

Effect of Additive Elements on Electrochemical Behaviour of Passive Films on Fe-18Cr Alloy

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Electrochemical behaviour of Fe-18Cr-X (X: Al, Si, Ti, Mn, Ni, Cu, Zr, Nb, Mo, and W, 0.5-4 at.%) alloy thin films deposited on Si wafer by ion beam sputtering technique was examined in order to discuss the effect of alloying elements which are completely dissolved in the alloy. Polarisation curves measured in 0.1 kmol m⁻³ H₂SO₄ revealed that active dissolution was suppressed by Ni, Nb, Mo, Cu and Ti, but was almost not affected by Al, Si, Mn. Pitting corrosion resistance in acid chloride solutions was extremely improved by Nb, Mo, Ti. On the other hand, Al, Si, Mn exhibited almost no change in pitting potential. Reactivation in sulphuric acid was suppressed by Mo, Nb, Ni, Ti, but not affected or slightly enhanced by Si and Mn. It is noticeable that addition of Nb is especially beneficial for preventing both pitting corrosion and reactivation. The corrosion behaviour of Fe-Cr alloys are discussed in terms of the stability of passive film which is influenced by minute additives incorporated in the film.

Keywords : passivity, stainless steels, minute additives, pitting, reactivation

1. Introduction

The corrosion resistance of Cr containing iron base alloy is derived from Cr enriched passive film, and is highly influenced by minute elements that are usually contained in commercial steels. Such elements are added in order to improve their corrosion resistance, mechanical properties and others. Alloying elements usually form structural defects, such as inclusion, segregation, precipitate along grain boundary, and *etc.* For instance, minor elements in stainless steels are usually added as stabiliser for N and C, de-oxidiser, former or de-former for some phases, and others. However, such structural inhomogeneities affects corrosion behaviour. Therefore, changes in the corrosion behaviour due to additives are not necessarily attributed to properties of passive film itself.

Property of passive film highly influences the corrosion behaviour of stainless steels. Properties of passive film might be highly influenced by alloying elements. Therefore, it is necessary to understand the role of additive elements on the electrochemical behaviour of passive films. However, as described above, most of alloying elements do not dissolve homogeneously in the alloy, but alter its structure to change corrosion behaviour. Therefore, it is necessary to prepare materials in which alloying elements are completely dissolved as solid solution. As

reported previously,¹⁾ thin sputtered film produced by ion beam sputtering technique is equiaxed nano-crystalline without any precipitate. Such material is suitable to examine the chemical effect of alloying element on the corrosion property of passive film. In the present work, Fe-18Cr alloys with various additives that are completely dissolved were examined in order to discuss the effect of minute additives on the electrochemical behaviour of passive film.

2. Experimental

Materials testes were thin alloy films prepared by ion beam sputtering technique.¹⁾ The deposition system consists of three Kaufman type ion beam guns of 3 cm in diameter (Ion Tech, Inc., Ft. Collins, CO) ; two for sputtering and the other one for assist bombarding. The process chamber was designed attainable to a vacuum level of about 1x10⁻⁸ torr. using a cryopump. In the present work the chamber was evacuated to be less than 3 x 10⁻⁸ torr. before the deposition process. Two Ar⁺ ion beams emitted from the two ion beam guns bombarded simultaneously two targets. One of the targets was Fe-18Cr alloy sheet of 100x150 mm² and the other was desired additive element sheet. The chemical composition of the Fe-18Cr was as follows ; C: 0.065, Si: 0.58, Mn: 0.82, P: 0.029,

S: 0.002, Ni: 8.75, Cr: 18.29, Mo: 0.14, Cu: 0.14 (mass%), and Fe: bal. The substrate for deposition was mirror finished silicon wafer of 100 mm in diameter, which was employed by Newman et al.^{2,3)} for corrosion study and was reported to have advantage of providing ideally flat. The substrate was put on a holder which is water cooled and rotated. In order to clean up, the substrate was bombarded by Ar⁺ ion emitted by assist ion gun with acceleration of 300 V prior to sputtering. The deposition time was typically 2 hours. In the present work, Al, Si, Ti, Mn, Ni, Cu, Zr, Nb, Mo, and W were used as additives. The amount of alloying component was controlled by adjusting the ion beam current on additive element target. The thickness of the film after 2 hours deposition was typically 300 nm.

The thin film adherent to the silicon wafer was cleaved into typically 10x10 mm² square specimen. For the electrochemical measurements, the cleaved specimen was mounted on an acrylic coupon, attached a lead wire on the film surface with electro-conducting paste, then covered with epoxy resin leaving an exposed area of 5x5 mm². A conventional 3 electrodes system was employed for electrochemical measurements with using a Ag/AgCl/3.3 kmol(m⁻³ KCl reference electrode. Test solutions were dilute sulphuric acid and NaCl + HCl solutions prepared with reagent grade chemicals and distilled water.

3. Results

3.1 Polarisation curves

Potential-dynamic polarisation curves were measured for deposited thin alloy films in 0.1 kmol m⁻³ H₂SO₄ solution. Figure 1 summarises current density at the active peak potential for various alloys as a function of the amount of additive element. As shown in this figure, most of alloying elements, especially Mo, Cu, Ni, Nb, suppress gradually active dissolution with increasing additives, whereas Al, Mn and Si do not change or slightly increase active dissolution current. The minimum current density in the passive range has been also described in Fig.2, which shows almost no change in the minimum current density by additives.

3.2 Pitting potential

Figure 3 shows typical potential-dynamic polarisation curves to measure the pitting potential in 0.1 kmol m⁻³ HCl + 10 % NaCl. As shown in this figure, pitting potential shifts in noble direction with increasing Cu contents. It is to note that conventional Type304 stainless steel never shows passive state in this solution. As already reported,¹⁾ thin sputtered film reveals extremely high corrosion

Fig. 1. Variation of active peak current density in the potential-dynamic polarisation curves of Fe-18Cr alloy thin films with additives.

Fig. 2. Variation of minimum current density in the passive region in the potential-dynamic polarisation curves of Fe-18Cr alloy thin films with additives.

Fig. 3. Polarisation curves to measure pitting potential of Fe-18Cr alloy thin films with various amounts of Cu.

resistance. Variation of pitting potential with additive elements is summarised in Fig.4 as a function of the amount of additives. Most of additive elements, except for Si, Al, Zr, change pitting potential more noble with increasing additives, then inhibit pitting corrosion. Especially, pitting corrosion is completely inhibited by a small addition of Nb and Mo. On the other hand, Mn usually known to promote initiation of pitting corrosion. With increasing Mn content, however, pitting potential initially decreased slightly, then turned to increase. This means Mn addition improved pitting corrosion resistance. Gradual decrease in pitting potential was observed only for Al addition.

3.3 Reactivation potential

Specimen was potentiodynamically polarized from -1000 mV, which is in the hydrogen evolution region, to -200 or +500 mV in the passive region. Then the applied potential was kept at the constant potential for 1 hour to obtain stable passive film. Subsequently, the applied potential was scanned in less noble direction with very slow sweep rate, *i.e.* -0.1 mV s^{-1} . During the return sweep, the potential passed through the active potential region of Fe and Cr. Therefore, passivity might be reactivated, if passive film were unstable to be reduced easily. Figure 5 schematically shows the procedure of the reactivation test. Case 1 in this figure illustrates the reactivation. The current decreases with decreasing applied potential to be negative value, then turns to increase toward positive direction due to reactivation. The potential at which the current varies from negative to positive is defined as a reactivation potential. The less noble reactivation potential means the more stable passivity. Occasionally, as shown in Case 2, the current changes exponentially in negative direction with decreasing applied potential to evolve hydrogen without any reactivation. Changes in the reactivation potential with increasing additives are summarized in Figs.6(a) and (b) for specimen polarized at -200 mV and at +500 mV, respectively. As shown in Fig. 6(a), reactivation potential was little affected by Al and W, and was slightly shifted in noble direction by Mn, Si, that is, passivity was deteriorated by these elements. On the other hand, Ni, Cu, Mo, Nb, Ti, and Zr similarly shift reactivation potential in less noble direction. Therefore, these alloying elements modify passivity of Fe-18Cr alloy more stable. As shown in Fig.6(b), variation of reactivation potentials for specimen passivated at 500 mV is more complicated. For some alloying elements, that are Cu, Mn, and Ti, reactivation potential changed not monotonously, but exhibited increase and decrease. On the other hand, for the most of alloying elements, the increasing additive

Fig. 4. Variation of pitting potential of Fe-18Cr alloy thin films with additives.

Fig. 5. Schematic drawing of the process of reactivation test.

elements lower the reactivation potential, then inhibit reactivation beyond a critical content of additives. The variation of the critical content to suppress reactivation is more significant for the test passivated at 500 mV compared to that at -200 mV. The smaller critical content to inhibit reactivation was observed in the order of Mo, Nb, Zr, and Ni, as indicated by short vertical lines in Fig.6(b).

4. Discussion

As known very well, corrosion resistance of stainless steel is mostly determined by its Cr content, and also by other minute elements, depending on the environment in which the steels are exposed. Structure of passive film formed on stainless steel accommodates the environment. Therefore, corrosion resistance of stainless steels should be evaluated in each environment. Nevertheless, passive film might be discussed generally independent of specific condition. In the present work, we tried to characterise passive film using some electrochemical tests. As already

Fig. 6. Variation of reactivation potential of Fe-18Cr alloy thin films with additives passivated at (a) -200 mV, and (b) +500 mV.

described, the specimen employed in the present work has actually no defect, that is, alloying element completely dissolved in the matrix. Therefore, the electrochemical properties revealed in the present study reflect the property of passive film itself. The role of additive elements are discussed in terms of changes in chemical property of passive film in the following.

As described in the polarisation curves, most of alloying elements suppressed active dissolution. As is not shown in this paper, XPS analysis on the passive film on thin alloy films revealed that additives did not significantly affect Cr content in the passive film. Therefore, the additives might promote the formation of passive film or make the property of passive film more protective toward active dissolution. On the other hand, current density at passive potential region was not so changed by additive elements. It is to note that these polarisation curves were measured with a fairly rapid scanning rate of 10 mV s^{-1} in order to avoid disappearance of very thin specimen during active dissolution. Therefore, it is highly possible that current density after polarisation of longer period varies depending on the additive element. The results exhibited by reactivation test are more suggestive on the role of additives. Measurement of reactivation potential of Fe-Cr alloys with various Cr content in 0.1 kmol m^{-3} H_2SO_4 was already reported by Fujimoto *et al.* using thin alloy film formed by ion beam sputtering.²⁾ It was revealed that reactivation potential shifts in the less noble potential with increase in the Cr content. Steep changes in the reactivation potential were found at 12~13at.% Cr and at 16~17 at.% Cr depending on the passivation potential. Such thresholds were discussed in terms of the critical Cr content to form Cr-like passivity of Fe-Cr alloys.⁴⁾ Cr

like passivity is attained when Cr is sufficiently enriched in the passive film. Reactivation of Cr-like passivity seems to occur due to reduction of Fe ions in the passive film to expose substrate alloy to the solution at the active potential region of Fe, resulting in active dissolution. Therefore, the reactivation potential shifts less noble with increasing Cr content, because Cr content in the passive film increases with increasing Cr in the alloy. It is noticeable that reactivation occurred for all Fe-Cr alloy tested (up to about 30 at.% Cr). Therefore, reactivation might be inevitable in acid solutions for Fe-Cr alloys. On the other hand, it is revealed in the present work that reactivation was inhibited for Fe-18Cr alloys with some additives. As shown in Fig.6(b), Mo, Nb and Ni are extremely effective. The reactivation is inhibited due to suppressed reduction of Fe^{2+} and/or Fe^{3+} ions in the passive film. It is already confirmed by XPS analysis that additive elements not necessarily enriched in the passive film. Therefore, small amount of such additives increased stability of Fe ions toward reduction. Mechanism to suppress reactivation might be different for each alloying element.

In the present work, role of the additive elements on the corrosion behaviour of stainless steels are characterised electrochemically and discussed in terms of stability of passive film. Pitting corrosion test might evaluate the resistance against harmful attack by Cl^- ions to breakdown passive film. For commercial steels, pitting corrosion tends to initiate at precipitates, such as MnS . The material tested in this work is free from such defects. Therefore, the additive elements which suppress pitting corrosion might protect nano-scale weak site in the passive film or promote repassivation of nono-scale broken site formed by Cl^- in

the passive film, as known for Mo and N. It is interesting that Mn, which is usually known to stimulate pitting corrosion due to formation of MnS, does not necessarily decrease pitting potential, because Mn is dissolved completely in the material used in the present study. Reactivation test revealed that elements that are known to improve corrosion resistance in acid media suppress reactivation, that is, reduction of Fe ions in the passive film. Mo and Nb are revealed extremely effective to prevent reactivation. In the present work, role of additives is characterised only electrochemically. It is necessary to analyse the location and state of minute elements in the passive film, and also to characterise in terms of electronic structure of passive film to discuss the mechanism to improve corrosion resistance.

5. Conclusion

Electrochemical property of Fe-18Cr alloy with various additive elements was studied systematically in terms of stability of passive film. Fe-18Cr alloys with small amount of additives were prepared using ion beam sputtering. Most of additives which suppress reactivation also

decrease active dissolution rate. Namely, Nb, Mo, Cu, Ni, and Ti are beneficial to prevent corrosion in acid. On the other hand, elements to suppress pitting corrosion are not necessarily coincide with the elements which improve resistance to corrosion in acid. Mo, Nb, Ni, and Cu are effectively suppress pitting corrosion. Mo is well known to prevent localised corrosion in Cl⁻ containing environment, and is also beneficial to suppress active dissolution in acid. On the other hand, Nb is often added in the stainless steels to stabilise C, N, but is proved to be extremely beneficial to prevent both pitting corrosion and active dissolution in acid.

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