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EFFECT OF N_2^+ ION IMPLANTATION ON THE OXIDATION BEHAVIOUR OF $Fe_{50}Ni_{50}$ ALLOY

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The high temperature oxidation behavior of $Fe_{50}Ni_{50}$ alloy foils implanted with 100 keV N_2^+ ions at a different dose values is studied by using the technique of conversion electron Mössbauer spectroscopy (CEMS). It has been shown that the implanted foils exhibit considerable adherence of scales and higher oxidation resistance as compared to the virgin foils. This excessive adherence of scales to the surface and higher resistance to oxidation of implanted samples is attributed to nickel enrichment in the surface layers. Various oxides of Fe, Ni and Fe-Ni are identified from the hyperfine interaction parameters of the corresponding CEMS spectra and also from x-ray diffraction measurements.

1. INTRODUCTION :

During the past decade a number of investigations /1-3/ have been carried out on the kinetics and mechanism of oxidation of Fe-Ni alloys. From the practical standpoint the need to acquire knowledge of the high temperature oxidation behaviour of these alloys is essential since various compositions are used in industry because of their magnetic behaviour, their thermal expansion properties and their ability to participate in glass to metal seals /4/.

In the present work we report the results of our study of the influence of ion implantation on the high temperature oxidation behavior of $Fe_{50}Ni_{50}$ alloy foils. This study is a continuation of our previous work /5/ of similar nature in which we have studied the low temperature oxidation behavior of $Fe_{50}Ni_{50}$ alloy foils. We have employed CEMS technique complemented by x-ray diffraction measurement and XPS depth profiling technique to investigate oxide formation in air at 800°C and 1100°C on implanted and virgin alloy foils. Emphasis has been placed on oxide identification and scale composition, although information on overall oxidation rates of the implanted and virgin alloy foils has also been obtained by gravimetric analysis.

2. EXPERIMENT :

Pure $Fe_{50}Ni_{50}$ alloy foils (99.9%) obtained from GoodFellow metals (England) were used in the present investigation. Samples having thickness of 0.5mm were cut in the size of 1cm x 1cm and were cleaned by employing a proper recommended procedure. These samples were implanted with 100 keV N_2^+ ions at a dose of 3×10^{16} and 1×10^{17} ions/cm^2, using a machine developed in our laboratory /6/. The implanted as well as virgin foils were oxidised at 800°C and 1100°C in air for one minute. The CEMS spectra of the samples were recorded by using a conventional constant acceleration Mössbauer set up. For obtaining the Mössbauer spectra a single line 50 mCi ^{57}Co source in Rhodium matrix was used. The CEMS spectra were least square fitted by using the standard MOSFIT programme to obtain the best fit hyperfine interaction parameters. X-ray diffraction measurements were carried out by using a Fe K_α source.

3. RESULTS AND DISCUSSION :

The computer fitted values of hyperfine interaction parameters corresponding to the CEMS spectra of virgin, implanted and implanted-oxidized $Fe_{50}Ni_{50}$alloy foils are summarised in Table-I. The x-ray diffraction data of all the samples of interest is presented in Fig-1. While analyzing the data it is important to note that the CEMS technique reveals information from the top (~2000 Å)surface layers whereas the x-ray diffraction technique probe deeper (i.e. ~ few microns).

The CEMS spectrum corresponding to virgin $Fe_{50}Ni_{50}$ alloy foil can be fitted with a sextet having a hyperfine field value of ~ 310 kOe which is characteristic of $Fe_{50}Ni_{50}$ alloy in the as received state /2/. Upon oxidation at 800°C, the CEMS spectrum for the corresponding sample indicates the presence of only α-Fe_2O_3 phase. The x-ray diffraction pattern corresponding to the sample oxidized at 800°C [Fig.1(b)] reveals the significant differences when compared with the pattern obtained for as received foil [Fig.1(a)]. The latter pattern contains three lines at 2θ values of 99.4°, 65.2° and 55.6° which are characteristic lines of $Fe_{50}Ni_{50}$ alloy whereas the former pattern indicates the presence of various oxide phases. The lines at 2θ [Fig.1(b)] values of 45° and 82° correspond to nickel ferrite phase while other peaks show the presence of Fe-Ni, Ni_2O_3 like phases. Thus, it seems that the surface of the oxidized $Fe_{50}Ni_{50}$ alloy foils consists of three distinct layers. The top layer contains α-Fe_2O_3 followed by Ni_2O_3 and $NiFe_2O_4$ layers. This observation is consistant with the results reported by Channing et al./7/. When the as received alloy foil is oxidized at 1100°C the CEMS spectrum and the x-ray diffraction pattern reveal similar features as that of the virgin samples oxidized at 800°C. In this case α-Fe_2O_3 scales were also formed, however their adherence to the substrate material was found to be poor.

When the as received alloy foils are implanted at a dose of 3×10^{16} N_2^+ ions/cm^2, corresponding CEMS spectrum shows slight increase in the value of isomer shift and decrease in the value of internal magnetic field. It has been reported that /8/ under tensile stress, increase in isomer shift could be observed for various iron alloys. At a dose of 3×10^{16} ions/cm^2 one can not expect the presence of large amount of tensile stress, however at a higher dose value such stresses may be present. Since the isomer shift is stress dependent, the effect of tensile stress in the implanted sample can be detected through CEMS measurement. The decrease in the value of internal magnetic field in the case of implanted sample indicates that the surface layers are enriched with nickel upon ion bombardment. In order to supplement this observation we performed depth profiling XPS studies on the as received and as implanted samples. These studies revealed that the average Fe/Ni ratio decreases after implantation in the near surface region.

When the implanted sample is oxidized at 800°C, first observable effect is that the adherence of the scales is increased. The corresponding CEMS spectrum could be fitted with two magnetic components having field values of ~485 kOe and 546 kOe ;and another sextet having an internal field value 510 kOe which is attributed to the α-Fe_2O_3 phase. The two sites at 485 kOe and 546 kOe correspond to the nickel ferrite phase with a resonably high concentration of nickel /9/.

Table I : The computer fitted values of hyperfine interaction parameters

Sample $Fe_{50}Ni_{50}$	IsomerShift mm/sec	Internal Magnetic Field kOe	Possible Phase(s)
i) as-received	0.039	310	FeNi
ii) oxidised at 800°C	0.36	512	α-Fe_2O_3
iii)low dose implanted	0.043	304	FeNi
iv) low dose implanted	0.35	510	α-Fe_2O_3
oxidized at 800°C	----	487	$NiFe_2O_4$
	----	547	
v) high dose implanted	0.082	302	FeNi
vi) high dose implanted	0.33	515	α-Fe_2O_3
oxidized at 800°C	----	488	$NiFe_2O_4$
	----	540	

This may be contrasted with the case of identically treated as received sample which shows the presence of only α-Fe_2O_3 phase in the CEMS spectrum. The x-ray diffraction patterns in the two cases [Fig.1(b) and 1(c)] exhibit same features, however the peak intensities are different in the two cases. Specifically the peak intensities corresponding to the nickel ferrite phase are increased in the case of implanted oxidized sample as compared to the oxidized virgin sample. Thus it can be concluded that the nickel rich ferrite layer formed in implanted case is more effective in limiting the diffusion of Fe atoms across the oxidation front as compared to the case of the as received sample. Upon further oxidation at 1100°C, the CEMS results and x-ray diffraction pattern show similar oxidation behavior as above and there is nothing interesting to bring out by way of comparison with the case of the unimplanted sample. However when the as received sample is implanted with a higher dose (1×10^{17} ions/cm^2) prior to oxidation at 800°C; significant changes are seen to occur in the rate of oxidation.

The CEMS spectrum of implanted ($1x10^{17}$ ions/cm^2) and oxidized at 800°C shows similar behavior as above. The x-ray diffraction pattern corresponding to the high dose implanted-oxidized sample shows the presence of Ni_2O_3, nickel ferrite and Fe-Ni as well. Presence of solid solutions with other composition form the extra peaks in the tail portion of Fe-Ni peaks. Also, prefered orientation of grains takes place as seen from the increase in the peak intensity at the 2θ value of 65.2°. When this sample is further oxidized at 1100°C, similar results are obtained as in the previous case.

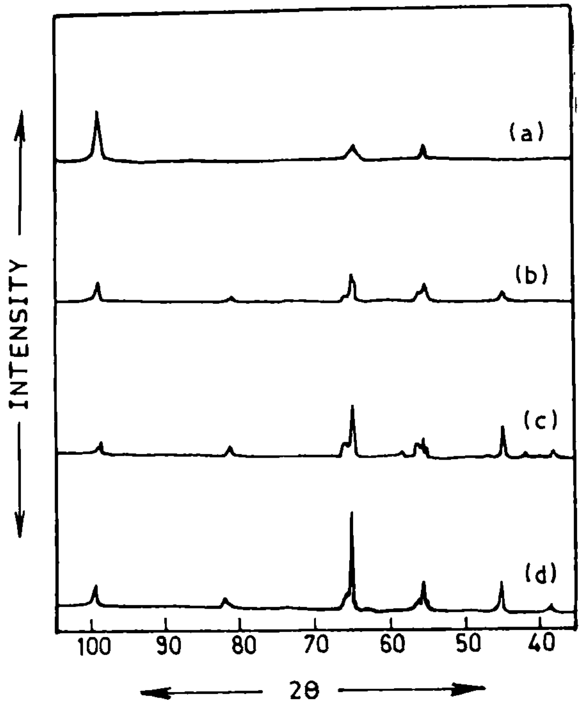

Fig.1 : X-ray diffraction patterns for $Fe_{50}Ni_{50}$ alloy foils(a) in as received form;(b) oxidized at 800°C; (c) low dose ion implnted and oxidized at 800°C; (d) high dose ion implanted and oxidized at 800°C.

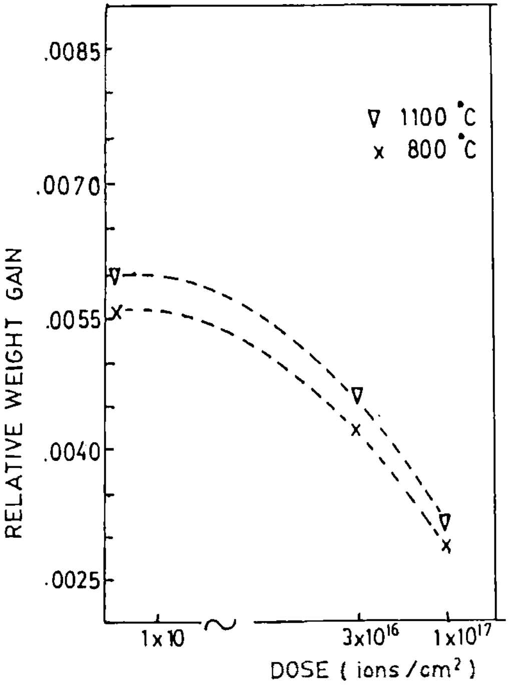

Fig.2 : Results of gravimetric analysis for the N_2^+ ion implanted alloy foils at varying doses.

From CEMS and x-ray diffraction analysis of as received and nitrogen implanted samples, it is observed that stoichiometry of the surface product is more or less same although the detailed composition is different in all the cases. The extent to which various phases exist could not be determined by the present investigation, however it is interesting to compare the oxidation behavior of the as received, low dose implanted and high dose implanted alloy foils via determination of the relative weight gain after oxidation at 800°C and 1100°C. The results of such estimates obtained from gravimetric analysis are shown in Fig.2. The cross marks correspond to the oxidation at 800°C while the triangles represent the oxidation at 1100°C. It is clearly seen that the low dose implanted sample exhibits less relative weight gain as compared to the as-received sample and the high dose implanted sample reveals much less relative weight gain as compared to the cases of both the as-received and the low dose implanted sample. The same trend is observed for oxidation at 1100°C. XPS and CEMS results suggest that Ni enrichment takes place on the surface after ion implantation. It has been shown that in nickel rich ferrite the diffusion rates for atomic transport are very low /11/ and hence the oxidation process is reduced as well. This is found to be the case in the present studies. In all the cases however , α-Fe_2O_3 is a surface product after oxidation. The surface energy of Fe being lower as compared to Ni, the surface is Fe rich and tends to form Fe oxides.

The intensities of x-ray patterns for ferrite phase remains the same in all implanted-oxidized cases. This is expected because for Fe K_α radiation, the x-ray scattering depth is quite low (1.2 μ) /11/. Therefore CEMS and x-ray diffraction data is not sufficient to quantify the extent of oxidation. Further work is in progress to estimate the extent of oxygen incorporation as well as nickel content in surface layers.

4. CONCLUSION :

The high temperature oxidation behavior of nitrogen ion implanted $Fe_{50}Ni_{50}$ alloy foils is studied by using the technique of conversion electron Mössbauer spectroscopy. The x-ray diffraction technique and x-photoelectron spectroscopy have also been used to obtain supplementary information. It has been shown that nitrogen ion implantation leads to considerable enhancement of the oxidation resistance of the alloy foils.

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