TEM study of interfaces in transition metal nitride thin films and their influence on their properties

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Titanium nitride and other transition metal nitrides were introduced in the early 1980s as single-phased protective coating materials for cutting and forming tools to prevent surface damage by abrasion. They exhibit a columnar growth mode, with crystalline interfaces as shown schematically in Figure 1(a). In order to enhance the hardness of these films the columnar growth has to be prevented. One of the solution is to grow coatings, consisting of alternating layers of two hard crystalline phases (e.g. TiN with CrN or NbN) or one crystalline and one amorphous phase (TiN/a-SiN) called multilayers. The achieved hardness enhancement reaches a factor of two, when the thickness of the individual layers is of the order of several nanometers [2]. Analogous, it is possible to deposit thin films, which show similar hardness enhancement by combining two non-miscible phases with distinct phase boundaries. This means that crystalline grains with a size of the order of 3-10 nm are embedded into an amorphous matrix, Figure 2(a), resulting in a so-called nanocomposite structure [3]. In all three types of structures the scientists aim to achieve the highest hardness values possible. Therefore the presence and microstruture of grains, interfaces and defects, which are obstacles for free dislocation movement inside the coatings is crucial for obtaining a hardness enhancement.
TEM is the perfect tool to investigate the defects inside the grains as well as the interfaces between crystalline-crystalline and crystalline-amorphous phases in columnar, multilayered and nanocomposite structures. Thus conclusions on the influence of the boundaries structure on the properties of the coating-substrate system can be drawn.
The columnar coatings, analyzed on the example of TiN in Figure 1(b), do not exhibit a single-crystalline structure, but are composed of multiple zones of different crystallographic orientations inside the column boundaries. The boundaries between those zones are obstacles for dislocation movement therefore these coatings reach hardness values up to 20GPa. Another obstacle for dislocations to surmount is the interface between two crystalline layers in the structure shown in Figure 1(c), where 50 repetitions of 25 nm of CrN and 25 nm NbN were combined to form a multilayer coating. It is very interesting to notice that in the dark field image only the CrN/NbN interfaces in the growth direction are visible. On the contrary, the columns seem to grow in a not disturbed way through the NbN/CrN interface. Another very interesting example is the TiN/SiN multilayered structure, where 1nm of amorphous SiN is sufficient to prohibit the growth of crystalline TiN columns having also the size of 1nm, Figure 1(e).
Silicon, when added into TiN is known to prohibit the columnar growth of the TiN grains by forming an amorphous matrix around the latter ones resulting in a nanocomposite structure, Figure 2(b). As already mentioned above, the condition to form a nanocomposite with an enhanced hardness is the presence of two immiscible phases with sharp boundaries. An example what happens to the microstructure in a system with not very well defined boundaries is AlSiN, Figure 2(c), where only a very faint increase in hardness is observed, Figure 3(b), because 6at.% can be dissolved in the AlN.

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Another concept is to replace in the TiSiN system the Si by Ge, which is in the group IV of the periodic table similar to Si, in order to extend the knowledge on the ternary multiphase nitride films. With several complementary investigation techniques including among other TEM and EELS, we succeeded to demonstrate that the Ge atoms segregate to the TiN crystallite surface thus limiting the crystal growth by forming the $TiGe_y$ amorphous phase. Moreover a hardness increase of about 30% has been achieved, Figure 3(a).

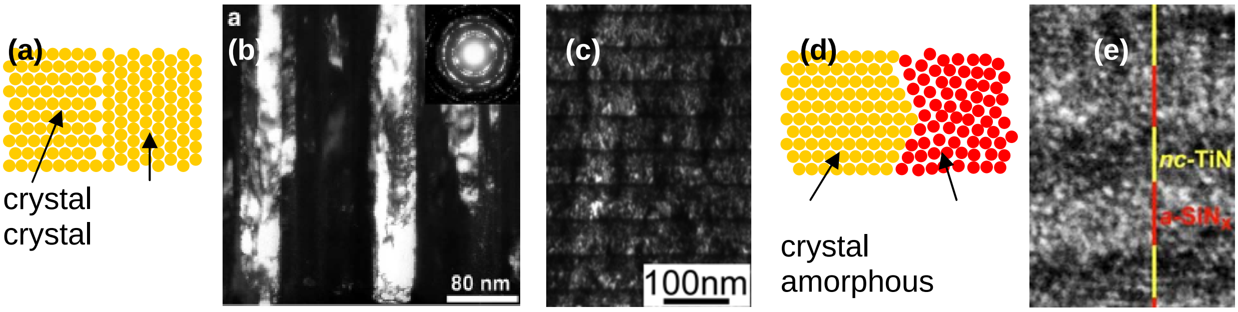

Figure 1 (a) Schematic view of the atomic arrangement between two crystalline structures; (b) TEM dark-field cross-section through a columnar TiN coating showing interfaces between the respective columns; (c) Dark filed image of a cross-section through a multilayered NbN/CrN coating (see text for details); (d) Schematic view of the atomic arrangement between a and an amorphous structure; (e) HRTEM image of a cross-section through a multilayer system of TiN/amorphous-SiN with the respective layer thickness of 1nm.

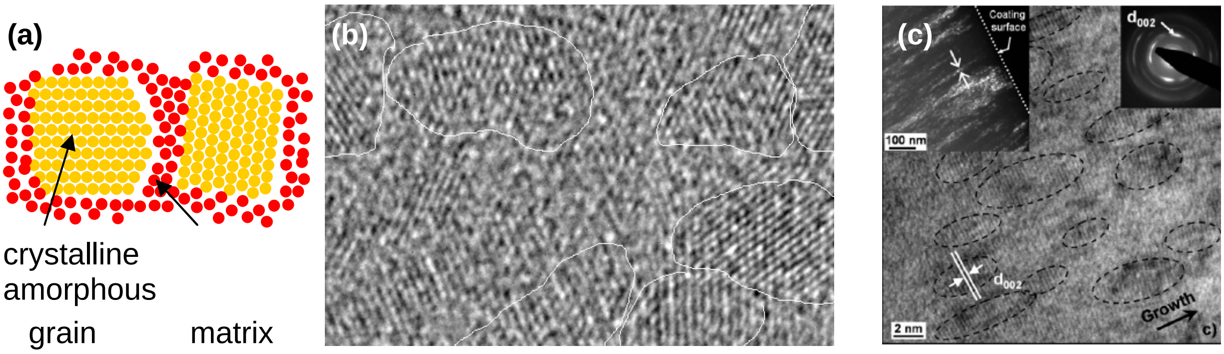

Figure 2 (a) Schematic view of the atomic arrangement of two crystalline grains surrounded by an amorphous matrix (nanocomposite structure); (b) HRTEM image of a TiAlSiN nanocomposite structure with crystalline TiAlN grains embedded in an a-SiN matrix; (c) HRTEM image of a AlSiN composite.

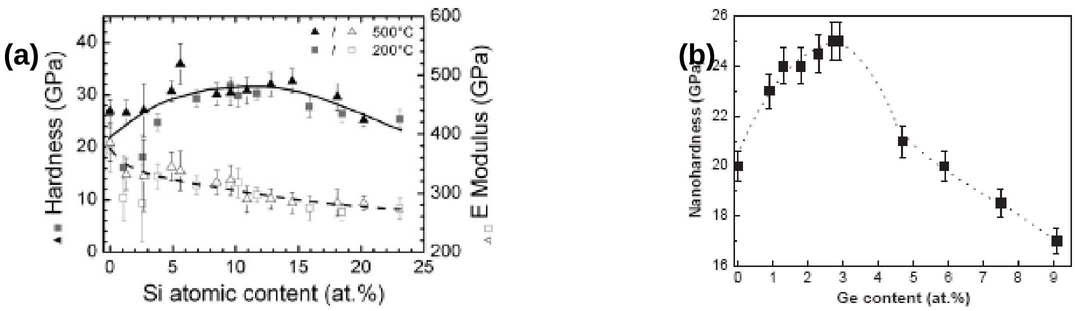

Figure 3 Hardness evolution for the: (a) AlSiN coating as a function of the Si concentration: the maximum is very faint; see text for explanation; (b) TiGeN film as a function of the Ge concentration: a clear maximum is observed for the nanocomposite structure.

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