Effect of Deformation Structure of AISI 316L in Low-Temperature Vacuum Carburizing

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Abstract: The effect of plastic deformation applied to AISI 316L in low-temperature vacuum carburizing without surface activation was investigated. To create a difference in the deformation states of each specimen, solution and stress-relieving heat treatment were performed using plastically deformed AISI 316L, and the deformation structure and the carburized layer were observed with EBSD and OM. The change in lattice parameter was confirmed with XRD, and the natural oxide layers were analyzed through TEM and XPS. In this study, the carburized layer on the deformed AISI 316L was the thinnest and the dissolved carbon content of the layer was the lowest. The thickness and composition of the natural oxide layer on the surface were changed due to the deformed structure. The natural oxide layer on the deformed AISI 316L was the thickest, and the layer was formed with a bi-layer structure consisting of an upper Cr-rich layer and a lower Fe-rich layer. The thick and Cr-rich oxide layer was difficult to decompose due to the requirement for lower oxygen partial pressure. In conclusion, the oxide layer is the most influential factor, and its thickness and composition may determine carburizing efficiency in low-temperature vacuum carburizing without surface activation.

Keywords: plastic deformation; deformed structure; low-temperature vacuum carburizing; expanded austenite; natural oxide layer

1. Introduction

Austenitic stainless steels (ASSs) are the materials used in various industries due to their formability and weldability based on excellent corrosion resistance. However, ASSs have the disadvantage of a lack of durability due to their relatively low mechanical properties (hardness, strength, and fatigue resistance) in manufacturing parts, so a thermochemical process is required [1,2]. While conventional thermochemical treatment methods such as carburizing and nitriding have been applied, the inherent corrosion resistance of ASSs is impaired due to precipitates such as carbide and nitride [3,4]. To overcome this problem, a low-temperature hardening process, which is carried out below precipitate formation temperature, has been developed [5]. The low-temperature surface hardening process is a method in which carbon or nitrogen is supersaturated in the interstitial site of the FCC at a relatively low temperature [6–8]. The interstitial atoms can be supersaturated due to the influence of alloying elements, thereby increasing surface hardness, wear resistance, and fatigue resistance, because those induced the compressive stress at the surface as the lattice expands due to supersaturation. For this reason, the low-temperature hardening layer, which is supersaturated by the interstitial atoms, is called expanded austenite (or the supersaturated layer), and the inherent corrosion resistance of ASSs can be also maintained.
However, there is one important thing to assess before carrying out the thermochemical surface hardening process that can improve the mechanical properties and maintain the inherent corrosion resistance of ASSs. It is precisely to consider the effect of plastic working imparted to the material before the thermochemical surface hardening process. Plastic working causes metallurgical changes in ASSs such that the grain size is reduced, strain-induced martensite is formed, or the formation of Cr precipitates is accelerated, and these changes affect the result of the thermochemical surface hardening process. It has been reported [9–11] that the carburizing and nitriding performed in a low-temperature region are also affected by whether plastic deformation of the material is applied or not. They reported that on equiaxed tensile strained AISI 304, strain-induced martensite was formed thereby increasing the formation rate of the low-temperature nitride layer and CrN precipitates. Other research results have been published that show that the formation rate of the low-temperature nitride layer was increased when deformation was applied to the surface through the Surface Mechanical Attrition Treatment (SMAT) process [12,13]. On the other hand, in the case of AISI 316L, in which martensite was not easily formed by plastic working, the depth of the low-temperature hardening layer was not measurably affected by whether to generate plastic deformation or not [14].

However, the results of the above research, although desirable, may tend to be inconsistent when the process method is changed. This is because the researchers removed the natural oxide layer and Beilby layer of ASSs with a surface activation step using electro-polishing or halogen gases (NF₃, HCl, etc.) before low-temperature surface hardening [15,16]. If these layers were present, it would have been difficult to confirm the clarity of the study because the natural oxide layer and Beilby layer interfere during the diffusion and solid solution of nitrogen. The removal process of these layers (surface activation) is considered an essential step in the low-temperature surface hardening of ASSs using gas atmosphere, but it is not required in low-temperature vacuum carburizing, which is being recently researched [17–20]. This is because low-temperature vacuum carburizing is the technology that simultaneously performs the removal of the oxide layer (surface activation) using the strong active characteristics of acetylene, and also because the natural oxide layer is spontaneously decomposed due to the low partial pressure of oxygen generated by the reaction of the process gases in a vacuum atmosphere [21]. Therefore, the state of the natural oxide layer can be a major factor in the carburizing efficiency of the low-temperature vacuum carburizing process. This is because the deformed structure and phase formed by plastic working not only affect the diffusion of carbon atoms but also the formation of a natural oxide film. Research on the correlation between a plastically deformed structure and carburizing efficiency in low-temperature vacuum carburizing has been reported in [18], but it focuses mainly on the deformed structure and diffusion. It was reported that the deformed structure was formed as nano-sized grains on the outermost surface, thus causing a low carburizing efficiency because diffusion was interrupted by the changed grains. In addition, it also showed that the plastically worked material was inefficient for carburizing because the oxide layer was formed thickly by the deformed structure (nano-sized grain) and that it can be removed with a suitable range of oxygen partial pressure by controlling the ratio of acetylene and hydrogen. However, research data are insufficient to apply low-temperature vacuum carburizing quickly and easily to the industries. Therefore, it is necessary to improve the low-temperature vacuum carburizing efficiency by studying the natural oxide film changes because the deformed structure including the diffusion interference factors has already been studied.

In this study, the step of low-temperature vacuum carburizing without surface activation was performed on AISI 316L which had a plastically deformed structure and a natural oxide layer. In order to control the accumulated strain and microstructure, solution and stress-relieving heat treatment were performed on the plastic-worked AISI 316L, and the formation rate and characteristics of the low-temperature carburized layer according to the decreasingly deformed structure by heat treatment were investigated. Based on the experimental results, the changes in the natural oxide layer and deformed structure of ASSs due
to plastic deformation and recovery are confirmed, and its effect on the low-temperature vacuum carburizing process is discussed.

2. Materials and Methods

2.1. Material and Heat Treatment

The specimens of cold-worked AISI 316L (ASTM A193-B8M CL2) used in this study were manufactured by drawing and were made in the form of disks (diameter (D) and thickness (T) of 32 and 7 mm, respectively). The specimen showed a tensile strength of 758 MPa, yield strength of 675 MPa, elongation of 28%, reduction in area of 68%, and average hardness of 342 HV$_{0.3}$. The stress-free specimen was prepared via solution heat treatment at 1353 K for 3 h using the cold-worked specimen. To obtain stress-relieving specimens, the cold-worked specimens were subjected to heat treatment in an argon atmosphere for 1 h at 973 and 623 K, which are the stress-relieving temperatures of general ASSs. After heat treatment, the Vickers hardness of the material was measured as 150 HV$_{0.3}$, 250 HV$_{0.3}$, and 280 HV$_{0.3}$, respectively, in the order of the heat-treatment temperature. After each treatment, the specimens were ground with silicon carbide papers from 180 to 2000 grit. Mechanical polishing with a 1 µm diamond suspension was conducted to achieve a mirror-like surface finish. The polished specimens were exposed to an atmosphere of 50 °C and 50% humidity for 3 h in the environmental test chamber in order to make a uniform passive layer. Immediately after the exposure, the low-temperature vacuum carburizing process was performed.

2.2. Low-Temperature Vacuum Carburizing

Low-temperature vacuum carburizing was performed in a commercial vacuum carburizing furnace (VH556-10, Rübig, Austria). High purity acetylene (C$_2$H$_2$, 99.80%) and hydrogen (H$_2$, 99.999%) were used as the process gases. Low-temperature vacuum carburizing was carried out for 10 and 14 h with a carburizing potential (Kc) of 1.41 at a working pressure of 800 Pa and a temperature of 723 K. After carburizing, the specimens were cooled to a temperature below 473 K in 60 s under a pressure of 5 bars of nitrogen gas to control any unexpected irregular phase transformation. At the end of this process, the specimens attained the ambient temperature in 10 min.

2.3. Characterization

The specimens after carburizing were etched in aqua regia for 3 min and observed using optical microscopy (OM; Nikon Eclipse LV 150NL, Nikon, Tokyo, Japan). The changes in the average grain size and grain boundary dependent on the heat treatment were analyzed by electron backscattered diffraction (EBSD; SU6600, Hitachi, Tokyo, Japan). The EBSD data were analyzed using orientation imaging microscopy software (OIM Analysis, EDAX, Draper, UT, USA). X-ray diffraction (XRD) analysis was conducted for phase identification at room temperature using the conventional symmetric Bragg–Brentano geometry by an X-ray generated by monochromatic Cu-Kα radiation (Ultima IV, Rigaku, Tokyo, Japan). The XRD measurements were conducted at 30 to 90 degrees and used radiation operating at 40 kV and 30 mA with a step size of 0.02. The detector used was a dual-type ultra-silicon strip (D/TeX) with an 8 mm first slit and 0.3 mm second slit, and the radius of the horizontal goniometer combined with D/TeX was 185 mm. The (111) γ peak of austenite was defined with ICDD pdf #00-033-0397. An X-ray photoelectron spectroscopy (Sigma probe XPS system, Thermo fisher Sci., Waltham, MA, USA) depth profile was obtained with a beam size of 400 µm to analyze the thickness and composition of the natural oxide layer in the initial and heat-treated specimens. Al-Kα X-rays (hν = 1486.74 eV) were used as the primary radiation source. Analysis parameters were 1 eV for the survey scan and 0.1 eV for the high resolution scan energy step size, in CAE scan mode with 37° of take-off angle (TOA). The ion beam sputter raster size was 2 mm, and the etched rate was 0.18 nm/s. The XPS spectra were recorded in the depth direction from the surface every 10 s for a total of 300 s. The XPS spectra were recorded for a 2p3/2 level of Ni, Cr,
and Fe and for a 1 s level of O and C. Quantitative elemental analyses were performed using Avantage software (Thermo Fisher Sci., Waltham, MA, USA). The quantification was carried out using relative sensitivity factors (RSF) provided in the database of the Avantage software. In addition, to analyze the natural oxide layer of the specimens, specimens were prepared in a cross-section using a focused ion beam and observed under 200 kV using transmission electron microscopy (JEM 2010, JEOL, Tokyo, Japan). The TEM specimen preparation process was as follows: a pure Pt coating was applied to the polished material to prevent further oxidation and contamination. After that, specimens were collected using FIB and TEM images were measured.

3. Results and Discussions

The heat treatment was respectively conducted to compare the state of the plastic deformation and the gradually relieving stress, because diffusion, the driving force behind low-temperature vacuum carburizing, is affected by the state of the material. These AISI 316L specimens subjected to either plastic deformation, solution heat-treatment, or stress-relieving treatment (623 K, 973 K) were measured by Electron Backscatter Diffraction (EBSD) to observe the microstructure and strain distribution.

Figure 1 shows EBSD results images and values of the low-angle grain boundary (LAGB), high-angle grain boundary (HAGB), and kernel average misorientation (KAM) for each specimen. The grain boundary, which is the main diffusion pathway, showed differences according to the deformation states of the specimens. The plastically deformed (Deformed AISI 316L) specimen was found to have the highest amount of LAGB and HAGB. Stress-relieving heat-treated (SR AISI 316L) specimens were shown to have a lower amount of HAGB and LAGB relative to the deformed AISI 316L due to grain growth and recovery. In the case of the solution heat-treated (Solution AISI 316L) specimen, HAGB and LAGB were significantly reduced as recrystallization and grain growth had occurred. The change in misorientation (KAM value) was confirmed since the misorientation of the local grain is also a factor that can affect the diffusion of atoms. From the KAM map in Figure 1e–h, it was confirmed that the Deformed AISI 316L had many deformed structures due to plastic working, and these were uniformly distributed throughout the material. On the other hand, in the SR AISI 316L (623 K, 973 K) specimens of Figure 1f, g, it was confirmed that the misorientation within the grain structure was reduced as the heat treatment temperature increased. In case of the Solution AISI 316L specimen, the deformed structure disappeared due to recrystallization and the misorientation was only observed in a few grain boundaries. The plastic equivalent strain was confirmed in order to represent at a glance each specimen in a metallurgically different state by plastic deformation and recovery heat treatment. The plastic equivalent strain rate of specimens in this study was quantified and compared using the following Equation (1) revealed in the study of Githinji et al. [22]. KAM_{e} and ε are average KAM values and equivalent strain, respectively. The equivalent strain of each specimen was derived as 0.74 (Deformed AISI 316L), 0.66 (SR at 623 K), 0.58 (SR at 973 K), and 0.02 (Solution at 1323 K), showing a similar trend to the EBSD analysis result.

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KAM_{e} = 3.314 - \frac{3.014}{1 + (\frac{\varepsilon}{0.770})^{1.178}}
\]

The EBSD results showed that the Deformed AISI 316L had a lot of grain boundaries which are the main path of diffusion and the misorientations which indicate geometrically necessary dislocation (GND). When the deformation was relieved through heat treatment, the grain boundary and the misorientation tended to decrease as the heat treatment temperature increased. The plastic equivalent strain and KAM value did not decrease significantly up to 973 K, but it was confirmed that the grain gradually recovered and the misorientation inside the grain progressively decreased with an increasing heat treatment temperature. Therefore, it was predicted that the Deformed AISI 316L would have the highest carburizing efficiency when low-temperature vacuum carburizing was carried out.
This was because the diffusion path was the greatest in the Deformed AISI 316L among the plastically deformed specimens. In order to confirm whether the carburizing result according to this prediction occurred, specimens with different amounts of deformation were subjected to low-temperature vacuum carburizing.

![Inverted pole figure and KAM map of AISI 316L with different deformed states](image)

**Figure 1.** Inverse pole figure and KAM map of AISI 316L with different deformed states; (a,e) plastically deformed AISI 316L, (b,f) 623 K stress-relieving treated, (c,g) 973 K stress-relieving treated, and (d,h) 1353 K solution-treated AISI 316L.

Deformed, Solution, and SR (623 K, 973 K) AISI 316L specimens were subjected to the low-temperature vacuum carburizing process unrequired for the surface activation step for 10 h. The formation rate of the carburized layer was different depending on the strain rate within the specimen, and the low-temperature carburizing layer was shown in Figure 2. In the Deformed AISI 316L specimen, the carburizing layer was not formed uniformly (Figure 2a) and only an island-shaped carburizing structure at a depth of approximately 9.2 μm was observed. On the contrary, a uniform carburized layer of about 14.8 μm was formed in the Solution AISI 316L specimen (Figure 2d). It can be seen that the SR AISI 316L specimens with an intermediate deformation between Deformed AISI 316L and Solution AISI 316L were non-uniformly formed from 3.8 to 13.5 μm in terms of carburizing layer thicknesses. In order to confirm whether a similar pattern was observed when the carburizing time was increased, low-temperature vacuum carburizing was carried out for 14 h and the results were shown in Figure 2’s inset images. After carburizing for 14 h, the thicknesses of the carburized layers that formed uniformly on all specimens increased to 14.5~18.7 μm. However, grain boundaries and deformed structures originating from the base material were observed within the carburized layer, except for the Solution AISI 316L specimen. In general, the defects (e.g., twins and grain boundary) could not be observed within the carburized layer due to expansion of the lattice by the interstitial solid solution of carbon atoms after low-temperature carburizing. The situation in this study (the situation in which
the defects were observed) that the grain boundaries were observed within the carburized layer may have appeared because the lattice expansion did not sufficiently occur due to low carbon content dissolved into the layer. Therefore, it was considered that the difference in dissolved carbon content occurred according to the deformed state of the specimen before carburizing. To confirm in more detail the point predicted from the OM result, the carburized layer was analyzed through XRD.

![Figure 2](attachment:figure2.png)

**Figure 2.** Cross-section of microstructure of austenitic stainless steel after low-temperature vacuum carburizing process for 10 h and 14 h (inset images); (a) plastically deformed AISI316L, (b) 623 K stress-relieving treated, (c) 973 K stress-relieving treated, and (d) 1353 K solution-treated AISI 316L.

The information from the ICDD pdf file 00-033-0397 exhibited the common name as AISI 304. Its chemical composition is different from AISI 316L. In the case of 316L with a higher Mo content, the (111) γ peak occurs at a lower angle because the lattice constant must be larger due to the influence of Mo. However, in the XRD results of cold-worked AISI 316L and heat-treated AISI 316L before carburizing in this study, (111) γ peaks were confirmed in the range of 43.60° ~ 43.65°. This opposite peak shift in the base material was presumed to be the effect of plastic deformation. However, the XRD results were used for the purpose of comparing after carburizing only according to the degree of deformation of the material. Thus, the values of Figure 3b were calculated based on two theta of (111) γ of the ICDD pdf 00-033-0397 (43.60°). The (111) γ peaks of austenite after the low-temperature carburizing process were shifted more toward the lower two theta than the peak of the base material because lattice expansion occurred due to a supersaturation of carbon without precipitation. Furthermore, the peaks were shifted to the lower two theta when a higher amount of carbon was dissolved. Figure 3 shows the results of X-ray diffraction analysis, confirming the lattice expansion of the specimen before and after carburizing. In the diffraction pattern of the (111) γ plane measured on the specimen subjected to carburizing treatment for 14 h, it was confirmed that low-temperature carburizing was performed well because all peaks of the carburized specimens were shifted to a lower two theta compared to the base material before carburizing (Figure 3a). It was also shown that the peaks of the (111) γ plane tended to be narrower and shifted to a lower angle in accordance with a reduced deformed structure by heat treatment (from 42.85° to 42.65°). The lattice
expansion rate was calculated by d-spacing obtained using Bragg’s law and shown in Figure 3b. The lattice of the Deformed AISI 316L specimen was expanded by 1.67%. As the temperature of the heat treatment increased, the lattice expansion rate increased by 1.78%, 2.01%, and 2.12%, respectively. Figure 3b also showed the predicted carbon content derived by Equation (2) based on the lattice constants. The predicted carbon content in Figure 3b was derived using the research results of Hummelsjø et al. [23]. Equation (2) is shown below (a is the lattice constants, $X_c$ is the weight percent of carbon):

$$a = 0.35965 \text{[nm]} + \left(0.0028 \pm 9.07 \times 10^{-5}\right)X_c \text{[wt.%C]} \quad (2)$$

The carbon content in the Deformed AISI 316L specimen was predicted to be 2.05 wt.%C, and the carbon content in the SR AISI 316L specimens increased when the stress-relieving treatment temperature increased. In the case of the Solution AISI 316L specimen in which the deformed structure was almost removed, the highest carbon content among the specimens was shown—2.64 wt.%C. From the above results, it was confirmed that the lattice expansion and the dissolved carbon content were increased when the decreased deformed structure was made by plastic deformation. Similar to the OM analysis result, the XRD result also confirmed that the lattice expansion of the Solution AISI 316L specimen was the greatest, and the carbon content of the carburized layer was relatively uniform through the small FWHM.

Figure 3. The results of phase analysis of AISI316L carburized for 14 h; (a) peak shift and broadening of (111)$\gamma$ plane, (b) d-spacing of (111) $\gamma$ plane and estimated carbon concentrations.

According to other studies [9,10,24], it was found that the increase in dislocation density and the formation of strain-induced martensite in accordance with plastic working did not affect the formation of the carburized layer or rather increased the carburizing rate. In this study, however, it was confirmed that the carbon content and thickness of carburized layer were decreased after low-temperature carburizing when the many deformed structures remained. Since these conflicting results, it may be surmised that other reasons be at play due to differences in the process. By comparison with the results of other studies, it was inferred that there were other reasons why the formation of the low-temperature carburized layer was disturbed by the deformed structure. As in the results of Li et al. [25], the nano-grained Beilby layer generated by plastic working may interrupt the diffusion of carbon. Alternatively, it may be because the natural oxide layer was formed differently from the conventional state on the nano-sized deformed layer generated with plastic working, as in the research of Ge [18]. As a result of this study, carried out without the surface activation step, it was confirmed that the carburized structure (expanded austenite) was formed only in some regions in the Deformed AISI 316L specimen during
the 10 h carburization, and in the case of the Solution AISI 316L specimen, the shape of the layer was formed in the same process. When the carburizing was performed for 14 h, although the shape of the carburized layers was almost formed in all specimens whether the deformed structure remained or not, the thicknesses were different for each specimen. In carburizing for 14 h, the difference in the thickness of the carburized layer meant that the diffusion of the interstitial atoms was disturbed by the deformed structure in each specimen. In addition, as previously mentioned in [18], there was another reason for the difference in carburizing efficiency, because the natural oxide layer formed differently from the conventional state on the nano-sized deformed layer generated with the plastic working. It was regarded that the required time for decomposition of the natural oxide layer during the carburizing process was different, because all specimens in this study stabilized the natural oxide layer in the same environment after polishing. Therefore, the natural oxide layer of specimens before carburizing, in which the deformation state was changed by plastic working and heat treatment, was concretely analyzed.

The natural oxide layer formed on the surface of all carburized specimens was analyzed in the depth direction by X-ray photoelectron spectroscopy and the result is shown in Figure 4a. Iron (Fe) content on the outmost surface was lower than 20 at.% but gradually increased below a depth of 7 nm. In addition, it was shown in the surface region that Fe content tended to be relatively higher as the heat treatment temperature was increased. Chromium (Cr) content was less than 7 at.% at the outermost surface, but it was immediately increased in an inward direction and stabilized at 12~14 at.% below a depth of 10 nm. However, it was shown that Cr content was increased rapidly to about 15 at.% at a depth of 2 nm for the Deformed and SR 623 K AISI 316L specimen, and then decreased and stabilized below a depth of 7 nm. In the other two specimens, also, Cr content increased from 7 at.% to 10~12 at.% up to a depth of 2 nm; however, there was no significant change after 2 nm. Oxygen content was measured about 45–53 at.% at the outermost surface in all specimens, and rapidly decreased in a depth direction and stabilized below a depth of 5 nm. A large amount of the oxygen content was measured in the order of the quantity of retained deformed structure, and the thickness of the natural oxide layer (*1/2 point of maximum oxygen content (please note: this follows the SEMI F60 standard for indirect verification)) was also 2.1 nm (Solution), 2.8 nm (SR 973 K), 3.2 nm (SR 623 K), and 3.9 nm (Deformed). In other words, the oxygen content and the thickness of natural oxide layer increased as the amount of deformed structure increased. This tendency was confirmed more specifically with the images taken by transmission electron microscopy shown in Figure 4. In the SR 623 K AISI 316L specimen, the deformed structure was mostly maintained and a natural oxide layer with a thickness of about 2.7 nm was observed (Figure 4b, black arrows). Nevertheless, the existence of oxide clusters over 5 nm was observed in some areas (Figure 4b, white arrow) On the other hand, in the case of the Solution AISI 316L specimen, the deformed structure was not observed, and a uniform oxide layer of 1.2 nm was formed without oxide clusters (Figure 4c).

As mentioned in the previous results, the thickness and composition of the natural oxide layer were changed according to the difference and presence in the deformed structure formed by plastic working and post-heat treatment. The natural oxide layer of the Deformed AISI 316L specimen was the thickest when the deformation structure was reduced due to an increase in heat-treatment temperature, and the thickness of the natural oxide layer decreased linearly. The composition of the natural oxide layer showed a tendency divided into particular differences with a heat-treatment temperature based on about 623 K. In terms of diffusion, the formation of a thick oxide layer in the Deformed AISI 316L specimen may be supposed to be due to the many diffusion paths generated by plastic working. Additionally, it was considered that the main diffusion path was the high-angle grain boundary. Although the LAGB significantly decreased only in the Solution AISI 316L specimen, the thickness and composition of the natural oxide layer were gradually changed according to the heat-treatment temperature. This means that pipe diffusion of oxygen atoms through the dislocation of strain-hardened austenitic stainless
steel did not significantly affect the formation of the natural oxide layer. Therefore, it was considered that diffusion of oxygen atoms and oxygen-friendly metal-based atoms through the high-angle grain boundary had a greater effect on the formation of the natural oxide layer [26]. In this aspect, the results of composition analysis, that the CrOy was formed more dominantly than FeOx until a depth of 5 nm in the natural oxide layer on the Deformed AISI 316L specimen, can be considered as follows: Cr atoms that have higher oxygen affinity than other metals were diffused relatively quickly along the high-angle grain boundary, and when more high-angle grain boundaries generated by plastic working remained, a relatively high Cr concentration was induced on the surface region of the natural oxide layer. This was because Cr (and substitutional metal) atoms were fixed in the grain boundaries and the dislocations at the non-equilibrium state generated by plastic working, and then the Cr atoms rapidly diffused outward through the path when the surface was exposed to oxygen from the outside [27,28]. As a result, a relatively thick oxide layer was formed and the Cr-rich oxide layer was more predominantly formed on the outermost surface because there were many grain boundaries from the fine grains by plastic working. This result was also found by Gui et al. [29], who reported that a natural oxide layer having a bi-layer structure composed of an upper Cr-rich oxide film and a lower Fe-rich oxide film was formed on the fine grain in the surface region by plastic working.

(a)

![Graph](image)

(b)

![Micrograph](image)

(c)

![Micrograph](image)

**Figure 4.** (a) The results of depth profiling of Fe, Cr, and O by XPS analysis of specimens heat treated in various temperature conditions before low-temperature vacuum carburizing (non-treatment, 623 K, 973 K, and 1323 K), and microstructures of natural oxide layer by TEM after heat treatment at (b) 623 K and (c) 1323 K before low-temperature vacuum carburizing.
The natural oxide layers, with different thicknesses and compositions, also affected the carburizing efficiency. For the same reason as a natural oxide layer, the Deformed AISI 316L specimen with the most dislocations and grain boundaries should have higher carburized efficiency or not negative significant influence since carbon diffusion is faster than stress-relieved specimens. However, the opposite result was obtained; it is confirmed from this result that the decomposition of the natural oxide layer affects the carburizing efficiency more in the absence of the surface activation process. In low-temperature vacuum carburizing only using acetylene and hydrogen, there were typically two known decomposition methods of the oxide layer (surface activation). These were influenced by the thickness and composition of the oxide layer. In the first method, as mentioned in our previous result [20], the free radicals, which were generated during the carburizing reaction, removed the natural oxide layer [17,18]. The second method was to keep the oxygen partial pressure low so that the oxide layer spontaneously decomposed [18]. When the free radicals generated during the reaction of unsaturated hydrocarbon gas decomposed the thick and/or dense natural oxide layer, it took long time to remove it. Additionally, the oxygen partial pressure for spontaneous decomposition of the Cr-rich oxide layer was about $10^{-10}$ bar lower than that of the Fe-rich oxide layer. Therefore, the thicker the Cr-rich oxide film, the more difficult it is to remove. Thus, it was considered that the removal of a thick Cr-rich oxide layer formed by plastic working was difficult during the low-temperature vacuum carburizing process. As a result, the carburizing rate is inevitably slowed.

In this study, it was conjectured that the carburizing efficiency was relatively low because of the thick Cr-rich natural oxide layer and non-uniform natural oxide cluster that formed in some regions of the Deformed AISI 316L specimen. In addition, since the removal time of the natural oxide layer and the clusters increased relatively, the diffusion time was lacking compared to the total process time so that the carbon content was relatively reduced. In order to confirm this conjecture, the natural oxide layer was removed using a commonly known mixture of nitric acid and hydrofluoric acid (nitric–hydrofluoric acid). After that, low-temperature vacuum carburizing was performed to confirm carburizing efficiency (Figure 5). When the natural oxide layer was effectively removed, a carburizing layer of similar thickness was formed regardless of the deformed structure. In conclusion, the thickness and composition of the natural oxide layer were the most important factors for carburizing efficiency in the low-temperature vacuum carburizing process without a surface activation step.
In conclusion, a deformed structure by plastic working is the most important factor for carburizing efficiency could be improved. In conclusion, a deformed structure by plastic working is the most important factor for carburizing efficiency could be improved.

4. Conclusions

In this study, the effect of plastic deformation applied to AISI 316L in the low-temperature vacuum carburizing process without the surface activation step was investigated. In the case of AISI 316L, with many deformed structures, the natural oxide layer was formed more thickly, with a bi-layer structure consisting of an upper Cr-rich layer and a lower Fe-rich layer, and the Cr-rich oxide layer being more predominantly formed on the outermost surface. When the low-temperature vacuum carburizing was performed for a relatively short time, the carburized layer on the specimen with a deformed structure was thin, or only carburized clusters were formed, and even if the carburizing time was increased, the carburizing efficiency was not improved. However, when the deformed structure was reduced by heat treatment, the natural oxide layer was thinner and the Cr-rich oxide layer was reduced, thereby increasing carburizing efficiency. Consequently, when the thick and Cr-rich oxide layer was formed by a deformed structure, it was considered that the efficiency of surface activation by free radicals was further reduced and the lower oxygen pressure required for spontaneous decomposition of oxide was demanded, thereby slowing the carburizing reaction. Therefore, it was found that to obtain a uniform carburized layer on the plastic worked AISI 316L, a longer process time was required in the low-temperature vacuum carburizing. In addition, it was confirmed that when the plastic worked AISI 316L was subjected to heat treatment to recover the deformed structure, the low-temperature vacuum carburizing efficiency could be improved. In conclusion, a deformed structure by plastic working is the most important factor for carburizing efficiency in the low-temperature vacuum carburizing process without a surface activation step because it changes the composition and the thickness of the natural oxide layer.

Figure 5. Cross-section of microstructure of austenitic stainless steel after 14 h low-temperature vacuum carburizing process with surface activation; (a) plastically deformed AISI316L, (b) 623 K stress-relieving treated, (c) 973 K stress-relieving treated, and (d) 1353 K solution-treated AISI 316L.
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References
1. Michal, G.M.; Ernst, F.; Heuer, A.H. Carbon paraequilibrium in austenitic stainless steel. Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 2006, 37, 1819–1824. [CrossRef]
2. Bell, T. Surface engineering of austenitic stainless steel. Surf. Eng. 2002, 18, 415–422. [CrossRef]
3. Collins, S.R.; Williams, P.C.; Marx, S.V.; Heuer, A.H.; Ernst, F.; Kahn, H. Low-Temperature Carburization of Austenitic Stainless Steels. In ASM Handbook, Volume 4D: Heat Treating of Irons and Steels; Dossett, J., Totten, G., Eds.; ASM International: Materials Park, OH, USA, 2014; Volume 4, pp. 451–460. ISBN 978-1-62708-066-8.
4. Tsujikawa, M.; Yoshida, D.; Yamauchi, N.; Ueda, N.; Sone, T.; Tanaka, S. Surface material design of 316 stainless steel by combination of low temperature carburizing and nitriding. Surf. Coat. Technol. 2005, 200, 507–511. [CrossRef]
5. Ichii, K. Structure of the ion-nitrided layer of 18-8 stainless steel. Technol. Rep. Kansai Univ. 1986, 27, 135.
6. Cao, Y.; Ernst, F.; Michal, G.M. Colossal carbon supersaturation in austenitic stainless steels carburized at low temperature. Acta Mater. 2003, 51, 4171–4181. [CrossRef]
7. Ernst, F.; Avishai, A.; Kahn, H.; Gu, X.; Michal, G.M.; Heuer, A.H. Enhanced carbon diffusion in austenitic stainless steel carburized at low temperature. Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 2009, 40, 1768–1780. [CrossRef]
8. Martin, F.J.; Natishan, P.M.; Lemieux, E.J.; Newbauer, T.M.; Bayles, R.A.; Kahn, H.; Michal, G.M.; Ernst, F.; Heuer, A.H. Enhanced corrosion resistance of stainless steel carburized at low temperature. Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 2009, 40, 1805–1810. [CrossRef]
9. Bottoli, F.; Winther, G.; Christiansen, T.L.; Somers, M.A.J. Influence of Plastic Deformation on Low-Temperature Surface Hardening of Austenitic Stainless Steel by Gaseous Nitriding. Metall. Mater. Trans. A Phys. Metall. Mater. Sci. 2015, 46, 2579–2590. [CrossRef]
10. Bottoli, F.; Winther, G.; Christiansen, T.L.; Somers, M.A.J. Influence of Plastic Deformation on Low Temperature Surface Hardening of Austenitic and Precipitation Hardening Stainless Steels by Gaseous Nitriding. HTM J. Heat Treat. Mater. 2015, 70, 228–238. [CrossRef]
11. Peng, Y.; Gong, J.; Jiang, Y.; Fu, M.; Rong, D. The effect of plastic pre-strain on low-temperature surface carburization of AISI 304 austenitic stainless steel. Surf. Coat. Technol. 2016, 304, 16–22. [CrossRef]
12. Chemkh, M.; Retraint, D.; Roos, A.; Garnier, C.; Waltz, L.; Demangel, C.; Proust, G. The effect of surface mechanical attrition treatment on low temperature plasma nitriding of an austenitic stainless steel. Surf. Coat. Technol. 2013, 221, 191–195. [CrossRef]
13. Balusamy, T.; Sankara Narayanan, T.S.N.; Ravichandran, K.; Park, I.S.; Lee, M.H. Influence of surface mechanical attrition treatment (SMAT) on the corrosion behaviour of AISI 304 stainless steel. Corros. Sci. 2013, 74, 332–344. [CrossRef]
14. Peng, Y.W.; Gong, J.M.; Jiang, Y.; Fu, M.H.; Rong, D.S. Influence of Plastic Pre-Strain on Low-Temperature Gas Carburization of 316L Austenitic Stainless Steel. Appl. Mech. Mater. 2016, 853, 178–183. [CrossRef]
15. Collins, S.R.; Schiroky, G.H.; Marx, S.V.; Williams, P.C. Concurrent flow of activating gas in low temperature carburization. U.S. Patent 10,246,766 B2, 2 April 2019.
16. Somers, M.A.J.; Christiansen, T.L. Gaseous processes for low temperature surface hardening of stainless steel. In Thermochemical Surface Engineering of Steels: Improving Materials Performance; Mittemeijer, E.J., Somers, M.A.J., Eds.; Woodhead Publishing Series in Metals and Surface Engineering; Woodhead Publishing: Sawston, UK, 2014; pp. 581–614. ISBN 978-0-85709-592-3.
17. Christiansen, T.L.; Hummelshøj, T.S.; Somers, M.A.J. Gaseous carburising of self-passivating Fe–Cr–Ni alloys in acetylene–hydrogen mixtures. Surf. Eng. 2011, 27, 602–608. [CrossRef]
18. Ge, Y. Low-Temperature Acetylene-Based Carburization and Nitrocarburizing of 316L Austenitic Stainless Steel. Ph.D. Thesis, CASE Western Reserve University, Cleveland, OH, USA, 2013.
19. Ge, Y.; Ernst, F.; Kahn, H.; Heuer, A.H. The Effect of Surface Finish on Low-Temperature Acetylene-Based Carburization of 316L Austenitic Stainless Steel. Metall. Mater. Trans. B Process Metall. Mater. Process. Sci. 2014, 45, 2338–2345. [CrossRef]
20. Song, Y.; Kim, J.H.; Kim, K.S.; Kim, S.; Song, P.K. Effect of C2H2/H2 Gas mixture ratio in direct low-temperature vacuum carburization. Metals 2018, 8, 493. [CrossRef]
21. Hsieh, M.-C.; Ge, Y.; Kahn, H.; Michal, G.M.; Ernst, F.; Heuer, A.H. Volatility Diagrams for the Cr-O and Cr-Cl Systems: Application to Removal of Cr2O3-Rich Passive Films on Stainless Steel. *Metall. Mater. Trans. B* 2012, 43, 1187–1201. [CrossRef]

22. Githinji, D.N.; Northover, S.M.; Bouchard, P.J.; Rist, M.A. An EBSD Study of the Deformation of Service-Aged 316 Austenitic Steel. *Metall. Mater. Trans. A* 2013, 44, 4150–4167. [CrossRef]

23. Hummelshøj, T.S.; Christiansen, T.L.; Somers, M.A.J. Lattice expansion of carbon-stabilized expanded austenite. *Scr. Mater.* 2010, 63, 761–763. [CrossRef]

24. Peng, Y.; Chen, C.; Li, X.; Gong, J.; Jiang, Y.; Liu, Z. Effect of low-temperature surface carburization on stress corrosion cracking of AISI 304 austenitic stainless steel. *Surf. Coat. Technol.* 2017, 328, 420–427. [CrossRef]

25. Li, Z.; Illing, C.; Heuer, A.; Ernst, F. Low-Temperature Carburization of AL-6XN Enabled by Provisional Passivation. *Metals* 2018, 8, 997. [CrossRef]

26. Gulbransen, E.A. Kinetic and Structural Factors Involved in Oxidation of Metals. *Ind. Eng. Chem.* 1949, 41, 1385–1391. [CrossRef]

27. Benafia, S.; Retraint, D.; Yapi Brou, S.; Panicaud, B.; Grosseau Poussard, J.L. Influence of Surface Mechanical Attrition Treatment on the oxidation behaviour of 316L stainless steel. *Corros. Sci.* 2018, 136, 188–200. [CrossRef]

28. Gupta, R.K.; Birbilis, N. The influence of nanocrystalline structure and processing route on corrosion of stainless steel: A review. *Corros. Sci.* 2015, 92, 1–15. [CrossRef]

29. Gui, Y.; Zheng, Z.J.; Gao, Y. The bi-layer structure and the higher compactness of a passive film on nanocrystalline 304 stainless steel. *Thin Solid Films* 2016, 599, 64–71. [CrossRef]