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STRUCTURE AND STABILITY OF THE ANODICALLY FORMED FILMS ON 304 STAINLESS STEEL IN SULFURIC ACID

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ABSTRACT

The structure and composition of the passive films formed on 304 stainless steel in deaerated 1N H_2SO_4 were studied by RHEED, XPS and AES. The stability of the passive films as a function of passivation potential and passivation time were investigated. The role of bound water in affecting the stability of the passive films is discussed.

INTRODUCTION

Recently, Okamoto (ref. 1) has proposed a model for the structure of the passive films formed on 304 stainless steel that lays emphasis on the role played by bound water in affecting the stability of the passive films in acidic sulfate and sulfate/chloride solutions at various anodic passivation potentials. Using radiotracer techniques, Okamoto noted a decrease in the amount of bound water in the film with increasing passivation potential especially above 0.4V (SCE). This variation in bound water in the film was found to be related to a compositional transition around 0.4V. According to this model, the passive films formed on 304 stainless steel are amorphous consisting of hydrous oxides of iron and chromium. Initially, these films are enriched in water as H_2O-M-H_2O networks which deprotonate to HO-M-OH and finally to O-M-O. It was proposed that the passivation potential and passivation time either collectively or separately control the deprotonation process.

In our previous RHEED studies (ref. 2) of 304 stainless steel, we have shown that there is a high degree of crystallinity in the potentiostatically formed films on 304 stainless steel in deaerated 1N sulfuric acid. There was also a remarkable agreement between the structure of various compounds detected in the passive film and the nature of passive film conceived by Okamoto. But, since these studies involved transfer of the samples into the electron microscope through air, it was necessary to check whether such a transfer introduced an artifact in the structural information obtained from such films owing to the

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modification of the surface film by atmospheric oxygen. We, therefore carried out another set of polarization experiments in a cell enclosed in an environmental chamber that was purged with prepurified nitrogen. Subsequently, the samples were transferred in an argon saturated transfer device to the electron microscope. In order to acquire an overall picture of the nature of the passive films, we also carried out XPS and AES analysis and we have attempted to compare the information obtained in these analyses with those of RHEED results.

The major objective of the present work is to characterize the structure and composition of the passive films formed on 304 stainless steel and hence, to test the validity of the model of the structure of the passive films already presented in the literature. Another important objective of this investigation is to study the stability of the film due to aging at a given potential.

EXPERIMENTAL

Samples of 304 stainless steel were vacuum annealed at 1100°C for 3 hours, quenched in water and polished to a 1 micron Cr_2O_3 finish. To remove the surface films formed during mechanical polishing, the samples were cathodically polarised at -600 mV for 15 minutes (ca. $10^3 \mu A\ cm^{-2}$) in deaerated 1N sulfuric acid and potentiostated for 1 hour at the passivating potential of interest. Subsequently, the samples were cleaned with deaerated doubly distilled water, dried in argon and immediately transferred to the electron microscope or electron spectrometer either through the atmosphere or argon. The structural and compositional analyses were done on separate freshly prepared samples. All the RHEED patterns were obtained using a Phillips EM 300 electron microscope at 100 KeV. The structural information was obtained by calculating the interplanar spacings employing a thin film of gold as a standard to calculate the camera constant. XPS and AES analyses were performed with a V.G. Scientific ESCA3MK II system. All XPS and AES measurements were carried out in a vacuum of ca. 5×10^{-10} torr. The composition depth profile of the passive films were carried out using AES in conjunction with Ar ion etching.

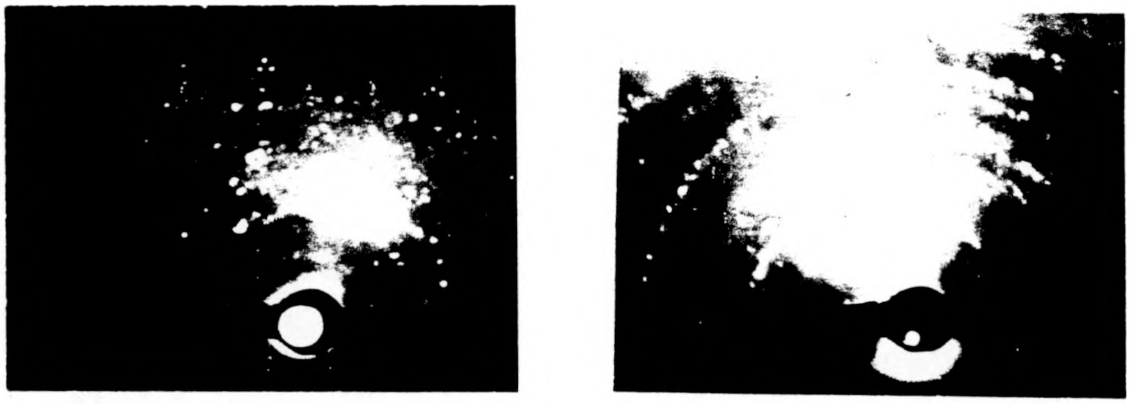
RESULTS

The potentials chosen for the present passivation studies were 0.25V, 0.40V and 0.55V (vs SCE). The RHEED results are summarized in Table I which presents the structures of the various compounds detected following both aerial and Ar transfer. Typical diffraction patterns acquired from high potential and low potential films are presented in Figures 1a and 1b. It is evident from the diffraction patterns that the passive films formed on 304 stainless steel display a high degree of crystallinity. At 0.25V and 0.40V, an iron-based compound resembling the structure of Green rust II ($4Fe(OH)_2.2Fe(OH)_3.FeSO_4.XH_2O$) (ref. 3) was detected in the film. The passivation of the 304 stainless steel

TABLE 1

RHEED analysis of the passive films formed on 304 stainless steel in 1N sulfuric acid.

Potential	Mode of Sample Transfer	d Spacing	Phases Observed
0.25V	Aerial	3.54, 3.21, 2.85, 2.46, 2.21, 1.88, 1.7, 1.6, 1.31	Green rust II, γ-CrOOH
	Argon	5.48, 3.65, 2.75, 2.66, 2.46 2.2, 1.94, 1.71, 1.59, 1.53	Green rust II, γ-CrOOH
0.40V	Aerial	6.0, 4.24, 3.54, 3.27, 2.86, 2.57, 2.25, 2.2, 1.84, 1.75, 1.71	Green rust II, γ-CrOOH α-FeOOH
	Argon	7.48, 5.52, 3.85, 3.63, 3.43, 3.26, 2.76, 2.65, 2.44, 2.12, 2.05, 1.96, 1.74, 1.67	Green rust II, γ-CrOOH γ-FeOOH
0.55V	Aerial	3.23, 2.73, 2.35, 2.18, 1.88, 1.69, 1.43, 1.19, 1.16	γ-FeOOH, γ-CrOOH
	Argon	6.34, 3.52, 3.33, 3.13, 2.76, 2.47, 2.35, 2.19, 2.11, 2.04 1.86, 1.81, 1.71, 1.67	γ-FeOOH, γ-CrOOH



(a) (b)

Fig. 1a and 1b. RHEED patterns obtained from the passive films formed on 304 stainless steel in deaerated 1N H_2SO_4 following argon transfer at (a) 0.25V (SCE), (b) 0.55V (SCE).

above 0.4V resulted in the formation of γ-FeOOH while chromium was present at all potentials as γ-CrOOH. No nickel compounds were found in the film. Figure 2 presents the XPS spectra of oxygen obtained from the 304 stainless steel passivated at 0.25V and 0.55V in 1N sulfuric acid while Figures 3a and 3b show the

AES depth profiles of the stainless steel following passivation at these potentials.

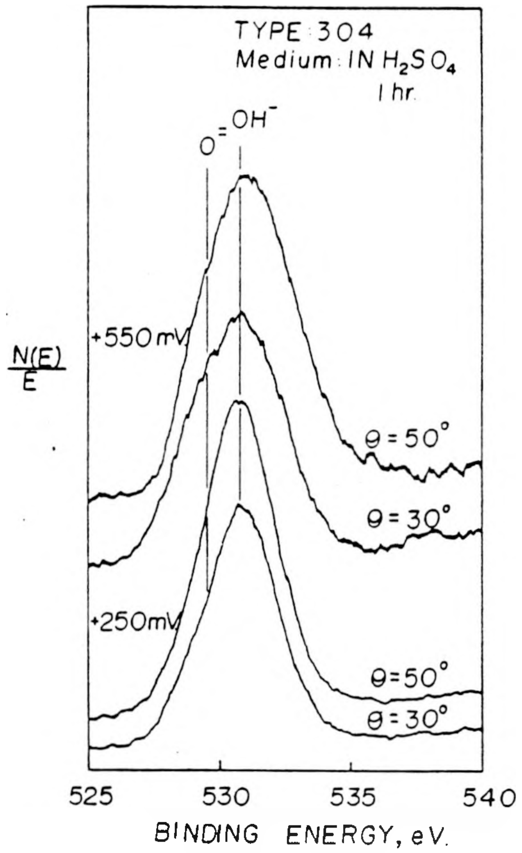
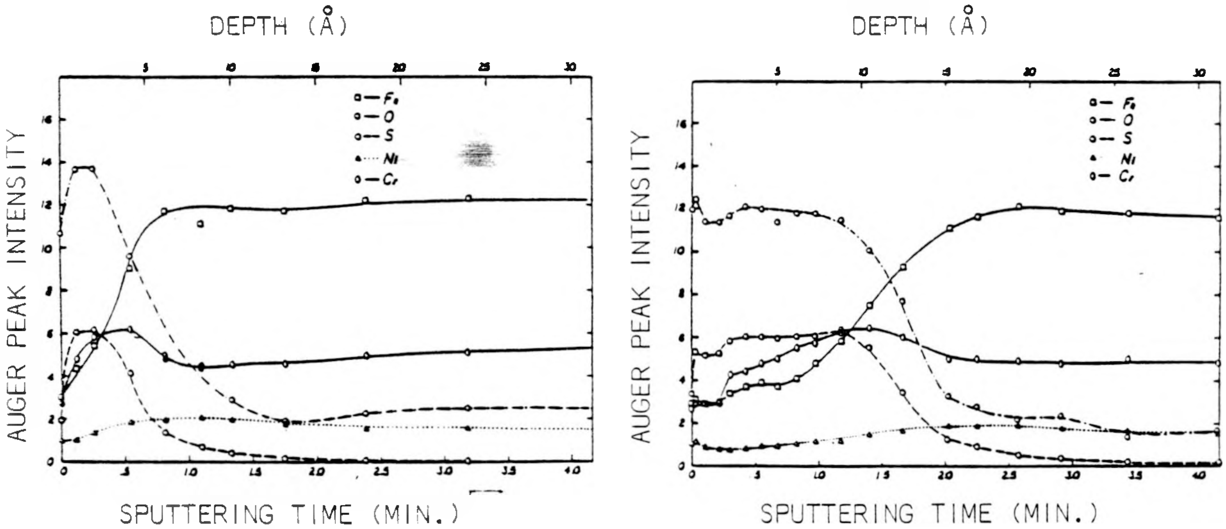


Fig. 2. O1s XPS spectra obtained from the passive films formed on 304 stainless steel in deaerated IN H_2SO_4 at 0.25V (SCE) and 0.55V (SCE).



(a)

(b)

Fig. 3a and 3b. AES composition depth profiles of 304 stainless steel passivated in deaerated IN H_2SO_4 at (a) 0.25V and (b) 0.55V (SCE).

DISCUSSION

It is apparent from the RHEED data that the structure of the passive films are strongly dependent on the passivation potential and time of passivation. The passive films formed on stainless steel are found to consist of both iron and chromium compounds in polycrystalline form as evidenced by continuous rings observed in our RHEED patterns. This is contrary to the assumption of Okamoto (ref. 1) and several other investigators (Refs. 4, 5) who contend that the passive films formed on stainless steel are amorphous. Both aerial and argon transfer resulted in the polycrystalline films. It was found that the aerial transfer of the passivated samples resulted in formation of α-FeOOH at 0.40V which was not observed in the samples transferred through argon atmosphere. It may be noted in this connection that Misawa et al (ref. 3) have shown that α-FeOOH may be formed by aerial oxidation of γ-FeOOH. Hence, it is clear that in order to obtain very reliable structural information from the RHEED data, it is important to avoid the exposure of the passivated specimens to atmospheric oxygen. Henceforth, our discussions in this section will be presented with respect to the results involving argon transfer. It is noted that the low potential films (<0.40V) contain γ-CrOOH and predominantly complex hydroxy compounds of iron with a significant amount of bound water as seen from the green rust II structure. At high potentials (>0.40V), the passive film exists in the form of oxyhydroxides (γ-FeOOH and γ-CrOOH). The XPS spectra which we have previously published (ref. 6) show the presence of Fe^{3+}, Fe^{2+} and Cr^{3+} peaks in low potential range and predominantly Fe^{3+} and Cr^{3+} peaks at high potentials showing a good agreement with the RHEED results. The relative amounts of Fe^{2+} and Fe^{3+} will be reported later in a more comprehensive paper (ref. 7). The narrow scan of O1s spectra given in Figure 2 shows the peaks corresponding to OH^- at 0.25V and O-OH at 0.55V. The AES depth profiles of the passivated stainless steel indicates an increase in film thickness with potential of passivation.

It is interesting to note that the hydroxide based green rust II phase has a significant amount of entrapped water. We also observed from AES analysis apparent enrichment of chromium at higher potentials. These results brings into question Okamoto's assumption that the bound water tends to be exclusively associated with chromium compounds in the film. Further studies in this area are necessary before this controversy can be resolved. In the passive film aging experiments reported by Okamoto, it is assumed that the chromium compounds are responsible for the high degree of deprotonation observed. To test this assumption, we carried out passivation experiments for a prolonged period (3 hours) in 1N sulfuric acid at 0.25V followed by RHEED analysis. In this work, we observed the complete transformation of γ-FeOOh from green rust II while chromium evidently remained unaltered as γ-CrOOH. Thus, the RHEED data presents evidence that the deprotonation is largely associated with the highly hydrated iron based compounds which is contrary to Okamoto's model. Despite these contradictions, the type of bonding between metal and oxygen in the films proposed by Okamoto for low potential and high potential films fits very well into the structures indicated by the RHEED data. The compositional transition observed at 0.40V was accommodated well by a structural transition wherein only iron compounds were involved as evident from the presence of green rust II and γ-FeOOH at 0.40V. This transition was found to be the intermediate stage between the transformation of a metastable compound (green rust II) in the film to a more stable compound (γ-FeOOH) and hence, the film structure at 0.40V exhibits the characteristics of both low and high potential films.

SUMMARY AND CONCLUSION

The passive films formed on 304 stainless steel were found to be polycrystalline incorporating varying amounts of bound water depending on the potential and time of passivation. Two iron compounds were detected in the films such as green rust II (<0.40V), γ-FeOOH (>0.40V). γ-CrOOH was observed at each of the three potentials investigated viz., 0.25-0.55. The unstable nature of low potential film was evident by aging experiments which showed their transformation from the original green rust II structure to γ-FeOOH. The passive films analyzed by RHEED following argon transfer showed very little difference in the structure from the ones which were analyzed following aerial transfer except for the formation of an additional phase (α-FeOOH) at 0.40V by aerial oxidation.

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