A new surface modification technique, called “iron-powder pack (IPP) treatment”, has been proposed. During IPP treatment, carbon and nitrogen diffuse into a metal substrate by treating it with a mixture of iron and carbon powders at high temperature in a nitrogen flow. This paper describes the effects of adding alumina to the mixture of iron and graphite powders on the microstructures and hardness of SUS430 ferritic stainless steel after IPP treatment. The alumina powder was added to prevent powder mixtures from sintering. A 7:3 (volume ratio) mixture of iron and graphite powders was used as a “base powder”, and the volume ratio of the alumina powder added to the base powder was varied from 0:1 to 50:1. A steel pipe packed with SUS430 steel and powder was heat-treated at 1 273 K for 3.6 ks in a nitrogen flow and then rapidly cooled in water. A surface-modified layer formed on the SUS430 steel through IPP treatment. When IPP treatment was performed using only the base powder, carbon was detected in the surface-modified layer. Both carbon and nitrogen diffused when alumina was added to the base powder. However, the thickness of the surface-modified layer gradually decreased from 380 to 125 μm with an increase in the amount of alumina. A similar tendency was observed in the surface hardness of the steel. In addition, the effects of subzero treatment and immersion in an aqueous nitric acid solution on the modified steel are discussed.

KEY WORDS: ferritic stainless steel; iron powder; graphite; alumina; carbon; nitrogen; diffusion.

1. Introduction

Surface modification techniques of stainless steels have been studied extensively to improve both corrosion and wear resistances.1–6) In general, gas carburizing and gas nitriding, which are industrially used to harden steel surfaces, are difficult to apply to stainless steels. Since they contain sufficient chromium and their surfaces are covered with a thin protective film of chromium oxide, it is necessary to remove the film from the surface before carbon and nitrogen can diffuse. Therefore, surface modification has been mainly performed by using plasma nitriding,1) plasma carburizing,2,4) and vacuum carburizing.6) Since these need special equipment and complicated process flows, a simpler method is desired.

The authors have reported a novel surface modification technique called “iron-powder pack (IPPS) treatment”,7–9) wherein stainless steel is carburized.7) In particular, a steel pipe, which is packed with a stainless steel specimen and a mixture of iron and carbon powders, is heated at 1 273 K for 3.6 ks in a nitrogen flow and then cooled rapidly in water.

Despite the simple and easy treatment, a surface-modified layer containing carbon forms in the obtained specimen. As just described, the most important point of IPP treatment is that iron powder is added to the carbon powder. It is known that this operation leads to the generation of carbon monoxide (CO) gas in the heating step, whereas the CO concentration detected in the holding step is very low.7,10) The CO gas is exhausted via the nitrogen flow from the electric furnace during heat treatment. Therefore, it is thought that the consumption of oxygen in the furnace contributes to the lowering of the oxygen partial pressure around the specimen. In addition, it has been experimentally confirmed that the iron powder acts as an important agent for enhancing the migration of carbon from the powder mixture to the specimen.10)

In IPP treatment, a powdery mixture of iron and carbon becomes solid by heating at high temperatures which should be avoided for sample recovery after heat treatment. Therefore, alumina powder was added to the iron and carbon powders as an anti-sintering agent. The purpose of the present study is to investigate the effects of alumina on the microstructures and hardness of SUS430 ferritic stainless steel modified by IPP treatment.
2. Experimental Procedures

An SUS430 ferritic stainless-steel plate with a thickness of 5 mm was used in the present study. This contained 16.44 mass% Cr, 0.06 mass% C, 0.62 mass% Si, 0.50 mass% Mn, 0.026 mass% P and 0.004 mass% S. The plate was cut into a rectangular shape with dimensions of approximately 40 mm × 10 mm, and subsequently cold-worked into a round bar with a diameter of 5 mm. After annealing at 1 173 K for 3.6 ks in an evacuated silica tube, the round bar was cut and cylindrical specimens with a diameter of 5 mm and height of 5 mm were prepared. The surface of the specimen was finished with a piece of #4000 waterproof abrasive paper before IPP treatment. Then the specimen was degreased in acetone using an ultrasonic cleaner and dried with hot air.

Scanning electron microscopy (SEM) images of the iron and carbon powders used, which were commercially available as carbonyl iron and graphite powders, are shown in Figs. 1(a) and 1(b), respectively. The iron powder contained 0.75–0.90 mass% C, 0.65–0.90 mass% N and 0.15–0.40 mass% O. Each powder was added to a graduated measuring glass by tapping until the necessary volume was obtained, and then the iron and graphite powders were mixed in a beaker to afford a 7:3 mixture of iron and graphite powders. This ratio was determined by using the method reported in our previous study, and this mixture was referred to as the “base powder”. Alumina powder, which is shown in Fig. 1(c), was added to the base powder as an anti-sintering agent. The volume ratio of the alumina powder to the base powder was varied from 0:1 to 50:1.

As shown in Fig. 2, two cylindrical specimens of SUS430 steel and a powder mixture were packed into a steel pipe having an outside diameter of 10 mm, an inside diameter of 9 mm, and a length of 50 mm. Both ends of the pipe were not completely sealed to take in nitrogen gas during heating. The pipe filled with the specimens and the powder mixture was placed in an electric furnace to apply IPP treatment. After repeatedly evacuating the furnace using a rotary vacuum pump and refilling it with nitrogen gas a few times, the pipe was heated at 1 273 K for 3.6 ks in a nitrogen flow and then removed from the furnace to rapidly cool in water. The nitrogen gas had a purity of > 99.99 vol%, and its flow rate was 500 mL/min. In some cases, the pipe subjected to water quenching was immediately put in liquid nitrogen and held for 1.8 ks, i.e., a subzero treatment was applied.

After IPP treatment, X-ray diffraction (XRD) measurements and Vickers hardness tests were conducted on the bottom surface of the cylindrical specimens of the SUS430 steel. XRD measurements with Cu Kα radiation were performed at a tube voltage of 40 kV and a tube current of 40 mA. In the hardness tests, a load of 2.94 N was applied at room temperature for 15 s. Thereafter, the specimen was cut in half to reveal the microstructure. The cross section was ground with waterproof abrasive papers and then mirror-finished using a diamond slurry with a particle size of 0.5 μm. The microstructure was examined by using optical microscopy, SEM, and electron probe X-ray microanalysis (EPMA). The accelerating voltage during SEM observation and EPMA analysis was 15 kV. Before optical microscopy and SEM, the specimens were etched in a solution of 5 g of copper chloride, 100 mL of hydrochloric acid, 100 mL of methanol and 100 mL of aqueous hydrogen peroxide. In addition, Vickers hardnesses of the cross sections were mea-
sured under a test load of 0.49 N to examine the relationship to the distance from the surface.

Several cylindrical specimens modified by IPP treatment were immersed in an aqueous solution of nitric acid (10 vol% HNO₃ and 90 vol% H₂O) for a predetermined amount of time, and mass changes per unit area were determined.

3. Results and Discussion

3.1. Microstructures after IPP Treatment

Figure 3(a) shows an optical micrograph of the cross section of SUS430 ferritic stainless steel before IPP treatment. The steel was cold worked into a round bar with a diameter of 5 mm and annealed at 1 173 K for 3.6 ks in an evacuated silica tube. Equiaxed ferrite (α-Fe) grains were observed in the steel. The steel specimens were packed into a steel pipe together with the base powder, which was a 7:3 (volume ratio) mixture of iron and graphite powders. These were held at 1 273 K for 3.6 ks in a nitrogen flow and then rapidly cooled in water. A cross sectional image of the SUS430 steel obtained by using IPP treatment is shown in Fig. 3(b). There were two characteristic microstructures within the range indicated by the double-headed arrow. In one region, there were several products, and the other was a white region. These regions were referred to as a surface-modified layer. On the other hand, in the lower side of the micrograph, a microstructure having many island-shaped white products was observed. As we reported previously, it is thought that this area is not affected by IPP treatment. In other words, we think that martensitic transformation of an austenite (γ-Fe) phase, which partially forms in the SUS430 steel at a temperature of 1 273 K, has occurred.

Alumina powder was added to the base powder to prevent sintering. Figures 3(c) and 3(d) show optical micrographs of the cross sections of the SUS430 steel after IPP treatment at 1 273 K for 3.6 ks in a nitrogen flow using 9:1 and 50:1 mixtures of alumina and base powders, respectively. The specimens could be easily separated from the powder mixtures. The microstructures are similar to that in Fig. 3(b). However, the thickness of the surface-modified layer, which is indicated by a double-headed arrow, decreased with an increase in the amount of alumina powder. Figure 4 shows the relationship between the alumina powder/base powder ratio and the thickness of the surface-modified layer. The thicknesses of the specimens were measured at several positions, and the mean value and the standard deviation were calculated. As the amount of the alumina powder in the mixture was increased, the thickness of the surface-modified layer gradually decreased from 380 to 125 μm.

A backscattered electron image of the SUS430 steel modified by using the base powder is shown in Fig. 5. The right side of the upper micrograph is continued to the left side of the lower one. A number of gray precipitates were observed near the substrate surface. The results of elemental mapping near the surface are shown in Figs. 6(a)–6(e). As shown in Fig. 6(d), carbon was detected in the steel. The diffusion of carbon from the base powder has been confirmed in our previous study. This phenomenon means that the chromium oxide film on the surface of the SUS430 steel decomposes during IPP treatment. Since carbon monoxide (CO) gas, which is generated in the heating step of IPP treatment, is exhausted via the nitrogen flow from the electric furnace, the oxygen partial pressure should be low around the SUS430 steel. Therefore, it is thought that this...
environment contributes to the decomposition of the oxide film on the steel surface. On the other hand, the diffusion of nitrogen from the heating atmosphere scarcely occurred, as shown in Fig. 6(e).

The precipitates formed near the substrate surface were composed of iron, chromium and carbon. The average chemical composition of some of the precipitates was quantitatively determined by using EPMA to be 40.5 mol% Fe, 34.2 mol% Cr and 25.3 mol% C. In comparison with the XRD pattern in Fig. 7(a), the precipitates were identified as M7C3. On the other hand, the chromium concentration in the substrate was affected by the formation of the precipitates, and it was determined to be 8.0 mol% Cr (7.5 mass% Cr), which is considerably smaller than that before IPP treatment (16.44 mass% Cr).

In Fig. 7(a), a diffraction peak for γ-Fe was observed. From a Fe–Cr–C ternary phase diagram reported in the literature, it is thought that γ-Fe is easily generated at high temperatures by a decrease in the chromium concentration due to the formation of a carbide, like M7C3, and is retained even after water quenching.

Figures 6(f)–6(j) show the results of elemental mapping close to the surface of the SUS430 steel after IPP treatment at 1273 K for 3.6 ks in a nitrogen flow using a 9:1 mixture of alumina and base powders. Both carbon and nitrogen were detected in the steel. This suggests that the alumina powder, which was added as an anti-sintering agent for the base powder, contributes to maintaining the flow path of the
nitrogen gas in the powder mixture. Therefore, the nitrogen gas easily reaches the steel surface. In comparison with Fig. 6(a), the precipitates are smaller. The distributions of carbon and nitrogen of the precipitates were different. From quantitative analysis, it was found that they contained 17.1 mol% Fe, 54.4 mol% Cr, 8.0 mol% C and 20.5 mol% N on average. This result suggests that an M$_7$C$_3$-type compound forms.

In this case, the substrate contained approximately 12.8 mol% Cr (12.0 mass% Cr). The value is higher than that when no alumina was added to the base powder. This indicates that the chromium concentration in the substrate is closely related to the number and size of precipitates formed by the diffusion of carbon and nitrogen. Therefore, the steel shown in Fig. 8, which was modified by using a 50:1 mixture of alumina and base powders, had the highest chromium concentration.

**Figure 9** shows the relationship between the average carbon concentration and the distance from the surface in the SUS430 steel after IPP treatment at 1 273 K for 3.6 ks in a nitrogen flow using various powder mixtures. The EPMA measurements were conducted within a cross section of approximately 600 µm x 400 µm after preparing a calibration curve for carbon. Although the carbon concentration is the mean value of those obtained from precipitates and the substrate, the baseline corresponding to the initial concentration of carbon in the SUS430 steel was unexpectedly high. This may be due to contamination of the area during analysis. The carbon concentration gradually decreased toward the inside of the steel in all cases. In addition, an increase in the amount of the alumina powder led to decreases in the carbon concentration at the substrate surface and the diffusion distance of the carbon into the steel due to the relative decrease in the amount of the base powder, which was the carbon source for IPP treatment. Moreover, decreasing the amount of the base powder increases the time required for decomposition of the chromium oxide film on the SUS430 steel. On the other hand, the values of the nitrogen concentration were too small to make a plot like that in Fig. 9.

### 3.2. Characteristics after IPP Treatment

**Figure 10** shows the surface hardness of SUS430 steel after IPP treatment at 1 273 K for 3.6 ks in a nitrogen flow in relation to the ratio of the alumina and base powders. The measurements were conducted more than 5 times on the bottom surface of each cylindrical specimen, and the mean value and the standard deviation are shown. The steel modified by using the base powder had a hardness value of around 1 000. On the other hand, the hardness value of the steel modified by using a 50:1 mixture of alumina and base powders was approximately 600 and is sufficiently higher than that before IPP treatment (160). As shown in Fig. 8, this steel did not have many precipitates in the vicinity of the surface. Therefore, the large hardness value is mainly due to the hardening of the substrate. This indicates that the diffraction peaks for α-Fe in Fig. 7(c) denote the formation of a martensitic phase formed during IPP treatment since it...
is difficult to distinguish these diffraction peaks.

The SUS430 steel modified by using a 9:1 mixture of the alumina and base powders had relatively high surface hardness, as shown in Fig. 10. The relationship between the hardness and the distance from the surface in this steel is shown by the white circles in Fig. 11. The hardness increased and decreased within a distance of 200 μm from the surface. From Fig. 3(c), this region had many gray grains colored by metallographic etching. At a position far from there, the hardness decreased with an increase in the distance. To examine the reason for the change in the hardness in the vicinity of the surface, the bottom surface of the cylindrical steel was mechanically ground, and XRD measurements were conducted at given positions away from the original surface, as shown in Fig. 12. In comparison to the intensities of the diffraction peaks for γ-Fe in Fig. 7(b), the peaks were intense. This indicates that γ-Fe phase easily forms at 1 273 K and remains at room temperature even after water quenching. Therefore, the presence of γ-Fe is responsible for the decrease in the hardness close to the surface.

To inhibit the γ-Fe phase, the steel subjected to IPP treatment was immediately immersed in liquid nitrogen for 1.8 ks as a subzero treatment. The black circles in Fig. 11 show the hardness values after subzero treatment. An improvement in the hardness was observed within a distance of 200 μm from the surface.

The combination of IPP and subzero treatments on SUS430 steel was helpful for improving its surface hardness. However, the lower chromium concentration in the substrate due to precipitates, like M7C3, exert a negative impact on corrosion resistance of the steel. Murakami et al. have reported the acid resistivity of Fe–Cr binary alloy in an aqueous nitric acid solution.12,13) In their reports, the amount of dissolution of the alloy decreases with an increase in the chromium concentration, and Fe-16 mass% Cr alloy does not dissolve in the solution. To study the influence of IPP treatment on the corrosion resistance of the SUS430 steel, the steels modified by using various powder mixtures were immersed in a 10 vol% aqueous nitric acid solution. Figure 13 shows the relationship between the immersion time and their mass changes. IPP treatment was carried out at 1 273 K for 3.6 ks in a nitrogen flow without the application of subzero treatment. The SUS430 steel before IPP treatment was immersed in the solution for comparison, and its mass remained unchanged during testing. However, the steel modified by using the base powder (0:1 mixture in the figure) was remarkably corroded, and there was a drastic decrease in the mass. On the other hand, for the steel treated using a 9:1 mixture of alumina and base powders, the dissolution of the steel was consider-
ably suppressed because the diffusion of carbon from the powder mixture was suppressed, as shown in Fig. 9, and a high chromium concentration remained in the substrate. IPP treatment using mixtures of iron, graphite and alumina powders is a beneficial technique for increasing the surface hardness of stainless steel, affording excellent corrosion resistance.

4. Conclusions
IPP treatment using mixtures consisting of alumina powder and base powder (iron:graphite = 7:3 by volume ratio) was applied to SUS430 ferritic stainless steel, and the effects of the alumina were examined. IPP treatment was conducted at 1 273 K for 3.6 ks in a nitrogen flow, and water was used as a coolant. The main results are summarized as follows:

(1) As the amount of the alumina powder was increased in the mixture, the thickness of the surface-modified layer formed on the substrate surface became small. However, both carbon and nitrogen were detected in the surface-modified layer, and the number and size of precipitates formed by the diffusion of these atoms were smaller.

(2) The Vickers hardness of the surface of the steel modified by using a 50:1 mixture of the alumina and base powders was approximately 600 and was sufficiently higher than that before IPP treatment.

(3) In the vicinity of the surface of the modified steel, there was a region with a low hardness due to the formation of γ-Fe remaining even after treatment. This region can be recovered by applying subzero treatment.

(4) The steel modified by using a 9:1 mixture of alumina and base powders was immersed in a 10 vol% aqueous nitric acid solution. The dissolution of the steel was considerably suppressed because of the higher chromium concentration in the substrate as compared to that when only the base powder was used.

Acknowledgements
The authors would like to express their appreciation to N. Matsuda for his kind assistance in the experiments. The authors also thank M. Onishi of Asahi Chiyoda Kogyo Co., Ltd. for the helpful comments. This work was supported by ISIJ Research Promotion Grant and JSPS KAKENHI Grant Numbers JP15K06509 and JP19K05045.

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