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RAPID PUBLICATION

A Combinatorial Screening Method for Corrosion Research Using Ion-Beam-Deposited Thin-Film Alloys and Microelectrochemical Measurements

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A combinatorial screening method for corrosion research using an ion beam co-sputtering system and a microelectrochemical probe was proposed. Small chips of pure Cr and Mo were placed on a large Fe-11%Cr plate, and those were used as a complex target for co-sputtering. The composition gradients of the sputter-deposited films were found to be controllable by the arrangement and the number of pure Cr and Mo chips. The optimum condition for fabricating Fe-Cr-Mo combinatorial libraries was investigated, and Fe-19%Cr-x%Mo ($5 < x < 48$) and Fe-7%Cr-x%Mo ($3 < x < 46$) films were prepared. A microelectrochemical technique was applied to measure the corrosion behavior of the restricted small area on the combinatorial libraries. The small diameter of microelectrochemical probes was appropriate for suppressing the measurement error arising from the compositional gradient within an measured area. The influence of Mo content on the polarization behavior of Fe-Cr-Mo alloys in 1 kmol·m^{-3} H_2SO_4 and 1 kmol·m^{-3} NaCl were investigated. The results obtained were similar to those previously reported for bulk Fe-Cr-Ni alloys, which indicated that the combinatorial screening method proposed in this study would be used for high-throughput tests for corrosion research. [doi:10.2320/matertrans.M2009130]

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1. Introduction

Combinatorial chemistry is a relatively new experimental methodology developed in pharmaceutical industry to reduce the time and cost for drug development. Generally, combinatorial chemistry involves the rapid synthesis and evaluation of a large number of compounds in parallel and have been applied to materials science.[1–4] Combinatorial screening methods for corrosion resistant materials, however, has been limited.[5] Conventional macroscopic polarization measurements can not be applied to combinatorial screening because experimental error was originated from the compositional gradient within an electrode. The size of electrode area in conventional macroscopic polarization measurements was generally 10 × 10 mm.

Microelectrochemical techniques[6–14] have been widely applied to characterize microscopic non-uniformity on metal surfaces, such as inclusions, grain boundaries, and roughness. Even though the specimens have macroscopic compositional gradients with centimeter (cm) order, microelectrochemical probes can measure the precise polarization behavior of a local area with a given composition because the diameter of the electrode area was typically less than 500 µm.

Ion-beam-sputter deposition (IBSD)[15–17] is the preferred method to fabricate multi-element materials, such as binary, ternary, or quaternary alloys. In an IBSD system, target materials are sputtered by inert gas ions and sputtered particles are deposited on a substrate to form a film. The point for establishing a combinatorial screening method is to find out the procedure that can produce compositional gradient-controlled thin-films. In this study, we have used a co-sputtering target[18–23] composed of small chips of alloying metals and a large plate of a matrix.

The combination of a microelectrochemical probe and an ion beam co-sputter deposition system allows establishing the combinatorial screening method for studies of corrosion resistant materials. The objective of this study was to propose the experimental procedure of the combinatorial screening method by combining ion-beam-sputtered thin-film alloys and microelectrochemical measurements. The concentration-gradient-controlled thin films, Fe-19%Cr-x%Mo ($5 < x < 48$) and Fe-7%Cr-x%Mo ($3 < x < 46$) combinatorial libraries, were prepared and the anodic polarization curves for the combinatorial libraries were measured in 1 kmol·m^{-3} H_2SO_4 and 1 kmol·m^{-3} NaCl solutions.

2. Experimental

2.1 Sample preparation

Compositional gradient-controlled thin Fe-Cr-Mo films were prepared using an IBSD system (Tokyo Denshiyakin, DIBS-3000HC TDY-0395) with a Kaufman-type ion source (Ion Tech, model 3.0-1500-100FHC). Figure 1 shows the schematic of IBSD apparatus used and the appearance of a complex target for co-sputtering. High purity Ar (99.9999 vol%) was used for sputter source. The complex target consisted of a commercial Fe-11%Cr (Cr: 10.96, Ni, 0.37, Cu: 0.03, Si: 0.15, Mo: 0.02, C: 0.022, Mn: 0.87, S: 0.001%) stainless steel plate, 130 × 130 mm, and pure metal chips (99.9% Cr or 99.9% Mo). The point of this complex target was that the number of pure metal chips in each row was different, which could provide the compositional gradient of alloy elements in sputtered thin films. The size of pure Cr and Mo chip was 10 × 10 mm. The base pressure of the system was lower than 7.5×10^{-5} Pa, and the working pressure lower than 3.3×10^{-2} Pa. The ion source was operated at a beam voltage of 750 V, a beam current of 13 mA, an accelerator voltage of 150 V, and an Ar flow rate of 4 sccm (standard cubic centimeters per minute). The thickness of sputtered films was kept at around 100 nm by controlling deposition time.

Glass plates of 10 mm width were aligned and used as substrates as shown in Fig. 1(b). The surfaces of the plates were degreased with an alkaline solution, followed by

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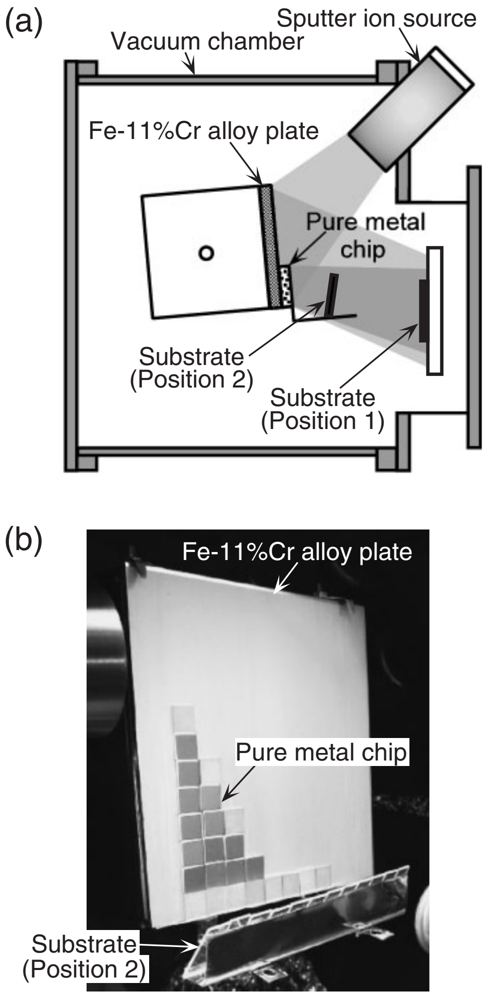

Fig. 1 (a) Schematic illustration of ion beam co-sputter-deposition system and (b) appearance of the complex target composed of Fe-Cr alloy plate and pure metal chips.

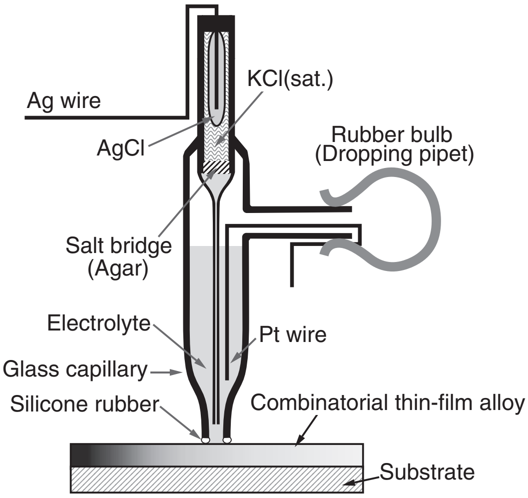

Fig. 2 Schematic illustration of microelectrochemical probe.

ultrasonic cleaning in pure water and ethanol, and finally dried with a N_2 gas stream. The distance between the target and the substrate was 130 mm (position 1) and 20 mm (position 2), respectively. After sputtering, anodic (+2 V) and cathodic (−2 V) voltages were alternately applied to the thin-film alloys in 5 mL of 1 kmol·m^{-3} H_2SO_4 so that the thin films were entirely dissolved in the solution. The dissolved solutions were diluted to 50 mL by the addition of pure water, and these solutions were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-8100) and the alloy composition was determined at intervals of 10 mm on the combinatorial thin Fe-Cr-Mo films.

2.2 Electrolytes

Electrochemical polarization measurements were performed in 1 kmol·m^{-3} H_2SO_4 and 1 kmol·m^{-3} NaCl solutions. These solutions were prepared from deionized water and analytical grade chemicals. All measurements were conducted at 298 K in the naturally aerated solutions.

2.3 Microscopic electrochemical measurements

A microelectrochemical probe similar to that developed by Suter *et al.*[6] was used to measure the polarization behavior of a restricted small area on the sputtered Fe-Cr-Mo films. Figure 2 shows the microelectrochemical probe used. The microelectrochemical probe consisted of two glass capillary tubes. The electrolyte was filled with the outer tube, and the inner tube was used as a Luggin capillary to allow measuring electrode potentials precisely even in the case of dilute solutions. A micro Ag/AgCl electrode filled with a saturated KCl solution was connected to the inner tube through a salt bridge. The agar salt bridge was made with a saturated KCl solution. When the electrolyte did not contain chloride ions, a saturated K_2SO_4 solution was used to make a salt bridge in order to keep chloride out of the test electrolyte. A counter electrode was a 0.5 mm platinum wire. All potentials cited in this paper were recalculated versus a Ag/AgCl (3.33 M KCl) electrode. The electrode area of this microcell was determined to be 1.0×10^{-7} m^2 (360 μm in diameter) by measuring the electropolished area on the stainless steel surface in microelectrochemical experiments.[14] A battery-powered low current potentiostat[14] was used to measure the current in the range of pA (10^{-12} A) to mA (10^{-3} A). Potentiodynamic polarization curves were measured at a scan rate of 3.8×10^{-4} V·s^{-1} (23 mV·min^{-1}). The surface of the combinatorial films for microelectrochemical measurements was the as-deposited condition. No heat-treatment was applied to the deposited films.

3. Results and Discussion

3.1 Composition of sputtered thin-film alloys

The optimum target arrangement for producing combinatorial Fe-Cr-Mo films was investigated. Figure 3 shows the target arrangement of pure Mo chips and a Fe-11%Cr stainless steel plate and the concentration profiles of the deposited film. In this case, the substrates were placed at the position 1 shown in Fig. 1(a). The compositional gradient of Mo in the sputtered films was 46 to 51%. The Cr content of the films was around 4 to 5%, even though target consisted of the large Fe-11%Cr steel plate. The small variation in Mo content was probably due to (1) the small variation in the number of Mo chips in the each row on the target and (2) the long distance between the target and the substrate.

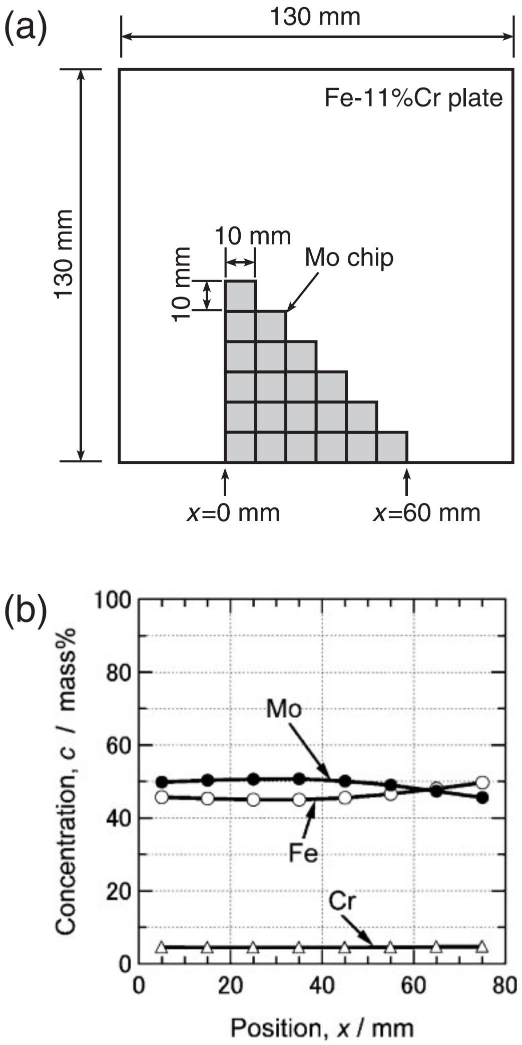

Fig. 3 (a) Complex target arrangement of pure Mo chips and Fe-11%Cr stainless steel plate and (b) concentration profiles of deposited film analyzed by ICP-AES.

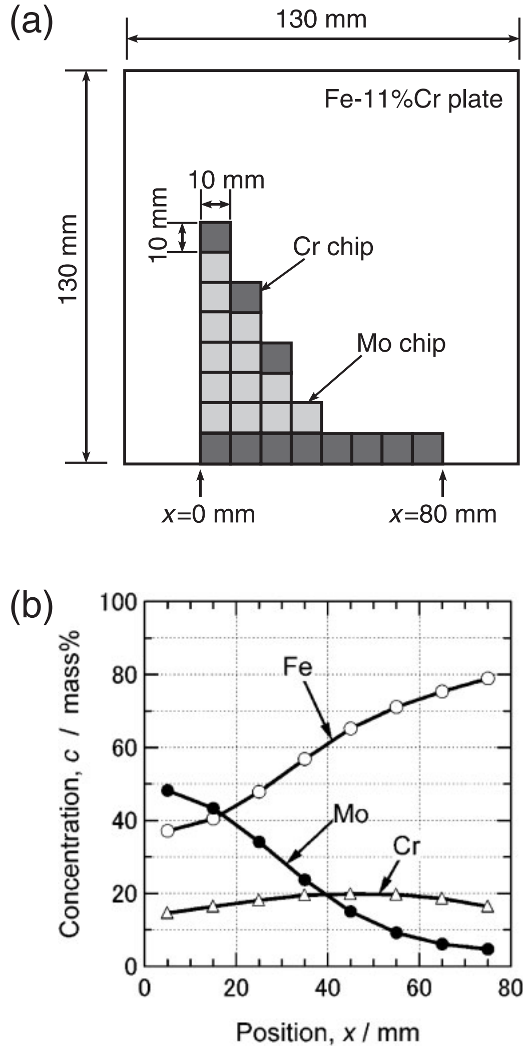

Fig. 4 (a) Complex target arrangement of pure Cr and Mo chips and Fe-11%Cr stainless steel plate and (b) concentration profiles of deposited film analyzed by ICP-AES.

To compensate the decrease in Cr content in the sputtered film, the addition of pure Cr chips was also thought to be necessary.

Figure 4(a) shows the modified target arrangement of pure Mo and Cr chips and a Fe-11%Cr stainless steel plate. In this case, the substrates were placed close to the target at the position 2 in Fig. 1. As seen in Fig. 4(b), a Fe-19%Cr-x%Mo ($5 < x < 48$) thin-film library could be prepared in this condition. The target configuration for co-sputtering and the distance between the substrate and the target were found to be the predominant factor producing combinatorial thin-film alloys using IBSD.

3.2 Effect of Mo content on electrochemical property for stainless steels

The effect of Mo content on the electrochemical property for Fe-19%Cr-x%Mo ($5 < x < 48$) stainless steels was investigated using the microelectrochemical probe. Figure 5 shows the anodic polarization curves in $1\,kmol{\cdot}m^{-3}$ H_2SO_4 solution measured on the combinatorial Fe-19%Cr-x%Mo ($5 < x < 48$) library at the position corresponding to 6%, 9%, 15%, 24%, and 34% Mo. No active dissolution region

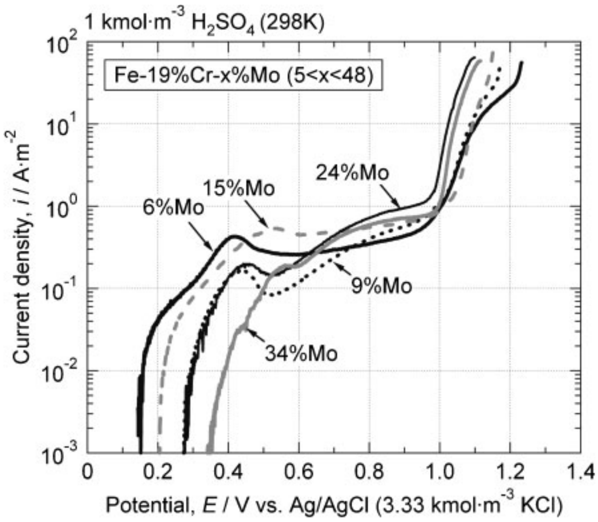

Fig. 5 Microscopic polarization curves in $1\,kmol{\cdot}m^{-3}$ H_2SO_4 solution measured on the combinatorial Fe-19%Cr-x%Mo ($5 < x < 48$) film at the position corresponding to 6%, 9%, 15%, 24%, and 34% Mo.

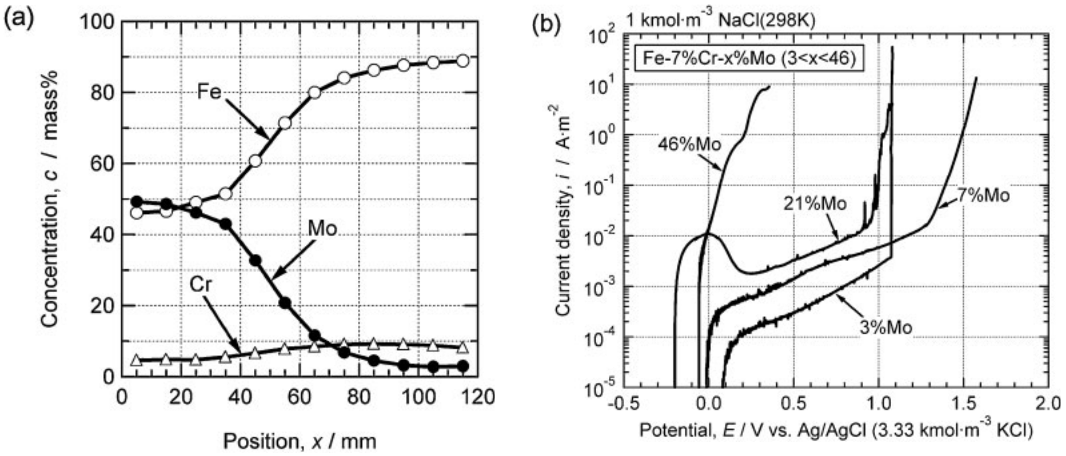

Fig. 6 (a) Concentration profiles of deposited film analyzed by ICP-AES and (b) microscopic polarization curves in $1\,\mathrm{kmol{\cdot}m^{-3}}$ NaCl solution on the combinatorial Fe-7%Cr-x%Mo ($3 < x < 46$) film at the position corresponding to 3%, 7%, 21%, and 46% Mo.

was observed for all the positions because the Cr content of 19% and the Mo content more than 6% allowed self-passivation of stainless steels.

As shown in Fig. 6(a), a Fe-7%Cr-x%Mo ($3 < x < 46$) thin-film library were prepared to know the effect of Mo content on the anodic polarization behavior of stainless steels in chloride environments. Figure 6(b) shows the anodic polarization curves in $1\,\mathrm{kmol{\cdot}m^{-3}}$ NaCl solution measured on the combinatorial Fe-7%Cr-x%Mo ($3 < x < 46$) library at the position corresponding to 3%, 7%, 21%, and 46% Mo. In the case of 3% Mo, pitting occurred at around 1.1 V. The position of 7% Mo, however, did not suffer pitting $1\,\mathrm{kmol{\cdot}m^{-3}}$ NaCl solution. The increase in current density above 1.3 V was due to mainly oxygen evolution. As many researches have already revealed,[23–25] Mo addition improves the pitting corrosion resistance of stainless steels. A similar effect of Mo addition is observed in Fig. 4, indicating that the proposed combinatorial screening method in this study would be used for high-throughput tests for corrosion research.

In the case of 21% and 46% Mo positions, an increases in current density was observed at around 0.9 and 0 V, respectively. This might be due to transpassive dissolution of Mo[26] in stainless steels because with increasing Mo content the onset potential of the current increase gradually approachs to the transpassive dissolution potential for pure Mo.[27] The combinatorial screening method proposed in this study can be utilized for alloy design of new corrosion resistant materials.

4. Conclusions

(1) The complex target composed of the small chips of pure Cr and Mo placed and a large Fe-11%Cr plate was suitable for co-sputtering to produce combinatorial Fe-Cr-Mo libraries. The composition gradients of the sputtered-films would be controlled by changing arrangement and the number of pure Cr and Mo chips.

(2) The combinatorial Fe-19%Cr-x%Mo ($5 < x < 48$) and Fe-7%Cr-x%Mo ($3 < x < 46$) films were prepared and the microelectrochemical technique was successfully applied to measure the polarization curves at the position corresponding to different Mo content.

(3) The combinatorial screening method using co-sputtered films and a microelectrochemical probe is a promising method for high-throughput tests in corrosion research.

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