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Hydrothermal corrosion of TiAlN and CrN PVD films on stainless steel

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Abstract

Hydrothermal corrosion of thin TiAlN and CrN PVD films (of 3μm thickness) in 100 MPa water over a temperature range of 20–950 °C is compared to the behavior of TiN films over the same *T*–*P* conditions. Corrosion resistance increases in the sequence TiN → TiAlN → CrN. A $FeTiO_3$ (ilmenite) layer on the surface of the TiAlN film is almost chromium-free and provides protective properties up to 700 °C, whilst ülvospinel formation leads to spallation of oxide scale due to high level growth stresses. Formation of a very stable spinel scale on the surface of the CrN films provides long-term corrosion protection in 100 MPa water up to 800 °C. Nitride films on low-alloyed steel can substitute for expensive super alloy in wet air oxidation systems, with working temperatures up to 700 °C in the case of TiAlN, or 800 °C in the case of CrN coatings.

Keywords: Titanium–aluminum nitride; Chromium nitride; PVD film; Hydrothermal corrosion

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1. Introduction

Metallic nitrides are widely used as a barrier thin film in electronics, as hard coatings and as special refractory materials. In all cases, corrosion resistance is very important and nitride coatings can significantly improve the corrosion performance of steel [1–3].

Water–solid surface interaction has great importance in many research fields. The oxidation efficiency of water at room temperature is much lower than that of oxygen [4], because surface hydroxyl groups reduce the oxidation ability of water. In the case of protective coatings, however, it is possible that open porosity and pinholes are formed during the deposition process [5–7]. These localized defects form a direct pathway between the corrosive environment and the substrate. At this point, the substrate is exposed to the electrolyte, and a galvanic cell is formed between the noble coating and the substrate. This corrosion mode leads to more deleterious damage than potential corrosion occurring on a bare substrate.

Recently we showed that commercial TiN PVD coatings can be used on low alloy steel in wet air oxidation systems, instead of expensive super alloys, with operating temperature up to 600 °C [8]. The authors [9,10] believe that the efficiency of wet air oxidation systems can be increased in enhanced temperature and pressure reaction conditions, but this requires new materials, which are effective under severe operating conditions.

TiAlN films [11,12] and dense bodies [13,14] were prepared in order to test the oxidation resistance of TiN, which showed that the oxidation resistance of TiAlN in air (and corresponding drill cutting performance) is increased with Al content [11]. CrN PVD coatings have the highest corrosion resistance in airflow oxidation conditions, compared to TiN and TiAlN, and can be used up to 700–800 °C [15].

However, information on corrosion resistance of coated materials in high temperature–pressure water is limited. There are no reliable data concerning hydrothermal corrosion of TiAlN films, although Kawana et al. [5] report excellent corrosion resistance of CrN compared to TiN films in water at 290 °C and 8.6 MPa, during a 1000 h circulating loop type experiment.

The goal of our research is to evaluate the corrosion resistance of commercial TiAlN and CrN films within the widest range of test conditions: i.e. temperature range 20–950 °C; water pressure 100 MPa; and exposure up to 750 h, in different pH solutions, which are compared to decomposition in waste water. In this paper only hydrothermal corrosion of TiAlN and CrN films in pure water is discussed.

2. Materials and experimental details

Japan Coating Center Co., Ltd produced the TiAlN and CrN PVD films that were deposited on a SUS-304 substrate. The chemical composition of the steel expressed as wt%, is: Cr-18.0; Ni-12.0; Mo-2.5; Si-1.0; C-0.3 with Fe making up the rest. The initial thickness of the films was 3 μm, and they all exhibited typical defect concentrations (for example, about 1% pinholes according to [5]). Moreover,