Available online at www.sciencedirect.com
ScienceDirect
Surface & Coatings Technology 201 (2007) 9299–9303
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Wear properties of MOCVD-grown aluminium oxide films studied by cavitation erosion experiments

Christian Pflitsch [a,*], Benjamin Curdts [a], Volker Buck [b], Burak Atakan [a]

[a] *Thermodynamics, IVG, Department of Mechanical Engineering, University of Duisburg-Essen, Campus Duisburg, Lotharstr. 1, D-47057 Duisburg, Germany*
[b] *Thin Film Technology, Department of Physics University of Duisburg-Essen, Campus Duisburg, Lotharstr. 1, D-47057 Duisburg, Germany*

Available online 3 May 2007

Abstract

Thin aluminium oxide films are of interest due to many technical applications, such as hard coating, electrical insulator, or antireflective coating. It is obvious for such applications that the used films should have a good contact with the substrate underneath, be well adhering and be mechanically resistant. Therefore, cavitation experiments according to the ASTM G32-92 standard were now used to study the adhesion and wear resistance of CVD-grown aluminium oxide films. It is shown that amorphous alumina films (0.75 μm thick) which are grown in a hot wall reactor on steel are enduring the cavitation erosion better than the clean and uncovered steel, and are thus very promising for technical applications. After 30 min cavitation, no damages are observed on the coated samples by SEM while uncoated steel is clearly damaged. After 180 min, the mass loss of the specimen caused by cavitation erosion is more than 7 times lower than the one of coated steel.

Keywords: Aluminium oxide; Cavitation erosion; Hard coating; Steel; MOCVD; Wear properties

1. Introduction

Aluminium oxide films have attracted much interest in the recent years for several technical applications, e.g. hard coatings [1], antireflective coatings on glass substrates [2], electrical insulators in electronic devices [3,4], or diffusion barriers in multilayer coatings which are protecting steel against high temperature oxidation [5,6]. Thereby several growth techniques were used to deposit the films, the most important ones being physical vapour deposition (PVD) [7] and chemical vapour deposition (CVD). A brief review on the latter method is given in Ref. [8]; for newer information of CVD-growth of aluminium oxide films see e.g. the introductory parts of Refs. [9,10].

The CVD-growth of thin aluminium oxide films on stainless steel substrates (AISI 304) was also studied by us recently [9]: films were deposited from an organometallic precursor, aluminium acetylacetonate ($Al(acac)_3$), which reacted with oxygen in an oxygen enriched atmosphere. A hot wall reactor (HWR) was used for film deposition at atmospheric pressure. Measurable decomposition starts at 580 K and the reaction is kinetically controlled at these temperatures. Above 770 K gas phase reactions and a depletion of the precursor are observed due to the relatively long dwell time in the hot zone. As a consequence, only deposition temperatures between 580 K and 770 K are useful in the HWR, and as a result of this low temperature the grown films are amorphous. Nevertheless, these amorphous films seem to be well adhering at first sight. Further details on the HWR-experiments are found in [9]. In order to deposit crystalline α-alumina films, high deposition temperatures above 1273 K are necessary, this can be achieved in a cold wall reactor (CWR) [10] where higher deposition temperatures are reached without precursor depletion. Unfortunately, the films grown at that high temperatures on steel substrates are spalling.

While most studies on aluminium oxide films, including our own (Refs. [9,10]), report detailed information on film deposition and film composition, often less attention has been paid on film adhesion. In part this is reasoned by the lack of reliable methods for the quantification of adhesion and also of wear resistance. Often simply the Scotch tape test is made, which only gives binary results and does not allow the comparison of different films. Only few methods for the more or less quantitative evaluation of film adhesion are reported in the literature, e.g. the scratch test, the bending test, the impact test, the Rockwell test, the Laser-acoustic

* Corresponding author. Fax: +49 203 379 1594.
E-mail address: christian.pflitsch@uni-duisburg-essen.de (C. Pflitsch).

0257-8972/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2007.04.092

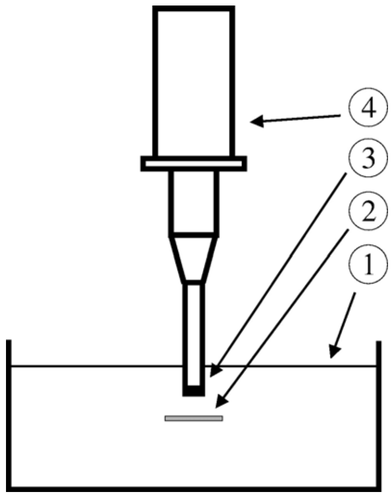

Fig. 1. Schematic diagram of the vibratory cavitation test set-up: (1) water bath filled with de-ionized water, (2) specimen, (3) sonotrode, (4) ultrasound generator 20 kHz and ±25 μm.

technique, or the cavitation erosion test [11]. Nevertheless, a "general" evaluation is not possible and some methods are not feasible for all substrates and films. In case of hard coatings on steel, a comparative study of the above mentioned methods was reported recently [11]: Different methods were used there to evaluate the known adhesion behaviour of TiN coatings on steel; it turned out that some of the above mentioned methods failed, e.g. the impact test or the Rockwell test, other ones evaluated the adhesion behaviour properly, e.g. the cavitation erosion test. Cavitation erosion was also successfully used to study the adhesion behaviour on other systems, e.g. diamond coatings on hardmetal tools [12] or metal coatings on polymer substrates [13]. Thus it seems to be well suited for 'hard systems' and 'soft systems'. These findings make cavitation tests also promising for the aluminium oxide/steel system.

Cavitation erosion experiments are utilized in the present study to analyze the adherence and the wear resistance of some of the recently grown films. The experiments were performed according to the ASTM G32-92 standard [14]. Thereby, the grown amorphous aluminium oxide films (HWR) are of special interest, because they are easily prepared and seem to adhere well at first glance; both of which make them very promising for technical application. Thus, steel substrates (AISI 304) covered with amorphous aluminium oxide films were analysed and also uncovered steel samples were measured. The resistance of the uncovered and covered samples to cavitation erosion was studied.

2. Experimental details

2.1. Film preparation

Technical details of the used HWR set-up and more detailed information on the depositions are reported in Ref. [9]. Basically, the set-up consists of a single zone heated furnace which was heated to 773 K during the present experiments. The pressure within the furnace was 1000 hPa (atmospheric pressure). Aluminium acetylacetonate was sublimated in a fluidized bed evaporator at constant temperature, 413 K, and the vapour was transported to the furnace with a carrier gas flow of 0.6 standard liters per minute (slm) synthetic air (20.5% oxygen in nitrogen). The feed pipes and the nozzle were heated to 423 K in order to prevent condensation. Additionally, 1.4 slm synthetic air was fed in, in order to increase the flow velocity. The deposition was performed on small stainless steel plates (AISI 304, DIN 1.4301) sized 2 cm × 3 cm. Before deposition, the substrates were cleaned for 10 min in an ultrasonic bath filled with de-ionized water.

2.2. Cavitation erosion experiments

Ultrasonic equipment according to ASTM G32-92 [14] was used for cavitation erosion tests of the MOCVD-grown aluminium oxide films. The set-up is sketched in Fig. 1. Basically, it consists of an ultrasound generator, a sonotrode, and a bath filled with de-ionized water. The temperature of the water was around 20 °C for all experiments. The lower end of the sonotrode consists of a titanium tip with 10 mm diameter. It was dipped 10 mm deep into de-ionized water and the sample was positioned 0.8 mm below the tip. The set-up was working at a frequency of 20 kHz. A peak-to-peak displacement amplitude of 50 μm was used, as it is proposed in the ASTM standard. During cavitation erosion test, the high frequency vibrations of the sonotrode produce a cavitation bubble field in front of the substrate surface, which is originated by the pressure fluctuations at the tip of the sonotrode. As a result, microjets are induced by the imploding bubbles. They hit the surface, and, after a certain time, damage it. In the present study, the samples were exposed stepwise to the cavitation erosion for a certain time. After each run they were cleaned carefully in an ultrasonic bath, then they were completely dried, and finally they were weighed with a high precision balance. The mass loss of the samples as function of erosion time was used to characterize the degree of erosion.

Table 1
List of selected cavitation erosion tests on films reported in the literature

Specimen		Cavitation erosion test		
Material	Film thickness	Incubation time (t_1)	Maximum rate of erosion	Film loss/time
Stainless steel[a] (AISI 304)	no film	~50 min	0.8504 μm/h	–
Amorphous aluminium oxide on steel[a]	0.75 μm	~70 min	0.2553 μm/h	75%/ 180 min
Diamond film on hardmetal tools[b]	<1 μm	40 s	–	40%/ 140 s
	3 μm	–	–	<1%/ 14 h
Ag film on PET[c]	–	–	–	100%/ 8 s
Al film on PET[c]	–	–	–	100%/ 166 s
Sn film on PET[c]	–	–	–	100%/ 200 s

[a]This study.
[b]Taken from Ref. [12].
[c]Taken from Ref. [13].