

CHARACTERISATION OF NANOSTRUCTURED HARD COATINGS PRODUCED BY CHEMICAL VAPOUR DEPOSITION

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INTRODUCTION

The use of nanostructured materials as wear resistant coatings on cutting tools has emerged, due to their superior physical properties. Novel analytical techniques allow the study of nanostructures and therefore their modification by parameter changes during the production process. Especially nanoscale multilayers show improved hardness and toughness, owing to the hindering of dislocation motion ^[1, 2]. The recent development of nanostructured AlTiN by spontaneous self-organisation, using chemical vapour deposition (CVD) suggests, that this technique can be extended to other metal nitride combinations ^[3]. AlZrN presents itself as a promising candidate for coating applications, as ZrN has similar properties to TiN, with advantages in drilling tests and a lower friction coefficient ^[4, 5]. HfN on the other hand shows good chemical inertness as well as thermal stability and when combined with aluminium nitrides in a mixed layer, wear resistance properties comparable with those of CrAlN ^[6]. However, knowledge about AlZrN and AlHfN coatings deposited by CVD is scarce.

The objective of this work is the production and investigation of chemical vapour deposited AlZrN and AlHfN coatings. The main focus is set on analysing the microstructure, crystal structure and elemental composition of the coatings, as well as optimising the deposition processes.

EXPERIMENTAL PROCEDURE

AlZrN and AlHfN coatings were produced using CVD based on previous work ^[7]. By overflowing metallic Zr/Hf and Al pellets at elevated temperature with HCl gas in two separate reactors, gaseous metal chlorides were produced in situ. Using H₂ as the carrier gas, the AlCl₃ and ZrCl₄ respectively HfCl₄ gases were then mixed and subsequently transported to the deposition reactor. Due to temperatures above 900 °C and the separately introduced mixture of NH₃ and N₂, the coatings were deposited on hardmetal inserts, which were coated with a TiN intermediate layer beforehand. All experiments were conducted at a deposition time of 25 min.

RESULTS AND DISCUSSION

AlZrN and AlHfN coatings with layer thicknesses up to 30 µm were generated, which indicates a high reactivity of the reaction gases. The SEM images of both coatings showed homogeneous surface structures with small cracks, which most likely occur due to differences in the thermal expansion coefficient, leading to residual stresses in the coatings.

Throughout the cross section of the AlZrN coatings, a gradient of the elemental composition was observed. Zooming in, a porous, nano-crystalline ZrN layer on the TiN could be detected, which then transforms into a dense pillar structure, as soon as Al is built into the coating (Fig. 1). This suggests either the preferred nucleation of ZrN on the TiN surface or a faster reaction of ZrCl₄ with NH₃ and N₂ compared to AlCl₃. Further investigations of the pillar structure led to the observation of slightly higher amounts of Zr in correlation with crystalline phases in the columns, surrounded by

more amorphous Al rich phases. This indicates the influence of the crystallinity by the amount of Al and Zr in the coating.

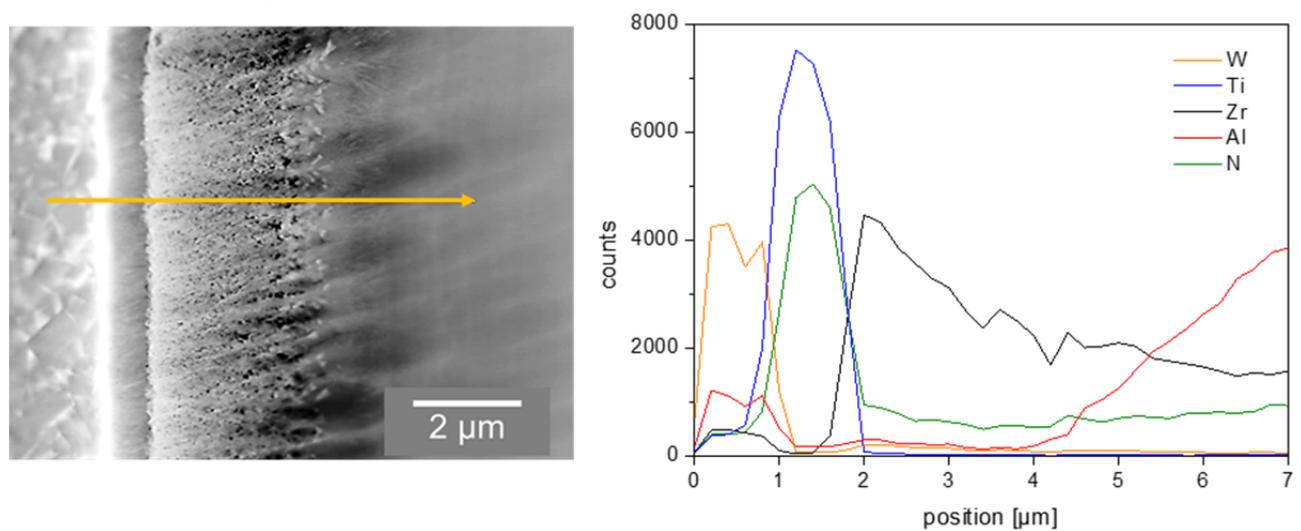


Fig. 1: EDX line scans, using TEM, examining the cross-section of the AlZrN coating.

The results of AlHfN revealed the formation of dense coatings with columnar microstructures, which occur due to changes of the phase composition. Additionally an amorphous HfN intermediate layer in the range of 2 nm between TiN and AlHfN was found.

CONCLUSION

Nanostructured AlZrN and AlHfN coatings were generated by CVD. The high reactivity of the reaction gases led to high deposition rates, which influenced the structure and elemental composition of the coatings. Additionally, a correlation between the Al/Zr or Al/Hf ratio in the coatings and the crystallinity of the structures was observed. We suspect, that by lowering the deposition rates more uniform structures and homogeneous elemental compositions throughout the coatings are achievable. The obtained results give new information on structures of AlZrN and AlHfN coatings, which will further help to optimise CVD processes.

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