

Atomic-scale structural and elemental analysis of novel substoichiometric transition metal diboride coatings

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This study addresses the atomic structure and local chemistry of novel substoichiometric transition metal (TM) diboride coatings by employing a range of transmission electron microscopy (TEM) techniques, through which the atomic scale mechanism for accommodating a boron deficiency in these substoichiometric line-compounds has been identified.

Binary TM diborides are regarded as an extremely hard ceramics owing to their high chemical stability, wear and corrosion resistance combined with superb thermal and electrical conductivity as well as high melting point [1]. Currently, magnetron sputtering is the primary approach for depositing coatings of such materials. The obtained TM diboride coatings typically exhibit a nanocolumnar microstructure with pronounced texture and are overstoichiometric in boron ($B/TM > 2$). TM diborides are typically linecompunds that only crystallize in the perfect stoichiometry. Accordingly, excess boron segregates to the nanocolumnar grain boundaries and forms amorphous tissue phase granting the super-hardness of the coatings [2]. A recent breakthrough in achieving full control of the B/TM ratio during the deposition process resulted in synthesis of novel substoichiometric $B/TM < 2$ coatings [3,4]. In order to attain a fundamental understanding of the atomic structure and local chemistry of novel substoichiometric TM diboride coatings, detailed analysis was performed by aberration-corrected TEM.

In this contribution, we fill a current knowledge gap, and locate the relative excess TM (Ti and Cr) with respect to the lattice in the $TiB_{1.9}$ and $CrB_{1.9}$ substoichiometric coatings, respectively. This is accomplished by using a combination of high-spatial resolution high angle annular dark field scanning TEM imaging (HAADF-HRSTEM), selective area electron diffraction (SAED) and electron energy-loss spectroscopy (EELS) spectrum imaging. Cross-sectional and plan-view characterization was performed using the Linköping double Cs corrected FEI Titan³ 60-300, operated at 300 kV. The experimental findings were verified using density functional theory (DFT) calculations and HRSTEM image simulations.

Figure 1 shows a plan-view (along [0001]) HAADF-STEM image together with the corresponding SAED pattern (inset) from $TiB_{1.9}$ (Figure 1a) and $CrB_{1.9}$ (Figure 1b) coatings. Both coatings exhibit planar-like defects with the dimensions reaching few tens of nm in size. SAED reveals discrete diffraction spots, which is expected from a hexagonal TM boride crystal structure along the [0001] zone axis, and indicate a high-crystal quality of the investigated coatings. Exploiting the relative orientation between the SAED pattern with respect to the defects, it is found that the defects are residing on the $\{1-100\}$ prismatic planes of the $TiB_{1.9}$ and $CrB_{1.9}$ crystal structure. STEM-EELS showed the B-deficiency and TM-enrichment in the planar defects.

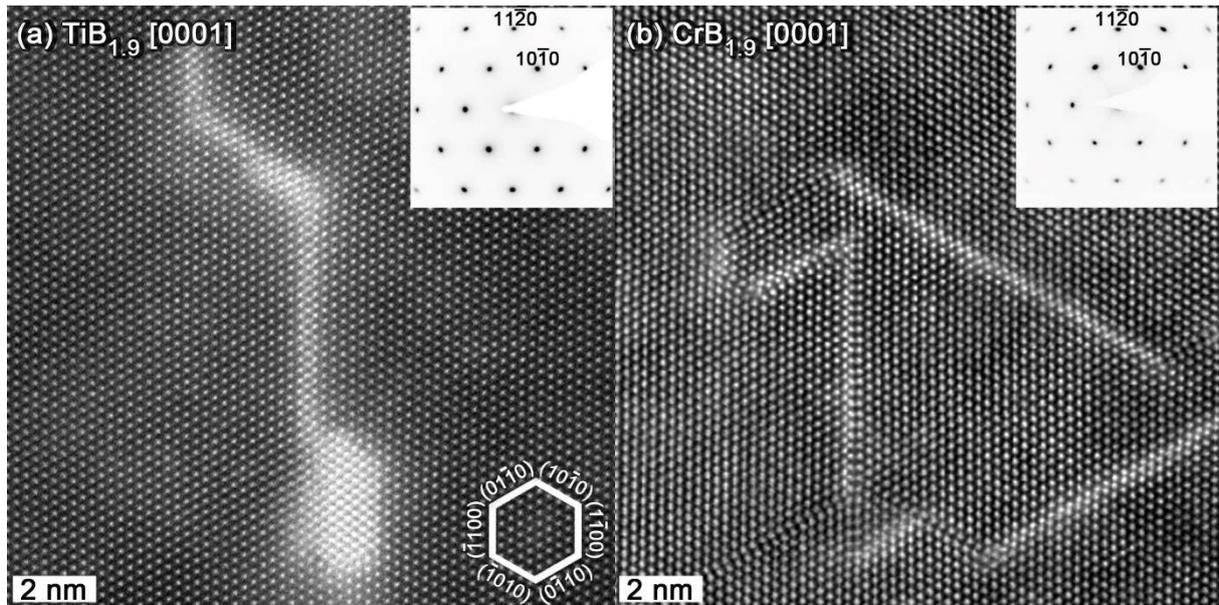


Figure 1: HAADF-STEM image showing the microstructure of (a) $\text{TiB}_{1.9}$ and (b) $\text{CrB}_{1.9}$ coating along the $[0001]$ zone axis. The inset shows the corresponding SAED patterns.

The study elucidates the atomic structure, shape, local chemistry, confinement, interface coherence and crystallographic relationship of the planar TM defects with respect to surrounding lattice of the TM diborides. This enable to deduce the B-deficiency as the driving force for TM-rich planar defect formation in the TM diboride crystal structure and attribute their formation mechanisms to the nature of the line compound. The results stand in strong contrast to the common observations of overstoichiometric $\text{TiB}_{2+\Delta}$ and $\text{CrB}_{2+\Delta}$ coatings.

The collection of results provides the direct evidence for decoding the atomic structure of substoichiometric TM boride coatings. It enables to explain the B deficiency in the coating which is directly associated with the formation of TM-rich planar defects [5,6,7].

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