# Chemical and Structural Modifications of AlCrN Coatings by Room-Temperature and Hot Nitrogen Ion Implantation

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### 1. Introduction

AlCrN coatings are widely applied to cutting and forming tools due to their high hardness and excellent oxidation resistance, making them a promising nextgeneration coating to replace conventional TiN and CrN. However, in practical applications, localized damage such as cracks or edge failures still occurs in regions where stress is concentrated, including tool edges, upper surfaces, and sidewalls. These failures are closely related not only to the intrinsic durability of the coating but also to localized fracture behavior under concentrated stress. Ion implantation has attracted attention as a method to selectively reinforce coatings by inducing chemical and structural modifications at the surface layer. In particular, nitrogen ion implantation can promote phase transformation, alter bonding states, and increase nitrogen concentration within the coating, thereby enhancing both wear and oxidation resistance. In this study, nitrogen ion implantation was performed on AlCrN coatings under both room-temperature and high-temperature conditions. Beam incidence angles were controlled to selectively strengthen specific regions. The objective was to identify the chemical and structural advantages of high-temperature implantation compared to room-temperature treatment.

#### 2. Methods and Results

The effects of nitrogen ion implantation on AlCrN coatings were investigated through a combined experimental approach, including ion beam implantation, structural analysis by XRD, chemical bonding analysis by XPS, and mechanical evaluation by nanoindentation hardness testing..

# 2.1 Ion beam experiments

AlCrN-coated specimens were implanted with mixed nitrogen ions (N $^+$ /N $_2$  $^+$ ) at 120 keV and a fluence of  $5\times10^{17}$  ions/cm $^2$ . The implantation experiments (Fig. 1) were conducted at room temperature and at 300 °C, with beam incidence angles of 90°, 60°, and 45° to enable selective reinforcement of stress-concentrated regions such as punch tops, edges, and sidewalls.

## 2.2 XRD Analysis

XRD analysis revealed that room-temperature

implantation formed a superficial hardened layer, but also induced brittle phases such as h-Cr<sub>2</sub>N (Fig. 2). As a result, the hardened layer was shallow and hardness decreased rapidly with depth. In contrast, high-temperature implantation facilitated nitrogen diffusion and migration, forming a continuous reinforced layer that extended deeper into the coating. During this process, brittle phase formation was suppressed, and stable growth of the fcc-AlN/CrN phase was observed.

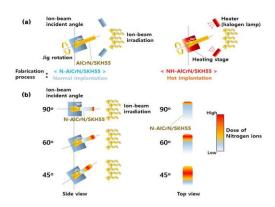


Fig. 1. (a) Schematic diagram of the nitrogen ion implantation process for AlCrN-coated samples under room-temperature and high-temperature conditions. (b) Beam incidence angle control for selective reinforcement of specific regions in the material geometry

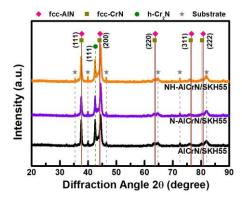


Fig. 2. XRD patterns of AlCrN coatings after nitrogen ion implantation at room and high temperatures. Hot implantation suppresses the brittle h-Cr<sub>2</sub>N phase and stabilizes the fcc-AlN/CrN phases, demonstrating improved structural integrity.

## 2.3 XPS Analysis

The effects of nitrogen ion implantation were examined

using ion beam processing, XRD, XPS, and hardness measurements. Among these, XPS analysis of the N 1s spectra revealed the most significant chemical differences between room-temperature and high-temperature implantation. For the room-temperature sample, the N 1s peak showed low intensity and was dominated by weakly bonded nitrogen states, indicating limited incorporation restricted to the surface. In contrast, the high-temperature sample exhibited a stronger N 1s signal with higher binding energy components corresponding to Al-N and Cr-N bonds. This result demonstrates that hot ion implantation enhanced nitrogen diffusion and bonding rearrangement, leading to greater chemical stability within the AlCrN lattice. Thus, the N 1s spectrum clearly highlights the superior effect of high-temperature implantation in reinforcing the chemical and structural integrity of AlCrN coatings.

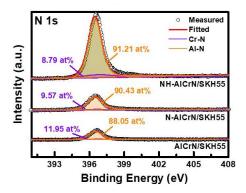


Fig. 3. XPS N 1s spectra of AlCrN coatings after nitrogen ion implantation at room and high temperatures, showing enhanced Al–N and Cr–N bonding under hot implantation.

### 2.4 Hardness Evaluation

Nanoindentation measurements (Fig. 4) showed that room-temperature implantation improved hardness only at the immediate surface, with values decreasing rapidly with penetration depth. In contrast, high-temperature implantation maintained hardness above 20 GPa throughout the subsurface region, demonstrating the formation of a deep and continuous strengthened layer. These results highlight the advantage of high-temperature implantation in achieving not only surface hardening but also long-term structural stability.

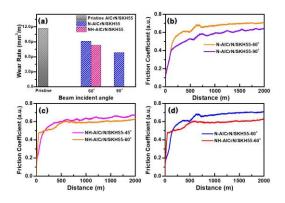


Fig. 4. Friction coefficient and wear rate of AlCrN coatings implanted at room and high temperatures. Hot implantation results in a lower and more stable friction coefficient together with a significantly reduced wear rate, confirming the enhanced tribological performance.

#### 3. Conclusions

This study compared the effects of room-temperature and high-temperature nitrogen ion implantation on AlCrN coatings. Room-temperature implantation contributed to a temporary increase in surface hardness but was limited by the formation of brittle phases and shallow hardening depth, which compromised structural stability. On the other hand, high-temperature implantation promoted nitrogen diffusion and migration, resulting in the formation of continuous and deep reinforcement layers. It also suppressed h-Cr<sub>2</sub>N formation, stabilized the fcc-AlN/CrN phase, and increased Al–N and Cr–N bond ratios, thereby enhancing both oxidation resistance and impact toughness.

Therefore, high-temperature ion implantation provides a clear advantage over room-temperature treatment in improving the reliability and service life of AlCrN coatings, particularly under high-load and severe operating conditions.

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