

EFFECT OF N_2^+ ION IMPLANTATION ON THE ELECTROCHEMICAL CORROSION BEHAVIOUR OF Fe-Ni ALLOY IN .1N H_2SO_4 SOLUTION

Ni

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A three sweep potentiokinetic technique was employed to study the electrochemical corrosion behaviour of Fe-50at%Ni in .1N H_2SO_4 solution. The as received foil did not show any passivation but it was observed in case of Fe-Ni samples implanted with N_2^+ ions at an energy of 100keV. Also it was seen that the primary passivation potential E_{pp} and the critical current density in the corrosion experiment decrease as the implanted nitrogen ion dose increases from 5×10^{15} to 1×10^{17} ions/cm². The identification of products formed during corrosion experiment has been attempted with the help of conversion electron Mössbauer spectroscopy (CEMS), X-ray diffraction (XRD) and X-ray photoemission spectroscopic (XPS) techniques, and the possible mechanism of reactions is discussed with reference to their results.

1. INTRODUCTION:

Fe-Ni binary systems are interesting to study since these alloys exhibit some distinct physico-chemical properties (viz. low thermal expansion, unique magnetic characteristics at 30-50% Ni etc.) and hence have earned tremendous technological importance. Although a lot of work has been done on the aqueous corrosion with different compositions of these alloys /1/ in the sulphuric acid solution, the effect of ion beam treatment on the corrosion behaviour of these alloys still remains unexplored. It is by now well established that ion beam treatment of solid surfaces has capability of increasing corrosion resistance of the material by virtue of forming metastable solid solutions near the surface/2/. In the present work, the effect of nitrogen ion implantation (fluence up to 1×10^{17} ions/cm²) on the corrosion behaviour of Fe₅₀Ni₅₀ alloys has been studied with the help of Conversion Electron Mössbauer Spectroscopy (CEMS) and X-Ray Photoelectron Spectroscopic (XPS) techniques. This work was undertaken primarily to study the influence of N_2^+ implantation on the surface corrosion properties which are likely to change not only due to change in the surface composition but also due to the formation of nitrides with the constituents of the Fe-Ni alloy.

2. EXPERIMENTAL:

Fe₅₀Ni₅₀ foils (99.9% pure) obtained from Goodfellow metals were used in the experiment. Samples of 4 sq. cm. were cleaned by recommended etching procedure to remove surface contamination. A number of freshly prepared samples were subjected to N_2^+ and Ar⁺ ion implantation (energy:100keV; dose:0.5- 10×10^{16} ions/cm²; vacuum; 10^{-6} Torr) to induce sufficient structural changes near the surface of the alloy. Some of the implanted as well as the unimplanted samples were electrochemically corroded in a corrosion cell whose details are described elsewhere /3/. The electrochemical corrosion measurements were carried out in 0.1 N H_2SO_4 solution using a three sweep potentiokinetic technique. A scan rate of 1.33 mV/sec was used with a voltage scan from -1250 mV to +1250 mV. The as-received, implanted and corroded samples were characterized by CEMS, XRD and XPS techniques. In the CEMS study, a single line Co⁵⁷ source embedded in Rhodium matrix was used. The recorded Mössbauer spectra were fitted by using the standard MOSFIT program /3/ to obtain the best fit values of hyperfine parameters wherever necessary. Le Caers fourier

decomposition procedure was used to analyse the complex Mössbauer spectra. Fe K α radiation was used in X-ray diffraction measurements.

3.RESULTS AND DISCUSSIONS:

Fig.1(a) shows final sweeps of potentiodynamic curves for the unimplanted sample as well as for implanted ones at various doses by N_2^+ ions, in 0.1 N H_2SO_4 solution. There is definite improvement with dose in the corrosion behaviour on implantation, in terms of the critical current density (i_{crit}) and the primary passivation potential (E_{pp}). Typically, passivation potential decreases up to 5×10^{16} ions/cm 2 dose and remains almost the same at 1×10^{17} ions/cm 2 dose while the (i_{crit}) decreases with dose. The decrease in i_{crit} is by almost one order while going from 1×10^{16} to 1×10^{17} ions/cm 2 dose. Also, current after passivation is seen to be lower by an order of magnitude at 1×10^{17} ions/cm 2 dose as compared to 1×10^{16} ions/cm 2 dose, indicating relatively less porous as well as stable film in the former case. When compared with the behaviour of pure Ni under identical conditions, it is observed that, for Ni, E_{pp} is lower as compared to ion implanted Fe-Ni, while current density after passivation is higher (~ 250 uA/cm 2) as compared to ion implanted Fe-Ni (~ 70 uA/cm 2). Thus effect of nitrogen implantation in improving corrosion behaviour can include two factors (i) Ni enrichment of the surface, (ii) Chemically active role of nitrogen.

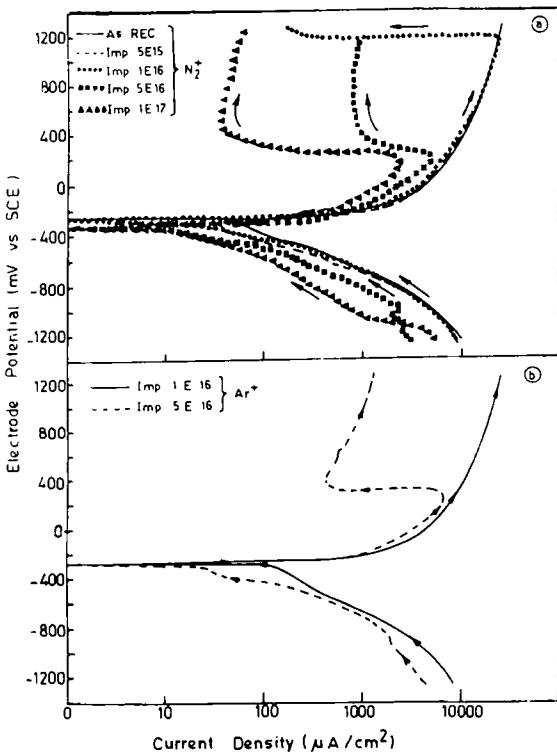


Fig.1. Final sweep of potentiokinetic curves in 0.1N H_2SO_4 solution for (a) N_2^+ implanted (Imp) (b) Ar^+ implanted at various dose on $Fe_{50}Ni_{50}$.

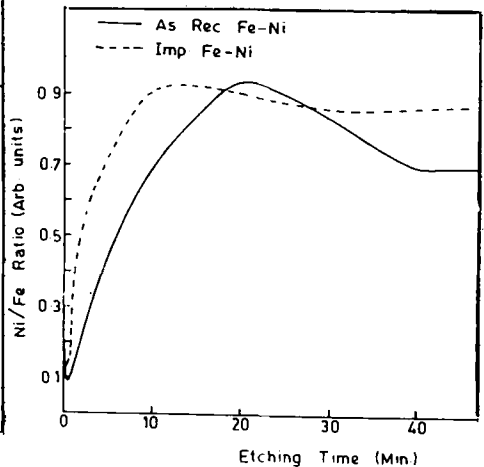


Fig.2. The plot of variation in area ratio of Ni/Fe in XPS dept. profiling study.

In order to find the compositional changes induced by implantation, XPS depth profiling is carried out. The results of the depth profiling as seen in Fig.(2) show that Ni enrichment indeed does take place near the surface. It is seen from the same figure that, the as-received Fe-Ni alloy surface is already Fe rich which is so because the surface energy of Fe is lower as compared to Ni. Thus, Ni rich region is expected below the Fe rich surface. The implanted ions reach this Ni rich region and create a defective region behind their track. This leads to out-diffusion of mainly Ni under radiation enhanced diffusion. This argument is further supported by the observation that when Fe-Ni is subjected to Ar^+ ion bombardment at a dose of $5 \cdot 10^{16}$ ions/cm², E_{pp} and i_{crit} are seen to follow a similar trend as in the case of N_2^+ ion implantation to a similar fluence (as seen in Fig.1 (a) and (b)). Since Ar^+ is not expected to play chemically active role, Ni enrichment indeed becomes one of the major causes for improved corrosion behaviour. This also indicates that nitrogen does not play any chemically active role.

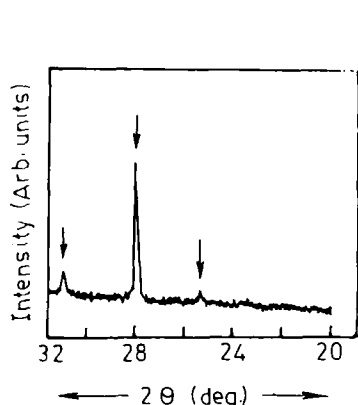


Fig.3. XRD pattern of $Fe_{50}Ni_{50}$ sample corroded in 0.1 N H_2SO_4 solution after implanting N_2^+ ions at a dose of $5 \cdot 10^{15}$ ions/cm².

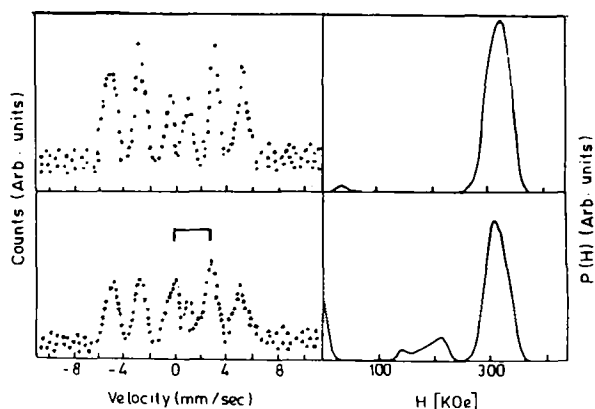


Fig.4. CEMS spectra and corresponding hf distribution curves for (a) $Fe_{50}Ni_{50}$ as-received & corroded (b) $Fe_{50}Ni_{50}$ implanted ($5 \cdot 10^{15}$ N_2^+ ions/cm²) and corroded.

In order to study the nature of the film formed after corrosion in various cases discussed above, conversion electron Mössbauer spectra (CEMS) were recorded. A sextet with hf value of 310 kOe could be fitted in the case of as received alloy. When corroded in 0.1 N H_2SO_4 solution, the spectrum could be fitted with two sextets of 317 kOe and 286 kOe field values. The spectrum and its field distribution are shown in Fig.4(a). As this sample did not passivate, the presence of two sextets in place of one suggests that one of the components is preferentially going in the solution. With this assumption, 317 kOe sextet can be attributed to the original Fe-Ni (Ni 50 at%) /4/ phase, while the other one with hf value of 286 kOe /4/ to the Ni rich phase close to the surface /4/. Thus, Fe could be preferentially going into the solution. Ni is known to be nobler than Fe, hence preferential loss of Fe can explain the presence of Ni rich phase in corroded sample. When sample implanted at $5 \cdot 10^{15}$ ions/cm² with N_2^+ is corroded, its CEMS spectrum (Fig.4(b)) shows one sextet with 306 kOe field and a doublet (Q.S.= 2.335 mm/sec, I.S.= 1.163 mm/sec w.r.t. α -Fe) corresponding to $FeSO_4$ /5/. The XRD pattern (Fig.3) for this sample shows $FeSO_4 \cdot 4H_2O$ and $FeSO_4 \cdot 5H_2O$ as the main contributors to the corrosion film. Possibility of $Fe_6S_8O_{33}$ is also indicated by a peak at 2θ value of 30.9° (fig.3). Thus, the implantation enhances the rate of

formation of sulphates (a precursor for passivating film) on the surface of the sample and eventually helps to reduce the rate of corrosion. This effect is more clearly brought out by the comparison between the CEMS spectra recorded for the sample implanted at 1×10^{17} ions/cm² and subsequently subjected to aqueous corrosion ($E_{pp} = 250$ mV). The CEMS spectrum of the implanted sample shows two sextets, one with $hf = 329$ kOe while the other with $hf = 295$ kOe. Clearly, the effect of ion implantation is seen to be that of Ni enrichment, resulting into two solid solutions of Fe-Ni at the surface, one being Fe rich (329 kOe) /4/ and the other Ni rich (295 kOe) /4/. After corrosion, the fitted spectrum shows sextet corresponding to $hf = 306$ kOe. Thus, iron rich solid solution is corroded and the remaining Ni rich phase gets passivated. The XRD pattern does not reveal any phase on the surface, because of the very small amount of corrosion products.

4. CONCLUSION:

We have shown that there is an improvement in the corrosion resistance of Fe₅₀Ni₅₀ alloys upon N₂⁺ ion implantation. The primary passivation potential and the critical current density, both decrease with an increase in the dose. The CEMS technique along with the XPS depth profiling and XRD analysis has been used to show that there is Ni enrichment of the surface upon implantation which is responsible for the observed improvement in the corrosion behaviour. This has also been made clear from the comparison with Ar⁺ ion implantation.

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