

Article

Effect of Active Screen Plasma Nitriding on Mechanical Properties of Spheroidal Graphite Cast Iron

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Abstract: Spheroidal graphite cast iron is a material with a wide range of uses such as in automobile parts. By applying active screen plasma nitriding (ASPN) treatment, the use of spheroidal graphite cast iron is expanded, and it can be expected to be used under special load conditions. In this study, we evaluated the effect of ASPN treatment on the mechanical properties of spheroidal graphite cast iron. With ASPN treatment, a nitride layer was formed on the sample surface and a diffusion layer was formed further inside the nitride layer. The thickness of nitride layer increased as the treatment temperature increased. The hardness was improved by ASPN treatment. The abrasion resistance was improved by ASPN treatment, and longer treatment time resulted in higher abrasion resistance. The fatigue strength was improved by ASPN treatment, and longer treatment time resulted in higher fatigue strength. ASPN treatment also improved the corrosion resistance.

Keywords: active screen; plasma nitriding; mechanical property; spheroidal graphite cast iron



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1. Introduction

Cast iron is used as a raw material for various products, such as industrial and mechanical parts. However, depending on the application, treatments aimed at appropriate surface modification are performed to improve the wear resistance and fatigue strength of cast iron [1–4].

One of the methods used for surface modification is plasma nitriding. In plasma nitriding, an external heating device is unnecessary since the material to be treated is heated by the collision energy of ions. The treatment time is short as it utilizes nitrogen in the active plasma state. Moreover, the process is economical as there is less consumption of energy and gas, and there is no burden on the environment because toxic substances are not employed by utilizing abundant resources of nitrogen and hydrogen. In plasma nitriding, the surface temperature of the material to be treated is increased, and its surface is cleaned by the sputtering action of a mixed gas of nitrogen and hydrogen. However, since current is directly applied to the material to be treated, there is a possibility of defects in the treated material, such as edge effect, arcing, and hollow cathode discharge. Therefore, a new technique, known as active screen plasma nitriding (ASPN), has been developed [5–18]. In ASPN, the material to be treated is insulated; a mesh-like metal screen is placed around the material and used as the cathode, and the furnace wall is used as the anode. A voltage is applied between the cathode and anode to allow nitrogen to diffuse into the material to be treated. In other words, because a glow discharge is generated between the furnace wall and the screen, rather than on the surface of the material to be treated, the constituent atoms of the screen and its nitrides in addition to nitrogen molecules, atoms, ions, and electrons exist in the plasma formed on the screen surface. The nitrides formed on the screen flow through the gas stream in the furnace and reach the surface of the material to

be treated, causing diffusion of nitrogen atoms into the material to be treated. Therefore, no edge effect, arcing, and hollow cathode discharge occur.

Attempts have been made to evaluate the hardness and wear resistance of ASPN-treated austenitic stainless steel [6,9,10]. From the analysis, it was found that the formation of a nitride layer improves the fatigue strength of ASPN-treated austenitic stainless steel [19,20]. Since ASPN treatment can be processed at a relatively low temperature, there is little structural change or deformation due to thermal effects, and a dense hardened layer can be obtained in a short time. In addition, ASPN treatment can form a uniform nitride layer on the surface of the material. Spheroidal graphite cast iron is a material with a wide range of uses, such as in automobile parts. By applying ASPN treatment, the use of spheroidal graphite cast iron is expanded, and it can be expected to be used under special load conditions. However, to date, there have been no reports on the application of ASPN treatment in cast iron. Therefore, in this study, we subjected spheroidal graphite cast iron, equivalent to FCD400, to ASPN treatment and evaluated the resulting structure and mechanical properties to ascertain the effect of ASPN treatment on the mechanical properties of cast iron.

2. Materials and Methods

Ferritic spheroidal graphite cast iron, equivalent to FCD400 (Fe-3.5mass%C-3.0mass%Si-0.02mass%P-0.01mass%S-0.1mass%Ti-0.1mass%Cr-0.6mass%Mn), was used, and three types of plate samples (10 mm × 20 mm × 5 mm for structure observation, 20 mm × 40 mm × 5 mm for wear test, and 15 mm × 20 mm × 5 mm for corrosion test) and ϕ 15 mm round bar samples (parallel portion length of 25 mm, parallel portion diameter of 8 mm) were prepared. Figure 1 shows a schematic of the device used for ASPN treatment. The ASPN treatment was performed using a direct current plasma nitriding device. The sample was placed in an insulated state, and a screen (diameter of 170 mm and height of 220 mm) made of mesh-like SUS304 was placed around it. The ASPN treatment was performed under the following conditions: treatment time of 4 h, treatment temperatures of 783–843 K, pressure of 100 Pa, and at a ratio of $N_2/H_2 = 1:1$. The ASPN-treated samples were evaluated by X-ray diffraction (RIGAKU, Japan, RINT-2550V) test using $CuK\alpha$ radiation, cross-sectional SEM observation (JEOL, Japan, JSM-6060LV), electron probe microanalysis (EPMA; JEOL, Japan, JXA-8800), glow discharge spectrometry (GDS; HORIBA, Japan, GD-Profilr 2) analysis, Vickers microhardness (Matsuzawa, Japan, MXT50) test, Suga-type abrasive wear (Suga Test Instruments, Japan, NUS-ISO-3) test, and Ono-type rotary bending fatigue (Shimadzu, Japan, H-6) test.

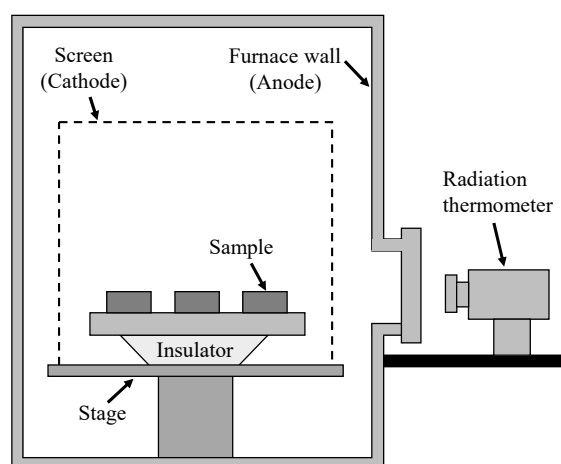


Figure 1. Schematic of device used for active screen plasma nitriding (ASPN) treatment.

In the Suga-type abrasive wear test, the abrasion wheel with SiC emery paper #600 rotated against the reciprocating sample surface under a load of 6.4 N. When the sample

was reciprocated for a cycle, the abrasion wheel was rotated 0.9° , and the emery paper was changed after one revolution of the wheel (400 cycles of reciprocating motion of the sample) to ensure the sample surface always contacted with fresh abrasive. The amount of wear of sample was measured by electronic scale every 200 cycles of reciprocating motion of sample. Each sample was tested for 2000 cycles to determine the amount of wear. The Ono-type rotary bending fatigue test was performed under a rotating speed of 3400 rpm. Stresses of different magnitudes were applied to the round bar sample, the number of repetitions until the sample broke was measured, and the stress that did not break even when the sample was repeatedly stressed 10^7 times was defined as the fatigue strength. To evaluate the corrosion resistance of the nitride layer obtained by ASPN treatment, a corrosion test was performed on the plate sample having the thickest nitride layer. The corrosion test was performed by immersing the ASPN-treated sample in 1 N hydrochloric acid, sulfuric acid, and nitric acid for 5 h.

3. Results and Discussion

Figure 2 shows the X-ray diffraction patterns of the non-treated and ASPN-treated plate samples. Diffraction peaks of Fe_{2-3}N and Fe_4N were detected in the ASPN-treated samples. Furthermore, with an increase in the treatment temperature, the intensity of the diffraction peaks corresponding to $\alpha\text{-Fe}$ decreased and that of Fe_{2-3}N comparatively increased. It is considered that this is because the nitrided layer became thicker as the treatment temperature increased.

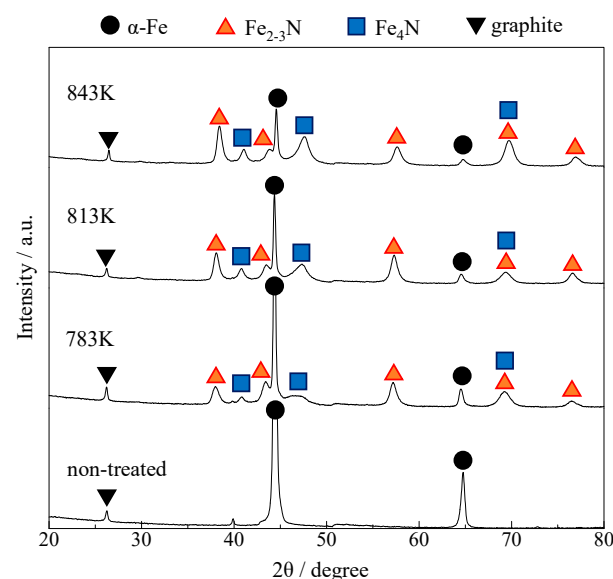


Figure 2. X-ray diffraction patterns of ASPN-treated plate samples.

Figure 3 shows the cross-sectional SE images of the non-treated and ASPN-treated plate samples, and Figure 4 indicates the nitrogen mapping images obtained by EPMA for the ASPN-treated plate samples. In the ASPN-treated sample, the presence of a layer different from the base material was confirmed on the surface, in which nitrogen was concentrated. The thickness of this layer was 1.9, 2.8, and $4.6\ \mu\text{m}$ at 783, 813, and 843 K, respectively, indicating that the thickness increased as the treatment temperature increased. From the X-ray diffraction pattern shown in Figure 2, this layer is hypothesized to be a nitride layer composed of Fe_{2-3}N and Fe_4N . The observation that the intensity of the diffraction peak corresponding to $\alpha\text{-Fe}$ decreased as the treatment temperature increased and that of Fe_{2-3}N comparatively increased, as shown in Figure 2, is believed to be due to the formation of a thicker nitride layer as the treatment temperature increased. The plausible reason behind the formation of a thicker nitride layer with the increase in treatment temperature is that the increase in treatment temperature increases the amount of

sputtering on the screen surface and thereby increases the deposits, which are the source of nitrogen, as well as the diffusion rate of nitrogen. Further inside the nitride layer, nitrogen was concentrated along the grain boundaries and the presence of a diffusion layer, in which nitride was formed along the grain boundaries, was confirmed. The nitride layer of the ferritic spheroidal graphite FCD400 radical nitrided at 803 K for 10 h in a mixed gas of H_2 and NH_3 is 2 to 3 μm [21]. The treatment time in this study was 4 h, but the thickness of the nitrided layer of the samples treated at 783 and 813 K was similar to the thickness of the nitrided layer of the radical nitrided sample.

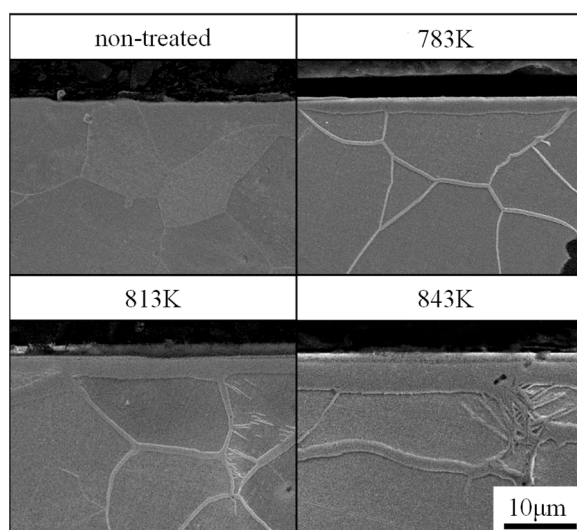


Figure 3. Cross-sectional SE images of ASPN-treated plate samples.

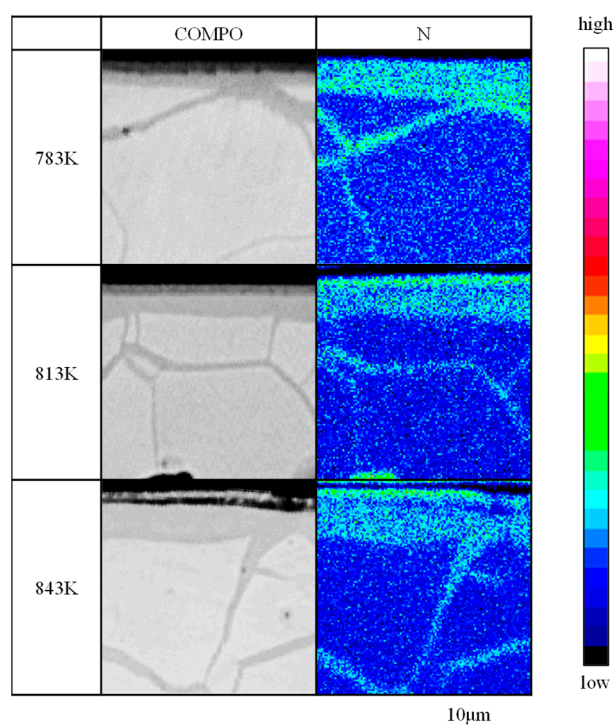


Figure 4. BSE images and nitrogen mapping images obtained by EPMA for ASPN-treated plate samples.

Figure 5 shows the results of GDS analysis of the ASPN-treated plate samples. Concentration of nitrogen on the surface of the ASPN-treated sample was confirmed, and nitrogen was observed to diffuse further inside as the treatment temperature increased. In all

ASPEN-treated samples, the nitrogen concentration dropped sharply within a few μm from the surface. In each sample, the position where the nitrogen concentration substantially decreased coincided with the thickness of the nitride layer confirmed in Figure 3.

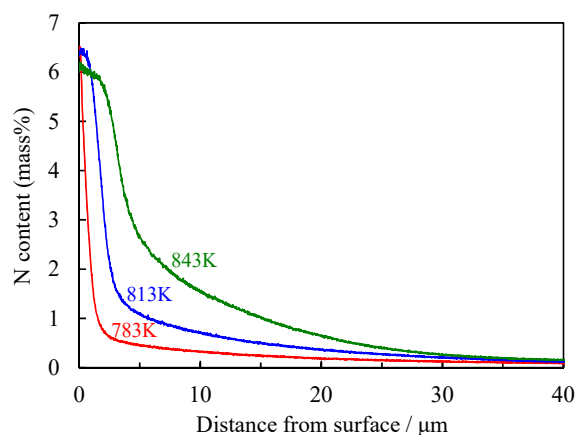


Figure 5. GDS analysis of ASPN-treated plate samples.

According to the results of GDS analysis of the ASPN-treated samples for regions further inside the nitride layer, nitrogen diffused up to depths of approximately 180, 250, and 300 μm at treatment temperatures of 783, 813, and 843 K, respectively. From this result, it was considered that the total thickness of the nitride layer (thickness of the combined layer of the nitride and the diffusion layers) obtained in this study was a maximum of approximately 300 μm . In addition, it has been reported that the total thickness of the nitride layer was 200–300 μm , as obtained by plasma nitriding-based treatment of ferrite-based spheroidal graphite cast iron at 843 K for 4 h [22,23]. Thus, it was confirmed that similar thickness of the total nitride layer was attained by ASPN treatment. The diffusion layer of the ASPN-treated sample was thicker than the diffusion layer (150 μm) of the radical nitrided sample [21].

Figure 6 shows the surface hardness of the ASPN-treated plate samples. The surface hardness increased by ASPN treatment. This can be attributed to the formation of a nitride layer (a combined layer consisting of nitride and diffusion layers) on the surface. Furthermore, the surface hardness increased as the treatment temperature increased. This is considered to be due to the formation of a thicker nitride layer with increase in the treatment temperature.

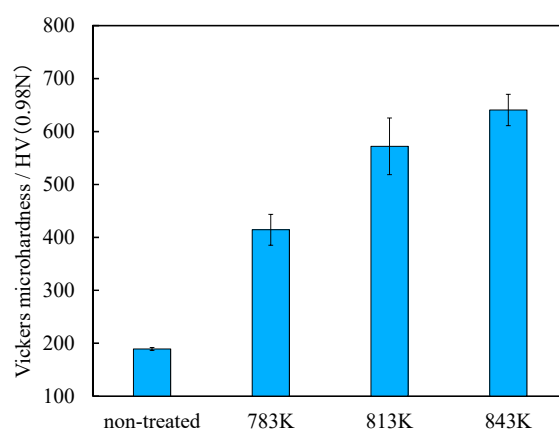


Figure 6. Surface hardness of ASPN-treated plate samples.

On the nitride layer of the ASPN-treated sample in Figure 4, a nitrogen-enriched layer with a thickness of 1.0 to 1.5 μm can be confirmed, and the nitrogen-enriched layer is a deposition layer consisting of nitride sputtered from the active screen. It is considered

that by applying the ASPN treatment, a nitride layer was formed on the surface of the spheroidal graphite cast iron by nitrogen diffusion from the deposition layer as in the case of other materials [5].

Figure 7 shows the cross-sectional hardness of the ASPN-treated plate samples. The hardness of all ASPN-treated samples decreased from the surface toward the inside. The possible reason is that a nitrogen-rich diffusion layer was formed closer to the surface and the nitrogen concentration decreased toward the inside, as indicated in Figure 5. Further, in the region near the surface, the hardness improved toward the inside with increase in the treatment temperature. It is considered that the higher the treatment temperature, the higher is the nitrogen concentration close to the surface, resulting in the formation of a harder diffusion layer. The hardness of the ASPN-treated sample was about the same as that of the radical nitrided sample (740 HV) [21].

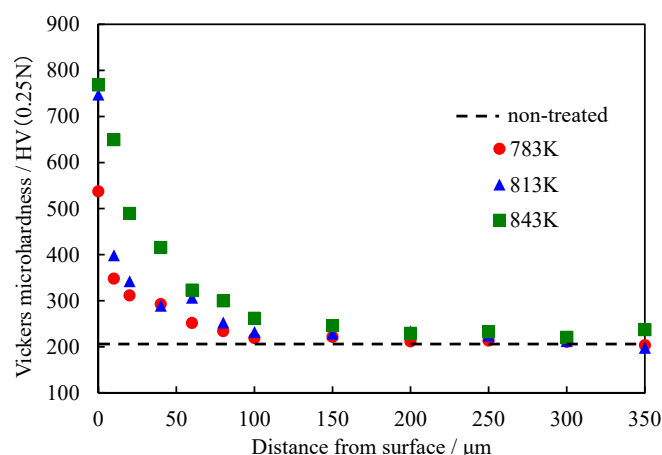


Figure 7. Cross-sectional hardness of ASPN-treated plate samples.

Figure 8 shows the Suga-type abrasive wear test results of the ASPN-treated plate samples. With the ASPN treatment, the amount of wear decreased and the wear resistance increased as the treatment temperature increased. The possible reason is that the hard nitride layer became thicker as the treatment temperature increased and the depth of the hardened layer increased, as shown in Figure 7.

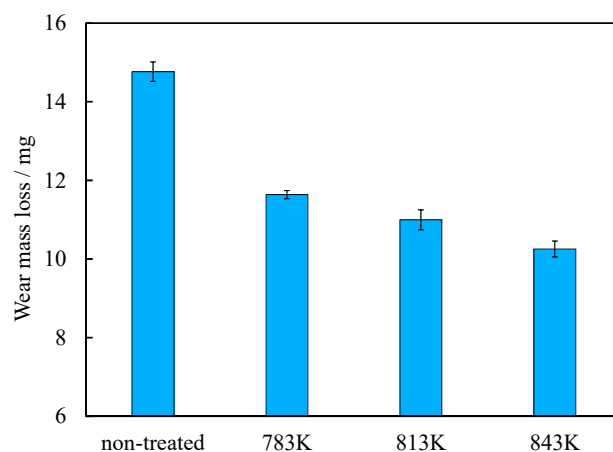


Figure 8. Suga-type abrasive wear test results of ASPN-treated plate samples.

Figure 9 shows the cross-sectional SE images of the ASPN-treated samples after immersion in acid. Severe corrosion and unevenness was observed on the surface of the non-treated sample, whereas the ASPN-treated sample, though slightly corroded, did not exhibit unevenness found in the non-treated sample. It is considered that the formation of

the nitride layer on the surface improved the corrosion resistance, suppressing the extent of corrosion.

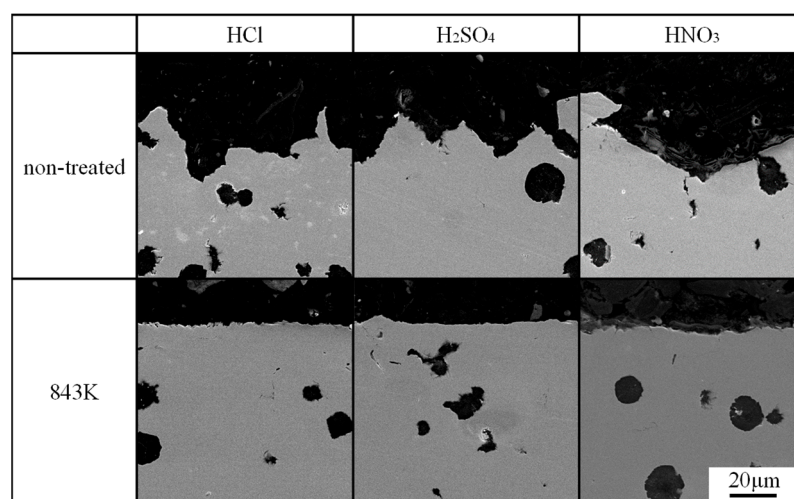


Figure 9. Cross-sectional SE images of ASPN-treated samples after immersion in 1N HCl, H₂SO₄, and HNO₃.

Figure 10 shows the fatigue strength of the ASPN-treated round bar samples, and Figure 11 shows the SE images of the fracture surface of the non-treated and ASPN-treated samples. It was observed that ASPN treatment improved the fatigue strength. The fatigue strength increased as the treatment temperature increased. From Figure 11, it was confirmed that both the non-treated and the ASPN-treated samples underwent brittle fracture in the rotary bending fatigue test. However, a quasi-cleavage fracture surface was confirmed near the surface in the non-treated sample, whereas grain boundary fracture was observed in the ASPN-treated sample. This grain boundary fracture was confirmed to occur further inside the sample as the treatment temperature increased. Accordingly, it is surmised that the starting point of the crack moved to the inside of the sample by ASPN treatment, increasing the fatigue strength. The fatigue strength of the ASPN-treated sample was higher than that of the radical nitrided sample (approximately 300 MPa). It is considered that this is because the diffusion layer was thicker in the ASPN-treated sample [21].

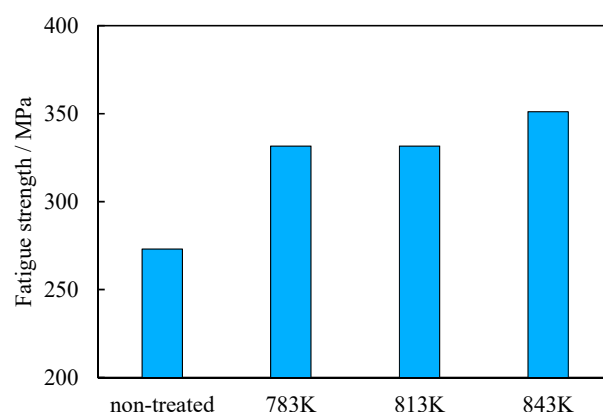


Figure 10. Fatigue strength of ASPN-treated round bar samples.

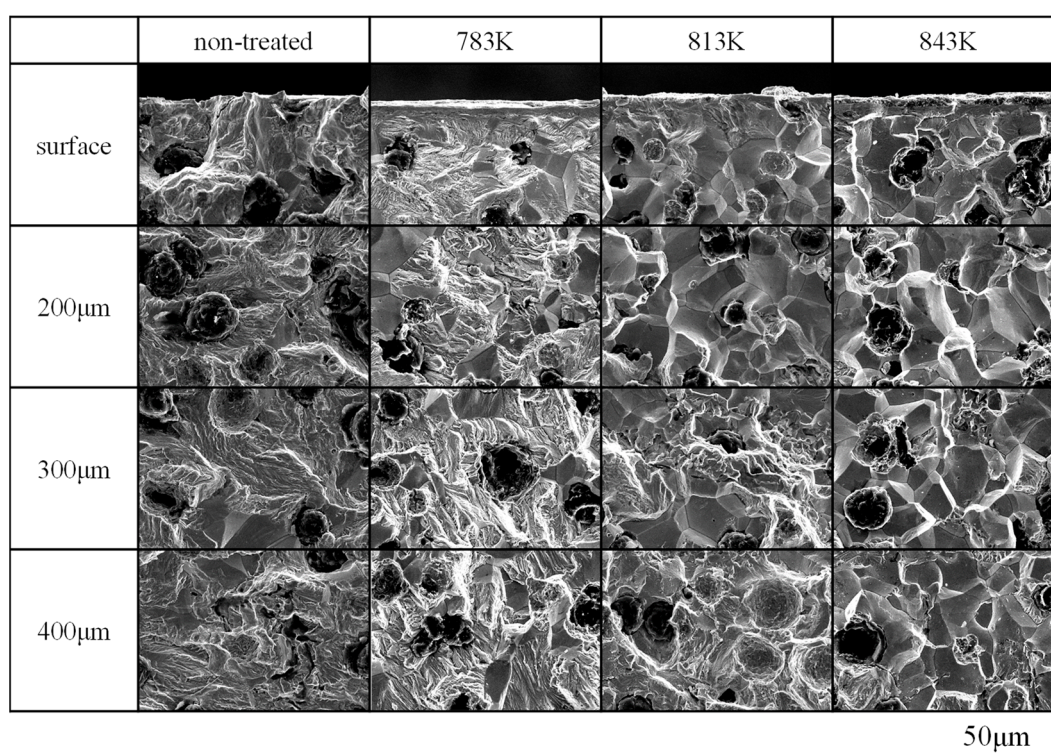


Figure 11. SE images of fracture surface of ASPN-treated samples.

4. Conclusions

In this study, FCD400-equivalent spheroidal graphite cast iron was subjected to ASPN treatment and its microstructure and mechanical properties were evaluated:

- (1) With ASPN treatment, a nitride layer was formed on the sample surface and a diffusion layer was formed further inside the nitride layer.
- (2) The thickness of the nitride layer increased as the treatment temperature increased.
- (3) The hardness increased as the treatment temperature increased.
- (4) The wear resistance increased as the treatment temperature increased.
- (5) The fatigue strength increased as the treatment temperature increased.
- (6) ASPN treatment improved the corrosion resistance.

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