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Structure and morphology of TiB_2 duplex coatings deposited over X40 CrMoV 5-1-1 steel by DC magnetron sputtering

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A B S T R A C T

The deposition of titanium diboride (TiB_2) films over tool steel substrates (AISI H13 premium/EN X40 CrMoV 5-1-1) is being investigated due to its excellent corrosion resistance and chemical stability against liquid aluminium. The use of nitrided steels as substrates for TiB_2 deposition may contribute to increase its adhesion and the overall steel resistance in applications such as forging, extrusion and die casting of aluminium. Duplex coatings were obtained by the PVD deposition of TiB_2 films over heat treated and nitrided steel using non-reactive DC magnetron sputtering from a TiB_2 target, varying the substrate bias voltage. Well structured and crystalline TiB_2 films were obtained for the selected deposition conditions, the best crystalline coatings being obtained for the positively biased substrates. Selected films produced over die-casting pins at a bias voltage of +50 V were tested for resistance to liquid aluminium soldering by immersion tests, and compared with the nitrided steel. The duplex TiB_2 coating has a much larger chemical resistance to attack by molten aluminium alloy than the just nitrided steel. Where there is soldering, steel is rapidly attacked and a complex Al–Fe–Si intermetallic forms.

1. Introduction

In the Aluminium die-casting industry quenched and tempered EN X40 CrMoV 5-1-1 (AISI H13) steel is widely used in the die-casting moulds in the areas that contact with molten aluminium [1,2]. This type of tool steel is commonly used for components such us cavities, inserts, pins, runners, etc, due to its properties, namely, its ability to resist to thermal fatigue, while maintaining a good toughness and hot hardness levels during service. In order to improve both the wear and chemical resistance of this hot work tool steel grade, surface engineering techniques can be applied, like the application of thermochemical heat treatments and PVD-coatings. Typical examples are the nitriding as a thermochemical treatment [3] and TiAlN and AlCrN, among other coatings as PVD-techniques [4–6]. The duplex coatings, i.e. deposition of PVD-coating over a nitrided surface, may ensure a longer life of mould components that are severely damaged by aluminium erosion and adhesion.

TiB_2 is a well known material in the aluminium liquid processing industry due to its chemical resistance against liquid aluminium [7]. These characteristics and fact that TiB_2 has high wear resistance, high hardness and good thermal properties make coatings of this material a very interesting approach concerning its application in die-casting dies. Previous work showed that crystalline TiB_2 coatings can be successfully obtained over quenched and tempered AISI H13 substrates, by applying positive substrate bias [8].

The chemical resistance of TiB_2 coatings and nitrided AISI H13 steel to attack by molten aluminium alloy used in die casting is tested and reported in the present work. TiB_2 films are produced as duplex coatings over nitrided surfaces of heat treated steel to further enhance corrosion resistance of the nitrided steel. Studying the effect of a first nitrided layer on the deposition and corrosion behaviour of TiB_2 coatings is another objective of the present work.

2. Experimental procedure

In this work a nitrided EN X40 CrMoV 5-1-1 steel was used as the substrate material. After a heat treatment, described elsewhere [8], and polishing, the samples were low pressure gas nitrided (Alnit®) under NH_3 atmosphere during 10 h at 540 °C. Substrate

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microstructure was observed by optical and scanning electron microscopy and the substrate microhardness profile was determined by Vickers (0.2 kg) indentation technique. Prior to the deposition, the samples were cleaned in ultrasonic baths of acetone and ethanol and then placed in the DC magnetron sputtering chamber at a substrate-magnetron distance of 70 mm. The TiB_2 target used for the sputtering process was a 76 mm diameter disc homemade by hot pressing high purity stoichiometric TiB_2 powders. The deposition chamber was evacuated to the pressure of 5×10^{-6} mbar and the substrates were cleaned by argon sputtering during 20 min before the non-reactive deposition using a bias of +100 V and an argon pressure of 6×10^{-3} mbar. The same pressure was used for 2 h long depositions under magnetron current emission of 0.5 A and substrate bias from −150 V to +150 V. The phase identification and texture of the coatings were determined by X-Ray diffraction using CuKα radiation. Immersion tests in liquid aluminium alloy were performed for the +50 V biased and nitrided samples. These samples were pin shaped, having 11 mm diameter and 40 mm long. Samples were dipped during 150 min in an EN DIN Al–12Si–1Cu(Fe) melt kept at 650 ± 10 °C. After the immersion, the samples were cut and polished for metallographic characterization of the cross section. The films morphology, chemical composition and thickness, as well as the immersed samples were characterized by scanning electron microscopy assisted by electron dispersive X-ray spectroscopy.

3. Results and discussion

The substrates used for the TiB_2 deposition were disc shaped samples of nitrided hot work tool steel. After nitriding heat treatment the samples exhibit two layers, with a total thickness of about 0.15 mm, as is shown in the optical micrograph of Fig. 1a. The external one consists of a thin compact and continuous (white) layer with hardness level exceeding 1000HV and the inner, named diffusion layer, has lower hardness towards the sample core (Fig. 1b) as a consequence of the presence of smaller and fewer nitrides precipitates. The nitrides were identified as Fe_3N and Fe_4N using X-ray diffraction.

The main deposition parameters were selected based on previously published work [8], using a sample-magnetron distance of 70 mm and an emission current of 0.50 A that originate 12 nm/min deposition rate for the unbiased samples. In this work, the effect of the bias voltage on the films crystallinity, morphology and growth kinetics was studied. Using X-Ray diffraction technique it was observed that negative bias does not promote the formation of crystalline structures, while the positive bias leads to the formation of strong textured TiB_2 films in the (001) plane (Fig. 2). This means that ion assisted deposition (negative bias) resulted in amorphous films and on the other hand, electron assisted process (positive bias) produces crystalline films due to the enhancement of surface mobility of adatoms [9]. Negatively biased samples have deposition rates slightly lower than positive ones. The measured values were 7.1 and 5.8 nm/min respectively for the −150 V and −50 V samples. The positively biased samples have deposition rates of 7.5 and 10.4 nm/mm for the +50 V and +150 V respectively.

On what respects morphology, the TiB_2 films appear differently according to the negatively and positively biased or unbiased films, as can be seen in the micrographs of Fig. 3. Scanning electron microscopy analysis to the substrate showed a porous nitrided outside layer (Fig. 3a). The films morphology at positively biased samples (Fig. 3b–d) partially mimics the nitrided substrates morphology (Fig. 3a). The films microstructures are granular and become finer as the bias voltage is decreased. The unbiased samples (Fig. 3e) also reveal the substrate topography but in a more compact way. The effect of the substrate topography on the films surface is attenuated when the sputtering is negatively bias assisted

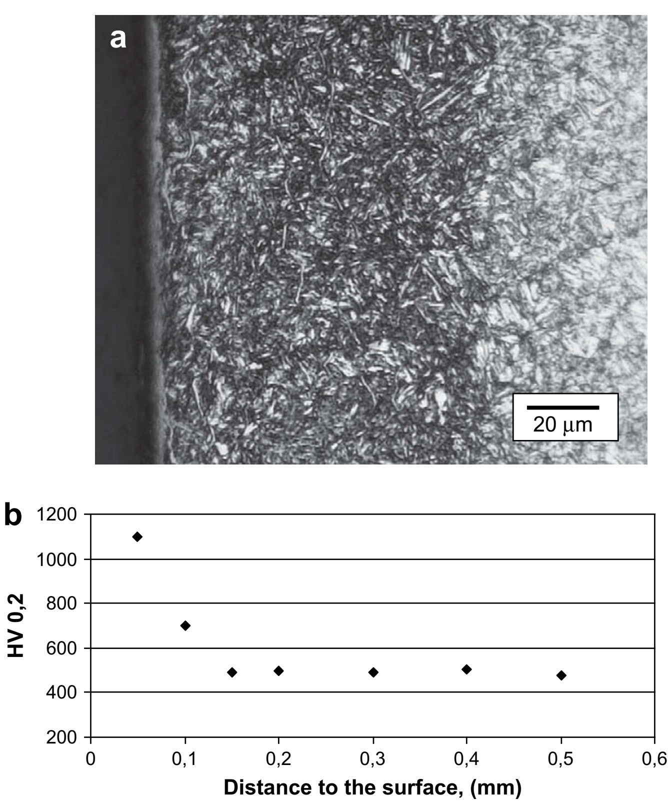

Fig. 1. Nitrided samples: a) microstructure taken from optical microscopy, b) Vickers hardness profile.

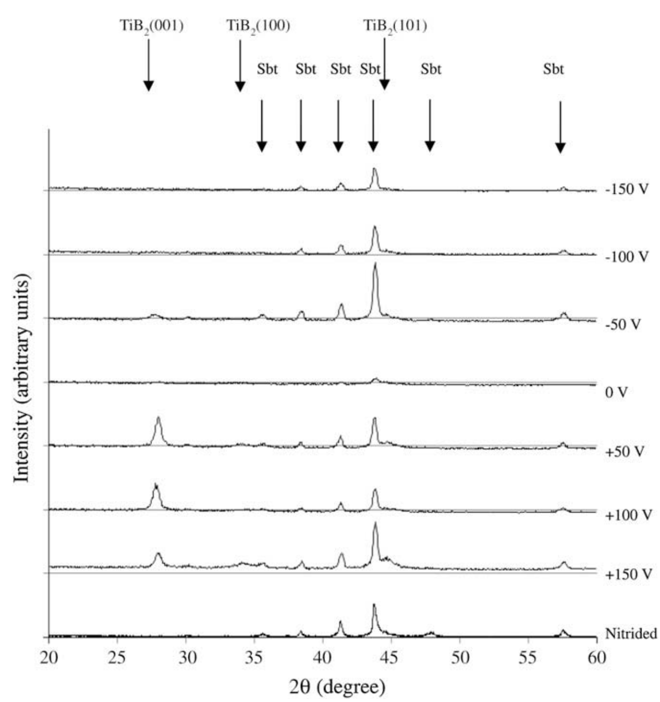

Fig. 2. X-Ray patterns of films produced varying substrate bias from +150 V to −150 V. (sbt – substrate).