INFLUENCE OF THIN COATINGS DEPOSITED BY PECVD ON WEAR AND CORROSION RESISTANCE OF MOULDS FOR SEMI-SOLID PROCESSING

O. Kyrylov, R. Cremer and D. Neuschütz

Lehrstuhl für Theoretische Hüttentechnik
Rheinisch-Westfälische Technische Hochschule Aachen
D-52056 Aachen
Germany

Abstract
Mould surfaces strongly suffer from abrasive and corrosive wear during the semi-solid processing of aluminium and steel. Thus the protection of the die surface by coatings is an important issue. For the coating of complex shaped tools, Plasma Enhanced Chemical Vapor Deposition (PECVD) has gained interest in the last years. Due to the significantly higher pressures as compared to PVD and low deposition temperatures as compared to thermal CVD, this technique allows the convenient coating of complex shaped three-dimensional parts at temperatures below the annealing temperature of many tool steels.

In this paper, hot work toolsteel H11 and the molybdenum based superalloy TZM were coated with (Ti,Al)N or Al₂O₃, respectively. The performance of the tools has been evaluated by thermal shock experiments and liquid corrosion as well as contact corrosion experiments. For the semi-solid processing of aluminium, (Ti,Al)N coatings with a high Al content performed best in all tests. Al₂O₃ coatings offered superior protection in case of steel casting. Both coatings were able to reduce the adhesion of the liquid metal significantly and exhibited a good behavior in thermal shock experiments. Optimized coatings showed good corrosion and oxidation resistance, thus proving the suitability of these coatings for the protection of dies during the semi-solid processing of aluminium alloys and steel.

Keywords: Corrosion resistant, PECVD coatings, semi-solid metal forming
INTRODUCTION

Semi-solid forming as a new near-net-shape process promises significant economical gain by reduction of material, energy and time input for parts production. Furthermore, parts with high surface quality and fine structure (small grain size) can be obtained. Analogous to traditional casting, this technology can be divided into low temperature aluminum and magnesium processing on one hand and high temperature copper and steel processing on the other hand.

One of the major challenges for the successful introduction of this technique is the successful protection of the mould surfaces thus enabling a longer lifetime of the tool [1, 2]. During semi-solid processing the surface of tools suffers from severe and complex wear. The major mechanisms leading to die failure are erosion or washout, as a result of the influence of the solid fraction of the alloys, chemical interactions between melted part of alloys and die surface, thermal shock, as a result of the high temperature gradient between the moderately cold die and the hot metal, oxidation, and cycled mechanical load [3].

Due to the higher temperature during semi-solid processing of steel alloys all these mechanisms are accelerated and result in increased surface damage of the tools. Suitable surface treatment can reduce corrosion and erosion of the die and thus enable an increased lifetime of the tools [4, 5].

Nowadays various surface treatments and coatings have been investigated and are used for tool protection. Films on Ti or Cr basis such as TiN, (Ti,Al)N, Ti(B,N), CrN and TiB$_2$ exhibit high hardness and good corrosion properties at moderate temperatures [6, 7]. Oxide ceramics such as ZrO$_2$ or Al$_2$O$_3$ have a significantly increased chemical stability at high temperatures.

Different methods are available for the deposition of protective coatings. Besides PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition), the PECVD (Plasma Enhanced Chemical Vapor Deposition) is a relatively new technology which combines the performance of PVD and CVD methods [8, 9, 10]. Due to the significantly higher pressures as compared to PVD and low deposition temperatures as compared to thermal CVD, this technique allows the convenient coating of complex shaped parts at temperatures below the annealing temperature of many tool steels.

In this work, (Ti,Al)N with various Al contents and Al$_2$O$_3$ coatings were deposited by PECVD and have been tested with respect to their wear behav-
ior, corrosion resistance in contact with aluminum alloys and steel in liquid and semi-solid states and with respect to their ability to withstand cycling thermal shock tests.

**EXPERIMENTAL**

The specimens of the hot work tool steel 1.2343 (AISI H11) and the molybdenum based alloy TZM (Mo98%;Ti0.5%;Zr1%) were coated in a PECVD-systems, described elsewhere [11]. The depositions were carried out from AlCl$_3$-TiCl$_4$-O$_2$-H$_2$-N$_2$-Ar gaseous mixtures in unipolar and bipolar pulsed glow discharges at typical processing temperatures between 500°C and 550°C which is below the annealing temperature of the hot work tool steel.

The metastable (Ti,Al)N layers were deposited with different Al/Ti ratios. Depending on the Al content of the film, they either had a single phase cubic structure or consisted of a mixture of cubic and hexagonal wurtzite type phase. Crystalline $\gamma$-Al$_2$O$_3$ layers were deposited under similar conditions. The properties of the deposited layers are given in Table 1. The corrosion resistance of the coatings for semi-solid processing was determined by liquid corrosion experiments and contact corrosion tests. The ability of the films to withstand a thermal shock in combination with an applied pressure was investigated by means of a modified thermal shock set up as reported in [9]. For liquid corrosion experiments specimens were dipped in the liquid aluminum alloy A356 (7%Si;0.5%Mg) and in the steel M2 (0.8%C;6%W;5%Mo;2%V;4%Cr) for 24 hours at 740°C and 1280°C, respectively. Contact corrosion experiments were carried out only for aluminum alloys. In this case, a billet of the aluminum alloy A6082 (1%Si,1%Mg) was pressed against the specimens with an initial pressure of 100 MPa and annealed for 6 hours at 600°C under ambient air. During thermal shock tests the specimens were pressed against the heated plate at 600°C and 1000°C with a pressure of 78 MPa for 5 s. After separation, the samples were cooled with ambient air or N$_2$ for 10 s. This cycle was repeated until failure was observed.

After corrosion and thermal shock experiments changes in structure and morphology as well as delaminations were investigated by means of SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray Analysis).
Table 1. Properties of coatings deposited by PECVD

<table>
<thead>
<tr>
<th></th>
<th>TiN</th>
<th>TiAlN</th>
<th>Al₂O₃</th>
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<tbody>
<tr>
<td>microhardness</td>
<td>2200 HV₀.₀₅</td>
<td>according to the structure: 2000–4000 HV₀.₀₂</td>
<td>1100 HV₀.₀₂ for amorph</td>
</tr>
<tr>
<td></td>
<td>1900 HV₀.₀₂ for γ-phase</td>
<td></td>
<td>mixture</td>
</tr>
<tr>
<td>critical load</td>
<td>up to 50 N</td>
<td>up to 40–45 N</td>
<td>up to 30 N</td>
</tr>
<tr>
<td>thickness</td>
<td>4–8 µm</td>
<td>3–5 µm</td>
<td>3–7 µm</td>
</tr>
<tr>
<td>deposition temp</td>
<td>500°C</td>
<td>500°C</td>
<td>500–550°C</td>
</tr>
<tr>
<td>gasmixture</td>
<td>TiCl₄-Ar-N₂-H₂</td>
<td>TiCl₄-Ar-N₂-H₂-AlCl₃</td>
<td>Ar-O₂-H₂-AlCl₃</td>
</tr>
<tr>
<td>deposition pressure</td>
<td>1.5 mbar</td>
<td>1.5 mbar</td>
<td>1.5-1.75 mbar</td>
</tr>
<tr>
<td>Al/Ti input ratio</td>
<td>0.5–3</td>
<td></td>
<td></td>
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</tbody>
</table>

RESULT AND DISCUSSION

After deposition all films showed a fine and dense structure with smooth surfaces. According to their chemical composition and deposition parameters the morphology varies from columnar to fine globular structure (Fig. 1).

All of the investigated coatings show reliable corrosion resistance in liquid Al alloys. Fig. 2 shows that the melted Al-alloy was not able to attack the steel through the protective layer. For comparison, micrograph c) shows the corrosion of the steel substrate after a delamination at the edge of a sample has occurred. This failure might be explained by the difference in the thermal expansion coefficient of the layers and substrate material, thus leading to spallation at the edges of the sample [9].

(Ti,Al)N and Al₂O₃ coatings exhibited the same behavior in the contact corrosion experiments, which were carried out only for aluminum alloys. After the experiments the billet could be completely removed from the specimens and no damage of the layers was observed. Although the experiments were carried out under ambient air, no oxidation of the coatings in the area which was not in contact with Al-billet was observed.
Both coatings, (Ti,Al)N and Al₂O₃, were tested for the semi-solid processing of steel. Fig. 3 shows the micrographs after liquid corrosion tests. The (Ti,Al)N coatings form a broad diffusion zone with the steel. In contrast to this, the Al₂O₃ films did not exhibit any solubility in the steel nor any chemical erosion.

The mechanisms leading to crack formation within the films were investigated by thermal shock experiments. (Ti,Al)N coatings consisting of two phases exhibited good results after the thermal shock experiments at 600°C. After 5600 cycles the surface was smooth and no delaminations were found (Fig. 4). Fig. 5 shows the surfaces of (Ti,Al)N and Al₂O₃ films after thermal shock experiments at 1000°C after 200 cycles. (Ti,Al)N coatings consisting of two phases showed good properties and only one delamination was found on the tool surface. The micrograph distinctly shows that the first cause leading to the destruction of the surface is the sticking of the liquid steel on the surface. The chemical composition of the sample given in Fig. 5 b) was determined by EDX. Point 1 corresponds to the TZM substrate, point 2 corresponds to the detached layer with parts of steel and point 3 to the remaining (Ti,Al)N layer. The alumina layers exhibited no sign of diffusion or chemical erosion after the tests, the surface was free of delaminations but a compaction of the film was observed (Fig. 6).
CONCLUSIONS

Appropriate surface treatment is able to protect the dies for semi-solid processing from wear and corrosion. Various Ti- and Al-based coatings have been deposited by PECVD on steel and the molybdenum alloy TZM and subsequently analyzed with respect to corrosion and wear resistance. (Ti,Al)N, with high Al content as well as $\gamma$-$\text{Al}_2\text{O}_3$ exhibited a reliable protection of the dies in case of aluminum semi-solid forming. At the high temperatures of steel semi-solid processing, the major influence on the surface damage was chemical erosion and diffusion from liquid parts of the alloy. In this case the best results were obtained with alumina coatings, not exhibiting any solubility with the melted steel. The experiments demonstrate that the
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Figure 3. Micrographs of samples after liquid corrosion tests in steel M2 at 1280°C.

(a) (Ti,Al)N with a broad diffusion zone. (b) $\text{Al}_2\text{O}_3$ protects the TZM substrate from the molten steel.

Figure 4. (Ti,Al)N surfaces

(a) After deposition. (b) After thermal shock tests, 5600 cycles at 600°C.

PECVD technique has high potential to produce protective coatings for die casting and semi-solid processing of aluminum alloys and steel.

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REFERENCES
(a) $\text{Al}_2\text{O}_3$ without cracking of the surface
(b) (Ti,Al)N with delaminations.

Figure 5. Micrographs of the surfaces after thermal shock experiments at 1000°C, 200 cycles

Figure 6. Cross-sectional micrograph of $\gamma$-alumina films deposited on TZM substrate after thermal shock experiments at 1000°C, 200 cycles.


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