Surface & Coatings Technology 340 (2018) 121–125

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Ion beam sputter coating in combination with sol-gel dip coating of Al alloy tube inner walls for corrosion and biological protection

Sevda Ayata[a,b], Wolfgang Ensinger[b,*]

[a] Chemistry Department, Faculty of Science, Dokuz Eylül University, Izmir, Turkey
[b] Department of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany

A R T I C L E I N F O

Keywords:
Ion beam sputter coating
Tube coating
Diamond-like carbon
Corrosion

A B S T R A C T

Aluminium alloy AlCuMg is an alloy with high mechanical strength and fracture toughness, but it suffers from poor corrosion resistance and friction behaviour. With a combined process of sol-gel deposition of zirconium oxide and a top coating of diamond-like carbon formed by ion beam sputtering with a movable conical sputter target inside the tube, the inner walls of AlMgCu tubes were homogeneously coated with a duplex coating with high resistance against corrosion in chloride solution. When Ag was added to the carbon sputter target, a DLC coating that contained Ag was obtained. Microbial tests showed that the coating is effective against pathogenic *E. coli* bacteria.

1. Introduction

Aluminium alloy AlCuMg is a material which has been designed for an improved mechanical strength in comparison to pure aluminium. Its shear strength is relatively high while still maintaining a good plasticity [1]. A disadvantage of this material is its poor aqueous corrosion behaviour, and also the tribological performance is not favourable. Both corrosion and tribology can be improved when the material is protected with an appropriate coating. If a coating is required that does not too much effect the workpiece dimensions on one hand, and does not lead to difficulties with heat treated alloy by using too high a process temperature, there are not so many techniques for reliable coating available. Another restriction is based on the workpiece dimensions. It is particularly difficult to coat three-dimensional workpieces and it is even more difficult to do so with the interior wall of such a workpiece. In the present paper, a duplex technique is described which combines two different methods for homogeneously coating the inner walls of small tubes at moderate temperature, yielding coatings with very good protection against aqueous corrosion.

The first coating was performed with the sol-gel-method [2] in combination with dip coating and heat treatment. Sol-gel based oxide coatings are well suitable for corrosion protection [3].

With this technique, a zirconium oxide coating was deposited. It is known from the literature, that such coating offers corrosion protection of steels [4–6]. The second technique is a sophisticated ion beam sputter method where a thin film of diamond-like carbon (DLC) was deposited on top of the ZrO_2 coating. The function of this film is to further reduce corrosion that takes place due to the microporosity of the zirconia coating on one side, and to yield a better tribological behaviour by reducing the friction coefficient on the other side. The secondary coating was deposited by pushing a conical sputter target through the tube under ion bombardment along the tube axis [7]. Deposition of the carbon atoms under simultaneous irradiation with scattered ions yields an amorphous diamond-like carbon film. In a third step, additionally silver was used with the carbon sputter target resulting in Ag-containing DLC films.

2. Experimental

Tubes of AlMgCu 2124 with an inner diameter of 16 mm, a wall thickness of 1 mm and a length of 170 mm were polished with diamond past by means of a rotating cotton bud with a suspension of 3 µm diamond particles. Afterwards, the tubes were cleaned with isopropanol with ultrasonification for 30 s and eventually with deionized water.

For sol-gel coating, the sol was prepared from a solution of 70% zirconium *n*-propoxide in *n*-propanol as the precursor. 50 ml were mixed under stirring with 25 ml 99% anhydric acetic acid. Then, 25 ml acetyl acetone were added as a stabilizing agent. Eventually, a water/propanol mixture with 70 ml of propanol and 10 ml of water was added. The solution was stirred for 1 h. Shortly before using it, it was cleaned from particles by means of a 0.45 µm mesh nylon filter.

The dip coater consisted of a self-made apparatus with an electromotor and a spindle, controlled by a computer. The tubes were immersed into the solution and pulled out along their axis. The pull speed

* Corresponding author.
E-mail address: ensinger@ma.tu-darmstadt.de (W. Ensinger).

https://doi.org/10.1016/j.surfcoat.2018.02.065
Received 30 September 2017; Received in revised form 15 February 2018; Accepted 18 February 2018
Available online 20 February 2018
0257-8972/

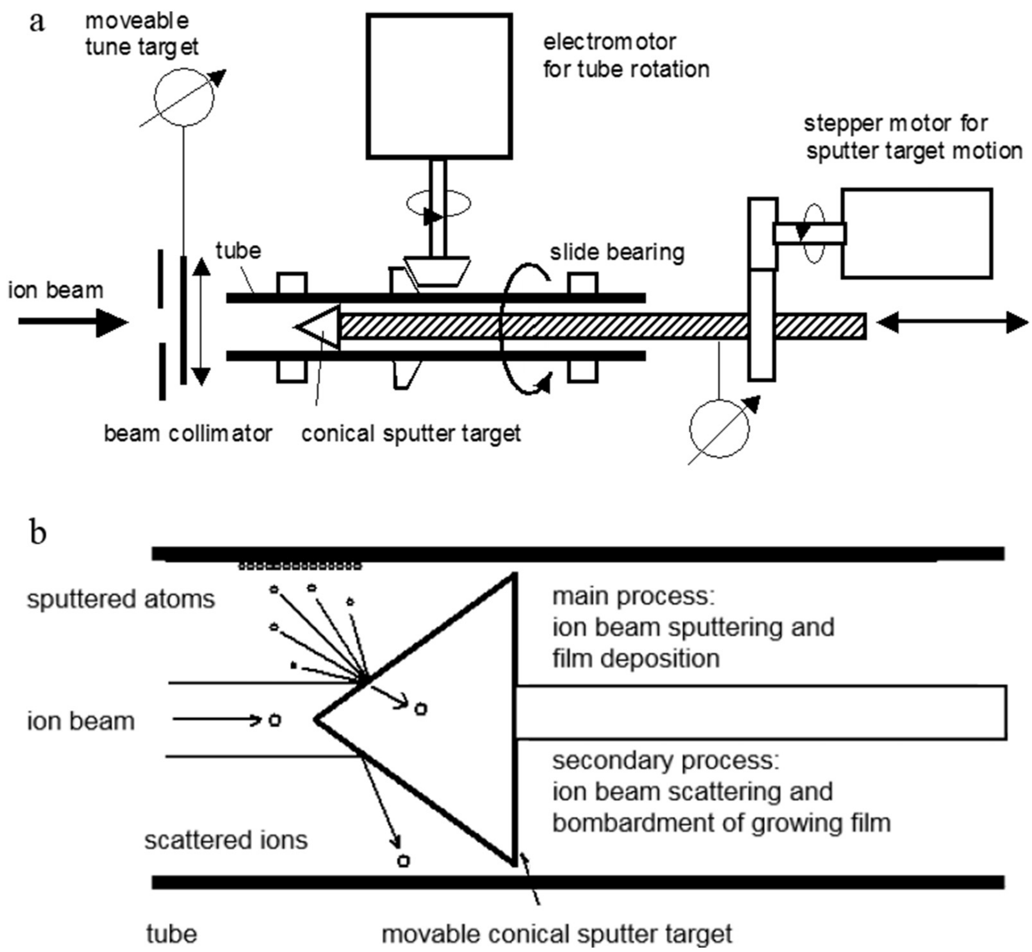

Fig. 1. a) Schematic presentation of tube sputter coater, b) The two main processes are sputtering and redeposition (film growth), and ion reflection (ion beam mixing and ion bombardment of growing film).

was controlled between 10 and 120 mm/min. The set-up was kept in a glove box to avoid dust and air turbulences. After coating, the tubes were kept on air for 1 h for drying. Here, particularly the solvent isopropanol, also water, evaporated. During this period, the tube was additionally covered to avoid deposition of dust onto the drying film. In the final step, the coating was calcinated at 200 and 300 °C, resp., in an oven on air. The samples were heated up at a rate of 3 K per min until the calcination temperature was reached, then they were kept there for 1 h.

Deposition of a film of diamond-like carbon was performed in an ion beam sputter coater. A graphite cone with an angle of 60° was moved through the tube along its axis. A collimated 40 keV Ar^+ beam was guided into the tube along its axis. The ion beam hit the graphite sputter target at an incidence angle of 60° and deposited carbon atoms onto the inner tube walls. For a uniform deposition, the tube was rotated. Fig. 1 shows the set-up and the processes taking place schematically. Details about this technique can be found elsewhere [7–9]. In order to add silver to the carbon coating, 1 mm thick Ag wire was wrapped around the sputter target.

After coating, the tubes were cut into segments. In order to facilitate this process, the tubes were pre-sectioned with grooves into eight segments, each one corresponding to 45° of the circumference, see Fig. 2. In this way, the final cutting process did not require sawing with large forces and creation of metal particles. The stripes were cut into smaller pieces.

Film adhesion was tested by means of the pin pull test. Pins with 2 mm diameter were glued onto the film with epoxy resin. In order to avoid tension, the originally flat pin heads were shaped so that the

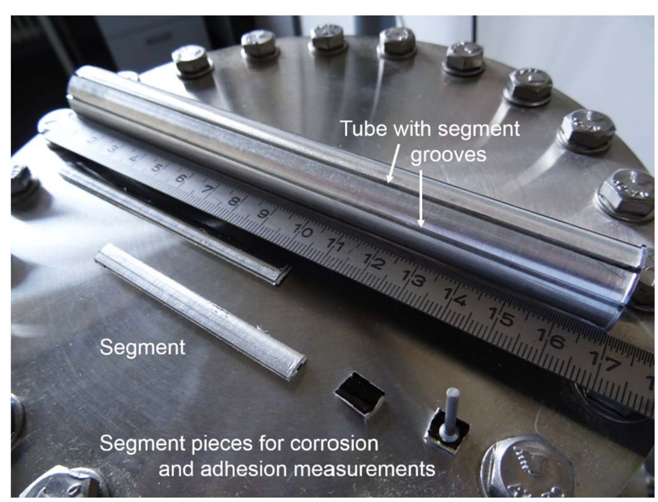

Fig. 2. Presegmented Al alloy tube, two partial segment stripes, two pieces of a segment of a DLC-coated tube, for corrosion, Auger spectroscopy and pin pull measurements.

curvature was identical to the one of the tube segments. By means of an electromotor, the pins were pulled off perpendicularly. The failure load, either of film to substrate or of the resin itself, was recorded.

Electrochemical corrosion tests were carried in a three-electrode setup with Standard Calomel Electrode (SCE) as reference electrode and a platinized Titanium foil as counter electrode. The corrosive environment consisted of a 3.5% aqueous NaCl solution kept at 25 °C by means