Enhanced High-temperature Oxidation Resistance of Hard TiB_2-rich $Ti_{1-x}Al_xB_y$ Thin Films

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Ultra-high-temperature refractory transition-metal (TM) diborides are considered as promising candidates for extreme environments. However, they typically do not exhibit sufficiently high oxidation resistance required for harsh environmental conditions. Here, we study the effect of Al addition on the high-temperature oxidation resistance of TiB_2-rich $Ti_{0.68}Al_{0.32}B_{1.35}$ thin films. The films, grown by hybrid high-power impulse and dc magnetron co-sputtering (Al-HiPIMS/TiB_2-DCMS) in pure Ar atmosphere at ~475 °C, exhibit hexagonal columnar nanostructure. While the column boundaries of $TiB_{2.4}$ layers grown by DCMS are B-rich, the $Ti_{0.68}Al_{0.32}B_{1.35}$ alloys consist of Ti-rich columns surrounded by an Al-rich $Ti_{1-x}Al_xB_y$ tissue phase which is highly B deficient. The observed transition in the nanostructure is attributed to the lower formation enthalpy of AlB_2 than TiB_2 together with enhanced atomic mobility caused by intense Al^+ ion bombardment during HiPIMS pulses. $TiB_{2.4}$ films readily oxidize at temperatures above ~300 °C, as evidenced by X-ray photoelectron spectroscopy, with oxidation products consisting of a tetragonal rutile-TiO_2 structure filled with an amorphous BO_x phase. Air-annealing at 700 °C for 1 h results in the formation of a thick double-layer oxide scale on $TiB_{2.4}$, ~510 nm, where the outer layer is composed of sub-micrometer crystallites and the inner layer has a porous and V-shape columnar structure. Compared to $TiB_{2.4}$, $Ti_{0.68}Al_{0.32}B_{1.35}$ alloys show significantly higher oxidation resistance, while retaining high hardness. In addition, the Ar content is significantly reduced, from 1.2 to 0.5 at.%, due to the use of pulsed substrate bias synchronized to the Al-rich phase of the HiPIMS pulses.

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