Chapter 6
THERMAL STABILITY AND SELF-ARRANGEMENT OF NANOCRYSTALLINE HARD COATINGS

P. H. Mayrhofer
Department of Physical Metallurgy and Materials Testing, University of Leoben, 8700 Leoben, Austria

Nanocrystalline hard coatings have attracted increasing interest in modern development of hard coatings. Their increased volume fraction of interfaces is often responsible for superior properties, but they stimulate also microstructural processes. Whereas for single-phase coatings a remarkable reduction in hardness occurs around 500°C, nanocomposites maybe stable up to 1000°C. In physical vapor deposited (PVD) hard coatings nanostructures can arise during growth or during a post annealing treatment. In non-reactively sputtered overstoichiometric TiB₂ coatings the excess of boron forms a tissue phase surrounding TiB₂ crystals. Thus, a nanocolumnar structure with a diameter of about 5 nm is formed during the deposition process. Another example for segregation driven formation of a nanostructure is TiN-TiB₂, where the coating consists mainly of TiN and TiB₂ nanocrystals of about 3 nm due to their extremely limited solubility. Nanostructures can also arise during annealing of supersaturated coatings. Thermal treatment of Ti₁₋ₓAlₓN coatings causes the metastable phase to decompose into its stable constituents TiN and AlN. Initially Ti₁₋ₓAlₓN coatings undergo spinodal decomposition generating an increase in hardness at elevated temperatures. The results presented show that next generation’s coatings with increased ability for self-arrangement can effectively be prepared by PVD.

Keywords: hardening, nanocomposite, spinodal decomposition, thermal stability, self-arrangement.

1. INTRODUCTION

In the last few years, several hard coating materials with unique properties have been developed or even transferred to industrial applications. Essentially, two different coating material groups can be distinguished. The first one includes materials with inherent unique properties, e.g., diamond-like carbon DLC [1], diamond [2] and cubic boron nitride [3] as inherently hard or even superhard (where the hardness exceeds 40 GPa) materials or aluminum oxide as thermally extremely stable coating [4]. The second group covers heterostructures. Unlike the multilayer coatings like the commercially...
applied TiC-Al\textsubscript{2}O\textsubscript{3}-TiN coatings deposited by CVD techniques with layer thicknesses in the order of a few to several tenth of microns [5], nanoscaled heterostructures allow the design of unique properties or property combinations. The first attempts to deposit these structures have been made with the goals (1) to create new superhard materials (see e.g., the review by Vepřek [6]) or to combine properties like high hardness with (2) high toughness [7] or (3) a low friction coefficient [8,9]. The latter task focuses on the design of functional coatings where nanodispersive structures consisting of hard (e.g., TiN) and lubricant phases (e.g., DLC, MoS\textsubscript{2}) have been suggested. Here, this topic will not be discussed further. This paper mainly deals with the optimization of mechanical properties represented by hardness and its thermal stability by the formation of heterostructures, which arrange themselves during growth of the coating or during a thermal treatment after deposition.

The science of materials is to a large extent couched in terms of length scales and their interactions. Thus, the mechanical response of materials can be understood from the point of view of the interaction of a characteristic length, which may be the dislocation radius at a given stress, with a size parameter describing the microstructure (e.g., grain size, column diameter, particle size, film thickness) [10]. Hardening of metals is caused by providing obstacles for the dislocation movement, these mechanisms can also be applied to some extent to hard coatings. Hindering of dislocation movement can be achieved by, (1) high density of point and line defects generated by energetic ion bombardment during growth, (2) internal boundaries like grain and column boundaries, (3) second phase particles and (4) solutes. Solutes in a crystal act as obstacles to dislocation motion through their elastic and/or chemical interactions with dislocations. Most solutes are weak hardeners except for the (technologically) important class of interstitial solutes that induce anisotropic distortions of the lattice. Second phase particles are generally the most potent strengthening agent in practical high strength engineering materials, their mechanisms can be divided into coherency, chemical, order, stacking-fault and modulus hardening [11,12].

The different mechanisms are individual in their effectiveness of hardening and especially in their effectiveness during a thermal treatment, which will be discussed in the following chapters.

2. THERMAL STABILITY OF SINGLE-PHASE HARD COATINGS

In single phase hard coatings like TiN a hardness increase can be obtained either by high energetic bombardment during growth of the films causing high compressive stresses or by a reduction of the grain size [13]. The effect of smaller grain sizes on the yield stress is classically described