Effects of Heat Treatment Conditions on Formation of Expanded-Austenite Phase in Austenitic Stainless Steels by Combining Active Screen and DC Plasma Carburizing Processes

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A low temperature plasma carburizing process can produce an expanded-austenite layer (generally called the S phase), which has high hardness and corrosion resistance at the surface of austenitic stainless steels. We have investigated S phase formation behaviors by using a combined process of active screen and DC plasma carburizing for austenitic stainless steels such as JIS SUS304 and 316 with the aim of developing a highly effective and efficient production technique. The influence of carburizing parameters (processing temperature, time, gas atmosphere, etc.) on the formation of the S phase was studied in terms of thickness, hardness, carbon concentration, lattice constant, and residual stress. The mechanical properties and corrosion resistances of the obtained S phases were also evaluated by using a ball-on-disk test and a salt spray test (SST). The results show that S phases produced efficiently by the combined process under a condition of 733 K and a 10.5 vol% of CH4 gas ratio have both excellent wear and corrosion resistances. [doi:10.2320/matertrans.H-M2017822]

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1. Introduction

Austenitic (γ) stainless steel is widely used in industrial and household products because of its excellent corrosion resistance and heat resistance. Additionally, γ stainless steel is non-magnetic, so it is useful for things negatively affected by magnetism, such as system parts (e.g., cases and bearings) installed in equipment used for transporting non-magnetic parts. However, γ stainless steel does not have high enough hardness and wear resistance for structural steels, unlike other low-alloyed steels.

Gas carburizing and gas nitriding are the most effective surface hardening processes to improve wear and/or mechanical properties of steels. However, as γ stainless steel contains a high concentration of chromium, chromium carbide (Cr7C3, Cr5C2) or nitride (CrN, Cr2N) is precipitated on the grain boundary at typical carburizing temperatures: 1173–1253 K in gas carburizing or 773–863 K in gas nitriding11). This inhibits the formation of a passivation film composed of chromium oxide because of the depletion of chromium in solid-solution, so corrosion resistance decreases.

In the mid 1980s, Zhang-Bell2) and Ichii et al.3) found that an expanded austenite phase (S phase) had both high corrosion resistance and high hardness. It is formed at the surface when nitrided at a low temperature such as 673 K for γ stainless steel. Since then, S phase formed by gas carburizing/nitriding or plasma carburizing/nitriding has been studied widely4–8).

The direct current plasma (DCP) method is a conventional plasma treatment. Because plasma is discharged on processing targets directly, the S phase is highly efficiently formed. However, a uniform and smooth treated surface is difficult to obtain because of arcing, a hollow cathode effect, and an edge effect on the surface9).

On the other hand, an active screen plasma (ASP) method does not discharge plasma on processing targets directly. Therefore, reactive species generated from plasma discharge occur on a screen, and they deposit themselves so as to surround the processing targets to be treated9). Consequently, a remarkably homogeneous S phase can be obtained. However, an S phase is formed less efficiently by using the ASP method than the DC plasma method. Further, in both methods, screen components are deposited on processing targets, which can inhibit S phase formation10).

External heaters were used for controlling carburizing temperature, so both the proportion of direct resistance heating and edge current density on the target specimen could be reduced. Additionally, reactivated species were used for carburizing that had been generated by discharging on not only a target specimen but also a screen.

Therefore, we have attempted to form S phases by using a combined process of ASP and DCP carburizing to develop a highly effective and efficient S phase production technique.

This paper studies the effects of carburizing conditions on S phase formation and the corrosion and wear resistances of the S phase.

2. Experimental Procedure

2.1 Plasma carburizing equipment

A plasma carburizing process was performed using a 300W × 280 × 250 mm plasma carburizing furnace (made by NDK Inc.) (Fig. 1). For the screen cage material, stainless wire mesh made of SUS304 steel was used. According to Nishimoto et al.11), efficiency of S phase formation is increased by decreasing the open area of wire mesh, so 6.5 mesh (wire diameter: 0.9 mm, opening width: 3.01 mm,
open area percent: 59.2%) was selected for the screen cage. The screen cage was prepared as a dual structure. Height and diameter of the external screen cage were 150 mm; similarly, the internal cage’s height and diameter were 142 mm. The specimen stage with pillars was completely made of SUS304 steel. The stage was 100 mm in diameter and 5 mm thick. In this study, plasma was generated on the specimen directly so as to monitor specimen temperature, and a thermocouple was set at a depth of 1 mm in the dummy specimen (made of SUS304 steel with 24 mm dia.). The plasma was generated using a pulsed power supply (up to 1 kV-120 A, made by Rübig GmbH & Co. KG). An external heater was also used to control specimen temperature.

2.2 Specimen and carburizing conditions

The chemical compositions of the steels used as specimens are listed in Table 1. Specimens were disk-shaped, 24 mm in diameter, and 8 mm thick. Their surface was mechanically ground and polished to a mirror finish.

The carburization conditions are shown in Fig. 2. The surface contamination and oxide film were removed by an ion bombardment process using a gas mixture of argon (Ar) and hydrogen (H2) for 3.6 ks. Then, while the furnace pressure was kept at 40 Pa, methane was varied in the range of 4.8 d 100 vol% by adjusting H2 gas volume, at specimen temperatures of 613, 733, and 833 K for 14.4 ks. After carburization, the specimens were cooled in the furnace.

The plasma generated during the ion bombardment and carburizing processes was measured by using emission spectrometry in the wavelength range of 200 d 1000 nm, as an average of 10 measurements of 10 ms integrations.

2.3 Analysis of S phase

The microstructures of the surface layer of carburized specimens were analyzed by optical microscopy. Hardness distributions were measured using a micro-Vickers hardness tester, where a load of 0.098 N was applied for 10 s.

The carbon concentration depth-profiles were measured by field emission scanning electron microscopy/wavelength dispersive X-ray (FE-SEM/WDX) using a calibration curve method.

The lattice structure of the carburized layer was analyzed by using X-ray diffraction (XRD) (Co Kα). The lattice constants were also precisely calculated from the relationship between the diffraction peak value (incident angle of 9 deg) of γ phase and sin2θ by using XRD methods. The residual stress in the carburized layer was estimated by using a 2θ-sin2ψ XRD method with a CrKβ ray. The stress constant necessary to measure stress was calculated by using a 46.85 deg diffraction angle of γ(200) in SUS316 steel that had a Young’s modulus of 200 GPa, Poisson ratio of 0.3, and −1258 MPa/deg12 in a non-strain state.

2.4 Evaluation of wear and corrosion resistance

The wear resistance of carburized specimens was evaluated in a ball-on-disk test. Sliding speed was 31.4 mm/s and sliding distances were 50 and 250 m at a 2 N load under dry conditions. An alumina ball (4.8 mm dia.) was used for a counterpart material. The surface roughness (Ra) of the specimen was adjusted to be 0.19 d 0.20 μm.

A salt spray test (SST) was carried out to evaluate corrosion resistance of the carburized specimens in accordance with JIS Z 2371. The duration range was up to 240 h. Further, STTs were also conducted for carburized specimens that had surface layers removed at depths of 0.5, 2, 7, and 21 μm by using a glow discharge optical emission spectrometer (GD-OES).

3. Results

3.1 Microstructure of carburized layers

Figure 3 shows optical micrographs of SUS304 steels treated at several CH4 gas ratios of 4.8, 10.5, 17.6, 36.5, and 100 vol% and at carburizing temperatures of 613, 733, and 833 K for 14.4 ks. Carburized layers 5 and 30 μm thick were formed at 613 and 833 K, so the thickness of the carburized layer increased as carburizing temperature increased. However, a dark-etched layer was observed on the surface of the specimen carburized at 833 K.

At the CH4 gas ratios below 17.6 vol% at 733 K, a white layer (which is explained later to be a high carbon layer, so it is hereinafter referred to as a carburized layer), which is hard to etch and thought to be carburized, is observed on the
specimen surfaces. Carburization at the CH₄ gas ratio of 10.5 vol% at 733 K obtained the thickest white layer: about 20 μm (Fig. 3). However, the carburized layer became thinner as the CH₄ gas ratio increased to 17.6 vol%. When the CH₄ gas ratio is over 36.5 vol%, no carburized layer is observed. Surfaces of specimens carburized at the CH₄ gas ratios of 36.5 and 100 vol% were covered with soot. Therefore, carburization is thought to be inhibited by soot at CH₄ gas ratios higher than 17.6 vol%.

Figure 4 shows optical micrographs of SUS304 steel carburized with current values of 0.1 and 0.5 A at a carburizing temperature of 733 K and the CH₄ gas ratio of 10.5 vol% for 14.4 ks. As current value is increased, the carburized layer thickens.

Figures 5 and 6 show the hardness distribution and the corresponding carbon concentration distribution of the surface layer of SUS304 steel carburized at various temperatures under the CH₄ gas ratio of 4.8 vol% (Figs. 5(a) and (b)) and various CH₄ gas ratios under a carburizing temperature of 733 K (Figs. 6(a) and (b)).

As carburizing temperature increases, both hardness and carbon concentration increase. Also, the hardness profiles agree with the carbon concentration profiles at all carburizing temperatures. The depth of increasing hardness and carbon concentration also coincide with the thickness of the carburized layer. Figure 7 shows the relationship between hardness and carbon concentration of the layers carburized at the CH₄ gas ratios of 4.8, 10.5, and 17.6 vol% and temperature of 733 K. Even though the S phase hardness depends on the thickness, hardness is found to increase almost proportionally to the amount of penetrating carbon. The hardness of the carburized layer is represented by the following relational expressions.

\[
\text{Hardness (HV)} = 181 \times C \text{conc. (mass%)} + 314 \text{ (20-μm-thick carburized layer)}
\]

\[
\text{Hardness (HV)} = 149 \times C \text{conc. (mass%)} + 262 \text{ (8-μm-think carburized layer)}
\]

Even at the same carbon concentration, a thicker carburized layer is much harder than a thinner one. This is because that compressive residual stress is much higher in the thicker layer than in the thinner layer, as will be described later.

The CH₄ gas ratio of 10.5 vol% is also found to be the most effective for penetrating carbon most deeply.

Figure 8 shows the XRD analysis results for a surface layer of SUS304 steel carburized at 733 K. The peak positions of γ(111) and γ(200) of SUS304 steel carburized at CH₄ gas ratios of 36.5 and 100 vol% correspond with those of untreated SUS304 steel.
On the other hand, in SUS304 steels carburized at CH₄ gas ratios lower than 36.5 vol%, which have an obviously carburized layer, these peaks are shifted to a lower angle side. This means that the lattice constant of γ phase in the surface layer is increased by the carburization. Hummelshøj et al. reported eq. (3)\(^1\text{3}\), which describes the relationship between lattice constant and carbon concentration of the S phase.

\[
a = 3.5965 + (0.6029 \pm 0.0189) \times 10^{-2} \times \text{yc} \\
\text{yc: Carbon concentration (at%)}
\]
Lattice spacing was calculated from diffraction peak values of $\gamma(111)$, $\gamma(200)$, and $\gamma(220)$ that were determined by using the 9-deg X-ray incident angle of a thin film method. Then, the lattice constant corresponding to each surface was calculated. Thereafter, each lattice constant was determined as a function of $\sin^2\theta$, by extrapolation, that is, as a value of when $\sin^2\theta$ is zero. Obtained lattice constants are plotted in Fig. 9. The relationship between the carbon concentrations at the depth of 1 $\mu$m and the lattice constants agrees well with Hummelshøj’s equation. Therefore, carburized layers in this study can be assumed to be an S phase.

Furthermore, Christiansen and Somers\(^{12}\) reported that the S phase has a compressive residual stress. The measured residual stress distributions in the S phases (SUS316) formed in this study are shown in Fig. 10. The compressive stress remains at a depth corresponding to S phase thickness. As an S phase becomes thicker, compressive residual stress becomes larger. The maximum compressive residual stress is 1400 MPa.

### 3.2 Wear properties

Figure 11 shows the results of a ball-on-disk test for SUS304 steel under a contact load of 2 N. Even after the sliding of 50 m, wear volume of the untreated specimen is 0.046 $\text{mm}^3$ and increases as sliding distance increases (0.31 $\text{mm}^3$ when sliding distance is 250 m). The wear volume of specimens with an S phase is still under 0.002 $\text{mm}^3$ even after sliding of 250 m. Thus, the S phase formed on the surface remarkably improves wear resistance.

Figure 12 shows cross-sectional profiles, wear track surface, and cross-section micrographs of wear track of the untreated SUS304 steel specimen and SUS304 steel specimen carburized with a 20-$\mu$m-thick S phase after sliding of 250 m. Wear width and depth of the untreated specimen are approximately 800 and 18 $\mu$m, respectively. On the other hand, for the specimen with an S phase, changes in cross-section profile and cross-section microstructure under wear track are not as clear after the test. As already discussed, an S phase formed on the surface by carburizing has a high hardness and a high compressive residual stress. Therefore, because the S phase inhibits the initiation and growth of surface cracks during the wear test, it is thought that the wear resistance can be improved.

### 3.3 Corrosion behavior

Figure 13 shows salt spray test (SST) results for untreated SUS316 steel and SUS316 steels with an S phase on the surface formed by carburization at 733 and 833 K. After 240 h, the entire surface of the specimen carburized at 833 K is covered with red rust. For this specimen, a dark-etched layer at the surface is observed mainly along the grain boundaries as shown in Fig. 3. This dark-etched layer is formed after aqua regia etching by precipitation of carbides at the grain boundary during the carburization. This grain boundary precipitation phase should be composed of chromium-related carbides because the steel contains around 18 mass% of chromium, which is a strong carbide-forming element. This carbide precipitation at the grain boundary is thought to cause a solute chromium poor zone to form around the grain boundary, resulting in decreased corrosion resistance. Therefore, the chromium carbide that precipitates on the grain boundaries during carburizing at 833 K is presumed to reduce the corrosion resistance.

However, red rust also formed on the specimen carburized at 733 K, on which no dark-etched layer was observed along the grain boundaries.

Figure 14 shows that many granular deposits of the order of 100 nm were observed on the surface of the specimen by FE-SEM observation. The granular deposits observed in this study are extremely small. In addition, the components of
Fig. 12  Cross-section profiles and optical images of cross-section of SUS304 steel with and without S phase after ball-on-disc test.

Fig. 13  Surface appearance of plasma-carburized SUS316 steel specimens compared with that of untreated specimen after 240 h in salt-spray test. Plasma carburizing were conducted under a atmosphere of CH₄ gas ratio of 10.5 vol% at 733 K and 833 K for 14.4 ks.

Fig. 14  FE-SEM images of plasma-carburized and untreated SUS316 steel surfaces.
the specimens (SUS316 steel) and the screen (made of SUS304 steel) are similar, so components of the screen are difficult to discriminate from those of the specimens by normal EDX qualitative analysis. Nii and Nishimoto\(^{14}\) reported that, based on SEM-EDX analysis results, screen components were deposited on specimens during nitriding because Ni derived from screen components made of SUS304 steel was detected on a specimen made of ferritic stainless steel SUS420 (0.09% C-0.003% Si-0.82% Mn-0.23% Ni-16.13% Cr).

We assume that the granule deposits formed by sputtering from the screen decreased corrosion resistance. Therefore, the specimens used for the SST were those with a 20-μm-thick S phase that had 2-, 7-, and 21-μm-thick surface layers removed and that with an 8-μm-thick S phase that had a 0.5-μm-thick surface layer removed by sputtering using a GD-OES device. As shown in Fig. 15, surface rust is not observed on the sputtered area of every specimen. Even after the 0.5-μm-thick surface layer is removed (Fig. 15(e)), no rust is found to form for up to 240 h, through rust water around the sputtered area dripped on to the sputtered area. These results show that layers with poor corrosion resistance are present only on the top surface of specimens and that the S phase almost the same corrosion resistance as untreated specimens.

4. Discussion

4.1 Formation mechanism of S phase

The mechanism of DC plasma carburizing using CH\(_4\) gas is thought to be an attachment of the capture and carbon ions by the catalytic action of the steel or a similar implantation of carbon ions in a steel surface\(^{15}\). Figure 16 shows optical emission spectra during the sputtering process using a mixture of Ar and H\(_2\) and the carburization process in an atmosphere of CH\(_4\) gas with a ratio of 10.5 vol%. H\(_\alpha\) (wavelength of 656 nm) and H\(_\beta\) (486 nm) originating from the Balmer series of hydrogen are shown. Emissions from a CH radical by B\(_2\Sigma\rightarrow X^2\Pi\) (389 nm) and A\(^2\Delta\rightarrow X^2\Pi\) (431 nm) were also revealed. Four emission peaks were identified. The highest peak intensity is H\(_\alpha\), the excitation process equation of which is eq. (4).

\[
\text{CH}_4 + e^- \rightarrow \text{CH}_3 + H^+ + e^- \quad (4)
\]

The second highest intensity is due to an excitation process of CH (431 nm), the reaction of which is expressed as eq. (5)\(^{16}\).

![Fig. 16 Optical emission spectra at (a) Ar/H\(_2\) sputtering process and (b) plasma-carburizing process.](image)

Fig. 15 SST test results (after up to 240 h) of SUS304 and SUS316 steels specimen surfaces sputtered using GD-OES up to a depth of 25 μm after plasma-carburizing: SUS304; (a)–(d), and SUS316; (e).
Conceivably, CH₄ gas excited by plasma generated on the screen and the specimen surface becomes the hydrocarbon radical cation (CH⁺) and carbocation (C⁺), respectively, as shown in reactions (6) to (8), and they can diffuse from the surface to the inside of a steel specimen.

\[
\text{CH}_4 + e^- \rightarrow \text{CH}^+ + \text{H}_2 + \text{H} + e^- \quad (5)
\]

Solved carbon in a regular octahedron site of γ phase with a face-centered cubic (fcc) crystal structure is the regular octahedron structure for an interstitial solid solution. Thus, the maximum crystallographic solid solubility of carbon in γ phase is 50 at%. Hence, assuming that Ni and Cr are uniformly solved in SUS304 steel as a substitutional atom and the chemical components of the steel are Ni: 8 mass%, Cr: 18 mass%, and Fe: 74 mass%, the maximum crystallographic solved carbon concentration is estimated to be approximately 17.6 mass%. According to Christiansen and Somers¹², the maximum solved carbon concentration given to the S phase by carburization is approximately 16 at%. This value is converted to 5.7 mass%. In this study, the maximum crystallographic solved carbon concentration is estimated to be approximately 17.6 mass%. According to Christiansen and Somers¹², the maximum solved carbon concentration given to the S phase by carburization is approximately 16 at%. This value is converted to 5.7 mass%. In this study, the maximum solved carbon concentration in the S phase is measured to be approximately 3 mass%. Therefore, although 3 mass% carbon concentration is already a supersaturated state, it might be possible to gain a much higher solved carbon concentration.

However, when carburized at a CH₄ gas ratio over 36.5 vol%, the specimen surface was covered with soot, which significantly inhibits carburization. This is because the amount of carbon supplied on the specimen surface exceeds the diffusion rate of carbon at the carburizing temperature, leading to carbon depositing on the specimen surface. Although the generation of soot can be inhibited by decreasing CH₄ gas ratio during carburization, a decrease in CH₄ gas ratio decreases the formation efficiency of the S phase. Therefore, the optimum CH₄ gas ratio is considered to be 10.5 vol% at a carburizing temperature of 733 K.

4.2 Hardening mechanism of S phase

Solid solution carbon definitely hardens S phase. Figure 17 shows hardness as a function of the carbon concentration, which is put in the data of normalized and annealed (γ and α’ ) stainless steel¹⁷) and quenched (0.11–0.34%)Cr-12%Cr steels¹²) in Fig. 7. The S phase is clearly much harder than these steel matrices with a comparable amount of carbon. The hardening of the S phase should be attributed to not only the solid solution strengthening of carbon but also the high compressive residual stress of up to 1400 MPa.

High compressive residual stress is generated because the lattice constant of the S phase (fcc, a = 3.6712 nm) is 2.1% larger than that of the matrix (fcc, a = 3.5969 nm) in addition to the formed S phase being comparatively thin (20 μm at most). The S phase obtained in this study, which contains carbon of 2.4 mass%, has a hardness of approximately 800 HV, which is equivalent to that of a quenched α’ stainless steel matrix with a carbon concentration of 0.38 mass%.

5. Conclusion

Effects of CH₄ gas ratio and temperature during carburization on forming of the S phase were studied by using a combined process of active screen plasma (ASP) and direct current plasma (DCP) carburizing of γ stainless steel (SUS304 and SUS316 steel) to develop an effective and efficient S phase production technique.

The results obtained can be summarized as follows.

(1) When the CH₄ gas ratio is 17.6 vol% or less at 733 K, an S phase can be formed without soot on the surface of a specimen. Moreover, the CH₄ gas ratio of 10.5 vol% is the most efficient to form an S phase.

(2) Hardness of the S phase increases in proportion to the amount of carbon penetrated by diffusion during carburization. Moreover, since a compressive residual stress of up to 1400 MPa is also imparted to the S phase, the S phase is harder than stainless steel containing the same amount of carbon.

(3) An S phase thicker than 10 μm remarkably improves resistance to wear.

(4) At under 733 K, though there is a layer that has poor resistance to corrosion at a depth of up to 0.5 μm, the S phase that has its surface layer removed has the same excellent resistance to corrosion as γ stainless steel before carburization.

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