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Oxide Surface Analysis of Nickel Based Chromium Alloys with the Aid of Auger Electron Spectroscopy

Aezeden[1] Mohamed and Jack Cahoon[2]
[1]Faculty of Engineering and Applied Science, Memorial University, St. Johns, NL, Canada, A1B 3X5
[2]Faculty of Engineering, University of Manitoba, St. Winnipeg,, MB, Canada, R3T 2N2

Abstract:- Auger Electron Spectroscopy (AES) has been used to study the surface compositions of three types of nickel based chromium alloys. These alloys are IN600, IN601 and C22. AES analysis indicated the presence of chromium and oxygen on their surfaces. The formation of this chromium oxide surface layer, 3 nm thick, provides excellent corrosion resistance. For alloy C22, no molybdenum was indicated on the surface, but it was found in the alloy bulk. Mo supposedly enhances the pitting resistance of an alloy.

Keywords:- analysis, chromium, layer, molybdenum, oxides, surface.

I. INTRODUCTION

Results from Auger Electron Spectroscopy (AES) of the surface composition of passive oxide films have been reported for Ni–Cr-Mo based alloys [1-3]. The presence of an inner oxide layer rich in Cr (barrier layer) is shown to be a primary factor in creating this passivity. The main effect of Mo content is to enhance the corrosion resistance of Ni-Cr-Mo based alloys but the mechanism is less well understood than for Cr content. It has been postulated that Mo on the alloy surface preferentially locates at local defects, which otherwise would act as dissolution sites [4], and slows anodic dissolution because of its higher metal–metal bond strength [5]. An alternative hypothesis is that MoO_4 is formed in the solid state in the exterior regions of the film. This MoO_4 layer is cation selective and resists the incorporation of anions, such as Cl^- and OH^-, which allows for the growth of a CrO inner barrier layer. The resulting bipolar film stabilizes the oxide phase [6].

The mechanism by which Mo enhances the corrosion resistance of Hastelloy C22 is not yet understood and a variety of possible mechanisms have been suggested. It has been postulated on the basis of surfaces analyses that the high-Cr alloys were able to build thick oxides with a layered structure, consisting of an inner Cr–Ni oxide layer and an outer Mo-Cr oxide. By contrast, such a high-Cr content inner layer and structured elemental distribution were not achieved with alloys having lower bulk Cr than alloys IN601 and C22 [7]. Surface preferentially locates at pits, which otherwise would act as dissolution sites, and slows anodic dissolution because of its higher metal–metal bond strength [8-11].

The aim of this paper is to report on surface analyses of IN600, IN601 and C22 alloys.

II. EXPERIMENTAL PROCEDURE

The IN600, IN601, and C22 alloys used in this study were pitted due to subject to aggressive environments. Auger electron spectroscopy (AES) was undertaken in an attempt to relate the corrosion behavior of these alloys to the nature of the surface oxide film.

In Auger Electron Spectroscopy (AES), an electrically conducting sample is bombarded with an electron beam having an energy of 20keV. These bombarding electrons cause a core electron from an atom in the sample to be ejected, resulting in a photoelectron and an atom with a hole in a core electron shell. The atom then relaxes via an electron with a lower binding energy from an outer electron shell dropping into the core hole, thus releasing some energy. The energy released results in the emission of an electron called an Auger electron after Pierre Auger who discovered this relaxation process. The energy of the Auger electron is characteristic of the element that emitted it and upon being measured can be used to identify the element. Since these ejected Auger electrons have very low energies and can escape only from the first few surface atomic layers, the composition of the surface layers can thus be determined.

Scanning electron microscopy (SEM) was also used to observe passive film breakdown in the form of pits.

III. RESULTS AND DISCUSSIONS

Auger analyses for IN600, IN601 and alloy C22 before sputtering and after sputtering are presented in Figures 1 (a), 2 (a), and 3 (a) and Figures 1 (b), 2 (b), and 3 (b) respectively. Sputtering involves removal of surface layers by an argon ion beam so that before-sputtering results are indicative of the surface composition whereas after-sputtering results represent the bulk composition of the alloy.

Both IN600 and C22 as in Figures 1 (a), 3 (a) show the presence of C on the surface but not in the bulk alloys as in Figures 1 (b), and 3 (b).

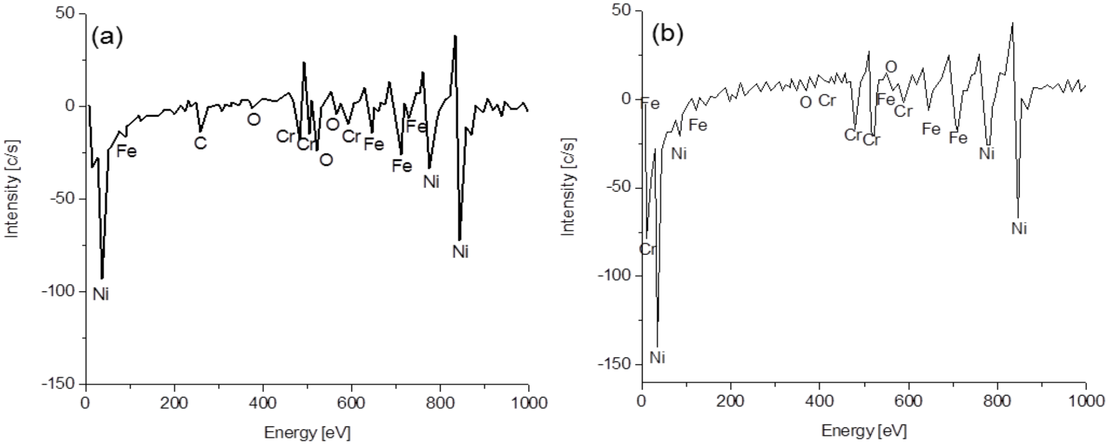

Fig. 1: AES surface analysis results for IN600 (a) before sputtering, and (b) after sputtering.

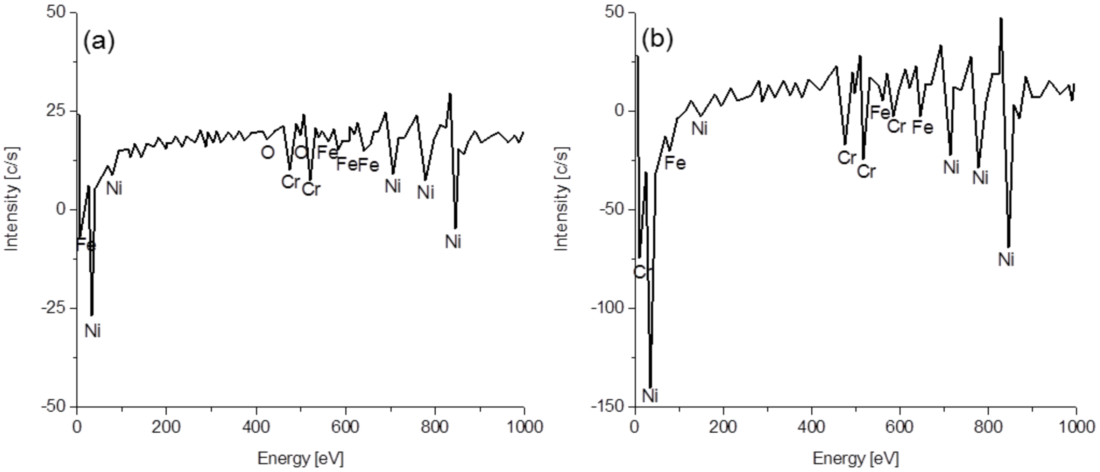

Fig. 2: AES surface analysis results for IN601 (a) before sputtering, and (b) after sputtering.

Since these alloys contain very little carbon, it is highly probable that the presence of C on the surface results from CO_2 in the atmosphere.

The most interesting result of these analyses is that the surface of alloy C22 does not exhibit any Mo as in Figure 3 (a) even though the bulk contains considerable Mo as in Figure 3 (b). This is puzzling since Mo supposedly enhances corrosion resistance. The absence of Mo on the surface of austenite stainless steel was also reported by Bandy [12].

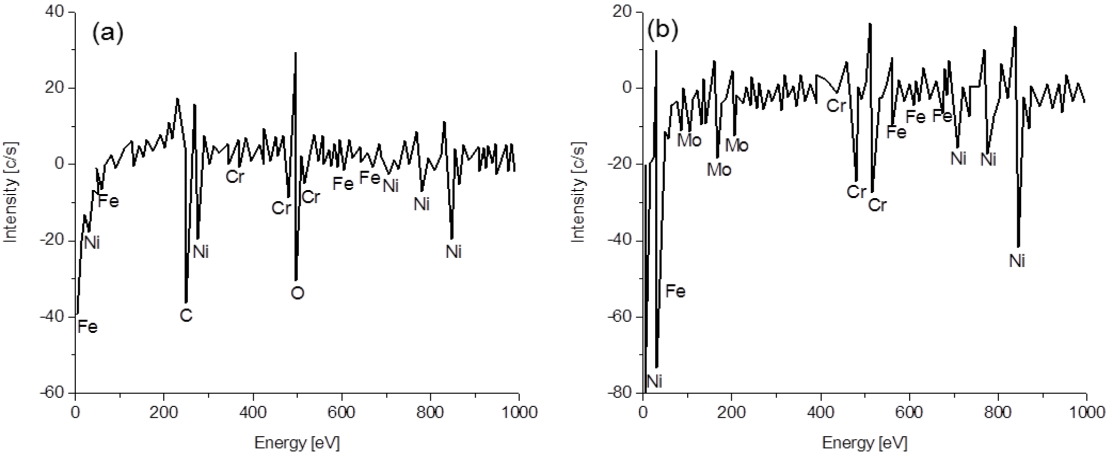

Fig. 3: AES surface analysis results for C22 (a) before sputtering, and (b) after sputtering.

Auger electron spectra were recorded in as-received samples of each alloy to determine the oxides as in Figures 1 (a), 2 (a), 3 (a). Clean surfaces of the samples were obtained by removing C and O atoms as in Figures 1 (b), 2 (b), and 3 (b) by means of an Argon (Ar^+) ion beam etching to remove the top 200 nm to 250 nm. Figures 4 (a), 4 (b), and 4 (c) show Auger depth profile results for IN600, IN601 and C22, respectively. These show that for each alloy Cr and O, presumably in the form of Cr_2O_3, tend to replace Ni and Fe on the surface. The Mo depth profile for alloy C22 also shows an absence of Mo on the surface. It was also indicated that the thickness of the oxide film is typically about 3 nm ($30A^o$) (Figure 4).

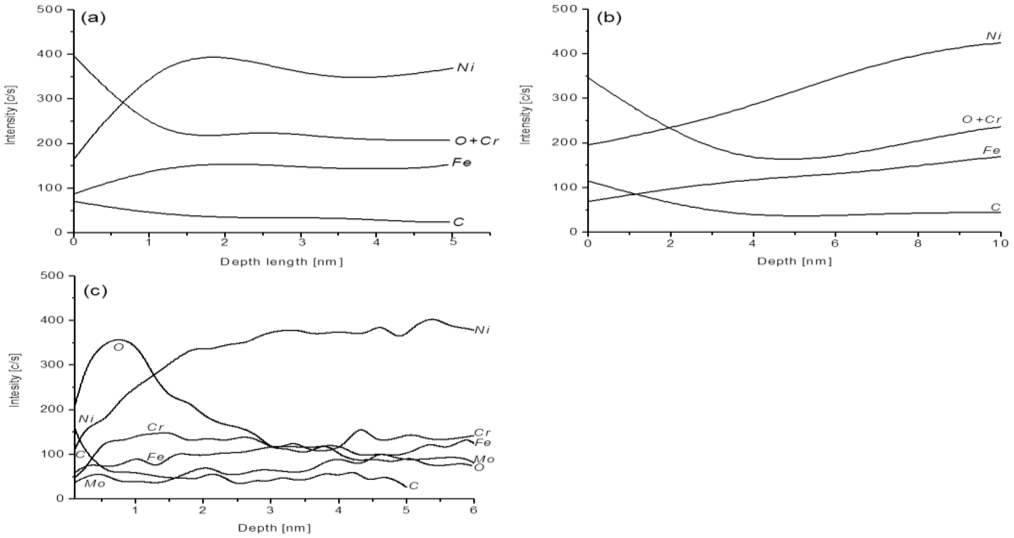

Fig. 4: AES depth of profile for (a) IN600, (b) IN601, and (c) C22.

A scanning electron microscopy (SEM) micrographs of an as received sample prior to immersion in a corrosive environment is shown in Figure 5 (a). SEM micrographs of these three alloys taken after immersion of samples in corrosive solutions as shown in Figure 5 (b), 5 (c), and 5 (d) indicated a morphology of surface pits for samples of IN600, IN601 and C22. Surface pits were more pronounced in the IN600 sample as in Figure 5 (b) and least pronounced in the IN601 and C22 samples Figures 5 (c) and 5 (d). The sample of alloy C22 showed no surface pits, thus indicating that the passive oxide layer from the addition of molybdenum and chromium is effective.

Fig. 5: SEM micrograph show (a) a representative samples before immersion, (b) IN600, (c) IN601 and (d) C22. (b, c, d) samples after immersion indicate from sever surface pits to slight surface pits respectively.

IV. CONCLUSIONS

Auger analysis indicated that Cr and O was present on the surfaces of samples from the IN600, IN601 and C22 alloys and is likely in the form of a Cr_2O_3 layer. Further, this layer extends to approximately 3 nm into the bulk of these alloys. Auger results did not show any Mo on the surface of alloy C22. However, a bulk, Mo content of 13.5% was noted. This is a puzzling result in that Mo supposedly enhances the pitting resistance of an alloy.

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