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# Looking into the Past for Materials of the Future

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The Gupta period Delhi Iron Pillar (see **Figure 1**) is testimony to the high level of skill achieved b ancient Indian iron smiths in the extraction and processing of iron. This Pillar has attracted the attention of corrosion technologists because it has withstood corrosion for the last 1600 years. The presence of relatively high phosphorus (0.25 wt-%) in the forge welded Delhi Iron Pillar plays a ma role in its excellent corrosion resistance [1, 2]. The presence of phosphorus leads to the formation o protective passive film on the surface, which provides the Pillar its exceptional corrosion resistance properties. However, in modern steel making process, the phosphorus content is controlled to 0.05 % because phosphorus segregation to grain boundaries reduces ductility of steel.

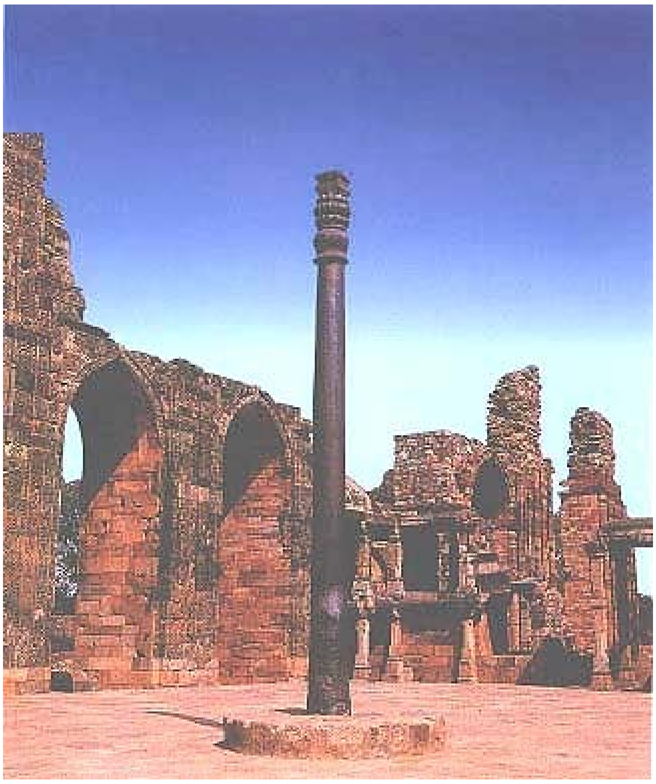

**Figure 1**: Delhi Iron Pillar at Qutub Minar complex in New Delhi.

The phase diagram of iron-phosphorus shows a (alpha + gamma) dual phase region at high tempera (see **Fig. 2**). If a phosphoric iron in the composition range 0.25 and 0.50 wt % P, is soaked in the tw phase region (temperature between $1000^{o}$C and $1100^{o}$C), then austenite phase ($\gamma$) will precipitate o the grain boundaries of ferrite phase ($\alpha$). This is well known in physical metallurgy. Austenite has higher solubility for carbon than phosphorus and therefore all the carbon is pushed to the grain boundary region while the phosphorus is removed from the grain boundary region. After a suitable soaking time at high temperature, the phosphoric irons can be air cooled to room temperature. The beneficial aspect of this treatment is that phosphorus, which was removed from the grain boundary

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regions, does not go back to these regions during air cooling because phosphorus requires time to diffuse to the grain boundary regions. In this manner, a high temperature soaking in the two phase region and subsequent air cooling should result in good ductility for phosphoric irons.

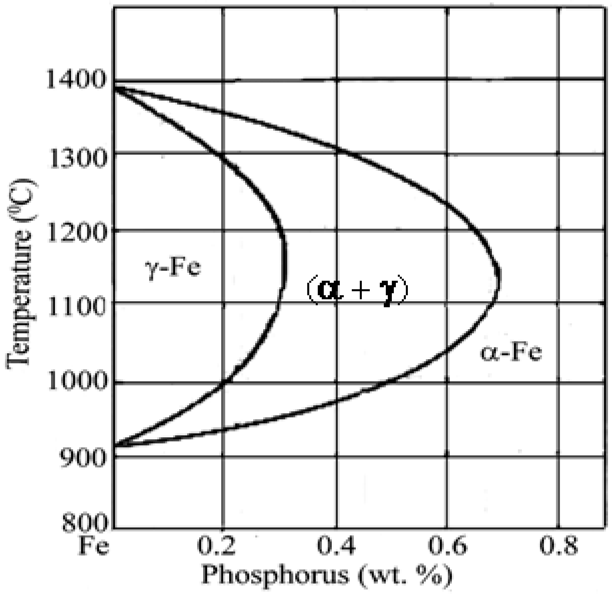

Figure 2: The high temperature gamma loop region of the Fe - P phase diagram.

How do we use the knowledge learnt from the study of the Iron Pillar for modern day technologica applications? In order to provide answers to this question, a detailed study was undertaken by a Ph student, **Gadadhar Sahoo**, under the guidance of Professor R. Balasubramaniam of the Materials a Metallurgical Engineering Department to understand possible industrial applications of phosphoric irons. The first aim was to render the phosphoric irons ductile. The second aim was to locate a mod application wherein the corrosion resistance of phosphoric irons could be put to good use. We shall delve into these aspects in this story of the week.

Ductility is a very important property from the point of practical application of any engineering material. How do we make phosphoric irons ductile? It is known that phosphorus segregation to th grain boundaries makes these locations weak and results in poor ductility. Therefore, the first aim the work was to find out methods to keep phosphorus away from the grain boundary. It was first realized that phosphorus will not be present in regions where carbon is located in the iron matrix because phosphorus is a substitutional solute element whereas carbon is an interstitial solute eleme Therefore, a small amount of carbon needs to be maintained in phosphoric irons. The next challeng to locate these carbon atoms along the grain boundaries, thereby keeping the phosphorus atoms aw from these locations. In order to achieve this, an intelligent use of the phase transformations in the iron-phosphorus system was applied.

In order to test this hypothesis, three phosphoric irons P1 (0.11 wt. % P), P2 (0.32 wt. % P) and P3 (0.49 wt. % P) were ingot cast and later forged to rods. In all these phosphoric irons, a small amou (0.02 wt. %) of carbon was maintained. Appropriate heat treatments were devised for these irons, a per the philosophy outlined above. Tensile testing of triplicate samples indicated good ducitlities f phosphoric irons, especially P1 and P2 (see **Fig. 3**). In the same figure, the tensile test result of a commercial reinforcement bar (TISCON of Tata Steel) used for concrete reinforcement application also shown.

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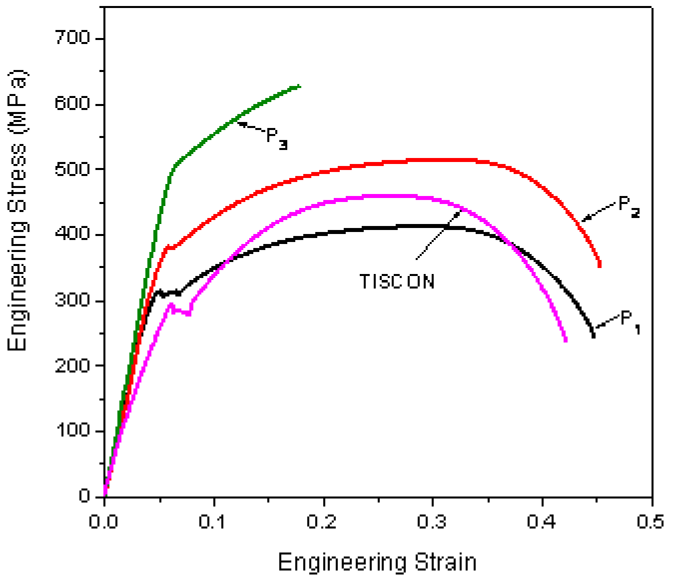

**Figure 3**: Typical engineering stress-strain curve of the specimens P1, P2, P3 and TISCON.

Good ductilities were obtained for phosphoric irons because phosphorus was kept away from the g boundaries. This was confirmed by microscopy (see **Fig. 4**). In this figure, the optical micrograph P2, that was soaked in the (alpha + gamma) dual phase region is shown, after etching with Nital. T light contrast at the grain boundaries indicates locations of low phosphorus content. Interestingly, t structure is known as a "**ghost" structure** because although the entire structure is ferrite at room temperature, the location of prior austenite and prior ferrite is revealed by the contrast that obtains to differences in phosphorus contents. Well, this is not important anyway here, but the idea of "gho does also apply in metallurgy!

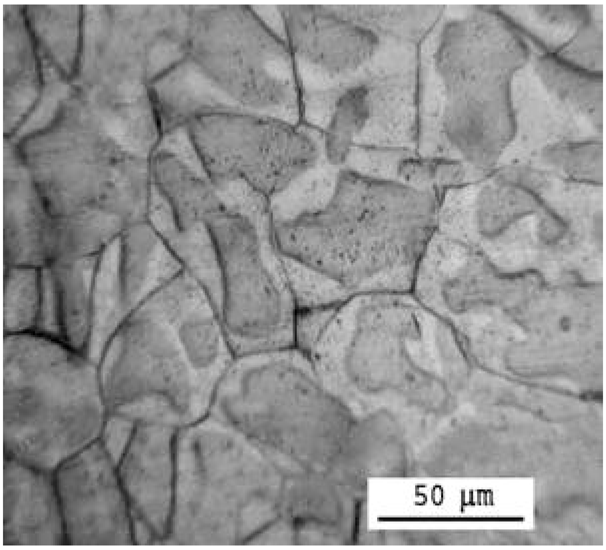

**Figure 4**: Optical micrograph of heat-treated specimen P2 after etching with Nital.

The good room temperature ductility obtained in phosphoric irons will remain as long as the materi are not exposed to the temperature range of $200^{o}$C to $600^{o}$C for long times. When phosphorus containing steels are exposed in this temperature range, phosphorus diffuses and segregates to the g boundaries, leading to their embrittlement. This is known as temper embrittlement. In case phospho irons have to be applied commercially in ambient temperature conditions, there would be absolutel problems regarding their ductility. We need to keep this in mind while looking for suitable applicat where phosphoric irons can be applied.

In this context, it is important to consider the production of reinforcing bars in concrete because a l tonnage of steel produced in a developing country like India is used for reinforcement of concrete i structural applications. The reinforcement bars have to possess the necessary strength, ductility and corrosion resistance. Modern-day reinforcement bars are strengthened by three methods, namely, microalloying with costly elements like Nb, Ti, etc., cold twisting (which used to be popular earlie and by controlled cooling in the bar mill plus cooling process. The last process is increasingly becoming popular in India and you must have noticed the advertisements for bars indicating that th are ?TMT bars? which stands for ?thermo-mechanically treated bars.? Phosphoric irons can be processed by a similar method utilizing the existing arrangements, with the major difference being ingot soaking, bar quenching and further cooling arrangements have to be fine tuned to produce phosphoric iron with a tough surface and a strong interior. This can be achieved by suitable design criteria [3].

The corrosion behavior of phosphoric irons has been evaluated in a wide variety of environments [ It was concluded that phosphoric irons possess necessary corrosion resistance in near neutral and alkaline conditions. A typical industrial application for which phosphoric irons may be applied is fo reinforcing concrete. Therefore, the corrosion resistance of phosphoric irons was evaluated extensi in simulated concrete environments and compared with commercially available material from Tata Steel, Jamshedpur . The results of the detailed study indicate the superior corrosion resistance of phosphoric irons in concrete conditions. For example, the corrosion rate of TISCON was much hig compared to phosphoric irons. Interestingly, phosphoric irons exhibited good passivity in concrete environments. A wide variety of techniques was used to study corrosion in concrete conditions [4]. These included polarization methods (linear and Tafel polarization), potentiodynamic polarization potentiostatic polarization, electrochemical impedance spectroscopy, salt fog immersion, complete immersion and atmospheric immersion experiments. Apart from samples exposed to aqueous solutions, cement-grouted samples were also tested to simulate actual application conditions

It is known that chloride ions are damaging to surfaces because they generally tend to destabilize th protective passive films on the surface. Surprisingly, phosphoric irons showed excellent corrosion resistance even in their presence. This significant result indicates that phosphoric irons will provide good service in environments where chloride ions are present, like in case of structures near seacoa As India possesses a large coast line, there is wide scope for using phosphoric irons in reinforced concrete structures near coastal areas, which generally call for higher material quality. This is the reason that the major steel makers in India , SAIL and TATA STEEL, market another quality of reinforcement bars, which they call CRS indicating "corrosion resistant steel." Generally, these stee contain a little amount of Cu and Cr as alloying additions and they are costly compared to normal reinforcement bars. Phosphoric irons can perform as good as, if not better, than these commercial C materials. An added advantage is that they will not be costly compared normal TMT bars.

In order to visually show the good corrosion behavior of phosphoric irons, the result of immersion testing in saturated $Ca(OH)_2$ solution containing 5 % NaCl is shown in **Figure 5**. The nature of sur after 125 days of immersion can be noted for three phosphoric irons and two commercial grades of reinforcement steels from Tata Steel (TISCON and CRS). The severe nature of corrosion in case of P1 , TISCON and CRS is quite clear. Phosphoric iron P3 is the most resistant, followed by P2 and t P1. These visual images clearly prove the beneficial effect of phosphorus in conferring corrosion resistance, especially in simulated concrete pore solution containing a relatively high concentration aggressive chloride ions [5].

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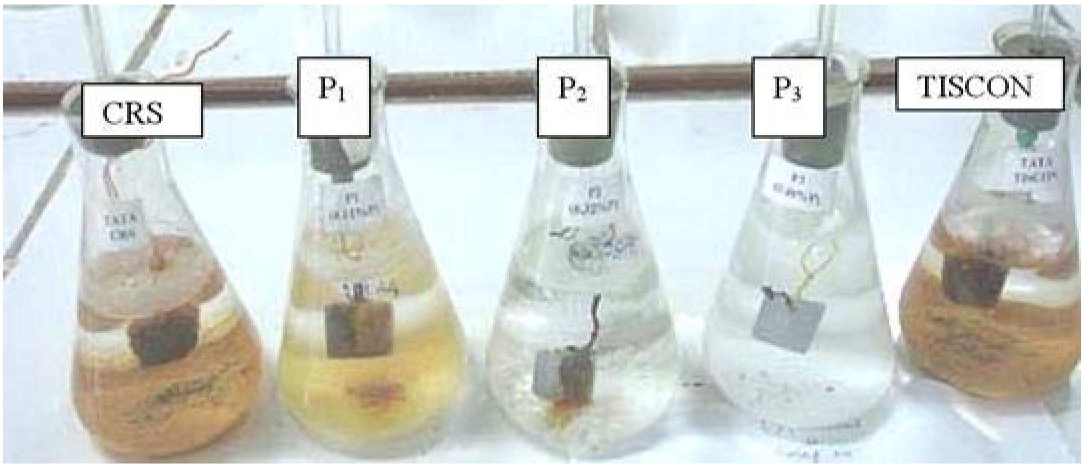

**Figure 5:** Immersion testing samples after 125 days of immersion in saturated Ca $(OH)_2$ solution containing 5 % NaCl.

We realize that ideas for developing phosphoric irons originated from the study of the Metallurgica Wonder of India - the Delhi Iron Pillar. You will all now, we hope, believe in the old adage that "th best of the new is often the long forgotten past."

## References:

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