

Improvement of Corrosion Resistance and Structural Change in 304 Stainless Steel by means of Ion-Mixing

Yasuyuki Masumoto^{1, *}, Mitsuhiro Takeda², Takanori Suda¹, Seiichi Watanabe¹,
 Soumei Ohnuki¹, Toshiaki Ohtsuka¹ and Kazuhiro Ikezawa³

¹Department of Material Science, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

²Department of Materials Science and Engineering, Miyagi National College of Technology, Natori 989-1239, Japan

³Domestic Research Fellow, JSTCC, WERC, Tsuruga 914-0192, Japan

High-energy ion-beam mixing technique was applied for the surface modification of austenitic stainless steel, followed by electrochemical characterization and microstructural observation. The co-mixing of silicon and chromium resisted the passivation current to 1/1000 relative to the un-modified condition. The corrosion resistance improved remarkably. Microstructural observation revealed that the enhanced diffusion and induced amorphous structure introduced by the co-mixing of silicon and chromium, which played a very important role in the improvement of electrochemical behavior at surface.

(Received November 14, 2001; Accepted March 12, 2002)

Keywords: ion-beam mixing, surface modification, austenitic stainless steel, corrosion resistance

1. Introduction

Many methods have been used for improving material surface properties such as ion-implantation,¹⁾ laser heating²⁾ and other surface coatings. High-energy ion-beam implantation enables to add various solutes with non-equilibrium concentration in sub-micron surface area. In the case of direct implantation of heavy elements, the concentration can be saturated at low level due to sputtering. On the other hand, the ion-mixing method which substitutes physically deposited elements for those of material can be expected to achieve efficient modification by low ion dose.

In general, chromium coating is an effective way for improving aqueous and high temperature corrosion properties, but the coating requires a relatively thick layer and good contact on the substrate. Ion mixing is potential technique to modify the surface film properties, such as stabilizing layer structure, creating non-equilibrium phase and interface bonding. Moreover, silicon is one of important element³⁾ for improving corrosion property in chromium-oxide film. The objective of this study is to apply the ion mixing for the surface modification of SUS304L (Table 1) and to examine the electrochemical properties and microstructural change.

2. Experimental Procedure

The samples used in this work were SUS304L which was heat-treated at 1323 K, 15 min. The shape of the samples for an anode polarization curve was 0.3 mm × 10 mm ×

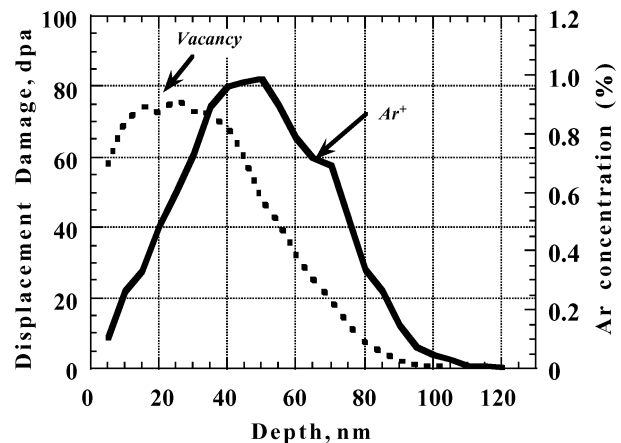


Fig. 1 TRIM96 calculation for Argon ion of 100 keV irradiated to $5 \times 10^{16}/\text{cm}^2$.

10 mm. All the specimens were polished to the mirror surface and were carefully cleaned with alcohol before deposition. Chromium and silicon were deposited in the vacuum of 3×10^{-5} Pa. Co-mixing samples were deposited in silicon followed by chromium. The thickness of coated films was about 20–30 nm. Argon ion of 100 keV was irradiated to $5 \times 10^{16}/\text{cm}^2$ at room temperature. From TRIM96 calculation (Fig. 1), the peak depth of the defects was estimated to be about 40 nm. From the irradiated surface the displacement of atom was 80 dpa in the maximum, and the remaining of argon was estimated to be less than 1 at% at the coated layer.

The electrochemical behavior was characterized by Potentio-dynamic measurements as a standard method; a silver-silver chloride reference electrode, a platinum counter electrode and 0.5% H_2SO_4 electrolyte were used. The microstructural observation was performed by transmission electron microscope (TEM) at 200 kV.

Table 1 Chemical composition of SUS304L.

C	Si	Mn	P	S	Ni	Cr
0.022	0.44	0.85	0.029	0.010	9.44	18.33

(mass%)

*Graduate Student, Hokkaido University.

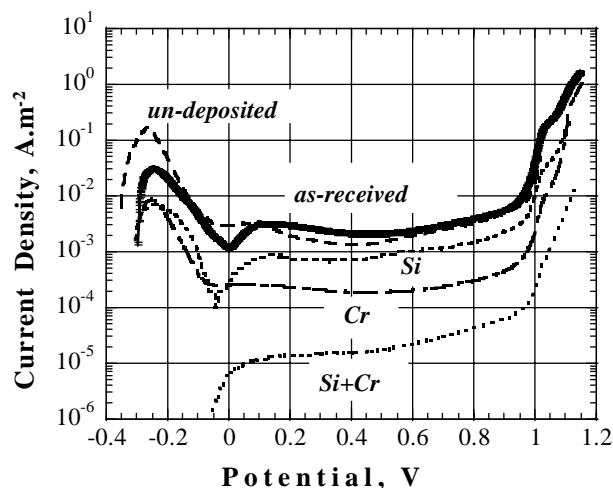


Fig. 2 Anodic polarization curves with and without ion mixing to $5 \times 10^{16} \text{ Ar/cm}^2$.

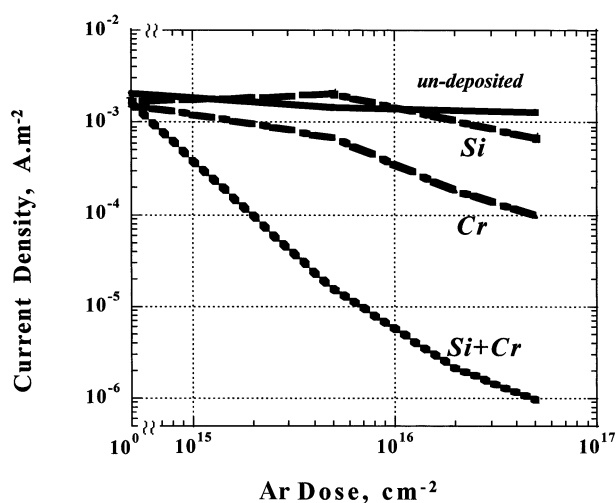


Fig. 3 Dose dependence of improving in anodic polarization (constant passivation current 0.4 V).

3. Results

3.1 Improvement of electrochemical property

Figure 2 shows the data of anodic polarization for several samples, which include un-deposited, deposited and ion mixed condition. In the case of as-deposited samples without ion mixing, there was no obvious changing comparing with any deposited samples. It can be assumed that deposited particles did not contact on the substrate due to the natural oxide layer covered on the metallic surface. This coating condition is not stable for the electric solution.

In the case of ion mixed samples, each of chromium or silicon deposition affected on the polarization curves; passivation currents decreased from the level in un-deposited sample. The ion mixing of other co-deposition of both silicon and chromium showed drastically reducing to 1/1000 in passivation current (C_p), constant passivation current (C_{cp}) and over passivation current (C_{op}), as showed in Fig. 2. This improvement in co-mixed specimens depended strongly on ion dose. Figure 3 shows C_{cp} for several specimens as the function of ion dose. Argon ion irradiation has effective reduction in C_{cp} . Co-mixing effect can be confirmed at relative dose level. The

slope of the graph descended when the implantation dose becomes more $5 \times 10^{15} \text{ cm}^{-2}$ and atom mixing was better done. $5 \times 10^{15} \text{ cm}^{-2}$ was in the order of 2–7 less than to do only an ion implantation. This is the result which shows the utility of the ion mixing. It should be noted that effective dose of ion is in the order of 10^{16} cm^{-2} for improving passivation current property.

3.2 Microstructural and compositional change in deposited layer

In Fig. 4, the pictures in the upper showed microstructures of only deposited samples. From microstructural observation of as-deposited samples, chromium deposited layer included small cracks in Fig. 4(b), which results in the agglomeration of chromium particles, whereas, silicon layer was amorphous structure in Fig. 4(c), confirmed by halo ring in diffraction pattern. The co-deposited layer of silicon and chromium showed simply superimposed microstructure, as shown in Fig. 4(d). It means that the structure is composed of fine crystalline chromium layer covered with amorphous silicon layer.

In Fig. 4, the pictures in the below showed microstructures of ion-mixing samples. In case of chromium layer, the small cracks spread and the small particles grew large in Fig. 4(f). In case of silicon layer, there were many black dots in the substrate, and the surface layer was amorphous by halo ring in diffraction pattern, in Fig. 4(g). As shown in Fig. 4(h), argon bubbles were confirmed after ion mixing, but the changing in diffraction pattern indicated that the amorphization was progressed slightly by the mixing; the deposited layer turn to be amorphous mixture of chromium and silicon.

Figure 5 shows the concentration change before and after ion implantation by SIMS (Secondary Ion Mass Spectroscopy). No obvious proof on compositional changing of chromium due to ion mixing, but silicon was spread widely after the mixing. It should be noted that silicon is a fast diffusive element and radiation-induced diffusion may occur, even at room temperature.

From those experimental evidences, remarkable improving effect on electrochemical property result in following factors; the physical joining between surface layer and substrate, stabilizing surface layer due to enhanced local diffusion, and amorphization of homogeneous layer. The irradiation-produced defects and implanted argon may be so minor for improving electrochemical properties in this condition.

4. Conclusion and Discussion

The ion mixing of silicon and chromium was carried out at 304L austenitic steel and evaluated the electrochemical surface characteristic and the structure change of the surface layer.

(1) The corrosion resistance was not affected after as-deposited condition, where deposited particles or layers may not bond with the substrate.

(2) After the mixing each of chromium or silicon, the corrosion property was improved, where the physical mixing may stabilize the bonding condition between deposited layer and substrate.

(3) The ion mixing after co-deposition of silicon and

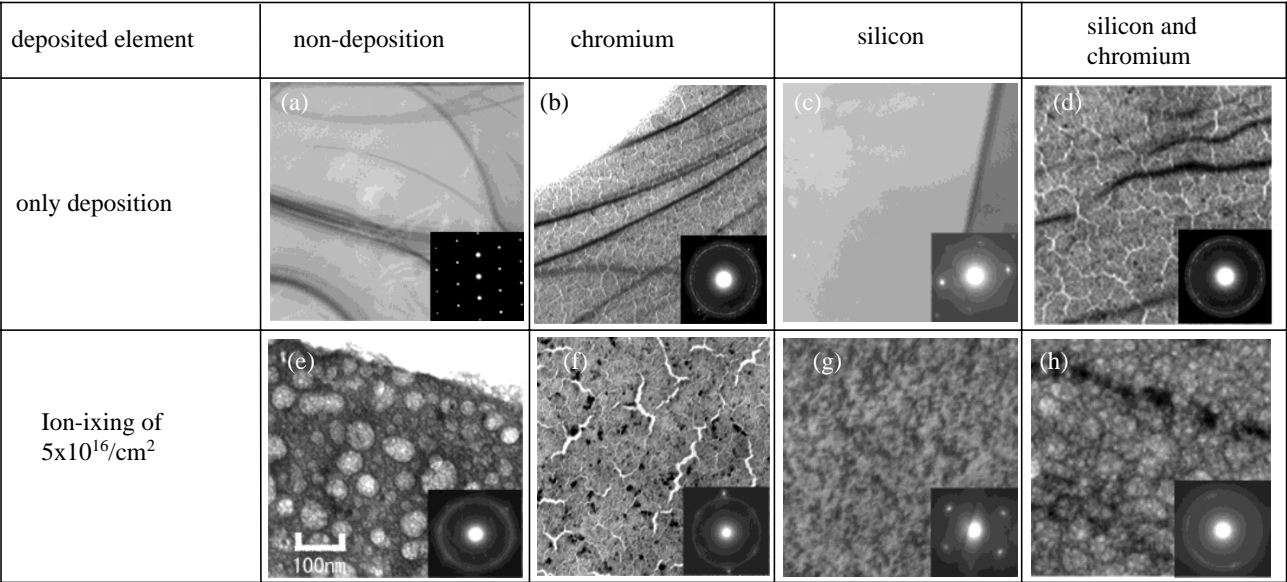


Fig. 4 Microstructure and diffraction pattern in SUS304L. The upper (a, b, c, d) showed the microstructures of only deposited condition and the below (e, f, g, h) showed those after ion-mixing.

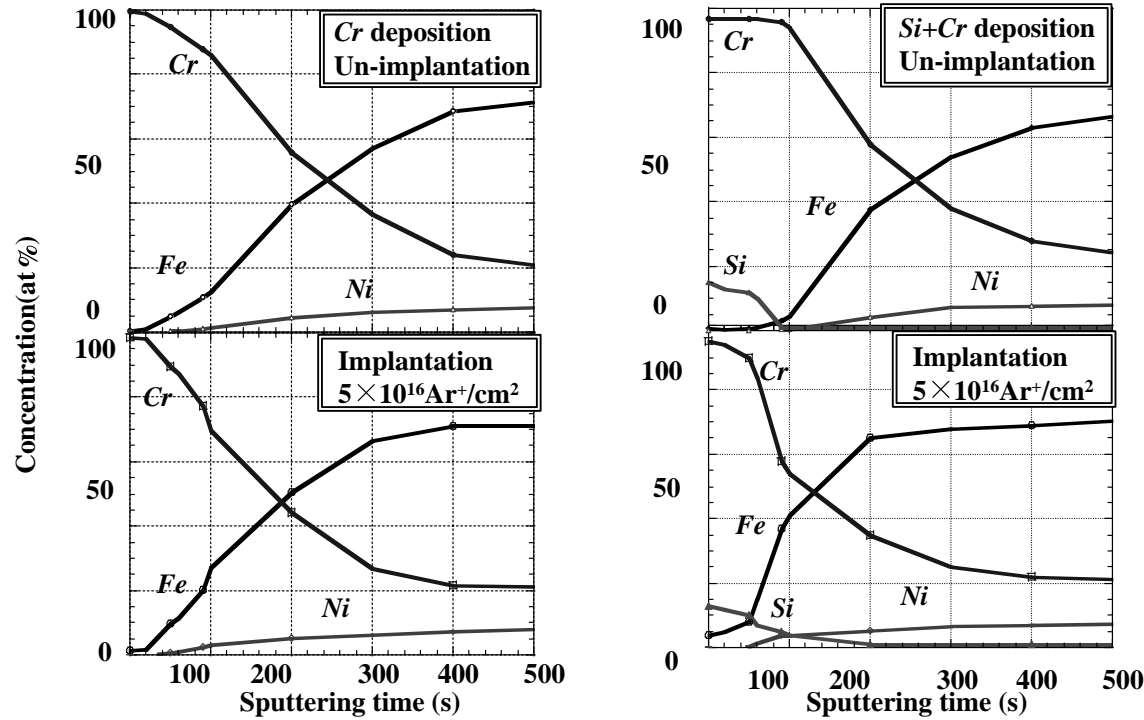


Fig. 5 The concentration change before and after ion implantation by SIMS. The ion dose was $5 \times 10^{16}/\text{cm}^2$.

chromium reduced intensively the passivation current to 1/1000. This improvement relates to the amorphization in the layer and the change in interface structure between the layer and the substrate.

(4) The ion-mixing plays important roles of radiation-enhanced diffusion and induced amorphization, as well as non-equilibrium concentration of additional element.

REFERENCES

- 1) J. L. Pérez, P. H. Sakanaka, M. A. Algatti, J. G. Mendoza-Alvarez and A. Cruz: *Orea Appl. Surf. Sci.*, **175–176** (2001) 703–708.
- 2) S. Gulizia, M. Z. Jahedi and E. D. Doyle: *Surf. and Coatings Technology* **140** (2001) 200–205.
- 3) R. Nishimura, K. Yamakawa, J. Ishiga, Y. Matsumoto and H. Nagano: *Mater. Chem. Phys.* **54** (1998) 289–292.