners**. However, this necessitates that the phosphorous is atomically dissolved and not precipitated as the phase diagram demands for nirvana (equilibrium). In addition, it should not be concentrated in grain boundaries either. Here is what Samantha found (turned 90° and augmented by me) in comparison to what well-known Hungarian / Czech Republic researchers [1](#) found:



Samantha Rubinson's data are a bit strange. While quite a few points inside the range outlined in blue would fall on the expected linear increase line (that means doubling the P-concentration would double the hardness; the red line shows the slope), many samples are much harder than one would expect from only their phosphorous content, and few are softer. That could only mean that

- there was no appreciable precipitation of  $Fe_3P$ , and
- there must be additional hardening, probably because some carbon was also present and cementite has formed.

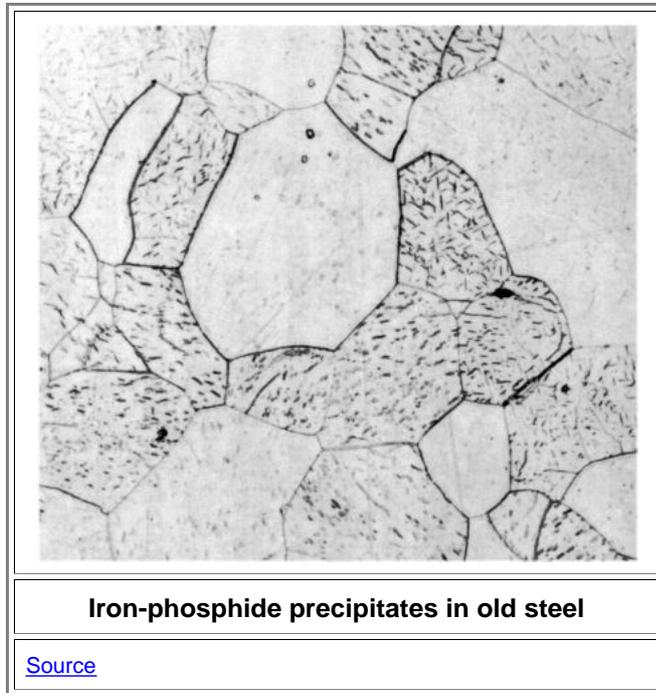
The data from Thiele and Hosek (matched in scale to the data of Rubinson) agree in general terms but not in detail,

showing once more that things are complex.

Whatever, while a hardness around 200 is not breathtaking if you think about the cutting edge of swords, it is respectable and quite sufficient for many other steel uses. The ancient smiths must have been puzzled no end that some initially hard steels could be further hardened by quenching but not always. Well, if an initial 200 hardness was due to phosphorous and not to carbon, quenching cannot produce martensite and thus extreme hardness.

So no **Fe<sub>3</sub>P precipitates** in all the samples above?. That could well be the case. The precipitation of phosphorous is difficult because it has to happen at relatively low temperatures. We might establish a "no Fe<sub>3</sub>P precipitates" rule at this point. In fact, Samantha Rubinson, while spelling out "phosphoric iron" a few 100 times in her [thesis](#), never ever mentions Fe<sub>3</sub>P precipitates.

But we should be careful about generalizations. Buchwald has encountered old steel that did contain iron-phosphide precipitates (and thus was rather soft for its phosphorous concentration). Here is the relevant picture:



The little black dashes are iron-phosphide precipitates according to Buchwald. Why that exception to the "no Fe<sub>3</sub>P precipitates" rule? Well, maybe that sample has gone through some annealing that just happened to be perfect for inducing precipitation. Maybe most of the precipitate growth happened in the 1000+ years the sample was hanging around at room temperature? Maybe those "little black dashes" aren't Fe<sub>3</sub>P precipitates but some stuff containing arsenic? (Buchwald couldn't yet know about that possibility).

Your guess is as good as mine: We need to wait until more research clears up the topic.

What about **arsenic steel**? Is there such a thing as iron with (almost) only arsenic (As) as alloy element? Well - not quite. Samantha Rubinson did find a few pieces with high arsenic concentrations of up to 1 %, but always mingled with the other stuff. She figures that it was in there unintentionally - in contrast to phosphorous.

So arsenic is not interesting? Note quite so. We will encounter it again in the context of the so-called "[white weld lines](#)". This is another still mysterious topic that needs elucidation.

All things considered, we do not need to be overly worried about arsenic in iron. One must keep an open mind, though.

Why is phosphoric steel more **corrosion resistant**? Because it is more homogeneous than carbon steel. There are no cementite particles sticking out into the surface that can't be covered by a [passivating oxide](#). In addition, some corrosion inhibiting phosphates might form as [outlined before](#). Note that phosphoric iron is not "stainless", it just rusts slower than comparable carbon steel. The [practical consequences](#) may have been considerable, however. No big mystery here - although the details are far from clear.

As the last point, we need to consider the "**whiteness**" of phosphoric iron or "silvery iron" as it was sometimes called according to Samantha Rubinson. All I can tell you is that I know a lot about why materials appear more or less colored if viewed with normal light, that it can't be explained in simple terms, and that I do not have a clear idea about how a little bit of phosphorous changes the appearance of a piece of iron.

Of course, you never look at a piece of iron but always at a piece of iron covered by some *thin layer of oxides*. These oxide influence the "color", the appearance to the naked eye. So maybe the oxides on phosphoric iron are different from those on regular steel an "make" the silvery-white appearance? I have a clear answer to that: I don't know.

▶ All things considered, phosphoric iron has quite a lot going for it. It has two big disadvantages, however:

1. It promotes brittleness, in particular cold-shortness.
2. It does not allow high hardness levels since no martensite can be formed.

The second point is not a problem for many applications but cold-shortness is. Or is it?

To be sure: phosphorous does cause cold-shortness and the "silvery iron" or whatever else it was called in ancient times was known to become brittle when cold. At least most of the time. We are allowed to wonder, however, if there might have been ways to make phosphoric iron from some bloomeries, containing slag particles and a little bit of this and that, less brittle than the "common" variants if treated "right"?

If we look into [cold shortness scientifically](#), and into the [influence of small amounts of impurities](#) and alloy atoms, we find that we look into an extremely complex issue. Phosphorous causes extreme cold-shortness and parts of the mechanism behind that is its tendency to precipitate into grain boundaries. Avoid that and you get non-brittle or ductile phosphoric iron?

- To quote S. Rubinson once more: "[In most archaeological artifacts there is no evidence of brittleness in the phosphoric iron microstructure ... . Vallbona \(1997\) suggested that this was the result of the presence of slag](#)". Maybe the ubiquitous slag particles in bloomery steel are good in this case? Hard to know because modern steel that is typically used for experiments does not have slag inclusions. Well, modern phosphoric iron has a champion on its own, [E. Balasubramaniam](#), who we have met not that long ago. He looked into the issue in some detail: "[In order to understand the possible method by which the ancient blacksmiths overcame the problem of embrittlement in phosphoric irons, a very careful study of the microstructures of several ancient Indian irons \(dating from the 5th Century AD up to the 19th Century AD\) was undertaken.](#)" I give you the whole 2003 paper in [this link](#).

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▶ Enough! Throughout the history of iron up to modern times, phosphorous in steel has provided for much trouble but was nevertheless extensively and deliberately used. The last word to that topic needs yet to be spoken!

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<sup>1)</sup> [Ádám Thiele and Jirí Hošek](#): "Estimation of phosphorus content in archaeological iron objects by means of optical metallography and hardness measurements", Acta Polytechnica Hungarica, after 2012 (no more data given)