

Original Paper

Effect of Phosphorus on Reheat Cracking of Cr-Mo Steels

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This study was devoted to the influence of phosphorus on reheat cracking sensitivity of Cr-Mo steels from the view points of the combined effect of phosphorus, chromium and molybdenum. The synthetic Cr-Mo steels melted in our laboratory were used. Their phosphorus contents were varied from 0.004 to 0.1wt% for five sets of Cr-Mo contents. The cracking sensitivity of steels was evaluated by the term of critical restraint stress to produce cracking obtained by the modified implant method for reheat cracking. The cracking sensitivity was discussed being related to the phosphorus segregation to prior-austenite grain boundary. The phosphorus concentration of grain boundary was semi-quantitatively determined by measuring the depth of grain boundary etched by a certain etchant. The results are summarized as follows. (1) There exists a critical phosphorus content, P_{crit} , from which the cracking sensitivity remarkably increases with the increase of phosphorus content. P_{crit} values are: above 0.02, 0.01, 0.008, 0.014 and below 0.01wt% for 0Cr-0.5Mo, 0.5Cr-0.5Mo, 1Cr-0.5Mo, 1.3Cr-0.5Mo and 2Cr-1Mo steels, respectively. (2) Phosphorus segregated to the prior-austenite grain boundary as early as in as-welded condition, and the degree of segregation corresponds to the degree of cracking sensitivity. (3) The grain boundary concentration of phosphorus becomes the maximum by tempering at about 500°C, which corresponds to the temperature of crack initiation.

1. Introduction

In the previous reports¹⁾²⁾, the combined effect of chromium and molybdenum on the reheat cracking sensitivity was examined at the fixed phosphorus contents of 0.02 and 0.01wt%. And the cracking sensitivity of Cr-Mo steels was newly expressed on a Cr-Mo content diagram where the contour lines of the critical restraint stress to produce cracking, $\sigma_{AW-crit}$ (Fig.1). From these results, it

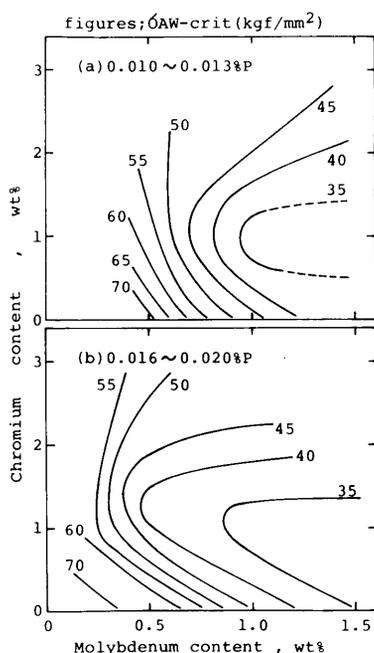


Fig.1 Contour lines of critical restraint stress ($\sigma_{AW-crit}$) shown in the Cr-Mo content diagram (a) 0.010 to 0.013 wt% P (b) 0.016 to 0.020 wt% P

can be pointed out that the effect of reducing phosphorus content from 0.02 to 0.01 wt% differs depending on the Cr-Mo contents. That is, the increase in the critical restraint stress is about 20 kgf/mm² at 1%Cr-0.5%Mo, but it is below 5 kgf/mm² in the composition range of 0 to 1%Cr-1%Mo.

In this study, the critical restraint stress were determined on five Cr-Mo steels, whose phosphorus content was varied continuously in a wide range in order to clarify the combined effect of phosphorus, chromium and molybdenum. And such combined effect of these elements was discussed from the view point of phosphorus segregation. It has usually been thought that phosphorus hardly segregated in the heat affected zone (HAZ) during welding and it segregated when the HAZ was reheated. But it is found by this research that phosphorus segregates already in as-welded condition. The mechanism of phosphorus segregation caused by welding was discussed from the view points of the α/γ transformation and the distribution of phosphorus between both phases during weld thermal cycle.

2. Experimental procedures

2.1 Materials

The twenty-six synthetic Cr-Mo steels were prepared in our laboratory by an induction furnace. Electrolytic iron, pig iron and ferro alloys were melted in air using a mullite crucible. Then the molten steel was deoxidized with metallic silicon and manganese in such quantities that the residual silicon and manganese contents would be about 0.3 and 1 wt%, respectively, and ferro phosphorus was intentionally added to the molten steel. Then the molten steel was poured directly into a cold steel split mold whose shape was 60 mm in diameter and 300 mm in height. The chemical compositions of steel specimens were shown in Table 1. These steel specimens are classified into five groups by the basic Cr-Mo contents, that is 0%Cr-0.5%Mo, 0.5%Cr-0.5%Mo, 1%Cr-0.5%Mo, 1.3%Cr-0.5%Mo and 2%Cr-1%Mo. The phosphorus content of each group was varied in a wide range (about 0.004 to 0.01 wt%).

Each ingot of 60 mm in diameter was hot forged into a steel bar of about 16 mm in diameter. And then the steel bar was quenched from 950°C, and tempered at 700°C for 1 hour. The implant shown in Fig.2(a) was machined from the heat treated steel bar. The implant was notched in order to ensure that the reheat cracking initiated and propagated within a coarse grained region of HAZ. The base metal plate shown in Fig.2(b) was machined from a commercial high strength

Table 1 Chemical compositions of 5 types of Cr-Mo steels containing 0.004 to 0.107wt%P (wt%)

No	C	Si	Mn	P	S	Cr	Mo
PA-1	0.17	0.28	0.53	0.011	0.018	0.00	0.45
PA-2	0.16	0.36	0.97	0.013	0.019	0.11	0.48
PA-3	0.12	0.42	1.06	0.020	0.018	0.04	0.51
PA-4	0.17	0.29	0.82	0.031	0.019	0.04	0.49
PA-5	0.18	0.25	0.78	0.085	0.020	0.01	0.48
PB-1	0.16	0.25	0.65	0.006	0.019	0.50	0.48
PB-2	0.17	0.28	0.57	0.010	0.014	0.46	0.47
PB-3	0.12	0.39	1.06	0.018	0.019	0.58	0.54
PB-4	0.17	0.28	0.84	0.060	0.020	0.49	0.50
PB-5	0.17	0.40	0.76	0.094	0.017	0.45	0.51
PC-1	0.17	0.36	1.12	0.006	0.020	1.13	0.47
PC-2	0.19	0.28	0.83	0.008	0.018	1.05	0.46
PC-3	0.16	0.39	0.75	0.011	0.014	0.99	0.47
PC-4	0.12	0.34	1.08	0.016	0.016	1.10	0.53
PC-5	0.19	0.29	0.84	0.021	0.019	1.05	0.45
PC-6	0.18	0.26	0.81	0.096	0.014	0.97	0.43
PD-1	0.18	0.37	1.11	0.014	0.020	1.25	0.49
PD-2	0.16	0.44	1.27	0.023	0.014	1.28	0.47
PD-3	0.17	0.30	0.97	0.063	0.018	1.42	0.49
PD-4	0.16	0.45	1.19	0.098	0.019	1.39	0.50
PD-5	0.17	0.31	0.97	0.107	0.020	1.30	0.42
PE-1	0.20	0.26	0.93	0.004	0.019	2.21	0.84
PE-2	0.18	0.25	0.84	0.012	0.015	2.19	0.94
PE-3	0.20	0.24	0.87	0.013	0.017	2.03	1.03
PE-4	0.13	0.38	1.16	0.019	0.020	2.03	0.93
PE-5	0.18	0.26	0.86	0.102	0.019	1.89	0.85

plate.

2.2 Reheat cracking test

The reheat cracking sensitivity of the steels were evaluated by the magnitude of the critical restraint stress, $\sigma_{AW-crit}$ obtained by the modified implant test for reheat cracking³⁾. The smaller the critical restraint stress is, the more sensitive the steel is. The conditions of welding and post weld heat treatment are shown in Table 2. This cracking test was performed under the condition of constant displacement(constant strain), and the restraint stress loaded before reheating (the initial restraint stress; σ_{AW}) was decreased during reheating. Therefore the critical stress includes two main factors; i) stress relaxation characteristics and ii) the grain boundary strength of prior-austenite at elevated temperature. The influence of phosphorus on these factors will be also discussed in detail later.

2.3 Grain boundary etching method

The grain boundary etching method was employed for the examination of grain boundary segregation of phosphorus. This method was proposed by T.Ogura et.al.⁴⁾ as a technique analyzing the amount of phosphorus segregation. And it was reported that the depth of grain boundary grooved by a certain etchant was proportional to its phosphorus concentration obtained by Auger analysis⁴⁾. Therefore, in this study the phosphorus concentration at grain boundary was

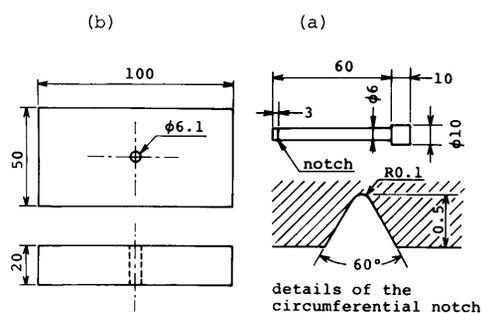


Fig.2 Dimensions of the specimen for reheat cracking test

(a) implant (b) base metal plate

Table 2 Conditions of welding and postweld heat treatment

welding conditions	
electrode	JIS DT2416 dried at 350°C for 1 hour
welding current	180 A
arc voltage	25 V
welding speed	15 cm/min
preheat	150 °C
post weld heat treatment	
heating rate	200 °C/hr
holding temperature	600 °C

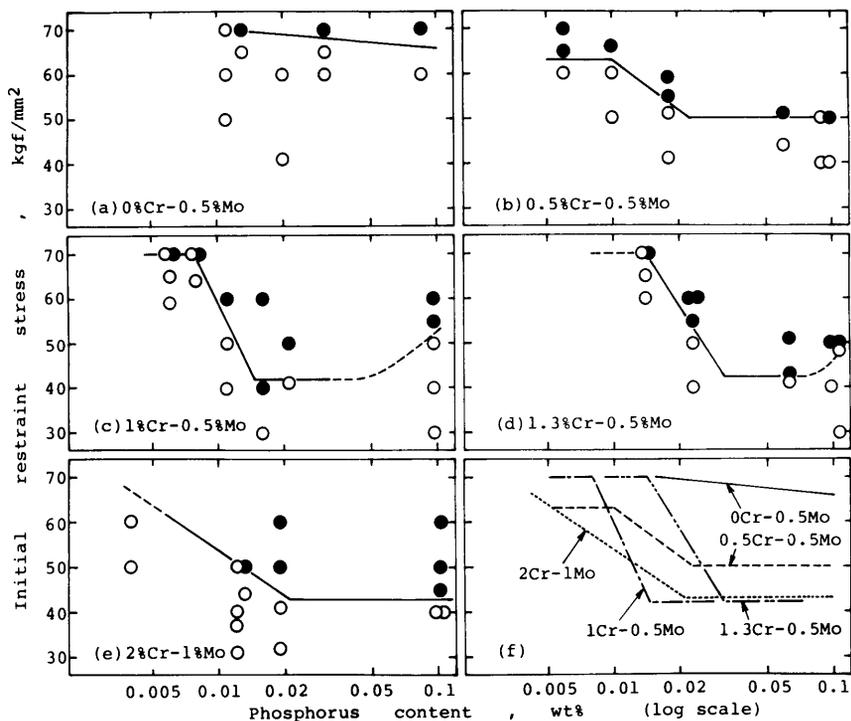


Fig.3 Influence of phosphorus on the critical restraint stress ($\sigma_{AW-crit}$) of 5 types of Cr-Mo steels

semi-quantified in term of the depth of etched grain boundary.

The etchant was prepared by mixing solutions A and B in the ratio 5:3 by volume just before using it.

Solution A: saturated aqueous solution of picric acid, solution B: aqueous solution of 3% laurylbenzenesulfonic acid sodium salt.

Etching conditions were listed below. Temperature of etchant: 20°C, etching time: 3 hours, amount of etchant: 80 ml/30 mm² of specimen surface.

3. Results of cracking test

Fig.3 shows the effect of phosphorus content on the cracking test results of the steel specimens divided into five Cr-Mo groups. Phosphorus content are plotted in the abscissa on a logarithmic scale. A mark ● denotes the initial restraint stress by which cracking occurred and a mark ○ denotes that by which cracking did not occur. A solid line separating cracking- and no cracking fields corresponds to the critical restraint stress, $\sigma_{AW-crit}$.

In the case of 0%Cr-0.5%Mo steel (Fig.3(a)), the critical restraint stress is decreased from 70 to 65 kgf/mm² with the increase of phosphorus content from 0.01 to 0.1wt%. The cracking sensitivity of these steels is generally even though the phosphorus content is as high as 0.1wt%, and the harmful effect of phosphorus is hardly recognized with these steels.

In the case of 0.5%Cr-0.5%Mo steel (Fig.3(b)), the critical restraint stress is 63 kgf/mm² in a phosphorus content range of below 0.01wt%. When the

phosphorus content is between 0.01 and 0.02wt%, the critical restraint stress is steeply decreased as phosphorus content increases. But it is not decreased any further, though the phosphorus content is increased over the range of above 0.02wt%. As mentioned above, there are two critical values of phosphorus content on the view point of the effect of phosphorus on cracking sensitivity. The lower critical value is regarded as threshold value for preventing the reheat cracking by decreasing phosphorus content. Therefore, this phosphorus content is named " the critical phosphorus content, P_{crit} ". P_{crit} of 0.5%Cr-0.5%Mo steel is 0.01 wt%. In the cases of 1%Cr-0.5%Mo and 1.3%Cr-0.5%Mo steels (Fig.3(c) and (d)), the variation of the critical restraint stress with the increase of phosphorus content had the tendency similar to that of 0.5%Cr-0.5%Mo steel. P_{crit} are 0.008 and 0.014wt%, respectively for 1%Cr-0.5%Mo and 1.3%Cr-0.5%Mo steels.

In the case of 2%Cr-1%Mo steel (Fig.3(e)), P_{crit} is not determined exactly, but it is assumed to be between 0.004 and 0.01wt%.

The critical restraint stress lines of five Cr-Mo groups are compared in Fig.3(f). Following facts can be pointed out. (1) When the phosphorus content is lower than P_{crit} of each Cr-Mo group, there is little difference in the critical restraint stress among these groups. (2) When the phosphorus content is between two critical values, the inclination of the line is increased with the increase of chromium content. (3) The critical phosphorus content, P_{crit} decreases with the increase of chromium content up to 1%Cr. When the chromium content exceeds 1%, P_{crit} increases conversely. (4) When the phosphorus content is larger than the upper critical value, the critical restraint stress decreases with the increase of chromium content.

4. Effect of phosphorus on stress relaxation characteristics

The critical restraint stress is determined by two factors in case of the constant strain type cracking test³). One of them is the strength of prior-austenite grain boundary at elevated temperature and the other is the stress relaxation characteristics. That is,

$$\sigma_{AW-crit} = \frac{100}{100 - R_{Tf}} \times \sigma_{PW-crit}$$

where R_{Tf} is the stress relaxation ratio at the temperature of T_f , at which the crack initiates. And $\sigma_{PW-crit}$ is the strength of prior-austenite grain boundary at the temperature of T_f . However, the $\sigma_{PW-crit}$ could not be measured directly, because the reheat crack is usually arrested when the initial restraint stress was slightly larger than the critical restraint stress. Therefore, in this report only the effect of phosphorus on the stress relaxation ratio was discussed by assuming that T_f would be 550°C on the basis of the data of some commercial Cr-Mo steels in the previous paper⁵). The stress relaxation ratio at 550°C was calculated by the following equation.

$$R_{550^\circ C} = \frac{\sigma_{AW} - \sigma_{PW 550^\circ C}}{\sigma_{AW}} \times 100 \quad (\%)$$

Fig.4 shows the effect of phosphorus on the stress relaxation ratio at 550°C for five Cr-Mo groups. The data indicate a large spread of value. So the

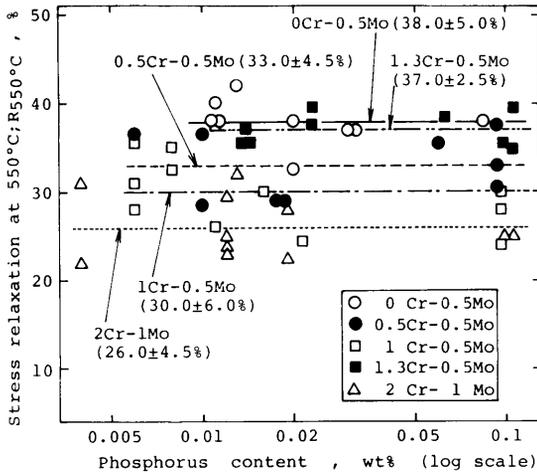


Fig.4 Influence of phosphorus on stress relaxation ratio at 550°C

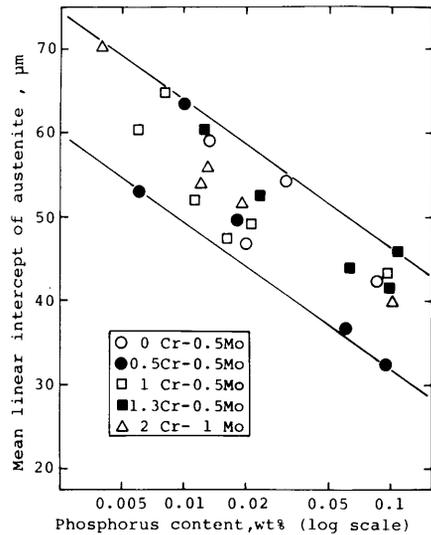


Fig.5 Influence of phosphorus on austenite grain size in HAZ

mean value of the stress relaxation ratio was calculated for each Cr-Mo group, and it was denoted by each line in the figure. It can be considered that the stress relaxation ratio of each Cr-Mo group is little affected by varying the phosphorus content even with an extremely wide range.

5. Phosphorus segregation to the prior-austenite grain boundary

As mentioned in the previous section, the stress relaxation ratio is little affected by varying the phosphorus content. Therefore, it is considered that the effect of phosphorus for increasing the cracking sensitivity illustrated in Fig.3 is attributed to its effect of decreasing the grain boundary strength, $\sigma_{PW-crit}$, due to its segregation to the grain boundary. If the prior-austenite grain size is not altered by the phosphorus content for each Cr-Mo group, the phosphorus concentration of grain boundary will be in proportion to the bulk concentration of phosphorus. However, Y.Ohmori⁶⁾ has recently reported the grain refining effect of phosphorus. So, the effect of prior-austenite grain size was preliminarily discussed before the examination of phosphorus segregation.

5.1 The effect of phosphorus on prior-austenite grain size

Fig.5 shows the effect of phosphorus on the mean linear intercept of austenite. The mean linear intercept decreases as the phosphorus content increases in every Cr-Mo groups.

It can be considered that the phosphorus concentration at grain boundary, P_{GB} is in proportion to the bulk concentration of phosphorus, P_B and in inverse proportion to the area of grain boundary which is included in unit volume of steel, S_V . That is,

$$P_{GB} = k P_B \frac{1}{S_V} \quad (k:\text{constant})$$

While it has been known that S_V is twice the value of the reciprocal of the mean linear intercept, \bar{L} ⁷⁾. Therefore,

$$P_{GB} = k' P_B \bar{L} \quad (k' = \frac{1}{2} k)$$

From the experimental results of Fig.5, \bar{L} is decreased only slightly from 65 to 40 μm as P_B increases very largely from 0.005 to 0.1wt%. Therefore it can be concluded that the grain refining effect of phosphorus scarcely influences the grain boundary segregation.

5.2 Phosphorus segregation in as-welded condition

Fig.6 shows the effect of phosphorus on the depth of groove of prior-austenite grain boundary for five Cr-Mo groups. The depth of groove; d value is increased generally with the increase of phosphorus content, but the inclinations of their lines vary with the Cr-Mo contents. That is, in the case of 0%Cr-0.5%Mo, d value scarcely increases with the increase of phosphorus content. The inclination of the line steeply increases with the increase of chromium content, and it has a maximum at 1%Cr. When the chromium content is increased further, the inclination of the line decreases. The tendency that d value has a maximum at 1%Cr corresponds well to that the cracking sensitivity has a maximum at 1%Cr.

The relation between d value and P_{crit} is qualitatively represented as follows. By decreasing the phosphorus content in Fig.6, five lines gradually approach to the value of d_0 , which is denoted by a broken line. The value of d_0 is considered as the fundamental depth of groove of etched grain boundary, which will be brought some fundamental factors other than the phosphorus segregation. The phosphorus content at which each line separates from d_0 line is found to correspond to the P_{crit} for each Cr-Mo group obtained in Fig.3. The P_{crit} values of 0%Cr-0.5%Mo and 2%Cr-1%Mo steels were not determined exactly from the results of cracking test. They can be estimated from d values as 0.05 and 0.004wt% for 0%Cr-0.5%Mo and 2%Cr-1%Mo steels, respectively. These estimated values are also

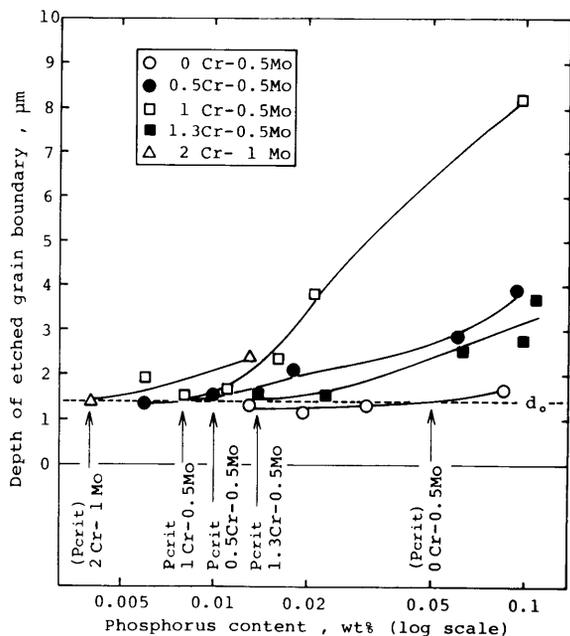


Fig.6 Influence of phosphorus on the depth of etched grain boundary of austenite

indicated in Fig.6 as the mark (P_{crit}).

From the experimental results mentioned above, the followings can be pointed out.

- (1) In the case of the cracking sensitive steel, phosphorus segregation has already found at prior-austenite grain boundary in as-welded condition. It will be reasonably to be considered that such segregation will be produced at elevated temperature at which the steel has been in austenite state.
- (2) The intensity of phosphorus segregation, and the phosphorus content above which the segregation occurs depend considerably on the Cr-Mo contents of steel.

It is the new idea of this research that the phosphorus has already segregated at austenite grain boundary during weld thermal cycle. If phosphorus would segregate simply by reheating below A_1 temperature, phosphorus should segregate at not only prior-austenite grain boundary but also ferrite grain boundary. This idea makes it very easy to explain the main problem why the reheat cracking initiates only at prior-austenite grain boundary.

5.3 Phosphorus segregation in tempering process

Fig.7 shows the changes of d value with rising the tempering temperature for some selected steel specimens. These weld specimens were tempered up to the appointed temperature at the heating rate of 200°C/hr , and then quenched immediately in water. In the case of $1\%Cr-0.5\%Mo-0.1\%P$ steel, d value decreases at the tempering temperature of 300°C , and then it is increased as the temperature rises. d value has a maximum at 500°C . Similar tendency is found for $1\%Cr-0.5\%Mo-0.02\%P$ steel.

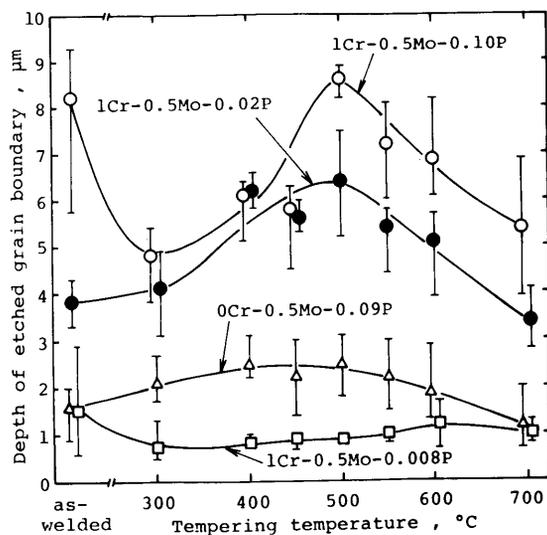


Fig.7 Influence of tempering temperature on the depth of etched grain boundary of austenite

$1\%Cr-0.5\%Mo-0.008\%P$ steel has the same Cr-Mo contents as two steels mentioned above, but this is insensitive to reheat cracking because of its low phosphorus content. In the case of this steel, d value is very small and the peak of d value is not found. While, $0\%Cr-0.5\%Mo-0.09\%P$ steel contains a large amount of phosphorus, but this is insensitive to cracking because of chromium free. In the case of this steel, d value is small and the peak of d value is lower. The results mentioned above indicates that there exists the strong mutual effect among chromium, molybdenum and phosphorus in the phosphorus segregation phenomenon.

6. Consideration on the mechanism of phosphorus segregation

An interesting experimental results was obtained in this research that

phosphorus segregated in certain extent as early as in as-welded state. The phosphorus segregation in this case is expected to be originated by rapid heating during welding. From such view point, a discussion is made on the segregation mechanism of phosphorus mainly in simple Fe-P-C alloy being referred to reactions indicated in the ternary diagram of Fe-P-C system.

6.1 Phase diagram of Fe-P-C system

Phase diagram of Fe-P-C system was proposed originally by Vogel⁸⁾, and in later its iron corner was modified by Langenscheid⁹⁾. The qualitative diagram of this system is shown in Fig.8*. The ternary and binary reactions in Fe-P-C system and the equilibrium distribution ratio of phosphorus among coexisting phases are shown in Table 3. They are arranged in the table in the order of falling temperature.

6.2 Segregation process of phosphorus during rapid heating

Fe-P-C alloy experiences the following reactions (transformations) during heating.

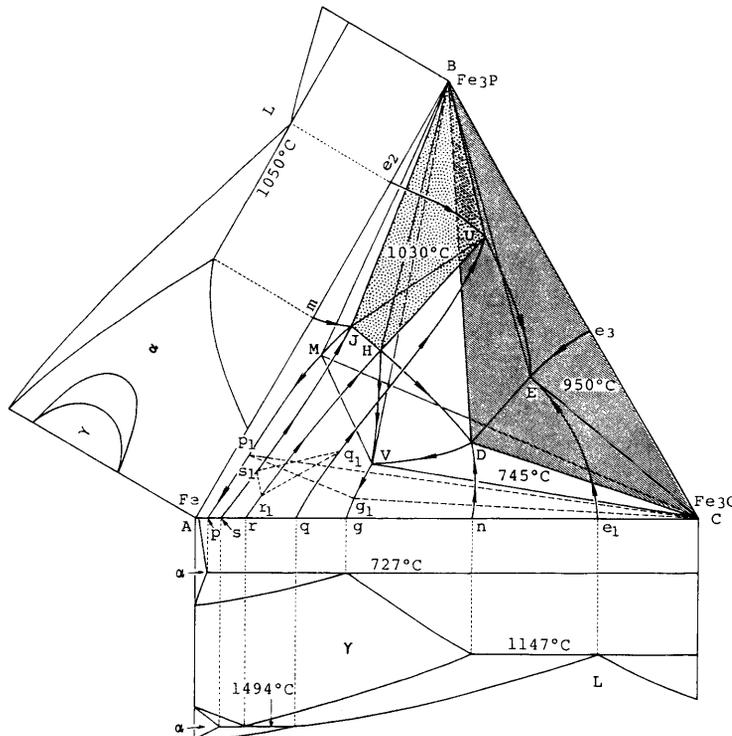


Fig.8 Fe-P-C ternary diagram (qualitative diagram)

* The temperature of the invariant ternary plane in Fig.8 are given by the authors referring to the data of Vogel, Langenscheid and others^{10) 11)}

Table 3 Phase changes occurring in Fe corner of Fe-P-C system

classification	temperature range	phase change	equilibrium distribution ratio of P
(3)	1030~1494°C	binary peritectic reaction $L + \delta(\alpha) \rightleftharpoons \gamma$	$C_L^P : C_\alpha^P : C_\gamma^P = 3.5 : 1 : 0.4$ (1250°C*)
(4)	1030°C	peritectic-eutectic reaction $L + \delta(\alpha) \rightleftharpoons \gamma + Fe_3P$	
(5)	745~1030°C	phosphide precipitation (1) $\gamma \rightleftharpoons \gamma + Fe_3P$ $(\gamma + \alpha) \rightleftharpoons (\gamma + \alpha) + Fe_3P$	
(2)	745~1030°C	α/γ transformation $\gamma \rightleftharpoons \alpha + \gamma$	$C_\alpha^P : C_\gamma^P = 1 : 0.37$ (900°C)
(7)	745°C	ternary eutectoid reaction $\gamma + Fe_3P \rightleftharpoons \alpha + Fe_3C$	
(1)	727~745°C	binary eutectoid reaction $\gamma \rightleftharpoons \alpha + Fe_3C$	$C_\alpha^P : C_\gamma^P : C_{Fe_3C}^P = 1 : 0.4 : 0$ (740°C*)
(6)	R.T. ~ 745°C	phosphide precipitation (2) $\alpha \rightleftharpoons \alpha + Fe_3P$	

* estimated value

Note; this table was composed by the authors using the data of R.Vogel⁸⁾ G.Langenscheid⁹⁾ H.Kaneko et al.¹⁰⁾ and R.Tanaka.¹¹⁾

- i) $\alpha + Fe_3C \rightarrow \gamma$ (727~745°C) ——— (reaction 1)
 ii) $\alpha + \gamma \rightarrow \gamma$ (745~1030°C) ——— (reaction 2)
 iii) $\gamma \rightarrow L + \delta(\alpha)$ (1030~1494°C) ——— (reaction 3)

The phosphorus segregation produced by these three steps of reactions is discussed below.

(a) First step of segregation by $\alpha + Fe_3C \rightarrow \gamma$

The segregation process of phosphorus during rapid heating can be explained in a simplified manner when the following assumptions is adopted: i) the equilibrium distribution of phosphorus will be always established at α/γ interface during the course of transformation, ii) the diffusion rate of phosphorus is so small that it diffuses little from α/γ interface to the original ferrite phase.

Phosphorus contained in alloy R, for example is distributed among ferrite,

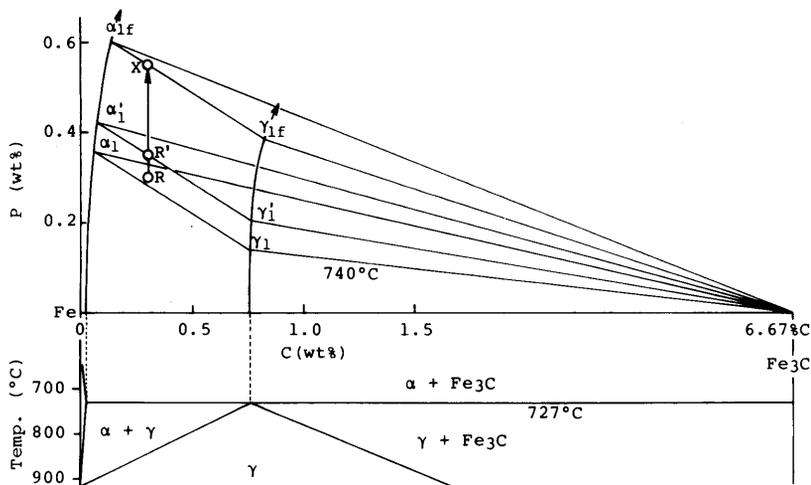


Fig.9 Phosphorus distribution in α , γ and Fe_3C phases in Fe-P-C alloy when binary eutectoid reaction $\gamma \rightleftharpoons \alpha + Fe_3C$ occurs

austenite and cementite in the following ratio at 740°C as shown in the phase diagram of Fe-P-C system of Fig.9.

$$[P]_{\alpha 1} : [P]_{\gamma 1} : [P]_{Fe_3C} = 0.36\% : 0.14\% : 0\% = 1 : 0.4 : 0$$

By assuming that this ratio is the same between 727 and 745°C, the distribution ratio of phosphorus will generally be expressed as:

$$C_{\alpha}^P : C_{\gamma}^P : C_{Fe_3C}^P = 1 : 0.4 : 0 \quad (727 \text{ to } 745^{\circ}\text{C})$$

On the basis of the assumptions and the data, the pattern of phosphorus concentration near α/γ interface at the beginning of the reaction(1), which occurs when the alloy is heated rapidly from lower temperature up to 740°C, will be schematically drawn as Fig.10(a). The maximum concentration, which corresponds to $[P]_{\alpha 1}$ of Fig.9, appears at the ferrite side of α/γ interface.

The subsequent transformation will occur in the adjacent zone d_1 , producing new α/γ interface in it. The average concentration of transforming zone is to correspond to that of new α/γ interface, which is shown hereafter by the notation of $[P]_{av-\alpha/\gamma}$. The concentrations of ferrite, austenite and $[P]_{av-\alpha/\gamma}$ at the new interface will be $[P]_{\alpha 1}'$, $[P]_{\gamma 1}'$ and $[P]_{R'}$, for example, as shown in

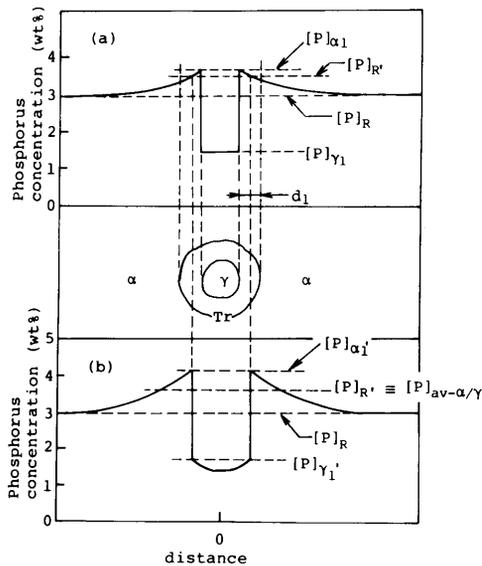


Fig.10 Distribution patterns of phosphorus near α/γ interface at the beginning (a) and the subsequent (b) instances of reaction $\alpha + Fe_3C \rightarrow \gamma$, at 740°C

Note, α :original ferrite, γ :austenite produced by the reaction at the beginning instance, Tr:transition zone in which the subsequent transformation is going to occur

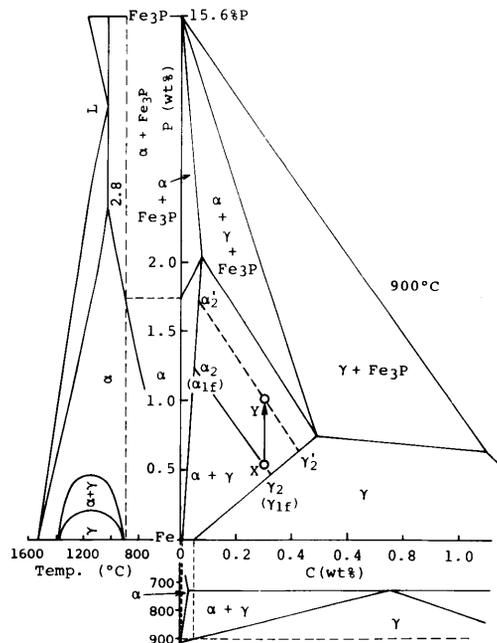


Fig.11 Phosphorus distribution in α and γ phases in Fe-P-C alloy at the temperature range in which α and γ phases coexist

Fig.9 and Fig.10(b).

As the results of reheating such sequences, $[P]_{av-\alpha/\gamma}$, $[P]_{\alpha}$ and $[P]_{\gamma}$ at the interface at each time increase progressively and reach finally the concentrations of $[P]_X$, $[P]_{\alpha 1f}$ and $[P]_{\gamma 1f}$ of Fig.9, respectively, at the end of the reaction(1).

(b) Second step of segregation by $\alpha + \gamma \rightarrow \gamma$

Phosphorus segregation caused by the reaction(1) will be intensified by the succeeding reaction(2), because the distribution ratio $C_{\alpha}^P : C_{\gamma}^P$ in this case is 1 : 0.37 which is the same as the case of reaction(1). The segregation sequence when the alloy is heated rapidly from 740°C up to 900°C, for example, is shown in Fig.11. $[P]_{av-\alpha/\gamma}$ corresponding to $[P]_X$ in the figure, which was attained by the reaction(1) at 740°C, will further increase up to $[P]_{\gamma}$ during the reaction(2) at 900°C by the same mechanism mentioned above.

(c) Third step of segregation by $\gamma \rightarrow L + \delta(\alpha)$

The distribution ratio of phosphorus among three phases concerning to the reaction(3) can be read from the reaction plane at 1250°C of phase diagram of Fig.12 as:

$$C_{L}^P : C_{\alpha}^P : C_{\gamma}^P = 3.5 : 1 : 0.4$$

Phosphorus is concentrated markedly into liquid phase. When the alloy is heated rapidly from 900°C up to 1250°C, α/γ interface zone having $[P]_{av-\alpha/\gamma}$ corresponding to $[P]_{\gamma}$ will produce liquid phase by the reaction(3). Phosphorus concentration of such liquid phase is as high as $[P]_{L3}$ in Fig.12.

As can be seen from the discussion above, phosphorus is progressively concentrated into α/γ interface by the reaction (1) and (2), and finally, α/γ interface zone produce liquid phase extremely rich with phosphorus. Such phenomenon has been known as the partial melting as grain boundary.

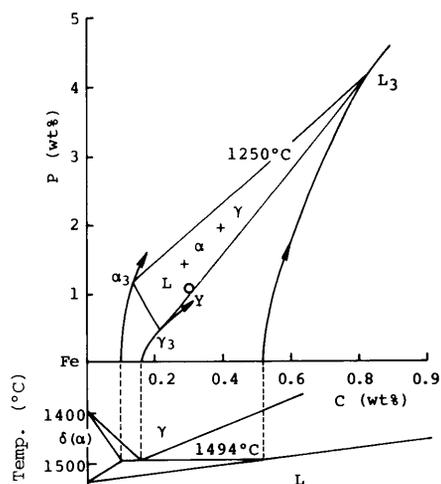


Fig.12 Phosphorus distribution in α , γ and liquid phases in Fe-P-C alloy when binary peritectic reaction, $L + \alpha \rightleftharpoons \gamma$ occurs

6.3 Effect of carbon on segregation process

Carbon will remarkably promote the phosphorus segregation of Fe-P-C alloy as explained below, for example, on the reaction(1).

By the reaction(1), a series of alloys, whose chemical compositions lie on the straight line $\alpha_1\gamma_1$ in Fig.9, produces at α/γ interface the same set of phosphorus concentrations, $[P]_{\alpha 1}$ and $[P]_{\gamma 1}$. The straight line $\alpha_1\gamma_1$ is shown by the formula,

$$(P) = -0.3(C) + 0.35$$

where, (P) and (C) are the phosphorus and carbon contents (wt%) of an alloy. If the second term of the above formula can be regarded as the same as $[P]_{\alpha_1}$ (Fig.9), the formula can be written as,

$$(P) = -0.3(C) + [P]_{\alpha_1}$$

By assuming that the lines $\alpha_1\gamma_1'$, $\alpha_1''\gamma_1''$ --- at several temperature are approximately in parallel to the line $\alpha_1\gamma_1$ in a certain chemical composition range, the phosphorus concentrations at several α/γ interfaces can generally be expressed as,

$$[P]_{\alpha} = (P) + 0.3(C)$$

Therefore, from the view point of phosphorus segregation, the increase of carbon content will bring the similar effect as the increase of phosphorus content.

6.4 Effects of chromium and molybdenum on segregation process

Ternary diagrams of Fe-Cr-C and Fe-Mo-C systems¹²⁾ indicate that chromium and molybdenum lower largely the temperature of reaction(3) of binary Fe-C system. The lower the temperature of the reaction is, the higher the phosphorus concentration of liquid phase will become⁸⁾. Therefore, it will reasonably be expected that those elements will increase largely the phosphorus concentration of liquid phase produced by reaction(3).

It will be also expected that those elements increase the ratio $C_{\alpha}^P/C_{\gamma}^P$ in the reaction(1) and (2), since they act as ferrite formers as phosphorus does. But the experimental data on such effect of them is very few.

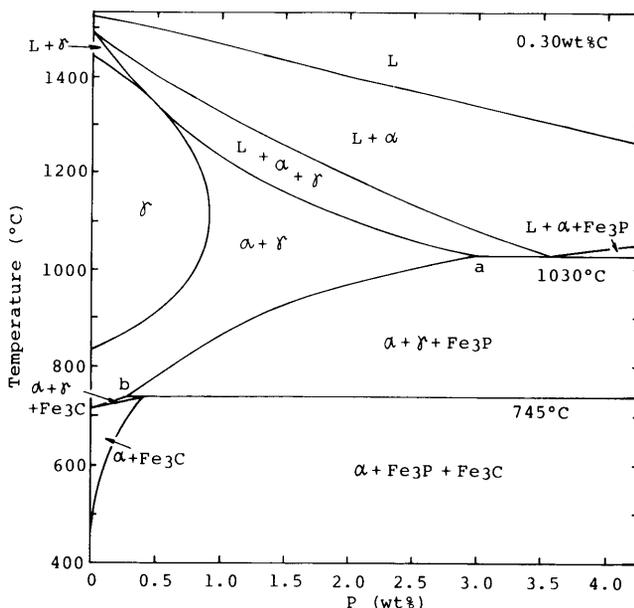
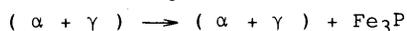


Fig.13 A vertical section of Fe-P-C ternary diagram at 0.30wt%C
 Note: this section was composed by the authors using the same data quoted in Table 3

6.5 Precipitation of phosphide during cooling

The cooling process begins at a certain temperature at which the partial melting occurs. During cooling, iron phosphide Fe_3P may be produced in prior-austenite grain boundary depending on the phosphorus concentration of grain boundary, $[P]_{gb}$ and the cooling rate. Fe_3P is produced by the following reactions.



The precipitation process is explained below by referring to 0.3%C section of Fe-PC diagram shown in Fig.13.*

(a) $[P]_{gb}$ being larger than point a of Fig.13

When $[P]_{gb}$ is so large as above the point a of Fig.13, Fe_3P is produced by the peritectic-eutectic reaction(4) at $1030^\circ C$. Falling temperature from $1030^\circ C$ reduces the solubility of phosphorus in austenite and ferrite, and Fe_3P precipitates as the reaction(5).

When the temperature reaches $745^\circ C$, a part of Fe_3P is redissolved into ferrite matrix by the following ternary eutectoid reaction.



Falling temperature from $745^\circ C$ reduces the solubility of phosphorus in ferrite, and Fe_3P precipitates again by the reaction(6). When the cooling rate through about $745^\circ C$ is large enough, martensite(M) will be produced by the reaction(8) instead of the reaction(7) and (6).



(b) $[P]_{gb}$ lying between points a and b

The same reaction mentioned above, except for the reaction(4), will occur in grain boundary.

(c) $[P]_{gb}$ being smaller than point b

Fe_3P will precipitate from ferrite in the temperature range below about $700^\circ C$ with the smaller cooling rate.

6.6 Effect of chromium and molybdenum on the solubility of phosphorus

The additions of chromium and molybdenum reduce markedly the solubility of phosphorus in ferrite and austenite of Fe-P-C alloy¹⁰⁾. Some examples of the effect of those elements are shown in Fig.14¹⁰⁾. The solubility of phosphorus in ferrite of Fe-P alloy is reduced to as smaller as one-twentieth by alloying 1%Mo or 5%Cr.

Therefore a large part of phosphorus in grain boundary will be present as phosphide rather than as dissolved phosphorus. The types of phosphide, such as iron, chromium and molybdenum phosphides¹³⁾ and their configurations may play an important role in the mechanism of reheat cracking which is induced by phosphorus segregation at the grain boundary.

* In order to simplify the explanation, the carbon concentration of grain boundary is assumed here to be constant as 0.3%.

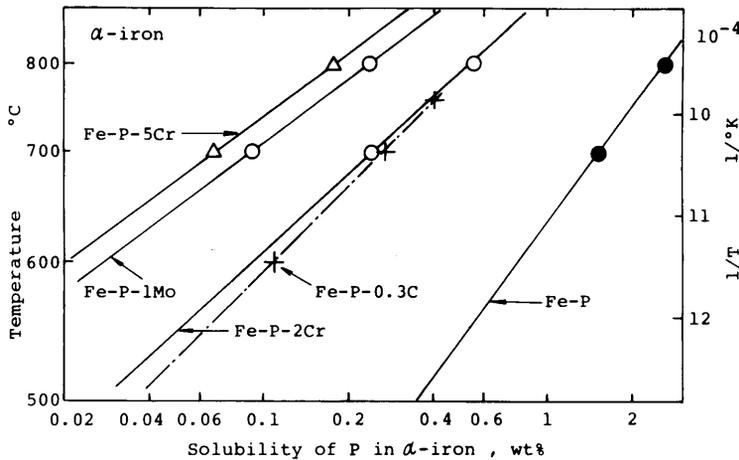


Fig.14 Effect of Cr and Mo on the solubility of P in α -iron¹⁰⁾

7. Conclusions

(1) The critical restraint stress for producing the reheat cracking were determined on five Cr-Mo steel groups, whose phosphorus content was varied in a wide range (0.004 to 0.1wt%). There exists a critical phosphorus content, P_{crit} , from which the critical restraint stress steeply decreases with the increase of phosphorus content. P_{crit} values are: above 0.02, 0.01, 0.008, 0.014 and below 0.01wt% for 0%Cr-0.5%Mo, 0.5%Cr-0.5%Mo, 1%Cr-0.5%Mo, 1.3%Cr-0.5%Mo and 2%Cr-1%Mo steels, respectively.

(2) The phosphorus concentration of prior-austenite grain boundary was semi-quantified by measuring the depth of grain boundary grooved by a etchant containing picric acid, and the following facts were pointed out. i) Phosphorus segregates to the grain boundary as early as in as-welded condition. ii) The degree of segregation in this condition corresponds very well to the degree of cracking sensitivity. iii) The grain boundary concentration of phosphorus becomes the maximum by tempering at 500°C, which corresponds to the temperature of crack initiation.

(3) The following mechanism of phosphorus segregation during rapid heating was proposed. i) Austenite produced by α/γ transformation should reject excess phosphorus toward the original ferrite through α/γ interface, because phosphorus can be distributed in austenite in smaller concentration than in ferrite. But phosphorus hardly diffuses in ferrite at the condition of rapid heating, and therefore, it is accumulated progressively at α/γ interface. ii) Phosphorus concentration at α/γ interface, which becomes finally austenite grain boundary, is increased markedly by the subsequent reaction, $\gamma \rightarrow \alpha + L$, because the phosphorus concentration of this liquid is extremely large than that of austenite.

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