Aqueous corrosion behavior of Ce-implanted ZrN coating

Q. G. ZHOU, X. D. BAI*, Y. H. LING, D. Q. PENG
Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, P.R. China
E-mail: zhouqg99@mails.tsinghua.edu.cn

J. XU, D. R. WANG
Beijing Great Wall Ti-Gold Co. Ltd., Beijing 100095, P.R. China

Zirconium nitride (ZrN) is applied as a decorative and hard coating because of its integrated properties of high hardness, optical properties, electrical and heat conductivity. The durability of ZrN coating depends not only on the properties, but also on its microstructure. In erosive environments, the major corrosion problem of coated steels is due to the defects in the coating, which may form direct path between the substrate and the exposed environment [1]. The application of an interlayer between the substrate and nitride coating was used to reduce the influence of defects and to improve the corrosion resistance of the substrate.

As an effective method to improve the surface properties, to a depth about 100 nm, the ion implantation or bombardment technique has been employed for further study of ZrN coatings performance. Cobalt [2] and silicon [3] have been implanted in ZrN coatings to improve the structure and mechanical properties. The influences of ion bombardment on the corrosion characteristics [4] and the optical properties [5] of ZrN coatings have also been investigated. However, there is little information about the effect of implantation on the electrochemical behavior.

In the present work, the ZrN coatings prepared by cathodic are deposition were implanted with cerium using a metal vacuum vapor arc (MEVVA) ion source implanter. The influence of cerium ion implantation on the residual stress and electrochemical behavior were investigated.

The substrates used in these experiments were $10 \times 15 \times 0.8$ mm commercial AISI 304 stainless steel. The samples were mechanically ground with 200–800 grade abrasive paper, polished with 1.0-μm diamond paste, ultrasonically degreased in ethanol and acetone, and finally rinsed in deionized water.

The ZrN coating was prepared using a cathodic arc deposition system, where the target was made of zirconium of 99.9% purity. Prior to deposition, the chamber was evacuated to below 1×10^{-3} Pa, and the sample holder was heated to $300\,^{\circ}$C. High purity argon gas was introduced to etch the substrate. To provide better adhesion between the substrate and the coating, a zirconium interlayer was then deposited prior to the final ZrN coating. High purity nitrogen gas was then introduced and used to deposit zirconium nitride, using a

bias voltage of -180 V, an arc current of 60 A, and a nitrogen pressure of 0.6 Pa.

The ZrN-coated samples were placed on the sample holder in the target chamber of the MEVVA source implanter under a background pressure of 1.0×10^{-3} Pa. The implanted area was 12 cm in diameter. The extracted cerium ions consisted of 3% Ce^+, 83% Ce^{2+}, and 14% Ce^{3+}, giving an average charge of approximately 2.1. Implantation ion doses of 5×10^{16}, 1×10^{17} and 2×10^{17} ions/cm^2 were used, at an extraction voltage of 40 kV and a beam current density of 15 μA/cm^2. The maximum temperature of the samples was $150\,^{\circ}$C. The temperature was determined by a variety of factors including the extraction voltage, beam current density, implantation time, and the properties of the implanted ions and the base material.

To evaluate the electrochemical performance of the Ce-implanted ZrN samples, potentiodynamic polarization was carried out in 0.5 M H_2SO_4 aqueous solution at room temperature using a Zahner IM6e electrochemical workstation. Potential scans were employed starting from a cathodic region of -1.0 V to the anodic region of 2.0 V. X-ray photoemission spectroscopy (XPS) was employed to analyze the composition and the valence states of the surface layer of the ZrN samples. In addition, X-ray diffraction (XRD) was used to examine the phase transformation due to the cerium ion implantation.

The crystallographic structure of the ZrN thin films was characterized by XRD. The XRD pattern shown in Fig. 1 accords well with the JCPDS card No. 35-0753, which showed that the film structure is equiaxed, and this could greatly reduce the corrosion rate compared to that for a columnar structure.

The Ce3d and Zr3d spectra of Ce-implanted ZrN samples are shown in Fig. 2(a) and (b), respectively. In Fig. 2(a), there are many peaks of Ce spectra including the Ce 3d peak in metallic Ce and CeO_2 and satellite lines of the as-implanted ZrN. CeO_2 is probably produced during MEVVA treatment, resulting from the moderately $(1.0 \times 10^{-3}$ Pa) remnant atmosphere in the chamber. Also in Fig. 2(b) there are peaks corresponding to Zr $3d_{5/2}$ and $3d_{3/2}$ of ZrN. Compared with Fig. 2(a), it can be concluded that cerium should preferentially combine with oxygen before zirconium.

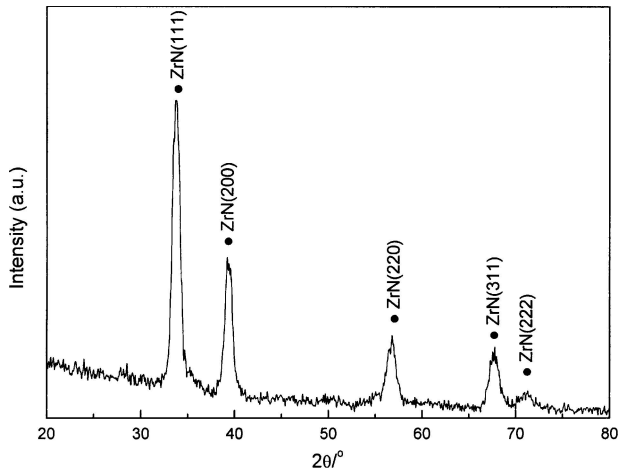*Author to whom all correspondence should be addressed.

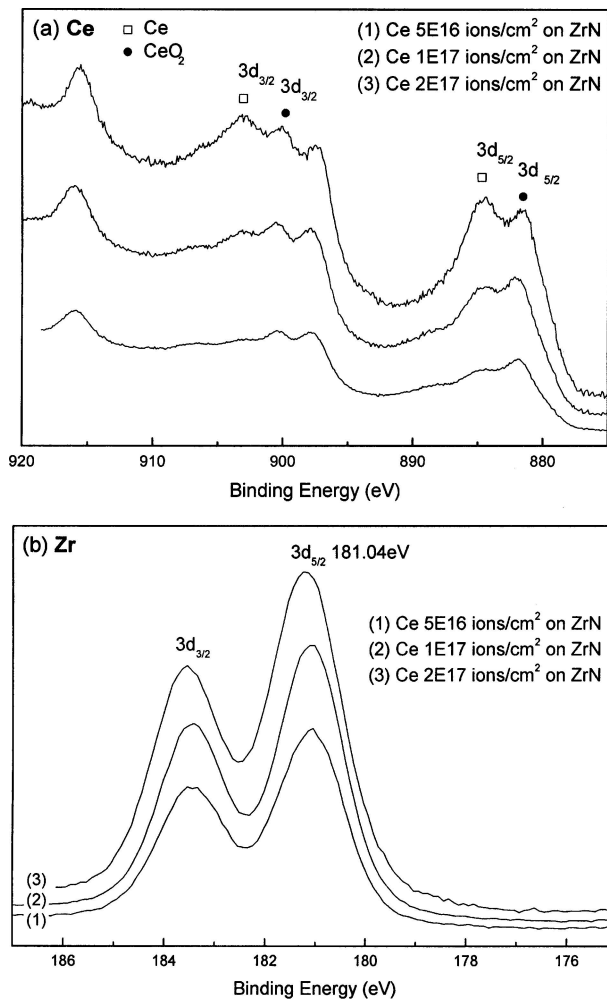*Figure 1* XRD pattern of as-deposited ZrN coating.

Figure 3 The polarization curves of as-deposited and Ce-implanted ZrN coatings.

Figure 2 XPS spectra of (a) Ce $3d_{5/2}$ and (b) Zr $3d_{5/2}$ in ZrN coatings implanted by cerium with dose of 5×10^{16}, 1×10^{17}, and 2×10^{17} ions/cm^2.

The potentiodynamic measurements were carried out in 0.5 M H$_2$SO$_4$ aqueous solution at a sweep rate of 2 mV/s. Before measurement, the solution was deaerated by introducing nitrogen for 1 hr, and the working electrode was exposed to the electrolyte for 10 min. Referring to the saturated calomel electrode (SCE), the potentiodynamic measurement began from a cathodic potential of -1.0 V and ended at an anodic potential of 2.0 V. A series of polarization curves for
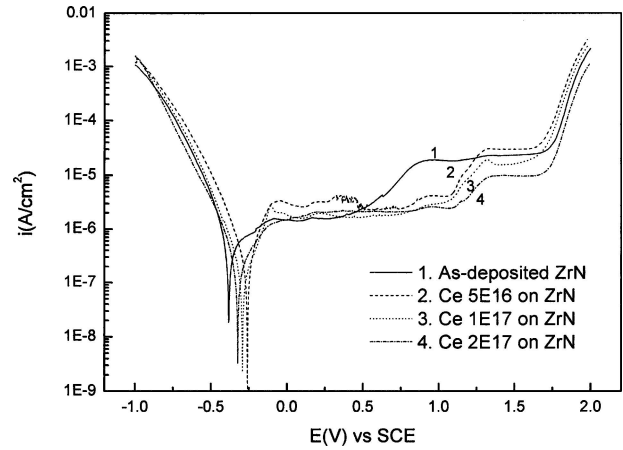
different cerium ion doses was obtained, as shown in Fig. 3.

The polarization resistance R_p was calculated according to the Stern–Geary equations [6]:

$$R_p = \frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c) i_{corr}} \quad (1)$$

where ΔE, ΔI are the differential results of E and I near the linear polarization region, and β_a, β_c are Tafel slopes of anodic and cathodic polarization curve, respectively, and i_{corr} is the corrosion current.

To evaluate quantitatively the corrosion resistance, the passive current density i_p and the polarization resistance R_p of ZrN coating are plotted as a function of cerium doses, as shown in Fig. 4. Compared with the as-deposited ZrN, with increasing ion dose, the passive current density (i_p) of Ce-implanted ZrN decreased, while the R_p values increased, which should increase the corrosion resistance with increasing ion dose.

The failure of the materials resulted from the corrosion of the substrate under the coating pinholes, while ZrN coating is chemically inert in acid solution. As shown in Fig. 2(a), with increasing ion dose, some cerium remains in metallic form; accordingly, the corrosion potential E_{corr} increases with ion dose (Fig. 5). Nevertheless, the values are higher than that of the
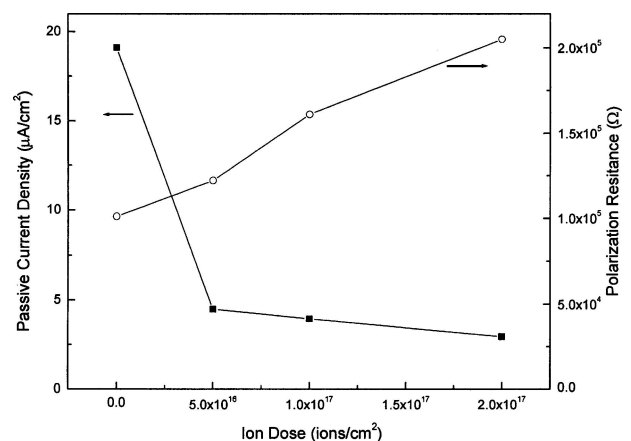

Figure 4 Passive current density and polarization resistance of as-deposited and Ce-implanted ZrN coatings with various doses.
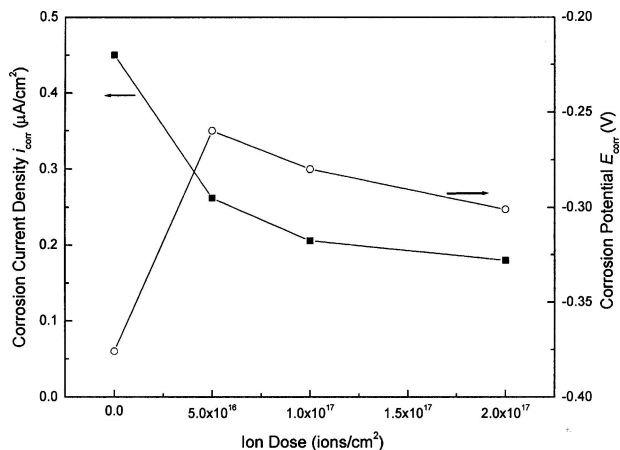
Figure 5 Corrosion current density and corrosion potential of as-deposited and Ce-implanted ZrN coatings with various doses.

as-deposited ZrN coating. With increasing ion dose, the passive current density and corrosion current density decreased, while polarization resistance increased, as shown in Figs 4 and 5. On the basis of a similar experiment [7], it could be deduced that the cerium ion implantation could result in a denser coating morphology and thereby the porosity could be reduced. Therefore, the corrosion rate of the Ce-implanted ZrN coatings decreased markedly.

The electrochemical behavior of as-deposited and Ce-implanted ZrN samples has been studied. XRD pattern shows that the microstructure of as-deposited ZrN coating is equiaxed. Cerium preferentially combined with oxygen, but it exists both in oxide and metallic form in high dose. Accordingly the corrosion potential E_{corr} increases with ion dose. Ce-ion implantation could greatly improve the corrosion resistance of ZrN coatings. With increasing ion dose, the passive current density and corrosion current density decreased, while polarization resistance increased.

References

1. W. TATO and D. LANDOLT, *J. Electrochem. Soc.* **145** (1999) 4173.
2. D. ZANGHI, A. TRAVERSE, M. D. M. ALVES, T. GIRARDEAU and J. P. DALLAS, *Nucl. Instrum. Meth. B.* **155** (1999) 416.
3. T. MAE, M. NOSE, M. ZHOU, T. NAGAE and K. SHIMAMURA, *Surf. Coat. Technol.* **142** (2001) 954.
4. E. KELESOGLU, C. MITTERER and M. URGEN, *ibid.* **160** (2002) 82.
5. C. MITTERER, P. H. MAYRHOFER, W. WALDHAUSER, E. KELESOGLU and P. LOSBICHLER, *Surf. Coat. Technol.* **109** (1998) 230.
6. M. G. FONTANA, "Corrosion Engineering," (McGraw-Hill Book Company, New York, 1986).
7. P. LOSBICHLER and C. MITTERER, *Surf. Coat. Technol.* **97** (1997) 567.