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Improvement of physical and chemical properties of steel implanted with Cr^+, Ti^+, Si^+ ions

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Low carbon steels (St3, St45) and a chromium doped steel (St40Cr) were implanted with 15–20 keV Ti^+, Cr^+ or co-implanted with $(Ti+Si)^+$, $(Cr+Si)^+$ ions to a dose of 8×10^{16} ions cm^{-2}. The composition of the surface region was examined by RBS and nuclear resonance scattering techniques. These analyses showed a relationship between the implanted ion doses and the oxygen concentration in the layer. The hardness of the implanted surface grew with increasing ion dose. This effect is associated with radiation damage and chemical compounds created in the surface regions of the ion-implanted steels. The corrosion properties of the steels were studied and the first results from electrochemical analysis of corrosion behaviour of samples in de-aerated borate buffer solution (pH = 6.5) are discussed.

1. Introduction

The use of accelerated ion beams for improving the physical and chemical properties of metals has been studied for a long time [1–3]. We investigate the application of ion-beam techniques to modify the adhesion of rubber to low carbon steels. There are known attempts to reduce the rate of the residue creation on the surface of a press-form by changing the rubber content [4]. In our study different species were implanted into steel which is used for press-form preparation with the aim to change its composition and properties. Preliminary results of the study show that it is possible to replace electrochemical methods of steel surface protection by ion implantation. For a better understanding of the role of ion implantation on adhesive and corrosion resistance the composition of the implanted steels, and hardness and corrosion behaviour were studied.

2. The mechanism of pulsed explosive ion emission

The steels used in this work are low carbon St3, St45 and St40Cr whose composition has been indicated separately. Cylindrical specimens with a diameter of 10 mm and a thickness of 3 mm were used. The specimens were carefully polished with a diamond paste of 0.5 μm at the final stage. Implantations were conducted using an ion source described previously [5]. Samples were implanted with 15 and 20 keV Cr^+, Ti^+, $(Cr+Si)^+$, $(Ti+Si)^+$ to doses ranging from 8×10^{15} to 8×10^{16} ions cm^{-2}.

Hardness was measured using the Vickers technique. Ten indents were made on each sample and the average hardness was calculated. For the composition investigations of the treated steel surfaces RBS and RS techniques were used in conjunction with changes to the experimental geometry and computer simulation. The energy of He ions was 1.25 MeV (RBS) and 3.047 MeV for resonance scattering for oxygen detection. Each set of implantation was followed by a Be sample. Therefore there was additional information available about the amount of additional impurities introduced into the samples. Corrosion behaviour of the samples was evaluated with electrochemical measurements in de-aerated borate buffer solution of pH = 6.5.

3. Results and discussion

The depth distributions of chromium and titanium implanted into steel St40Cr with an energy of 15 keV and associated oxygen incorporation are shown in figs.

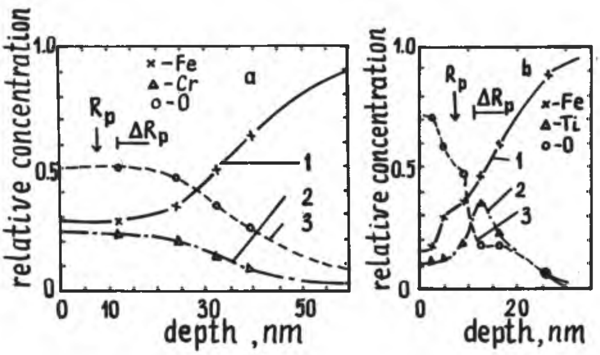

Fig. 1. Relative concentration profiles of iron (1), chromium or titanium (2), and oxygen (3), in steel St40Cr implanted with 15 keV (a) Cr^+ ions, dose 8.7×10^{16} cm^2, (b) Ti^+ ions, dose 4.8×10^{16} cm^{-2}.

1a and 1b, respectively. The titanium profile is in qualitative agreement with the theoretical prediction, although the maximum concentration depth is approximately 20% greater than the calculated R_p, fig. 1b. The peak concentration of O for the sample implanted with Ti^+ is in the near surface region. The amount of oxygen is given by an approximate composition of Me(= Ti, Fe)O_2.

Curve 2 in fig. 1a shows that the implanted Cr profile is distributed in steel St40Cr considerably deeper than expected from theoretical prediction. The oxygen profile has almost the same depth distribution as chromium. This suggests that the oxygen is connected with Cr atoms according to the formula Me(= Cr)O_2.

Table 1
Vickers hardness [kgf/mm^2] of the steels St3, St45, St40Cr implanted with 15 keV Ti^+ ions, doses $\sim1.8\times10^{16}$ cm^{-2}

	St3	St45	St40Cr
Virgin	151 ± 19	196 ± 11	276 ± 25
Implanted	170 ± 9	269 ± 14	394 ± 31

In the cases of co-implantation of $(Ti + Si)^+$ and $(Cr^+Si)^+$ ions the depth distribution of the implanted species agrees with that theoretically predicted.

An interesting feature of the distributions of Cr, Ti, O in fig. 1 is the presence of the "tails" of these elements at depths which are several times larger than the projected ranges of ions. Probably this effect is associated with the nature of pulse implantation using our ion source. Some details of it have been already discussed theoretically [6] and in experiments [7]. Partly the depth distribution of the elements might be connected with high energy density (more than 1 eV/at) deposited in collision cascades [8].

The Vickers hardness data of the Ti^+ ion implanted steels are presented in table 1. The measured hardness is a function of impurity concentration in the steel and the relative increase of the hardness after Ti^+ implantation also depends on the presence of carbon and especially of chromium. Therefore the observed behaviour can be explained by the influence of the impurities implanted or present before in the steel on the movement of dislocations during indenter loading. It is known that chemical compounds (MeC, MeN, etc.) are created in metals under ion implantation. Hence they

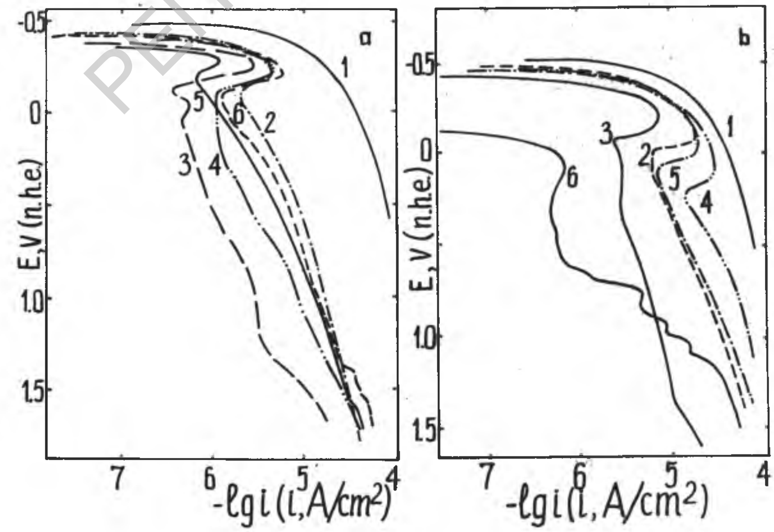

Fig. 2. Anodic potentiodynamic polarization (3.6 V/h) curves of steel St3 (a) and St40Cr (b) in borate buffer solution (pH = 6.5) at 25°C before (1) and after ion implantation of Ti^+ (2,3) and $(Ti+Si)^+$ (4–6) with the following ion doses: (2,4) 8×10^{15} cm^{-2}, (3) 2×10^{16} cm^{-2}, (5) 1×10^{16} cm^{-2}, (6) 1.5×10^{16} cm^2.

also may cause increased hardness of the surface layers in the ion-implanted steel as it was shown for different thin films [9].

At the co-implantation of $(Ti + Si)^+$ ions the relative increase of hardness in steel is less than for the case of only Ti^+ ion implantation, table 2. Such behaviour of the steel hardness may be explained with the known fact that titanium carbide is harder than titanium silicide and compounds such as carbosilicides. Implantation of Cr^+ ions into the investigated steels leads to increasing hardness with ion dose. But note that the amount of the relative hardness increase in this case lies between the data obtained for Ti^+ and $(Ti + Si)^+$ ion implantation.

The electrochemical analysis of the corrosion behaviour of our samples showed that the characteristics of implanted (Ti^+, $Ti^+ + Si^+$, $Cr^+ + Si^+$) carbon steels improved both in the active and passive regions: the establishment of more positive values of corrosion potentials E_{cor}, a decrease in the dissolution rate and the appearance of passive state (fig. 2). The most pronounced effect after titanium implantation into steel St3 is observed when the highest ion dose was used. The anodic dissolution current density (CD) of this sample decreased in the active region by 1.5–2 orders of magnitude and the passivation ability increased, which was manifested in the lowering of the critical passivation CD and potential values (i_{cr}, E_{cr}) as well as passive CD (i_p) of more than 1.5 order of magnitude (fig. 2a). It was found that Ti^+ implanted samples of steel St3 and St45 exhibited no significant differences in corrosion–electrochemical properties. At the same time the corrosion resistance of titanium implanted steel 40Cr samples was higher over steel St3/Ti^+ samples under similar implantation conditions (fig. 2b). The most significant effect is observed for sample St40Cr/Ti^+, as in the case of St3/Ti^+, with the highest ion dose (fig. 2b, curve 3). The main corrosion–electrochemical characteristics of steel St3 materials co-implanted with $(Ti + Si)^+$ ions are listed in table 3.

The results presented both in table 3 and in fig. 2a indicate that corrosion resistance of co-implanted steel materials is improved again with an increase in ion dose. E_{cor} of the most resistant sample is established in the active–passive transition region and the passive CD is equal to that of the best St40Cr/Ti^+ sample.

Table 2
Vickers hardness [kgf/mm^2] of the steel St40Cr co- or single-species-ion implanted

Dose [$\times 10^{16}$ cm^{-2}]	$(Ti+Si)^+$	Ti^+
1.8	295 ± 11	394 ± 31
3.0	411 ± 25	527 ± 44

Table 3
The critical passivation current (i_{cr}), E_{cor} and passive current (i_p) of steel St3 co-implanted with $(Ti+Si)^+$ ions

	Dose [cm^{-2}]		
	8×10^{15}	1.2×10^{16}	3×10^{16}
i_{cr} [A/cm^2]	3×10^{-5}	2×10^{-5}	8×10^{-7}
i_p [A/cm^2]	1.6×10^{-5}	8×10^{-6}	5×10^{-7}
ΔE_{cor} [V]	0.06	0.06	0.4

It is important to note that the modified surface layer of the most resistant steel St3/$Ti^+ +$ Si^+ sample is rather thin; at voltages above + 0.4 V a passive state breakdown is observed. The latter conclusion is confirmed by the prolonged potentiostatic tests under corrosion-free and passive state (+0.1 V) potentials. The sample surface after corrosion tests ($t = 24$ h) is covered by friable corrosion products on the basis of Fe_2O_2, and E_{cor} of the implanted material is shifted to E_{cor} values of the unimplanted substrate already in 1.5 h.

The most pronounced effect in sample St40Cr after co-implantation of $Ti^+ + Si^+$ ions is slightly less strong than for the best sample of steel St3/$Ti^+ + Si^+$: passive CD is 2–3 times lower.

The corrosion properties of co-implanted ($Ti^+ +$ Si^+) steel St45 samples are inferior to those of co-implanted steel St3 and steel St40Cr. It should be noted also that no significant difference was observed between ($Cr^+ + Si^+$) and ($Ti^+ + Si^+$) co-implanted samples under similar implantation conditions as well as between steel St45 and steel St40Cr substrates in the case of ($Cr^+ + Si^+$) co-implantation.

4. Summary

Surface analysis using Rutherford and resonance backscattering showed that ion implantation of Cr^+ produced 2.5–3 times thicker modified layers than Ti^+ ion implantation. In both cases, the concentration of oxygen in ion-implanted regions is rather high; i.e. sufficient to create compounds with the formula MeO_2.

The hardness of the investigated steel samples grows with increasing of Cr^+, Ti^+ or $(Cr + Si)^+$, $(Ti + Si)^+$ ion doses. The most pronounced effect was observed during ion implantation into steel St40Cr. Increase of the hardness in ion implanted steels is associated with the appearance of radiation damage and with the creation of chemical compounds with iron and implanted species.

The corrosion resistance and passivation ability of carbon steels are improved with increasing ion dose. The effect of surface modification on the corrosion–electrochemical properties is more pronounced in the case of steel St40Cr substrate. It was difficult to reveal the nature of the implanted species (Ti^+, $Ti^+ + Si^+$, $Cr^+ + Si^+$) on the corrosion behaviour of steels, but co-implantation with $Ti^+ + Si^+$ is more effective. It is still an open question under which implantation conditions the most advantageous changes of the corrosion characteristics may be obtained. However, the formation of chemically modified surface and subsurface layers with high strength Me–C and Me–Si (Me = Fe, Ti, Cr) covalent bonds seems to play an important role in this context [10]. The surface modification with corrosion resistant components (Cr^+, Ti^+, Si^+) on the one hand decreases the anodic reaction rate on the implanted steels, and on the other hand the passivation ability of implanted steels is increased as a result of formation of transition metal carbide and silicide precipitates which change the reaction kinetics.

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