

Original Paper

Micro-segregation of Phosphorus in a Fe-P-C Alloy Caused by Rapid α/γ Transformation

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The mechanism of phosphorus segregation caused by rapid heating was clarified experimentally using Fe-0.6wt%P-0.3wt%C alloy. The alloy was heated rapidly up to 950°C followed by quenching, and the phosphorus distribution was examined by EDX micro-analysis on the specimen consisting of austenite (martensite) and a little ferrite. As the result, phosphorus is enriched in ferrite region by rapid α/γ transformation in over ten times as much as its content of the bulk alloy. The rapid heating also brought a fall of the temperature of initiating liquation, which was confirmed by microscopic observation.

Those experimental results could clearly prove the authors' theoretical prediction that i) phosphorus is forced to enrich in the original ferrite, as it can be dissolved only a little in austenite produced by a rapid transformation, ii) the region in which ferrite transforms finally becomes the austenite grain boundary, the greater the phosphorus concentration in the grain boundary, the lower the temperature of its liquation becomes.

The procedure of determining the correlation curve of the intensity of $K_{\alpha-P}$ vs. phosphorus concentration is explained in detail.

1. Introduction

The authors have previously discussed the mechanism of the reheat cracking of Cr-Mo steels and pointed out that i) the reheat cracking is induced mainly by the phosphorus segregation at the prior-austenite grain boundary, ii) this segregation is originated in as-welded condition, and is intensified further by reheating¹⁾.

In the previous paper²⁾, the authors have proposed a theoretical mechanism of phosphorus segregation caused by rapid heating on the basis of the phase diagram of Fe-P-C system. The outline of this theoretical prediction is

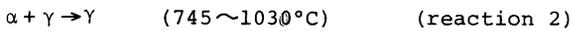
introduced again in the beginning part of the paper.

This prediction was proved experimentally in this investigation by using Fe-0.6wt%P-0.3wt%C alloy and the micro-analysis by EDX (energy dispersive X-ray spectrometer). A great effort was made for applying EDX to a full-quantitative analysis of phosphorus in micro-areas of the alloy.

2. Theoretical prediction on segregation process of phosphorus caused by rapid heating

2. 1 Segregation in α/γ region

According to the phase diagram of Fe-P-C system, an iron base alloy experiences three types of reactions (transformations) when it is heated from the room temperature up to about 1400°C as ³⁾⁴⁾,



The following segregation process of phosphorus will be expected by assuming that (i) the equilibrium distribution of phosphorus between ferrite and austenite will be always attained at α/γ interface during the transformation, (ii) the diffusion rate of phosphorus from α/γ interface into ferrite phase will be smaller than the velocity of transformation.

The phosphorus distribution near α/γ interface at the time when an austenite particle is formed in a homogeneous ferrite region by reaction 1 or 2 is illustrated in Fig.1(a). $[P]_R$, $[P]_{\alpha 1}$ and $[P]_{\gamma 1}$ are the phosphorus concentrations in ferrite matrix region, austenite particle and ferrite at α/γ interface, respectively. The distribution ratio of phosphorus between both phases, $C_{\alpha}^P/C_{\gamma}^P$ is $1/0.4$ ⁴⁾. Consequently, immediately after the transformation, phosphorus should be discharged from austenite particle to ferrite matrix region through α/γ interface. As the result, the phosphorus concentration reaches the maximum at the ferrite side of the interface

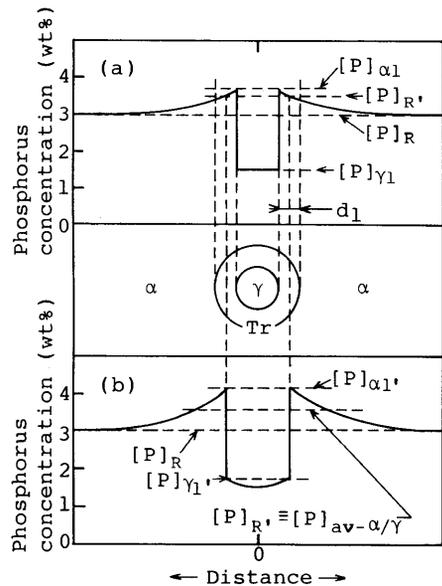


Fig.1 Phosphorus distribution near α/γ interface (a) beginning instance of α/γ transformation (b) succeeding instance of transformation

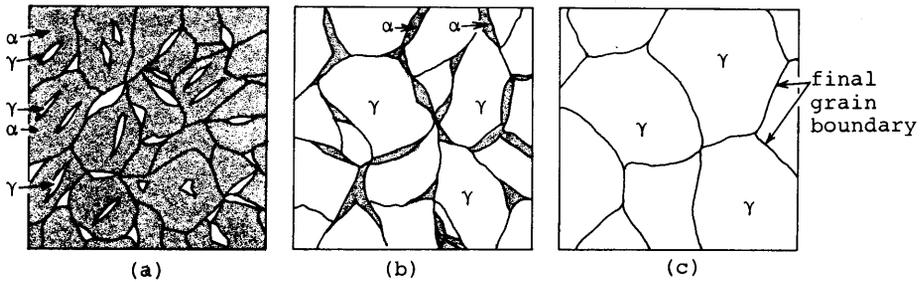


Fig.2 Progress of α/γ transformation and corresponding segregation zone (schematic representation)

- (a) near the beginning of transformation; phosphorus is concentrated at α/γ interface
- (b) near the end of transformation; phosphorus concentration at the interface is increased
- (c) transformation finishes and austenite grains are growing; phosphorus is confined at austenite grain boundary at the beginning of this stage

as $[P]_{\alpha 1}$ in Fig.1(a). Subsequent transformation occurs in a micro-region of d_1 , whose average concentration, $[P]_R$, is larger than that of original ferrite matrix, $[P]_R$. After this transformation, the new maximum concentration of $[P]_{\alpha 1}'$ ($>[P]_{\alpha 1}$) is attained as shown in Fig.1(b). A series of succeeding transformation in the same manner increases progressively the maximum phosphorus concentration at α/γ interface.

The transformation completes as the temperature rises (Fig.2(a) and (b)). When the heating rate is sufficiently great, the region of austenite grain boundary, in which ferrite transformed finally, will be enriched by phosphorus as shown in Fig.2(c). But when the heating rate is not so great, the segregation does not occur, because phosphorus will diffuse into austenite rather than will be confined in the grain boundary.

2. 2 Segregation caused by liquation

By a subsequent heating after the transformation, a part of the alloy will begin to melt; this stage of melting is called "liquation". This liquation is brought by the reaction 3. The temperatures of initiating the reaction 3 for three alloys, for example, P_1 , P_2 and P_3 are shown in the diagram of Fe-P-C system of Fig.3²⁾³⁾⁴⁾. It shows that (i) the temperature of initiating the reaction falls with increasing the phosphorus content of the alloy, (ii) the equilibrating distribution ratio of phosphorus among three phases are; $C_L^P : C_\alpha^P : C_\gamma^P = 9 : 2.5 : 1$. That is, liquid phase produced by this reaction is enriched by phosphorus in nine times as much as the original austenite phase.

By assuming that (i) and (ii) will be also valid for a micro-region of grain boundary, it is expected that the grain boundary region where phosphorus segregates will begin to liquate at a lower temperature than the bulk alloy does.

In actual welding process, liquation is used to occur at a lower temperature by phosphorus segregation, the width of liquated zone will be expanded, and this makes the steel more sensitive to the grain boundary embrittlement and cracking.

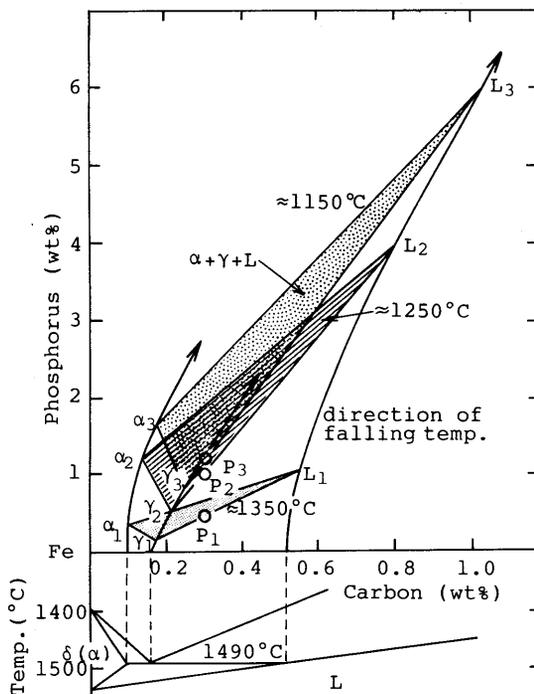


Fig.3 Some horizontal sections of Fe-P-C ternary diagram showing (i) temperatures of initiating the reaction, $\gamma \rightarrow L + \delta(\alpha)$ for the alloys of P_1 , P_2 and P_3 , and (ii) phosphorus distribution among α , γ and liquid phases

3. Conditions of quantifying phosphorus by EDX micro-analysis

3. 1 Considerations on the back ground intensity

The method of EDX micro-analysis is very useful for analyzing several elements in a smallest area (0.1 μ m in diameter). But its application is usually confined to semi-quantitative analysis. Various preliminary experiments for each element is required for applying it to the full-quantitative analysis.

The phosphorus concentration in a Fe-P-C alloy, [P] can be determined by the fraction $I_P / (I_P + I_{Fe})$ using the correlation curve of [P] vs. the fraction. I_{Fe} ; the integrated X-ray intensity of iron K_{α} line in a energy range, for example, 6.20 to 6.60keV (the nominal value is 6.398keV). I_P ; that of phosphorus K_{α} line in a energy range, for example, 1.90 to 2.14keV (the nominal value is 2.013keV).

I_{Fe} and I_P are shown schematically in Fig.4. The back ground intensity increases with decreasing the energy and reaches the maximum when the energy is about 2keV, which corresponds, unfortunately, to that of $K_{\alpha-p}$ line. Consequently, for obtaining the I_P value, a reasonable amount of the back ground intensity, I_P should be canceled from the measured value, I_{P-mes} .

That is,

$$I_{P-mes} = I_P + I_{BG} \text{ ---- (1)}$$

In this research, the following procedure was adopted for deciding I_{BG} .

An integrated intensity of back ground ranging from 2.16 to 3.00keV was used as a reference value, I_{BG-ref} , and its average intensity H_B was defined as;

$$H_B = \frac{I_{BG-ref}}{(3.00-2.16)/0.02 + 1} \text{ --- (2)}$$

where, 0.02(keV) is the possible smallest energy interval for measuring the individual X-ray intensities. The integrated intensity of back ground, I_{BG} , was defined as;

$$I_{BG} = H_B [(2.14-1.90)/0.02 + 1] = \frac{(2.14-1.90)/0.02 + 1}{(3.00-2.16)/0.02 + 1} I_{BG-ref} = 0.30 \cdot I_{BG-ref} \text{ ---- (3)}$$

3. 2 Preliminary experiment on the optimum conditions

Two main factors which affect the result of analysis will be the acceleration voltage of the anode and the tilt angle of the specimen surface, which is defined in Fig.5. Some preliminary experiments were made for determining the optimum combinations of those factors.

Specimen An ingot of Fe-0.6wt%P-0.3wt%C alloy was made by melting electrolytic iron, pig iron and ferro-phosphorus in an induction furnace in air and deoxygenized by metallic silicon and manganese, and then casting it into a steel mold. The ingot of 8kg, 60mm in diameter and 300mm in length was hot-forged into a 10mm square bar. It was then homogenized at 1200°C for 44 hours in vacuum, and quenched in water. Its chemical composition is shown in Table 1. The specimen consists of a single phase of martensite. The specimen surface to be analyzed was ground by grinding machining in water flow and then by a cloth with chromium oxide. The surface was etched slightly by nital.

Experiments The integrated X-ray intensities of phosphorus (I_P), iron (I_{Fe}) and back ground (I_{BG}) were determined on a fixed spot (0.1µm in diameter) of the specimen by varying the two factors; acceleration voltage

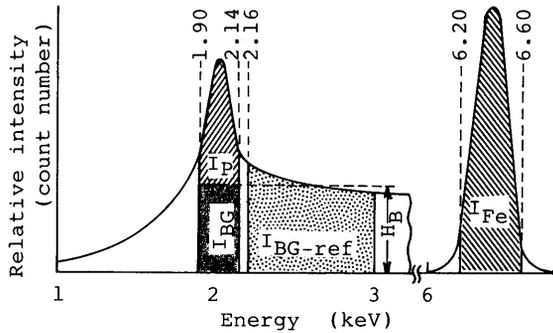


Fig.4 X-ray intensities of I_P , I_{BG} , I_{BG-ref} and I_{Fe} illustrated in a chart of energy level and X-ray count number

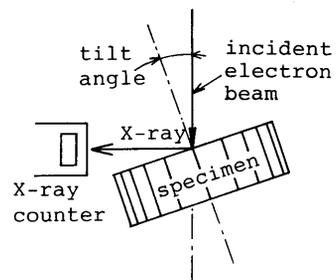


Fig.5 A sketch representing the tilt angle

Table 1 Chemical compositions of tested material (wt%)

C	Si	Mn	P	S
0.28	0.10	0.50	0.579	0.02

of 5 to 30kV and tilt angle of 0 to 60 degree.

The counting time of 100sec and a magnification of 3000 were selected.

The experimental results of Fig.6 show that (i) I_P , I_{Fe} and I_{BG} increase generally with increasing the acceleration voltage up to 25kV; the greater those intensities are, the more precise measurements can be conducted, but (ii) I_P/I_{Fe} ratio increases with decreasing the voltage down to 10kV; I_{Fe} is not detectable for 5kV, and also (iii) I_P/I_{BG} increases with decreasing the voltage for a fixed tilt angle, (iv) I_P/I_{BG} increases with increasing the tilt angle up to 60 degree for a fixed voltage. However, the practice of focusing and observation becomes difficult when the tilt angle increases.

From those discussion, it will be concluded that the acceleration voltage of 10kV and the tilt angle of 45 degree are the optimum conditions for analyzing phosphorus in a Fe-P-C alloy.

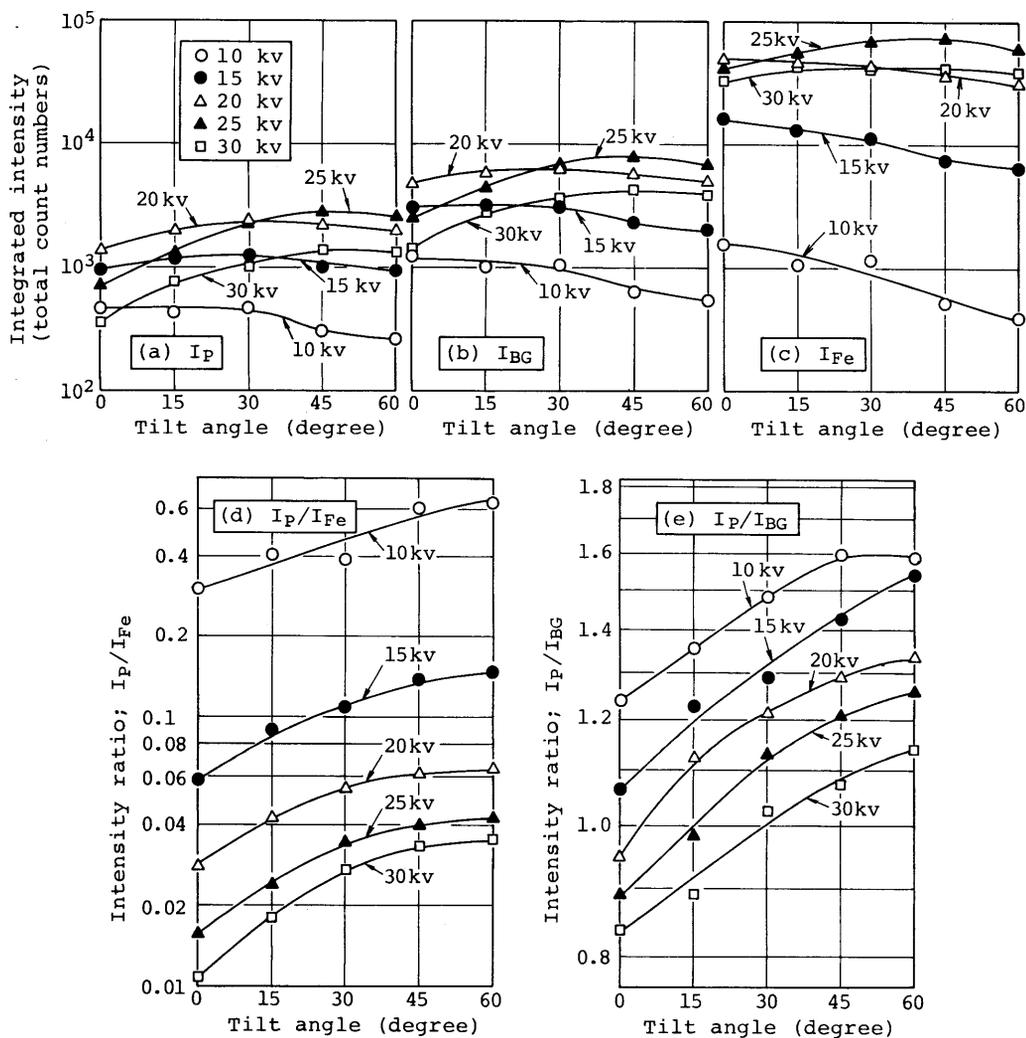


Fig.6 Relations among integrated intensities, acceleration voltage and tilt angle; I_P , I_{Fe} and I_{BG} ; integrated intensities of P, Fe and back ground (relative values)

3. 3 Correlation curve

A correlation curve between the phosphorus concentration [P] and $I_P/(I_P + I_{Fe})$ was drawn by the following procedure. Standard specimen A; Fe-0.6wt%P-0.3wt%C alloy which is the same as used in 3.2. Standard specimen B; Fe-5wt%P alloy which was homogenized in vacuum at 1030°C for 40 hours and quenched in water. Its microstructure consists of ferrite and Fe₃P. Only ferrite part, which dissolves 2.64wt% of phosphorus as can be seen in the equilibrium diagram of Fe-P system in Fig.7, was used for the analysis. Standard specimen C; Fe-12wt%P alloy, which is cast in a steel mold pre-heated at 1000°C, is used in as-cast condition. Its microstructure consists of primary crystal of Fe₃P (15.6wt%P) and eutectic (ferrite+Fe₃P) as can be seen from Fig.7. Only the primary crystal was used for the analysis.

180 spots in the area of 1.8mm² were analyzed on the specimen A. 50 spots in the area of 0.5mm² were analyzed on the specimens B and C.

The correlation curve obtained is shown in Fig.8(a). The plots A, B and C denote the mean values of analysis on the specimens A, B and C, respectively.

It will be considered that the

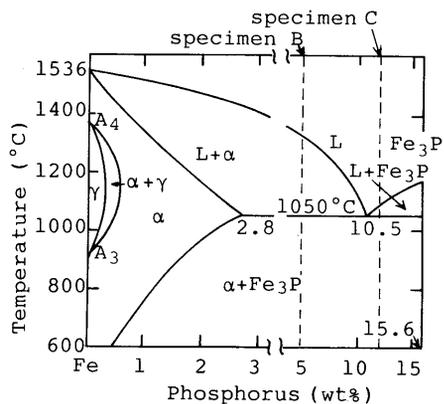


Fig.7 Fe-P binary diagram

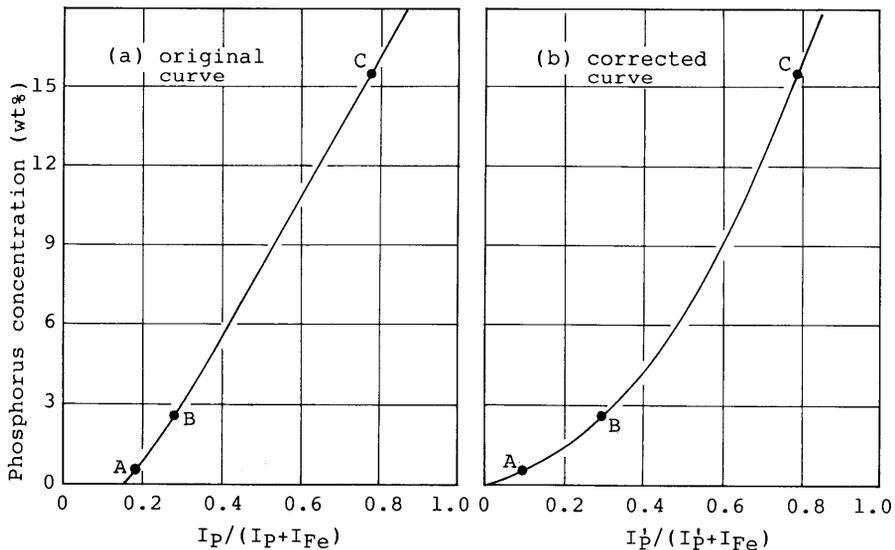


Fig.8 Correlation curves of X-ray intensity fraction vs. phosphorus concentration in the Fe-P-C alloy

I_P ; original value of the integrated intensity of $K_{\alpha-P}$, I_P' ; its corrected value, I_{Fe} ; original value of the integrated intensity of $K_{\alpha-Fe}$

correlation curve of $[P]=0$, $I_P/(I_P+I_{Fe})=0$, but this original curve does not. This error would be brought by the error in sharing I_{P-mes} into I_P and I_{BG} (equation(1)). Then, I_P and I_{BG} are modified by a trial-and-error method as,

$$I_{P-mes} = I_P^1 + I_{BG}^1 \text{ ----- (4)}$$

where, $I_P^1 = I_P - 70$, $I_{BG}^1 = I_{BG} + 70$. The corrected correlation curve between $[P]$ and $I_P^1/(I_P^1+I_{Fe})$ is shown in Fig.8(b).

4. Experimental results on phosphorus segregation in a Fe-P-C alloy

4. 1 Effect of heating rate on phosphorus segregation

Fe-0.6wt%P-0.3wt%C alloy was used for the experiments. The phases existing in this alloy at each temperature are shown in the 0.3wt%C section of Fe-P-C ternary diagram of Fig.9.

The phosphorus concentrations in micro-areas were measured on the specimens which were heat-treated as follows (Fig.10). (O) as cast, (H) as homogenized followed by water quenching, (A) after heating the specimen (H) at 700°C for 3 hours, the temperature was elevated rapidly (20°C/sec) up to 950°C and kept it for 10 min followed by quenching. Keeping the specimen at 700°C was made for the purpose of reducing Fe_3P by dissolving it into ferrite matrix. (B) the temperature was elevated slowly (0.06 °C/sec) from 700°C up to 950°C and kept it for 10 min followed by quenching. (C) the temperature was elevated rapidly (20°C/sec) from 700°C up to 950°C and kept it 44 hours followed by quenching.

180 spots in an area of $1.8mm^2$ were analyzed; the diameter of each spot was 0.1 μm . The phosphorus concentration in

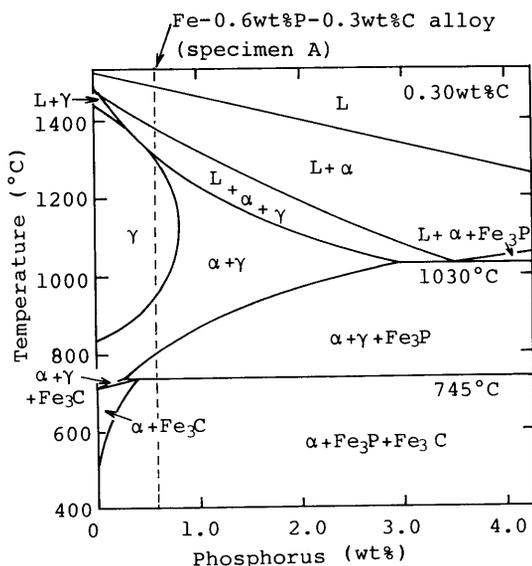


Fig.9 A vertical section of Fe-P-C ternary diagram at 0.30wt%C²⁾

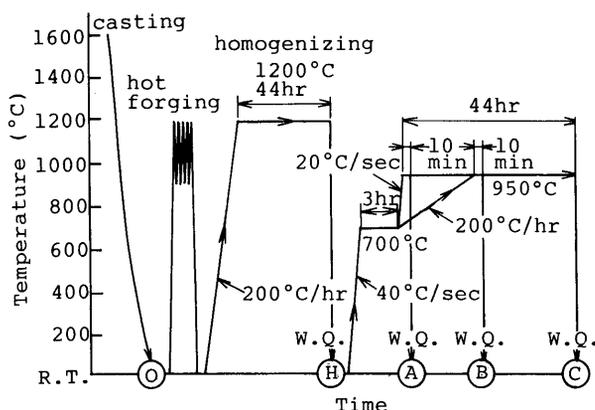


Fig.10 Heat treatments used to investigate the effect of the velocity of α/γ transformation on the phosphorus segregation

each spot was determined by the correlation curve of Fig.8. As the result, the phosphorus distribution of each specimen is shown by a histogram as in Fig.11.

In as-cast specimen which is composed of ferrite and pearlite, the maximum concentration of phosphorus as high as 7% is seen in the ferrite region (Fig.11(O)). This type of micro-segregation is caused by a rapid solidification. By hot forging and subsequent homogenizing treatment, the phosphorus segregation of as-cast condition is disappeared as shown in Fig.11(H).

By heating rapidly the specimen up to 950°C, the phosphorus segregation is newly produced in ferrite region; its maximum concentration is as high as 6% as shown in Fig.11(A).

On the contrary, the phosphorus segregation is hardly recognized when the specimen is heated slowly up to 950°C as shown in Fig.11(B).

The phosphorus segregation caused by the rapid heating is reduced considerably by holding the specimen at 950°C for as long as 44 hours as shown in Fig.11(C).

A series of the experimental results proves clearly the theoretical prediction explained in 2.1.

4. 2 Effect of heating rate on liquating temperature

To examine the second prediction that the liquation will begin at much lower temperature than the equilibrating solidus temperature when phosphorus segregates by rapid heating, following experiments were made.

The homogenized alloy is reheated at 700°C for 3 hours for dissolving Fe_3P

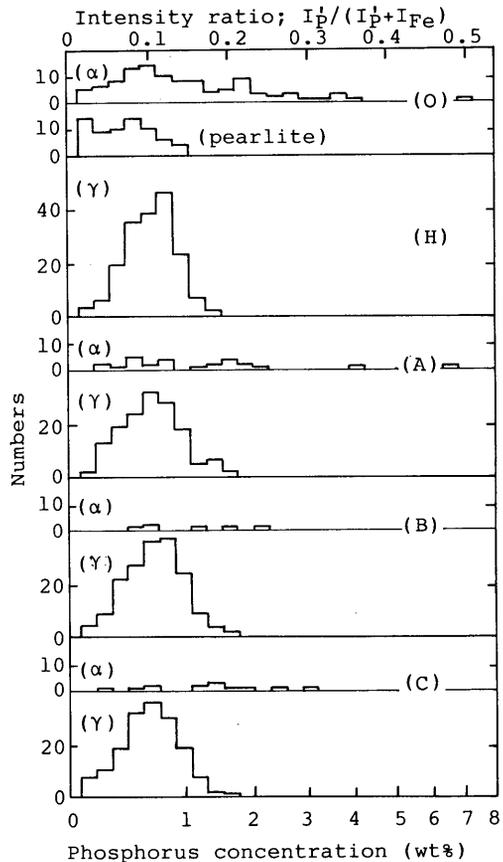


Fig.11 Distributions of phosphorus concentrations in specimens heat-treated as follows;
specimen(O); as-cast
specimen(H); as homogenized
specimen(A); transformed by rapid heating up to 950°C and held for 10 min
specimen(B); transformed by slow heating up to 950°C and held for 10 min
specimen(C); transformed by slow heating up to 950°C and held for 44 hours

into ferrite matrix and then quenched. After that, it is heated by different heating rates (0.06 to 200°C/sec) up to different temperatures (1000 to 1400°C) and quenched immediately. Those heat treatments are illustrated in Fig.12. The occurrence of liquation was observed by a microscope under magnification of 200. The results are shown in Fig.13. The mark o shows that liquation occurred by those maximum temperature and heating rate, and the mark ● shows that it did not occur. The curved line shows the temperature of initiating liquation. The equilibrating solidus temperature (1290°C) falls with increasing the heating rate when it exceeds 30°C/sec. The temperature fall is largest in the heating rate of 50 to 80°C/sec.

The distribution of phosphorus before liquation initiates was measured on

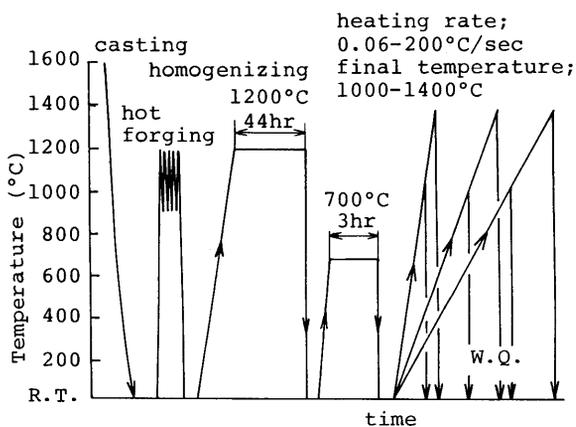


Fig.12 Heat treatments used to investigate the effect of heating rate on the temperatures of initiating liquation

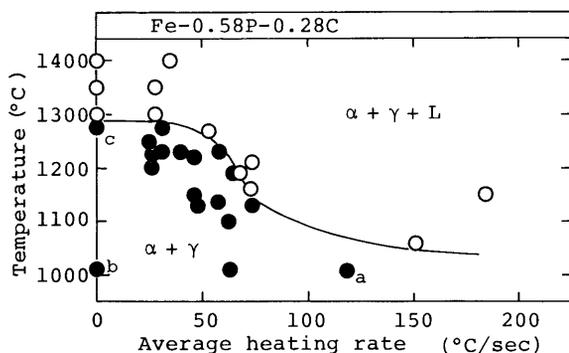


Fig.13 Relation between heating rate and partial melting temperature

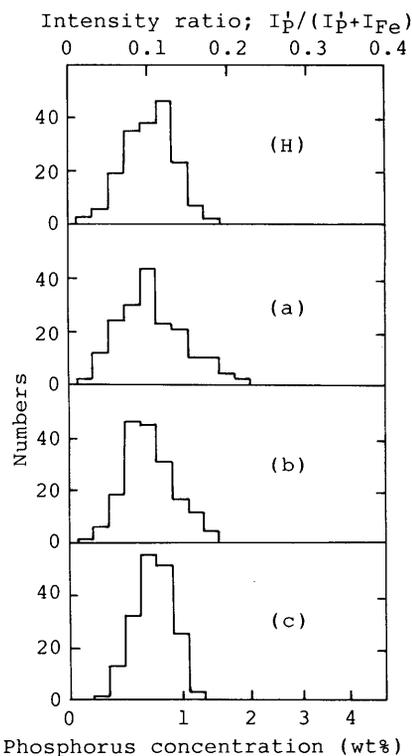


Fig.14 Distributions of phosphorus concentrations in specimens heat-treated as follows; specimen(H); as homogenized specimen(a); transformed by rapid heating up to 1010°C with 120°C/sec specimen(b); transformed by slow heating up to 1010°C with 200°C/hour specimen(c); transformed by slow heating up to 1275°C with 200°C/hour

the specimen "a" in Fig.13 (heated rapidly up to 1010°C) by the same method of analysis as in Fig.11. The result of Fig.14(a) shows again that rapid heating produces the phosphorus segregation. However, its maximum concentration (2.5wt%) is smaller than that of the specimen "c" of Fig.11(c) (7wt%), which was heated rapidly up to 950°C. Such decrease of the maximum concentration may be caused by the phosphorus diffusion during heating from 950 to 1010°C, because the diffusion rate of phosphorus in this temperature range will be very great as explained in 2.1.

The specimens "b" and "c" in Fig.13 (heated slowly up to 1010 to 1275°C) do not exhibit the phosphorus segregation as shown in Fig.14(b) and (c), respectively.

4. 3 Consideration on the temperature-time region of producing the segregation

A continuous-heating-transformation diagram of Fe-0.6wt%P-0.3wt%C alloy was composed by microscopic observations on the specimens heated up to several temperatures with several heating rates. This diagram is shown in Fig.15. It is assumed that there are two fields in the diagram concerning to the segregation and the diffusion behaviors of phosphorus. Field I; the time-temperature field in which phosphorus will prefer to segregate. Field II; the time-temperature field in which phosphorus will prefer to diffuse.

When the heating rate is sufficiently great as ① in Fig.15, phosphorus confined in the austenite grain boundary by heating through the field I will hardly diffuse towards the austenite matrix by succeeding heating. And then liquation occurs in the grain boundary at a low temperature as shown in the figure.

When the heating rate is medium as ② although phosphorus is once confined in the grain boundary by heating through the field II. As the result, liquation at lower temperature does not occur.

When the heating rate is sufficiently small as ③, phosphorus does not segregate during α/γ transformation as shown in the figure.

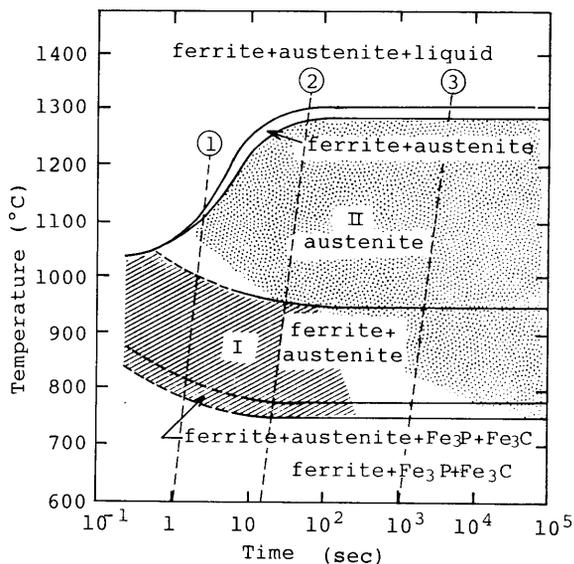


Fig.15 Relation between the segregation field and solidus temperature illustrated on the continuous-heating transformation diagram of Fe-0.6wt%P-0.3wt%C alloy
Field I; the time-temperature field in which phosphorus will prefer to segregate
Field II; the time-temperature field in which phosphorus will prefer to diffuse

5. Conclusions

The mechanism of the phosphorus segregation during rapid heating was examined by several experiments using Fe-0.6wt%P-0.3wt%C alloy and EDX micro-analysis.

- (1) The optimum conditions of EDX micro-analysis for phosphorus were defined as; acceleration voltage 10kV, tilt angle 45 degree.
- (2) The correlation curve between the phosphorus concentration, [P] and the fraction of integrated intensity, $I_P^2/(I_P^2+I_{Fe})$ was proposed for Fe-P-C alloys.
- (3) The following sequence of phosphorus segregation was recognized.
 - (i) The phosphorus segregation is initiated by rapid α/γ transformation in the manner that phosphorus is enriched in the original ferrite phase.
 - (ii) The phosphorus-rich region will become later the austenite grain boundary.
 - (iii) Liquation occurs in this region producing the liquid of a very large concentration of phosphorus. The greater the heating rate is, and therefore, the larger the phosphorus concentration is, the lower the temperature of initiating liquation becomes.

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