

CORROSION BEHAVIOURS OF ION IRRADIATED Ta AND Co-Cr-W FILMS ON STAINLESS STEEL

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ABSTRACT

Thin films of Ta or Co-Cr-W deposited on 2Cr13 stainless steel were irradiated with 200 keV Xe⁺ or 190 keV N⁺ at room temperature. The results of electrochemical corrosion behaviour of the resulting films in H₂SO₄ solution show that the corrosion resistance is greatly improved compared with that of virgin steel. Energy dispersive X-ray analysis, Rutherford backscattering spectrometry and X-ray photoelectron spectrometry were used to determine the surface composition of the irradiated layers, and Ta depth profile and chemical states.

Keywords: Ion-irradiation Electrochemical corrosion Corrosion resistance

1 INTRODUCTION

Ion irradiation of the film deposited on substrate materials may enhance the adhesion between film and substrate, and effectively modify the surface properties of the substrate materials.

Ta and Co-Cr-W alloys are potentially good candidates for forming highly protective passive films and the purpose of the present study was to examine the corrosion behaviour of films of these materials deposited on 2Cr13 stainless steel after ion irradiation. The motivation is that ion irradiation of film deposited on substrate is capable of overcoming the limit of added element concentration on the substrate surface by using ion implantation,^[1] and is also a powerful technique for producing multi-element surface alloy films on the protected materials with good adhesion.^[2]

2 EXPERIMENTAL

2Cr13 stainless steel was used as substrate in these experiments and its composition is (0.16–0.24)C–(12–14)Cr–bal. Fe. These substrates were 1000–1050 °C water quenched then 700–900 °C tempered, and polished, degreased prior to deposition. The Ta or 65Co–30Cr–5W was deposited on the 2Cr13 substrates by dc magnetron sputtering with a thickness of about 60 nm, then the deposited Ta

specimens were irradiated at room temperature with 200 keV Xe⁺ to a dose of 3×10^{16} ion/cm² and the deposited Co-Cr-W specimens were irradiated with 190 keV N⁺ to a dose of 4×10^{16} or 8×10^{16} ion/cm², the current density of Xe⁺ or N⁺ was limited at 3–4 μ m/cm² in order to minimize heating effects.

Corrosion tests were performed at room temperature (25 °C) using a potentiodynamic polarization technique in 0.5 mol/l H₂SO₄ solution. This electrochemical arrangement consisted of a three electrode polarization cell: A platinum sheet was used as an auxiliary electrode and a saturated calomel electrode (SCE) served as a reference. The solution was activated by argon gas bubbling to prevent concentration polarization and, to a lesser extent, for deaeration purposes. A cathodic current of 250 μ A was run for 3 min in order to dissolve the oxide film formed in air before the corrosion tests. After the electrode attained a steady-state the polarization curve was obtained automatically from –2000 mV to 2000 mV. EDAX measurements have been used to gain information about the surface composition of the samples at various points before and after the polarization tests. In addition some samples of Ta film with Xe ion irradiation were measured with RBS and XPS in order to get some information about depth profile and chemical state of the samples before or after corrosion tests.

3 RESULTS AND DISCUSSION

The electrochemical parameters of the anodic polarization tests for the various irradiated films on 2Cr13 stainless steel are shown in Table 1. For comparison, polarization parameters for the base material tested under the same conditions are also shown in Table 1.

Table 1
The electrochemical parameters of samples in 0.5 mol/l H₂SO₄ solution

Specimen	Critical current density I_c (mA · cm ⁻²)	Passive current density I_p (mA · cm ⁻²)	Corrosion potential E_n (mV)	Passivation range ΔE (mV)	Potential of passivation failure E_p (mV)
2Cr13	5.45×10^{-1}	4.37×10^{-2}	–460	910	1080
2Cr13+Ta	2.5×10^{-2}	1.05×10^{-2}	–450	1170	1720
2Cr13+CoCrW 8×10^{16} N ⁺ /cm ²	2.69×10^{-4}	1.1×10^{-4}	–459	1370	1130
2Cr13+CoCrW 4×10^{16} N ⁺ /cm ²	1.91×10^{-2}	7.24×10^{-3}	–464	780	1280

The data show that the critical current density I_c as well as the passive current density I_p for ion irradiated specimens are much less than for the base material. The values of I_c and I_p decreased by more than three and two orders of magnitude, respectively, for the deposited CoCrW specimens with N⁺ dose of 8×10^{16} cm⁻², but

those values for specimens with N^+ dose of $4 \times 10^{16} \text{ cm}^{-2}$ were as not good as the above. The passivation range ΔE for the specimens with $8 \times 10^{16} \text{ N}^+/\text{cm}^2$ irradiation was extended by about 400 mV, but ΔE was not changed for ones with $4 \times 10^{16} \text{ N}^+/\text{cm}^2$. For the irradiated Ta specimens, all the electrochemical parameters were improved especially the potential of passivation failure E_p was greatly risen up to 1720 mV compared with 1080 mV for base material.

Table 2

Composition of specimens before and after anodic polarization measured by EDAX

Specimen	Composition (wt %)	
	Before corrosion	H ₂ SO ₄ corrosion
2Cr13+Ta	90.27Ta-2.50Cr-7.23Fe	35.24Cr-64.76 Fe (dark location) 2.91Ta-14.12Cr-82.97Fe
2Cr13+	2.16W-6.07Cr-67.38Co-24.39Fe	1.87W-12.41Cr-85.72Fe (dark location)
Co-Cr-W	$8 \times 10^{16} \text{ N}^+/\text{cm}^2$	2.01W-13.03Cr-0.40Co-84.56Fe
	2.44W-6.64Cr-64.97Co-25.93Fe	2.27W-15.80Cr-81.93Fe (dark location)
	$4 \times 10^{16} \text{ N}^+/\text{cm}^2$	2.41W-13.79Cr-2.05Co-81.75Fe

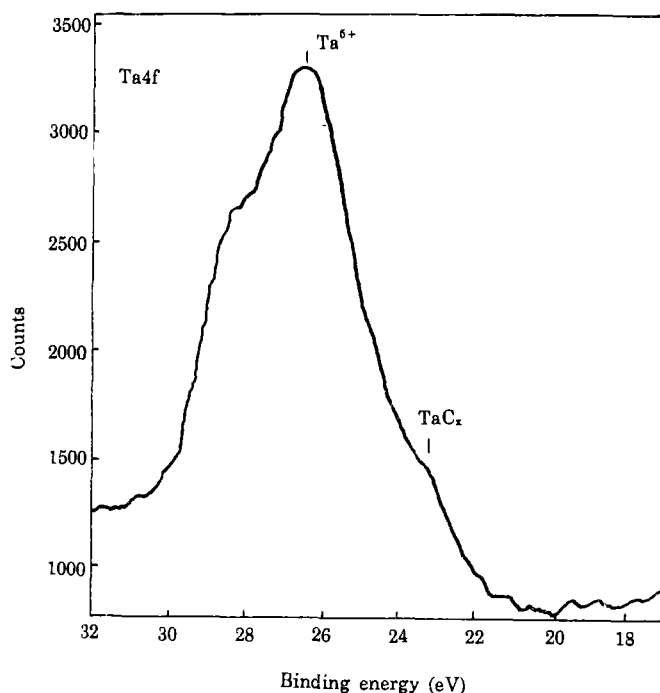


Fig.1 XPS spectrum of ion irradiated Ta film on steel

The surface composition of the specimens was measured by EDAX before and after polarization and summarized in Table 2. These values indicate that preferential dissolution of certain species took place during corrosion. It was found that some localized anodic dissolution at small pits of the order of about $5 \mu\text{m}$ diameter happened on the surface of the specimens. Comparing 2Cr13 substrate with 1Cr13 one

which has a lower carbon content, the values of I_c and I_p for the Ta-2Cr13 specimen are higher than those for the Ta-1Cr13 specimen.^[3] XPS analysis of these specimens shown in Fig.1 indicates that $TaC_x(x=0.71-1.00)$ was formed on the surface of these specimens. This means that the formation of such a compound not only reduced the Ta content, which would normally have a tendency to form a protective passive layer, but also acted as microcathode during corrosion, resulting in accelerating the dissolution of iron.

The values from Table 1 indicate that I_c or I_p for the deposited Co-Cr-W specimens using an irradiating nitrogen ion dose of 8×10^{16} ion cm^{-2} is much lower than that using 4×10^{16} ion cm^{-2} . It seems that a nitrogen ion dose which was not enough to form the complete nitride layer but was in excess of solid solubility in the matrix led to a deterioration in corrosion resistance. Isolated nitride particles and radiation induced segregation occurs along the crystal boundaries. The resulting material is prone to suffer intergranular corrosion due to the internal stresses produced at these boundaries^[4].

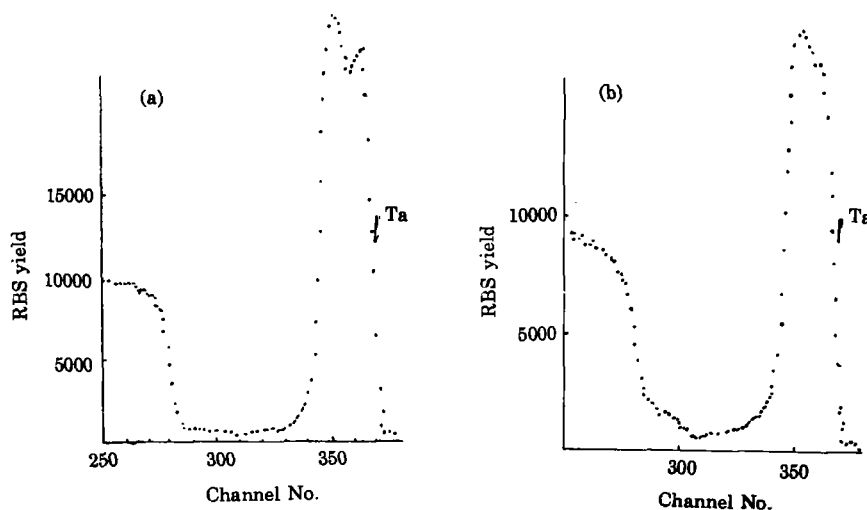


Fig.2 Depth profile of ion irradiated Ta film on steel measured by RBS

(a) Before polarization (b) After polarization in H_2SO_4 solution

RBS analysis was made for the irradiated Ta specimen shown in Fig.2. It could be found that the part of Fe reached ~ 300 channels after polarization in H_2SO_4 solution. It means that some part of Fe has been exposed at the surface of samples after polarization. One of the explanation might be small holes in Ta film were produced by polarization. The improvement of corrosion resistance of the base material by ion irradiated Ta specimens is due to the ability of Ta to form and self-repair easily the passive and protective oxide film on its surface in H_2SO_4 solution. The composition of the surface oxide films has been identified as Ta_2O_5 by XPS analysis shown in Fig.1.

Usually, the Cr level over that necessary to form carbide phases was the most important factor controlling the corrosion resistance properties of the Co–Cr–W alloy. In the situation of ion irradiated Co–Cr–W specimens, not only chromium which formed an extremely protective passive Cr_2O_3 film determined by XPS,^[4] but also a micro-cathodic source-free unitary metastable alloy, which may be formed by the ion irradiation processing, are beneficial to improvement in corrosion resistance of substrate material.

4 CONCLUSIONS

The polarization tests and EDAX, RBS, XPS analyses have been studied for the ion irradiated Ta or CoCrW films on 2Cr13 steel. The main conclusions are given below.

a. Ion irradiation of thin films of Ta or Co–Cr–W on 2Cr13 stainless steel can effectively improve the corrosion resistance of base materials in H_2SO_4 solution.

b. The carbon from substrate influenced improvement of corrosion resistance in H_2SO_4 solution for the ion irradiated Ta film on 2Cr13 steel.

c. The magnitude of N^+ ion irradiating doses affected the degree of improvement in corrosion resistance in H_2SO_4 solution for the ion irradiated CoCrW film on 2Cr13 steel.

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Corrigenda

The 1st line of p.222 Vol.2 No.4: 25 % instead of 50 %

The 7th line in Tab.2 p.223 Vol.2 No.4: 0.035(4) instead of 0.35(4)