# The final report for the project 22-4: Environment-friendly materials processing: physical vapor deposition of advanced functional coatings with reduced energy consumption

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The activities started with the successful postdoc recruitment of Bartosz Wicher who has been employed (50%) in this project between 1st of August 2023 and 31st of July 2025.

The first phase of the project (WP1-WP2) was devoted to very extensive plasma characterization. Systematic ion-energy distribution function measurements for relevant compound targets ($TiB_2$, $AlB_2$, $HfB_2$) were performed according to the plan. In addition, ion fluxes present during sputtering using hybrid configurations such as $TiB_2$-HiPIMS/$AlB_2$-DCMS and $AlB_2$-HiPIMS/$TiB_2$-DCMS were also tested (here HiPIMS = high power impulse magnetron sputtering and DCMS = direct current magnetron sputtering). We found out that the ionization of the DCMS flux is much higher in the former case due to the difference in the first ionization potentials and the ionization probabilities of sputtered metals.

Following that the experiments with film growth by magnetron sputtering were conducted for binary and ternary diboride systems (WP3-WP7). $Ti_{1-x}Al_xB_2$ films have been grown with either $Al^+$ or $Ti^+$ ion assistance. The metal-ion-synchronized substrate biasing for control of metal-ion energy, and, hence, subplantation depth was also used. Films were grown without external substrate heating to minimize process energy consumption. The substrate temperature during growth was lower than 180 ºC. All layers were thoroughly characterized (XRD, SEM, TEM, XPS, nanoindentation). The effects of ion type ($Al^+$ *vs.* $Ti^+$) and ion energy on nanostructure, kinetic solubility limits, phase content, mechanical properties, and high-temperature stability were studied. It was found that alloying with Al improves the high-temperature oxidation resistance: the thickness of the oxide-scale forming after 1 h anneal at 800 ºC decreased more than 15 times upon increasing the Al fraction x in $Ti_{1-x}Al_xB_2$ from 0.36 to 0.74. $Ti_{1-x}Al_xBy$ films with $0.58 \leq x \leq 0.67$ offered the best compromise between high-temperature oxidation resistance and mechanical properties with an average oxide scale thickness 90–180 nm and the hardness of 34–38 GPa. Results are published in high IF journal *Materials and Design* (see Ref. 1).

Very promising results summarized in the first publication inspired the follow up study (see Ref. 2), in which the role of Al concentration in $Ti_{1-x}Al_xB_y$ diboride thin films on the high-temperature oxidation resistance was studied in more detail. This is a very crucial aspect. All reported diboride films are inherently hard, however, they suffer from poor oxidation resistance and readily oxidize above 400 ºC, which hinders applications. Our study revealed the crucial role of the starting Al content (varied in a wide range $0.36 \leq x \leq 0.74$) on the high-temperature oxidation resistance. Films with the Al fraction lower than 0.49 performed poorly in oxidation tests: rapid B loss through evaporation of boria lead to the formation of a highly porous nanostructure that facilitated rapid oxygen diffusion, leading to a high rate of oxidation and, eventually, scale spallation. In contrast, films with $x \geq 0.58$ showed a much better oxidation resistance: a dense, amorphous Al-rich oxide

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scale was observed to grow on top of the original diboride layers, thus passivating the surface against further oxidation at temperatures higher than 800 ºC.

An additional study (not included in the original project plan) dedicated to the growth of purely boron films by low frequency magnetron sputtering was also conducted (cf. Ref. 3). Deposition of dense B films was demonstrated. The substrate temperature was lower than 150 ºC as no external heating was used during the synthesis. The contamination levels were below 5.9 at.%, which is markedly lower than previously reported. The mechanical properties were impressive with hardness and elastic modulus of 29.1 and 438.7 GPa, respectively. At the same time the residual stress was lower than - 1.1 GPa.

Two more manuscripts based on the results generated within the project are still in preparation.

In total, the financial support from the Åforsk grant 22-4 was acknowledged in 11 regular publications (Refs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11), one invited review article (Ref. 12) and 8 presentations at international conferences (including 6 invited talks).

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