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High temperature oxidation protective chromium-based coatings prepared by IBAD and PACVD methods

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ABSTRACT

Chromium nitride films were prepared by high energy (90 keV) IBAD method and chromium oxide films were prepared by PACVD method on AISI 316 stainless steel. The chemical composition was evaluated by electron beam microanalysis. The mechanical properties of coatings were tested by Vickers indenter, scratch tester and calotest. The films were hard and exhibited a satisfactory adhesion to the steel substrate. The corrosion resistance of the coatings was tested at 700–1000 °C in oxidizing atmosphere (air). The corrosion kinetics was evaluated by the gravimetric method. The total corrosion exposure was up to 1000 h. The films decreased high temperature oxidation of stainless steel substrates.

1. Introduction

Chromium-based films (chromium nitride and chromium oxide) combine anti-corrosion properties with satisfactory wear resistance. Various unconventional deposition processes, including IBAD (Ion Beam Assisted Deposition) and PACVD (Plasma Assisted Chemical Vapour Deposition), have been used to produce these protective coatings. Chromium nitride films were prepared by IBAD method but only at low values of ion energy (<2 keV). At high values of ion energy, an improved adhesion of the films can be expected and from corrosion point of view the adhesion is a very important property.

Data dealing with IBAD and PACVD anti-corrosion coatings are published relatively seldom. Some papers on chromium nitride films dealt with their corrosion properties, both in electrolytes and at high temperatures in air. Some properties of coatings (e.g., porosity, adhesion, thickness etc.) influence their behaviour in both these corrosion environments. Hones et al. [1] and Senf with Broszeit [2] confirm that magnetron CrN_x coatings have an excellent resistance to high temperature oxidation. In addition, they show a good wear resistance. These coatings have been deposited on low alloy steels and aluminium alloys. Bertrand [3] has deposited chromium nitride coatings by magnetron using AISI 304 stainless steel substrates. These coatings had very good tribological properties but their corrosion resistance was somewhat restricted by the presence of pores. Wang et al. [4] have studied oxidation behaviour of CrN coatings, which were deposited on AISI 304 steel. Samples have been tested at temperature 300–800 °C for 60 min. Oxidation of the nitride was observed at temperature over 500 °C. As regards to the temperature stability of nitride coatings there are similar conclusions in paper [5]. We have had previous experience [6,7] with IBAD SiN_x coatings acting as a protection of low alloy and CrNi stainless steels against high temperature corrosion. These coatings decreased corrosion in long-term corrosion test cycles at 500–700 °C in oxidizing and sulphidizing–oxidizing atmospheres.

In the case of chromium oxide, the most coatings were deposited by magnetron sputtering and mechanical properties were investigated. Pang et al. [8] deposited chromium oxide coatings on low-carbon steel by magnetron sputtering. Hardness and adhesion were investigated by indentation tests. When the coating hardness was increased the adhesion was weakened. Hones et al. [9] deposited the chromium oxide films on HSS substrates also by magnetron sputtering. The chemical composition was measured by electron probe microanalysis. Chromium oxide thin films exhibit high hardness values. Dayung et al. used unbalanced magnetron sputtering process for the deposition of chromium oxide thin film. Excessive thermal stress in the films resulted in cracking of chromium oxide exposed to high temperatures [10].

2. Experimental

Two kinds of high temperature oxidation protective chromium-based coatings were prepared by IBAD and PACVD methods: chromium nitride by IBAD method and chromium oxide by PACVD method. The coatings were deposited on samples (diameter 20 mm and thickness 4 mm) made of stainless AISI 316 steel. Substrate

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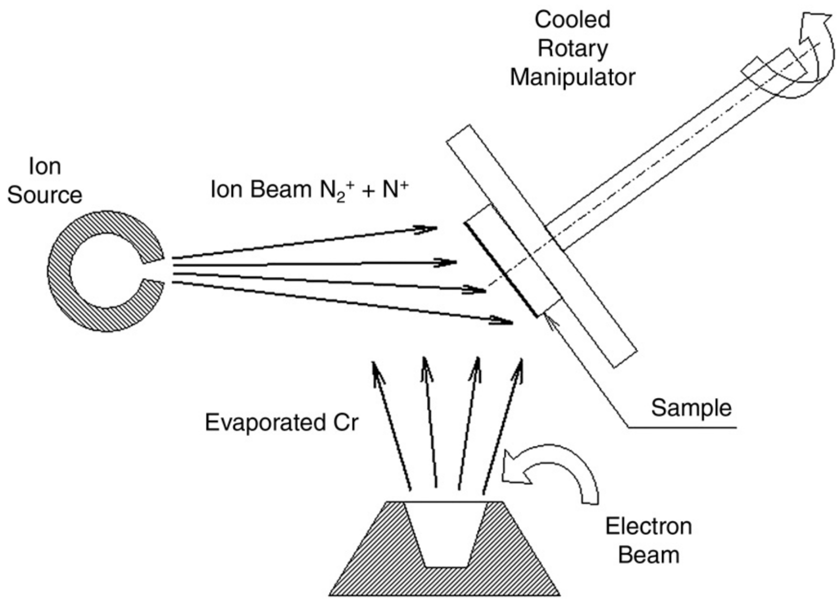

Fig. 1. Principle of IBAD process.

surface was mechanically grinded and polished. Before deposition process the samples were ultrasonically degreased in acetone.

The IBAD process (Fig. 1) was conducted as a simultaneous evaporation of chromium (flux 1.8×10^{18} $m^{-2}s^{-1}$) and bombardment with nitrogen ions (flux 3.9×10^{17} $m^{-2}s^{-1}$). Nitrogen ions energy was 90 keV. Thickness of coating was approximately 2 µm.

PACVD deposition (Fig. 2) was conducted from chromium acetylacetonate and oxygen (1:1) at 70 Pa and 400 °C, using rf plasma (13.56 MHz, 200 W). Thickness of coating was approximately 5 µm. The thickness of coatings was evaluated by calotest method (i.e. coatings were ground through by rotating ball and the thickness was measured on grinded surface by light microscope).

Chemical composition of coatings in as deposited state was investigated by EPMA (Electron Probe Microanalysis) with wave dispersion of emitted X-rays at electron beam energy 10, 15 and 20 keV. The Vickers microhardness (HV) of coatings was measured by special adaptor on light metallography microscope at applied loading 5 g. Adhesion of coatings was measured by scratch tester (with cone tip).

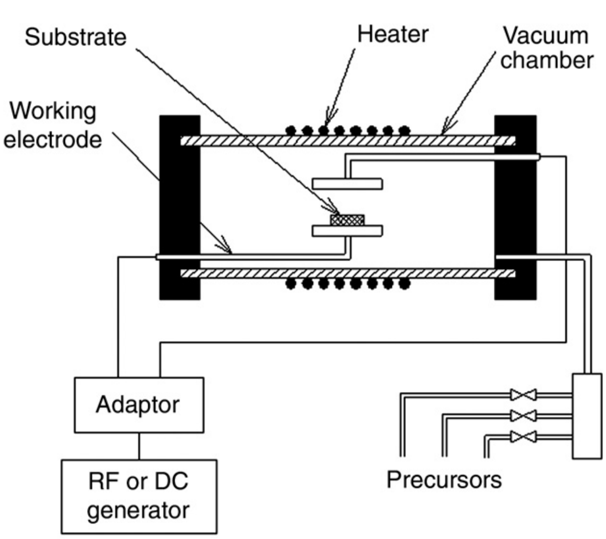

Fig. 2. Layout of PACVD apparatus.

Corrosion resistance was investigated in corrosion tests which were taken in air at temperatures 700 °C, 800 °C and 900 °C for total time 200 h in the case of 2 µm IBAD chromium nitride coatings and at temperatures 800 °C, 900 °C and 1000 °C for total time up to 1000 h in the case of 5 µm PACVD chromium oxide. The tests were interrupted after defined intervals of elapsed time. Corrosion kinetics was evaluated by gravimetric measuring of weight gains during each test interruption. Each point in the diagrams represents the arithmetical average from weighing of 10 samples.

3. Results and discussion

Microanalysis of IBAD coatings in as deposited state was made at electron beam energy 10, 15 and 20 keV. Results are in Table 1. Results of chemical analysis show, that all coatings contain large amount of non-reacted chromium in addition to chromium nitride. The content of nitrogen increases with increasing electron beam energy because of relatively broad Gaussian concentration profile corresponding to high energy nitrogen ion implantation at 90 keV. Coatings prepared at low energy (up to 2 keV) have a homogeneous compositional ratio of nitrogen and chromium across the coating. When high energy ions are used (of the order of tens of keV) the composition of the coatings becomes inhomogeneous; gradient coatings are produced. The small concentration of iron noticed in the coating is produced by the high energy ion beam mixing which also contributes to the higher adhesion of coatings to the substrates.

Microhardness of IBAD chromium nitride coatings in as deposited state was approximately 1200 HV and force required for delamination

Table 1
Chemical composition of IBAD chromium nitride coating.

Beam energy [keV]	Composition [at.%]			Composition [wt.%]		
	Cr	N	Fe	Cr	N	Fe
10	79.8	19.7	0.5	93.0	6.2	0.8
15	79.6	19.9	0.5	92.8	6.3	0.9
20	76.3	23.2	0.5	91.8	7.5	0.7