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Tensile and plane bending fatigue properties of pure iron and iron-phosphorus alloys at room temperature in the air

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Abstract

In many low alloys as well as in plain carbon steels, segregation of trace element, especially phosphorus (P), sulfur (S), arsenic (As), etc. is really a great problem. Because, it induces brittleness in the steels and subsequently causes deterioration in mechanical properties. In this present work, commercial grade of pure iron with varying amount of phosphorus contents such as 0.001, 0.11 and 0.21 wt% were annealed at different temperatures and time periods to induce varying degrees of temper embrittlement. After annealing heat treatment, tensile and plane bending fatigue tests of these ferrous alloys were carried out at room temperature in the air. The tensile and fatigue fracture surfaces were observed under scanning electron microscope (SEM) to study various fracture features. It has been found that the addition of phosphorus in the pure iron increased the tensile strength, however, it decreased the ductility. The grain refining effects and increase in tensile strength due to additions of P were found to be very significant. However, with increase in annealing time at any temperature, the mechanical properties were found to deteriorate gradually and the fatigue fracture mode was also found to change from its transgranular cleavage type to intergranular type fracture.

1. Introduction

Reversible temper embrittlement has been frequently observed in many different low alloy steels serving at high temperatures, e.g. order of 500°C or during slow cooling from high temperature. This type of embrittlement might change the brittle transgranular fracture mode (either in fatigue or fast fracture) to intergranular one, with subsequence deterioration in fracture toughness [1-6]. In many cases, phosphorus plays an important role for inducing this type of unwanted effect in low alloy steels. So, in general, phosphorus is considered as a detrimental element in low alloy steels. For interstitial free or low carbon structural steel, it also has a great tendency to segregate at grain boundaries and/or other microstructural sites during cooling period after hot working [7-9]. In many cases, hot rolled steel is cold worked for some special properties, e.g. good surface finish, better dimensional tolerances and/or better strength. However, the fatigue properties of the cold worked steels are deteriorated severely [10-11].

There is no doubt that phosphorus, in general, induces temper embrittlement and degrades the mechanical properties of many steels. However, careful control of the thermomechanical treatment, phosphorus in steel might be beneficial in many cases. As per Hall-Petch relationship given below, refining in grain sizes means heightening the tensile strength of the steel.

$$\sigma_o = \sigma_i + KD^{-1/2} \qquad (1)$$

Where σ_0 is yield strength, σ_i is friction stress, K is locking parameter and D is the grain diameter. Additions of small amount of phosphorus in iron/steel decreases the prior austenite as well as the ferrite-pearlite grain sizes. It also increases the strength of steels by solid solution strengthening mechanism [12,13]. In order to improve the corrosion resistance of thermomechanically treated (TMT) structural steels bars used for reinforcement of concrete, P-added TMT (TMT-P) steel has also been developed [14-17]. The purposes of this research work is to have a better understanding concerning the improvement of tensile as well as fatigue lives by adding phosphorus in iron and the possible deterioration in various mechanical properties if these steels are annealed.

2. Experimental

The materials used in this work were commercial grade of pure iron and phosphorus added iron (0.11% P: Fe-P-I and 0.21% P: Fe-P-II) alloys. The chemical compositions of these three alloys are presented in Table 1. These alloys were melted in vacuum by induction melting and forged at National Institute of Materials (NIMS), Japan. In order to change the grain sizes of these test alloys, they all were annealed at different temperatures such as 700, 800 and 900°C. All test alloys were annealed for three different time periods as 5 minutes, 1 hour and 10 hours at 700°C. However, for 800 and 900°C only one hour annealing period was used.

Table 1 : Chemical compositions (wt %) of the iron and Fe-P alloys used.

Material Identification	*C*	*Si*	*Mn*	*P*	*S*
Pure Iron	0.003	<0.001	<0.001	0.001	0.001
Fe-P-I Alloy	0.003	<0.001	<0.001	0.110	0.017
Fe-P-II Alloy	0.003	<0.001	<0.001	0.210	0.005

After annealing, metallographic samples were prepared and etched with 5% Nital following the standard procedure. They were then observed under the SEM to identify the microstructures and establish the grain sizes. The average ferrite grain sizes of all annealed steels were measured and presented in Table 2. After necessary heat treatment, tensile tests were carried out by a Universal tensile testing machine at room temperature in the air. Using a plane bending fatigue testing machine (Tokyo Koki Seizosho, Ltd., Model: PBF-30C), fatigue tests were also conducted at room temperature in the air. For all alloys, fatigue tests were carried out at a frequency of 1000 cycle per minute (cpm). The geometries of the tensile and fatigue specimens are shown, respectively, in Figs. 1 and 2. In order to have a complete *S-N* (stress versus number of fatigue cycle) curves about six specimens under all annealing conditions were tested starting from different levels of initial bending stresses.

Table 2 : Average ferrite grain sizes (mm) of the alloys after annealing.

Material Identification	*Annealing Temperature and Time Periods*				
	700°C/ 5min	*700°C/ 1h*	*700°C/ 10h*	*800°C/ 1h*	*900°C/ 1h*
Pure Iron	35	40	44	58	83
Fe-P-I17	18	21	27	42	
Fe-P-II	15	16	18	24	40

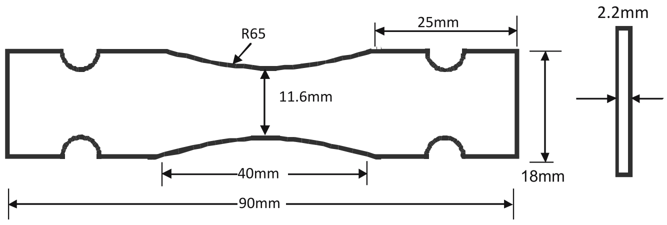

Fig. 1 : Geometry of fatigue test specimen.

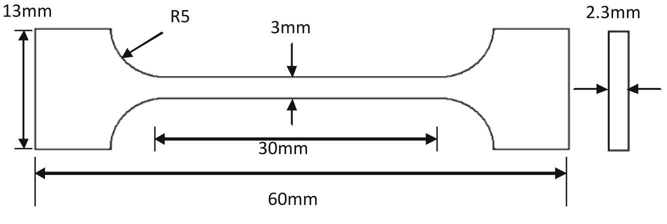

Fig. 2 : Geometry of tensile test specimen.

3. Results and discussion

3.1 Tensile behaviour

3.1.1 Effect of annealing time on tensile properties

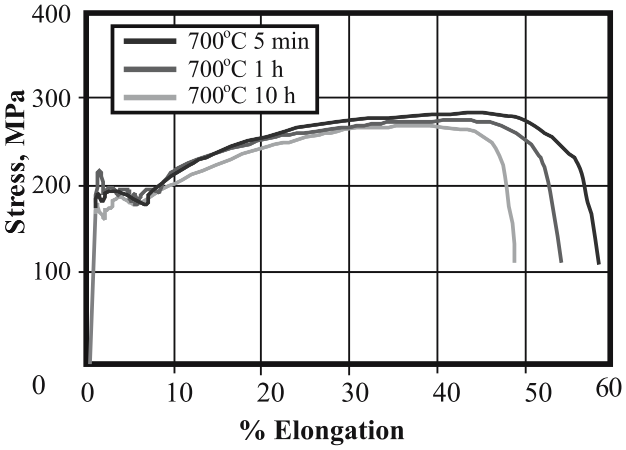

Fig. 3 : Nominal stress-strain curves of pure iron annealed at 700°C for different time periods.

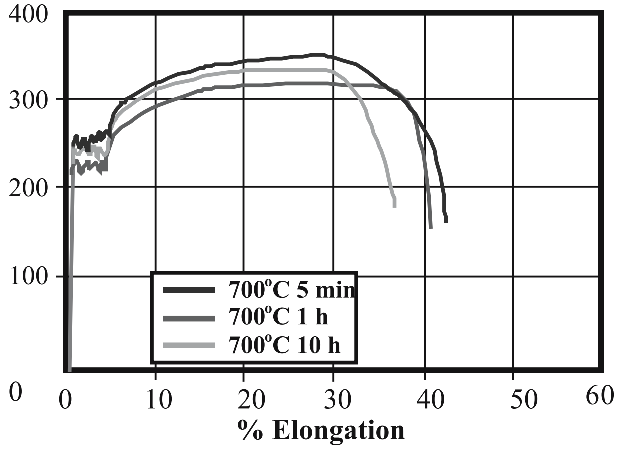

Fig. 4 : Nominal stress-strain curves of Fe-P-I alloy annealed at 700°C for different time periods.

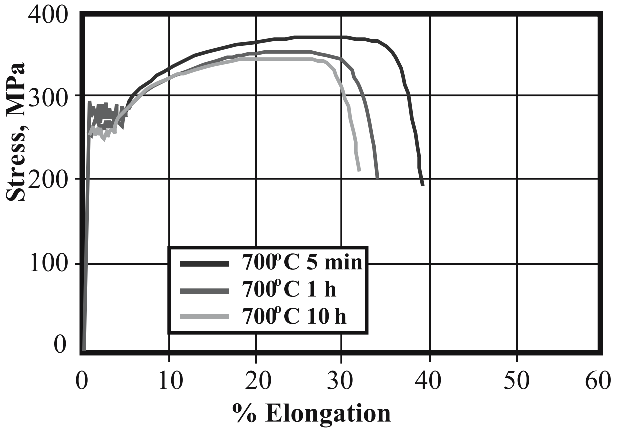

Fig. 5 : Nominal stress-strain curves of Fe-P-II alloy annealed at 700°C for different time periods.

The stress-strain curves of pure iron annealed at 700°C for different time periods are presented in Fig. 3. From these curves, it is clear that, with increase in the annealing time, both the tensile strength and percentage of elongation decreased. Similar trends have also been found for both Fe-P alloys, Figs. 4 and 5. From Table 2, it is evident that annealing at 700°C for different time periods (e.g. 5 minutes, 1 hr and 10 hrs) did not change the ferrite grain sizes significantly. However, noticeable changes in tensile properties, especially in the elongation levels have been found for all test alloys.

For load bearing components, especially in the field of structural applications, ductility is a very important property. The average ductility and strength of any material is controlled by both the grains and grain boundaries. If the grain boundaries and other microstructural sites, e.g. carbide-matrix/inclusion-matrix interfaces become brittle by any reason, the ductile grains (e.g. ductile ferrite grain) alone can not contribute to provide a better overall ductility of the material. During annealing at 700°C, we might expect several changes in the structures of iron alloys such as ferrite grain coarsening, precipitation of iron carbides, segregation of phosphorus, etc. For iron-carbon alloy, general observation is that decrease in carbon (C) content means increase in ductility. Precipitation of iron carbide during annealing treatment means depletion of carbon in the ferrite grains, which might increase the ductility of the alloy. But, in the present study, ductility decreased. So, other parameters seemed to be operative that are responsible for this type of decreasing. It has been found that annealing at 700°C caused a very minor change in grain sizes, Table 2. So, segregation of trace element (here P because no other element is present in the test alloys) is the prime factor to control the mechanical properties. It is well known that phosphorus segregation to the grain boundaries makes these locations brittle [4-6] and results in poor ductility, which is popularly known as temper embrittlement in materials science. Phosphorus has a great tendency to diffuse to grain boundaries. However, this phenomenon is particularly effective in the steel where no carbon exists in the form of solute atoms. Solute carbon is a potential barrier for the P atoms to segregate at grain boundaries. The reason is that the atomic radius of P is higher than that of the host iron. So, phosphorus atoms form substitutional solid solution. In contrast, C atoms are smaller than the host Fe atoms and can fit in the interstitial position of the host iron with a little difficulty. Because of a wide range of mismatches (blank spaces) that commonly remain at grain boundary areas of any polycrystalline material (which is very clear in the micrograph presented in Fig. 6), C atoms get much more chance to be segregated there. As a result, carbon atom, even it is of very low concentration, segregates at grain boundaries faster than P [18-20]. As long as carbon atoms exist at grain boundaries, P atoms can not enter there. The commercially pure iron selected for this study has a very negligible amount of C (0.003%). During annealing, these C atoms formed carbide particles (white colour small particles), which is very clear from micrograph presented in Fig. 7. So, P atoms got opportunity to be segregated at grain boundaries as well as at carbide-matrix interfaces very easily by making them brittle. This type of segregation proceeds through a solid state diffusion, which is a slow process. So, it does not reach to the end. So, with time, accumulation of P atoms at grain boundaries increased with subsequent increase in the brittleness of grain boundaries and carbide-matrix interfaces. As a result, longer period of annealing at 700°C caused more deterioration in strength and ductility of all alloys.

The effect of carbide precipitation and its subsequent effect on P segregation are also evident from tensile fracture surfaces presented in Figs. 8 and 9. In Fig. 9, the voids created during the room temperature tensile tests are

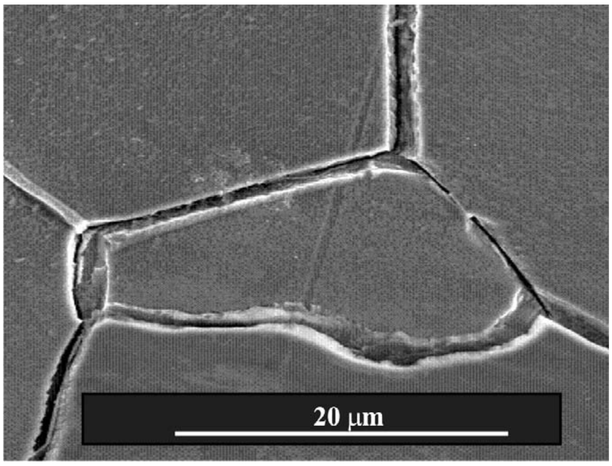

Fig. 6 : Optical micrograph showing the mismatches (blank spaces) between two adjacent grain boundaries of pure iron.

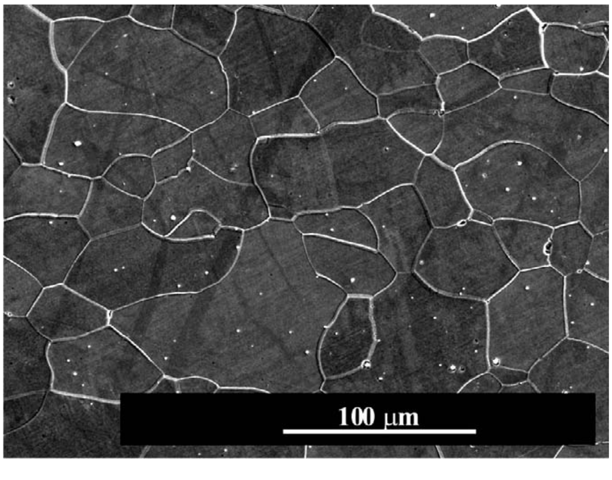

Fig. 7 : Carbide particles in the matrix of pure iron after annealing for 10 hours at 700°C.

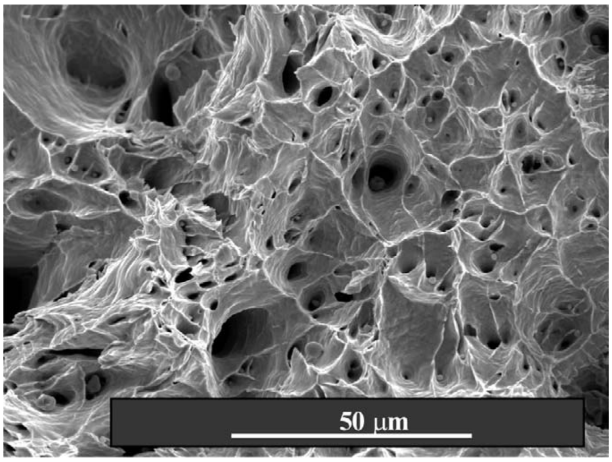

Fig. 8 : Tensile fracture surface of pure iron annealed at 700°C for 1 hour.

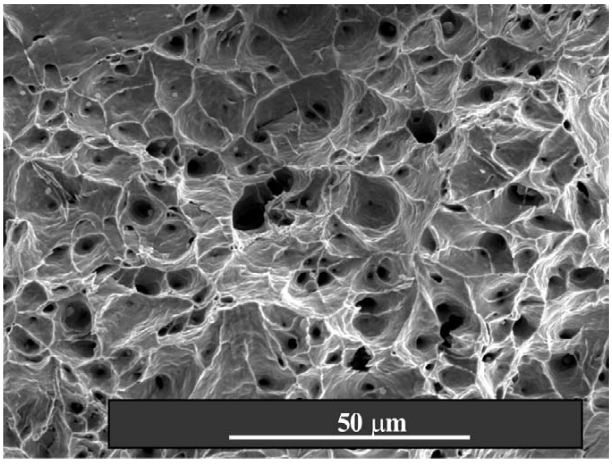

Fig. 9 : Tensile fracture surface of pure iron annealed at 700°C for 10 hours.

relatively finer compared to that observed in Fig. 8. During tensile tests, microvoids usually initiate from coarse inclusion particles for unembrittled iron alloys. Annealing for 10 hours formed carbide precipitates as well as their growth. This also resulted a very high level of phosphorus segregation at grain boundaries and carbide-matrix interfaces making them relatively more brittle. As a result, crack nucleation at carbide/ matrix interfaces arguably took place earlier. Compared to the inclusion particles, the population of carbide particles is much more enormous and they are closely spaced too. So, carbide nucleated voids remain relatively smaller in size, even after their gradual coalescence up to the final fracture.

3.1.2 Effect of annealing temperatures on tensile properties

Tensile tests were also carried out for specimens annealed at 700, 800 and 900ºC for one hour. The stress-strain curves of different alloys annealed at different temperatures are shown in Figs. 10-12.

From Figs. 10-12, it is clear that, for all alloys annealed for identical period of time, annealing at 700ºC resulted more deterioration in ductility levels. During reversible temper embrittlement, phosphorus preferentially segregates at grain boundaries due to existing difference in energy levels between grain boundaries and that within the grains. Usually, this difference strongly effective in the temperature range 200-650ºC [21,22]. Above 700ºC, the movement of foreign atoms along with parent atoms becomes gradually more random, i.e. difference between the energy levels of grains and grain boundaries becomes relatively insignificant. As a result, tendency of the preferential segregation of P at grain boundaries becomes to be negligible. At this situation, impurity atoms (here P, evidence of which will be provided later) remain well distributed at all microstructural sites. So, annealing at temperature 800ºC found to be slightly less effective for P segregation. At 900ºC annealing, phosphorus atoms were more mobile, which further limited the preferential P segregation at grain boundaries. However, in terms of deterioration in tensile properties, annealing at 900ºC resulted more P induced temper embrittlement compared to that samples annealed at 800ºC. Here it is to be mentioned that annealing at 900ºC caused excessive ferrite grain growth (Table 2), which reduced the total ferrite grain boundary areas significantly. During slow cooling through the critical temperature range in the furnace, P segregation took place. Because of significantly reduced grain boundary areas, samples annealed at 900ºC also experienced significant grain boundary P segregation. So, compared to 800ºC, annealing at this temperature caused more deterioration in mechanical properties.

3.1.3 Effects of phosphorus content on tensile properties

Addition of 0.11% phosphorus in pure iron significantly increased the tensile strength, but reduced the ductility, Figs. 10-12. However, further increase in tensile strengths due to addition of more phosphorus (e.g. 0.21%) was not very significant. Phosphorus increases the strength of parent iron by strengthening the ferrite matrix. It also has precipitation (Fe_3P) hardening effect [23]. However, it is very small particle to make visible under normal microscopic study. The third effect is through the grain refinement of ferrite. From Figs. 10-12, it is evident that 0.11% phosphorus addition significantly increased the strength of iron alloy due to pronounced ferrite grain refinement effect. Further, increase in P also increased the strength. But the strength increase was not proportional to the P addition. The reason is that more addition of P (after 0.11%) did not refine the ferrite grain size significantly, which is clear from Table 2. Refining in ferrite grain means more strengthening of ferrite. So, slight increase in the tensile strength of Fe-P-II alloy containing 0.21%P was possibly due to precipitation hardening effect.

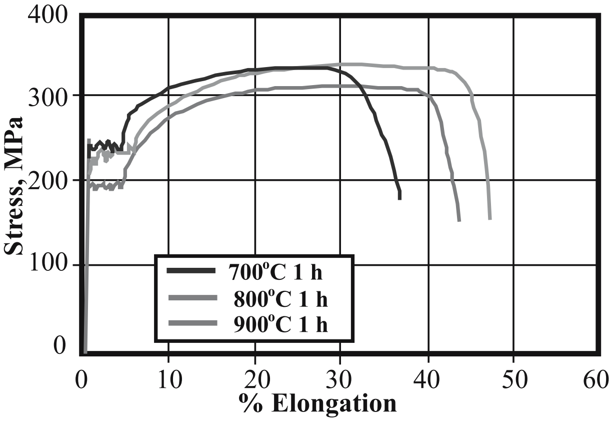

Fig. 10 : Nominal stress-strain curves of pure iron annealed at different temperatures for I hr.

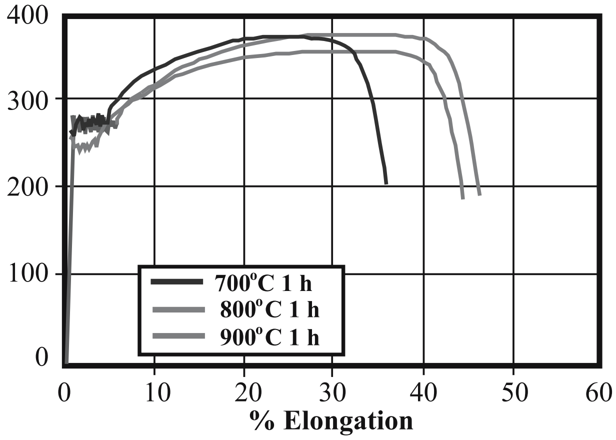

Fig. 11 : Nominal stress-strain curves of Fe-P-I alloy annealed at different temperatures for 1 hr.

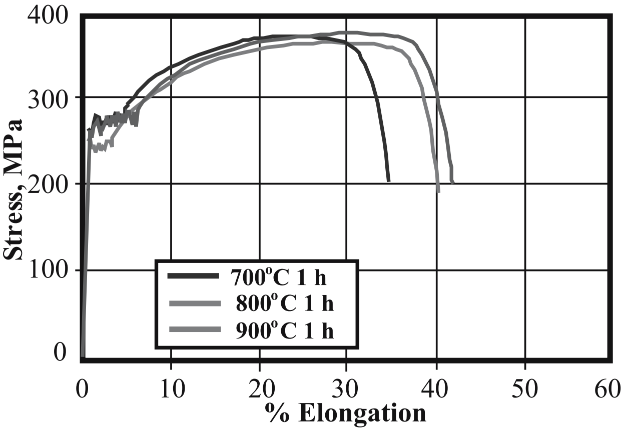

Fig. 12 : Nominal stress-strain curves of Fe-P-II alloy annealed at different temperatures for 1 hr.

3.2 Fatigue properties of the iron alloys

Fatigue tests were carried out on specimens of all alloys annealed at 700ºC 10 hours time periods only. Because, the degree of temper embrittlement effects in terms of tensile strength and ductility deteriorations were found to be more

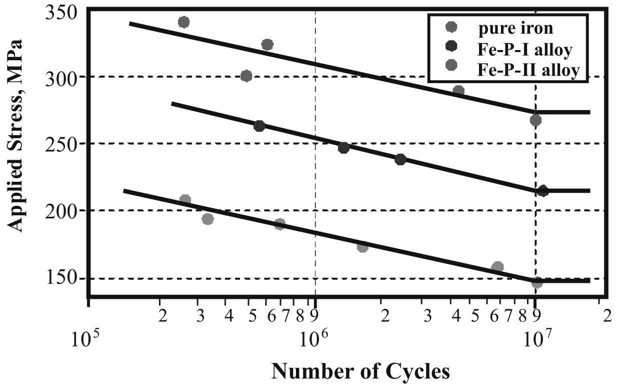

Fig. 13 : S-N curves of pure iron, Fe-P-I and Fe-P-II alloys annealed at 700ºC for 10h.

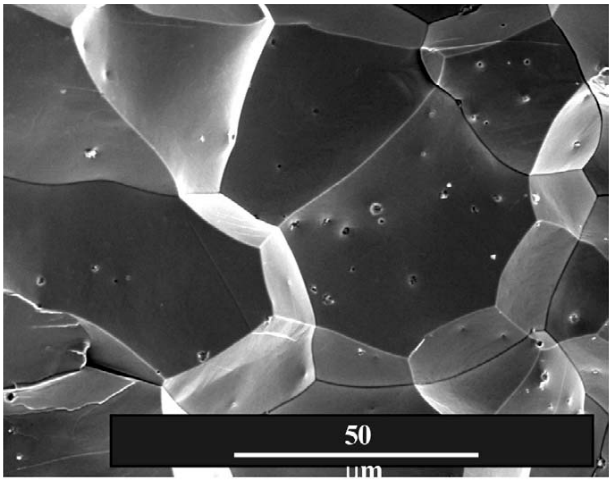

Fig. 14 : Intergranular fracture on fatigue crack of pure iron annealed at 700ºC for 10 hours.

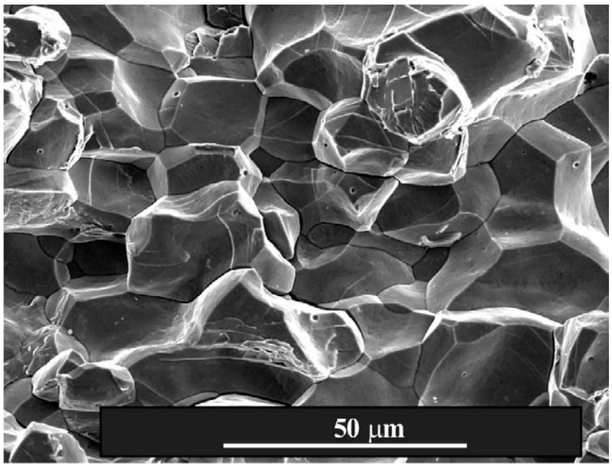

Fig. 15 : Intergranular fracture on fatigue crack of Fe-P-II alloy annealed at 700ºC for 10 hours.

severe under these annealing conditions. Similar to yield and tensile strengths, increase in P addition increased the fatigue limit of pure iron, Fig. 13. For all alloys, under these annealing conditions, the fatigue fracture modes were almost intergranular, Figs. 14 and 15. However, increase in the proportion of P content in the pure iron increased fatigue limits, which is quantitatively shown in Table 4. In this table the UTS values and fatigue limits of all alloys after 10 hours of annealing at 700ºC have been presented. A comparison of fatigue limit degradation due to temper embrittlement of all these three alloys annealed at 700ºC for 10 hours are presented in Table 4.

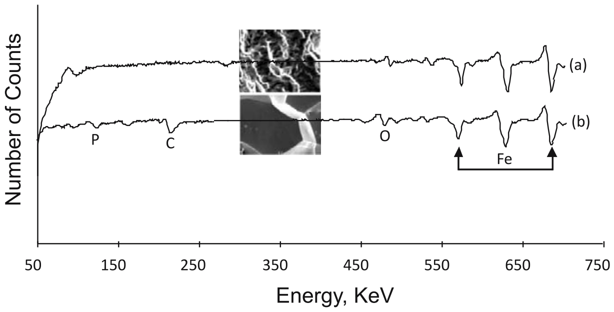

Fig. 16 : AES spectra (a) on transgranular cleavage facet of virgin pure iron (at the top) and (b) on intergranular facet of the annealed pure iron at 700ºC for 10 hours.

Table 4 : Ratio of fatigue limit to UTS of all alloys annealed at 700ºC for 10 hours.

Sample Identification	*Annealing Temp/Time*	*UTS (MPa)*	*Fatigue Limit (FL) (MPa)*	*% of FL in Terms of UTS*
Pure Iron	700ºC/10hour	275	150	54
Fe-P-I Alloy	700ºC/10hour	330	215	65
Fe-P-II Alloy	700ºC/10hour	350	270	77

From Table 4, it is clear that, in terms of tensile strength (UTS), pure iron experienced the most degradation in fatigue life after temper embrittlement and alloy Fe-P-II experienced the least. Fractographs presented in Figs. 14 and 15 also support these quantitative results. Compared to Fe-P-II alloys, intergranular fatigue fracture surface of pure iron is more clean-cut in nature, which also indicates the heavy P segregation at grain boundaries. The reason behind this is the very coarse ferrite grains in pure iron. Coarser ferrite grain means smaller grain boundary area and heavy phosphorus segregation. This encouraging result indicate the safe usability of high phosphorus steels as various load bearing components under both the monotonic and cyclic loading conditions at room temperature in the ambient air.

In the previous section, many times, it has been mentioned that annealing caused P segregation at grain boundaries as there was no other element to be segregated there and that intergranular fracture was caused mainly due to this grain boundary P segregation. In order to confirm the P segregation during annealing period and also to ensure the presence of heavy concentration of P on intergranular facets, the transgranular cleavage fracture of virgin alloy and intergranular facets of the annealed alloy were also analyzed by the Auger Electron Spectroscopy (AES), Figure 16. AES spectra on transgranular cleavage facet (brittle fracture of virgin pure iron) do not show any P peak, however, it is very clear in the spectra obtained from intergranular facets (brittle fracture of annealed pure iron). This observation clearly shows that during annealing treatment P segregated at the grain boundaries, which ultimately caused intergranular fracture during the fatigue tests of the samples.

4. Conclusions

In this works effect of phosphorus additions on tensile and plane bending fatigue properties of commercial grade of pure iron have studied after annealing them at various temperatures for different time periods. From the results of this research work following conclusions are drawn:

- Addition of 0.11% P caused more than 50% decrease in the ferrite grain size of the pure iron for any annealing conditions. However, making the P addition to around double (0.21%) resulted only a very minor effect on further grain refining (around 10%).
- Phosphorus addition in pure iron increased the tensile strength with decrease in ductility. These experimental results suggest that the strengthening of the pure iron is very much related to the degree of ferrite grain refinement rather than the amount of phosphorus addition in the pure iron.
- Compared to the ultimate tensile strengths of all individual alloys, phosphorus added alloys exhibited gradually better fatigue limit, which seems to be an encouraging route for strengthening iron alloys. These experimental results also suggest that the longevity of the product made from hot worked phosphorus added iron alloys will also be better under cyclic loading conditions at room temperature in the air.

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