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AN ATOM-PROBE STUDY OF PASSIVATED SURFACE OF A STAINLESS STEEL

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Abstract - The compositions of the passive film formed on stainless steel and the metallic phase below the film was analyzed by an atom-probe. FIM tips were prepared from a cold-worked type 316 stainless steel wire and field evaporated to obtain the clean surface. Then the tip was exposed to atomosphere and treated with nitric acid to form the passive film on the surface.

The analysis shows that the passive film formed is at most 4 monolayers thick and consists mainly of Cr-compound. The alloying elements Cr and Ni are enriched in the film. As the passivation time becomes longer, the Cr enrichment tends to progress. It is shown that Mo is enriched at the film-metal interface.

I INTRODUCTION

The surface of stainless steels has been the subject of numerous papers both in the field of corrosion and vacuum science. With the advent of surface sensitive analytical techniques combined with inert gas ion sputtering, the surface compositions and structures of the passive oxide film formed on the surface of stainless steels have been deduced /1,2/. Atom-probe is unique among the family of surface analytical techniques that have been introduced in recent years in that it examines only the outermost atomic layer of the surface. Due to its excellent spatial and depth resolution in combination with the facility for identifying chemically any impurities quantitatively, the atom-probe is ideally suited to the study of the composition of thin oxide films and the interface between the film and the metal.

This paper describes the atom-probe study of the compositions of the passive film formed on the surface of type 316 stainless steel and the distribution of alloying elements across the interface between the film and the metal.
II EXPERIMENTAL METHODS

Details of our energy-focusing TOF atom-probe have been described elsewhere /3/. The specimens were prepared from a cold-worked type 316 stainless steel wire of 0.2mm diam. A nominal composition of the wire was 18.65at%Cr, 11.40at%Ni, 1.46at%Mn, 1.03at%Mn and 1.19at%Si. The specimen tips were electrolytically etched using a solution of concentrated HCl at 2-3Vac, and rinsed with pure water. The as-etched tips were field evaporated at first to remove the contaminated surface layers until the bulk composition of the steel was obtained. Afterward, the specimen was removed from the atom-probe and exposed to air. Then it is immersed in a nitric acid solution to form the passivated surface. During the passivation no electrical potential was applied to the specimen. Nitric acid solutions of 10% and 30% concentrations were used and the passivation was carried out for 5min to 70hrs at 20°C and 60°C. The passivated specimens were rinsed with pure water and in some cases followed by acetone rinse. Then they were introduced into the atom-probe for compositional analysis. The atom-probe analysis was performed by superimposing pulse voltage on dc voltage at a ratio of 1 to 3 at 40K. The vacuum during the analysis was 10^-10^-11Torr.

III RESULTS AND DISCUSSION

Figure 1 shows an example of the atom-probe mass spectra obtained prior to and after passivation treatments in 10% nitric acid at 20°C for 15min and 30% nitric acid at 60°C for 90min. The spectra show contributions both from the passive film and the metal underneath the film. For the field evaporated clean surface only ions of the metallic constituents of the type 316 stainless steel are observed. For the passivated surfaces, ions of oxides, hydroxides, O, OH, H2O, H3O, C, N and CH3 appear in addition to the metallic ions. Carbon related ions and nitrogen seem to be resulted from contamination during the passivation and/or exposure to air.

For chromium containing species, a considerable number of oxide ions, CrO2+ and CrO22+ are present and several hydroxide ions, CrO(OH)2+ and CrOH+ as well. These ions are present only in the passive film which has at most a thickness of four monolayers, as shown later. Iron appears to be slightly oxidized in the film by judging from the presence of oxide and hydroxide ions fewer than the chromium containing species. The two other main alloying elements, nickel and molybdenum are present only in the form of metallic ions. It appears that the passive film consists mostly of slightly hydrated chromium oxide and lesser fraction of iron oxide.

Figure 2 shows the dependence of the concentration depth profile of Cr on that of Fe as a function of the passivation time in 10% nitric acid at 20°C. From the slope of the plots, it is suggested that the chromium enrichment progresses slowly with time and is limited in the passive film. Kinetic effects must be in control of the change of composition. The initially formed film contains a high concentration of iron due to its availability and prolonged exposure enriches chromium in the film.
Fig. 1: An example of atom-probe mass spectra of the type 316 stainless steel surfaces.

Fig. 2: Relation between Cr and Fe concentration depth profiles as a function of passivation time in 10% nitric acid at 20°C.
Figure 3 shows the layer to layer variation of the concentration of Fe, Cr and Ni. One monolayer is estimated to correspond to 20 ions from the intervals of ion detection. The average concentration of major constituents in the passive film is 60% Fe, 27% Cr and 13% Ni for the passivation in 10% nitric acid and 36% Fe, 45% Cr and 19% Ni for 30% nitric acid. It is clearly seen that chromium is enriched in the film and nickel also shows a clear indication of enrichment. The difference in the extent of enrichment between the two passivation treatment appears to arise from the progress of the passivation. As suggested previously, the chromium enrichment and iron depletion in the passive film may be a result of the selective dissolution of iron and preferential oxidation of chromium during the passivation treatment /2,4/. Nickel is not oxidized because of its high chemical stability in comparison with iron and chromium. The chromium enrichment shows the maximum in the outermost layer in the film for the 30% nitric acid passivation, while in the second layer for the 10% nitric acid passivation. The presence of a slight maximum in Cr concentration profile inside the passive film has been noticed by several workers /5,6/. This may be an indication of the progress of the passivation, that is, the early stage for the 10% and the later stage for the 30% nitric acid passivation. According to XPS studies of the passive film /2,4/, nickel does not appear to be enriched in the film, but in the metal underneath the film. However, the present results clearly show the enrichment of nickel in the film and this is simply due to the result of the selective dissolution of iron. Further the preferential oxidation of chromium may be considered to result in the concentration gradient shown in the figure.

Figure 4 shows the concentration depth profiles of chromium oxide and hydroxide, oxygen and water and molybdenum. The thickness of the passive film is estimated to be three to four monolayers from the depth where no increase in the number of oxide and oxygen ions is observed. This is in agreement with the thickness estimated in the XPS study of Mo containing stainless steels /4/. A considerable enrichment of molybdenum is found at the film-metal interface for the passivation in 10% HNO₃. Molybdenum content in the passive film has been investigated by several workers /2,4,7/. Following Olefjord and Elfstrom /7/, the molybdenum content in the film depends on the potential during the passivation and molybdenum is significantly enriched in the film at lower potentials. This is in accordance with our findings. During the selective dissolution of iron, molybdenum, chromium and nickel are enriched on the surface of the metal phase and during the development of the passive film chromium is preferentially oxidized while nickel and molybdenum are scarcely oxidized. The structure of the passive film may be deduced as follows. The number of detected OH⁻ and hydroxide is small compared to that of O²⁻ and oxide and at least in depth O²⁻ and oxide are dominant. After taking the previous studies by XPS into account /2,4/ it is concluded that the outermost layer of the passive film consists of CrO(OH) and the inner layer of Cr₂O₃.

The use of UHV analytical technique to study passivated surface is frequently criticized because of the possibility of dehydrating the passivated surface thus changing its composition. However the detection of H₃O⁺, H₂O⁺, OH⁻ ions in the stainless steel surface demonstrates that water is strongly bonded to the surface and its loss from the passivated surface is not an inherent consequence of placing it in the atom-probe.
Fig. 3 Layer to layer variation of the concentration of the major constituent

Fig. 4 The concentration depth profiles of chromium oxide and hydroxide, oxygen and water, and molybdenum
CONCLUSION

This study confirms the previous results that the passive film formed on the stainless steel surface consists mainly of chromium compounds, possibly the outermost layer of CrO(OH) and the inner layer of Cr$_2$O$_3$. The selective dissolution of iron in the acid results in the enrichment of chromium and nickel in the film and molybdenum at the film-metal interface. The thickness of the passive film is at most 3 to 4 monolayers and the composition of the film depends on the passivating conditions.

REFERENCES