Optimization of AlTi PLD coating by increasing Ti content, N2 and Annealing which used for SKD61 pins in aluminum die casting

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Cover Page Footnote
The authors are grateful to the Material and Metallurgical Engineering Department (postgraduate program) of University of Indonesia, BRIN photonics research center and PT XYZ Laboratory for providing research opportunity and assistance during the experiment and characterization processes.
Optimization of AlTi PLD Coating by Increasing Ti content, N2, and Annealing which used for SKD61 pins in Aluminium Die Casting

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Abstract. The Alumunium Titanium Nitrogen (AlTiN) coating is known as one of the best coating materials for protective coating, while Pulsed Laser Deposition (PLD) is a laser coating process used for electric layer and superconductor applications, producing thin films up to 20 µm in thickness. The combination of these two matters has already been researched and is still in progress. One major challenge in the aluminium casting industry is to minimize the damage caused to tool steel pins made from SKD61, when aluminium material sticks to the pin, and halting production. Therefore, research on effective coatings for tool steels and testing various basic mechanical properties, such as hardness, coating content, roughness, adhesive level, surface image, and microstructure, need to be conducted to address this issue. The research started by creating dummy blocks as samples from SKD61, followed by PVD-PLD with three coating materials, namely Al/Ti (50:50), Al/Ti (40:60), and Al/Ti (30:70). The PLD utilized an Nd:YAG laser with a 1064 nm wavelength, and a vacuum condition with 99.5% High Purity N2 gas, concluding with the annealing process. Several sample tests were conducted to assess the effectiveness of the coatings, including FESEM, SEM, EDS, surface roughness, VDI, and micro-hardness, which were analyzed at the BRIN Physics Research Center and PT XYZ Laboratory. The results indicated that the thin layer deposition improved mechanical properties. The coatings showed an amorphous Al-Ti-N morphology, with surface hardness ranging from 333-384 mHv (without annealing) and 410-455 mHv (with annealing). The roughness increased from 0.198-0.247 Rz (without annealing) to 0.318-0.916 Rz (with annealing). The coatings were ranked in ascending order of hardness as AlTi 40:60, AlTi 50:50, and AlTi 30:70. These findings provide valuable insights for further research, including exploring substrate heat treatment, fixture rotation, and casting effects.

Keywords: Coating material; Tool damages; PLD process; Nitrogen gas

1. Introduction

The coating is a process in which a substrate material is covered with a layer of a different material that does not alter the chemical composition of the substrate (Tracon 2007; Oerlikon 2012). The coating process typically involves three key components: the coating material, the coated substrate, and the application method.

The production of aluminum castings can be hindered by tool damage, especially at the die component due to die soldering. Die soldering occurs due to the sticking of aluminum material to the surface of the die, causing damage to the die and even the casting product. Repairs until ready for production again take more than 5 hours, so productivity decreases. Currently, there are several alternative options to minimize the occurrence of die soldering. Researchers have been done studying to use of alloying material (Kohlhepp et al. 2021; Fatmi et al. 2022;  

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At this point, our research emphasizes the selection of the best coating material with a particular coating process. According to multiple coating research references Chromium (Cr), Titanium (Ti), and Aluminum (Al) are common materials used in tool steels due to their ability to increase the critical temperature required for the bonding or soldering process to occur (Han & Viswanathan 2003). The use of hard alumina (Al₂O₃) coatings is a common strategy for improving resistance to abrasion and corrosion, while also enhancing electrochemical properties (Abdel-Gawad, Osman & Fekry 2019; Barakat et al. 2019; Barjesteh et al. 2019; Paz Martínez-Viademonte 2020; Feng et al. 2021). Coatings of Titanium (Ti), and Chromium (Cr) in the form of nitrides, such as Titanium nitride (TiN) and Chromium nitride (CrN), are also widely used due to their excellent hardness, resistance to oxidation, corrosion, and high temperatures (Chen et al. 2020; Cui et al. 2020). Additionally, nitride coatings can improve surface roughness, resulting in better surface adhesion (Bhushan et al. 2020).

Tiₓ⁻ₓ Alₓ N is a type of material that was developed using a combination of titanium (Ti), aluminum (Al), and nitrogen (N), which results in the formation of metastable cubic phase compounds. It was first introduced in the late 80s, TiAlN coatings have demonstrated excellent machining performance, that exceeds the capabilities of TiN, TiC, and CrN coatings. These coatings offer superior oxidation resistance, hardness, and stability at high temperatures. The annealing process applied to the AlTiN coating results in even greater system stability effects (Hörling et al. 2005; Giuliani 2019).

Pulse Laser Deposition (PLD) within the Physical Vapor Deposition (PVD) method is a popular approach for producing high-quality superconductive coatings, that find use in medical, magnetic, and electrical applications. Recent advancements have seen PLD being used to create crystalline oxide ceramic coatings, nitrides, and even for the synthesis of nanopowder and tubes (Pokropivny 2007).

NdYAG (Neodymium – dopped Yttrium Aluminum Garnet) is a laser material composed of solid-state crystals that has exceptionally hard, stable, and isotropic as well as possess superior optical qualities. The power of the laser beam generated by this material is determined by several factors, including the condition of the target material, the laser wavelength, and the amount of energy applied (Priadi, Suliyanti & Kosasih 2020).

The microstructure, mechanical, and electrochemical properties of a coating layer are significantly impacted by the application of heat treatment (Vangesa et al. 2022). The thermal stability of the TiAlN coating layer can also be affected by alterations to its microstructure (Chaar et al. 2021). Additionally, the process of anilization can influence the coating layer’s resistance to oxidation (Zhou et al. 2021; Chavee 2022).

2. Material and Methods

2.1. Substrate Materials

The substrate sample was made from SKD61 material with the sample size fabricated using a milling process on a Fanuc CNC machine and refined using a KURODA surface grinding machine. The cutting process involved a METKON cutting wheel machine, resulting in four rectangles measuring 10 x 10 x 2 mm³. The polishing procedure commenced with resin mounting, followed by sandpaper polishing from grid #600 to #4000 using a SRUERS polishing machine. Finally, diamond paste was applied as shown in Figure 1.
2.2. Coating/Target Material

The target samples, in the form of tablets, were procured from Loyal Technology China and were composed of AlTi in ratios of 50/50, 40/60, and 30/70, as shown in Figure 2.

2.3. PLD Process

In the PLD process, the main equipment, comprises a laser source, chamber and electric source as depicted in Figure 3. To execute the process, specific parameters such as wavelength, energy quantity, and processing time need to be set. For instance, the PLD-NdYAG was performed at a wavelength of 1064 nm, with the Q-switch set after a time delay of 160 µs, a pulse energy of 120 mJ, and a vacuum pressure ranging between 0.96 ~1.22 Torr for a duration of 10 minutes.
2.4. Annealing Process

The annealing process is carried out using a heat treatment furnace with a heating rate of 10°C/minute, which is carried out in stages over a temperature range of 25°C to 600°C, in 2 types of vacuum, namely vacuum atmosphere and vacuum N2. At a temperature of 600°C, the process was held for 2 hours, then the samples were allowed to reach normal temperature inside the furnace.

Figure 3 PLD main equipment (a) Laser source of PLD, (b) Chamber, and (c) Electric source
2.5. Research Focus

The primary objective of this research is to examine how the mechanical properties of the AlTiN coating layer on the SKD61 material surface are affected by three key factors, the Ti content, utilization of nitrogen gas, and the annealing process.

3. Result and Discussion

The PLD-NdYAG process was performed at the BRIN research facility. Following this, a visual examination of the AlTiN samples, with compositions of 50/50, 40/60, and 30/70, was conducted to assess their opacity after undergoing PLD process. The results revealed an increasingly opaque surface as the Ti content increased, as illustrated in Figure 5.

![Figure 5. Visual examination of AlTiN PLD samples](image)

The higher opacity observed on the AlTiN coating layer with increased Ti content can be attributed to its increased deposition onto the substrate’s surface. This can cause the surface to become increasingly uneven, resulting in greater light scattering and an opaquer appearance. In essence, the greater the number of Ti particles deposited onto the surface, the higher the likelihood of light scattering, leading to increased opacity.
3.1. **FESEM Result**

The Field Emission Scanning Electron Microscope (FESEM) analysis was performed using the SEM – FESEM FEI Helios Dualbeam, with a magnification capability of 20000 x. The resulting micrograph displayed an amorphous droplet-shaped microstructure as depicted in Figure 6.

![Figure 6](image)

**Figure 6.** Micro structure of (a) AlTiN 50/50, (b) AlTiN 40/60, and (c) AlTiN 30/70

The microstructure of AlTiN 50/50 exhibits an irregular clump droplet-like sponge, that is elongated and evenly spread. The droplets of AlTiN 40/60 are clump sponges in nature and tend to cluster together. AlTiN 30/70 has a slight clump sponge microstructure and tends to agglomerate to some extent. Generally, materials with a more sponge structure, are prone to exhibit degraded mechanical properties such as reduced elasticity, crack resistance, and rigidity (Kim et al. 2019; Vasiliev et al. 2023).

3.2. **SEM-EDS Result**

The scanning electron microscope (SEM) observation using JEOL JSM 6360 LA revealed that a coating layer was present on the surface area. However, upon observation of the sample cross-section, it was found that not all samples had a coating film. Only the cross-sectional samples of AlTiN 50/50 showed the presence of coating layers containing Al and Ti, with a thickness of approximately 1 to 2 μm. This condition may have arisen due to the non-uniform thickness of the coating as seen in Figure 7. It has been reported in previous research that the shape of droplets generated through PLD can lead to an uneven distribution of coating deposits (Panjan et al. 2021).
MDEV Test Result Summary

<table>
<thead>
<tr>
<th>Test Item</th>
<th>Coating Pin Dies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AITi (180/10)</td>
</tr>
<tr>
<td></td>
<td>AITi (180/20)</td>
</tr>
<tr>
<td></td>
<td>AITiN (50/50)</td>
</tr>
<tr>
<td></td>
<td>AlCr (180/20)</td>
</tr>
<tr>
<td></td>
<td>AITiN (40/60)</td>
</tr>
<tr>
<td></td>
<td>AITiN (30/70)</td>
</tr>
<tr>
<td>Microstructure</td>
<td>Martensite</td>
</tr>
<tr>
<td>SEM Thickness Coating (µm)</td>
<td>Undetected</td>
</tr>
<tr>
<td>SEM – EDS Cross section</td>
<td>Undetected</td>
</tr>
<tr>
<td>layer</td>
<td>Al &amp; Ti</td>
</tr>
<tr>
<td>Surface area</td>
<td>Al &amp; Ti detected</td>
</tr>
<tr>
<td></td>
<td>Al &amp; Cr</td>
</tr>
<tr>
<td></td>
<td>Al &amp; Ti detected</td>
</tr>
</tbody>
</table>

**Figure 7.** Surface area and Cross section area of coating AITiN after PLD

### 3.3. Hardness & Wear Resistance Test Result

The results of hardness & wear resistance testing using the VDI 3198 method, and the Hardness Rockwell Tester Future Tech indicate a decrease in hardness value as the Ti content increases (384 Hv – 333 Hv – 384 Hv). Previous research has shown that the hardness of the AITiN coating increases with the formation of Ti$_{1-x}$Al$_x$N (single phase center cubic), which is influenced by the Al content (Giuliani et al. 2019). In this research, the increase in Ti content caused a reduction in Al elemental content, resulting in decreased hardness. Additionally, the FESEM microstructure results showed an amorphous coating deposition condition, which can further reduce the coating’s mechanical properties. There were no visible differences in wear resistance and adhesion between the three types of coatings, with all levels being at HF1 (good level). Only the AITi sample changed from HF1/HF2, to stable HF1 after becoming AITiN, as shown in Figure 8.
MDEV Test Result Summary

<table>
<thead>
<tr>
<th>Test Item</th>
<th>Coating Pin Dies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AITi (180/10)</td>
</tr>
<tr>
<td>Wear Resistance (VDI 3198 Test)</td>
<td>HF1</td>
</tr>
<tr>
<td>Surface Hardness (HRC)</td>
<td>38</td>
</tr>
</tbody>
</table>

Figure 8. VDI 3198 Result for AITiN coating

3.4. Roughness Test Result

The Surfcom 480A machine was used to perform roughness testing, and the results indicated a decrease in roughness level as the Ti content increased (Table 1). The roughness value decreased from 0.065 RA to 0.046 RA then to 0.041 RA, in line with the increase in the Ti content, indicating that the coating surface became smoother. This correlation can be explained by the increase in amorphous structure observed in the FESEM microstructure as the Ti increased.

Table 1 Roughness Value of AITiN coating

<table>
<thead>
<tr>
<th>Sample</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AITiN 50/50</td>
<td>0.065</td>
</tr>
<tr>
<td>AITiN 40/60</td>
<td>0.046</td>
</tr>
<tr>
<td>AITiN 30/70</td>
<td>0.041</td>
</tr>
</tbody>
</table>

3.5. Annealing Result

The significant increase in hardness value after annealing (Figure 9), indicates the positive effect of this process on the mechanical properties of the coating. Theoretically, the annealing process can improve toughness, plasticity, and produce a certain microstructure. The hardness value of the AITiN layer increased from 333 Hv (before annealing) to 455 Hv (after annealing). Similar findings have been reported in previous research on various coatings, whether produced by PVD or CVD (Aissani et al. 2019; Zeng et al. 2021).

Another interesting result from this annealing process is that the vacuum annealing condition without N2 results in a higher hardness, compared to vacuum + N2. The phenomenon of decreasing mechanical properties of the AITiN coating layer due to annealing with N2 also occurred in several previous studies. The photocatalytic ability of the Black TiO2 layer decreases
when vacuum annealed with inner gas He and N2. The formation of oxygen vacancies (OVs) occurs more easily in an atmospheric vacuum (Zhang et al. 2021). In the process of annealing the AlN layer under N2 vacuum conditions, it was found that the surface O content decreased due to O outgassing from the AlN surface to the atmosphere of the N2 vacuum chamber. This decrease in surface O content will cause a decrease in hardness and an increase in surface roughness (Cheng et al. 2020).

**Table 2** Annealing of AlTiN

<table>
<thead>
<tr>
<th>Test Item</th>
<th>Coating Pin Dies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AlTiN 40/60</td>
</tr>
<tr>
<td></td>
<td>(Vacuum+N2)</td>
</tr>
<tr>
<td>Wear Resistance</td>
<td>HF1</td>
</tr>
<tr>
<td>Hardness (HRC)</td>
<td>39.5 ~ 44.9</td>
</tr>
<tr>
<td>Convert Vickers (HV)</td>
<td>383 ~ 440</td>
</tr>
</tbody>
</table>

**Figure 9.** Effect of annealing on the hardness of the AlTiN coating layer.
Figure 10 shows a significant increase in surface roughness value after annealing, with the roughness value increasing eight to 10 times. For instance, in the case of AlTiN 30/70, the roughness value increased from 0.041 RA to 0.318 RA. This effect can be attributed to the impact of annealing on the microstructure of the coating. Coarsening of the grains in the coating is caused by the degradation of the chain structure which weakens the strength of the molecular chain, changes in particle shape, and agglomeration, which results in an increase in surface roughness (Al Armouzi et al. 2019; Jiang et al. 2019). At the end, the coarsening grains will tend to make surface roughness increase.

4. Conclusion

This research demonstrated that the PLD method can optimize the AlTi coating by adding N₂ gas and applying an annealing process as a post-treatment. Increasing the Ti content in the AlTi coating led to a decrease in surface hardness, from 384 Hv to 333 Hv. By adding N₂ gas in the PLD process, AlTiN compounds were formed which are deposited onto the substrate surface as a coating layer. These AlTiN compounds have a better wear resistance performance in a stable (good) HF1 level attachment, superior to the AlTi compounds with HF1/HF2 level attachments. The resulting coatings exhibited sponge Al-Ti-N morphology, with surface hardness ranging from

<table>
<thead>
<tr>
<th>Sample</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlTiN</td>
<td>AlTi N 50/50</td>
</tr>
<tr>
<td></td>
<td>AlTi N 40/60</td>
</tr>
<tr>
<td></td>
<td>AlTi N 30/70</td>
</tr>
<tr>
<td>Annealing</td>
<td>AlTi N 50/50</td>
</tr>
<tr>
<td></td>
<td>AlTi N 40/60</td>
</tr>
<tr>
<td></td>
<td>AlTi N 30/70</td>
</tr>
</tbody>
</table>
333 to 384 mHv (without annealing) and 410 to 455 mHv (with annealing). Apart from that, annealing with vacuum N2 tends to produce a hardness value that is below the hardness value of a vacuum atmosphere. The hardness value of vacuum annealing with N2 range from 383 to 440 mHv. The roughness increased from 0.198 to 0.247 Rz (without annealing) to 0.318 to 0.916 Rz (with annealing). In order to further advance this research, the impact of substrate heating and target rotation on the PLD procedure needs to be examined.

Acknowledgments

The authors are grateful to the Material and Metallurgical Engineering Department (postgraduate program) of University of Indonesia, BRIN photonics research center and PT XYZ Laboratory for providing research opportunity and assistance during the experiment and characterization processes.

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Han, Q & Viswanathan, S, 2003, ‘Analysis of the mechanism of die soldering in aluminum die casting’, Metallurgical and materials transactions A, vol. 34, pp. 139-146, DOI: 10.1007/s11661-003-0215-9


