

The Corrosion Behaviour of Titanium, Surface Alloyed with Palladium by Implantation and/or Plasma Pulses, in a Simulated Flue Gas Environment

F.A. Bonilla¹, P. Skeldon¹, G.E. Thompson¹,
J. Piekoszewski^{2,3}, Z. Werner³,
A.G. Chmielewski², J. Stanislawski³

¹Corrosion and Protection Centre, UMIST,
P.O. Box 88, Manchester M60 1QD, UK

²INCT, Dorodna 16, Warszawa 03-195, Poland

³The Andrzej Institute for Nuclear Studies,
Otwock-Swierk 05-400, Poland

INTRODUCTION

Significant reduction in the emission of pollutants (e.g., NO_x, SO₂ and volatile organic compounds) from the metallurgical and thermal power industries has been achieved by electron beam treatment of flue gases (1). An essential component of this technology is a thin window through which the electrons access the reaction chamber. Titanium foil, 50 μm thick, is currently used due to its strength and to its good corrosion resistance. The current service life of windows is typically 2,000 hours, whereas, plant shut-downs are programmed for 10,000 hours.

EXPERIMENTAL

Degradation of Ti in the environment within the chamber has been simulated in 0.1 M H₂SO₄ solution at 80°C (2). For improved corrosion resistance of the window, the foil has been surface-alloyed with Pd using: (i) high intensity pulsed plasma beams (HIPPB) under a pulsed erosion mode of operation of a rod plasma injector (RPI); (ii) Pd pre-deposition onto Ti by e-gun evaporation and processing by HIPPB under a pulsed implantation doping (PID) mode; (iii) implantation of Pd into the Ti foil using a metal vapour vacuum arc (MEVVA) source followed by HIPPB under the PID mode (3). Nitrogen was used as the working gas for the HIPPB processes. Surface alloys of compositions in the range 0.7–17 at.% Pd, with smooth depth composition profiles (Figure 1), 30-900 nm thick were produced, as assessed by Rutherford backscattered spectrometry (RBS).

RESULTS

The behaviours of the Ti foil and the surface alloys in the simulated environment were evaluated from the open circuit potential (OCP) during immersion tests; the average weight loss rate was determined. The weight loss rate of Ti after 15 h immersion was ~ 45 g m⁻² d⁻¹ and the steady OCP was -780 mV (SCE). The results of 100 h immersion tests for the surface alloys indicate a reduction of at least 2 orders of magnitude in the weight loss rate compared with the Ti foil. The alloys with reduced Pd concentrations exhibited enrichment of the alloying element in the outer 20 nm of the alloy during immersion in the acid, as determined by medium energy ion scattering (MEIS) (Figure 2). For alloys with higher Pd concentrations, a crystalline Pd-rich film, (from electron diffraction and energy dispersive X-ray (EDX) analysis), was detached upon removal from the solution, as observed by the unaided eye and later by transmission electron microscopy. RBS and EDX analyses indicate that the proportion of the initial deposited Pd lost during immersion tests (13-99%) generally increased with increasing Pd concentration in the outer layers, for alloys prepared under similar conditions. Further, increasing amounts of deposited Pd did not necessarily result in a lower net average weight loss rate (total weight loss rate minus contribution of Pd). The net average weight loss rate for the surface alloys is about 0.14 g m⁻² d⁻¹ equivalent to 0.4 pm s⁻¹ or 1.3 μA cm⁻² (assuming

formation of Ti⁴⁺ ions). The OCP of the Pd-containing alloys is higher (up to 480 mV (SCE)), than that of Ti, consistent with the protection mechanism of Pd, whereby it enhances the cathodic reaction at the surface, effectively reducing the hydrogen overvoltage and hence, shifting the corrosion potential into the passive region of Ti (4).

CONCLUSIONS

The results suggest that during the immersion tests, selective dissolution of Ti (under the passive condition) occurs. For alloys with increased Pd concentrations, the enrichment associated with the selective dissolution of Ti, results eventually in detachment of a film, mainly composed of a network of Pd nanocrystals. The dissolution mechanism of Ti appears complex; depending upon the composition profiles and it may involve phase transformations, varying surface and volume diffusion rates and interaction between the noble metal and oxide passive films (5).

ACKNOWLEDGMENTS

European commission contract No. ICA2-CT-2000-10005

REFERENCES

- (1) A.G. Chmielewski et al., Radiat. Phys. Chem., **46**, 1063 (1995).
- (2) S.D. Barson et al., Corros. Sci., **42**, 1213 (2000).
- (3) J. Piekoszewski et al., Surf. Coat. Tech., **106**, 228 (1998).
- (4) M. Stern and H. Wissenberg, J. Electrochem. Soc., **106**, 759 (1959).
- (5) B.G. Ateya and H.W. Pickering, Corros. Sci., **38**, 1245 (1996).

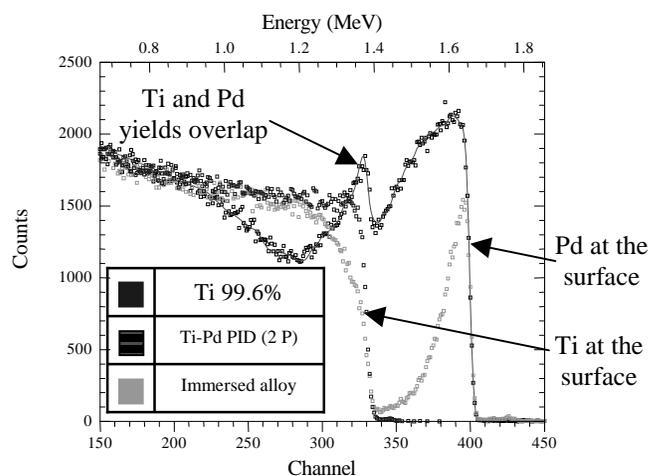


Figure 1 RBS spectra of untreated Ti, and Ti-Pd surface alloy (Pd pre-deposition followed by HIPPB PID) before and after immersion in 0.1 M H₂SO₄ at 80°C for 100 h

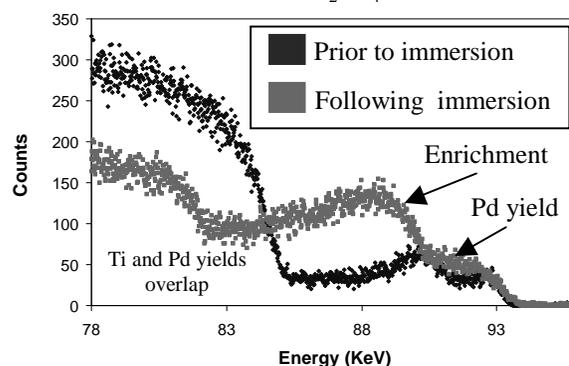


Figure 2 MEIS spectra at 90° scattering angle of Ti-Pd surface alloy produced by implantation with a MEVVA source followed by HIPPB PID (low Pd concentration)