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The Effect of C₂H₂/H₂ Gas Mixture Ratio in Direct Low-Temperature Vacuum Carburization

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Abstract: The effect of the acetylene and hydrogen gases mixture ratios in direct low-temperature vacuum carburization was investigated. The gas ratio is an important parameter for producing the free radicals in the carburization. The free radicals can remove the natural oxide film by the strong reaction of the hydrocarbons, and then thermodynamically activity can be increased. When the gas ratio was below 1, the supersaturation expanded austenite layers were formed on the surface of the AISI 316L stainless steel, which had the maximum carbon solubility up to 11.5 at.% at 743 K, were formed. On the other hand, when the gas ratio was above 1, the carbon concentration of them remained low even if the process time was enough increased to reach the maximum carbon solubility. As a result, the carbon concentration underneath the surface was determined to be highly dependent on the gas mixture ratio of acetylene and hydrogen. In conclusion, it is necessary to restrict the ratio of acetylene and hydrogen gases to total mixture gases to form the expanded austenite layer with the high carbon concentration in the direct low-temperature vacuum carburization.

Keywords: Direct Surface Activation; Low-Temperature Vacuum Carburization; Expanded Austenite; Supersaturation; Acetylene;

1. Introduction

Austenitic stainless steel is used in a variety of industrial applications due to excellent corrosion resistance, mechanical properties, and especially low-temperature toughness. However, it has poor wear resistance and hardness for the application of the parts requiring high mechanical properties. Meanwhile, surface hardening technologies such as nitriding, carburizing and nitrocarburizing have been extensively studied [1]. However, austenitic stainless steel has a limitation in that it has to need the low temperature in the surface hardening treatment such as above due to reducing the corrosion resistance. So, low-temperature carburization was proposed and commercialized to enhance surface mechanical properties such as hardness and wear resistance with keeping the inherent corrosion resistance of austenitic stainless steel [2–7]. It is because carbon atoms penetrate into the austenite matrix to be the supersaturated solid solution [8].

The natural oxide film on the austenitic stainless steel prevents the penetration of carbon atoms into the austenite matrix, and the solubility of carbon is extremely decreased [9,10]. Thus, the additional process must be required for removal and/or conversion of the natural oxide layer on the surface in order to improve the mechanical properties of austenitic stainless steel in low-temperature carburization. Such the surface activation has been researched to improve the

efficiency of carbon atoms penetration into austenitic stainless steel since the 1960s. The traditional surface activation methods can be classified as follows: a) to remove the oxide layer with a chloride resin [11], a metal halide salt bath [12], and a halide gases [13], b) to penetrate carbon atoms easily using the iron thin films [14] and c) to break the oxide layer by high energy ion bombardment such as plasma sputtering. [15] Compared with the traditional methods, the latest method of exposing to the halogen gas atmosphere containing gases such as HCl, NF₃, and Urea acid, etc., has been commercially used [2,7,13].

However, alternative ways are demanded to solve the environmental problems which those gases are very toxic. So, the acetylene gas (C₂H₂) as a carbon source is recently studied to remove the natural oxide layer and improve carburization efficiency in carburization [16–18]. The mechanism of carburization in acetylene is elucidated as follows: first, adsorption and decomposition of C₂H₂ gas on the solid surface at the certain temperature and it subsequently the carbon species to be a development of radical [19,20], those can be soluble into iron. At the same time, the natural oxide film can be removed by the activation energy of radical gas [20].

Such low-temperature carburization with C₂H₂ gas has been researched about the effects of activity and diffusion rate by changing of process temperature and time [17,21,22]. In carburization, C₂H₂ gas causes the sufficient reactions even with a small amount for carburization in a vacuum and a decrease of the oxygen partial pressure so that the natural oxide layer can be naturally decomposed [17,22]. Due to the characteristic of acetylene at the low-temperature regime, carburization in a vacuum was proposed to control soot and/or metal dusting easily. [16] And in another study has been researched the change of the carbon activity and the partial pressure of oxygen according to the ratio of the process gas. [17]

Nevertheless, it is lack of studies on the effect of the C₂H₂ gas ratio of total process gases in low-temperature vacuum carburization. Therefore, the theoretical and experimental studies are essentially demanded because the process gas ratio, an important experimental parameter that affects the carburization efficiency, produces radicals that cause strong reaction of the hydrocarbons and determines thermodynamic activity by vacuum degree and gas ratio [16,20].

In this study, we focused on the carburization effects according to a mixture ratio of C₂H₂ and H₂ gases in low-temperature vacuum carburizing process. After the treatment, the results of carburization thickness, carbon concentration, and hardness depth profiles were observed, and then the experimental data were compared with calculated data based on the other numerical study [4]. On the premise of validity, the influences of gas ratio on the carbon solubility (para-equilibrium carbon concentration) and the critical mixture value of C₂H₂ and H₂ gases confirmed by an increase of carburization time and the change of gas ratio during the process are discussed.

2. Materials and Methods

In this study, the numerical simulations were carried out by a computational calculation before direct low-temperature vacuum carburization to obtain a uniform carburization layer thickness of at least 20 μm. The numerical simulations were based on the finite difference method, where Fick's 2nd law was discretized as a finite difference approximation in the dimensions of the penetration depth of x (μm) and treatment time of t (s) [23,24]. The Crank-Nicolson algorithm was used for the computational calculations. The boundary conditions of AISI 316L stainless steel (ASS) were fixed, such as the maximum carbon solubility C_{max} at the gas-metal interface of 11.5 at%. pct [7] and diffusion coefficient D of 4.5×10^{-5} μm²/s at 743 K (470 °C) at infinite dilution obtained from research of Agarwala et al. [25]. However other studies [23,24] indicate that the diffusion coefficient depends on the concentration during diffusion of the dissolved carbon atoms into the metal. Therefore, the diffusion coefficient of D needs to be calculated by changing the concentration dependence of the diffusion coefficient of D' . The D' can be calculated from the well-known Equation (1).

$$D' = D \exp\left(k \frac{C}{C_{max}}\right) \quad \text{Equation (1)}$$

The ASS rods were made of round bar type and cut to $\Phi 31\text{mm} \times \text{T}7\text{mm}$ for the test samples. The chemical compositions of the samples are given in Table 1. Before carburization, the samples were annealed for 3hr at 1353K. Those were polished with silicon carbide papers from 180 to 2000 grit and mechanical at a final step with a $1\text{ }\mu\text{m}$ diamond suspension to achieve a mirror-like surface finish. Finally, surface contaminations were removed by ultrasonically cleaning in acetone and ethanol solution, respectively.

Table 1. Chemical compositions of commercial grade AISI 316L

	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Fe
AISI 316L	0.02	0.48	1.8	0.03	0.02	10.03	16.66	2.05	4.3	Bal.

Direct low-temperature vacuum carburization was performed in a commercial vacuum carburizing furnace (VH556-10, Rübiger, Austria) with detailed experimental conditions as shown in Table 2. The furnace chamber was evacuated to 1 Pa for 6 hours at 743K before the tests in order to remove the impurities in the furnace and stabilize the samples. Acetylene gas (C_2H_2) high purity (99.90%) and hydrogen gas (H_2) highest purity (99.999%) were used as the process gases. Those were mixed at a gas ratio of 0.05, 1 and 10 and introduced during the test. The total amount of the process gases was maintained a constant at 300 standard liter per hour (SLH), and the flow rate of those remained similar in all processes. Also, carburization was performed at a working pressure of 800Pa and temperature of 743K. After carburization, the samples were cooled to 473 K in 60 seconds with 5 bars of nitrogen gas to control the unexpected irregular changes and reached to room temperature in 10 minutes.

Table 2. Experimental conditions of direct low-temperature vacuum carburization.

Exp. No	Gas mixture ratio	Gas composition	Time (hour)	Temp (K)	Pressure (Pa)
A-1	0.05	0.05 C_2H_2 – 0.95 H_2	14	743	800
A-2	1	0.5 C_2H_2 – 0.5 H_2	14		
A-3	10	0.91 C_2H_2 – 0.09 H_2	14		
A-4	1	0.5 C_2H_2 – 0.5 H_2	42		
A-5	10	0.91 C_2H_2 – 0.09 H_2	42		
A-6	0.05	0.05 C_2H_2 – 0.95 H_2	3.5		
A-7	0.05	0.05 C_2H_2 – 0.95 H_2	7		
A-8	0.05 → 10	0.05 C_2H_2 – 0.95 H_2 0.91 C_2H_2 – 0.09 H_2	7 → 7		

All samples were examined after carburization as follows. The samples were etched in aqua regia for 10 minutes and observed using optical microscopy (OM) of Nikon Eclipse LV 150NL. Micro Knoop’s hardness was measured by a hardness tester of Mitutoyo HM210 with a load of 98 mN for 15 seconds. X-ray diffraction (XRD) analysis was applied to characterize the phase identification in the conventional symmetric Bragg-Brentano geometry with x-ray created by monochromatic $\text{Cu-K}\alpha$ radiation using Ultima 4 diffractometer (Rigaku, Japan). The carbon concentration and thickness of carburization layer were determined with the conditions of 700 V, 30 mA, 20 points/sec and cal. factor 0.7 by Glow Discharge Optical Emission Spectroscopy (GDOES), GDS850A spectrometer (LECO, USA).

3. Results

In this study, direct low-temperature vacuum carburization was conducted to investigate the effects of the C_2H_2 and H_2 gases mixture ratios on the formation of the carburization layer, which is

well known as expanded austenite layer. The ratios of C₂H₂ gas to the total gases and the process time were changed. The other conditions were constant at both working pressure 800 Pa and temperature 743 K in all carburization treatments as mentioned in the experimental method.

Fig. 1 shows the cross-sectional OM images of ASS samples carburized at various the gas mixture ratios of 0.05, 1 and 10. The expanded austenite layer clearly separated from the substrate can be observed in Fig. 1(a) and (b), cross-sectional images of samples carburized at the conditions of A-1 and A-3, respectively. While the expanded austenite layer was uniformly formed at the condition of A-1, it was not at the condition of A-3, in which the thickness deviation of 5 μm was observed. In Fig. 1(c), the sample carburized at a condition of A-4 appears the expanded austenite layer with a uniform thickness of about 35 μm . On the other hand, the sample carburized at a condition of A-5 showed the maximum thickness of about 30 μm in the expanded austenite layer, and it showed an ununiformed wave patterns with a thickness variation of 15 μm .

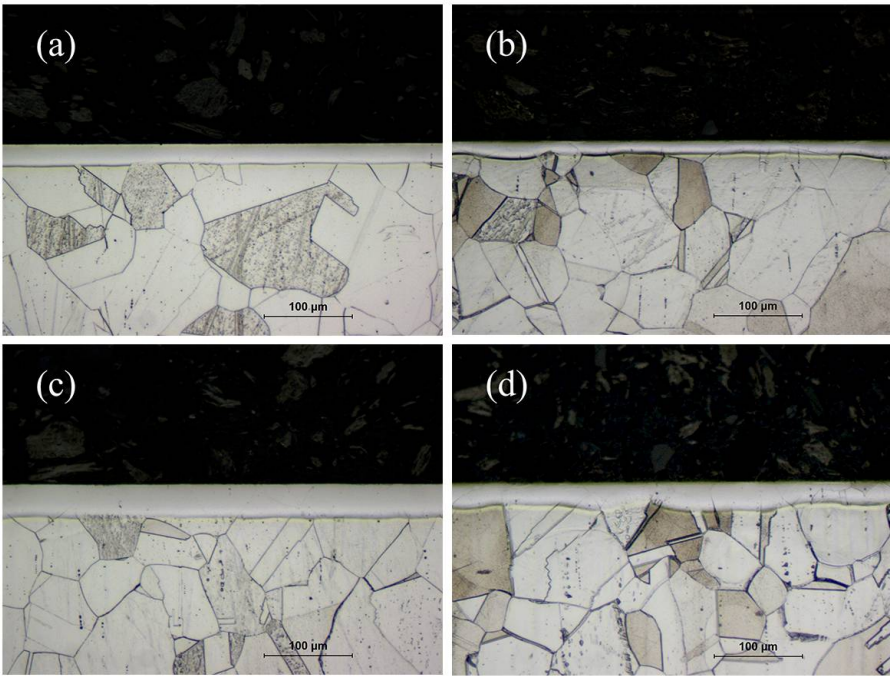


Figure 1. Cross-sectional optical microscope images of the ASS carburized with validation of gas mixture ratios (a) ratio 0.05 and (b) ratio 10 for 14h, (c) ratio 1 and (d) ratio 10 for 42h.

Fig. 2 shows the results of numerical simulation and experimental data obtained by GDOES analysis. In Fig. 2(a), the carbon concentration depth profiles were obtained from the calculated and experimental data of the ASS samples carburized for 14 hours at gas ratio of 0.05, 1 and 10. In numerical simulation, the boundary conditions applied the values mentioned in experimental to the diffusion equation. Further, the concentration dependence of diffusion coefficient was calculated using Equation (1). The simulated carbon concentration depth profiles from other researchers [24,25] presented the best fit corresponded to $k = 5.0$ at Equation 1 [4,24], but the profile obtained for the experimental data the best fit corresponds to $k = 2.0$ in this study. The difference of k value as compared with others results may be because the carbon concentrations effectively reach the para-equilibrium solubility limit at the beginning of the treatment by a removal of the natural oxide film before the low-temperature vacuum carburization[24,25]. Also, it is a difference between the calculated and experimental data that the carbon concentration underneath the surface is higher than that of maximum carbon solubility of 11.5 at. %. The reason is due to protruding a large amount of carbon sticking and/or absorbed to the surface at the beginning of the sputtering, which is inherent in the GDOES used to measure the carbon concentration [26]. So, the y-axis intercept, which is the value in the y-axis that meets by extending a straight line toward the surface from the slope at the point of 1 μm where the high concentration of the surface abruptly drops, is about 11.5 at.% and may be considered as the surface concentration in this study. The values of maximum carbon

concentration showed both 11.5 at.% at the conditions of A-1 and A-2, and gradually decreased toward the depth, which is equal to the substrate concentration of 0.1 at.% in the depth of 23 μm . On the other hand, the carbon concentration showed a maximum value of 7.5 at. % underneath the surface of the sample carburized at the condition of A-3 and is equal to that of the substrate in the depth of 17 μm . Fig. 2(b) shows the calculated and experimental data of the samples carburized at the conditions of A-4 and A-5. The calculated data was agreement with the experimental result obtained in the condition of A-4. The maximum carbon concentration appeared at 1 μm underneath the surface, and the concentration was more steeply decreased since about 20 μm and the shape of concentration profiles was almost the same as compared with the result obtained in the condition of A-2.

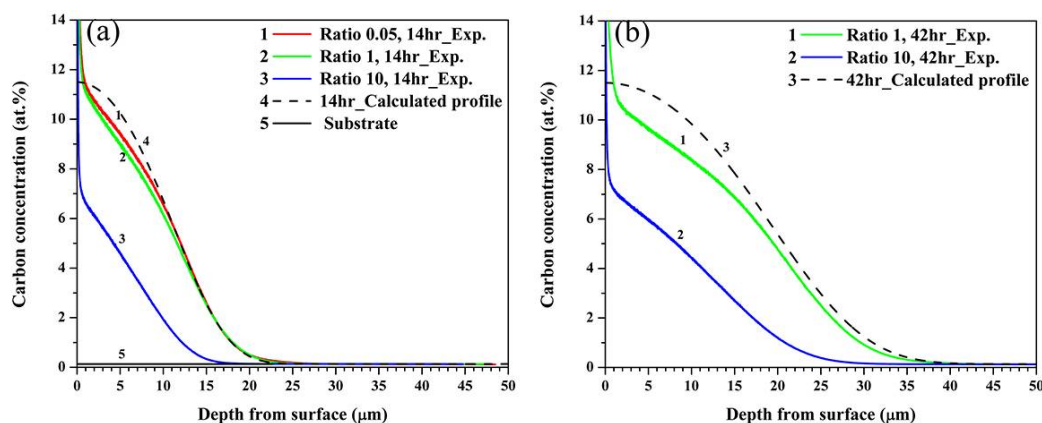


Figure 2. GDOES carbon concentration depth profile of the ASS samples carburized for (a) 14h and (b) 42h.

Fig. 3 presents the crystal structure of the ASS samples carburized with various the gas mixture ratios of 0.05, 1 and 10 by XRD analysis. In Fig.3 (a), the strong intensity peaks of γ -Fe phases, two preferred orientations of (111) and (200), were observed. The peaks of untreated sample were found at two-theta of 43.44° and 50.58° . However, it can be seen that the peaks of all the carburized samples shifted toward the lower angle direction than that of the untreated sample. In the condition of A-3, the peaks of (111) and (200) were found at two-theta of 42.77° and 49.39° , respectively. In the condition of A-1, the peaks of (111) and (200), which were the most shifted in XRD scans, were observed at two-theta of 42.35° and 48.96° , respectively. The shift of the peak means that the FCC lattice is expanded by increasing the lattice constant, a , which were 0.3606 nm in an untreated sample and 0.3694 nm in the condition of A-2

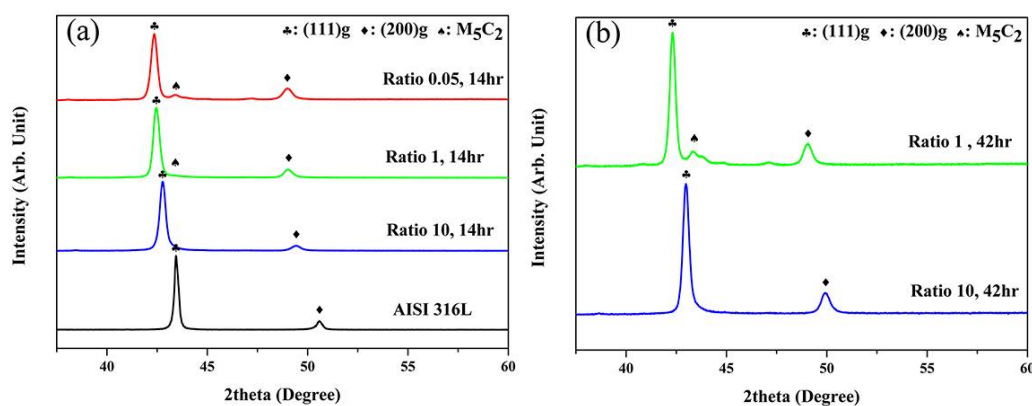


Figure 3. XRD diffraction patterns obtained from the ASS carburized for (a) 14h and (b) 42h.

Also, the weak intensity peak belong to a second phase was observed at two-theta of 43.33° corresponded to a plane spacing $d \approx 0.2086$ nm in results obtained at the conditions of the only A-1 and A-2, where the value of the maximum carbon concentration was about 11.5 at.%. As a result, it

can be presumed that the phase has a crystal structure of M_5C_2 , the Hägg carbide [4,27] which is known to form at more carbon concentration of 11 at.% in the previous studies [4]. In XRD results of Fig. 3(b), the (111) peak in XRD result of the sample carburized at the condition of A-4 was slightly shifted by 0.2° toward the lower angle than that obtained in the result obtained at the condition of A-2, and the Hägg carbide peak was also observed with slightly increased intensity. In the condition of A-5, however, XRD result was obtained almost same to the results of the sample carburized at the condition of A-3. That is, the (111) peak was observed at approximately the same position at the conditions of A-3 and A-5, but the peak of M_5C_2 was not detected.

In Fig. 4(a), the maximum hardness values of the samples carburized at the conditions of A-1 and A-2 were 812 and 747 $H_{K0.01}$ at 2 μm , respectively, but both the hardness values were sharply decreased from about 8 μm , and appeared the substrate hardness values of 150 $H_{K0.01}$ at 22 μm . On the other hand, the hardness value of the sample carburized at the condition of A-3 was max. 480 $H_{K0.01}$. It was rapidly decreased from about 2 μm and appeared 150 $H_{K0.01}$ at 17 μm . As shown in Fig. 4(b), the hardness value of the sample carburized in the condition of A-4 was max. 890 $H_{K0.01}$ at 2 μm , and it was kept above 550 $H_{K0.01}$ until about 20 μm and appeared the substrate hardness value at about 35 μm . In case of sample carburized at the condition of A-5, however, the maximum hardness value was slightly increased to 550 $H_{K0.01}$ as compared with the sample carburized at the condition of A-3. (See figure: error bars denote the standard error of the mean on the hardness values in the expanded austenite layer with the wide range deviations of $\pm 100 \sim 200 H_{K0.01}$, because this was represented by averaging the hardness values of each of thin and thickness layers to calculate the standard error.)

The values of the maximum carbon concentration and hardness of Fig. 2 and Fig. 4, were not largely changed as compared to the samples carburized for 14 hours despite having had enough carburization process time. However, the carbon concentration and hardness below maximum value area were high in the condition of 42hr as compared to the sample carburized for 14 hr. As follow these results, it was confirmed that the hardness depth profiles show a very similar behavior to the carbon concentration depth profiles.

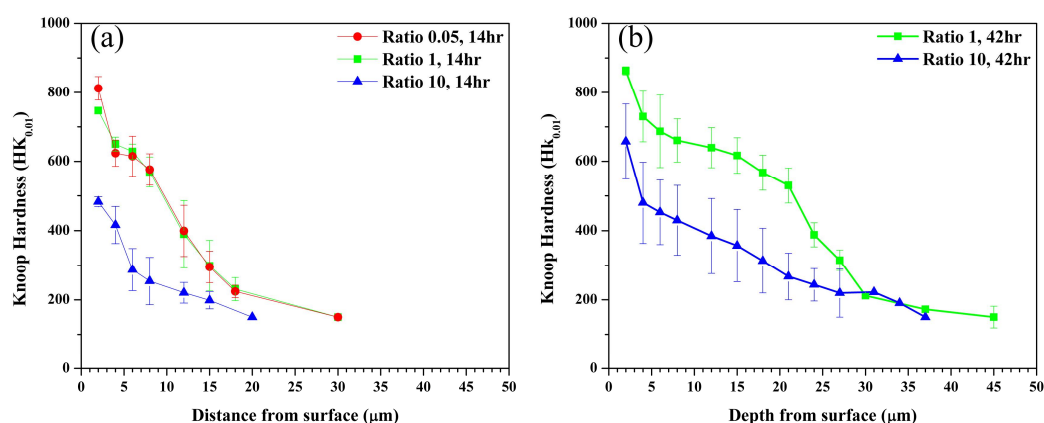


Figure 4. Hardness depth profile of carburized ASS for (a) 14h and (b) 42h.

In Fig. 5, the cross-sectional microstructure images, carbon concentration, and hardness depth profiles were appeared with the samples carburized for 3.5 hours, A-6 (a), 7 hours, A-7 (b), and for 7 hours at gas ratio 0.05 followed by 7 hours at gas ratio 10, A-8 (c). Fig. 5 (a), (b) and (c) show the cross-sectional images of samples carburized at the three conditions of the order mentioned in the previous sentence and in which expanded austenite layers are the thicknesses of 13, 15 and 17, respectively. The thicknesses are almost similar to those found from the results of the carbon concentration depth profiles in Fig. 5 (d) and the hardness depth profiles in Fig. 5 (e).

The carbon concentrations underneath the surface of the samples carburized at the conditions of A-6 and A-7 were similar to both about 11.5 at.% in Fig. 5 (d). In the condition of A-8, however,

the carbon concentration underneath the surface was decreased from the high concentration of 11.5 at.% formed after the sample carburized at the condition of A-7 and it is similar to the result obtained at the condition of A-3. As comparing the two results obtained at A-3 and A-8, it can be seen a difference that carbon concentration was slightly higher at the condition of A-8 since 5 μm . Fig. 5(e) shows the hardness profiles of samples carburized with previous mentioned the conditions of A-6, A-7 and A-8. The hardness appeared max. 680 $\text{Hk}_{0.01}$ of sample carburized at the condition of A-7, and then it was drastically decreased to that of substrate. In cases of the samples carburized at the conditions of A-3 and A-8, all the hardness values were similar and lower maximum 480 $\text{Hk}_{0.01}$ than that of the sample carburized at the condition of A-7. However, the expanded austenite layer of the sample carburized at A-8 was the thickness of about 20 μm due to the process time is equal to the result obtained at the condition A-3.

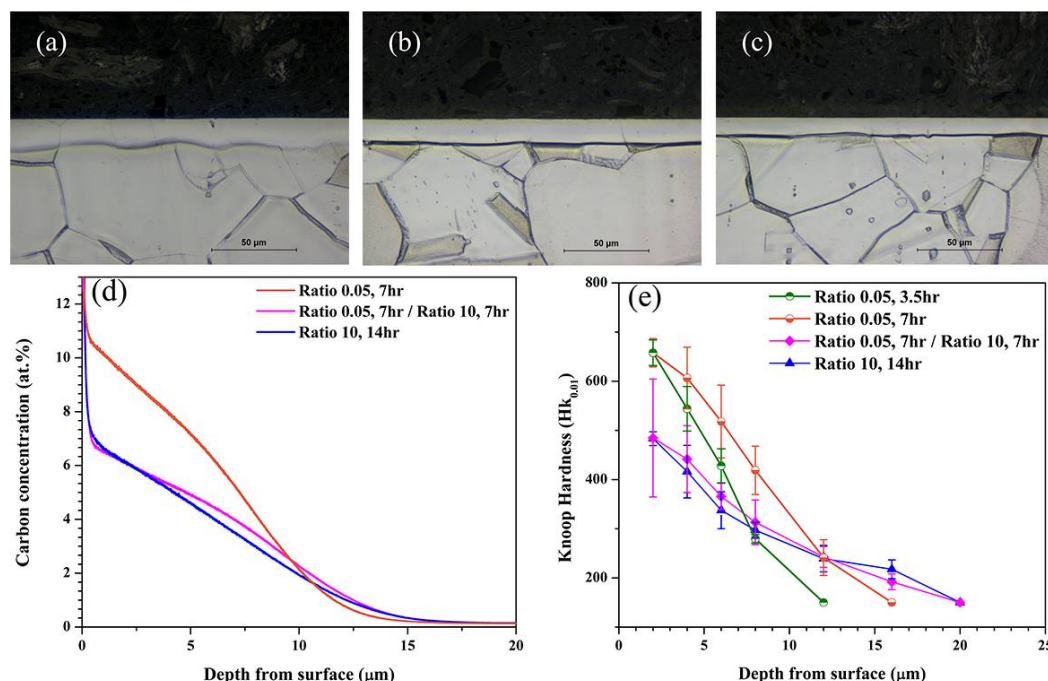


Figure 5. Cross-sectional optical microscope image of ASS carburized by gas mixture (a) ratio 0.05 for 7 hours followed by 10 for 10 hours, (b) ratio 0.05 for 7h and (c) ratio 0.05 for 3.5h, (d) GDOES carbon concentration depth profile of carburized ASS by gas mixture ratio 0.05 for 7h, ratio 0.05 for 7 hours followed by 10 for 10 hours and ratio 14 for 10 h and (e) hardness depth profile of carburized ASS by gas mixture ratio 0.05 for 7h, ratio 0.05 for 3.5h, ratio 0.05 for 7 hours followed by 10 for 10 hours and ratio 14 for 10 hours

4. Discussion

As shown in the experimental results, the yield of the expanded austenite layer depends on the gas ratio in direct low-temperature vacuum carburization using acetylene gas. The concentration of samples carburized at the conditions of A-1 and A-2 were similar to the maximum value of 11 ~ 12 at.% [4,28] and the thicknesses of expanded austenite layer were also similar to 22 μm . On the other hand, the carbon concentration and the thickness of the layer at the condition of A-3 were significantly lower than those at the less gas ratio. In particular, the thickness was uneven and 13 ~ 18 μm in the range of large standard error.

It is generally known that acetylene is adsorbed on the surface of a metal base material [20] and decomposed into hydrogen and carbon, which is diffused and dissolved in the interstitial site. In this study, however, the carbon concentration was the lowest at the condition of A-3, which has the highest amount of acetylene, even though it has much more carbon species which can dissolve in the substrate. This means that adequate amount of hydrogen is necessary for a certain temperature in low-temperature vacuum carburization using C_2H_2 gas [20,29]. Also, it is consistent with the study that flowing high C_2H_2 with nearly infinite carbon activity is expected to increase the carbon

concentration in ASS, but the actual carburization efficiency is very low [16]. The reason why the efficiency of carburization is lowered when the ratio of C_2H_2 is greatly increased can be expected as follows [16,17]: a) difficult to increase to para-equilibrium carbon solubility limit due to a lack of free radicals generated depending on the amount of introducing H_2 gas, b) the interruption of the transfer of soluble carbon species from the gas atmosphere into the solid because of the soot and metal dust formed by the high activity of C_2H_2 gas.

In this study, the expanded austenite layers were uniformly formed on the surface except for the specific conditions. However, the soot with dark grayish color was produced after low-temperature vacuum carburization under all of the process conditions because the acetylene activity was as high as about 103 ~ 105 even in a vacuum. Accordingly, it is not a point to be considered in this study as one among the reasons of deterioration of carburizing efficiency by the interruption of the transfer of soluble carbon species in (b) due to soot and metal dust. Therefore, the reduction of the carburization efficiency in the condition of A-3 was much probably the result of decreased radicals by a lack of hydrogen gas. Due to lack of free radicals, because, if the natural oxide layer is not completely removed or para-equilibrium carbon concentration is got lower, carbon is unevenly dissolved in the austenite matrix and the carbon concentration profile in the entire carburization layer may be not increased. Generally, the formation of the carburization layer takes concentration-dependent diffusion with a function of $\ln\sqrt{Dt}$. In the bulk material carburized at low temperature, therefore, the heterogeneous solid solution of carbon atoms may have occurred (or can occurs in initial diffusion regime) due to limited expansion of the lattice by the surrounding one, different of diffusion path, or difference of carbon diffusion rate depending on the crystal orientation [30,31]. At that time, if the carbon species continue to introduce from the surface, the ASS will be able to keep maximum para-equilibrium carbon concentration continuously, and then the internal carbon concentration can be gradually increased as the carbon continues to diffuse to the inward direction. However, if the natural oxide layer is not completely removed or para-equilibrium carbon concentration is got lower, the diffusion rate is inevitably slowed due to the lack of carbon species introduced from the interface of gas and solid. Therefore, it is presumed that the expanded austenite layer in the condition of A-3 have a relatively low carbon concentration as compared to the other conditions despite the carburization at the same time.

Carburization was carried out for 42 hours in order to confirm whether the carbon concentration in the expanded austenite layer is increased with process time even though free radicals are low and the results shown in Fig.3. At a condition of A-4, the adequate free radicals were produced by enough hydrogen gas. As a result, the sample obtained a carbon concentration and the thickness of the expanded austenite layer almost similar to the maximum carbon solubility of 11.5 at.% [28] and the predicted result by theoretical calculation, respectively. In a condition of A-5, however, the thickness of the expanded austenite layer was increased to a maximum 30 μm , but it was not constant and had a large deviation as shown by cross-sectional OM image. Also, the maximum carbon concentration was equal to 7.5 at.% as compared with the result obtained at the condition of A-3. Therefore, it is summarized that the para-equilibrium carbon concentration is not even increased with the process time when the numbers of free radicals generated by the small amount of hydrogen gas ratio in the total process gases are small. These results show that carbon species are continuously supplied only at a decided concentration by generated free radicals at each process condition even if process time increases.

In the experimental results of changing the gas ratio in-process shown in Fig. 5, it can be seen that the gas ratio has a great influence on the radical formation. In a condition of A-7, it is guessed that the surface was relatively quickly activated by a number of free radicals mentioned above and then carbon atoms diffused through the surface to the substrate, thus, the expanded austenite layer was formed thinly as a high hardness layer with a uniform and maximum carbon concentration of about 11 at. %. On the other hands, when the free radicals were reduced by changing the gas ratio from 0.05 to 10, it is presumed that it is similar to the sample carburized at the condition of A-3, because the carbon concentration at the interface between gas and metal was decreased with the free radicals.

Based on these results, Fig. 6 shows a schematic of the variance in carbon concentration profile due to changes the para-equilibrium carbon concentration according to the gas ratio. In Fig. 6 (a) and (b), the influence on the formation of the expanded austenite layer by the difference in para-equilibrium carbon concentrations, $C_{eqs-g}(0.05)$ at gas ratio 0.05 and $C_{eqs-g}(10)$ at gas ratio 10, was shown. When $C_{eqs-g}(0.05)$ is high, the surface carbon concentration $C_s(0.05)$ is reached to maximum value in a short time due to the high activity of acetylene. And when the carburization time increases, it is diffused in the depth direction while maintaining the surface concentration. In case of gas ratio 10, On the other hand, the carbon concentration $C_s(10)$ on the underneath of the surface becomes lower due to the insufficient radicals, and then it does not change even if the increase of the process time, only the diffusion occurs as shown in the experimental results of Fig. 5 (d).

As shown in Fig. 6 (c) and (d), after carburization, although the gas ratio was only changed in the same carburization time, the carburization depth and the surface carbon concentration were similar. It is guessed that if $C_{eq,s-g}(10)$ is decreased from $C_{eq,s-g}(0.05)$, the carbon atoms on the dissolved in the surface by carburization at gas ratio 0.05 only diffuse into the substrate because $C_s(0.05)$ is higher than $C_{eq,s-g}(10)$, no additional carbon atoms are supplied through the interface from gas atmosphere. As shown in Fig. 6 (d), however, the difference between carbon concentration profiles has appeared as follows: When the gas ratio is changed during the process in case of one in two carburization conditions, the expanded austenite layers at both conditions have the same thickness but the deviations in the middle parts of the carbon concentration profiles occur. This means $C_{total}(0.05, 7hr)$ (total carbon concentration in the expanded austenite layer formed by the carburization for 7 hours at gas ratio 0.05), is higher than $C_{total}(10, 7hr)$, (total carbon concentration in the expanded austenite layer formed by the carburization for 7 hours at gas ratio 10). Finally, when $C_s(10)$ will be lower than $C_{eq,s-g}(10)$, the carbon atoms are introduced from the outside of gas and continuously diffused toward the substrate.

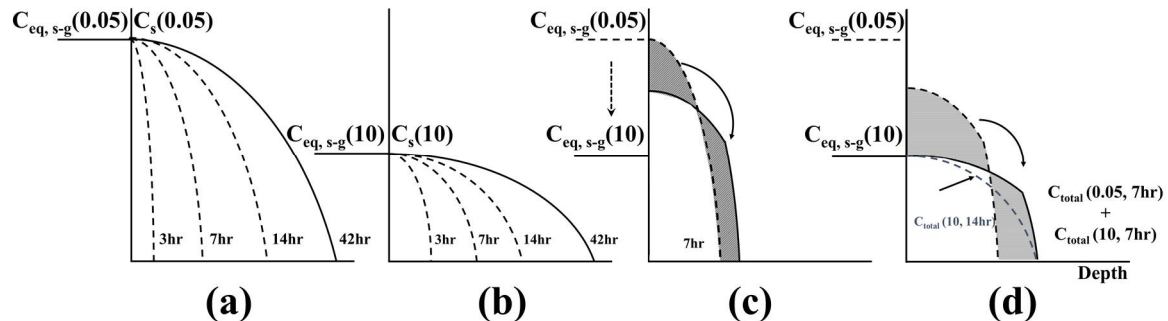


Figure 6. Schematic diagram of carbon concentration due to change of carbon para-equilibrium concentration according to the gas mixture ratio

5. Conclusions

In the present study, the effect of acetylene and hydrogen mixture gas ratios in direct low-temperature vacuum carburization was investigated. The results are summarized as follows:

AISI 316L stainless steel was carburized with the acetylene and hydrogen gas mixture ratio of 0.05, 1 and 10 at 800Pa for 14hours at 743K, these results show that an increase of acetylene gas ratio brings out lower surface carbon concentrate and thickness of the expanded austenite layer. The reason why the efficiency of the direct low-temperature vacuum carburization is decreased even though the amount of acetylene is greatly increased is as follows. The production efficiency of free radicals generated by acetylene decomposition depends on the gas ratio.

The main conclusions are as follows:

- The calculated carbon concentration profiles based on the diffusion model with concentration dependence of diffusion coefficient was agreement with the experimental results of

AISI 316L stainless steel carburized at the gas ratio of 0.05, 1 and 10 and 743 K. The calculated result presented the best fit corresponded to $k=0.2$.

- While the gas mixture ratio of acetylene increases, the efficiency of carburization decreases, which also depends on an amount of hydrogen gas in the total gases. That is, when the amount of hydrogen is smaller than the gas ratio 1 in this study, the generation of free radicals is reduced. As a result, the carbon atoms, supply directly affecting the natural oxide film and/or carburization, are significantly reduced.

- When the gas ratio of acetylene was changed in the middle of the carburization, the same expanded austenite layer thicknesses and carbon concentrations were obtained in the case of the samples carburized with changing a gas ratio 0.05 to 10 and without changing the gas ratio 10. In other words, the results obtained by the carburization at a constant gas ratio and changing the gas ratio during the process were very similar as the process time was the same. These results are explained in detail by the model shown in Fig. 6

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