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Heterostructural decomposition in V1-xWxB2-Δ films induced by B deficiency

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Transition metal borides (TMBy) represent a structurally rich group of materials with attractive physical properties, including high hardness and high melting points, making them promising candidates for applications in extreme conditions. Considerable attention has been paid to overstoichiometric TMB2+Δ films with hexagonal α-P6/mmm structure exhibiting super-hardness attributed to high cohesive strength between excess-boron tissue phase and crystalline nanocolumns. However, positive effects of reducing the boron content in terms of toughness and oxidation resistance have been reported. Lowering the boron to metal ratio can have various effects on structure and stability, depending on the specific diboride system and its affinity to boron vacancies. In this work, we study the influence of boron understoichiometry on structure and thermal stability of vanadium tungsten diboride films. We present results of high-resolution scanning transmission electron microscopy showing that boron deficiency leads to a high density of planar defects, including antiphase boundaries (APB-2i), the accumulation of which enables the formation of WB-Cmcm areas coherently included in the hexagonal VB2-P6/mmm structure. The observation is supported by density functional theory calculations showing that since the presence of vacancies is favored by the α-WB2 and not convenient for the α-VB2 system, there is an increased probability of decomposition into stoichiometric VB2 and boron deficient WBz<2 products. Additionally, we report on other types of planar defects, such as twinning, and discuss their role in local formation of other boride phases within the Cmcm structure.

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