Precipitation Behavior of Phosphides in the Centerline Segregation Zone of Continuously Cast Steel Slabs

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The precipitation behavior of phosphides which are the most important compounds in the centerline segregation zone of continuously cast (CC) steel slabs has been studied using the non-aqueous electrolyte-potentiostatic etching method (the SPEED method).

The results are summarized as follows.

(1) Iron phosphides were clearly observed in middle (0.16%C or more) and high carbon steel slabs as spheroidized eutectic compounds, but not observed in low carbon steels.

The spheroidized eutectic phosphides were identified as $(\text{Fe}, \text{Mn})_3\text{P}$, $(\text{Fe}, \text{Mn})_2\text{P}$ and steadite ($\text{Fe}_3\text{P}-\text{Fe}_3\text{C}-\text{Fe}$).

(2) The precipitation zone of the eutectic phosphides depends on the C and P contents of CC slabs, and the phosphide precipitates in slabs of about 0.16%C or more. Thus it is considered that the precipitation of the spheroidized eutectic phosphides depends on the primary austenite (γ) at solidification of CC slabs, and an increase in the γ quantity causes the solubility of P in the γ to drop. Therefore, the P segregates along γ grain boundaries, and then concentrates spheroidized and precipitates as the eutectic phosphides.

(3) The morphology and composition of the spheroidized eutectic phosphide, $(\text{Fe}, \text{Mn})_3\text{P}$, change into those of $(\text{Fe}, \text{Mn})_2\text{P}$ and FeP by heating at about 1173 K.

(4) The precipitation zone of the phosphides is in good agreement with both the weld cracking zone and the poor ductility zone concerning hot ductility in carbon steels.

Thus it is considered that the embrittlement owing to phosphorus is caused by the phosphides with low melting point.

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I. Introduction

Centerline segregation in the continuously cast slabs of steel (hereinafter referred to as CC slabs) is an important factor that governs the quality of steel products and is claimed to serve as initiation sites for hot cracking, lamellar tearing, hydrogen-induced cracking and other defects in steel products. Many studies have found that elements, such as phosphorus, sulphur, manganese, carbon and hydrogen, are concentratedly segregated in the centerline segregation zone of CC slabs. The morphology of these alloying elements existing in the centerline segregation zone of CC slabs has not been clarified. Thinking that the actual state of the centerline segregation zone should be investigated as an urgent issue to reduce the centerline segregation, the authors tried to determine the morphology of phosphorus, which is considered the most important of the centerline segregation elements, using actual CC slabs. Past examinations by the electron probe microanalyzer (EPMA) and other instruments showed that phosphorus is segregated to a high degree in the centerline segregation zone of CC

slabs. It is presumed from the research results of Adams⁽¹⁾ and the present authors⁽²⁾⁽³⁾ that phosphorus is precipitated as phosphide in the centerline segregation zone of CC slabs. This study was conducted to clarify the actual state of phosphides in the centerline segregation zone of CC slabs.

II. Experimental Method

1. Materials

About 100 samples were machined from the centerline segregation zone of CC slabs of extralow-carbon steel to high-carbon steel (1.5 mass% carbon)^{††} and were analyzed. The samples ranged from 0.010 to 0.030% in phosphorus content. The chemical compositions of typical samples are given in Table 1.

2. SPEED method

Phosphides were observed and analyzed by the SPEED method. Since the SPEED method is already described in detail in a previous report⁽⁴⁾, its explanation is omitted here. The following apparatus and reagents were used in the experiment:

(1) Potentiostatic electrolysis apparatus with

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†† In this report, solid compositions and liquid compositions are expressed in mass percent and volume percent, respectively.

Table 1 Chemical composition of typical steel samples (mass%).

	C	Si	Mn	P	S	Al
A	0.05	0.21	1.02	0.02	0.010	—
B	0.17	0.25	1.12	0.029	0.012	—
C	0.25	0.26	1.04	0.021	0.018	—
D	0.85	0.19	0.45	0.020	0.003	0.019
E	1.05	0.21	0.40	0.024	0.003	0.013

microcoulometer: Made by Fujiwara Scientific Company (Model FS-102). Potential setting: 0 to ± 2 V vs SCE. Coulomb scale: 0.1 to 9999.9 C.

(2) Electrolytic cell: Made by Fujiwara Scientific Company (Capacity: 400 cm³).

(3) Scanning electron microscope: Made by Hitachi (Model S-700). Equipped with an energy-dispersive X-ray spectrometer (EDX, Philips-ECON-3).

(4) Electrolyte: 10% acetylacetone-1% tetramethylammonium chloride-methyl alcohol (hereinafter abbreviated to 10% AA electrolyte).

The sample was wet polished to a mirror finish and was electrolytically etched in the AA electrolyte at a controlled potential. The microcoulometer was preset to keep the depth of etching at a few micrometers. After the electrolytic etching, the etched surface of the sample was washed in methyl alcohol until the red chelate of ferric acetylacetonate disappeared and was dried in a nitrogen gas stream or in a vacuum. The dry etched surface was observed under a scanning electron microscope (SEM), and the phosphides were qualitatively analyzed and identified by the energy-dispersive X-ray spectrometer (EDX) attached to the SEM as well as by an electron probe microanalyzer (EPMA) and an analytical electron microscope, among other instruments.

III. Experimental Results

1. Macrostructures of CC slabs

The macrostructures of the centerline segregation zone of CC slab samples etched by the SPEED method are shown in Fig. 1. The degree of segregation is high in the macrostructure shown in Fig. 1(a) and is relatively low in the macrostructure shown in Fig. 1(b). V segregation is observed in each macrostructure. The precipitation behavior of the phosphides in the centerline segregation zone of CC slabs was analyzed as described below.

2. Phosphides in centerline segregation zone of CC slabs

(1) Phosphides in centerline segregation zone of CC slabs of medium-carbon steel ($\sim 0.2\%$ C)

CC slab samples containing the centerline segregation zone were polished and etched by the SPEED method. When the etched surface of each sample was observed and analyzed by the SEM-EDX, no phosphides were confirmed in the centerline segregation zone of CC slabs of low-carbon steel ($\leq 0.1\%$ C). Phosphides of two morphologies were confirmed in the centerline segregation zone of CC slabs of medium-carbon steel ($\approx 0.16\%$). Typical phosphides confirmed are shown in Figs. 2 and 3.

Figure 2 shows acicular and planar phosphides, which are $(\text{Fe, Mn})_3\text{P}$ and $(\text{Fe, Mn})_2\text{P}$, according to the results of identification described latter. Figure 3 shows a spheroidized eutectic phosphide, which consists of $(\text{Fe, Mn})_3\text{P}$ and partly contains $(\text{Fe, Mn})_2\text{P}$.

Fig. 1 Centerline segregation zone of CC slabs.

Fig. 2 Observation of needle-like phosphide, $(\text{Fe}, \text{Mn})_3\text{P}$, $(\text{Fe}, \text{Mn})_2\text{P}$ in centerline segregation zone of middle carbon steel CC slab.

(2) Phosphides in centerline segregation zone of CC slabs of high-carbon steel (0.85C%)

The phosphides found in the centerline segregation zone of CC slab samples of up to 0.8%C are the spheroidized eutectic phosphides $(\text{Fe}, \text{Mn})_3\text{P}$ and $(\text{Fe}, \text{Mn})_2\text{P}$, as shown in Fig. 3. The precipitation of the phosphides along prior austenite grain boundaries was observed in samples containing 0.85%C or more. Typical examples of such phosphides are shown in Figs. 4 and 5. The phosphides confirmed in sample D are shown in Fig. 4 and the phosphides confirmed in sample E are shown in Fig. 5. Each phosphide is steadite, composed of Fe_3P - Fe_3C -Fe and exhibiting a ternary eutectic structure.

3. Identification Results of Phosphides

(1) Fine phosphides

The sample surface was etched by the SPEED method and treated to prepare an extraction replica. The extraction replica was observed under an analytical electron microscope (EDX, electron diffraction, for instance) to identify the phosphides confirmed as described in 2.(1). Typical results of identification are shown in Fig. 6. From Fig. 6, the fine planar phosphide can be identified as $(\text{Fe}, \text{Mn})_2\text{P}$. The presence of $(\text{Fe}, \text{Mn})_3\text{P}$ and other

phosphides made it impossible to distinguish between these phosphides according to their morphology alone.

(2) Spheroidized eutectic phosphides

The composition of spheroidized eutectic phosphides is expressed as $(\text{Fe}, \text{Mn})_3\text{P}$ according to the results of analysis by the SEM-EDX. A crystallographic analysis was also made. When microfocus X-ray diffraction was performed on large spheroidized phosphide particles using a micron-sized region X-ray diffractometer (JOEL JDX-MAPI), the pattern shown in Fig. 7 was obtained. The pattern was in good agreement with that of Fe_3P .

Steadite shown in Figs. 4 and 5 was similarly analyzed. The pattern shown in Fig. 8 was obtained. The pattern shows that, Fe_3P and Fe_3C were confirmed. When the phosphides were analyzed further for carbon, phosphorus and iron by the EPMA, their composition almost agreed with that of steadite investigated in the past (C: 2.2%, P: 10.5%, Fe: 87.2%). When the ternary eutectic phosphide was heated in an argon gas stream, it melted at 1253 K (980°C).

4. Precipitation region of phosphides

The precipitation region and morphology of the phosphides confirmed as described in III. 2 are arranged

Fig. 3 SPEED observation of spheroidized eutectic phosphide, $(\text{Fe, Mn})_3\text{P}$ in the centerline segregation zone of middle carbon steel CC slab.

in Fig. 9 according to the ladle analyses of carbon and phosphorus. In Fig. 9, acicular or planar phosphides are indicated by the $\bullet$ mark; the spheroidized eutectic phosphides $(\text{Fe, Mn})_3\text{P}$ and $(\text{Fe, Mn})_2\text{P}$ are indicated by the $\bullet$ mark; and the ternary or Fe_3P - Fe_3C -Fe eutectic phosphides (steadite) is indicated by the $\oplus$ mark. It was found that the precipitation of the spheroidized phosphide depends on the carbon content and occurs when the carbon content is about 0.16% or more.

IV. Discussion

It was confirmed that many types of phosphides are precipitated in the centerline segregation zone of CC

slabs of carbon steel as noted above. The precipitation mechanism of the phosphides, morphological and structural changes of the phosphides with heating and working, thermal characteristics of the phosphides, and the relationship between the precipitation region of the phosphides and the properties of steel are discussed below.

1. Precipitation mechanism of phosphides

The precipitation region of the phosphides is shown in Fig. 9. The precipitation mechanism of the representative spheroidized eutectic phosphides is discussed here. The precipitation of the spheroidized eutectic phosphides is confirmed when the carbon content is 0.16% and above,

Fig. 4 SPEED observation Fe_3P - Fe_3C -Fe (steadite) in centerline segregation zone of high carbon steel CC slab.

Fig. 5 SPEED observation of $(\text{Fe}, \text{Mn})_3\text{P}$ in the centerline segregation zone of high carbon steel CC slab.

as shown in Fig. 9. When Fig. 9 is compared with Fig. 10 in which a Fe-C phase diagram⁽⁵⁾ is shown, the precipitation of the spheroidized eutectic phosphides is related to

primary austenite on solidification. Particularly, the solubility of phosphorus in austenite decreases with increasing amount of austenite⁽⁸⁾. As a result, phosphorus is rejected to austenitic grain boundaries on cooling and is concentrated at the austenite grain boundaries. When it passes the eutectic temperature region on cooling, phosphorus forms a liquid film and turns into small spheres with the smallest surface tension. At the eutectic temperature, phosphorus is considered to precipitate as spheroidized eutectic phosphides. The precipitation mechanism of the spheroidized eutectic phosphides is summarized in Fig. 11.

When the carbon content is 0.85% or above, the spheroidized eutectic phosphide is considered to finally precipitate as a ternary eutectic phosphide (Fe_3P - Fe_3C -Fe, steadite) according to the above-mentioned reaction and the reaction with Fe_3C -Fe(γ) (ledeburite).

2. Changes in morphology and structure of phosphides with heating

A study was made of the changes in the morphology and structure of the spheroidized eutectic phosphides when heated for 1.8 to 3.6 ks (30 to 60 min) in the austenite region above 1173 K (900°C). The fine eutectic phosphide $(\text{Fe}, \text{Mn})_2\text{P}$ was confirmed when the spheroidized eutectic phosphide $(\text{Fe}, \text{Mn})_3\text{P}$ was heated for 1.8 ks and more. The simple phosphide FeP was confirmed, though in a small amount, when the spheroidized eutectic phosphide $(\text{Fe}, \text{Mn})_3\text{P}$ was heated for 3.6 ks. These findings indicate that the spheroidized eutectic phosphides are concentrated from $(\text{Fe}, \text{Mn})_3\text{P}$ to FeP when the phosphorus concentration is high in the vicinity of the spheroidized eutectic phosphides in the austenite region above 1173 K. Phosphorus and manganese are rejected from austenite to the grain boundaries, are enrich-

Fig. 6 TEM observation of $(\text{Fe, Mn})_2\text{P}$ in the centerline segregation zone of middle carbon steel CC slab.

Fig. 7 Micro-focus X-ray diffraction pattern of $(\text{Fe, Mn})_3\text{P}$ in the centerline segregation zone of middle carbon steel CC slab.

Fig. 8 Micro-focus X-ray diffraction pattern of $(\text{Fe, Mn})_3\text{P}$ and Fe_3C in the centerline segregation zone of high carbon steel CC slab.

ed in $(\text{Fe, Mn})_3\text{P}$, which is considered as a liquid existing at the grain boundaries, and are concentrated into $(\text{Fe, Mn})_2\text{P}$. When the phosphide concentration increases, the phosphide is considered to concentrate to FeP of higher melting point. The mechanism of this concentration is summarized in Fig. 12 and typical examples of $(\text{Fe, Mn})_3\text{P}$, $(\text{Fe, Mn})_2\text{P}$ and FeP confirmed are shown in Fig. 13. The results of analysis by the SEM-EDX showed typical phosphide compositions to be $(\text{Fe}_{0.9}\text{Mn}_{0.1})_3\text{P}$, $(\text{Fe}_{0.8}\text{Mn}_{0.2})_2\text{P}$ and $(\text{Fe}_{0.95}\text{Mn}_{0.05})\text{P}$.

3. Changes in phosphides with heating and rolling

The spheroidized eutectic phosphides were studied to see if they would change with hot rolling. Samples of 20 mm in thickness, were heated at 1173 K for 600 s and rolled to a thickness of about 3 mm by means of a small rolling mill. The resultant changes in the phosphides contained in the samples were investigated.

Phosphide particles of about 5 μm in diameter almost retained their original morphology, whereas phosphide particles of 10 to 20 μm in diameter cracked or elongated

Fig. 9 Precipitation zone and morphologies of the iron phosphides in centerline segregation zone of steel slabs.

Fig. 10 Phase diagram of the Fe-C system.

Fig. 11 Precipitation mechanism of the spheroidized eutectic phosphides $((\text{Fe}, \text{Mn})_3\text{P}, (\text{Fe}, \text{Mn})_2\text{P})$ in centerline segregation zone of steel slabs.

Fig. 12 Concentration mechanism of iron phosphide by heating at elevated temperature (1173 K).

during hot rolling. Phosphide particles cracked by hot rolling are shown in Fig. 14.

Fine spheroidized phosphide particles were present in the vicinity of the phosphide particles cracked by hot rolling and the concentration of soluble phosphorus was increased around the area where were many cracked phosphide particles. These findings suggest the dispersion and diffusion of spheroidized eutectic phosphides by hot rolling.

4. Thermal analysis of iron phosphides

The melting point of the iron phosphide Fe_3P is said to be 1373 to 1433 K (1100 to 1160°C), while the eutectic temperature of the iron phosphide $\text{Fe}_3\text{P}-\text{Fe}(\gamma)$ is said to be 1323 K (1050°C)⁽⁸⁾. The phenomenon of embrittlement by the eutectic phosphide $(\text{Fe}, \text{Mn})_3\text{P}$, already reported by the authors⁽³⁾, occurs at a temperature of approximately 1173 K and cannot be explained by the melting point of 1323 K. Differential thermal analysis (DTA) was carried out on a $\text{Fe}_3\text{P}-\text{Fe}$ synthetic reagent in an argon atmosphere during heating and cooling.

An example of measurement is shown in Fig. 15. The temperature measurements taken on heating show that the melting point are close to those Fe_3P and $\text{Fe}_3\text{P}-\text{Fe}$, but there is only one exothermic peak of 1173 K, considered as solidification point on cooling. It was recognized accordingly that the iron phosphide Fe_3P solidifies at 1173 K on cooling and remains as a liquid film down to 1173 K. This finding may be taken as evidence that can explain the phosphide embrittlement phenomenon at 1173 K⁽³⁾ as already reported and the changes in the morphology and structure of the phosphides in the vicinity of 1173 K as described in IV. 1 to 3.

5. Relationship between precipitation region of phosphides and properties of steel

The precipitation morphology of phosphides in the centerline segregation zone of CC slabs, the precipitation region of the phosphides and the changes in the morphology and structure of the phosphides with heating and rolling were mainly investigated as discussed above. The effect of these phosphides on the properties of steel is discussed here in comparison with the past research results.

Figure 16 shows the weld cracking region of F. Matsuda *et al.*⁽⁶⁾ and the poor hot ductility region of H. Suzuki *et al.*⁽⁷⁾ These results are arranged by the carbon and phosphorus contents of steel and closely agree with the phosphide precipitation region investigated by the present authors. It is thus presumed that weld cracking and poor hot ductility are caused by the precipitation of phosphides with low melting point.

V. Conclusions

The precipitation behavior of phosphides existing in the centerline segregation zone of continuously cast slabs of steel was investigated by the SPEED method and other techniques. The following findings were obtained:

Fig. 13 SPEED observation of the typical phosphides in steel slabs. (a): spheroidized eutectic $(\text{Fe, Mn})_3\text{P}$, (b): Spheroidized eutectic $(\text{Fe, Mn})_2\text{P}$, (c): $(\text{Fe, Mn})_2\text{P}$ with eutectic structure at its periphery and (d): $(\text{Fe, Mn})\text{P}$.

Fig. 14 SPEED observation of cracked phosphide, $(\text{Fe, Mn})_3\text{P}$ after hot rolling.

Fig. 15 DTA curves of Fe_3P .

Fig. 16 Effect of C and P on the phosphide the hot ductility and the cracking.

(1) Phosphides, such as fine phosphides $\{(\text{Fe, Mn})_3\text{P}$ and $(\text{Fe, Mn})_2\text{P}\}$ and spheroidized eutectic phosphides

$\{(\text{Fe, Mn})_3\text{P}$ and $(\text{Fe, Mn})_2\text{P}\}$, are precipitated in the centerline segregation zone of CC slabs of steel with a carbon content of 0.16% or more.

(2) When the carbon content is 0.85% or more, the ternary eutectic phosphide $\text{Fe}_3\text{P}-\text{Fe}_3\text{C}-\text{Fe}$ (steadite) is precipitated.

(3) The precipitation morphology and region of the above-mentioned phosphides were arranged by the carbon and phosphorus contents of steel.

(4) The precipitation of the spheroidized eutectic phosphide $(\text{Fe, Mn})_3\text{P}$ is related to primary austenite. A mechanism was proposed for the precipitation of the phosphide.

(5) The spheroidized eutectic phosphide $(\text{Fe, Mn})_3\text{P}$ changes in morphology and structure from $(\text{Fe, Mn})_3\text{P}$ to $(\text{Fe, Mn})_2\text{P}$ to FeP when heated in the vicinity of 1173 K.

(6) Spheroidized eutectic phosphide particles, measuring 10 to 20 μm in diameter, are cracked or elongated during hot rolling. Some are dispersed and diffused.

(7) The thermal analysis of iron phosphide indicates an exothermic peak of 1173 K, considered to be its solidification point on cooling and it remains as a liquid film down to 1173 K. The behavior of the phosphides discussed above can be explained by this finding.

(8) The precipitation region of the phosphides closely agrees with the region where weld cracking and poor hot ductility occur as previously reported. It is thus presumed that the conventional problems of weld cracking and poor hot ductility are caused by the precipitation of phosphides with low melting point.

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