HEAT TREATMENT OF Ni-P-Al_2O_3 ELECTROLESS COATINGS

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Abstract
The aim of this work was to describe the influence of heat treatment on structure and phase composition of Ni-P-Al_2O_3 coatings. Coatings were prepared using nickel lactate-hypophosphite bath; conventional AlSi10Mg0.3 cast alloy was used as a substrate. Composite coating was prepared using commercial Saffil fibers (Al_2O_3 with 4 wt. % SiO_2) as reinforcement. Coated samples were heat treated at 400–550°C for 1–8 hours, structure and phase composition were studied using light microscopy and XRD phase analysis. Ni-P coated samples were used as a reference. During the heat treatment at high temperatures, the nickel diffuse into the substrate and various intermetallic phases are formed on the boundary between the surface layer and the substrate. Due to the difference in the thermal expansion coefficient of these intermetallics and the substrate, the coating tends to scale-off during cooling to the room temperature. It was found that the scaling can be reduced by reinforcing the coating with Al_2O_3 fibers.

Keywords: electroless Ni-P coatings, heat treatment, composite coatings

1. INTRODUCTION
Due to their excellent castability, Al-Si alloys are suitable for large series production of complex-shaped castings, such as cylinder blocks, cylinder head, discs etc. For some applications, it is necessary to increase wear resistance of cast parts e.g. by wear-resistant coating. PVD (physical vapour deposition) or galvanic coatings have sufficient hardness and wear resistance, however coating of complex-shaped parts is very problematic. These problems can be partly solved by using electroless autocatalytic coating. Electroless Ni-P coatings are sufficiently wear and corrosion resistant [1]. Further improvement of mechanical properties can be achieved by preparation of hard particle (carbides, oxides etc.) reinforced Ni-P coatings or by heat treatment [2-5]. Generally, 400°C/1 h is considered as optimal, being given this regime yields maximal coating hardness [6]. This is attributed to the decomposition of formerly amorphous Ni-P phase, formation of crystalline Ni and precipitation of fine Ni_3P phosphide particles [7]. Annealing at higher temperatures for longer periods leads to gradual hardness decrease caused by Ni and Ni_3P grains coarsening, therefore these heat treatment regimes are not used. It should be noted that some Al-Si cast engine components may be exposed to elevated temperatures even for relatively long periods. Besides Ni grains crystallisation, phosphides precipitation and subsequent growth of these phases, solid state reactions on the substrate-coating boundary may occur during heat treatment at elevated temperatures. Hardness of formed intermetallic phases is often higher than that of optimally (400°C/1 h) heat treated Ni-P coating. During cooling from the annealing temperature, the adhesion...
between formed intermetallic layer and substrate may be severely decreased due to the coefficient of thermal expansion (CTE) difference [8]. It is expected that adhesion of fibre-reinforced Ni-P coating will be significantly better.

2. EXPERIMENT

Commercial AlSi10Mg0.3 (wt. %) alloy was used as a substrate. The material provided by an industrial supplier was remelted in an electric resistance furnace and cast into metal mould. Samples of 10 mm in thickness were cut out from cylindrical ingots having 20 mm in diameter and length of 200 mm. Samples were progressively ground using P60 – P1200 SiC papers and ultrasonically degreased for 15 minutes in acetone. Before being transported into the plating bath, samples were etched for 60 s in solution containing 5 ml HNO₃, 2 ml HF and 93 ml H₂O. Electroless plating conditions are summarized in Table 1.

Table 1. Conditions used for electroless deposition

<table>
<thead>
<tr>
<th>bath composition</th>
<th>nickel lactate</th>
<th>30 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nickel hypophosphite</td>
<td>20 g/l</td>
</tr>
<tr>
<td></td>
<td>lactic acid</td>
<td>10 ml/l</td>
</tr>
<tr>
<td>pH adjustment</td>
<td>3 x 5 ml 1 M NaOH solution</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(at the start and subseq. after 40 minutes of plating)</td>
<td></td>
</tr>
<tr>
<td>bath temperature</td>
<td>90±2°C</td>
<td></td>
</tr>
<tr>
<td>bath volume</td>
<td>250 ml</td>
<td></td>
</tr>
<tr>
<td>fibre content</td>
<td>2,5 g/l (composite coating)</td>
<td></td>
</tr>
<tr>
<td>coating time</td>
<td>120 minutes</td>
<td></td>
</tr>
</tbody>
</table>

Commercial Saffil fibres (Al₂O₃ with 4 wt. % SiO₂) were used as reinforcement. To enhance their wettability, fibres were stirred for approx. 12 h in small amount of demineralised water using magnetic stirrer (400 rpm) before being added into the bath. Coated samples were subsequently heat treated in an electric resistance furnace under argon atmosphere (flow rate of 0.5 l/min) using different annealing regimes. Cooling down to the room temperature was performed in air. Structure and phase composition was studied using light microscopy (Olympus PME3) and x-ray diffraction analysis (XRD XPERT Pro + High Score Plus).

3. RESULTS

3.1 Microstructure

Fig 1. and Fig. 2 present LM images of cross-sectioned Ni-P-Al₂O₃ coatings both after deposition and after heat treatment. The coating thickness is approx. 10 μm, coating is homogeneous and shows a relatively good adherence to the substrate. Fibres are incorporated predominantly parallel to the surface. After annealing at 400°C/1 h (Fig. 1a) there is seemingly no change from the as-deposited state. However, during this treatment regime significant changes in the internal structure of coating occur. Formerly amorphous nickel phase crystallises and very fine phosphide particles precipitate. These changes are not observable by means of light microscopy and will be indicated by XRD patterns (Fig. 4). During heat treatment at 450°C/8 h at least one intermetallic layer occurs on the substrate-coating boundary (Fig. 1b). Phase is formed mainly due to the nickel diffusion into the substrate, not due to the aluminium diffusion into the layer. This is demonstrated by the fact that there are no
fibres in the emerging intermetallic layer. At 550°C, annealing for 1 h is enough to induce intermetallics formation; two sub-layers are formed on the boundary (Fig. 2a). During annealing at the same temperature for 8 h, no further changes of microstructure are observed except for layers growth (Fig. 2b). Despite the intermetallics layer thickness no scaling was observed after annealing at 550°C/8 h. Visible pores on the substrate-coating boundary are formed during sample preparation as a result of silicon particle chipping.

**Fig. 1.** Structure of Ni-P-Al₂O₃ coating (cross-section, light microscope):
a) 400°C/1 h, b) 450°C/8 h

**Fig. 2.** Structure of Ni-P-Al₂O₃ coating (cross-section, light microscope):
a) 550°C/1 h, b) 550°C/8 h

Fig. 3 shows LM micrograph of cross-sectioned Ni-P coating after annealing at 550°C. It is evident that coating and intermetallic layers delamination is more significant than in case of Ni-P-Al₂O₃ coatings. After 1 h, local delamination of surface layer occurred (Fig. 3a), after 8 h, massive cracks are formed on the substrate-coating boundary (Fig. 3b).
3.2 Phase composition

Development of phase composition during heat treatment (Fig 4) was observed using Ni-P coated samples. After deposition, only broad peak of amorphous Ni-P phase and sharp diffraction lines of Al-Si substrate are visible. During annealing at 400°C Ni₃P phase precipitates as a result of nickel and phosphorus diffusion. However, diffusion rate of nickel is not sufficient to induce intermetallic sub-layers formation. At 450°C Al₃Ni intermetallic phase is formed by solid state reaction on the substrate-coating boundary. Preferential formation of aluminium-rich phase proves that the phase formation is controlled mainly by the nickel inward diffusion and not by the diffusion of aluminium towards the surface. With increasing temperature and time of heat treatment, phase with higher nickel content Al₃Ni₂ is formed and phosphides composition is gradually changed from Ni₃P to Ni₁₂P₅ and subsequently to Ni₂P.

Fig. 4. XRD analysis – influence of heat treatment regime on coating phase composition (measured on Ni-P coating)
4. CONCLUSIONS

Due to the heat treatment at high temperatures, various phase transformations and chemical reactions take place on the substrate-coating boundary of the Ni-P coated sample. This sequence can be written as follows:

1. Ni-P (amorphous) $\rightarrow$ Ni (crystalline) + Ni$_3$P (crystalline)
2. Ni + Al $\rightarrow$ Al$_3$Ni
3. Al$_3$Ni + Ni $\rightarrow$ Al$_3$Ni$_2$
4. Ni$_3$P $\rightarrow$ Ni$_{12}$P$_5$ + Ni
5. Ni$_{12}$P$_5$ $\rightarrow$ Ni$_2$P + Ni

Being given the fact that Al$_2$O$_3$ fibres are not contained in the formed intermetallic sub-layers, it can be said that intermetallics on the substrate-coating boundary are formed mainly due to the inward diffusion of nickel. This is further proved by the preferential formation of aluminium-rich phase (Al$_3$Ni) and delayed formation of phase with higher nickel content (Al$_3$Ni$_2$).

Intermetallic layers thickness increase with increasing temperature and time. In case of Ni-P coatings, this leads to the severe decrease of substrate-coating adhesion and finally to the coating delamination. Using fibre-reinforced coating, the delamination can be significantly reduced.

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LITERATURE