Vacuum 105 (2014) 52–58

Contents lists available at ScienceDirect

Vacuum

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

Influence of plasmochemical modification of Al–Cu–Mg alloys on surface structure and functional properties

Karol Kyzioł [a,*], Magdalena Mędala [b], Łukasz Kaczmarek [c]

[a] Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Mickiewicza 30, 30 059 Kraków, Poland
[b] Institute of Technology, Pedagogical University, Podchorążych 2, 30 084 Kraków, Poland
[c] Institute of Materials Science and Engineering, Lodz University of Technology, Stefanowskiego 1/15, 90 924 Łódź, Poland

ARTICLE INFO

Article history:
Received 26 January 2014
Received in revised form
16 February 2014
Accepted 18 February 2014

Keywords:
Aluminum alloys
Surface modifications
Aluminum nitride
Coating deposition
Mechanical properties

ABSTRACT

The article presents the results of the study of the composition and selected functional properties of Al–Cu–Mg alloys modified by RF CVD technique (Radio-Frequency Chemical Vapor Deposition). The type and composition of the deposited SiNH and carbon doped SiNH layers was altered in the experiments. The samples were pretreated with argon plasma etching and N^+ ion implantation.

On the basis of the experimental evidence it is concluded that the deposition of an anti-wear SiCNH coating (using SiH_4:CH_4:N_2 = 1:1:2 gas mixture) improves both the investigated mechanical properties (hardness ca. 10 GPa, Young modulus ca. 95 GPa) and tribological performance of the control (unmodified) alloy sample as well as those of the modified alloy samples whose outer layer is SiNH.

1. Introduction

One of the challenges that materials science has recently undertaken to tackle is the search for low-density materials with high fatigue and high wear resistance. There is a strong demand for such materials for applications in automotive, aircraft and arms industries [1,2] motivated by the need to increase the range and load-bearing capacity and to decrease maintenance and fuel costs. These problems can be remedied by reducing the weight of vehicles, which is to say, reducing the weight of functional components of which vehicles are built [3], which is exactly the reason why out of light alloys based on aluminum [4,5], magnesium [6,7] or titanium [8,9] aluminum alloys appear to be the most applicable due to their low density, high strength-to-weight ratio and responsiveness to mechanical treatment [10–12].

New technologies in this area are expected to increase hardness and corrosion resistance of these materials, improve their tribological performance and reduce contact fatigue as these are the constraints on the range of possible applications of aluminum alloys as functional materials [13–15]. For that purpose, coatings, including gradient coatings, are deposited on the surface of alloys that contain carbon, nitrogen, titanium and hydrogen atoms [16–18]. For example, depositing an AlN phase on the surface of aluminum alloy by, among others, nitrogen ion implantation and/or by plasma nitriding increases the range of viable applications of these alloys whenever low weight and high tribological performance are required [16,19,20]. Along currently used methods of surface treatment of alloys (e.g. shot peening) [13,21], thermo-chemical treatment techniques are also used in order to obtain anti-wear coatings (with pre-generated compressive residual stress in the alloys undergoing treatment). These techniques include, among others, methods of chemical and physical coating formation from gas phase [22] such as plasma-based ion implantation [11,16], arc ion plating [23], microarc oxidation [24].

One of the more promising methods of aluminum alloy surface modification is the technology of chemical coating deposition from gas phase, which includes PA CVD technique (Plasma Assisted Chemical Vapor Deposition). The method allows researchers to select optimal parameters and therefore enables generation of a coating with a pre-determined atomic structure. Designing technology in this field involves not only the selection of reactive gas mixture and plasma generation parameters but also determination of the time span and temperature of the processes performed. Ensuring high adhesion of generated coatings to aluminum alloys may significantly improve functional properties of these materials, e.g. hardness, Young modulus and tribological performance [25].

The foregoing paper reports on the investigation into coatings deposited on Al–Cu–Mg alloys (2024 series) by RF CVD method

* Corresponding author. Tel.: +48 12 617 24 65; fax: +48 12 617 24 93.
E-mail address: kyziol@agh.edu.pl (K. Kyzioł).

http://dx.doi.org/10.1016/j.vacuum.2014.02.006
0042-207X/

(Radio Frequency Chemical Vapor Deposition) conducted with a view of developing anti-wear low friction coatings. Selected mechanical and tribological properties were scrutinized of the systems (aluminum base – coating) obtained after plasmochemical modification. Structure and composition of coatings were analyzed based on the results of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), infrared spectroscopy (FTIR), surface topography (AFM) and phase composition (XRD) examination. Functional properties were determined based on hardness and Young modulus measurements whereas tribological performance was examined on the basis of scratch testing results.

2. Material and methods

2.1. Preparation of coatings

Modification of aluminum alloys was performed at an RF CVD reactor, excitation frequency of 13.56 MHz and maximum plasma generator power of 300 W (Elettrorava S.p.A., Italy) – Schematic 1.

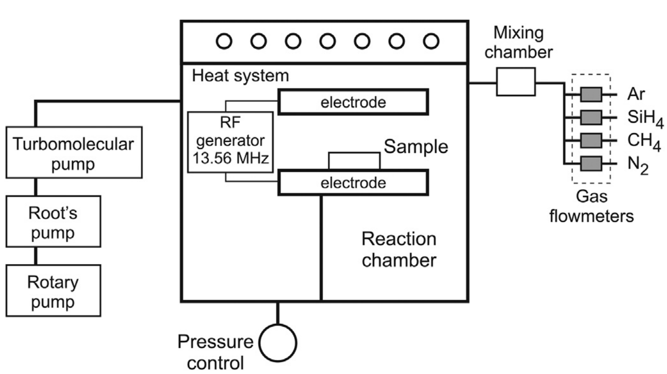
Disc-shaped, diameter of φ 35 mm, height of 7 mm, commercial 2024 aluminum alloy samples were used for modification, the mass fraction (weight percent) composition of which is presented in Table 1.

Prior to the deposition process, the aluminum alloy samples were subject to precipitation hardening by solution heat treatment (at the temperature of 773 K for 6 h) and aging (393 K, 1 h). The processes performed in the RF CVD reactor (after the shot peening) involved two-stage treatment of the alloy samples. The synthesis of the coatings on the surface of the 2024 aluminum alloy samples was performed simultaneously during the second stage of the substrate aging.

Prior to the placement in the reaction chamber, the samples were degreased with isopropyl alcohol in an ultrasonic bath for 10 min at room temperature. Next, the substrates were rinsed with distilled water and dried under a stream of nitrogen.

Four independent series of experiments were performed in the RF CVD reactor. The samples were subject to plasma etching, N^+ ion modification (plasma nitriding), and subsequently, (depending on the series of the experiment), to the deposition of SiN:H or SiCN:H layers (Table 2, Schematic 2).

In order to remove adsorbed gases and activate surfaces, in each of the four series of tests, the Al–Cu–Mg alloys were subjected to argon plasma etching for 20 min (in an Ar flow at the flow rate of 200 cm^3/min). Next, the substrates were modified by N^+ ion implantation in hydrogen/nitrogen atmosphere (1:3 mixture composition) for 120 min. Depending on the type of modification used (i.e. the series of the tests), the surface of the pre-treated substrate was once again activated, which, in the case of the M4 sample, resulted in



Schematic 1. Schematic of the RF CVD apparatus used for the deposition of the coatings.

Table 1
Chemical composition of Al–Cu–Mg alloy (weight %), EDS analysis.

Element	Cu	Mg	Mn	Si	Fe	Zn	Ti	Al
Wt. (%)	4.5	1.37	0.61	0.07	0.27	0.02	0.02	Balance

the formation of an additional layer, namely a SiN:H (SiH_4:N_2 = 1:2) layer. In the successive series of tests, SiCN:H coatings of various carbon content were obtained on the aluminum substrates pretreated by N^+ ion modification, in the methane flow at the flow rate of 8 and 16 cm^3/min in the reaction mixture for the M6 sample (SiH_4:CH_4:N = 1:1:2) and M8 (SiH_4:CH_4:N = 1:2:2) respectively.

2.2. Method analysis

As previously stated, physicochemical analysis of the obtained coatings included examination of their structure, phase composition and selected practical properties of the modified surface of Al–Cu–Mg alloys.

Microstructural tests were performed at the Scanning Electron Microscopy and Microanalysis Laboratory of the Faculty of Materials Science and Ceramics, AGH University of Science and Technology, with a Nova NanoSem 200 (FEI, USA) scanning electron microscope with EDAX Genesis energy dispersive X-ray spectrometry attachment (EDS). Atomic structure of the coatings was analyzed with an FTS-60 V Fourier transform infrared spectrometer (FTIR) by the American company Bio-Rad.

Surface topography analysis was carried out with a Bruker Multimode 8 instrument for atomic force microscopy (AFM) with PeakForce Tapping technique.

Phase composition was determined on the basis of X-ray diffraction analysis (XRD) performed with an HZG-4 apparatus with CuKα radiation.

A G200 (MTS System) nano indenter with the Continuous Stiffness Measurement (CMS) technique was used to examine hardness and modulus distribution. In the tests performed, the penetration depth was 1000 nm, surface approach velocity 10 nm/s, frequency target 45 Hz, Poisson's ratio 0.25, strain rate target 0.005 l/s and maximum force of 70 mN. A conical diamond stylus with the cone angle of 60° and tip radius $R = 1$ μm was used in the tests.

Adhesion of the coating to the substrate was determined on the basis of scratch testing by calculating the critical delamination force Fc. The following parameters were set for the tests: scratch velocity of 1 μm/s, max. scratch load 15 mN, scratch length 50–70 μm, profiling velocity 10 μm/s, load applied during profiling 100 μN, loading rate of 0.2 mN/μm.

Five measurements were taken during each test, mean values of which were used for analysis. Delamination points were determined by investigation of the coefficient of friction μ as a function of scratch length and force applied as well as by microscopic analysis of load penetration curves.

3. Results and discussion

3.1. Structural, chemical and topography properties

The analysis of the microstructure and chemical composition of the coatings shows that in each of the obtained series (see Schematic 2 above) their structure is rather amorphous without visible defects such as chipping or flaking (Fig. 1), which may translate into high adhesion of the obtained coatings.

The visibly lighter micro spots (Fig. 1(a)) are areas with high iron and copper content. The remaining images (Fig. 1(b)–(e)) show granularity of the obtained structures.