Characterization of film properties on the Ni–Cr–Mo Alloy C-2000

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ARTICLE INFO

Article history:
Received 3 October 2012
Received in revised form 8 November 2012
Accepted 9 November 2012
Available online 19 November 2012

Keywords:
Passive film
Ni–Cr–Mo alloys
Alloy C-2000
XPS
ToF-SIMS

ABSTRACT

The passive and transpassive film properties grown at various potentials on a Ni–Cr–Mo alloy, Alloy C-2000 (Ni=23Cr=16Mo=1.5Cu), were investigated by surface-sensitive techniques such as Angle-Resolved X-ray Photoelectron Spectroscopy (AR-XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and SEM. The presence of a layered structure in the passive film has been demonstrated, with the outermost surface being enriched in Cu (or Cu oxide) and Mo oxide, the intermediate region dominated by Cr/Ni hydroxides, and the inner region comprising Cr/Ni oxide. As the potential increases from –0.4 to 0.6 V (vs. Ag/AgCl in saturated KCl), the film thickness increases, and the relative Cr content of the film increases while that of Ni decreases. The passive film (0 V) has a relatively thicker inner oxide layer and higher Cr2O3 content in the inner layer, compared to the transpassive film (–0.4 V). In the transpassive region (0.6 V), the anodic oxidation of Cr(III) to Cr(VI) in the barrier layer of the film and its subsequent dissolution leads to the loss of the Cr2O3-rich inner layer and the destruction of passivity. Destruction of the barrier layer proceeds non-uniformly on the alloy surface.

1. Introduction

It is well known that Ni–Cr–Mo alloys exhibit exceptional corrosion resistance under extreme environment conditions. These alloys are widely used by chemical processing industries, in the areas of energy, health and environmental, oil, gas and pharmaceuticals. Their high corrosion resistance is generally attributed to their elemental composition and the passive behavior it induces; the combination of high Cr and Mo contents leading to the formation of a Cr-dominated passive oxide film [1–5]. Since the properties of passive films control overall corrosion behavior, a wide array of in situ and ex situ analytical techniques [1,3,6–10] has been employed to assess the passive behavior and passive film properties on Ni–Cr–Mo alloys. Additionally, the high percentage of \[\sum_{i}^{3}\] grain boundaries limits the initiation of localized corrosion at these locations [11] and the high Mo content limits propagation and promotes rapid repassivation if initiation of localized sites does occur [12].

Lloyd et al. [1–3] determined the film composition and thickness, and the effect of the alloying elements, Cr, Mo, and W, on the composition and thickness of the passive film on a number of Ni–Cr–Mo (W) alloys in acidic solutions. The oxide film consists of a Mo, Cr, and Ni oxide, with Cr present as Cr(III) and Mo present in several oxidation states. The film was found to be only a few nanometers thick (<5 nm), and the thickness increased with increasing potential in the passive region. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) showed that the high-Cr alloys were able to build thicker oxides with a layered structure consisting of an inner Cr–Ni oxide layer and an outer Mo/W oxide when anodically oxidized in 1.0 M NaCl + 0.1 M H2SO4 solution (pH 1). The presence of Mo and W in the outer regions of the oxide is thought to suppress passive dissolution at high potentials, when Cr(VI) release appears to start. A similar layered oxide was observed to form on Alloy-22 (Ni=22Cr=13Mo=3W) in extremely saline (5 M NaCl) neutral solutions [13], over the potential range –0.4 V to 0.2 V. A Cr(III) oxide barrier layer was shown to grow and thicken with increasing potential, again accompanied by the segregation of Mo, and to a lesser degree W, to the outer regions of the film.

The oxide film properties have also been characterized by electrochemical impedance spectroscopy (EIS) [6,8,14]. MacDonald et al. [8] characterized the oxide properties on Alloy-22 over the potential range from –0.2 to 0.7 V. The polarization resistance \(R_p\), dominated by the barrier layer resistance, measured in hot, slightly acidic solution (pH 3, saturated NaCl, 80 °C), initially increased with applied potential within the passive range achieving values >10^5 \(\Omega\) cm^2 consistent with passivity. At a sufficiently high potential \(E>0.2V\), close to the initiation of the transpassive state, \(R_p\) begins to decrease with increasing potential. The film exhibited n-type semiconducting properties in the passive region (<0.4 V) with
a transition to p-type behavior as the oxide thinned and cations were oxidatively ejected from the barrier layer in the transpassive region [14].

Recently, Jakupi et al. [6] characterized the oxide film properties on Alloy-22 in near neutral pH, 5 M NaCl solutions, at 30 °C. A similar variation in film resistance with applied potential was observed, the impedance properties being divided into three applied potential ranges. More recently, the evolution of surface composition in these three regions has been determined by XPS [13]. Over the potential range −0.6 V to −0.3 V, the film resistance increases with potential accompanied by an increase in Cr(III) content indicating the formation of a protective barrier layer. Both the film resistance and the Cr(III) content of the oxide increase to their maximum values in the potential range −0.3 V to −0.2 V accompanied by a decrease in the relative concentration of Ni in the film [13]. Within this range the Mo content of the film (as Mo(II), Mo(IV), Mo(VI) and non-stoichiometric MoO3O4) does not vary significantly with potential [13]. For potentials >0.3 V, both the film resistance and the Cr(III) content decrease accompanied by significant increases in Cr(OH)3, Mo(VI) and W(VI), indicating the injection of cation defects into the Cr(III) oxide-dominated barrier layer in the early stages of transpassivity.

Crevice corrosion experiments conducted under galvanostatic conditions showed that a potential >0.2 V was required to initiate and stabilize active crevice corrosion at 120 °C in 5 M NaCl. This apparent threshold for initiation is consistent with a susceptibility to crevice corrosion only when defect injection into the Cr(III) oxide barrier layer occurs, as identified by XPS and impedance measurements.

The susceptibility of Ni–Cr alloys to crevice corrosion is clearly dependent on the composition of the alloy [15–17], although the critical compositional balance remains unelucidated. In an attempt to clarify the key compositional features we have been studying a range of alloys. In this paper we describe our studies on the oxide composition on Alloy C-2000 (Ni–23Cr–16Mo–1.6Cu) as a function of applied potential using Angle-Resolved X-ray Photoelectron Spectroscopy (AR-XPS) and ToF-SIMS.

2. Experimental
2.1. Materials and electrode preparation
Cylindrical specimens were cut from plate material supplied by Haynes International, Kokomo, Indiana (USA), with a diameter of 1 cm and a height of 0.5–1 cm. The cylinders were drilled at one end to allow electrical connection to a threaded rod of the same material. Prior to each experiment, the specimen surface (surface area of 0.785 cm²) was wet-polished with a series of SiC papers up to 1200 grit, and then polished successively with 5.0, 0.3, and 0.05 µm alumina powder suspensions. Specimens were then swabbed with cotton under running water to reduce the chances of staining, and finally rinsed with large amounts of Type 1 water, obtained from a Milli-Q Academic A-10 system. Specimens were immersed first in acetone and then in Type 1 water and ultrasonicated for 10 min to remove any attached polishing residue, rinsed again with large amounts of Type 1 water, and immediately placed in the electrochemical cell to minimize air oxidation.

2.2. Electrochemical film growth
A standard three-electrode, glass electrochemical cell housed in a grounded Faraday cage was used. The cell contains a working electrode (WE), a pure platinum (99.95% purity) counter electrode (CE), and an in-house fabricated saturated silver/silver chloride (Ag/AgCl) reference electrode (RE) (199 mV vs. SHE at 25 °C). Freshly prepared 5 M NaCl solutions were used as the electrolyte. The solutions were prepared from reagent grade NaCl and Type 1 water. Prior to starting each experiment, the electrolyte solution was purged for at least 1 h with UHP argon (Praxair) and purging continued throughout the experiment.

A Solartron 1284 multistat was used to apply a constant potential to the electrode, half-immersed in a stirred electrolyte. A period of 60 min of cathodic cleaning at −1.0 V was required to guarantee a reproducible surface. Subsequently, a film formation potential was applied for 44 h to grow an oxide film, and Corrware software (Scribner Associates Inc.) was used to record the data. The potential investigated were −0.4, 0, and 0.6 V to represent near-passive, passive and transpassive regions, respectively [1]. Experiments were performed at room temperature (22 ± 2 °C). The pH of the solutions was adjusted to 7.0 ± 0.2 with HCl and NaOH solutions.

After film-growth, the specimen was immediately removed from the cell, rinsed and ultrasonicated for 2 min in Type 1 water to remove any electrolyte left on the specimen surface. The specimen surface was then dried in a stream of argon gas, placed in a small tin box and stored in a desiccator. Subsequently, the specimen was analyzed using SEM, XPS and ToF-SIMS.

2.3 Surface analyses
SEM images were obtained on a Hitachi S-4500 field emission SEM equipped with an EDAX™ EDX system at Surface Science Western (SSW). All AR-XPS analyses were carried out with a Kratos Axis Ultra spectrometer at SSW using a monochromatic Al Kα (1486.6 eV) source. The instrument work function was calibrated to give an Au 4f7/2 metallic gold binding energy of 83.95 eV. The spectrometer dispersion was adjusted to give a binding energy of 932.63 eV for metallic Cu 2p3/2. The Kratos charge neutralizer system was used for all analyses. The apparent shifts of the spectra were calibrated using the C 1s peak set to 284.8 eV. High-resolution spectra were obtained using a 20 eV pass energy, whereas survey spectra were recorded using a 160 eV pass energy with an analysis area of ~300 µm × 700 µm. Two photoelectron take-off angles (measured from the sample surface), 30° and 90°, were used to analyze the oxide film on Alloy C-2000. By comparison of the information obtained at a grazing take-off angle (30°) to that at an angle close to the surface normal (90°), information on the variation of composition with depth can be obtained.

An ION-ToF Time-of-Flight Secondary Ion Mass Spectrometer (ToF-SIMS IV) was used to obtain the ToF-SIMS depth profiles and cross-sectional images for sputtered specimens. A 1 kV Cs+ ion beam was used to sputter an area of 200 µm × 200 µm on the specimen and negative secondary ions were collected from a 100 µm × 100 µm area within the sputter crater using a 25 kV monoisotopic Bi+ primary ion beam. A smaller analysis area was used within the sputter crater to avoid edge effects. Each ToF-SIMS mass spectrum was calibrated using the exact mass values of at least 3 known species in the spectrum collected during profiling.

3. Results
3.1. Electrochemical film growth
Fig. 1 shows log–log plots of current density transients recorded at the three potentials (−0.4, 0, and 0.6 V) in deoxygenated neutral 5 M NaCl at room temperature. These potentials cover the range from incomplete passivation (−0.4 V) to transpassivity (0.6 V) [1]. For times ≤ 10⁵ s the current is almost independent on time. This can be attributed to the change in composition of the cathodically reduced air-formed film remaining after the cathodic pretreatment. For t ≥ 3 × 10⁵ s, the transients recorded at −0.4 V and 0 V
show the decay expected for oxide film growth with the net current at −0.4 V becoming negative after 36 h. The current densities observed at the end of the film growth period are in the range of 100 nA cm⁻², confirming the establishment of passivity. The current density recorded at 0.6 V initially decreases due to film growth before eventually increasing slightly after 4 h, indicating the onset of transpassivity. This is consistent with the transpassive oxidation of Cr(III) in the oxide film to the more soluble Cr(VI), and the conversion of Mo from low to high oxidation states [2]. The slight decrease in current density after 27 h suggests that thickening of the transpassive oxide limits the oxidation of the substrate alloy.

3.2. SEM and ToF-SIMS imaging

SEM micrographs show that, except after polarization at 0.6 V, the oxide-covered electrode surfaces are featureless and not shown. Fig. 2 shows the alloy surface after polarization at 0.6 V for 44 h is not uniformly oxide-covered as observed at the lower potentials: some areas are covered by a dark gray product, suggesting transpassive oxidation is uneven.

ToF-SIMS images of the surfaces oxidized at 0 V and 0.6 V, Fig. 3, confirm the uneven nature of the transpassive oxidation at 0.6 V. At this potential the various species are inhomogeneously distributed.
on a scale which matches the dimensions of the dark gray areas in the SEM image. Chromium hydroxide is enriched in the dark gray areas in the SEM image, accompanied by enrichment in MoO$_2^-$ at the expense of MoO$_3^-$ at 0 V. Also, although less obvious, Ni and Cu hydroxides are enriched at the expense of the corresponding oxides. By contrast, all species detected in the film grown at 0.4 V are uniformly distributed on the surface.

This non-homogeneity in the distribution of species and the almost time-independent current density at 0.6 V, Fig. 1, indicate that transpassive oxidation tends to spread laterally across the surface. This suggests oxidation occurs at the edges of unconverted passive oxide and that the high oxidation states of Mo produced transpassively from a partially protective thicker transpassive film.

3.3 Angle-resolved XPS

Electrodes polarized at −0.4 V, 0 V and 0.6 V were analyzed by AR-XPS at take-off angles of 30° and 90°. Analyses performed at the take-off angle of 30° probe shallower depths than those recorded at an angle of 90°. Surface compositions determined from survey spectra recorded at the two angles are shown in Fig. 4. As expected, the O relative content of the surface is higher at 30° than at 90° at −0.4 V and 0 V, Fig. 4(a). At 0.6 V the O content measured at 90° is only marginally less than that at 30° consistent with an increase in film thickness after anodic oxidation at this transpassive potential. The cation composition of the oxide film, corrected for contributions from the metallic substrate (determined from high-resolution spectra), is determined by excluding the oxygen contribution in the spectral quantification, Fig. 4(b). The film was found to be composed of ~40–70% Cr, 20–45% Ni, 10–20% Mo and a detectable amount of Cu depending on the polarization potential. Comparison to the nominal composition of Alloy C-2000 shows a clear enrichment of Cr and depletion of Ni in the film, especially after polarization at 0.6 V in the transpassive range.

For both Cu and Mo, the content is higher at 30° than 90° for all three potentials, suggesting their enrichment in the outer regions of the film. However, the differences are small precluding any definite conclusions. A similar slightly more definite comparison suggests Ni, and possibly Cr, are enriched in the inner regions at the two lower potentials. At 0.6 V the Cr content is considerably lower and that of Ni slightly higher at 30° compared to 90°, consistent with the transpassive oxidation of Cr(III) to Cr(VI) in the barrier layer of the film and its subsequent dissolution. If confirmed this Cr/Mo segregation in the film is consistent with the results of Lloyd et al. obtained on Ni–Cr–Mo alloys in acidic sulphate solution [2].

High-resolution scans were recorded for the Ni 2p, Cr 2p, Mo 3d, Cu 2p, O 1s and C 1s peaks. Examples of the fitted O 1s, Ni 2p, Cr 2p and Mo 3d spectra, corrected using a Shirley background correction, are shown in Fig. 5, and the relative amounts of individual species in Fig. 6. The O 1s spectrum can be fitted with three component peaks (Fig. 5(a)); the peaks at 529–530 eV, 531–532 eV and ~533 eV are attributed to O$^{2-}$ in the oxide, OH$^-$ species or defective sites in the oxide, and adsorbed H$_2$O (or possibly O$_2$) [18], respectively. The relative amounts of O$^{2-}$ and OH$^-$ obtained by fitting the O 1s spectra at the three potentials are shown in Fig. 6(a). Large amounts of OH$^-$ are found at all three potentials, but especially at 0.6 V. The presence of large amounts of OH$^-$ is likely due to the prolonged cathodic pretreatment of the surface prior to anodic film growth. In addition, higher OH$^-$ and lower O$^{2-}$ contents are observed at 30° than at 90°, indicating hydroxides are located primarily in the outer, and oxides in the inner, regions of the film.

The Ni 2p spectra were deconvoluted using the parameter values published by Biesinger et al. [18,19], Fig. 5(b). The relative percentages (Fig. 6(b)) show similar amounts of metallic Ni at −0.4 V and 0 V at both angles, an observation apparently at odds with the signals for Cr and Mo (Fig. 6(c) and (d)) which both decrease over the potential range from −0.4 V to 0 V suggesting passive film thickening. The most likely explanation for this is that, while depleted in the Cr and Mo, Ni is slightly enriched in the alloy at the oxide/substrate interface. As expected, the metallic Ni content at 30° is smaller than at 90°. The absence of a signal for metallic Ni at both take-off angles at 0.6 V confirms the presence of a much thicker film at this potential. Comparison of the relative amounts of Ni(OH)$_2$ and NiO measured at the two angles shows a higher Ni(OH)$_2$ content and a lower NiO content at 30° than at 90°, in the passive and transpassive regions, consistent with inner oxide and outer hydroxide regions in the film as indicated by the O 1s spectra.

The Cr 2p spectra were fitted with the parameter values determined by Biesinger [19,20] (Fig. 5(c)), and the relative percentages are shown in Fig. 6(c). The relative percentages of Cr(OH)$_3$ and Cr$_2$O$_3$ are much higher and much lower, respectively, at 30° compared to 90°, consistent with an inner Cr$_2$O$_3$ barrier layer and outer hydroxide layer. Additionally, unlike for Alloy-22, the Cr$_2$O$_3$ content of the film is not significantly decreased at 0.6 V, suggesting the barrier layer may be more durable at 0.6 V in Alloy C-2000 compared to Alloy-22.

The Mo 3d high-resolution scans were fitted with spin–orbit pair intervals set at 3.13 eV and the parameters determined by McIntyre et al. [21] as shown in the example in Fig. 5(d). Mo was found to be present in the film in a range of oxidation states (IV, V, and VI), and the relative percentages are shown in Fig. 6(d). Comparison of the
Fig. 5. Examples of high-resolution fitted XPS spectra (a) O 1s (0 V, 90°), (b) Ni 2p (−0.4 V, 30°), (c) Cr 2p (−0.4 V, 30°), and (d) Mo 3d (0 V, 90°) recorded on Alloy C-2000.

Relative percentages of Mo species obtained at the two different angles indicates an enrichment of high oxidation states of Mo in the outer region of the film, especially at 0.6 V when the percentage of Mo(VI) increases markedly. Additionally, the percentage of Mo(V) measured at 90° is significantly larger than that at 30° at 0.6 V. In fact, at 30° the percentage of Mo(V) decreases with increasing potential whereas at 90° it increases, indicating a conversion of lower Mo oxidation states in the inner region of the film at 0 V to higher oxidation states in the outer regions of the film at 0.6 V.

A typical Cu 2p3/2 high-resolution XPS spectrum is shown in Fig. 7. A single peak with a binding energy ranging between 931.8 eV and 932.9 eV was obtained on all specimens. This is close to the

Fig. 6. Relative compositions of O (a), Ni (b), Cr (c), and Mo (d) species in the Alloy C-2000 surface after polarization at −0.4 V, 0 V, and 0.6 V (pH 7, 44 h) at take-off angles of 30° (solid lines) and 90° (dashed lines).
binding energy for both Cu metal and cuprous oxide, which are within 0.1 eV of each other and cannot be distinguished by XPS [22]. The well known shake-up satellite peak (5–10 eV higher on the BE scale than the principal Cu 2p1/2 line), indicative of the presence of the expected Cu(II) species [22–24] at high potentials, was not observed. The absence of Cu(II) species in the film may be due to the decomposition of Cu(OH)₂ to Cu(I) under X-ray exposure in the spectrometer [22].

3.4 ToF-SIMS results

ToF-SIMS depth profiles recorded for negative ions after polarization at −0.4 V, 0 V and 0.6 V are shown in Fig. 8. Fig. 9 shows the cross-sectional images for the ions reconstructed from the sputtering profiles. Since the sputtering rate is unknown, conversion of sputtering times cannot be accurately used to calculate film thickness. However, according to Lloyd et al. [1], the passive film thickness on this alloy in acidic solutions (pH 1) is about 2–3 nm. Since the negative ions detected in the ToF-SIMS spectra do not necessarily represent the species which exist in the oxide, the oxidation states of ions cannot be determined. However, in conjunction with other techniques (AR-XPS), ToF-SIMS data can be used to obtain the depth profiles for species within the film.

The sputtering profiles that each species exhibits a maximum intensity at a specific time, indicating its localization within the film. From the variation in these times, a layered structure of the film can be inferred. Based on peak locations, Cu and Mo oxides segregate to the outer surface of the film, hydroxides of Cr, Ni and Cu are located at intermediate depths, and the inner film region is enriched in Cr and Ni oxides. This layered structure is consistent with the AR-XPS results and is more clearly shown in the cross-sectional images in Fig. 9. It is worth noting that the analytical depth (proportional to sputtering time, Fig. 8) for the surface oxidized at 0.6 V is approximately 6 times larger than that at two lower potentials (as indicated by the arrow labeled “d” in Fig. 9). The much longer sputtering time required at 0.6 V indicates a significant increase in film thickness as indicated by AR-XPS.

While exact compositions cannot be obtained by this technique, the relative concentrations of various species can be determined if it is assumed that the various oxide components have identical sputtering efficiencies. Fig. 10 shows the Cr₂O₇⁻/MoO₃⁻ (solid line) and Cr₂O₇⁻/CuO⁻ (dotted line) ratios from the sputtering profiles. The increase in the Cr₂O₇⁻/MoO₃⁻ and Cr₂O₇⁻/CuO⁻ ratios from the outer to the inner regions of the film confirms the tendency for the alloy to form a Cr rich inner oxide layer with Mo and Cu segregated to the outer regions. The shorter sputtering time required to reach a peak in the Cr₂O₇⁻/CuO⁻ ratio, compared to that for Cr₂O₇⁻/MoO₃⁻, indicates a more emphatic surface segregation of Cu than of Mo, consistent with the AR-XPS results and published literature on stainless steels [25] and Fe–Cr alloys [26].

The larger Cr₂O₇⁻/MoO₃⁻ and Cr₂O₇⁻/CuO⁻ ratios obtained on the specimen polarized at 0 V compared to that at −0.4 V, show there is an increase in Cr₂O₇⁻ content of the inner regions of the film with potential, consistent with the development of a barrier layer oxide, as suggested by the AR-XPS results. The lower Cr₂O₇⁻/MoO₃⁻ ratio obtained after polarization at 0.6 V, together with the AR-XPS results, clearly shows the loss of Cr₂O₇⁻ from the film as CrO₄²⁻ [27], and the very broad and shallow peaks in
the Cr$_2$O$_3^-$/MoO$_3^-$ and Cr$_2$O$_3^-$/CuO$^-$ ratios at 0.6 V indicates the destruction of the Cr rich inner layer, leading to a highly defective transpassive oxide [26].

4. Discussion

As previously observed for Alloy-22, the oxide film on Alloy C-2000 exhibits a bilayer structure consisting of a Ni/Mo-containing inner Cr(III) oxide barrier layer formed directly on the alloy surface and an outer hydrous oxide layer formed by hydrolysis of cations ejected from the barrier layer. This separation between an oxide-dominated inner layer and an outer hydroxide-dominated layer is clearly demonstrated by AR-XPS.

As the applied potential is increased from $-0.4$ V (near passive region) to 0 V (passive region) the XPS results indicate an increase in film thickness accompanied by an increase in Cr(III) content of the inner oxide, consistent with previous observations for Alloy-22 [1,2,8,13]. The observation that the relative Cr content of the film increases while that of Ni decreases with potential leading to an increased Cr content of the inner oxide indicates the principle process leading to passivity is the dissolution of Ni and retention of Cr, in agreement with previous observations by Lloyd et al. in acidic sulphate solutions [2].

This improved passivity with increasing Cr(III) oxide content was demonstrated for Alloy-22 by EIS measurements [6] and confirmed for C-2000 in a similar manner [to be published]. It is worth noting that the Cr(III) oxide content of the inner layer for Alloy C-2000 in this study (>30%) is considerably higher than that obtained after anodic polarization of Alloy-22 (≤10%). This difference most likely reflects the longer duration of anodic oxidation in the present case (44 h) compared to the Alloy-22 study (2 h) rather than the influence of any specific differences in composition (the absence of W (3 wt.% in Alloy-22) and the presence of Cu (1.6 wt.% in C-2000)) although this remains to be unequivocally demonstrated [28].

The Cr/Mo segregation process, observed primarily by ToF-SIMS, has been previously observed for Mo-containing stainless steels [29] and Ni–Cr–Mo alloys [1–3]. It has been claimed that the Mo(VI) in the outer layer of the oxide is stabilized as MoO$_4^{2-}$ by the high electric field leading to deprotonation of OH$^-$ within the film which supplies O$^{2-}$ to enhance the formation of the Cr(III) inner oxide [30].

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**Fig. 9.** ToF-SIMS cross-sectional images for Alloy C-2000 reconstructed from sputtering profiles after polarization at (a) $-0.4$ V, (b) 0 V and (c) 0.6 V (pH 7, 44 h). The lighter colors indicate a higher content of the species shown in the images. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
The accumulation of a Cu layer on the surface of Ni–Cr–Mo alloys has not been observed previously. On 304 stainless steel containing 0.19 wt.% Cu, Ogle et al. [31] used linear sweep voltammery coupled to downstream atomic emission spectrometry (AES/EC) to show congruent dissolution of Fe, Cr, Ni, Mn and Mo but delayed release of Cu. EDX analysis of the surface layer on 304 stainless steel (1.9 wt.% Cu) showed an increase in Cu content to 6.91 wt.% confirming its retention on the steel surface [32]. The overall suppression of anodic dissolution was attributed to the accumulation of this layer [32]. Itzhak and Peled [33] claimed that the deposition of Cu on the surface of 316 sintered stainless steel containing 0.25–5.0 wt.% Cu improved the corrosion resistance. Seo et al. [34] found that Cu suppressed the anodic dissolution of Fe−26Cr in 1 M H2SO4. The morphology of the deposited Cu was found to vary on the surfaces of ferritic and austenitic steel [35], but a metallic Cu layer was found by most workers [32].

The beneficial effect of alloying with Cu has been attributed to the stability of deposited Cu on an anodically oxidized surface [36], but also to the presence of Cu in solid solution and Cu-rich phases in the matrix of the alloy, and to the rapid formation of a Cu-rich surface layer during active dissolution [37].

However, Seo et al. [34] claimed that Cu reduces the stability of the passive layer, and also the passive film on Cu-bearing stainless steels was destroyed by Cl− attack more easily than that on steel containing no Cu [35]. Lizovs [38] found that Cu reduces the stability of the passive layer on stainless steels containing less than 1% Mo, but this reduction was over-ridden when the Mo content was increased to 3%. In addition, the suppression of anodic dissolution by the deposited Cu was only observed in the potential range in which it was stable. At more positive potentials, Cu dissolved as CuCl2− in solutions of low pH and high Cl− concentrations, and the dissolution potential shifted in an active direction as the Cl− concentration was increased [31,35]. It was also suggested that the dissolution of Cu as complexes CuCl−, CuCl2−, CuCl3− and CuCl4− might assist the destruction of the passive film, making Cu harmful to the localized corrosion resistance of both ferritic and austenitic stainless steels [35]. The details of the effect of alloying with Cu remain uncertain.

The enrichment of Cu in the outer region of the oxide film on Alloy C-2000 is consistent with the results for stainless steels. However, the chemical state of the Cu is difficult to determine by XPS and ToF-SIMS techniques, due to the possibility of the reduction of Cu(II) species to Cu(I) under X-ray exposure [22]. Also, the closeness of the BE for Cu metal and cuprous oxide, makes their separation in XPS spectra extremely difficult. Based on thermodynamic evidence [35,39], metallic Cu would be expected on the surface of Alloy C-2000 at −0.4 V, while at 0 V and 0.6 V, Cu2+ and Cu3+ would be the stable forms, respectively. The CuO and Cu(OH)2 found in the surface of Alloy C-2000 by ToF-SIMS sputtering profiles and images may be due to the ion interactions in the sputtering/analysis chamber in the instrument, and cannot be used to confirm the oxidation state of the Cu. However, the SEM images show no evidence for the separation of any crystalline forms on the surface of the alloy in the passive (0 V) and transpassive (0.6 V) regions. This could suggest that the Cu is incorporated in the outer regions of the film in the Cu(I) and/or Cu(II) states, although the present analyses could not confirm this.

The composition and structure of the passive film change considerably when the film-growth potential is extended into the transpassive region (0.6 V). A much thicker but non-uniformly distributed film was observed. The transpassive oxidation of Cr(III) to Cr(VI) in the barrier layer of the film and its subsequent dissolution, leads to the destruction of the Cr2O3-enriched inner layer, as indicated by the extremely low relative oxide to hydroxide content in the AR-XPS results, and the loss of a peak in the Cr2O3−/MoO3− intensity ratio obtained from ToF-SIMS sputtering profiles. The oxidative dissolution of Cr(III) leads to the introduction of a large number of cation vacancies in the film and a decrease in polarization resistance [6,8]. This destruction of passivity allows the transport of Ni through the film and its dissolution at the oxide/solution interface. Also, the percentage of Mo(VI) increases markedly, indicating a conversion of lower Mo oxidation states in the inner regions of the passive film to higher oxidation states in the outer regions. Additionally, the AR-XPS data shows oxidation of Mo(V) to higher oxidation states takes place in the inner layer of the film.

The SEM evidence in Fig. 2 suggests this accumulation retards extensive dissolution. Although the XPS results (Fig. 6(c)) suggest the Cr(III) oxide content of the barrier layer is high at this potential it does not prevent the onset of transpassive behavior. This apparent contradiction may reflect the local nature of the onset of transpassivity (Fig. 2) with areas of intact passive film coexisting with transpassively degraded areas.

5. Summary and conclusions

The passive and transpassive properties of oxide films on C-2000 at various potentials were investigated by AR-XPS, ToF-SIMS and SEM. The presence of a layered structure in the passive film has been demonstrated, with the outermost surface being enriched in Cu (or Cu oxide) and Mo oxide, the intermediate region dominated by Cr/Ni hydroxides, and the inner region comprising Cr/Ni oxide.

As the film growth potential is increased into the transpassive region (0.6 V) the oxidative destruction of the Cr(III)-dominated barrier layer occurs non-uniformly on the surface of the alloy. This may account for the AR-XPS observation that the Cr2O3 content of the surface layer does not apparently decrease and indicates that transpassive oxidation tends to spread laterally across the surface and the higher oxidation states of Mo produced transpassively, and shown to accumulate by ToF-SIMS, form a partially protective film. This film is approximately six times thicker than the passive film present at less positive potentials.

As potential increases from −0.4 to 0.6 V, the film thickness increases, and the relative Cr content of the film increases while that of Ni decreases. The passive film (0 V) has a relatively thicker inner oxide layer and higher Cr2O3 content in the inner layer, compared to the near-passive film (−0.4 V). When the film-growth potential is extended into the transpassive region (0.6 V), the composition and structure of the film change considerably. The transpassive
oxidation of Cr(III) to Cr(VI) in the barrier layer of the film and its subsequent dissolution leads to the loss of the Cr₂O₃-rich inner layer and the destruction of passivity.

Acknowledgements

The authors gratefully acknowledge the U.S. Department of Energy and the National Science and Engineering Research Council of Canada (NSERC) for the funding sources, and Haynes International, Kokomo, Indiana, for their generous donation of materials. Special thanks go to Dr. Mark Biesinger, Dr. Heng-Yong Nie, and Mr. Ross Davidson at Surface Science Western (SSW), for their knowledge and assistance on the analytical techniques employed in this study.

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