ION IMPLANTATION FOR CORROSION INHIBITION OF ALUMINUM ALLOYS IN SALINE MEDIA

J. M. Williams, Oak Ridge National Laboratory,* Oak Ridge, TN

A. Gonzales, AVSCOM-DERSO, Corpus Christi, TX

J. Quintana, Corpus Christi Army Depot, Corpus Christi, TX

I-S Lee and R. A. Buchanan, The University of Tennessee, Knoxville, TN

F. C. Burns, R. J. Culbertson, and M. Levy, U. S. Army Materials Technology Laboratory, Watertown, MA

J. R. Treglio, ISM Technologies, Inc., San Diego, CA

Abstract

The effects of ion implantation treatments on corrosion of 2014 and 1100 aluminum in saline media were investigated. Implanted ions were N, Si, Ti and Cr. Techniques included salt spray testing, electrochemical studies, Rutherford backscattering spectrometry, and profilometry. It was concluded that ion implantation of Cr is of potential practical benefit for corrosion inhibition of 2014 Al in salt environments.

1. Introduction

Aluminum and its alloys are vulnerable to corrosion by pit initiation when exposed to saline environments such as sea water, salt spray and marine atmospheres. In particular, the wrought commercial alloy, 2014 Al, is more susceptible to corrosion in salt environments than some other aluminum alloys. Because of superior mechanical properties, however, this composition finds use in aircraft construction. Better protection of 2014 Al surfaces against pitting corrosion would result in more highly optimized components, and thus could contribute to better overall performance of aircraft systems.

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The results of the present paper form part of a larger and continuing study on use of ion implantation treatments for corrosion inhibition of aluminum in saline environments. Results are presented for the ion species, nitrogen, chromium, titanium and silicon, as implanted into 2014 Al. The engineering test consisted of salt spray exposure. Other techniques included electrochemical and Rutherford backscattering (RBS) analyses. For comparison with the results from 2014 Al, parallel studies have also been done on 1100 Al, a nominally pure commercial aluminum.

It will be concluded that ion implantation of chromium is quite effective as corrosion protection for 2014 Al.

2. Experimental Procedures

2.1. *Processing, testing, and analyses*

Ion implantations were performed by use of a Varian/Extrion 200–1000 implanter, a well-known design which provides for magnetic analysis of beam. The sample coupons were secured to a cooled Ni-block type of target holder for implantation. Temperatures of the block ranged from -10 to 40°C during the implantations. From previous tests it can be concluded that, for a ductile material such as Al, secured to the block, the sample temperature is no more than 5°C higher than the block temperature. Vacua during implantations ranged from 8×10^{-7} torr down to 2×10^{-7} torr. Fluencies and energies will be stated in the results, except for certain of the nitrogen implantations. Some nitrogen treatments were intended to produce more-or-less flat concentration profiles of specified concentration to depths of about 0.25 microns. The treatment consisted of three

implantations at combinations of fluences and energies designed by calculation [1] to achieve the desired concentration. For example, for 20 at.% N the parameters were $5.3 \times 10^{16}/\text{cm}^2$ at 17.5 keV, $6.0 \times 10^{16}/\text{cm}^2$ at 32 keV and $2.0 \times 10^{17}/\text{cm}^2$ for 65 keV. Proportional adjustments were made for the 10 at.% and 30 at.% profiles. Dosimetry was by current integration during implantation. For Cr and Ti implantations, dosimetry was confirmed by use of Rutherford backscattering spectrometry (RBS).

Salt spray (fog) testing was conducted according to the ASTM Standard Method described in ASTM Designation B 117-73 [2]. In concept, the test consists of placing the samples in a large chamber into which salt fog is continually introduced by atomization. In compliance with the specification, the environment temperature was $35 \pm 1^\circ\text{C}$, the pH was between 6.5 and 7.2, the NaCl concentration was 5 ± 0.5 wt.%, and the fog density was such as to produce 1.8 milliliters of condensate per hour (average) per 80 cm^2 at area.. Exposure time was 168 h.

For electrochemical experiments, samples were immersed in 1 wt.% NaCl deaerated solution. Studies consisted of potentiodynamic cyclic anodic polarization experiments.

Rutherford backscattering spectrometry (RBS) [3] analyses made use of He ions at 2.0 MeV incident energy. The scattering angle was 160° for all analyses.

Profilometry was by use of of a Dektak IIA profilometer equipped with a submicron stylus.

2.2. *Starting materials*

The composition of 2014 Al is nominally 4.4 wt.% Cu, 0.8 wt.% Si, 0.8 wt.% Mn, and 0.5 wt.% Mg, the balance being Al. The 1100 alloy is 99 wt.% Al minimum,

with the principal alloying constituent being Cu at the 0.1 wt.% level. The 2014 was in the hard form (T6).

Starting surfaces were prepared by two types of polishing processes. The first (named "A") was a metallographic technique which made use of a colloidal silica polishing compound. This compound has a pH of about 9. This treatment produced a very bright and mirror-like surface on 1100 Al. On 2014 Al the surface was also very bright but was considerably more wavy in texture than the surface on the 1100. This result is presumably connected with the presence of Cu precipitates in the 2014. The "mechanical" polish consisted of first grinding and polishing the surface to a finish of 0.1 micron RMS. Then the samples were further polished by use of 2-6 micron diamond paste. Although smooth, these surfaces were not as lustrous as those produced by the "A" polish. Starting surfaces for 1100 Al were produced only by the "A" polish. Either polish was used for respective samples of 2014.

Rutherford backscattering spectra for typical starting surfaces are shown in Fig. 1. The most important point is that the "A" polish produces some enhancement of Cu concentration at the surface of 2014 Al, apparently due to preferential removal of Al by the somewhat caustic polishing compound. This can be seen by comparing curves 1 and 2 in Fig. 1. It later turned out that samples with the "A" polish performed worse in pitting corrosion than samples with the mechanical polish. There was even some enhancement of Cu concentration at the surface of the 1100 Al (curve 4). Another spectrum for mechanically polished 2014 Al (curve 3) is also shown in Fig. 1. Comparison of curves 2 and 3 demonstrates that there was variability in the amount of O incorporated into the near-surfaces among mechanically polished samples. The amount of O in the near-surface for curve 2 (Mechanical 1) for example was $1 \times 10^{17}/\text{cm}^2$, whereas O was not detected for Mechanical 2. It is suspected that heating during the grinding process is the factor that determines the amount of O in the surface of as-prepared samples.

3. Results

Figure 2 is a photograph of coupons of 2014 alloy for the respective conditions indicated. The salient impression presented by the photograph can be taken as a rather accurate representation of the relative merits of these particular implantation treatments. The implanted area of Cr-implanted sample has no visible pits, but is in fact somewhat less bright than the new sample, due to addition of some O (see below). The Ti-implanted sample may be slightly under represented in merit by this particular lighting, but there are a few pits, particularly near the periphery of the implanted area. The low dose Si implant is of no benefit, and the high dose is of some slight benefit. Nitrogen implanted samples of 2014 Al (10 at.% N, 20 at.% N and 30 at.% N) are not shown. The N-implanted samples of 2014 Al were all indistinguishable from unimplanted ones after salt spray testing. Therefore, N-implantation of 2014 Al was considered to provide no benefit against corrosion in this severe salt spray test.

Oxide coatings from unimplanted areas are not reflective, but in some cases exhibit a white coloration. There are some small reflective areas in between the large patches of oxide.

Figure 3 is a profilometry trace for which the stylus has travelled from the implanted to the unimplanted area for the Cr-implanted sample of Fig. 2. The elevation of the original surface is well defined by the Cr-implanted area. On the unimplanted area large patches of oxide, which have apparently grown from pit nuclei, are 30 microns thick. Between these oxide areas are other areas which have not been severely oxidized, and which remain somewhat reflective. This oxide texture is typical of that for unimplanted samples for both 2014 and 1100 Al, except that for 1100, there are fewer pit

nuclei and oxide patches. The reflective areas in between the oxidized areas are somewhat more prominent for 1100.

Figure 4 shows RBS histograms for the Cr-implanted sample of Fig. 1 and for an as-implanted sample. For the implanted and tested sample it is evident that some O has been added by the 168-h salt spray exposure. The concentration of oxygen corresponding to the peak in the implanted and tested sample is $3.5 \times 10^{17}/\text{cm}^2$. If all of this oxygen were added by the test, the corresponding weight gain would be only $9.3 \times 10^{-6} \text{ gm}/\text{cm}^2$. The amount of O on the surface before implantation or after implantation for this particular sample is not known, however. Thus, the value quoted for added oxygen can be considered to be the maximum.

The Cr and Al edges remain at the same energies as before the test. Thus, it can be concluded that no unknown substances of appreciable thickness are covering the surface. Some implanted Cr is essentially all the way out to the surface for both cases. Owing to addition of oxygen within the implanted layer, the Cr peak just back of the surface has been somewhat broadened. The oxygen contributes to inelastic loss of the He ions, and thus spreads the Cr backscattering events out over a wider energy range than for the untested case. Within 3%, the amount of Cr in the two peaks is the same. Further quantification is presented below.

The RBS histogram for the Ti-implanted 2014 Al sample of Fig. 2 is qualitatively similar to that for Cr. About twice as much oxygen was added as for the Cr-implanted, and the Ti peak was somewhat more broadened than the Cr peak.

Figure 5 presents a summary of some electrochemical results for samples immersed in deaerated 1 wt.% NaCl solution. The results presented are the pitting potential and a potential that characterizes the resistance to pit propagation. This latter indication is taken as the potential at a current offset of $1 \text{ mA}/\text{cm}^2$. Potentials are represented relative to the standard hydrogen electrode (SHE). Although the results are

not presented graphically, it was observed that the open circuit corrosion potentials were generally unaffected by ion implantation for N and Cr treatments. Corrosion potentials were about -0.75 V for these cases and for unimplanted material. For Si and Ti treatments, the corrosion potential was increased to approximately -0.4 V, and for both Si fluencies the corrosion potential apparently exceeded the pitting potential for 1100 Al. Elevation of the surface to a high floating potential may be the reason that Si-implanted samples were rather susceptible to pitting in the salt spray test. For Ti-implanted Al the corrosion potential remained slightly less than the pitting potential.

The most striking positive indication of Fig. 5 is the marked improvement in pitting potential for 1100 Al for certain nitrogen implantations. These results for 1100 Al are in contrast to those for 2014 Al, for which nitrogen produced essentially no effect on the electrochemical indicators. Apparently for nitrogen, there is an optimal dose, which is less than the maximum. This result seems broadly in agreement with that of Venkatraman et al.[4]

Salt fog testing of N-implanted 1100 Al produced an oxide which differed considerably in appearance from that which was formed on unimplanted 2014 Al or on N-implanted 2014 Al. The coating on 1100 was smooth (profilometry) and of a rather uniform tan color. The appearance was independent of nitrogen dose for 10, 20, and 30 at. % treatments. The coating was essentially Al_2O_3 of some microns in thickness, as was determined by RBS analysis.

Oxides on many samples subjected to salt fog testing were surveyed by RBS, and the histograms were compared with that derived from a high-purity Al_2O_3 insulator. Although the spectra have not been analyzed in quantitative detail, it was judged that the composition of the oxides is generally close to the stoichiometry of Al_2O_3 . No Na or Cl was detected in corrosion products. Occasionally unexpected elements were detected. One batch of samples had appreciable carbon incorporated in the oxide.

In general 1100 Al performed better than 2014 Al for both salt fog testing and for electrochemical testing. This statement applies for unimplanted samples and for any given implantation treatment. The electrochemical indicators for the as-polished samples (Fig. 5) are exceptions. Likewise, mechanically polished 2014 Al performed better than "A" polished for given surface treatments and tests. These results are consistent with the idea that Cu concentration at the surface may be a key factor in susceptibility of 2014 Al to pitting corrosion.

Preliminary results on dose dependency for Cr implantations have indicated that the dose of $3 \times 10^{17}/\text{cm}^2$ at 150 keV may be about optimal for that energy. The improvement for $1.5 \times 10^{17}/\text{cm}^2$ is not as great. There is not much, if any, more improvement for $4.5 \times 10^{17}/\text{cm}^2$ than for $3.0 \times 10^{17}/\text{cm}^2$. From RBS the measured retained doses were 1.4 , 2.7 , and $3.7 \times 10^{17}/\text{cm}^2$ for the respective nominal doses (determined from current integration) of 1.5 , 3.0 , and $4.5 \times 10^{17}/\text{cm}^2$. At the lowest dose the difference of 7% is mostly due to error in either dosimetry, RBS determination or both. The progressively larger fractional differences at higher doses are due to saturation effects resulting from sputtering.

4. Conclusions and discussion

The most important among the results cited above is that Cr-ion implantation produced a large improvement in the pitting corrosion resistance of 2014 Al. The reason for this improvement is not known. It is well known that Cr provides pitting resistance in stainless steels and in nickel based alloys such as Hastelloys. Passive films based on chromium oxide are known to be more resistant to reduction by Cl than films based on aluminum oxide. In this connection, it may be significant that Cr_2O_3 and Al_2O_3 are completely miscible as an oxide alloy. Since much of the the susceptibility of 2014 Al

to pitting appears related to the presence of the Cu, it is also possible to speculate that some interaction with the Cu is a reason for the favorable result. For example Cr metal, like Cu, has little solubility in Al. Perhaps some of the implanted Cr joins preexisting Cu-rich precipitates to produce a more highly enhanced Cr concentration in the precipitates than in the Al matrix. The Cr does produce more favorable pitting and pit propagation potentials than any other implanted constituent in 2014 Al.

The chromium treatment has possible practical applications. One issue that pertains to some applications is the resistance of the surface treatment to corrosion and simultaneous fretting action. For such a situation the choice of best surface treatment may depend on the nature of the fretting action. Brittle coatings with sharp interfaces at the substrate (e.g. anodic oxide, CVD coatings) might be vulnerable to fracture, breakup and spalling due to various types of impact. As an integral part of a ductile substrate, an ion implanted surface might be resistant to a certain amount of peening action, but certainly could not resist severe gouging by sharp asperities.

Quality control throughout all phases of execution, including preparation of surfaces for implantation, could well be important for successful application. For example in the present study, the possibility of various amounts of oxygen being present on mechanically polished samples was not anticipated. This oxygen did not affect the main conclusions, but may have introduced uncertainty in quantitative results such as amount of oxygen added in certain tests, or in electrochemical potentials for control samples.

For a result such as that of the Cr-implanted sample, shown in Fig. 2, the question might arise as to whether the apparent success of ion implantation on that particular sample (part of surface treated and part untreated) is due to making the implanted area more noble, so that the untreated area becomes sacrificial. This issue will not be discussed, but there are reasons why we do not believe that is the case.

Nitrogen is an inexpensive treatment, and it would appear from the electrochemical studies that N-implantation is promising, at least for some aluminum alloys in some applications. In the severe tests of the present study, however, nitrogen produced no benefit for 2014 Al (consistent with the electrochemical results) and perhaps a marginal benefit for 1100 Al for 10, 20, and 30 at. % N. The $3 \times 10^{17}/\text{cm}^2$ treatment at 20 keV (Fig. 5) has not yet been tried with the salt fog.

It was judged that the salt spray results could be partially rationalized in terms of the electrochemical results.

References

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FIGURE CAPTIONS

Figure 1. Rutherford backscattering histograms for Al alloy samples that have been prepared for ion implantation and corrosion testing. 2.0 MeV He ions. 160° scattering angle.

Figure 2. Photograph showing coupons of 2014 Al, new, after various ion implantation treatments and salt fog testing, and as-tested with no ion implantation. Starting surfaces were all mechanically polished. Ion implanted areas were 2 cm in diameter, and the ion implanted samples were halved after salt testing. 168 h salt fog test. ORNL Photo 6784-90.

Figure 3. Profilometer trace over the transition from implanted area to unimplanted area for the Cr-implanted sample of Fig. 2. (ORNL-DWG 90-M-14917)

Figure 4. Rutherford backscattering histograms for the Cr-implanted sample of Fig. 1 (implanted and tested) and for a typical as-implanted sample for Cr. $3 \times 10^{17}/\text{cm}^2$ Cr at 150 KeV.

Figure 5. Electrochemical potentials characterizing pit initiation and pit propagation for 1100 Al and for 2014 Al for as-prepared samples and for samples with various ion implantation treatments. The as-polished 2014 sample had the mechanical polish. (ORNL-DWG 90-M-14614)

Will be improved

NEW SAMPLE - UNIMPLANTED, UNTESTED

PROFILER TRACE
Cr-IMPLANTED 2014 Al, $3 \times 10^{17}/\text{cm}^2$
ENGINEERING SURFACE
SALT FOG TESTED

ORNL-DW6

90-14917

M

Improved

version
underway
in ORNL Graphics

Will be improved.

Electrochemical Potentials Characterizing Pit Initiation and Pit Propagation for 1100 Al and for 2014 Al with Various Surface Treatments

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