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EFFECTS OF NITROGEN AND CARBON ION IMPLANTATION INTO AUSTENITIC STAINLESS STEEL ON HYDROGEN ABSORPTION

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ABSTRACT

The effect of implanted nitrogen and carbon ion into SUS 304 on the absorption of hydrogen by cathodic charging were studied. Implantations of N^+ , C^+ were performed with doses of 3×10^{17} ions cm^2 and 5×10^{17} N^+ cm^2 , and 5×10^{17} C^+ cm^2 at an energy of 90 keV. Nitrides and carbide were investigated by X-ray diffraction, Auger electron spectroscopy (AES) and scanning electron microscope (SEM). Formation of hydrides during cathodic charging were depressed by a modified surface layer. It is concluded that the both nitrides and carbides act as the barrier of hydrogen migration and the catalyst of desorption of cathodically charged hydrogen.

INTRODUCTION

Absorption of hydrogen by metals such as stainless steel and titanium alloys may lead to hydride formation and deterioration of the mechanical properties. Studies have been conducted concerning the possibility for protection against hydrogen absorption and embrittlement by mean of surface modification of the metals.^{1, 2)}

Although authors have reported the effect of nitrogen ion implantation into titanium alloys on the chemical composition and its inhibit action of hydrogen migration and take-up previously^{3, 4, 5)}, in this study, reduction of hydrogen absorption in austenitic stainless steel (SUS 304) by nitrogen ion and carbon ion implanted layer are reported.

EXPERIMENTAL

Mirror polished austenitic stainless steel (Cr; 18.25%, Ni; 8.45%, Fe; bal.) was implanted at room temperature with 90 keV nitrogen ion and carbon ion. The ion fluence was varied in the range of 3×10^{17} ions cm^{-2} to 1×10^{18} ions cm^{-2} . Hydrogen were charged cathodically in 1N $-H_2SO_4$ aq. solution for 8 and 16 hour. Modified surface layer of specimens were characterized by X-ray diffraction, Auger electron spectroscopy (AES) and Scanning electron microscope (SEM) which have been reported previously.^{3, 4)} Absorbed hydrogen content in the austenitic stainless steel was estimated apparently by glycerol displacement method.

RESULTS AND DISCUSSIONS

Figure 1 show X-ray diffraction patterns for nitrogen ion, carbon ion and $(N^+ + C^+)$ ions double implantation at 5×10^{17} ions cm^{-2} , respectively. The diffraction pattern for nitrogen ion sole implantation indicates that surface layer have Fe_2N , Cr_2N , Ni_3N phase. For carbon ion sole implantation, Fe_2C , $\text{Fe}_{2.5}\text{C}$ and $(\text{Cr}_3\text{Fe})_7\text{C}_3$ phase were observed in the surface layer. Further, $(N^+ + C^+)$ dual ion implanted modified layer indicates that complex mixed phase of Fe_2N , Fe_3C , Fe_3N , Ni_4N and $(\text{Cr}_3\text{Fe})_7\text{C}_3$ were formed.

An Auger sputtering profile of specimen before hydrogen charging are shown in Figure 2. Implanted nitrogen have maximum peak at sputtering time of 5 to 9 minute. Implanted carbon have broader distribution than that of nitrogen, having a maximum concentration peak at sputtering time of 8 to 11 minute. For $(N^+ + C^+)$ dual implantation, distribution of nitrogen was flattened, causing by influence of implanted carbon ion.

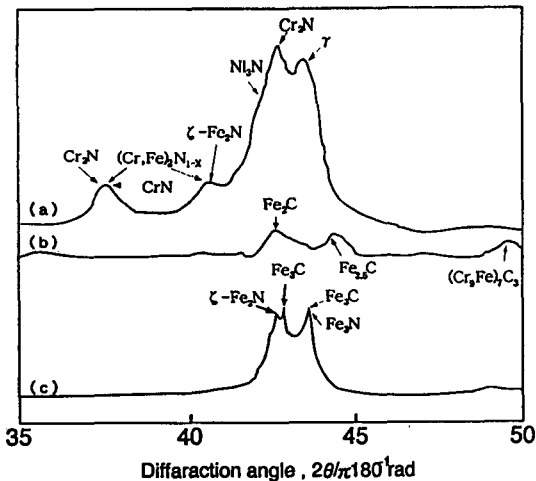


Fig. 1 X-ray diffraction patterns for sus304 stainless steel implanted with (a) $5 \times 10^{17} \text{N}^+ \text{cm}^{-2}$, (b) $5 \times 10^{17} \text{C}^+ \text{cm}^{-2}$ and (c) $5 \times 10^{17} \text{N}^+ \text{cm}^{-2}$ plus $5 \times 10^{17} \text{C}^+ \text{cm}^{-2}$

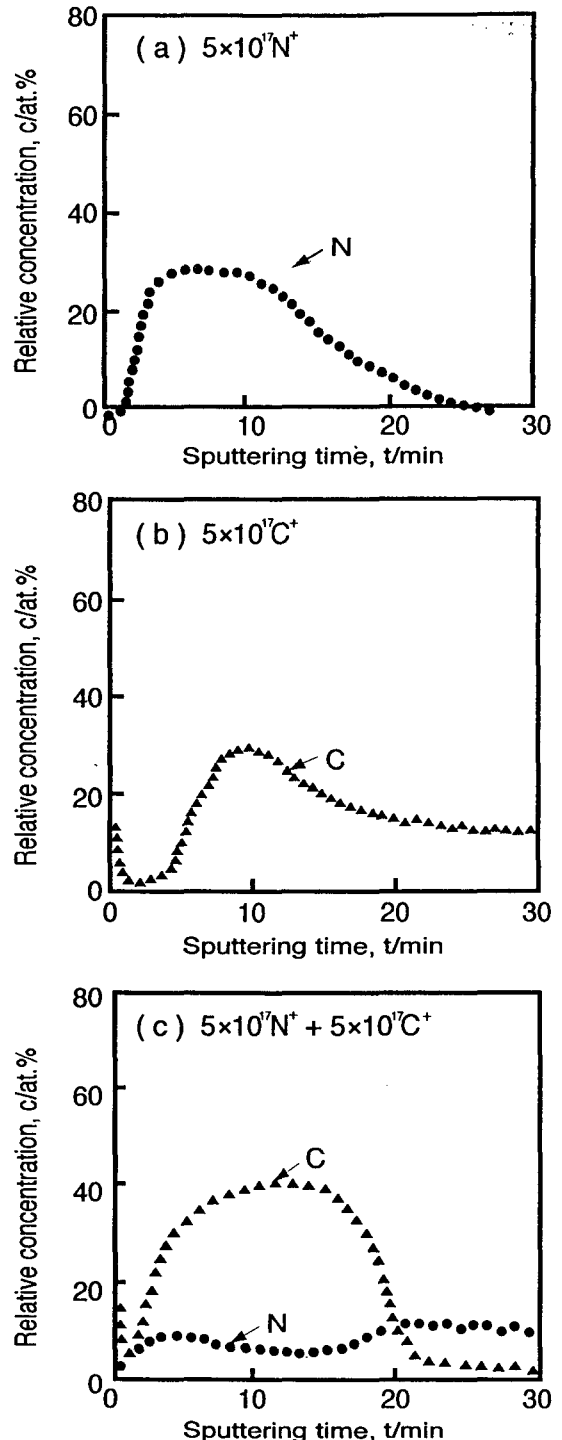


Fig. 2 Composition profiles for sus304 stainless steel implanted with (a) Nitrogen, (b) Carbon and (c) Nitrogen-plus-carbon.

After cathodic charging for 16 hour, surface phase of specimen were investigated by X-ray diffraction as shown in Figure 3. For unimplanted and nitrogen sole implanted specimen, hydrogen induced martensite ϵ and α' phase are detected. Carbon ion sole implanted specimen showed γ_H peak which is considered to depend on a solid solution of hydrides. Nitrogen and carbon double implanted specimen showed no detectable peak to correspond with ϵ , α' and γ_H phase. Depend on these results, it is deduced that greater reduction of absorption of the hydrogen which charged cathodically, is expected by both nitrogen and carbon ion implantation at fluence of 5×10^{17} ions cm^{-2} for austenitic stainless steel(SUS 304).

In order to elucidate the effects of modified surface of SUS304 by nitride and carbide, apparent hydrogen evolution volume were measured by glycerol displacement method. As shown in Figure 4, evolved hydrogen were indicated to saturate at volume of 0.16cm^3 and

20 ks for unimplanted and carbon ion implanted specimens. Nitrogen implanted specimen evolved about 0.06cm^3 and saturated within 10 ks. Whereas, nitrogen and carbon ion dual implanted specimen which can not be detected any sign of hydride for mation by X-ray diffraction, showed nearly zero volume of evolution of hydrogen. From these results, it is deduced that alloy elements of SUS 304 and its nitrides and carbides may have important role to reduce the absorption of hydrogen at modified surface layer.

Surface morphologies of specimens after hydrogen charged 16 hour are shown in Figure 5. Surface of unimplanted specimen were attacked uniformly by hydrogen charging, and grain boundary appeared clearly. Whereas the nitrogen sole implanted specimen are apparently undamaged. The carbon ion sole implanted specimen was observed a grain boundary and microcrack in the grain by etching. Surface feature of nitrogen and carbon ion dual implanted specimen was rela-

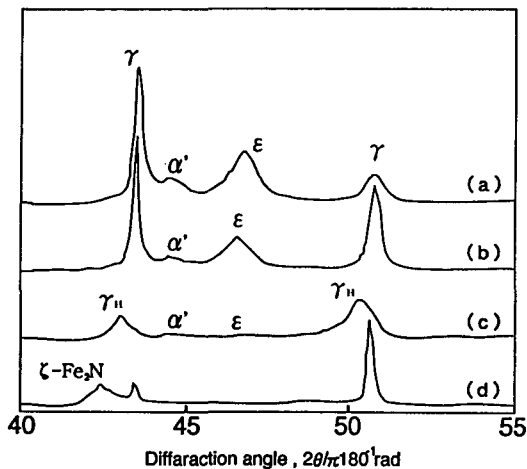


Fig. 3 X-ray diffraction patterns of sus304 steel which were charged with hydrogen at 1Acm^{-2} for 16h.
(a) unimplanted, (b) Nitrogen, (c) Carbon and (d) Nitrogen-plus-Carbon.

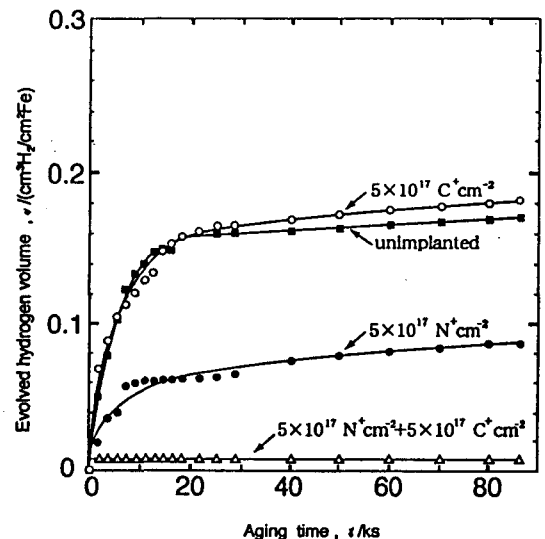


Fig. 4 The total volume of evolved hydrogen gas in sus304 steel as a function of aging time after hydrogen charging at 1Acm^{-2} for 16h.

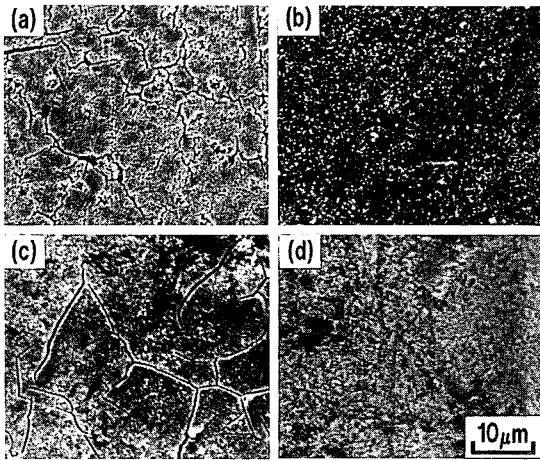


Fig. 5 SEM micrographs of SUS304 steel surfaces after hydrogen charging at 1Acm^{-1} for 16h. (a) unimplanted, (b) $5 \times 10^{17}\text{N}^+\text{cm}^{-2}$, (c) $5 \times 10^{17}\text{C}^+\text{cm}^{-2}$ and (d) $5 \times 10^{17}\text{N}^+\text{cm}^{-2}$ -plus- $5 \times 10^{17}\text{C}^+\text{cm}^{-2}$.

tively smoothed and observed no cracking in a grain.

These results are suggested that there are different action of two effects⁶⁾. One is the catalyzing action for hydrogen desorption, and other is the depressing action of migration of hydrogen in the metal. Further studies will be required to elucidate the mechanism of the action of nitrides and carbides in the modified layer.

CONCLUSION

Nitrogen ion implantation into SUS 304 showed excellent resistance to hydrogen absorption and migration. On the other hand, carbides which formed by carbon ion implantation showed lower resistance than the nitrides for the hydrogen absorption. Absorption and migration of hydrogen is reduced sig-

nificantly by $(\text{N}^+ + \text{C}^+)$ dual ion implantation.

The results may be explained in term of different action of two effects. One is the catalyzing action for recombination of hydrogen atom and the desorption of H_2 gas from modified metal surface, and other is the blocking the diffusion path for hydrogen from the surface to the bulk and protection from the hydrogen embrittlement of the metals.

Further studies will be required to elucidate in detail the mechanism of the protection by nitrides and carbides phase.

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