Oxidation and corrosion studies of Al-implanted stainless steel AISI 321 using nuclear reaction and electrochemical techniques

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The oxidation of Al-implanted (implantation energy 40 keV, dose 10^{16} - 10^{17} Al ions/cm^2) AISI 321 stainless steel samples in air has been studied at temperatures between 450 and 650°C using the ^{16}O(d,p)O nuclear reaction. The determination of the distribution of the implanted Al atoms has been performed using the resonance at 992 keV of the ^{27}Al(p,y)_{28}Si nuclear reaction. The determined oxygen profiles indicate that the implantation of 5 \times 10^{16} and 10^{17} Al ions/cm^2 leads to an improvement of the oxidation resistance of the studied steel samples. The passivation/corrosion behaviour of the Al-implanted steel samples in 0.5M aqueous sulphuric acid solution has also been investigated electrochemically using potentiodynamic and cyclovoltammetric techniques. The passivation potential values and the repassivation moving to more positive values indicate an improvement of the corrosion resistance of the Al-implanted steel samples.

1. Introduction

Ion implantation has been proven to be successful in modifying the properties of near-surface layers of materials without affecting the bulk. It is well known that ion implantation improves the thermal oxidation resistance of metals and alloys. This is due to both chemical and radiation damage effects [1]. The selection of the suitable thermal oxidation inhibitor is primarily based on its affinity to oxygen in comparison with that of the matrix atoms and its solubility in the metallic matrix.

During this work the thermal oxidation of Al-implanted (implantation energy 40 keV, dose between 10^{16} and 10^{17} Al ions/cm^2) austenitic stainless steel AISI 321 (Fe/Cr18/Ni8/Ti) samples has been studied in the temperature region between 450 and 650°C. Aluminum was chosen because of its high affinity to oxygen, as well as its ability to form double oxides and its solubility in iron.

The behaviour of the Al-implanted steel samples was also electrochemically investigated in acid solution (0.5M H_2SO_4) although the implantation of ions does not always improve the corrosion resistance of metallic surfaces (see e.g. refs. [2,3]).

2. Experimental

Stainless steel AISI 321 (Fe/Cr18/Ni8/Ti) samples (thickness 0.25 mm, supplied by Goodfellow) were implanted at room temperature with 40 keV Al ions (implantation dose between 10^{16} and 10^{17} Al ions/cm^2) using the 50 kV implanter of the Nuclear Physics Institute of the University of Frankfurt, Germany. The vacuum in the implantation chamber was better than 10^{-6} mbar. A liquid nitrogen trap was surrounding the target arrangement during the implantation. The Al^+ ion beam intensity was about 10 \mu A/cm^2.

The distribution of the implanted Al atoms on the sample surfaces has been determined by means of the resonance at 992 keV of the ^{27}Al(p,\gamma)^{28}Si nuclear reaction at the 2.5 MV van de Graaf accelerator of the same institute.

Implantations with 2 \times 10^{17} Al ions/cm^2 (E_{Al} = 40 keV) at 10^{-5} mbar oxygen partial pressure lead to the formation of gold-brown coloured layers with up to 50 at.% Al concentrations.

The implanted samples were oxidized in air at temperatures between 450 and 650°C. The duration of the oxidation varied from one to six days. The oxygen depth distribution on the oxidized samples was determined using the ^{16}O(d,p)O nuclear reaction at the 5 MV Tandem Accelerator Laboratory of the National Centre for Scientific Research "Demokritos", Athens, Greece.

Electrochemical investigation of the implanted steel samples has been performed in aqueous solution of 0.5M H_2SO_4 by means of potentiodynamic and cyclovoltammetric techniques using rapid (50 \text{V/h}) and slow (0.6 \text{V/h}) scan rates. The slow scan rates allow measurements under nonconstant conditions of the metal-
3. Results and discussion

The theoretical distribution of the implanted Al ions in the AISI-321 steel matrix, calculated using the computer code TRIM90 [4] in comparison with the experimental results obtained by means of the $^{27}$Al($p,\gamma$)$^{28}$Si nuclear reaction is given in fig. 1. The experimental aluminum profile, before the thermal treatment of the samples, is characterized by a lower mean ion range (ca 160 Å in comparison to the calculated value of 281 Å) and shows a diffusion tail form. The differences between the experimental and the calculated distributions are most probably due to sputtering effects. The aluminum profile of the thermally treated samples was also determined using the same technique. In both cases a 60° angle of the target surface to the proton beam direction facilitated the measurement of the rather narrow Al distribution, improving the depth resolution of the technique. The Al distribution in the implanted AISI-321 steel samples (dose; $10^{17}$ ions/cm$^2$) after thermal oxidation for one, two and four days at 650°C is given in fig. 2.

The oxidation of the studied Al-implanted steel samples in the temperature range between 450 and 650°C shows a parabolic behaviour ($\Delta m^2/S^2 = k_p t$, where $\Delta m/S$ is the mass increase per surface unit, $k_p$ the parabolic rate constant and $t$ the time). Fig. 3 gives the concentration of oxygen on Al-implanted steel samples at 450°C. The corresponding parabolic rate constants are $4.4 \times 10^{-6}$, $9.0 \times 10^{-6}$ and $2.1 \times 10^{-5}$ ((mg/cm$^2$)$^2$ per day), for the samples implanted by $10^{17}$, $5 \times 10^{16}$ and $10^{16}$ Al ions/cm$^2$, respectively. The value for the nonimplanted steel samples at 450°C is $2.3 \times 10^{-5}$ ((mg/cm$^2$)$^2$ per day). This is an indication that the oxidation resistance improvement by means of implantation of $10^{16}$ Al ions/cm$^2$ at 450°C is rather limited, whereas the implantation with higher dose leads to a more significant reduction of the oxidation rates. Fig. 4 shows the oxygen concentration on $10^{17}$ Al ions/cm$^2$ implanted stainless steel samples at 450, 550 and 650°C. There is a considerable difference in the oxidation behaviour at the 450 and 550°C on the one hand and the 650°C on the other hand, indicating the presence of different oxidation mechanisms. A preliminary evaluation of the Arrhenius plot of the parabolic rate constant $k_p$ in the case of the implantation with a dose of $10^{17}$ Al ions/cm$^2$ gave an activation energy value of $E_a = 26$ kJ mol$^{-1}$ for the temperature region below 550°C. The corresponding activation energy value for higher temperatures is about 7 times higher, also indicating the different oxidation mechanisms concerned. These results are in good agreement with data obtained during oxidation studies using Al-implanted pure iron [5]. It seems more likely that the low temperature (below 600°C) oxidation mainly proceeds, as in the case of pure iron, by fast diffusion paths transport,
Fig. 2. Experimental depth distribution of 40 keV Al ions (dose: $10^{17}$ cm$^{-2}$) on AISI-321 steel samples after oxidation in air at a temperature of 650°C for one ($\circ$), two (+) and four (++) days.

which is known to be less activated than the bulk diffusion taking place at higher temperatures. Aluminum being soluble in a-Fe is equally distributed between bulk and grain boundaries of iron oxides, slightly affecting both fast diffusion paths transport and bulk diffusion. The improvement of the oxidation resistance of the AISI-321 by implantation with a dose higher than $5 \times 10^{16}$ Al ions/cm$^2$ is of the order of a factor of 2, whereas the implantation of less soluble ions segregating to dislocations and grain boundaries could lead to better blocking effects and more drastic reduction of the low temperature oxidation rates.

There is an increasing number of publications dealing with the improvement of the corrosion resistance of ion-implanted metallic surfaces, especially iron and steel surfaces, in acid solutions (see e.g. refs. [2,3,6,12]). In most of the cases an improvement of the corrosion resistance of the implanted surfaces is observed, although it is well known that ion implantation is unsuitable for long-term corrosion protection, because of the rather limited width of the modified surface layer produced by low energy ions (implantation energies up to a few hundred keV). The partial or total amorphiza-
tion of the surface of the implanted substrates should, on the other hand, be thermodynamically more reactive in corrosive environments. However, the lack of defects, grain boundaries, etc., usually found in crystalline materials, leads to an improvement of the resistance of the amorphous state to pitting corrosion [13].

Most of the corrosion studies in solutions are using electrochemical techniques (potentiodynamic, potentiostatic and cyclovoltammetric methods), although these measurements cannot substitute long-term open-circuit immersion tests and can be, in most of the cases, interpreted only qualitatively.

Potentiodynamic measurements indicated a slight increase of the pitting potential (E_p) of the Al-implanted samples compared to the nonimplanted ones. The E_p values varied from 1300 for the nonimplanted to 1400 mV for the 10^17 Al ions/cm^2 implanted samples. The E_p values are characteristic of the potential region, where an intense anodic activation and pitting corrosion begins. The corresponding repassivation (E_r) and corrosion (E_corr) potentials varied from +900 to +950 mV and from −370 to +130 mV, for the above mentioned samples, respectively. The corrosion rate was found to be 27.8 and 20.2 × 10^{-5} mg s^{-1} cm^{-2} for the nonimplanted and the 10^{17} Al ions/cm^2 implanted AISI 321 steel samples in 0.5M H_2SO_4, respectively. The samples with lower Al dose showed similar behaviour with values between the above mentioned. All curves show a hysteresis loop during the reverse scan, indicating sensitivity to pitting corrosion. There are differences among the subsequent scans showing the gradual dissolution of the implanted layer.

4. Conclusions

There is an improvement of the oxidation resistance of almost a factor of 2 of the AISI 321 steel samples implanted with 5 × 10^{16} and 10^{17} Al ions/cm^2 in comparison with the nonimplanted material. The oxidation of the above mentioned Al-implanted samples in air at temperatures below 550°C seems to proceed by a different mechanism than at 650°C. In the former temperature region, the oxidation of the samples, as in the case of Al-implanted pure iron, most probably proceeds by fast diffusion paths transport, whereas at higher temperatures it proceeds by bulk diffusion.

The corrosion resistance of the AISI 321 steel in 0.5M H_2SO_4 solutions seems to be improved by Al implantation, as indicated by potentiodynamic measurements of the pitting, repassivation and corrosion potentials. On the other hand, the 40 keV Al implantation does not seem to provide, because of the limited width of the layer, any modified material surface suitable for any long-term practical application.

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