PRJ, Vol. 3 (January 1991); P. 57–62, 9 FIGS, 1 TABLE.

Short Note

SENSITIVITY OF PIPE-LINE STEELS TO HYDROGEN INDUCED CRACKING

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حساسية الفولاذ الكربوني للهيدروجين المسبب للتشققات

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تم اختبار عدة أنواع من الفولاذ الكربوني الذي سبق أن تعرض لغاز كبريتيد الهيدروجين المبلل ووجد أن هذا الفولاذ له استجابة للهيدروجين المسبب للتشققات.

بينت الإختبارات الميثالوغرافية وجود عروق من الفسفور وأن الهيدروجين المسبب للتشققات له علاقة بعرض العروق الفسفورية.

INTRODUCTION

According to the technical literature and experience, pipe-steels of the same grade working in almost the same environment containing H_2S have a different sensitivity to hydrogen induced cracking (HIC). Reaction of the wet hydrogen sulfide with iron produces the hydrogen atoms which can be easily absorbed by the iron matrix due to their small diameter and high coefficient of diffusivity at the ambient temperature. In some places as for instance interphase boundaries (Steel matrix-nonmetallic inclusions), the hydrogen atoms are recombining into molecules creating pressure in these sites. After a sufficient pressure build-up in these places, the blisters and stepwise cracks are observed [1]. Sensitivity of pipe-steels to HIC depends on many factors; namely chemical composition, metallurgical and environmental variables [2]. Presence of impurities like sulphur and phosphorous are known to affect the properties of steel adversely if they are not controlled. Presence of MnS inclusion in elongated shape [2] plays a major role in the initiation of HIC.

Effect of sulphur on HIC in steels has been extensively reported in the literature while that of phosphorous on HIC is hardly known. The present note reports some preliminary observations on the effect of phosphorous on HIC.

RESULTS AND DISCUSSION

Hydrogen Induced Cracking (HIC)

The samples were taken from three pipe-lines made of A53 steel grade of chemical composition listed in Table 1. Pipe (D) had 20 inch of diameter, pipes (P) and (E) were 30 inch diameters. Each pipe

Table 1. Chemical Analysis of the Three Steel Pipes

PIPE	CONTENT %									
	C	Mn	Si	S	P	Almet	Cr	Ni	Cu	V
(P)	0.22	1.20	0.37	0.029	0.046	0.02	0.06	Nil	N.T.	Nil
(E)	0.20	1.21	0.30	0.014	0.032	0.04	0.06	Nil	N.T.	Nil
(D)	0.23	0.90	0.35	0.033	0.054	N.T.	0.02	0.0075	0.015	N.T.

N.T. = Not Tested.

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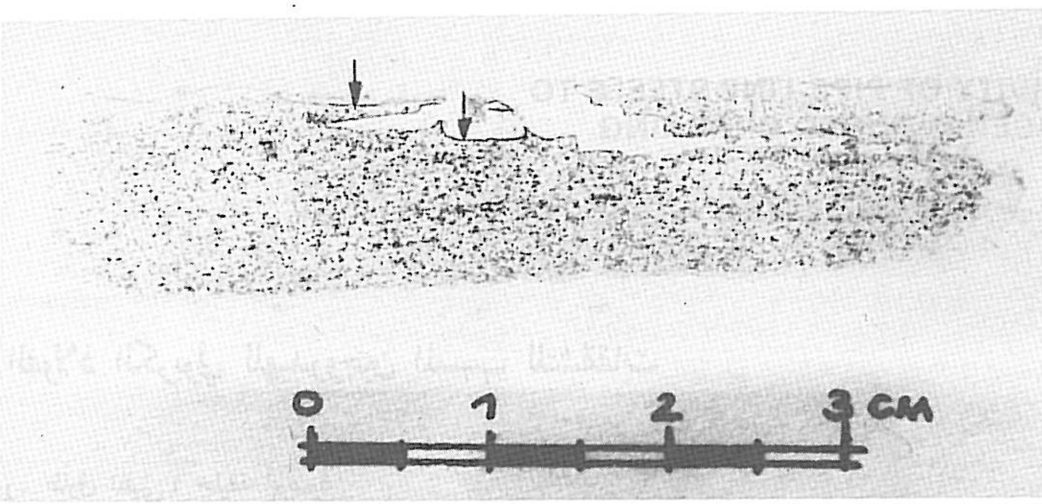

FIG. 1. Sulphur print made from the specimen of steel (P).

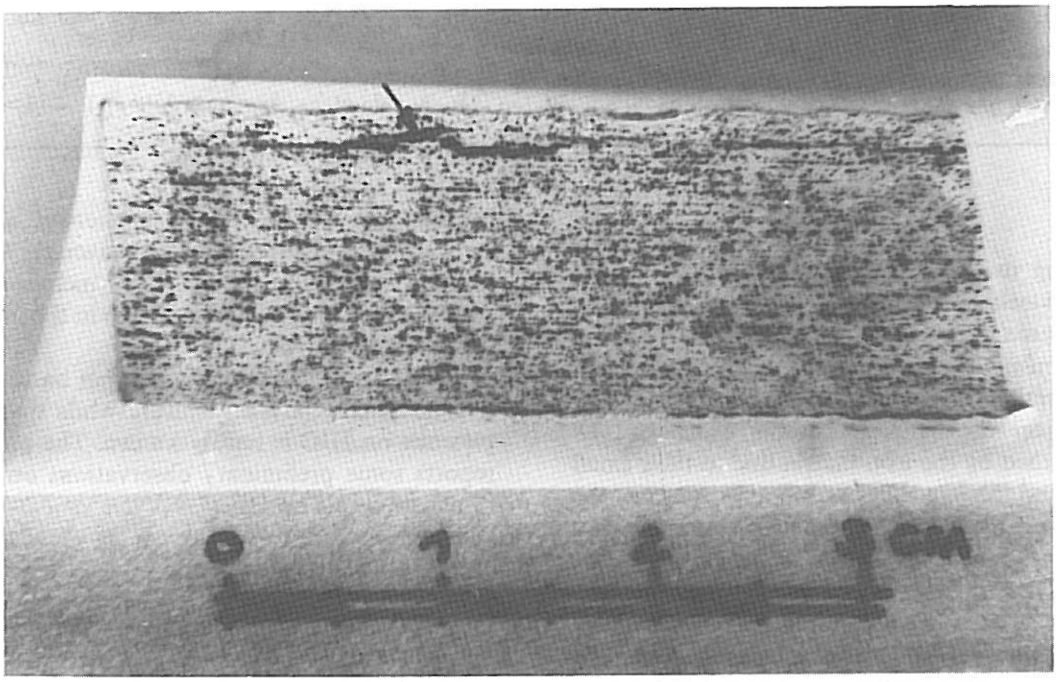

FIG. 2. Sulphur print of Steel (P) with stepwise crack. Dark deposit marked by arrow indicates that the crack had a direct contact with H_2S.

has been in sevice for about 17 years carrying a natural gas containing H_2S in amounts ranging from 500 ppm up to a few thousand ppm depending on the service period and operational circum-stances. The highest concentration up to 1040 ppm of H_2S has been found in pipe (E). The average pressure of the natural gas flowing through all these pipes was about 500 psi.

From each pipe the longitudinal specimens were taken for macro- and micro-observations. All specimens of pipe (P) exhibited many open blisters and inner cracks of lamination type; some of them formed the step wise cracks. Macro-sulphur print in Fig. 1 shows the cracks in the pipe-wall opened in the inner pipe surface. Figure 2 shows sulphur print with stepwise crack situated close to the inner pipe surface. The dark spots indicate the places occupied by non-metallic inclusions (Mn, Fe)S as impurities inherited after metallurgical processing. Black de-posit (FeS) along the cracks (See arrows in Fig. 1 and Fig. 2) are the product of reaction between wet H_2S environment and inner pipe surface. Cathodic reaction is hydrogen ion reduction as illustrated below:

$$Fe \rightarrow Fe^{++} + 2e^-$$

$$H^+ + e^- \rightarrow H \text{ adsorbed} \begin{cases} \nearrow H + H \rightarrow H_2 \\ \rightarrow H \text{ adsorbed by steel} \end{cases}$$

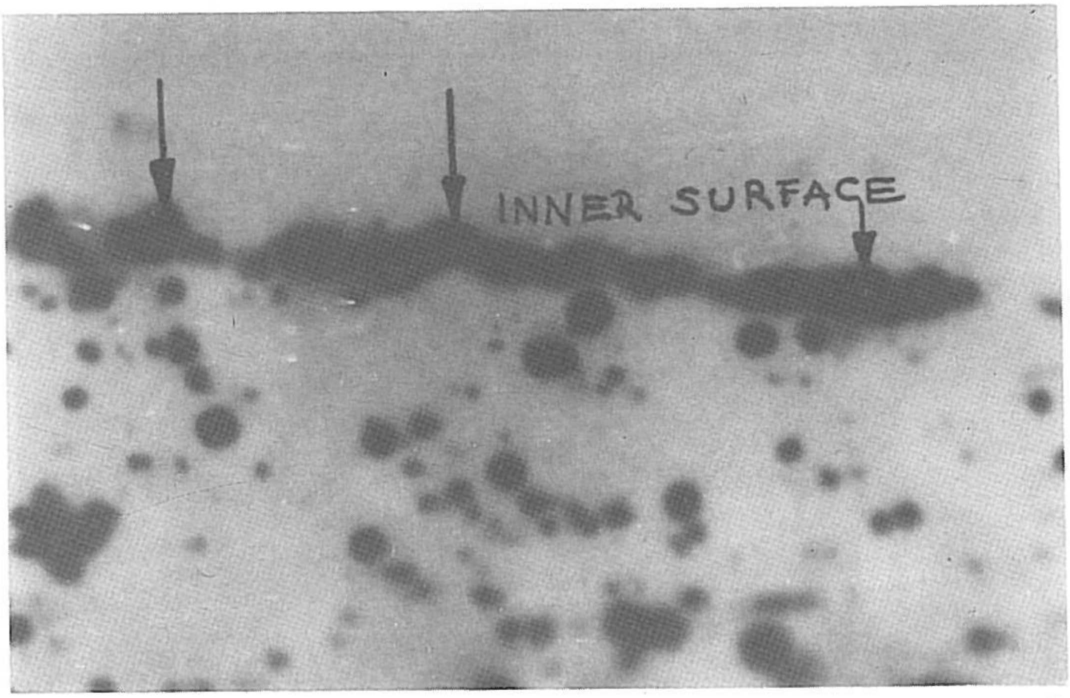

FIG. 3. FeS deposited at the pipe inner surface due to the reaction between H_2S and Fe. Sulphur print magnified 63×.

Part of the hydrogen atoms is absorbed by steel and can diffuse into the iron matrix producing hydrogen induced cracks (Blisters or stepwise cracks), the rest of the atoms recombine into molecules and flow away with the gas stream. This deposit, along the inner surface of the pipe, is shown after magnification in Fig. 3. Samples taken from pipe (E) did not exhibit hydrogen induced cracks in spite of the highest H_2S content in the gas.

Macrophotographs and macro-sulphur prints of samples taken from the pipe (D) are shown in Fig. 4. They are visible in cross-sections with stepwise cracks (see arrows) without black deposit that indicates no direct contact of the cracks with the pipe inner surface.

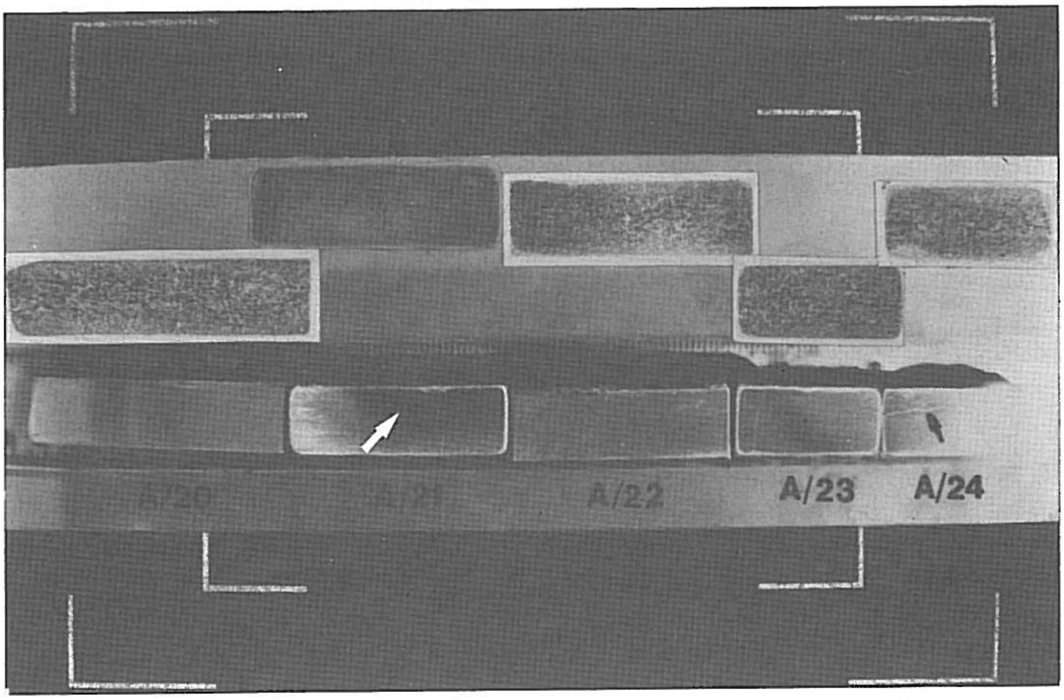

FIG. 4. Samples of A series cut from pipe of (D) type. The arrows are showing stepwise cracks in the section A/21 and A/24. Sulphur prints are showing the (Fe, Mn) S distribution in the cross-section.

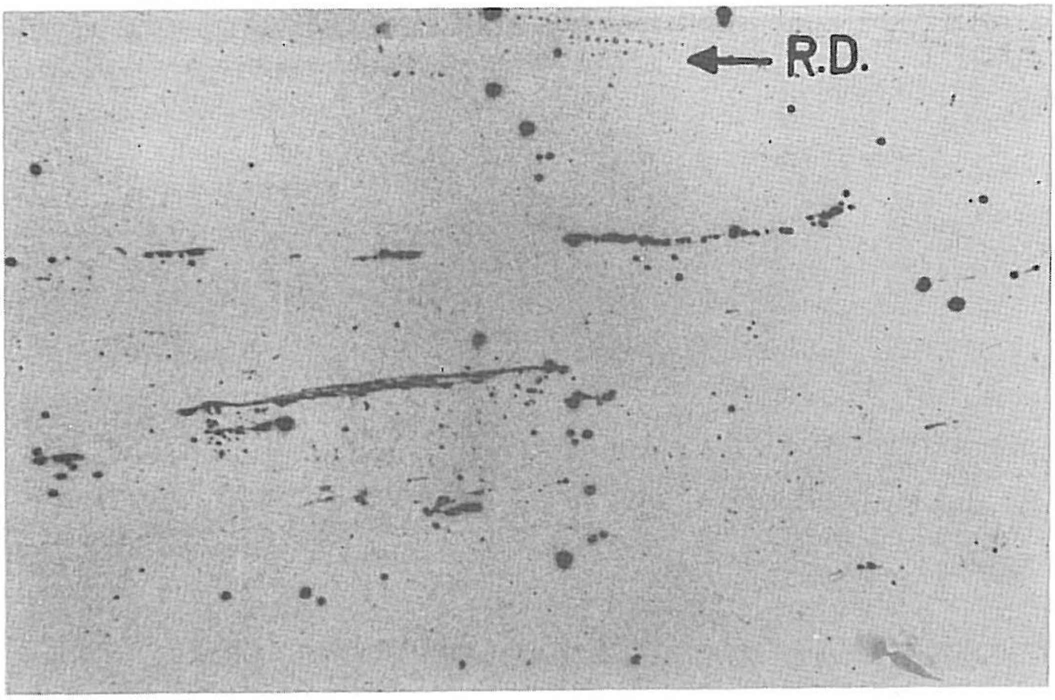

FIG. 5. Elongated non-metallic inclusions due to high deformation stage due to hot rolling. Magnification 130×.

The above observations have revealed a different sensitivity of tested pipes to hydrogen induced cracking. The relationship between phosphorous segregation and the hydrogen induced cracking (HIC) concept has been used, as a hypothesis explaining the above obsevations.

Phosphorous Segregation and HIC

Phosphorous segregation in steel can be easily revealed by using one of the well known etching techniques [3]. For this study Stead's and Oberhoffer's reagents have been used to get better reproducibility of etching results.

The steels used for pipe production have been hot rolled. This operation produced high directionality of structural constituents and non-metallic inclusions. Fig. 5 shows the nonmetallic inclusions elongated towards rolling direction (RD). Similarly, the segregation areas are elongated and form the bands shown for steel (E) in Fig. 6.

The distance between the enriched phosphorous band

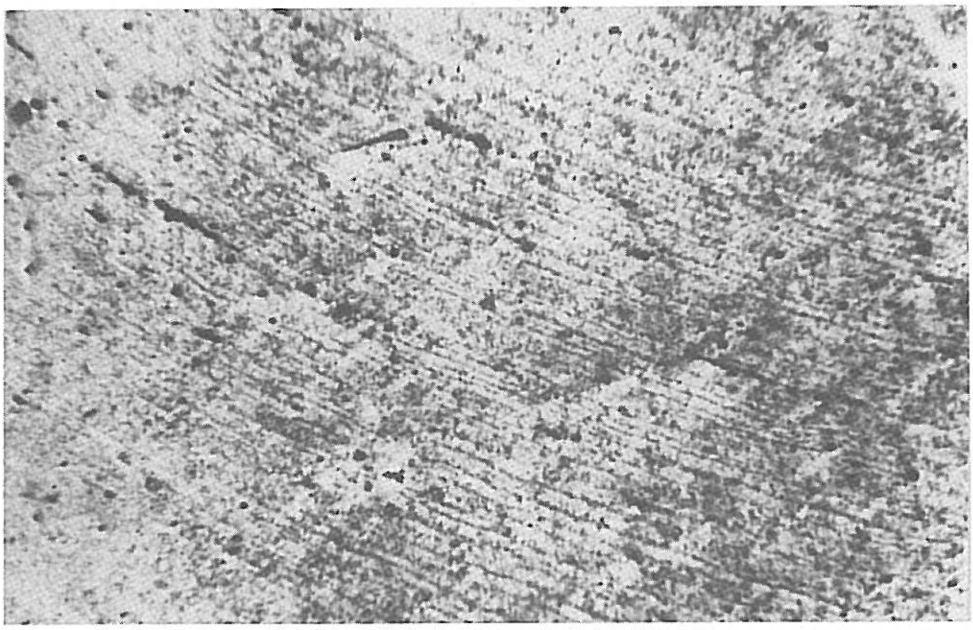

FIG. 6. Phosphorous segregation bands following the direction of plastic deformation in steel (E) Steads reagent. Magnification 63×.

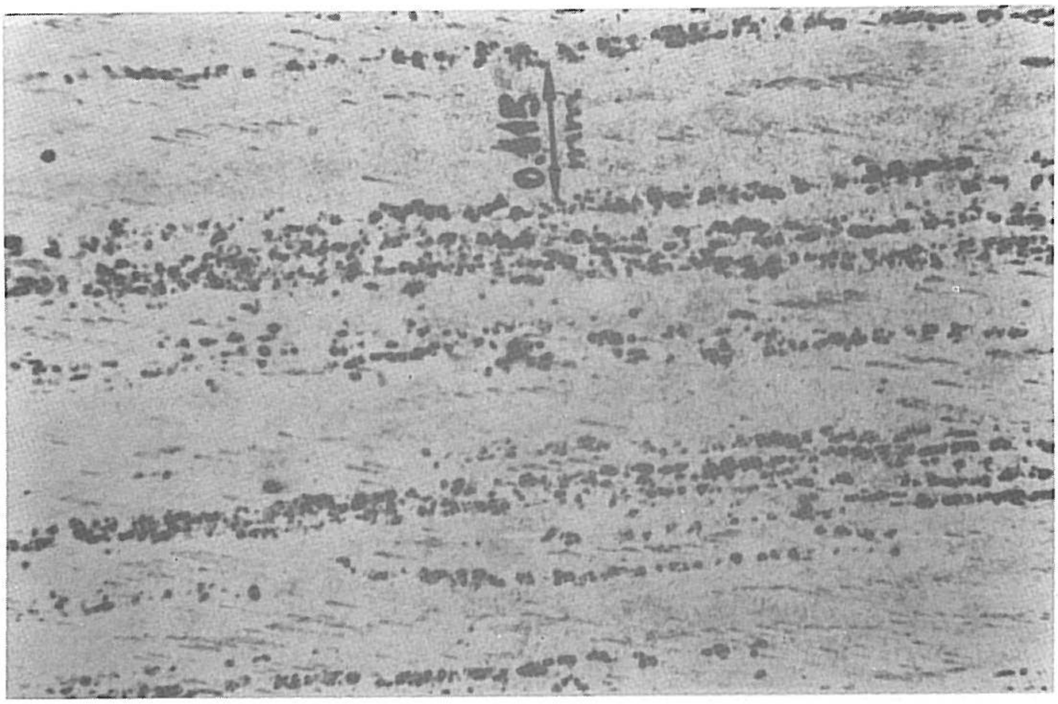

FIG. 7. Phosphorous bands of 0.115 mm of average width (light colour) in steel (P) Stead's reagent. Magnification 130 ×.

(light colour) and the depleted one (dark colour) for this steel is 0.03 mm. This steel was not sensitive to HIC. Fig. 7 shows for comparison the 0.115 mm wide enriched phosphorous bands in steel (P) that exhibited a great deal of HIC.

The stepwise cracks propagated usually along a wide 0.2 mm band enriched by phosphorous white (or light) bands (see Fig. 8). In the 0.25 mm wide band the stepwise cracks are propagating following the "rolling direction". Fig. 9 shows the two stepwise cracks following wide phosphorous band approaching the area in which 0.3 mm wide segregation bands became narrow and unfavourable for further crack propagation (see arrows). Extremly high forces developed at both crack tips produced deformation of the metallic fibers between these cracks. The above examples illustrate the fact that at the microscale in steel (D) the phosphorous segregation has changed from very

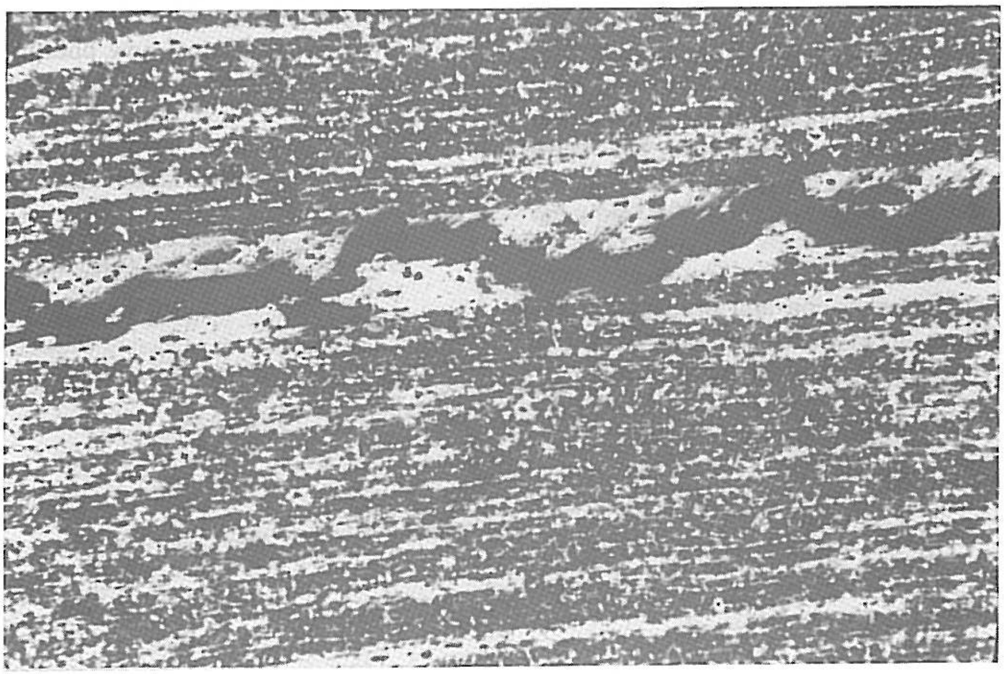

FIG. 8. Stepwise cracks in the 0.25 mm wide phosphorous band. Oberhoffer's reagent. Magnification 130 ×.

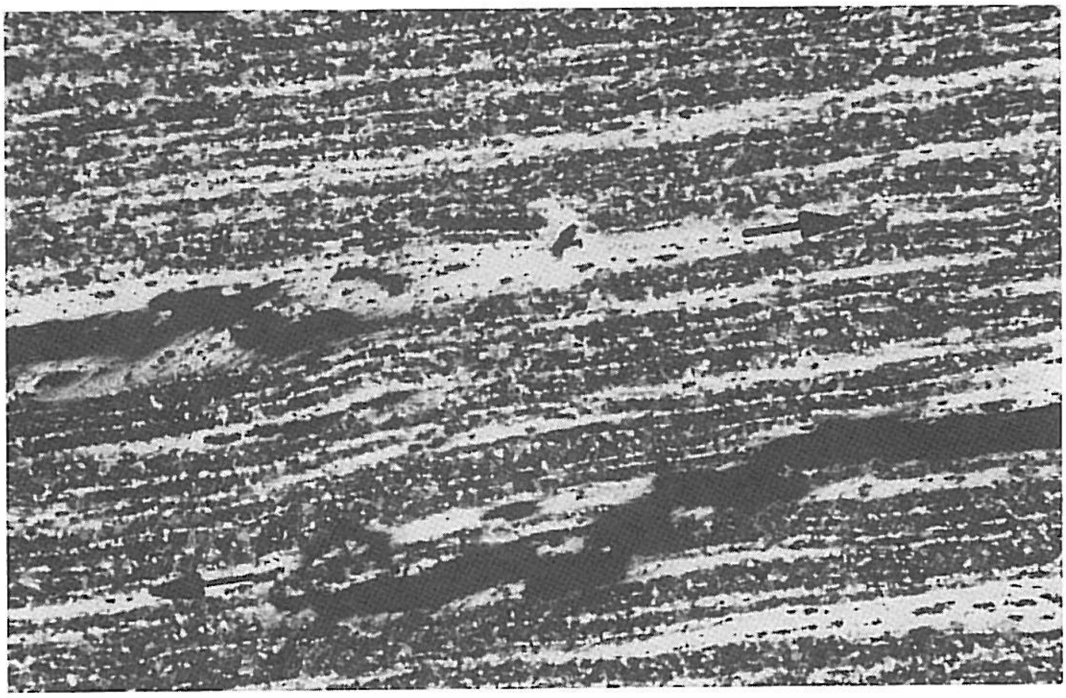

FIG. 9. The situation in the area where two stepwise cracks are arrested due to narrowing (see arrows) the phosphorous bands. Note a plastic deformation of the structure between both cracks ends. Oberhoffer's reagent. Magnification 63×.

wide enriched in phosphorous bands, in which many of stepwise cracks have been originated, to very narrow one in which stepwise cracks could not propagate. Probably, the high phosphorous content in this steel exceeded 0.05%, and the uncontrolled solidification process caused such complicated mode of phosphorous segregation and high susceptibility to stepwise cracking of the steel (D). All samples exhibited phosphorous bands wider than 0.1 mm. The steel (P) should be placed in the area of bands over 0.1 mm (measured average band was 0.115 mm). Steel (E) in which stepwise cracks have not been found exhibited bandwidth of about 0.03 mm. The rough estimation of the critical phosphorous segregation bandwidth gave the values between 0.03 mm and 0.1 mm. If the bands are below 0.03 mm the steel should not be sensitive to HIC. The steel is very sensitive to cracks nucleation and propagation due to the presence of H_2S in the natural gas if the phosphorous bands are wider than 0.1 mm.

CONCLUSIONS

(i) Results of metallographic study suggest that sensitivity of low carbon pipe-steel to HIC depends on phosphorous segregation in the pipe-wall cross-section.
(ii) It is believed that if the phosphorous band by width is below 0.03 mm the sensitivity is very small. Over 0.1 mm, the sensitivity is very high.
(iii) The mechanism of how phosphorous segregation affects HIC is not clear and further investigation is needed.

REFERENCES

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