Vacuum 122 (2015) 127–134

Contents lists available at ScienceDirect

Vacuum

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

Active screen plasma nitriding of Al using an iron cage: Characterization and evaluation

Arash Yazdani [a, b, *], Mansour Soltanieh [c], Hossein Aghajani [d]

[a] School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Narmak, Tehran, 16846-13114, Iran
[b] Central Reference Laboratory, Iran University of Science and Technology, Tehran, 16846-13114, Iran
[c] Centre of Excellence for High Strength Alloys Technology, School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, 16844, Iran
[d] Materials Engineering Department, Faculty of Mechanical Engineering, University of Tabriz, Tabriz, Iran

ARTICLE INFO

Article history:
Received 11 August 2015
Received in revised form
13 September 2015
Accepted 14 September 2015
Available online 15 September 2015

Keywords:
Iron nitride coating
Active screen plasma nitriding
Wear
Scratch hardness

ABSTRACT

In this research iron nitride coating was deposited on Al substrate using active screen plasma nitriding technique. Samples were plasma nitrided in an iron cage, at 550 °C, gas mixture of N_2:H_2% = 3:1 for 2.5, 5 and 7.5 h. The coatings were characterized using X-ray diffraction, scanning electron microscopy and atomic force microscopy. Corrosion resistance of samples was investigated using polarization technique. Mechanical properties including nano hardness, wear performance and adhesion strength were also studied. Results showed that the coatings were mainly consist of $Fe_{2-3}N$ particles whose size increased by nitriding at longer time periods. Moreover, it was found that at longer coating times such as 7.5 h, the nitrogen atoms diffused into the Al substrate and formed a thin layer of AlN under the $Fe_{2-3}N$ coating. Formation of the AlN coating increased the corrosion resistance of the coated sample, but it was still poor compared to uncoated Al. On the contrary, mechanical features of coated Al improved by increasing the nitriding time. Finally, the mechanical characteristics of the deposited coatings were compared to those of conventionally plasma nitrided Al. Despite the higher hardness of the AlN coating, $Fe_{2-3}N$ showed superior scratch hardness and wear resistance.

1. Introduction

Aluminum and it alloys have numerous applications in automotive and aerospace industries because of their outstanding features such as high specific strength, light weight and mechanical formability [1,2]. Nevertheless, their applicability has been restricted due to their low hardness, poor wear resistance and high pitting corrosion tendency [3]. Different types of coatings such as nitrides [4,5], oxides [6], intermetallics [7,8] and composite [9] have been applied by diverse techniques such as mechanical coating [9], plasma electrolytic oxidation [10], ion implantation [11], plasma nitriding [12] and so forth to improve the surface characteristics of Al alloys. Among the nitride coatings, TiN [4,13] and AlN [5,14] have received a great deal of attention due to their excellent features.

Iron nitride is another corrosion and wear resistant coating which has submitted promising results for protecting steel substrate [15,16]. Iron nitride coating could be easily deposited onto the steel surface using conventional plasma nitriding (CPN) technique [17]. Since the material of the coatings produced via CPN depends on that of the substrate to be coated, active screen plasma nitriding (ASPN) method should be employed for deposition of iron nitride coating on Al substrate. In this process, the entire workload is surrounded by a large metal screen on which a high voltage cathodic potential is applied. The worktable and the components to be treated are insulated from cathodic screen and the anodic chamber walls. The components are in a floating potential or subjected to a relative lower bias voltage [18]. Some inherent shortcomings for conventional plasma nitriding, such as damage caused to parts by arcing, the “edging effect”, “hollow cathode effect” and difficulty in maintaining a uniform chamber temperature, particularly in full workloads of components with uneven dimensions have been eliminated in the ASPN [19].

According to the literature, there is no report on the deposition of the iron nitride on the Al alloys to improve their functional properties. Moreover, plasma nitriding compared to other

* Corresponding author. School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Narmak, Tehran, 16846-13114, Iran.
E-mail address: arash_yazdani@metaleng.iust.ac.ir (A. Yazdani).

http://dx.doi.org/10.1016/j.vacuum.2015.09.018
0042-207X/

techniques used for producing iron nitride coating needs less sophisticated and cheaper equipments which facilitate its industrial applications. Hence, in this research we aim at the deposition of iron nitride coating on Al substrate through plasma nitriding method using an iron cage. Additionally, the corrosion and mechanical properties such as hardness, wear resistance and adhesion strength will be examined. Finally, produced iron nitride coatings were compared to the AlN one which was deposited via conventional plasma nitriding.

2. Experimental procedures

In this research, commercial aluminum with the purity of ~99.6% was used as substrate material. Chemical composition of the Al alloy is shown in Table 1.

Disk type specimens with 40 mm diameter and 4 mm height were prepared. Then they were cut into two equal parts along their axis. Upper and lateral sides of disks were ground and mirror polished with SiC papers from 120 to 1200 grit and 0.5 mm alumina powder, respectively. For nitriding, the polished samples were tightly fastened together and placed on an insulative porous chamotte in an iron screen with 0.8 mm thickness where they were plasma nitrided in a pulsed DC plasma reactor. The parameters related to screen and the location of sample in the screen are listed in Table 2.

Plasma nitriding chamber was evacuated up to10 Pa by a rotary pump. Nitriding process was carried out with 60% duty cycle, 10 kHz frequency, 500 ± 100 Pa pressure, an atmosphere of 75%N_2, 25%H_2 and at 550 ± 5 °C. Samples code and treatment specifications are summarized in Table 3.

The phase composition of the coatings was studied by X-ray diffraction (XRD) analysis using a PANalytical, X'Pert Pro MPD with a Cu $K\alpha_1$:$K\alpha_2$ radiation ($\lambda = 1.5418$ Å). The surface morphology and cross sectional microstructure of the coatings were studied using a VEGA II TESCAN scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS).

Surface topography and hardness were studied using AFM and depth-sensing indentation (Triboscope system, Histron Inc., USA) techniques, respectively. For each sample, five measurements were performed at different points on the surface and the average roughness value (R_a) has been reported. A Berkovich diamond indenter was used for performing indentation experiments. Prior to experiments, the tip area function was calibrated by using Oliver and Pharr methods [20] and a standard fused quartz sample. A typical loading-hold-unloading sequence was used for indentation experiments. After engaging of tip and sample surface, the load was increased at a constant rate until the 3 mN load (maximum indentation depth of 160 nm) was achieved. In order to reduce the creep effect, the max load was kept constant for 10 s. In the unloading segment, the tip was withdrawn from the sample surface at the same rate. For each sample, five indents were performed at different points on the surface. The Oliver and Pharr method was applied for analyzing the experiment data.

Dry sliding pin-on-disc wear tests were performed in a laboratory atmosphere at 30–40% relative humidity and a temperature of around 25 °C. The normal load of 10 N was used in the wear tests and the rotation speed was 0.2 m s^{-1} with a radius of 11 mm for 300 m sliding. The material of the pin was a cemented tungsten carbide pin of 5 mm in diameter with spherical tip of 2.5 mm in radius. The weight of each specimen before and after the wear test was measured using an electronic balance having a precision of 0.1 mg. The scratch hardness test (an indicator of coating adhesion [21]) was done according to ASTM-G171 standard using a scratch device (Parsa Polymer Sharif) equipped with Rockwell C indenter type. Scratch load and speed were 700 g and 3.5 mm/s, respectively. A scratch of length 3 cm was produced during each test. Four scratches with at least five scratch widths faraway from each other were produced at the tested load on each sample and the results were averaged.

Specimens were immersed in a 3.5% NaCl solution for potentiodynamic polarization studies. Corrosion tests were carried out with 0.001 mV/s scan rate. A three-electrode cell configuration was employed for the measurements consisting of a saturated calomel reference electrode (SCE), a platinum auxiliary electrode and a working electrode (specimen). All potentials in this study are referred to SCE. The measurements were carried out using an Autolab computer controlled measuring system.

3. Results and discussion

3.1. Structural characterization

SEM images obtained from the surface of coatings are shown in Fig. 1.

As seen the coating layer is consisted of very small particles of iron nitride. Such a particulate structure, hexagonal particles with regular distribution and well-defined boundaries, is one of the characteristics of coatings deposited by the active screen plasma nitriding technique. Moreover, it is observed that with increasing the coating time, the particles size increases. Coatings deposited for 2.5 h (AS2) have the particle size of about 180 nm (Fig. 1a), while it reaches to 210 (Fig. 1b) and 320 nm (Fig. 1c) by extending the nitriding time to 5 (AS5) and 7.5 h (AS7), respectively. The particle coarsening phenomenon is an evidence of the particle growth. Prolonged nitriding times will enhance the growth of primary nuclease and also formation of new nuclease of iron nitride. Consequently, the particle coarsening is expected. A typical cross sectional SEM image obtained from the sample AS7 is shown in Fig. 2.

As can be seen, a highly dense iron nitride coating with no defect, such as pores or cracks in either the coating itself or the interface region with the substrate, has been deposited on the Al. Such features could be considered as strong evidence of the high adhesion and cohesion strength of the produced coatings. Topology features of the deposited coatings were examined using AFM method as shown in Fig. 3. It is clearly seen that at shorter coating periods (2.5 and 5 h), the iron nitride particles grow semi-spherically (Fig. 3a,b). While, at a longer nitriding time (7.5 h), the height and width of the semi-spherical particles increase. Consequently, crater-like or inverted pyramid morphology becomes dominant (Fig. 3c). Similar results have been also reported for the deposition of the TiN coating via ASPN technique [22]. Moreover, traces of the polishing step could be recognized at Fig. 3a,b. By increasing the nitriding time to 7.5 h, less polishing traces are discernible which is due to the increase of the coating thickness.

Surface roughness and thickness of the coatings were assessed using AFM and cross sectional SEM images, respectively, and the

Table 1
Chemical composition of used aluminum alloy as substrate (wt %).

Al	Fe	Ni	Pb	Ca	Mg	Mn	Na	Sb	Si	Sn	Sr
99.635	0.226	0.016	0.006	0.002	0.003	0.004	0.002	0.004	0.094	0.007	0.001