1. Introduction

There are many carburizing methods, such as pack carburizing, liquid carburizing, gas carburizing, vacuum carburizing and plasma carburizing according to carbon source. Most methods are performed in an environment that contains oxygen or its compounds, except for vacuum carburizing and plasma carburizing. Such processes can induce the formation of an oxidation layer underneath the surface of the metal, called “the internal oxidation”, and this has deleterious effects on the mechanical properties. However, the plasma and vacuum carburizing methods are performed in vacuum furnaces, and the internal oxidation can be avoided. In particular, plasma carburizing uses a Glow-Discharge Methane Plasma at a power density range from 0.1 to 1 watt/cm², so the transition coefficient of carbon is sufficiently high to enable a direct implantation of the workpiece. Thus, superior surface quality is achieved in plasma carburizing with a much shorter process time than any other carburizing method. Plasma carburizing could reduce energy consumption and requires less capital equipment. Reduced impact on the environment is also one of the distinguished features of this plasma technology. For these reasons, many attempts have recently been made to industrialize plasma carburizing.

These carburizing processes are remarkable methods of enhancing the surface mechanical properties of materials used in shafts, gears, bearings, and other highly stressed machine parts. Furthermore, the compressive stress generated in the hardened surface layer is known to enhance fatigue resistance.

There are many factors that affect the fatigue resistance of carburized steel. These factors include effective case depth, hardness, residual stress, surface finish, grain size, morphology and distribution of carbides, intergranular oxidation, microcracking and the presence of retained austenite.

The purpose of this study is to characterize plasma carburizing itself and the fatigue properties of plasma carburized steel compared with gas carburized steel. To compare fatigue properties between gas and plasma carburized steels, effective case depth was set as the standard factor, and then other factors, such as surface carbon content, retained austenite, residual stress, grain size, and hardness distribution were analyzed.

2. Experiment

The chemical composition of the steel used in this investigation is listed in Table 1. The specimen is modified steel from a low carbon steel (0.176C, 0.119Si, 1.014Cr, 0.387Mo) widely used in carburizing. As shown in Table 1, the modified steel contained higher Mo to improve hardenability and lower Si to reduce internal oxidation. Figure 1 shows the hardness distribution of the common carburized steel, and that of the modified steel after plasma carburizing with the

| Table 1. Chemical composition of specimen. (wt%) |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Element | C   | Si  | Mn  | P   | S   | Cr  | Mo  | Al  | Cu  | Ni  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Composition | 0.176 | 0.119 | 0.779 | 0.010 | 0.019 | 1.014 | 0.387 | 0.041 | 0.102 | 0.101 |

Fatigue Properties of Plasma Carburized Low Carbon Cr–Mo Steel

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carburizing layer and the fractured surface were observed by scanning electron microscopy. Surface carbon content was defined at the 0.05 mm point away from the free surface and it was measured by Auger electron spectroscopy under an electron beam current of 60 nA and a voltage of 10 keV. The amount of retained austenite and residual stress at the casehardened layer were measured by X-ray analysis. The specimens were electrolytically polished from the surface to 400 μm depth for the depth profile analysis. Cu Kα radiation was used with 10 mA and 30 kV operation conditions. The volume fraction of retained austenite was calculated by the ratio of four diffraction peaks: {211} and {200} peaks for martensite, and {220} and {200} peaks for austenite.\(^8\) Residual stress was calculated by the slope of the relationship between \(2\theta\) and \(\sin^2\varphi\) and the range of \(2\theta\) was from 140°–170°.

\[
\text{Residual stress} = K \frac{\Delta(2\theta)}{\Delta(\sin^2\varphi)}
\]

\(K:\) stress constant \(= 64.13 \text{ kgf/mm}^2 \) \((-632.8 \text{ Mpa})\)

\(\varphi:\) angle between incident X-ray beam and diffracted beam

3. Results and Discussions

3.1. Plasma Carburizing

3.1.1. Hardness Distributions

To determine the hardness distribution with time, plasma carburizing experiments were carried out for various times. Boost-diffuse carburizing method\(^5,\(^6\) consisting of 15 min carburizing, 30 min diffusion and another 15 min carburizing, was performed at 900°C. Other carburizing conditions were as follows: reaction gas was CH\(_4\), pressure was 6 Torr (800 Pa), and current density 4 mA/cm\(^2\) with 100–1,500 V.

Figure 2 shows hardness profiles after plasma carburizing the specimen for 40 min. and 60 min, and after boost-diffuse carburizing for 60 min. The results were compared with those of the gas carburized specimen for 150 min at 925°C. Although plasma carburizing was performed at a lower temperature for a shorter time than gas carburizing, the effective case depths of the plasma carburized specimens increased 20–50% more than those of the gas carburized specimens. The reason was that carburizing gas such as methane was dissociated during plasma carburizing, and thus a high carbon potential can be established and maintained at the specimen surface even though the total temperature and pressure in the furnace were relatively low. The effective case depth of boost-diffuse carburized steel was deeper than that of normal plasma carburized steel, even if the carburizing time was shorter than the normal plasma carburizing time of 40 min. In the first carburizing cycle a large amount of carbon is adsorbed on the surface and diffuses into specimens by concentration gradient of carbon, and then the carbon concentration on the surface was diluted during the first diffusion cycle. After the first diffusion cycle, the specimen had a higher carbon potential than that of the gas carburized specimen.
3.1.2. Microstructure

During the gas carburizing, an oxidation layer was formed on the surface. Internal oxidation resulted in depleting the alloying element near austenite grain boundaries, which caused a local decrease in hardenability and promoted the soft transformation products in quenching.9) Also, the internal oxidation reduced fatigue resistance. 10) Figures 3(a) and 3(b) show surfaces of plasma carburized and gas carburized specimens respectively after oil quenching. The internal oxidation layer was observed to be about 10 $\mu$m thick in gas carburized steel but it did not appear in plasma carburized steel. The plasma carburizing process was carried out in a vacuum environment and did not contain oxygen, so internal oxidation was hardly observed. Figure 4 shows the surface oxidation layer in the gas carburized steel by SEM micrographs and line scanning. As shown in Fig. 4, the oxidation layer consists of Mn and Cr oxides because those elements have lower free energy of oxide formation than Fe and other elements.

3.1.3. Surface Carbon Content

Plasma carburizing depends on the adsorption rate of carbon at the surface and diffusion rate of carbon in steel. It means that the carburizing rate can be assessed according to surface carbon content. To confirm this fact, surface carbon content and effective case depth relationship was investigated in this study. Figure 5 shows the effective case depth and the surface carbon content of the plasma carburized specimen with various time at 900°C, 6 Torr (800 Pa) and 4 mA/cm$^2$. Surface carbon content was measured before the diffusion process. As expected, the effective case depth increased with surface carbon content. Surface carbon content increased rapidly at the beginning of the plasma carburizing process but after carbon content was reached near to the maximum carbon solubility about 1.22 wt% in steel, the carbon content was increasing slowly. Surface carbon content exceeded the equilibrium carbon solubility of austenite when the plasma carburizing time was longer than 60 min. The reason of exceeded carbon content on surface may be that plasma treatment increased real surface temperature higher than the measured temperature and the other reason was that many carbides were formed during plasma carburizing.

Figures 6(a) and 6(b) show boost-diffuse carburizing cycle and surface carbon content of boost-diffuse plasma carburized steel at 900°C, 6 Torr (800 Pa) and 2.5 mA/cm$^2$. The plasma was operated during the boost portion of the cycle and shut off during the diffusion portion. Total
process time was 60 min, which boost (20 min) and diffuse (20 min) were performed continuously or every 12 min respectively. In Fig. 6(b), hatched bars indicated carbon content of normal plasma carburizing for 20 min and 60 min. Surface carbon content was the highest at 5 times every 12 min cycle even if carburizing time is the shortest among plasma carburizing time. It was clear that the surface carbon content was more affected by times of cycles rather than by carburizing time. Also effective case depth increased with surface carbon content as shown in Fig. 5. The effective case depth of boost-diffuse carburized steel for 30 min was deeper than that of normal plasma carburized steel for 40 min (see Fig. 2). This boost-diffuse technique allows the use of a high carbon potential during carburizing, thereby providing an optimum rate of diffusion during the following diffusion cycle. Thus, the effective case depth is achieved in shorter time than when using a fixed carbon potential.

3.2. Fatigue Properties of Plasma Carburized Steel

Plasma carburizing and gas carburizing experiments were carried out for 60 min at 900°C, 6 Torr (800 Pa) and 2.5 mA/cm² and for 120 min at 920°C respectively for fatigue tests. After the carburizing process, diffusion and oil quenching was performed. Figures 7(a) and 7(b) show the schematic diagram of gas and plasma carburizing processes. Figure 8 shows hardness profile of plasma and gas carburized specimens for fatigue test. Dotted line for Hv 510 represents the effective case depth. As shown in Fig. 8 the plasma carburizing time, 60 min, was determined to have the effective case depth of plasma carburized steel nearly the same as that of gas carburized steel. The effective case depth of plasma carburized steel was lower than that in Fig. 2 because the plasma carburizing for fatigue test was carried out at lower current density than that of previous plasma carburizing. Surface hardness and effective case depth were almost the same. But the hardness profile near surface of plasma carburized steel was higher than that of gas carburized steel. Because surface carbon content as driving force for diffusion was higher in plasma carburized steel so diffusion of carbon into steel was faster even if carburizing time was shorter than gas carburizing time.
The result of high cycle fatigue test on carburized specimens is shown in Fig. 9. Fatigue limits of plasma carburized steels at $2 \times 10^6$ cycles were improved about 3.8% comparing to that of gas carburized one as expected. To find out the reasons of high fatigue limits of plasma carburized steels, grain size, fractography, surface carbon content, retained austenite and residual stress were investigated.

Grain size of both carburized steels was corresponding to about ASTM Number 10. In general fine-grained steels (over ASTM Number 7) show no grain growth until austenitizing temperature of 980°C. Carburizing and diffusion temperature was 900–920°C in this experiment so even if gas carburizing time was longer than plasma carburizing time, no grain growth was observed after gas carburizing.

Figure 10 shows fracture morphologies of plasma and gas carburized specimens after fatigue test. Fracture mode of plasma carburized steel was a mixture of intergranular and transgranular as shown in Fig. 10(a). However, gas carburized steels showed mostly intergranular as shown in Fig. 10(b) because internal oxidation made grain boundary so weak that crack was initiated easily at the grain boundary.

Figures 11 and 12 show the amounts of retained austenite and residual stress at surface measured by X-ray analysis. The presence of retained austenite in the hardened outer layer of carburized steels was due to the decrease of Ms (martensite starting temperature) below room temperature because of high carbon content. The amount of retained austenite was about 15–20% at the surface of plasma carburized steel and was about 5–10% at the surface of gas carburized steel. Carbon content of the fatigue tested specimens was measured by CS analyzer (carbon, sulfur analyzer, Leco CS3000) from surface to 75 μm depth. The result was that the plasma carburized steel contained 0.8752 wt% of carbon while the gas carburized one contained 0.7623 wt% of carbon. So the difference of the amount of retained austenite between the two carburized steels was due to the carbon content. Plasma carburized steels had a larger amount of retained austenite because high carbon content decreased Ms point more than that of gas carburized steel. Although the effect of retained austenite amount on fatigue properties is still controversial, large amounts of retained austenite are detrimental, since it diminish surface residual stress. However according to fracture mechanics, a plastic zone should form ahead of a growing crack tip. It is
also well known that martensitic transformation can take place when austenite is under plastic strain. Thus a fatigue crack running across a carburized layer could transform the retained austenite into martensite. Because of that, the optimum volume of retained austenite about 20–30% are known to be beneficial on fatigue endurance.15) So it was investigated whether martensitic transformation took place or not in this study. The hardness variation across the carburized zone on the fracture surface of specimen is shown in Fig. 13. Also it included the hardness curve of an untested specimen of the same plasma carburizing treatment. There was no difference of hardness distributions between the two specimens. Therefore, it seems that the martensitic transformation did not happen during fatigue testing that employed a completely reversed cycle of stress as in this study. Accordingly, small amount of retained austenite was considered to be beneficial to fatigue properties because it reduced less surface residual stress.

Residual stress is one of the most important factors that affects fatigue properties. Basically compressive residual stress which obstructed crack propagation occurred due to gradient of carbon concentration in the carburized steels. The Ms temperature was decreased with carbon content so Ms temperature at surface containing high carbon content was lower than that at core. It means that martensite transformation started firstly at core. Because of that, carburized steel has high compressive stress at the surface. Figure 12 shows residual stress of carburized steels. Compressive residual stress of the plasma carburized steel was higher than that of gas carburized steel. The oxidation layers were reported to reduce compressive residual stress.16–18) Internal oxidation layer was softer than martensite matrix so it relaxed compressive residual stress on surface and it occurred all grain boundaries in the gas carburized steel as shown in Fig. 4. And the other reason was the bombardment of the specimen's surface by molecules and ions with high kinetic energy during sputtering and carburizing.41 The bombardment may generate surface compressive stress like a shot peening in the plasma carburized steel.

Many factors such as hardness profile, oxidation layer, retained austenite, residual stress and grain size affecting fatigue properties were investigated between gas carburized and plasma carburized steels respectively. Among these, grain size and effective case depth were almost same, so retained austenite, residual stress and oxidation layer could have influenced the fatigue properties in this study. First of all, internal oxidation affected the fatigue properties greatly than any factors because it generated the cracks.

The plasma carburized steels had a larger amount of retained austenite that was not transformed into martensite and had a higher compressive residual stress on surface than that of gas carburized steel. The retained austenite did not diminish surface residual stress for plasma carburized steel.

Consequently, fatigue limit improvement of plasma carburized steel was that even if it had a higher amount of retained austenite, it did not contain the internal oxidation layer and have a higher compressive residual stress than that of gas carburized steel.

4. Conclusion

As the result of the studies, the main conclusions were derived as follows;

1) The effective case depth in plasma carburized steel at lower temperature for shorter time increased up to 50% in comparison with that of gas carburizing.

2) In case of boost-diffuse carburizing, the number of cycle times had a more effect than carburizing time on the surface carbon content.

3) Fatigue limits of the plasma carburized steel were higher than those of the gas carburized steel in the same effective case depth.

4) Transgranular fracture was the dominant failure in the plasma carburized steel.
The plasma carburized steels had a larger amount of retained austenite and had a higher compressive residual stress on surface. Among many factors that affect fatigue, internal oxidation layer and residual stress were the most important in this study.

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