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Influence of heat treatment on microstructure and adhesion of Al_2O_3 fiber-reinforced electroless Ni–P coating on Al–Si casting alloy

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ABSTRACT

Influence of heat treatment regime on microstructure, phase composition and adhesion of Al_2O_3 fiber-reinforced Ni–P electroless coating on an Al–10Si–0.3 Mg casting alloy is investigated in this work. The pre-treated substrate was plated using a bath containing nickel hypophosphite, nickel lactate and lactic acid. Al_2O_3 fibers pretreated with demineralised water were placed into the plating bath. Resulting Ni–P–Al_2O_3 coating thickness was about 12 μm. The coated samples were heat treated at 400–550 °C/1–8 h. LM, SEM, EDS and XRD were used to investigate phase transformations. Adhesion of coating was estimated using scratch test with an initial load of 8.80 N. It is found that annealing at high temperatures (450 °C and above) leads to the formation of hard intermetallic products (namely Al_3Ni and Al_3Ni_2 phases) at the substrate–coating interface. However, as determined by the light microscopy and by the scratch test, these phases reduce the coating adhesion (compared to coatings treated by the optimal annealing regime 400 °C/1 h). The analysis of scratch tracks proves that fiber reinforcement significantly reduces the coating scaling. However, due to the formed intermetallic sub-layers, partial coating delamination may occur on the samples annealed at 450 °C and above.

1. Introduction

Nickel-based coatings are widely used to improve mechanical properties and wear resistance of components. One of the great advantages of electroless Ni–P coatings, compared with the electrolytic Ni coatings, is their suitability for plating of complex-shaped components, such as those with internal surfaces or holes. This allows the use of Ni–P coatings in automotive and aerospace industry as a suitable surface finishing method to enhance wear resistance of complex-shaped Al–Si cast components such as pistons, cylinder heads or engine blocks.

Various procedures have been developed to produce Ni–P coatings on aluminium-based alloys [1,2]. As it has been reported in many studies, structure and properties of these coatings depend considerably on content of phosphorus, on bath composition, temperature and pH. Hardness of the as-deposited Ni–P coatings generally lies between 500 and 800 HV, it decreases with increasing phosphorus concentration and, unlike galvanic Ni coatings hardness, can be further increased by subsequent heat treatment [2–4]. Generally acknowledged optimal heat treatment regime is 400 °C for 1 h, being given it yields maximal hardness. This is attributed to the crystallization of Ni and precipitation of Ni_3P phase [4,5]. When higher annealing temperatures or longer periods are used, hardness of the coating progressively decreases due to the nickel grain growth and due to the phosphide particles coarsening. On the other hand, due to the diffusion on the

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substrate–coating interface promoted by higher temperatures various solid state reaction may occur [6,7]. It was found that the coefficient of thermal expansion (CTE) of intermetallic phases formed during annealing at temperatures above 400 °C differs significantly from that of the substrate [8]. This induces thermal stress in the vicinity of the coating–substrate interface during cooling down from the annealing temperature. The presence of thermal stress often results in severe decrease of coating adhesion and may lead to the coating delamination [9]. It should be noted that during operation Ni–P coated Al–Si components may be exposed to the temperatures above 400 °C even for longer periods. From the technological point of view it is thus important to closely describe above mentioned processes to be able to minimize risk of undesirable component failure.

It is expected, that by reinforcing the Ni–P coating with Al_2O_3 fibers it is possible to significantly reduce the scaling and thus improve mechanical properties, such as wear resistance, of Ni–P coatings. For this reason, the purpose of this work is to describe the influence of heat treatment conditions on microstructure, phase composition and adhesion of Al_2O_3 fiber-reinforced Ni–P coating.

2. Experiment

Conventional casting Al–Si10–Mg0.3 alloy (all concentrations in wt.%, unless stated otherwise) was used as a substrate for electroless deposition. The alloy provided by an industrial supplier was remelted in an electric resistance furnace and cast into a cast-iron mould to prepare cylindrical ingots of approximately 20 mm in diameter and 200 mm in length. Disc-shaped samples of approximately 10 mm in thickness were cut out directly from the ingots. Samples were ground using P60–P1200 SiC paper to obtain surface of defined roughness. Prior to plating, samples were pretreated by ultrasonic degreasing in acetone (15 min) and by deoxidizing in an etching solution (5 ml HNO_3, 2 ml HF, 93 ml H_2O). After each step, samples were rinsed in demineralised water and after the final rinsing, samples were immediately placed into the plating bath. The electroless deposition was carried out, according to the specification given in Table 1. Commercial Saffil fibers (Al_2O_3 with 4 wt.% SiO_2) were used as reinforcement (Fig. 1). Appropriate amount of fibers was mixed with approximately 10 ml of demineralised water and fibers were stirred using magnetic stirrer (400 rpm) for at least 12 h before being placed into the plating bath.

Table 1 – Conditions used for electroless deposition of Ni–P coatings.

Chemical composition	Nickel lactate $Ni(C_3H_5O_3)_2$ — 34 g/l Nickel hypophosphite $Ni(H_2PO_2)_2$ — 20 g/l Lactic acid $C_3H_6O_3$ — 10 ml/l
Temperature	90 ± 2 °C
pH	4.5–5.0 (maintained by triple addition of 5.0 ml of 1 M NaOH solution during the process)
Bath volume	250 ml
Deposition time	120 min
Number of samples	2 per bath
Stirring	400 rpm (magnetic stirrer)

The prepared samples were heat treated at 400–550 °C/1–8 h in an electric resistance furnace under argon protective atmosphere (flow rate of 0.5 l/min). Cooling to the laboratory temperature was performed in air. Structure and phase composition of both as-deposited and heat-treated samples were studied using light microscopy (LM), scanning electron microscopy (SEM) (Hitachi S 4700 operating at 30 kV), energy dispersive spectrometry (EDS) (Noran) and by X-ray diffraction analysis (XRD) (Philips X'Pert Pro, 30 mA, 40 kV, Cu Ka radiation).

Coating adherence was estimated by observation of the surface subjected to the scratch test with an initial load of 8.80 N. The load was gradually increased five times by 8.80 N. Tracks after the scratch test were observed using light microscopy (LM).

3. Results and discussion

3.1. *Structure and phase composition*

Fig. 2a to e show LM images of cross-sectioned Ni–P–Al_2O_3 coated samples both after the deposition and after the heat treatment. The as-deposited Ni–P–Al_2O_3 coating (Fig. 2a) having a thickness of approximately 12 μm shows good uniformity and adherence to the substrate. Concentration of phosphorus in the coating determined using XRF was 17.4 at.% which means the as-deposited nickel coating is probably amorphous. During pretreatment, a thin surface layer of α-Al phase of the Al–Si alloy was removed, which allowed emerging silicide particles to be partly incorporated in the coating. Al_2O_3 fibers are incorporated mainly parallel to the sample surface (Fig. 2b). Fig. 2b shows cross-section of sample annealed at 400 °C/1 h. The structure of the coating is apparently the same as that of the as-coated samples. However, it is known that during annealing at 400 °C/1 h coating undergoes significant changes. As it is indicated in Table 2, nickel crystallizes and Ni_3P phosphides precipitate. Fig. 2c presents the sample annealed at 450 °C/8 h. It was found that this regime allows at least one reaction product to form between the Ni–P layer and the substrate. The reaction product was determined as Al_3Ni intermetallic phase (Table 2). At 550 °C, 1 h is enough to induce reaction between the coating and substrate (Fig. 2d). The reaction products were identified as Al_3Ni (closer to the substrate) and Al_3Ni_2 (closer to the Ni–P coating). Prolonged annealing leads to further growth of both intermetallic layers, see Fig. 2e. Influence of heat treatment regime on coating and intermetallic sub-layers thickness is summarized in Fig. 3.

Development of phase composition during heat treatment is summarized in Table 2. The intermetallic layers thickness after heat treatment at elevated temperatures for longer periods was found to be greater than XRD analysis depth. Therefore, the phase composition was determined mainly by comparing previous results (XRD spectra, light micrographs, EDS analysis) obtained for Ni–P coatings [10] with EDS analysis results and light micrographs of Ni–P–Al_2O_3 coatings.

The only crystalline phases detected on the as-deposited sample were Al and Si (substrate) and the Al_2O_3 (fiber