An Investigation of Grain-Boundary Embrittlement in Fe-P, Fe-P-S, and Fe-Sb-S Alloys

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Grain-boundary embrittlement of pure iron due to phosphorous, antimony and sulfur is studied using fracture appearance transition temperature measurements and Auger electron emission spectroscopy chemical analysis of fractured surfaces. Phosphorous and sulfur are found to segregate to grain boundaries in the entire ferrite range. Segregation to grain boundaries of these elements in the austenite appears to be negligible. It is shown that the segregation of these elements to grain boundaries in iron does not conform to the Gibb's equilibrium segregation model. Sulfur appears to be a more severe embrittler of iron than does phosphorous.

THE deleterious effect of O, S, P, and Sb on the mechanical properties of iron has been well established. After certain heat-treatments, when these elements are present, the ductile-brittle transition temperature is raised with fracture occurring primarily along the grain boundaries. These elements are also known to play an important role in the fracture of low alloy steels. Low alloy Ni-Cr steels containing Sb, P, Sn, or As exhibit reversible temper-embrittlement[7] when they are held or slowly cooled during tempering through the temperature range of 575° to 350°C. In order to clarify the role of these elements in the embrittlement of iron and its alloys a detailed study of the effect of the impurities P, Sb, and S on the grain-boundary embrittlement of pure iron was undertaken.

Until the recent work by Rellick *et al.*[1] on Fe-Te system, the only work on the grain-boundary embrittlement in a binary iron-base system had been by Inman and Tipler[2] who studied the embrittlement of iron by phosphorous. They showed by bend tests that an iron containing 0.09 pct P was fully ductile at room temperature, but failed in a brittle intergranular manner at −78°C when furnace cooled from 1000°C. A short isothermal treatment at 700°C followed by a water quench produced a severe intergranular weakness at room temperature. They showed by radioactive tracer techniques that the concentration of phosphorous at the grain boundaries in the embrittled specimens (water quenched from 700°C) is as high as fifty times that of the grain interior. In some specimens the excess was equivalent to a layer of pure phosphorous more than 60Å thick. Cahn and Hilliard[3] demonstrated by thermodynamic calculation that phosphorous segregation in these amounts does not conform to an equilibrium segregation model.

Even though this study by Inman and Tipler provides some understanding of the problem of grain-boundary embrittlement of iron by phosphorous, more detailed study appears to be necessary on this system. Moreover, Auger electron emission spectroscopy provides a better tool for the analysis of fractured surfaces than the method used earlier by Inman and Tipler. Therefore, a study of the grain-boundary embrittlement in Fe-P and Fe-Sb systems was made using Auger Electron Emission Spectroscopy.

EXPERIMENTAL PROCEDURE

Alloy Preparation

Fe-P ALLOYS

Three alloys were used in this investigation.

1) Fe-0.2 pct P alloy obtained from the General Electric Research and Development Center. This alloy was also used as a master alloy for the next two alloys.

2) Fe-900 ppm P alloy was vacuum induction melted using Johnson-Matthey iron and the Fe-0.2 pct P alloy mentioned above.

3) Fe-500 ppm P alloy prepared in a way similar to the 900 ppm P alloy.

The $\frac{1}{2}$ in. diam ingots were hot forged at 1000°C to $\frac{3}{8}$ in. diam rods and then cold rolled and swaged to 0.162 in. diam rods. These rods were used for all the subsequent experiments on these alloys.

Fe-P-S AND Fe-Sb-S ALLOYS

Two phosphorous doped and two antimony doped irons were obtained from the General Electric Research and Development Center. These were made by vacuum melting high purity vacuum melted electrolytic grade iron. Phosphorous doped irons contained 500 to 600 ppm P and 200 ppm P by weight, respectively, and antimony doped irons contained 500 to 600 ppm Sb and 200 ppm Sb by weight, respectively. Chemical analysis of the ingots showed, in addition to the appropriate amounts of phosphorous and antimony, the presence of sulfur to the extent of 30 ppm by weight. These alloys were used to study the combined effect of phosphorous and sulfur, and antimony and sulfur in the embrittlement of pure iron. The $\frac{3}{4}$ in. diam ingots were hot forged, cold rolled, and swaged to 0.162 in. diam rods (as in the case of Fe-P alloys).

Heat-Treatment and Transition Temperature Measurement of Irons

Preliminary investigations were made to determine the heat-treating conditions in which failure occurred by intergranular fracture and also to determine how intergranular fracture could be avoided in these irons.

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A variety of heat treatments were given toward this end. As per the experiments of Inman and Tipler,[2] the initial treatment was to austenitize the binary Fe-P alloys at 1000°C and furnace cool one set of specimens and water quench the remainder. The water-quenched specimens were then treated for one hour at 700°C and again water quenched. Room temperature notched impact tests of furnace cooled specimens and those quenched from 700°C showed extremely brittle grain-boundary fractures. Next, a similar room temperature test was carried out on a specimen which was brine quenched from 1000°C. The fracture surface revealed a mixture of ductile and cleavage facets for the 900 ppm P and 500 ppm P doped irons, but it was completely intergranular for the 0.2 pct P iron.

Room temperature notched impact tests were also carried out on specimens which were water quenched from 800°, 850°, and 900°C after prior brine-quenching from 1000°C. In all these cases, the specimens fractured in a brittle manner along the grain boundaries. Thus it was found that a specimen, furnace cooled from 1000°C and one water-quenched from 700° to 900°C after prior brine-quench from 1000°C showed extreme intergranular weakness at room temperature. The 0.2 pct P iron showed intergranular weakness at room temperature under all heat-treating conditions. The only possible way to avert intergranular fracture in 900 and 500 ppm P doped irons was to brine quench from 1000°C.

Having established the room temperature fracture behavior, the next step was to determine the Fracture Appearance Transition Temperature (FATT) of the alloys. The transition temperature was determined after the following heat-treatments. The phosphorous doped irons were annealed at 1000°C for 1 h, furnace cooled to 700°C, held for 1 h, furnace cooled to 375°C, and water quenched. This treatment was followed to allow for optimum segregation. For the two low phosphorus irons, specimens brine-quenched from 1000°C were used as nonembrittled specimens to get an idea of the shift in transition temperature of embrittled irons.

Fig. 1(*a*) shows the specimens used for FATT measurement. The specimens were machined after heat-treatment. The tests were made at various temperatures using a Charpy machine with a constant low 15°C pendulum swing.

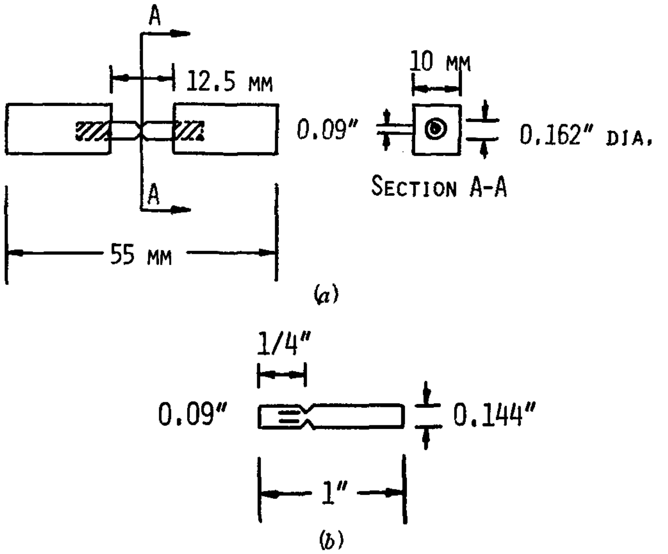


Fig. 1—(*a*) Specimen for impact test. (*b*) Specimen for Auger analysis.

The heat treating and testing procedures having been established, the ternary P-S and Sb-S irons were subjected to the same treatment and their fracture appearance transition temperature determined in a similar way. All heat-treatments were carried out in a tube furnace in a flowing argon atmosphere.

Auger Electron Analysis and Scanning Electron Fractography

Specimens for Auger analysis were given the same treatment as for transition temperature measurement. Fig. 1(*b*) shows the specimens machined for Auger analysis. The reader is referred to the work of Joshi and Stein[4] for details of this technique of surface chemical analysis.

Auger specimens were broken in the baked vacuum system and the fracture surfaces analyzed for segregates. After taking the Auger spectra, the fractured surfaces were sputtered layer by layer[4] (each layer 6 to 10Å deep) using Argon at 4 μ pressure. By this method a profile of the segregate from the grain boundary into the bulk could be obtained. The fractured Auger specimens (the half that was not sputtered) were used for scanning fractographic studies. The fractures were carefully examined for precipitates or any other feature that might be present.

Metallographic examination of the polished specimens was also carried out to ascertain the microstructure in these embrittled irons.

Auger analysis of the nonembrittled specimens was not possible since grain-boundary fracture was not obtained in this case.

RESULTS

Table I shows the chemistry of the alloys used for the present investigation. The Fracture Appearance Transition Temperature (FATT) data are shown in Table II. It is seen that in binary Fe-P alloys the transition temperatures in the embrittled condition lie in a narrow range for a wide range of phosphorous concentrations. For all these phosphorous doped irons (in the embrittled state), the FATT is less than 200°C. In the case of phosphorous doped ternary irons containing sulfur, the transition temperature is very high even though the sulfur content is only about 30 ppm. The

Table I. Table Showing the Composition of Alloys Used in This Study

	Composition, wt pct						
Alloy	P	Sb	S	C	Cr	Ni	Fe
A	0.2	–	–	–	–	–	balance
B	0.09	–	–	–	–	–	balance
C	0.05	–	–	–	–	–	balance
D	0.05-0.06	–	0.003	–	–	–	balance
E	0.02	–	0.003	–	–	–	balance
F	–	0.05-0.06	0.0035	–	–	–	balance
G	–	0.02	0.003	–	–	–	balance

Table II. Table Showing the Effect of Heat Treatment on the Fracture Appearance Transition Temperature and Type of Fracture of P, P-S, and Sb-S Irons

Alloy	Heat Treatment	FATT	Type of Fracture
A	a) W.Q. from 1000°C	R.T.	100 pct Ix
	b) a + 700°C 1h, W.Q.	150°C < FATT < 200°C	20 pct Ix at 175°C
	c) f.c. from 1000°C	150°C < FATT < 200°C	100 pct Ix at 150°C
B	a) Brine Q. from 1000°C	R.T.	mixed mode, mainly cleavage
	b) f.c. to 700°C from 1000°C hold 1 h, f.c. 375°C, W.Q.	150°C < FATT < 200°C	15 to 20 pct Ix at 175°C
C	a) Brine Q. 1000°C	0°C	20 to 25 pct Ix fr; rest cleavage
	b) f.c. 700°C from 1000°C hold 1 h, f.c. 375°C, W.Q.	100°C < FATT < 150°C	mixed fracture at 150°C, 20 to 30 pct Ix
D	a) Brine Q. 1000°C	R.T.	90 to 95 pct cleavage
	b) f.c. 700°C from 1000°C, hold 1 h, f.c., 375°C, W.Q.	FATT > 375°C	100 pct Ix at 375°C
E	a) f.c. to 700°C from 1000°C, hold 1 h, f.c. 375°C, W.Q.	FATT > 350°C	100 pct Ix at 350°C
F	a) Brine Q. from 1000°C	R.T.	mixed mode, 70 pct cleavage, 10 pct Ix
	b) f.c. to 700°C from 1000°C hold 1 h, f.c. 375°C, W.Q.	FATT > 300°C	90 to 95 pct Ix at 300°C
G	a) f.c. to 700°C from 1000°C, hold 1 h, f.c. 375°C, W.Q.	FATT > 100°C	100 pct Ix at 100°C
	b) Brine Q, from 1000°C +850°C, 1 h, W.Q.	R.T.	100 pct Ix

FATT for these alloys is over 300°C as compared to 175°C for a 900 ppm P doped iron. Fig. 2 shows the Auger spectrum of the fractured surface of 0.2 pct P doped iron quenched from 700°C. Figs. 3, 4, and 5 show the concentration profile from the grain-boundary into the bulk for the 0.2 pct P and the 900 ppm P irons and Fig. 6 shows the spectrum for the 0.05 pct P iron. Segregation of phosphorous is observed in 0.2 pct P iron under all heat-treated conditions. However, the segregation of phosphorous is less when quenched from 1000°C. Progressively less segregation of phosphorous is observed for 0.2, 0.09, and 0.05 pct P irons in the embrittled state.

An estimate of the concentration of phosphorous at the grain boundary can be made following Palmberg and Marcus,[5] assuming a linearity of peak height with concentration. Weber and Johnson[6] have argued on a theoretical basis that $dN(E)/dE$ (d^2N/dE^2 in figures), that is, the peak height of the Auger electron spectra is proportional to the atomic concentration of the element being analyzed. Since they were able to support the calculation with experimental results on potassium (deposited on germanium), it appears that the assumption of linearity of peak height with concentration is justified. The height of the phosphorous peak after a deep sputter (over 3600 layers) of the fractured surface in 0.2 pct P (0.35 at. pct) iron is used for calibration and calculation of the phosphorous concentration at the boundary. All phosphorous peak heights are normalized with respect to the iron peak height in the bulk of the 0.2 pct P iron (see Appendix).

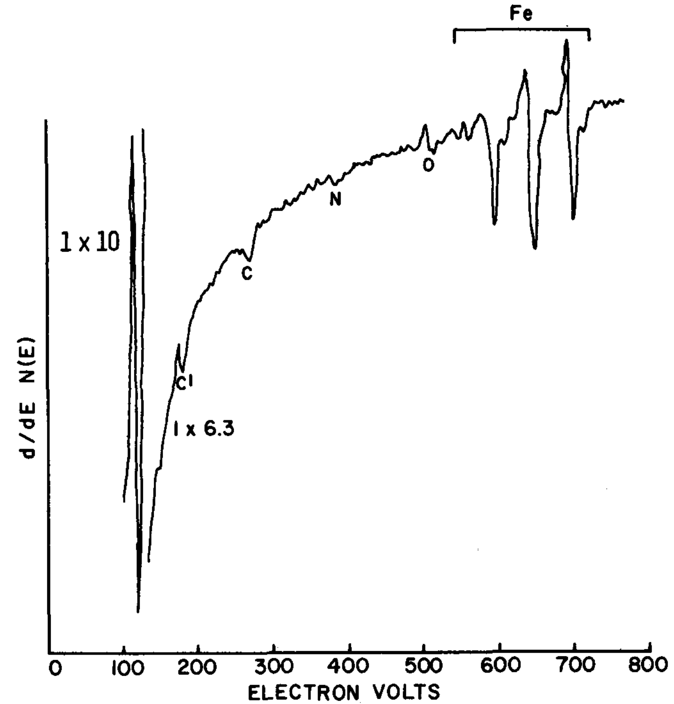


Fig. 2—Auger spectra of 0.2 pct P iron water quenched from 700°C.

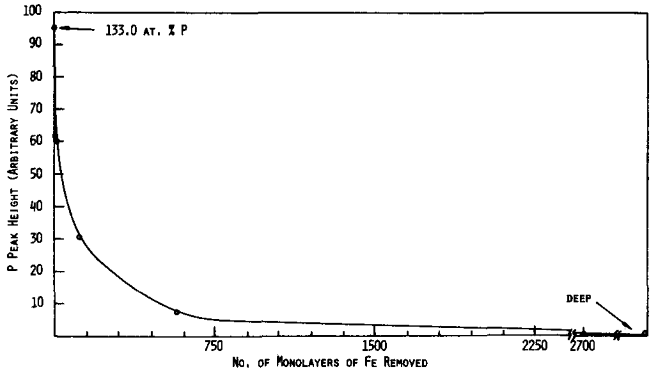


Fig. 3—Variation in phosphorous concentration with sputtering in 0.2 pct P iron furnace cooled from 1000°C.

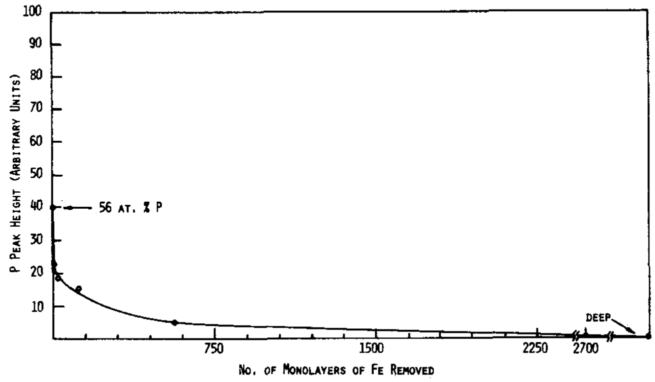


Fig. 4—Variation in phosphorous concentration with sputtering in 0.2 pct P iron water quenched from 1000°C.

According to these calculations 0.2 pct P iron (alloy A) shows 133 at. pct P at the grain boundary in the furnace cooled condition, and when quenched from 1000°C

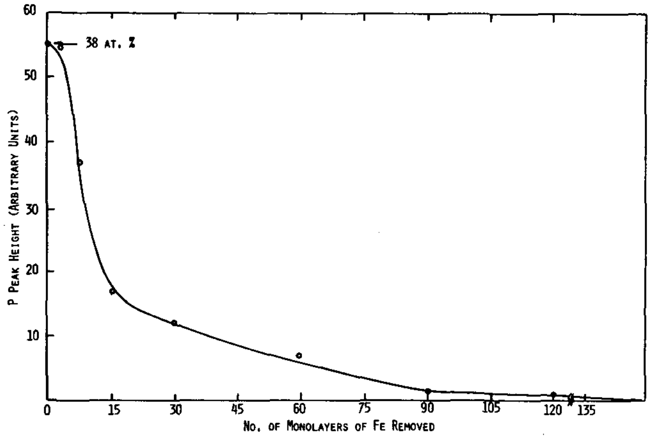


Fig. 5—Variation in phosphorous concentration with sputtering in embrittled 0.09 pct P iron.

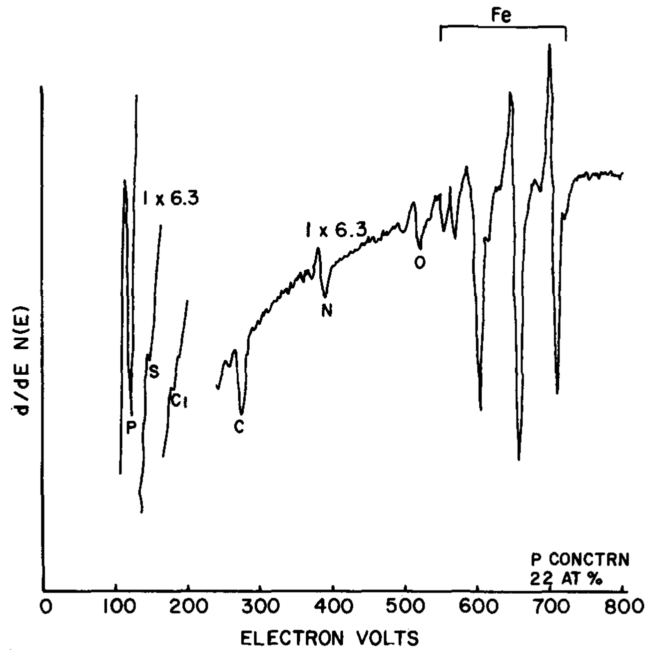


Fig. 6—Auger spectra of embrittled 500 ppm P iron.

the concentration at the intergranular faces dropped to 51 at. pct P. Alloy B containing 900 ppm P shows 38 at. pct P at the boundary in the embrittled condition. Values of over 100 at. pct P at the grain boundaries are obtained from extrapolation of peak heights obtained at low concentrations where slight errors may result in gross errors at higher concentrations. (The error is introduced mainly from the phosphorous peak height measurement in the spectrum obtained from deep sputtered 0.2 pct P iron. The phosphorous peak height is small so that its exact measurement is difficult. This could introduce an error of 25 to 30 pct.) However, it is clear that the phosphorous concentration at the grain boundaries of these alloys is very high and it approaches 100 at. pct.

Figs. 7 and 8 show the Auger spectra of the embrittled 200 ppm P and 200 ppm Sb irons containing sulfur and Figs. 9 and 10 show the sputtering profiles from the boundary into the grain of 500 ppm P and 500 ppm Sb irons containing sulfur. It may be noted that there is a pronounced segregation of sulfur even though it is present in very small amounts and its concentration in the bulk is far less than the concentration of phosphorous or antimony. In the 500 ppm P iron containing sulfur (alloy D), both sulfur and phosphorous are segregated to the boundary, though the segregation of sulfur is more pronounced. In the rest of the irons only sulfur is observed. It is surprising that there is very little indication of antimony segregation (antimony peaks show up at 460 eV energy in the Auger spectra) even in the iron containing 500 to 600 ppm Sb (alloy F). The small chlorine peak at 180 eV in Fig. 8 is possibly due to contamination from the atmosphere. Fig. 11 shows the Auger spectrum of 200 ppm P iron containing sulfur (alloy E), water quenched from 850°C after a prior quench from 1000°C. Even quenching from this high a temperature does not prevent the segregation of sulfur to the grain boundaries. It is difficult to estimate the amount of sulfur at the boundary as no standard alloy has been studied for calibration. However, since the electron energies for sulfur and phosphorous are close (150 and 120 eV, respectively), it is reasonable to estimate the sulfur concentration using the same calibration as used for phosphorous. Although

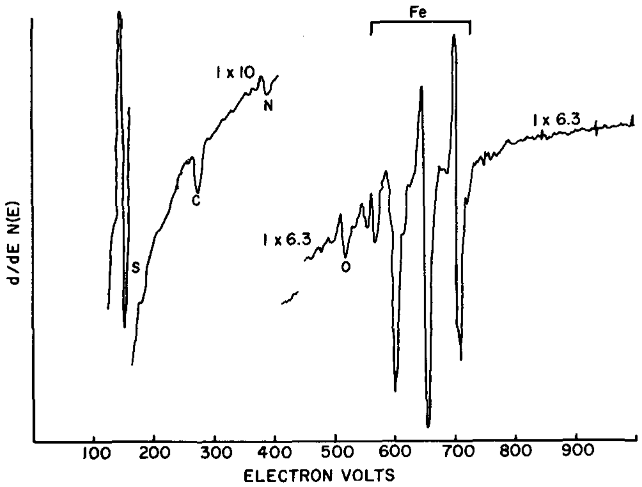


Fig. 7—Auger spectra of embrittled 200 ppm Sb-30 S iron.

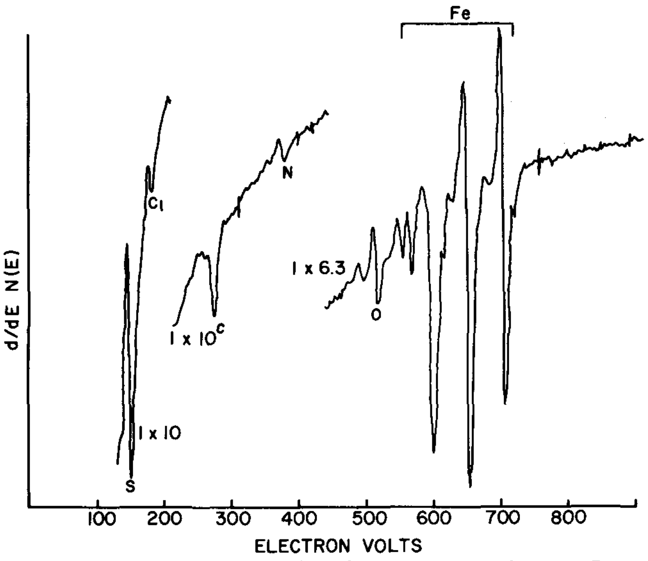


Fig. 8—Auger spectra of embrittled 200 ppm P-30 ppm S iron.

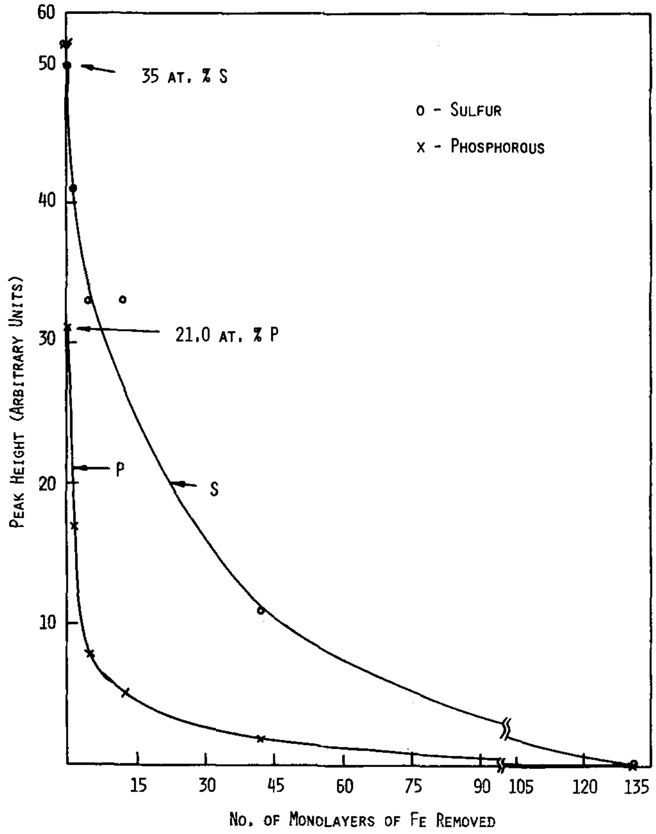


Fig. 9—Variation of phosphorous and sulfur concentration with sputtering in 500 ppm P iron containing sulfur.

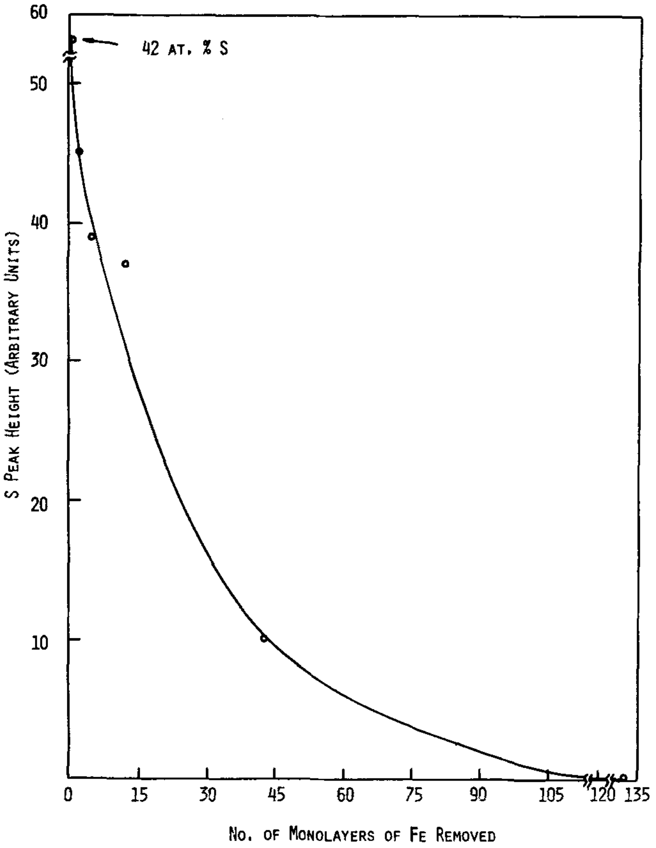


Fig. 10—Variation of sulfur in concentration with sputtering in 500 ppm P iron containing sulfur.

such an estimate may not be very accurate, it gives us an approximate idea of the extent of sulfur segregation. Accordingly, the concentration of sulfur at the boundary turns out to be almost 35 at. pct. All the irons studied showed excess of nitrogen at the grain boundary indicating segregation of this element (peak at 380 eV). The nitrogen content of the bulk was not determined.

Scanning electron fractograph of embrittled 500 ppm P iron is shown in Fig. 12(*a*). The low magnification pictures show clearly the intergranular nature of fracture.

DISCUSSION

Results on Fe-P, Fe-P-S, and Fe-Sb-S alloys show that the embrittlement occurring in these alloys is different from the reversible temper embrittlement known to occur in low alloy steels. The embrittlement in the alloys studied is found to be irreversible. Segregation of impurities occurs at all temperatures in ferrite. This is also clear from Tables III and IV of Inman and Tipler[2] where segregation of phosphorous to the grain boundaries in iron is reported irrespective of the heat-treatments undergone by the alloy sections. It appears that the segregation in austenite is negligible or very limited in extent. This is evident from the Auger spectra of alloy A (0.2 pct P iron) water quenched from 1000°C and the mechanical tests on alloys B, C, D, E, F, and G which produced mainly cleavage fractures after brine quenching from 1000°C. Fig. 13 shows the Fe-P phase diagram with the positions of alloys A and B in the diagram at 1000°C indicated. The alloy B containing 900 ppm P is close to the solid solubility limit of austenite and yet it does not fail by intergranular mode when it is quenched from 1000°C. Alloy A is in the two phase ($\alpha + \gamma$) region at 1000°C. The equilibrium composition of α and γ at 1000°C is about 0.4 and 0.1 pct P, respectively. This alloy shows up to 50 at. pct P at the grain boundary when quenched from 1000°C. Since the alloy B containing 900 ppm P did not show in-

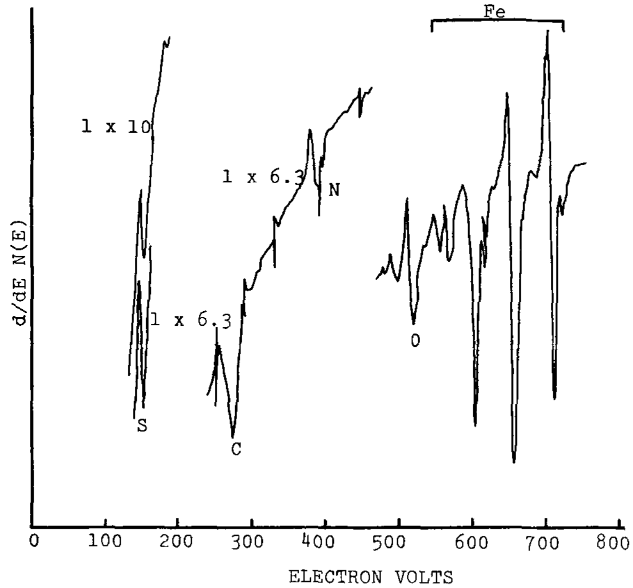
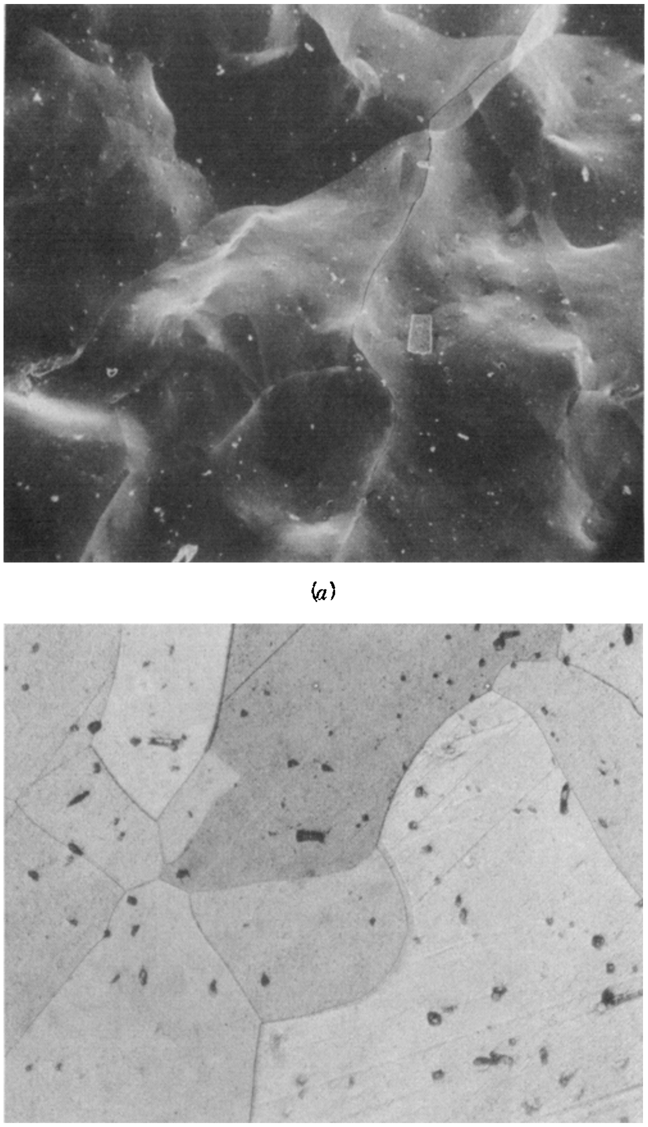


Fig. 11—Spectra of 200 ppm P-30 ppm S iron water quenched from 850°C.


(a)

(b)

Fig. 12—(*a*) Fracture surface of embrittled Fe-500 ppm P alloy. Magnification 110 times. (*b*) Micrograph of Fe-500 ppm P alloy showing ferrite grains. Magnification 170 times.

tergranular fracture (indicating negligible segregation), it appears that the segregation in alloy A has occurred from ferrite to the ferrite-austenite boundary. Thus, in spite of the much lower solubility of phosphorous in austenite than in ferrite, segregation appears to occur only in the ferrite. The absence of segregation in austenite in alloy B cannot be attributed to the high temperature of 1000°C and its effect on grain boundary energy, because alloy A is also treated at the same temperature.

Inman and Tipler estimated the amount of phosphorous segregated to the grain boundaries in Fe-900 ppm P alloy to be about 50 times that present in the bulk, by using radioisotope technique. They showed that in the extreme case, if phosphorous segregates as a layer of pure element, the total thickness of phosphrous layer lies in the range of 30 to 70Å. Present investigation shows the concentration of phosphorous at the boundary for Fe-900 ppm P alloy to be ~ 38 at. pct. For the 0.2 pct P iron in the furnace-cooled condition, however, the results show the presence of a layer of nearly pure phosphorous at the grain boundary. The thickness of the nearly pure phosphorous layer, considering both sides of the fracture surface, appears to be not more than 10 to 15Å. A sharp fall in the phosphorous concentration after sputtering two monolayers suggests that most of the phosphorous exists as a segregate in the elemental form rather than as a precipitate. Even though most of the phosphorous exists as a segregate, it is not unlikely that some of it could exist as precipitates. An indication of the presence of precipitates is obtained from the persistence of phosphorous signals when sputtering deep in the 0.2 and 0.09 pct P alloys.

Calculation of excess phosphorous at the boundary for Fe-900 ppm P alloy using the model of Cahn and Hilliard[3] confirms their view that the phosphorous segregation in iron does not conform to the equilibrium segregation model. The excess phosphorous atoms at the boundaries are found to be more than two times larger than the maximum number of atoms (0.19×10^{16} atom cm^{-2}) predicted by the model, even if one assumes that the grain boundary energy goes to zero. Similar calculations using Cahn and Hilliard model for sulfur also show that the segregation does not conform to that proposed by Gibbs. As equilibrium segregation is governed by factors controlling solubility, it would appear that for binary alloys of iron with elements such as phosphorous, which form substitutional solid solution, the segregation is governed by factors other than those that control solubility. Also, if solid solubility were to be the criteria for segregation, we should have observed

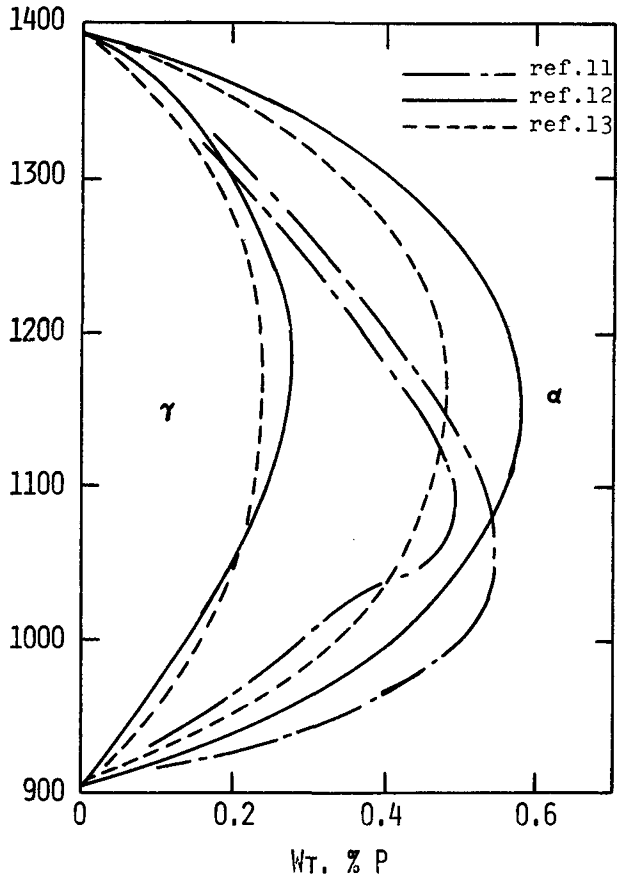


Fig. 13—Phase diagram of Fe-P system (from Hanson).[11]

larger amounts of segregation in the austenitic phase. It appears that the type of phase, the type of grain boundary (γ-α or α-α) or the vacancy solute interaction near the boundary in α phase may be responsible for the nonequilibrium segregation observed in binary and ternary irons studied.

Several conclusions can be made from the mechanical test data on the binary and ternary alloys studied. Alloy C containing 0.05 pct P has a transition temperature close to 140°C and the alloys A and B containing 0.2 and 0.09 pct P, respectively, show transition temperature close to 175°C. Considering that the phosphorous content at their boundaries in the embrittled condition is approximately 21, 100, and 38 pct, respectively, it would appear that there is no definite correlation between the concentration of phosphorous at the boundary and the transition temperature, at least beyond a certain phosphorous concentration level at the boundary. As the transition temperature remains the same (~175°C) for a wide range of phosphorous concentration at the boundary, it appears that the maximum transition temperature is a characteristic of the type of impurity present. This is also evident from the results on sulfur bearing irons. Alloy D (500 ppm P and 30 ppm S) shows a transition temperature greater than 350°C; alloy F (500 ppm Sb and 35 ppm S) has FATT greater than 375°C and alloy E (200 ppm P and 30 ppm S) also had FATT over 375°C. As only sulfur is seen segregated to the boundary in alloy E, it is reasonable to deduce that the high transition temperatures in these alloys are attributable to sulfur and that sulfur induces a characteristic maximum transition temperature of over 350°C when present as a segregate in iron. Thus, this investigation seems to indicate that sulfur has a much greater potential for producing intergranular fracture than phosphorous alone does. Low, *et al.*[7] showed that for a 3.5 Ni, 1.6 Cr, 0.4 pct C steel containing 500 ppm P, the transition temperature in the severely embrittled condition is 120°C which is less than that observed for the 500 ppm P iron (140°C). Therefore, it may be inferred from the present mechanical test results that in low alloy Ni-Cr-C steels the embrittlement (obtained by temper embrittling treatment) is not enhanced beyond that characteristic of the impurity element. As temper-embrittled Sb-doped Ni-Cr steels[7] have FATT ~600°C, it may also be inferred that antimony induces a high transition temperature when present as a segregate at the grain boundaries and that the FATT characteristic of antimony is over 600°C. It may be noted here that the presence of antimony at the grain boundaries in Ni-Cr steels in the embrittled condition was established by Joshi and Stein[4] by Auger spectroscopic study of fractured surfaces. Hence, the effect of different impurity elements such as P, Sb, As, Sn, and so forth, on the extent of temper embrittlement in steels may be explained by the extent of embrittlement they produce in iron.

The ability of different elements to impart varying degrees of embrittlement may be explained by the change in surface and grain boundary tensions they produce due to unit change in grain boundary composition. Hondrons, Low, and Joshi and Stein have dealt with this aspect in considerable detail. A general approach to the problem can be made using the Griffith equation for brittle fracture:

$$\sigma_F = \frac{2E\gamma}{\pi c}^{1/2}$$

where σ_F is the fracture stress at which a crack of length C becomes unstable and propagates. E is the elastic modulus of the material and γ is the work to form two new surfaces created as the crack increases in length.

Let us consider the case where there is a change in γ. For cleavage fracture γ is equal to $2\gamma_s$, where γ_s is the energy per unit area of the cleavage surface. For intergranular fracture, since the energy of the new surfaces is partly reduced by the energy of the grain boundary

$$\gamma = (2\gamma_s - \gamma_b)$$

where γ_b is the grain boundary energy per unit area. When an impurity segregates to the grain boundary due to Gibb's adsorption it reduces γ_b and contributes to an increase in σ_b. But most grain boundary active impurities are also surface active and hence decrease the surface energy γ_s. The degree to which an impurity affects the γ_s and γ_b term determines the extent of embrittlement that it produces in a material. Therefore, the ability of Sb, P, As, and Sn to impart variable degrees of embrittlement could be explained on the basis that their effect on γ_s and γ_b vary markedly. How valid this argument is for iron and steels is not clear because the discussion on the grain boundary energy is based on Gibb's adsorption and as we observed earlier, the segregation in binary and ternary irons studied do not comply with this mechanism.

The segregation of phosphorous and sulfur in irons and the subsequent intergranular fracture seems to occur along ferrite-ferrite boundaries rather than strictly along prior austenite boundaries (intergranular fracture in Ni-Cr steels occurs along prior austenite grain boundaries). This conclusion is based on a comparison of the grain size obtained from fractographs with the ferrite grain size obtained by optical metallography of published and etched specimens, Fig. 12.

Another conclusion can be made from the results on irons. The data clearly establishes that, in the absence of C, Ni, and Cr are not required for the embrittlement of irons. The presence of phosphorous, sulfur or possibly antimony alone at the grain boundary is sufficient to cause extreme brittleness in irons.

CONCLUSIONS

1) Phosphorous and sulfur segregate to grain boundaries in iron in the entire ferrite range.

2) There appears to be negligible segregation of these elements in austenite.

3) Sulfur appears to be a more severe embrittler (FATT > 350°C) than phosphorous (FATT ~ 175°C).

4) Segregation of phosphorous and sulfur to iron boundaries does not follow Gibb's adsorption mechanism.

APPENDIX

A) ATTENUATION

1 × 10, 1 × 6.3, and so forth, in Figures are the attenuation levels. When an Auger spectrum is compared with a standard to determine the composition, it should be at the same attenuation levels. The phosphorous

and iron peaks in the deep sputtered 0.2 pct P iron were made at an attenuation of 1 × 6.3. For the embrittled 0.2 pct P iron, the phosphorous peak was taken at a reduced attenuation of 1 × 10 as the 1 × 6.3 attenuation takes the phosphorous peak out of scale. The equivalent peak height attenuated to 1 × 6.3 is given by:

$$\frac{\begin{array}{c}\text{Actual measured peak height}\\ \text{from } (1 \times 10) \text{ attenuation}\end{array} \times 10}{6.3}$$

B) NORMALIZATION OF PEAK HEIGHTS

When comparing spectra to evaluate phosphorous composition, care was taken to see that the iron peak heights for the standard and the spectrum in question were the same. For example, let us say that the 650 eV Fe peak height for the deep sputtered 0.2 pct P iron standard is 35 arbitrary units. To compare another spectrum with this standard, the whole spectrum to be compared is proportionately reduced or increased in size (as the case may be) so that the 650 eV Fe peak is 35 arbitrary units. This procedure was found necessary because, under identical conditions, even for the same material, the peak heights obtained at different times are not exactly identical.

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