# Effect of atomic mixing on the electrochemical and corrosion properties of Ni-Ti surfaces

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Nickel films of 10nm thickness on titanium substrates were irradiated with 10keV $Ar^+$ ions to various fluences using dynamic recoil mixing (DRM) conditions, where sputtered nickel is continuously replenished. Rutherford backscattering (RBS) analysis of the resulting films shows considerable Ni-Ti mixing and the possible formation of a Ni-Ti compound. Potentiostatic polarisation curves for these mixed films indicate that their life for use as electrocatalytic electrodes for chlorine liberation is increased by a factor of five.

## INTRODUCTION

Ion implantation of metals as a means of modifying their surfaces for the production of electrodes with altered electrochemical properties has been the subject of several studies.[1-3] One possible application is the production of active corrosion-resistant electrodes based on passivation of metals for use as anodes in the electrolysis of acidic and weak alkaline solutions.[4]

In addition to ion implantation, atomic mixing as a technique for the modification of the surface properties of metals has also received some attention recently.[5] The material most widely used so far has been platinum or titanium but the high cost of platinum makes its use economically prohibitive and its replacement by nickel an attractive alternative. Under anodic polarisation conditions nickel possesses a sufficiently high electrocatalytic activity for chlorine liberation, although its low corrosion resistance in such an environment prevents its use. For this reason there is considerable interest in the formation of intermetallic compounds of nickel with metals such as titanium, tantalum, and molybdenum and the development of techniques to form such compounds. One such technique is atomic mixing of thin nickel films by energetic inert gas ions. For example Tomashov et al[6] have investigated the composition and electrochemical properties of nickel films deposited on titanium and irradiated by energetic $Ar^+$ ions. They have shown that the resulting surface has a composition of $Ti_2Ni$, consistent with its electrochemical properties in liberating chlorine from an acidic chloride solution. However, it is further reported that the mixing, beyond a bombardment dose of $10^{16}Ar^+$ ions/cm², is severely limited because of the sputtering of the nickel films. In the present study we have used a technique known as DRM, which replenishes the film material under controlled conditions during the bombardment process, thus overcoming the thinning of the film by sputtering experienced during more conventional mixing experiments. The composition and electrochemical properties of the resulting films are reported here.

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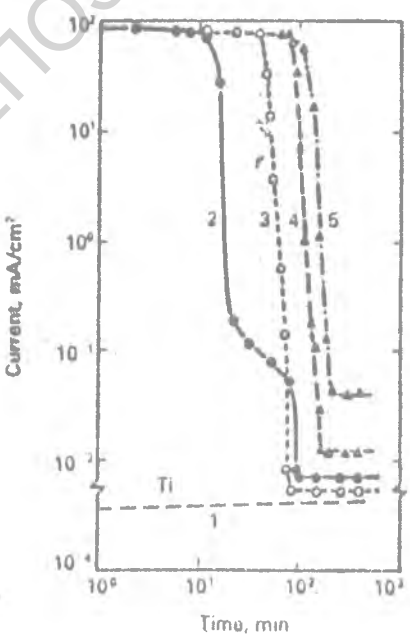
## EXPERIMENTAL PROCEDURE

The DRM apparatus used in the present experiments has been described elsewhere.[7] Nickel films 10nm thick were sputter deposited on to polished titanium substrates and these were irradiated with 10keV $Ar^+$ at room temperature with fluences $5\times10^{15}$, $1\times10^{16}$, and $3\times10^{16}$ ions/cm². The current density during the irradiation was 4μA/cm² for all samples. The ion bombardment was accompanied by simultaneous sputter deposition of nickel at a rate of 1nm/min to compensate for the sputter erosion of the films, and 2MeV $He^+$ backscattering with a scattering angle of 168° was used to study the composition of the resulting films. To improve the depth resolution of the system the samples were tilted by 70° to the incident beam, thus providing a total resolution of 1.8nm per channel for nickel.

Electrochemical tests were carried out in an alkali carbonate solution made from 180g/l $K_2CO_3$+120g/l $KHCO_3$ at a temperature of 20°C. Potentiostatic (current/time) curves at a potential of 1.7V relative to a silver chloride reference electrode were obtained.




*1 Potentiostatic curves for E=1.7V (1) Ti, (2) as deposited Ti-Ni, (3) samples after DRM with $5\times10^{15}$ 10keV $Ar^+/cm^2$, (4) DRM with $1\times10^{16}$ $Ar^+/cm^2$, and (5) $3\times10^{16}$ $Ar^+/cm^2$*

## RESULTS AND DISCUSSION

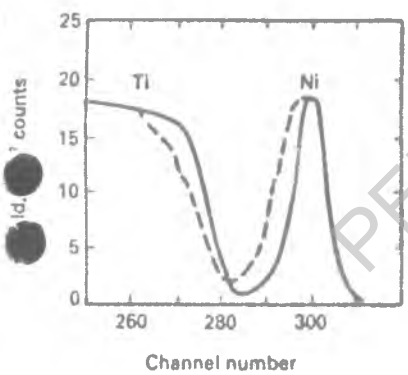
The experimental potentiostatic polarisation curves for Ti, for as-deposited Ni on Ti, and for atomically mixed Ni-Ti samples are shown in Fig.1. For titanium in the conditions used the current density is $4\times10^{-3}$mA/cm² because of the semiconducting properties of titanium oxide surfaces at high anode potentials. The current densities for the as-deposited Ni-Ti and the atomically mixed Ni-Ti films are 90mA/cm² during the initial test period. However the time of operation at this current density is markedly different for the as-deposited films and the corresponding recoil mixed films. The life of the mixed films is increased by over a factor of five in comparison with the as-deposited films, and Fig.1 also indicates that the stability of the electrodes also increases monotonically with an increasing $Ar^+$ fluence.

It is possible to cite several factors which lead to the increase in stability after recoil mixing. Firstly, there is the inclusion of an inert gas such as argon which may lead to the corrosion resistance of nickel, as has been seen for nickel bombarded by He atoms.[8] Secondly, the corrosion resistance of nickel increases as result of

enrichment of the nickel film by titanium as a result of atomic mixing. Such an increase in corrosion resistance in acidic chlorides as a result of addition of small quantities of titanium has also been reported.[9]

It must be noted that, during the process of simultaneous deposition and bombardment in DRM, the quantity of nickel was increased from $9.4\times10^{16}$ atoms/cm$^2$ to $1.3\text{-}1.4\times10^{17}$ atoms/cm$^2$ after bombardment with $5\times10^{15}$Ar$^+$ ions/cm$^2$. This increase is general for this process but is not sufficiently high to explain the increase in the life of the electrodes. For example, although the quantity of nickel increased by a factor of 1.5 after bombardment by $5\times10^{15}$Ar$^+$ ions/cm$^2$, the life of the electrodes for the corresponding samples increased by over a factor of 4 (see curves 2 and 3 in Fig.1).

The RBS spectra for the as-deposited film and those after DRM to an Ar$^+$ fluence of $3\times10^{15}$ ions/cm$^2$ are shown in Fig 2. In spite of the fact that for 10keV Ar$^+$ in nickel the maximum in the projected energy range curve lies a depth of $R_p$=5.1nm with a standard deviation $\Delta R_p$=3.8nm,[10] significant changes in the Ni-Ti interface have been observed. This is in agreement with Newcombe et al's work where it was shown that effective atomic mixing occurs in layers of thickness $R_p+4\Delta R_p$.




*2 RBS spectra for 2MeV He under optimum scattering geometry $\theta_1 = 70°$, $\theta_2 = 58°$. Ni (10nm) on Ti; —— as deposited; - - - - after DRM using $3\times10^{15}$ ions/cm$^2$ 10keV Ar$^+$*

An estimate from the shape of RBS spectra shows that, for irradiation by $3\times10^{15}$/cm$^2$ Ar$^+$, the quantity of nickel mixed with titanium is

$N_{Ni\ (Ti)} = 1.5\times10^{15}$/cm$^2$

The appearance of small steps on the nickel and titanium signals at the Ni-Ti interface suggest formation of Ni-Ti compounds, although the magnitude of these steps is too small to warrant any definite conclusion regarding the composition of their compounds. However, further evidence of such intermetallic compounds arises from the electrochemical properties of these films. To be specific, the dynamical reduction of the anode current after dissolution of nickel from the surface suggests the formation of a Ni-Ti compound. For example, as the Ar$^+$ fluence increases from $5\times10^{15}$ to $3\times10^{16}$ ions/cm$^2$ the time required to reach a steady current increases from 45 to 140min (curves 3 and 5 in Fig.1). In our opinion the transition part in the potentiostatic curves is likely to be connected with Ni-Ti intermetallic compound formation on the anode.

## CONCLUSION

A technique known as DRM was used to irradiate 10nm nickel films deposited on titanium with 10keV Ar$^+$ with varying fluence. An RBS analysis of the resulting films shows considerable Ni-Ti mixing and possibly the formation of small quantities of Ni-Ti compounds. The potentiostatic polarisation curves for these films indicates that their life increases by a factor of ~5 after DRM and that the stability of the electrodes increases monotonically with an increasing Ar$^+$ fluence. These changes are mainly attributed to the mixing of nickel and titanium ions, possible effects of the inclusion of argon in nickel, and formation of Ni-Ti compounds.

The results clearly indicate the need to further investigate the formation of stable and metastable metallic phases by ion beam mixing, and the identification and characterisation of such phases as well as their electrochemical properties.

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## [illegible] NEWS

### New forming method saves die costs

A way of making precision-formed metal components without incurring die costs has been developed by metal spraying specialist **Mineral and Chemical Products**. The technique, which is based on high temperature metal spraying, is said to be ideal for the short production runs that are most expensive in conventional tooling costs.

The MCP approach starts with a detailed model of the part carved in wood, plastics, or any other suitably stable material. This is then used to form a 'negative' mould in epoxy resin. The component itself is produced by arc spraying zinc on to the mould until a full-scale 'positive' has been formed. Any finish — from plating to paint — can then be applied to the component, which faithfully reproduces the shape and surface texture of the mould.

The metal atomised and deposited by the spraying system — the TAFA electric arc gun — has densities in excess of 90% with porosities as low as 0.17%. Its laid-down chemistry is essentially the same as that of the feed stock wire. However changes do occur in the physical properties during arc spraying and, for this reason, the process is not suitable for parts subject to high loading or stresses.

MCP believes a major area of application could be in the production of short runs of