Microstructural Changes in Low-carbon Steel Occurring by Heating in Mixtures of Iron, Graphite and Alumina Powders

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Carbon and nitrogen are easily diffused into stainless steel and titanium, when these are embedded in mixtures of iron, graphite and alumina powders and held at high temperatures in a nitrogen flow. To promote an understanding of this new diffusion technique, which we call “iron-powder pack treatment”, we focused attention on the microstructures of low-carbon steel subjected to such a treatment. The diffusion of carbon into the steel was understood by evaluating area fraction of pearlite emerging in ferrite. A pearlite area in the steel, which was heat-treated at 1,273 K for 3.6 ks using a mixture of iron and alumina powders, was larger than before heating, because the steel was carburized by carbon in the iron powder. On the other hand, an increase in the pearlite area was hardly observed in the case of a mixture of graphite and alumina powders. By replacing a part of graphite in this mixture with the iron powder, however, pearlite was most remarkably produced in the steel. Instead of the iron powder, the use of nickel powder did not exert a significant impact on the diffusion of carbon into the steel. These indicate that the iron powder acts as an important agent for enhancing the migration of carbon from a powder mixture to low-carbon steel. The relationship between a diffusion phenomenon of carbon and the generation of carbon monoxide gas in heat treatment is also discussed.

KEY WORDS: low-carbon steel; iron powder; graphite; alumina; nitrogen; carbon diffusion.

1. Introduction

A wide variety of stainless steels have been developed in accordance with the intended use. These contain sufficient chromium to form a passive film of chromium oxide, and show excellent corrosion and oxidation resistances. This also means that it is difficult to diffuse carbon and nitrogen into the stainless steel from the viewpoint of surface hardening. In fact, a modified layer due to the diffusion of carbon was not formed on ferritic stainless steel (SUS430), when we tried gas carburizing in an industrial furnace in operation. In other words, it is necessary to remove a stable oxide film from the surface of the stainless steel before diffusing carbon and nitrogen. Various carbon and nitrogen diffusion techniques, such as carburizing and nitriding in gas mixtures containing hydrogen,1) vacuum carburizing,2,3) plasma carburizing,4,6) plasma nitriding,7,8) and nitrogen implantation,9) have been studied to produce the stainless steel having both high surface hardness and excellent corrosion resistance. However, these techniques need special equipment and complicated process flows to obtain a modified layer.

The authors have found out a simplified technique for diffusing carbon into the stainless steel.10) Specifically, a stainless steel sample is embedded in mixtures of carbonyl iron and carbon (activated carbon and graphite) powders, and then heat-treated in the vicinity of 1,273 K in a nitrogen flow. Alumina powder is also added to surely prevent the powder mixture from sintering. Depending on the composition of the powder mixture, both carbon and nitrogen can be diffused into the stainless steel. In addition, this technique enables the formation of a Ti(C, N) layer on a metallic titanium substrate11) and the reduction and carbonitriding of an oxide film on an anodized titanium substrate.12) We have named this carbon and nitrogen diffusion technique “iron-powder pack (IPP) treatment”.

The feature of the IPP treatment is that carbon monoxide (CO) gas is generated in a heating step.10–12) This is probably due to a chemical reaction between carbon in the powder mixture and residual oxygen in an electric furnace. Oxygen in the furnace should be expelled, because the CO gas is exhausted with a nitrogen flow from the furnace. Accordingly, the oxygen partial pressure should be low around a stainless steel sample. Therefore, it is thought that this environment contributes to the decomposition of the oxide film and to the suppression of oxidation on the surface of the stainless steel, making it easy for carbon and nitrogen to diffuse into the steel.
Although we have proposed the above mechanism of the IPP treatment, the role of the iron powder in mixtures containing graphite and alumina powders has not been clarified in spite of being indispensable to this process. In the present study, low-carbon steel plates were heat-treated in a nitrogen flow using various powder mixtures and the effect of the iron powder in the mixture on the microstructures of the steel plates was investigated.

2. Experimental Procedures

A commercially-produced low-carbon steel plate with a thickness of 1.2 mm was used as a substrate. This is designated as electrolytic zinc-coated steel sheet, SECC, according to Japanese Industrial Standards (JIS G 3313), and contained 0.04 mass% C, 0.01 mass% Si, 0.20 mass% Mn, 0.012 mass% P and 0.009 mass% S. The steel plate was cut into square shapes with dimensions of 10 mm × 10 mm, and the surface was carefully finished with a #4000 water-proof abrasive paper to remove a zinc-electroplated film on the steel plate. The plates were degreased in acetone using an ultrasonic cleaner and dried with hot air.

Mixtures of commercially available iron, carbon and alumina powders were put into an alumina crucible, and low-carbon steel plates were embedded in the mixtures. Figure 1 shows scanning electron microscopic (SEM) images of the used powders. Carbonyl iron was used as an iron powder. It was fine and spherical as shown in Fig. 1(a), and contained 0.75–0.90 mass% C, 0.65–0.90 mass% N and 0.15–0.40 mass% O. Graphite and alumina powders were selected as a carbon source and anti-sintering agent, respectively. The total volume of the powder mixture in the crucible was 8 mL, including 3 mL of the alumina powder. For the remaining 5 mL, the volume ratio of the iron powder to the graphite powder was varied from 0 mL : 5 mL to 5 mL : 0 mL. Therefore, the composition of the powder mixture, which was 8 mL in total, is expressed by volume ratio. For example, 2:3:3 means 2 mL of the iron powder, 3 mL of the graphite powder and 3 mL of the alumina powder. Instead of the iron powder, low-carbon carbonyl iron (<0.03 mass% C, <0.01 mass% N, 0.12–0.30 mass% O) and pure nickel powders, which are shown in Figs. 1(d) and 1(e), respectively, were also prepared.

The crucible, which was filled with the low-carbon steel plates and the powder mixture, was placed in an electric furnace, as shown in Fig. 2. After repeatedly evacuating the furnace using a rotary vacuum pump and refilling it with nitrogen gas a few times, the crucible was heated in the temperature range of 1 073–1 273 K for 0.9–8.1 ks in a nitrogen flow. The nitrogen gas had a purity of >99.99 vol%, and its flow rate was 500 mL/min. The heat treatment without the powder mixture was also performed for comparison. All specimens were allowed to cool in the furnace to room temperature. In some cases, a detector of CO gas was attached to an exhaust port in the furnace, and its concentration was monitored during heat treatment.

The specimens were cut in half to reveal the microstructures. The cross sections were ground with waterproof abrasive papers and then mirror-finished using diamond slurry with a particle size of 0.5 μm. They were examined by
optical microscopy and electron probe X-ray micro analysis (EPMA). Before optical microscopy, the specimens were etched in methanol containing nitric acid (97 vol% CH₃OH and 3 vol% HNO₃).

3. Results and Discussion

3.1. Addition of Iron Powder to Graphite and Alumina Powders

Figure 3(a) shows an optical micrograph of the cross section of a low-carbon steel plate before heating. Black regions in the upper and lower sides in the micrograph correspond to resin for mounting the specimen. Although an electrolytic zinc-coated steel sheet was used in the present study, an electroplated film was sufficiently removed by mechanical grinding. The steel plate was composed mainly of ferrite grains with an average size of approximately 15 μm. Black particles dispersed in the plate were pearlite. A microstructure of the steel plate heat-treated at 1 273 K for 3.6 ks in a nitrogen flow without a powder mixture is shown in Fig. 3(b). Coarse columnar ferrite grains were observed in the vicinity of the steel surface, whereas there was no pearlite area in the steel. This indicates that decarburization was induced by oxygen existing in the electric furnace. In other words, residual oxygen in the furnace cannot be ignored, even though the steel plate was heated in a nitrogen flow.

Figures 4(a) and 4(d) show optical micrographs of the cross section of the steel plate heat-treated at 1 273 K for 3.6 ks in a nitrogen flow using a 5:0:3 mixture of iron, graphite and alumina powders. A pearlite area, which was black in color, increased in comparison with Fig. 3(a).

Fig. 3. Optical micrographs of a cross section of a steel plate (a) before and (b) after heat treatment at 1 273 K for 3.6 ks in a nitrogen flow without a powder mixture.

Fig. 4. Optical micrographs of a cross section of a steel plate heat-treated at 1 273 K for 3.6 ks in a nitrogen flow using (a) 5:0:3, (b) 0:5:3 and (c) 1:4:3 mixtures of iron, graphite and alumina powders. (d)–(f) Enlarged micrographs of the specimens shown in (a)–(c), respectively.
Since the used iron powder contained 0.75–0.90 mass% C, an increase in pearlite means that the steel plate was carburized by carbon in the iron powder. On the other hand, when a 0:5:3 mixture of iron, graphite and alumina powders was used, the heat-treated steel plate had a microstructure shown in Figs. 4(b) and 4(e). The area fraction of ferrite to pearlite was approximately 96:4, and the pearlite area was unexpectedly small. Although the steel plate was surrounded with graphite at a temperature of 1273 K, it was difficult to diffuse carbon into the steel.

The steel plate was set in a 1:4:3 mixture of iron, graphite and alumina powders and heated at 1273 K for 3.6 ks in a nitrogen flow. This corresponds to “IPP treatment”, which is described in the introduction. Optical micrographs of the cross section of the obtained plate are shown in Figs. 4(c) and 4(f). The metallic luster surface was retained even after heating, and the steel plate had a microstructure consisting of ferrite and pearlite. Surprisingly, the amount of pearlite remarkably increased. As shown in Fig. 5, the distributions of iron and carbon in the vicinity of the surface reflected a pearlite structure. Figure 6 shows the relationship between average carbon concentration and plate thickness obtained by EPMA analysis. The measurements were conducted within a cross section of approximately 1.2 mm × 1.2 mm after forming a calibration curve of carbon. The carbon concentration reached approximately 0.8 mass% in the vicinity of the steel surface, and gradually decreased toward the center in the plate. Meanwhile the distribution of nitrogen in Fig. 5(d) was not clear and the diffusion of nitrogen from the heating atmosphere seems to be quite small.

Figure 7 shows a cross-sectional image of the steel plate heat-treated at 1273 K for 3.6 ks in a nitrogen flow using a 2:3:3 mixture of iron, graphite and alumina powders. A ferrite + pearlite structure, as well as Fig. 4(c), was observed, and the pearlite area increased with increasing iron powder in the mixture. The relationship between the mixing ratio of the used powders and the area fraction of ferrite to pearlite in the steel plate heat-treated at 1273 K for 3.6 ks in a nitrogen flow is presented in Fig. 8. As shown in Fig. 4(b), when the mixture of graphite and alumina powders was used, an increase in pearlite was hardly observed. By replacing a part of graphite with the iron powder, however, the diffusion of carbon into the steel plate was promoted and...
a large quantity of pearlite was produced. In 2:3:3 and 3:2:3 mixtures of iron, graphite and alumina powders, the pearlite area occupied more than 60% of the cross section of the steel plate. This indicates that the addition of iron powder to graphite and alumina powders is beneficial in promoting the diffusion of carbon into the steel plate.

3.2. Replacement of Iron Powder

Iron powder used in section 3.1 contained 0.75–0.90 mass% C. To investigate the effect of the carbon content in the iron powder on the diffusion of carbon into steel, low-carbon carbonyl iron powder was prepared. The carbon content in the powder was < 0.03 mass%. As shown in Figs. 1(a) and 1(d), its particle size was equal to that of the iron powder dealt with in section 3.1. Figure 9(a) shows an optical micrograph of the cross section of a low-carbon steel plate heat-treated at 1 273 K for 3.6 ks in a nitrogen flow using a 1:4:3 mixture of low-carbon iron, graphite and alumina powders. A remarkable increase in pearlite, which is a black grain in the micrograph, was observed. The microstructure of the obtained plate was similar to that in Fig. 4(c).

Instead of the iron powder, nickel powder was added to the graphite and alumina powders. A microstructure of the steel plate heat-treated at 1 273 K for 3.6 ks in a nitrogen flow using a 1:4:3 mixture of nickel, graphite and alumina powders is shown in Fig. 9(b). The amount of pearlite was pretty small by comparison with Fig. 4(c).

These results indicate that the iron powder plays an important role in the diffusion of carbon into the steel heat-treated in the powder mixture, regardless of the carbon content in the iron powder.

3.3. CO Gas Measurement

2:3:3 and 3:2:3 mixtures of iron, graphite and alumina powders were extremely helpful to promote the diffusion of carbon into steel, as shown in Fig. 8. The former mixture was used to investigate the influences of the heating temperature and holding time on the formation of pearlite in the steel. In this section, high-carbon iron powder, as shown in Fig. 1(a), was added to the graphite and alumina powders.

Figure 10 shows optical micrographs of the cross section of a low-carbon steel plate heat-treated at 1 073 and 1 173 K for 3.6 ks in a nitrogen flow using a 2:3:3 mixture of iron, graphite and alumina powders. As the heating temperature
increased, pearlite areas (black particles in the micrograph) spread from the surface toward the inside of the steel plate. On the other hand, the microstructures of the steel plate heat-treated at 1273 K for 0.9 and 8.1 ks are shown in Fig. 11. White particles in Fig. 11(b) corresponded to ferrite. Including Fig. 7, the pearlite area increased according to a linear relationship to the square root of the holding time.

It is well-known that CO gas plays an important role in conventional carburizing techniques. Therefore, the CO concentration was monitored during heat treatment using mixtures of iron, graphite and alumina powders. Figure 12 shows measurement results of the CO concentration detected during heat treatment using 0:5:3, 2:3:3 and 5:0:3 mixtures of iron, graphite and alumina powders. Only the powder mixtures (8 mL) were held at 1273 K for 3.6 ks in a nitrogen flow. Although the steel plate was not embedded in the powder mixtures, there was no influence on the obtained data. A peak for the CO gas was observed in the vicinity of 973 K in a heating step. Its peak height increased with increasing iron powder and with decreasing graphite powder. This seems to be related to residual oxygen existing in the electric furnace, as mentioned in connection with Fig. 3(b). Oxygen in the furnace should be preferentially consumed by the oxidation of the iron powder at a temperature below 973 K, according to the Ellingham diagram for the Fe–O (iron oxides) and C–O (CO gas) systems. Furthermore, it is thought that iron oxides produced by residual oxygen were reduced by carbon in the powder mixture, because the free energy of formation for CO becomes lower than that for iron oxides around 973 K. Therefore, the peak height of the CO gas would show a good relationship
with the amount of the iron powder.

On the other hand, the CO concentration detected in a holding step was very low, regardless of the used powder mixture. However, there was a large difference in the formation of pearlite in the steel, as shown in Figs. 4 and 7. Since the CO gas generated in a heating step should be exhausted with a nitrogen flow from the furnace, it is difficult to think of a direct relationship between the CO gas and the diffusion of carbon into the steel.

As mentioned above, the free energy of formation for CO is lower than that for iron oxides in the vicinity of 973 K. Thus, at temperatures above 973 K, iron oxides covering iron powder in the mixture of iron, graphite and alumina powders should disappear. In addition, the low oxygen partial pressure should be retained in the powder mixture by the generation and exhaust of CO gas in a heating step. As a result of these actions, it is thought the clean surface of the iron powder is in direct contact with the graphite powder, and the movement of carbon is enhanced in the powder mixture. A diffusion phenomenon of carbon observed in the present study has not been reported to the best of our knowledge, and the details are still under our investigations. Interestingly, the iron powder had a ferrite structure in the powder mixture after heat treatment. In other words, the used high-carbon iron powder was decarburized, but not carburized.

Kashiwaya et al.\(^\text{[16]}\) and Yamamoto et al.\(^\text{[17]}\) have reported about the catalytic effect of metallic iron and iron oxide on gasification of coke in steel-making processes. Although the field of industrial application is different from the present study, the function as a catalyst is expected for the iron powder, which is an important agent for the diffusion of carbon into the steel.

4. Conclusions

To examine the role of iron powder in mixtures containing graphite and alumina powders, which were used in “IPP treatment”, low-carbon steel plates were embedded in various powder mixtures and then held in the temperature range of 1 073–1 273 K for 0.9–8.1 ks in a nitrogen flow. The main results were as follows.

1) The formation of pearlite was promoted in the steel plate by adding the iron powder to the graphite and alumina powders, regardless of the carbon content in the iron powder. In particular, a pearlite area occupied more than 60% of the cross section of the steel plate by using 2:3:3 and 3:2:3 mixtures of iron, graphite and alumina powders.

2) A mixture containing nickel powder, instead of the iron powder, did not have a significant effect on the diffusion of carbon into the steel plate.

3) The pearlite area spread from the surface toward the inside of the steel plate, as the heating temperature and holding time increased.

4) The remarkable migration of carbon from the powder mixture to the steel plate would be due to the direct contact between iron and graphite powders at high temperatures.

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