

Original Paper

Comparison of the Influences of Phosphorus and Sulfur on the Reheat Cracking Sensitivity of Cr-Mo Steels

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The influences of phosphorus and sulfur on the reheat cracking sensitivity of 1%Cr-0.5%Mo steels were investigated using experimental steel specimens doped with phosphorus or sulfur. The cracking sensitivity was evaluated by terms of critical restraint stress obtained by an implant test. And the metallurgical experiments were made on the phosphorus segregation to the austenite grain boundary, and on the diffusible sulfur concentration. Phosphorus segregation was measured by the grain boundary etching method, and sulfur was measured dividing into dissolved sulfur in iron matrix and combined sulfur as sulfide. As the results of the cracking tests, it was found that there exists a critical content of phosphorus for the reheat cracking sensitivity, above which the cracking sensitivity is steeply increased with an increasing phosphorus content. When the phosphorus content exceeds the critical value, it segregates to the austenite grain boundary during welding and its segregation is intensified by tempering after welding. In the case of sulfur-doped steels, the dissolved sulfur concentration is the major factor governing the cracking sensitivity. The critical value of its concentration, above which the cracking sensitivity is steeply increased, was determined. The dissolved sulfur concentration depends both on the bulk sulfur and manganese contents.

Key Words: reheat cracking, phosphorus segregation, dissolved sulfur, implant test, critical restraint stress, critical phosphorus content, critical dissolved sulfur concentration

1. Introduction

The authors have pointed out in the previous paper [1] that phosphorus increases the reheat cracking sensitivity by means that it segregates to the prior-austenite grain boundary during post-weld heat treatment at about 800 K, and makes the grain boundary weak and brittle.

It has been believed that phosphorus exists uniformly in iron matrix after welding, and moves to the grain boundary by diffusion during post-weld heat treatment [2]. This model proposed originally by D.McLean [3] explains the segregation of phosphorus to an usual grain boundary. But it can not explain why phosphorus prefers to segregate to the prior-austenite grain boundary of the reheated heat affected zone, and hence, a new model which can explain this special phenomenon will be required. The authors assumed that the phosphorus segregation to prior-austenite grain boundary would originate, when the steel was brought to the austenite condition by the weld thermal cycle. Its segregation would be intensified further by "the equilibrium segregation" during tempering process. In this investigation, they confirmed their assumption by some experimental works using the grain etching method.

Sulfur is another impurity element which increases the reheat cracking sensitivity of steel. It is considered that sulfur segregates to the grain boundary during welding and tempering processes in the same manner as phosphorus does. However, the component of sulfur which takes part in the segregation will be the free or dissolved sulfur, not be the combined sulfur forming sulfide. From this point of view, the influence of dissolved sulfur on the reheat cracking sensitivity was examined. Much attention was paid on the influence of manganese combining with that of sulfur in this investigation.

1%Cr-0.5%Mo steel was selected for the investigation, as it is known to exhibit the maximum sensitivity to reheat cracking among several Cr-Mo steels.

2. Experimental methods

2.1. Preparation of steel specimens

The influence of phosphorus on the reheat cracking sensitivity of 1%Cr-0.5%Mo steel was examined on the steel specimens containing 0.006 to 0.096%P, as shown in Table 1.

To clarify the combined influence of sulfur and manganese, four series of 1%Cr-0.5%Mo steel were used; 0.5 and 1.0%Mn series in which sulfur content was varied from 0.015 to 0.09%, and 0.015 and 0.08%S series, in which manganese content was varied from 0.01 to 1.3%, as shown in Table 2.

These steel specimens were prepared by the following

Table 1 Chemical compositions of P-doped 1%Cr-0.5%Mo steel specimens

No.	C	Si	Mn	P	S	Cr	Mo
P-1	0.17	0.36	1.12	0.006	0.020	1.13	0.47
P-2	0.19	0.28	0.83	0.008	0.018	1.05	0.46
P-3	0.16	0.39	0.75	0.011	0.014	0.99	0.47
P-4	0.12	0.34	1.08	0.016	0.016	1.10	0.53
P-5	0.19	0.29	0.84	0.021	0.019	1.05	0.45
P-6	0.18	0.26	0.81	0.096	0.014	0.97	0.43

Table 2 Chemical compositions of S-doped 1%Cr-0.5%Mo steel specimens

No.	C	Si	Mn	P	S	Cr	Mo
LM-1	0.19	0.24	0.43	0.01	0.019	1.03	0.55
LM-2	0.17	0.49	0.55	0.01	0.030	1.07	0.51
LM-3	0.20	0.19	0.41	0.01	0.054	1.06	0.57
LM-4	0.21	0.24	0.52	0.01	0.092	1.16	0.54
HM-1	0.18	0.36	1.14	0.01	0.016	1.07	0.51
HM-2	0.18	0.52	1.23	0.01	0.028	1.11	0.52
HM-3	0.18	0.41	1.12	0.01	0.049	1.16	0.52
HM-4	0.22	0.36	1.13	0.01	0.093	1.13	0.53
LS-1	0.20	0.20	0.29	0.01	0.017	0.93	0.56
LS-2	0.19	0.27	0.58	0.01	0.014	0.98	0.58
LS-3	0.20	0.47	0.84	0.01	0.016	1.08	0.57
LS-4	0.20	0.45	1.33	0.01	0.014	1.09	0.53
HS-1	0.21	0.25	0.11	0.01	0.080	0.94	0.59
HS-2	0.21	0.45	0.35	0.01	0.085	1.04	0.55
HS-3	0.18	0.28	0.76	0.01	0.176	0.94	0.55
HS-4	0.20	0.34	1.01	0.01	0.076	1.05	0.54
HS-5	0.18	0.34	1.20	0.01	0.077	1.09	0.55

procedures. Electrolytic iron, 1%C steel and ferro-alloys were melted together in a mullite crucible in air by using an induction furnace. The melt was deoxidized by metallic silicon and manganese, and then ferro-phosphorus or iron sulfide was added to the melt. The final temperature of the melt was 1840 K. The 8 kg melt was cast into a steel mold of 60 mm in diameter and 300 mm in height. These ingots were hot-forged at 1150 to 1250 K into a steel bar of 15 mm in diameter. The bar was oil-quenched from 1223 K and tempered at 973 K for 1 hour.

2.2. Procedures of reheat cracking test

The reheat cracking sensitivity of each steel specimen was evaluated by the magnitude of the critical restraint stress, $\sigma_{AW-crit}$ obtained by the modified implant test [4-6]. This cracking test was performed by the constant-strain type machine shown in the previous papers [6-8].

A set of implant test specimen is shown in Fig.1. The implant and the base metal plate were machined from the steel bar and a commercial high strength steel (0.67%Cr-0.24%Mo), respectively. The welded specimen was reheated at a rate of 200 K/hr up to 873 K, and kept at this temperature for 20 hours.

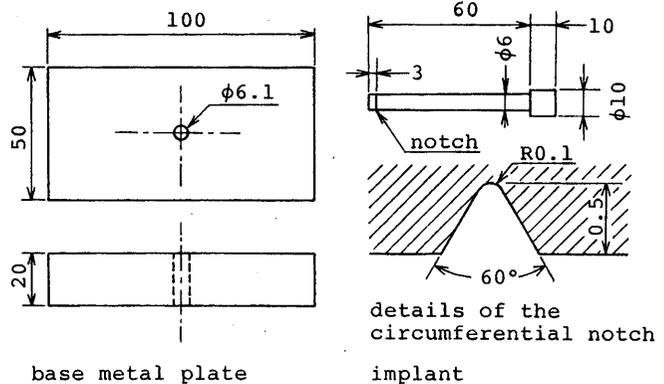


Fig.1 Dimensions of the specimen for reheat cracking test

3. Influence of phosphorus on the reheat cracking sensitivity

Fig.2 shows the results of cracking tests on the effect of phosphorus for the specimens of 1%Cr-0.5%Mo steels shown in Table 1. A logarithmic scale is used for the abscissa of the phosphorus content. The solid line in this figure corresponds to the critical restraint stress, $\sigma_{AW-crit}$, which is the boundary between cracking field (● mark) and no cracking field (o mark).

The authors assumed here that there will be three stages in the $\sigma_{AW-crit}$ -phosphorus content correlation curve; the upper shelf stage, the transition stage and the lower shelf stage, and that each stage in this curve will be approximated by a straight line. On the basis of this assumption, a bent line is drawn in the figure. Logarithmic scale was taken for the abscissa for the ease of straightening the curved line of the transition stage and reading micro-concentrations around the upper bend point.

The phosphorus content value corresponding to the upper bend point is named as "the critical content of phosphorus, P_{crit} ". The P_{crit} of this steel is 0.008%. The P_{crit} is regarded as the threshold value or the target value for

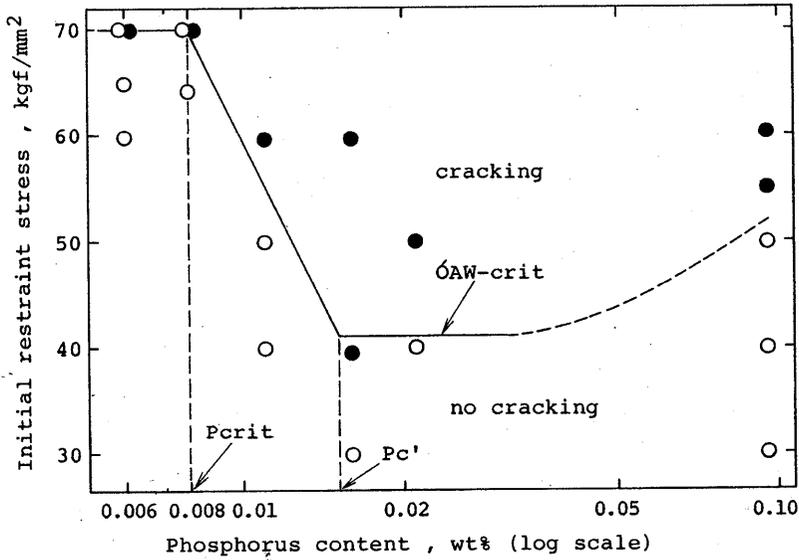


Fig.2 Influence of phosphorus on the critical restraint stress ($\sigma_{AW-crit}$) of 1%Cr-0.5%Mo steel

preventing the reheat cracking by means of decreasing the phosphorus content.

The lower bent point, $P_{c'}$ will be less important from the view point of preventing the reheat cracking.

4. Influence of sulfur on the reheat cracking sensitivity

4.1 Single influence of sulfur

The single influence of sulfur on the cracking sensitivity is shown in Fig.3. The meanings of the marks and line in this figure are the same as those in Fig.2. Fig.3(a) and(b) show the influence of sulfur at the constant manganese levels; 1 and 0.5%, respectively. These figures exhibit the tendency that the critical restraint stress decreases with an increasing sulfur content. However, the decrease of the critical restraint stress is less steep and the critical value of sulfur content, which was clearly seen in the case of phosphorus (P_{crit}), is not recognized in these figures.

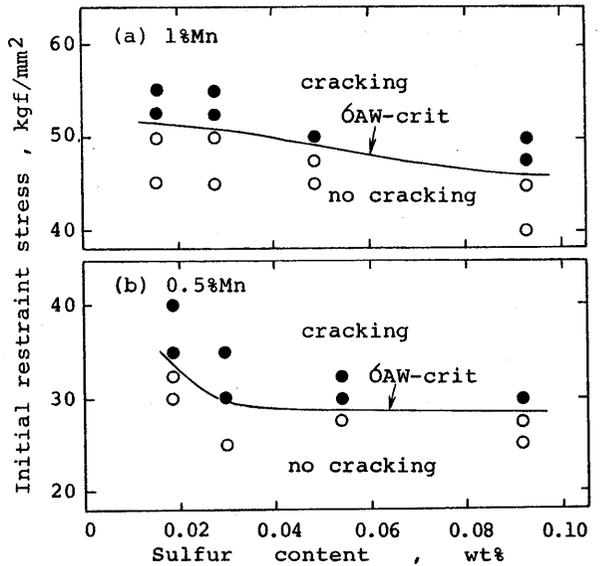


Fig.3 Influence of sulfur on the critical restraint stress of HM and LM series specimens

4.2. Influence of manganese in S-doped steel

Fig.4(a) and (b) show the influence of manganese at the constant sulfur levels; 0.015% and 0.08%, respectively. The beneficial effect of manganese in S-doped steel is clearly seen in the specimens of 0.015% and 0.08%S series. The critical restraint stress increases linearly with increasing the manganese content. The curves of both series are actually the same in shape, except for that of 0.08%S series locates in the lower side of that of 0.015%S series.

It can be concluded that the harmful effect of sulfur itself will be almost hidden by the strong beneficial effect of manganese in those expressions of Fig.3 and Fig.4.

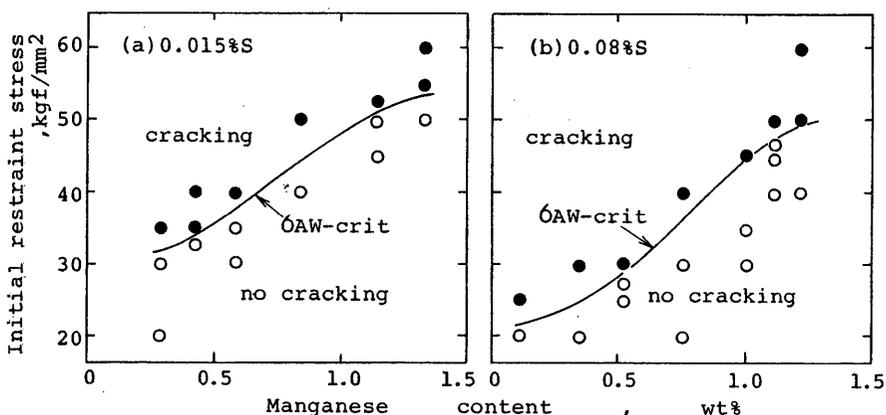


Fig.4 Influence of manganese on the critical restraint stress of LS and HS series specimens

4.3. Influence of dissolved sulfur

As mentioned above, the single influence of sulfur on the cracking sensitivity depends largely on the manganese content of steels. Sulfur exists in steels in the forms of dissolved atom and of combined atom forming sulfide. The concentration of dissolved sulfur together with the quantity of sulfide was determined by the following experimental procedure. The sulfide particles present in each specimen quenched from the temperature of 1573 K were extracted as the anode residue of the electrolysis. The electrolyte used was one liter aqueous solution of 15% sodium citrate and 1% potassium bromide (neutral solution). The electrolytic current density was 10 mA/cm². The weight of the steel specimen dissolved was about 20 g. The residue was collected on a grass filter (G4). It was washed with water followed by ethyl alcohol, and finally, dried at 323 K.

The extracted residue contains not only sulfide but also oxide and some quantity of iron hydroxide formed during the electrolysis. The weight of sulfur in the residue per 100 g bulk specimen, [S] was determined by the chemical analysis. The sulfide content was calculated from [S] with assuming that the sulfur concentration of each sulfide is the same as that of the stoichiometric MnS compound (36.9%S) [7], as shown in Table 3. The weight of dissolved sulfur per 100 g bulk specimen, (S) was obtained by reducing the [S] value from the

Table 3 Concentration of dissolved sulfur, quantity of sulfide and sulfide type

No.	Weight per 100g bulk specimen (g)						sulfide type
	bulk specimen		residue	combined sulfur [S]	dissolved sulfur (S)	sulfide	
	Mn (b)	S (b)					
LM-1	0.43	0.019	0.317	0.0081	0.0109	0.022	MnS
LM-2	0.53	0.030	0.362	0.0191	0.0109	0.052	MnS
LM-3	0.41	0.054	0.441	0.0413	0.0127	0.112	MnS
LM-4	0.52	0.092	0.473	0.0805	0.0115	0.218	MnS
HM-1	1.14	0.016	0.287	0.0101	0.0059	0.027	MnS
HM-2	1.23	0.028	0.393	0.0242	0.0038	0.066	MnS
HM-3	1.12	0.049	0.455	0.0423	0.0067	0.115	MnS
HM-4	1.13	0.093	0.501	0.0866	0.0064	0.235	MnS
LS-1	0.29	0.017	0.374	0.0066	0.0104	0.018	MnS
LS-2	0.58	0.014	0.312	0.0050	0.0090	0.014	MnS
LS-3	0.84	0.016	0.329	0.0091	0.0069	0.025	MnS
LS-4	1.33	0.014	0.338	0.0099	0.0041	0.027	MnS
HS-1	0.11	0.080	0.370	0.0602	0.0198	0.163	MnS
HS-2	0.35	0.085	0.419	0.0736	0.0114	0.199	MnS
HS-3	0.76	0.076	0.396	0.0680	0.0080	0.184	MnS
HS-4	1.01	0.076	0.327	0.0689	0.0071	0.187	MnS
HS-5	1.20	0.077	0.417	0.0709	0.0061	0.192	MnS

total weight of sulfur, S(b), as shown in the table.

As shown in Table 3, the concentration of dissolved sulfur is remarkably decreased with an increase of the manganese content, and increased little with the bulk sulfur content. On the contrary, the concentration of combined sulfur, is increased with the sulfur content. If the harmful effect of sulfur is due to the sulfur segregation to the grain boundary, the dissolved sulfur only is responsible for producing the reheat cracking. All the values of the critical restraint stress in Fig.3 and 4 were plotted against the parameter of the

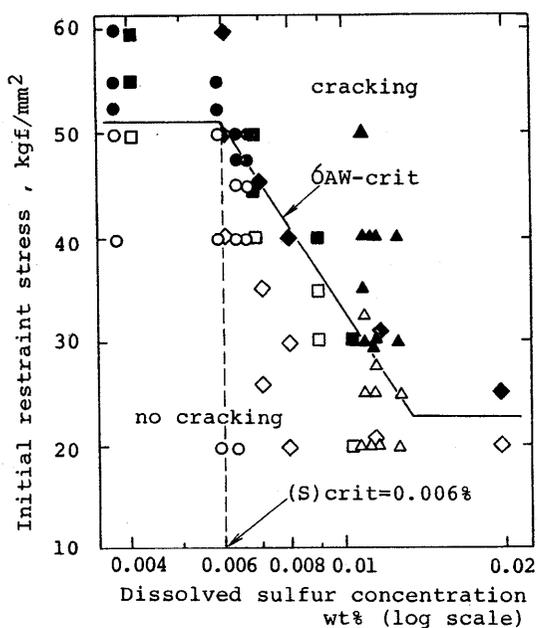


Fig.5 Critical concentration of dissolved sulfur, (S)crit shown on the critical restraint stress—(S) diagram of 1%Cr-0.5%Mo steel (0.01%P)

marks: ● ○ HM series(1%Mn)
 ▲ △ LM series(0.5%Mn)
 ■ □ LS series(0.015%S)
 ◆ ◇ HS series(0.08%S)

concentration of dissolved sulfur as shown in Fig 5.

The σ_{AW} -crit-(S) correlation curve is drawn with assuming that there are the upper shelf stage, the transition stage and the lower shelf stage, as explained in the case of phosphorus.

The (S) value corresponding to the upper bent point is named as "the critical concentration of dissolved sulfur, (S)crit". The (S)crit of this steel is 0.006%.

4.4. Comparison of the influence of sulfur with phosphorus

The influences of sulfur and phosphorus on the reheat cracking sensitivity have been discussed by comparing in each other by many researchers [8]. However, the magnitudes of influences of both elements can not be compared directly using their contents of a bulk steel, because sulfur exists in a steel in the dissolved and the combined forms, as mentioned above.

The influence of the former is assumed to be very much larger than the latter, and the comparison was made by using the same quantity of dissolved sulfur and phosphorus on the Fig.5 (S-doped steel) and Fig.2 (P-doped steel). Two curves in those figure inform that 1) the effect of dissolved sulfur for reducing the upper shelf stress is almost the same as that of phosphorus, 2) the difference between (S)crit and Pcrit is not so large. It can be concluded here that sulfur and phosphorus render the harmful effect of the same magnitude on the reheat cracking when the the influence of the former is restricted to that by the dissolved sulfur.

5. Phosphorus segregation to the prior-austenite grain boundary

5.1. Grain boundary etching method

"The grain boundary etching method" [9] is used to assess the local concentration of phosphorus segregating at the austenite grain boundary. It was pointed out that "the depth of etched grain boundary, d" by this method was proportional to its phosphorus concentration analyzed quantitatively by Auger electron spectroscope.

The etchant in this experiment was prepared by mixing the solutions A and B in the ratio 5:3 by volume immediately before using it. Solution A: saturated aqueous solution of picric acid, Solution B: aqueous solution of 3% dodecylbenzensulfonic acid sodium salt (a wetting reagent). The etching time was 10.8 ks at 293 K.

An indentation was made near the etched grain boundary by the diamond pyramid cone of a micro-hardness testing machine. This surface was polished until the etched grain boundary was worn out. The depth d corresponding to the thickness of the worn-out-layer was given by the reduction in the size of the indentation.

5.2. Initiation of phosphorus segregation during welding

The influence of phosphorus on the depth of etched grain boundary d is

shown in Fig.6 for 1%Cr-0.5%Mo steel in as-welded condition. The depth d is decreased with a decreasing bulk phosphorus content, and it reaches a shelf value, d_0 at the phosphorus content of 0.008%. This content agrees well with the P_{crit} obtained by the cracking test. Therefore, from the metallurgical view point, the P_{crit} will be the critical phosphorus content below which any segregation of it will not occur during welding.

Fig.6 informs an important fact that phosphorus is originally segregated to a certain extent at austenite grain boundary by the welding thermal cycle. This fact will be very useful for explaining the reason why the reheat cracking is not initiated along ferrite grain boundary existing in the reheating (tempering) stage but initiated along prior-austenite grain boundary produced in the welding stage.

The fundamental mechanism of producing the phosphorus segregation during welding has been proposed by the authors in the previous paper [10].

5.3. Intensification of phosphorus segregation during tempering

The depth d of the heat affected zone tempered at several temperatures was measured on the steel specimens of 1%Cr-0.5%Mo-0.008 to 0.10%P. They were heated up to each given temperature with a heating rate of 0.056 K/sec and quenched immediately in water.

Fig.7 shows changes of the depth d with a rising tempering temperature for each steel specimen. In cases of 1%Cr-0.5%Mo-0.10%P and 1%Cr-0.5%Mo-0.02%P steels, d values are increased by raising the temperature up to 773 K and then it is decreased as the temperature exceeds it. In the case of 1%Cr-0.5%Mo-0.008%P steel whose phosphorus content corresponds to P_{crit} , d values are generally small at every tempering temperature and a peak is not recognized in the curve.

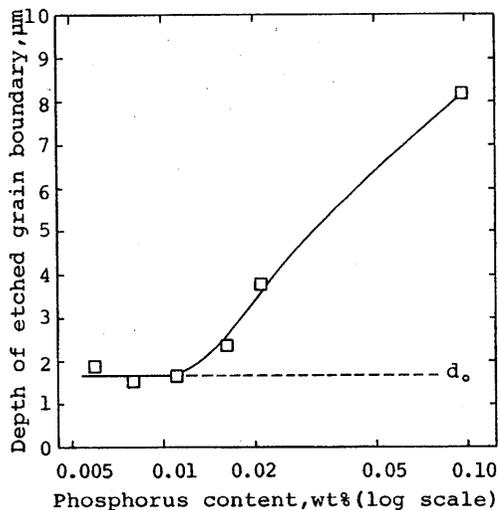


Fig.6 Influence of phosphorus on the depth of etched grain boundary of austenite

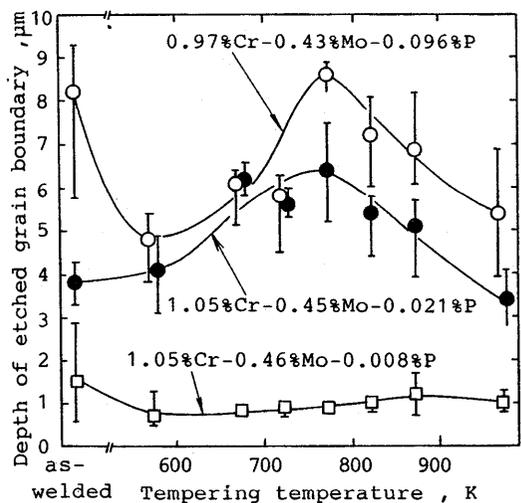


Fig.7 Influence of tempering temperature on the depth of etched grain boundary of austenite

Thus it is concluded that the phosphorus segregation produced initially by welding is generally intensified by subsequent tempering at 773 K at which the reheat cracking most likely initiates.

In steel, in which phosphorus did not segregate during welding (1%Cr-0.5%Mo-0.008%P steel), it does not segregate further during tempering.

A model of intensifying the phosphorus segregation is shown in Fig.8. Phosphorus concentrated to a zone around the prior-austenite grain boundary by welding is transferred further to a very narrow site by tempering, as shown in the figure. The segregation phenomenon of this case will occur subjecting to the mechanism of "The equilibrium segregation" proposed by D.McLean.

The intergranular fracture will occur when the $[P]_{GB}$ reaches the $[P]_{GBcrit}$ in Fig.8 under a certain applied stress.

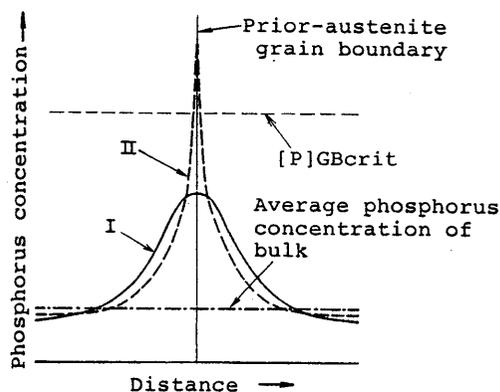


Fig.8 Profiles of phosphorus concentrations near the prior-austenite grain boundary cause by welding(I), and that caused by reheating(II)

6.Sulfur segregation to the prior-austenite grain boundary

Sulfur will segregate to the austenite grain boundary during welding by the same way as phosphorus does. In the case of the sulfur segregation during the tempering, following two processes will be expected to occur at or near the grain boundary; 1) Intensification of sulfur segregation which is subjected to the equilibrium segregation by the same way as phosphorus does, 2) Precipitation of sulfide from ferrite matrix which is super-saturated with sulfur. Although, it is not known at present which process prefers to occur, the possible states of grain boundary brought about by those processes will be assumed as below.

- 1) alone : Sulfide-free grain boundary
(excluding the sulfide produced during welding)
- 2) alone : Sulfide precipitating in a zone around the grain boundary.
- 1) followed by 2): Sulfide precipitating at the grain boundary
- 2) followed by 1): (impossible to occur.)

7.Conclusions

The influences of phosphorus and sulfur on the reheat cracking were compared on 1%Cr-0.5%Mo steel, the following results were obtained:

- 1) The influence of phosphorus can be summarized simply by the correlation curve of the phosphorus content--the critical restraint stress. In this correlation curve, there exists a critical phosphorus content, P_{crit} , below which the reheat cracking hardly occurs.

- 2) The influence of sulfur can not be summarized by the sulfur content alone. In this case a combined effect between sulfur and manganese should be considered.
- 3) The influence of sulfur under several manganese contents can be expressed simply by the term of "the dissolved sulfur concentration, (S)". There exists a critical value of (S) which corresponds to P_{crit} of P-doped steel.
- 4) Sulfur and phosphorus induce the harmful effect of the same magnitude on the reheat cracking when their effects were compared in the same quantity of the dissolved sulfur and the phosphorus.
- 5) A series of processes of impurity segregation in the prior-austenite grain boundary during welding and tempering was clarified with the case of phosphorus segregation.

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