Thin Films and Coatings

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TEM study of interface's impact on hardening mechanisms in transition metal nitride thin films

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The aim of this study was to identify the types of interfaces and their impact on hardening mechanisms of differently structured transition metal nitride coatings, by direct transmission electron microscopy (TEM) observations. The investigated coatings have been divided according to their structure into three groups: columnar coatings, multilayers and nanocomposites. The microstructural aspects of all three groups have been extensively studied by TEM in as-deposited and heat-treated state or after indentation in order to better visualize the mechanisms governing the coating behavior during plastic deformation. Also the combination of different chemical compositions and their influence on the coating's microstructure has been analyzed.

TEM studies down to the atomic scale, of a compositionally graded TiAlSiN coating allowed putting some light onto the mechanism of formation of the nanocomposite structure. The images taken in the Ti-rich part of the coating showed crystalline columns with neat interfaces, followed by a progressive appearance first of a crystalline and then of an amorphous boundary phase as the Al+Si concentration was increasing. At the top part of the coating the well-known nanocomposite structure consisting of crystalline grains surrounded by an amorphous matrix was observed, Figure 1(a). In addition it could be shown that the nanocomposite structure, exhibiting high hardness, can only be formed with two phases having sharp interfaces such as TiN/SiN, Figure 1(c). It was not possible to make a hardness enhanced nanocomposite out of AlN and SiN. This was due to local epitaxy at AlN/SiN interfaces, investigated on a models system of AlN/SiN multilayers. Indeed, it was found that 0.7 nm of SiN, corresponding to about two monolayers, grew crystalline on AlN favoring epitaxy, Figure 1(b) – (e).

The nanocomposite structure is not the only way to achieve a hardness enhancement in these coatings: also columnar coatings can be hard, provided a sufficient density of dislocation barriers, not in form of column boundaries, is present. Two solutions to increase the density of dislocation barriers are presented: one consists in the introduction of compositionally graded multilayers, which distort the lattice but do not obstruct the columnar growth. The second solution is a phase modulated structure i.e. inside the columns zones of different phases are formed as it is the case for cubic and hexagonal NbN, which nevertheless has a columnar structure.

In multilayered coatings three types of interfaces, influencing their properties were observed: completely epitaxial, such as in AlN10 nm/SiN<0.7 nm layers or NbN/CrN interfaces in the growth direction, Figure 1(d), semi-coherent, with local epitaxy and non-coherent such as in TiN/SiN coatings. All of them were barriers for dislocation movement making thus these coatings harder that their reference columnar layouts.

To better visualize and identify the hardening mechanisms based on dislocation blocking in metal nitride coatings, plastic deformation was deliberately induced by nanoindentation.

Columnar and multilayered coatings have been extensively investigated by post-mortem TEM observations of indents cross-sections. In general, all coatings containing TiN, independently on their structure or layer thickness, deformed by shear sliding at grain boundaries. This mechanism was observed on two different scales: either multilayer pieces or individual grains were vertically displaced over distances of several nanometers. It was particularly well visible for the NbN/TiN and the TiN/amorphous-SiN combinations.

By microstructural observations it could be shown that the substrate governs the deformation induced by nanoindentation with a Berkovich indenter tip in columnar TiN coatings. In the case of columnar TiN deposited on a soft Si substrate during indentation the columns underwent shear sliding at grain boundaries and were pushed into the substrate forming steps at the interface Figure 2(a) & (b). If columnar TiN is grown on polycrystalline, hard WC-Co substrate, cracks at columnar boundaries are generated and the columns are bent, Figure 2(c). However, the columns, which grow on the soft Co matrix, are also pushed into it, similarly to the TiN/Si combination. Conversely, those columns, which grow on the hard WC grains are bent and internally fractured, Figure 2 (d).

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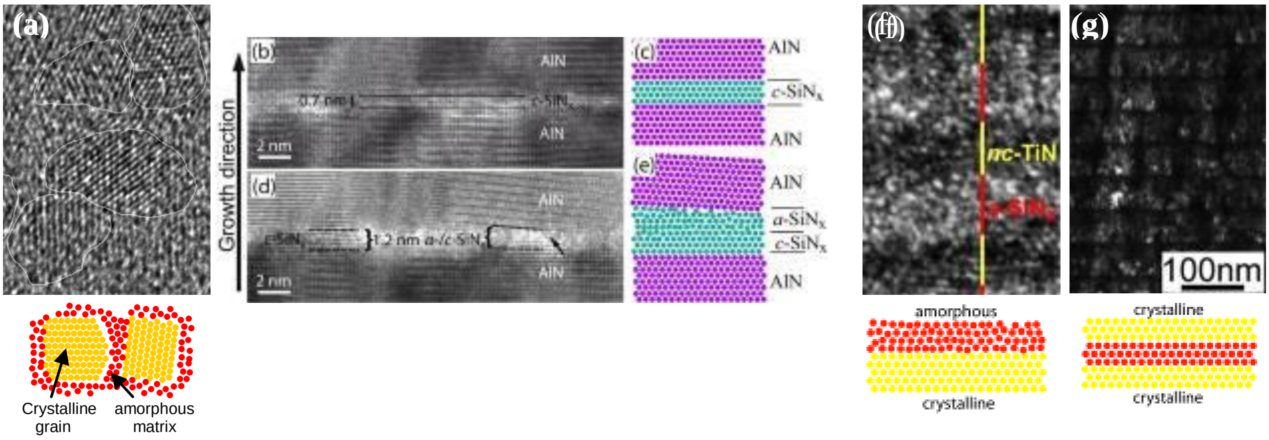

Figure 1. (a) HRTEM image of a TiAlSiN nanocomposite with a scheme of crystalline grains surrounded by an amorphous matrix; (b) & (d) Single crystalline AlN/SiN$_x$ multilayers with two different SiN$_x$ thicknesses together with (c) & (e) schematic models of the interlayer arrangement of the SiN$_x$ atoms; (f) HRTEM image of a cross-section through a of TiN/amorphous-SiN multilayers with the respective layer thickness of 1 nm and a schematic representation of the atomic arrangement. (g) Dark field image of a cross-section through a multilayered NbN/CrN coating and a schematic representation of the atoms in the multilayers.

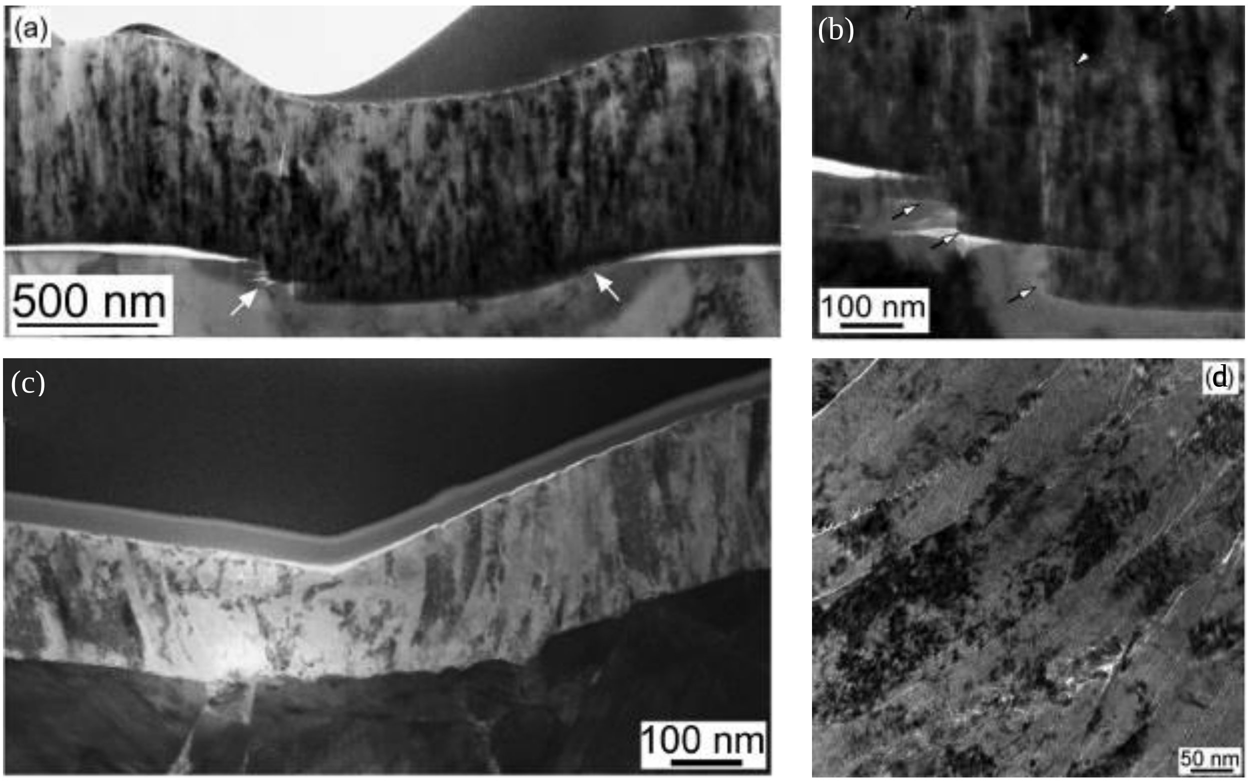

Figure 2. TEM bf images of cross-sections through a Berkovitch indent imprints in columnar TiN coatings grown on (a) soft Si (001) substrate; (b) hard polycrystalline WCCo substrate; magnified view of: (b) the steps formed by the columns pushed into the soft SI substrate due to grain boundary sliding; (d) Columns with intercolumnar and internal cracks.