Production of CrN/NbN superlattice coatings by cathode switching reactive cathodic arc evaporation

C. Pecchio¹, E. Bemporad², D. De Felicis², S. De Rossi¹ & F. Carassiti²
¹Surface Engineering Dept, Istituto Scientifico Breda S.p.A., Italy
²Mechanical and Industrial Engineering dept., Univ. “ROMA TRE” Italy

Abstract

CrN/NbN superlattice and CrN coatings, approximately 3 μm in thickness, have been deposited on tool steel samples by a modified reactive cathodic arc evaporation technique (CAE) in an industrial-size chamber. Superlattice deposition was achieved by triggering alternatively on Cr and Nb cathodes, obtaining layers of about 4-5 nanometers. X-ray diffraction, scanning and transmission electron microscopy, atomic force microscopy and energy dispersive X-ray analysis were used to determine microstructure and chemical composition of both coatings and coating defects. Diffraction techniques showed for the CrN coating a (220) preferred orientation and a strongly preferred (200) orientation for superlattice samples, with a lattice parameter intermediate between the CrN and the NbN ones. Defect evaluation was focused on shape, dimension, density, clustering and other process-sensitive features. In CrN/NbN superlattice coatings a separation between defects and the surrounding bulk coating was evident, in fact TEM analysis revealed a different microstructure and chemical composition in this area. On the basis of macroparticle formation theory an explanation of the experimental observations is proposed.

1 Introduction

The cathodic arc evaporation process has been applied extensively to deposit hard coatings for tribological applications due to its high ion current density and high energies (50-150 V) of metal ions: this means elevated deposition rate and
excellent coating adhesion that are the main characteristics of arc based coatings. However conventional cathodic arc evaporation suffers from macroparticle contamination. The formation of macroparticle relies on the process of arc discharge during coating, whose generation and sustaining require the arc triggering and a following high current input process. Such an energetic process not only produces highly ionised plasma but also ejects melt target material droplets. Macroparticle formation causes the local loss of coating adhesion, the increasing of overall surface roughness and the formation of nodule-like defects. These latter can be embedded within the coating, or can act as a precursor of craters and dish-like defects, due to droplet self-expulsion mechanism [1]. None of mentioned defects is advantageous for tribological application; moreover metallic macroparticles can be potential sites for the corrosion of coated steel samples [2-4] and also selective wear has been demonstrated at defect macroparticles in erosive slurry [5]. CrN/NbN superlattice coatings are deposited on industrial scale by cathode switching reactive arc evaporation. Superlattices are generally produced by a number of techniques, the most common of which is sputtering, using different evaporation sources in opposite targets configurations and rotating the substrate holder in order to alternately expose the substrate to the two materials. In this way the layer thickness is controlled by the substrate holder rotation rate at a constant material flux. These kind of systems can limit the geometry which can be accommodated or require complex and expensive reciprocating shutters to create controlled atmosphere separation, to restrain cross contamination [6]. On the contrary, using cathode switching reactive cathodic arc evaporation (S-CAE) all the intermixing mechanism, excepted diffusion deriving from the deposition of too thin layers, are eliminated using an interrupted deposition by alternatively triggering on the Cr or Nb cathodes. Superlattice samples are compared with two different kind of CrN samples: CrN coating produced in a standard cathodic arc mode and CrN coating produced in cathode switching mode i.e. alternatively triggering on two different chromium evaporators sets. This work evaluates droplet contamination influence on morphological and compositional properties of the droplet coating surroundings and analyse the correlation among generation, transport and features (number, density, geometry...) of macroparticle and process parameters.

2 Experimental

CrN/NbN superlattice and CrN coatings were prepared in a reactive cathodic arc deposition chamber [7] equipped with eight cathode flanges and a rotating biased carousel holding pieces for coating. Films were deposited on X82WMoV65 tool steel [8] previously polished to a roughness $R_s<0.02 \mu m$. In the case of superlattices deposition one Cr and one Nb cathode (fig.1) were mounted on each chamber side, in order to have a good plasma uniformity during both the CrN and the NbN layer deposition. Prior to loading into the chamber, the substrates were cleaned using a sequence of ultrasonically enhanced alkali washing stages followed by de-ionized water rinsing and hot air
drying. After loading, the chamber was pumped down to $1 \times 10^{-3}$ Pa and heated for about one hour to 350°C, after which the substrates were ion cleaned inside by an intensive bombardment with highly ionised plasma (first hydrogen and then chromium). After etching, a thin layer of chromium of about 0.05 µm was deposited in order to improve adhesion providing a smooth transition between the ion-cleaned substrate and the coating properties. Subsequently, CrN or CrN/NbN coatings were deposited, controlling the multilayer period during superlattices deposition by modifying the triggering time at constant deposition rate. Coating and defect properties were studied by means of Digital Optical Microscopy (using DF and DIC filters to enhance surface features), Electron Microscopy (SEM Philips XL 30 LaB₆, TEM Philips CM 120 LaB₆ both analytical), Atomic Force Microscopy (NT-MDT Smena contact mode, 7x7 µm, 1Hz line scanning speed) and XRD (Scintag mod. X1 with a Bragg-Bentano geometry, 40kV, CuKα radiation). A direct measurement of the superlattice period was made in the low angle region using the standard Bragg equation; the density modulation period was obtained using XTEM observation. Plan-view sample preparation consists of mechanical grinding, dimpling to about 5 µm and then a final step using ion milling (Baltec RES 100 with a 8kV double gun 12° grazing incidence till hole and 6kV double gun 5° for 1h). XTEM samples were prepared by the use of the tripod wedge polishing technique (30, 15, 6, 3, 1, 0.5 and 0.25 µm 3M abrasive sheet for thinning and polishing of one side; 6, 3, 1, 0.5 and 0.25 µm till transparency on the other side), and then ion milled (both faces, 12° for 2 hours and 6° for 1 hour).

Fig. 1. Schematic view of the CAE coating chamber showing the Cr and Nb cathodes arrangement.
3 Results and discussion

3.1 Coating structure

Three different kind of samples have been compared: a CrN/NbN superlattice, marked with (a), and two different CrN coatings obtained with switched deposition process (b) and normal deposition process (c). CrN samples, produced using both standard and cathode switching deposition mode, exhibit an NaCl face-centered cubic (fcc) unit-cell structure and a [220] texture (fig.2).

Fig. 2. X-ray diffraction pattern of a homogeneous (b) and (c)-type coating (scan step: 0.05º, count time: 3 sec).

Fig. 3. High and low angle (in frame) X-ray diffraction pattern of (a)-type coating; estimated period λ=5nm (scan step: 0.01º, count time: 4 sec).
High angle XRD 2θ scan for CrN/NbN superlattice deposited at a fixed triggering time (3 seconds) is shown in fig.3. When triggering time is low enough to obtain nanometric layers, X-ray diffraction pattern is equivalent to face centered cubic structure with a strong [200] preferred orientation and only one peak exists between the position of CrN (NaCl-type, \(a_{0}=0.414\) nm) and \(\delta\)-NbN (\(a_{0}=0.440\) nm). The lattice parameter calculated from [200] plane of the CrN/NbN superlattice with \(\lambda=5\) nm (corresponding to \(2\theta=42.14^\circ\)) is 0.429 nm, indicating that CrN and NbN distort each other. For all multilayered coatings, typical low angle X-ray reflection peaks due to chemical modulation period are observed. The two peaks shown in fig.3 (in frame) occurred at positions corresponding to the reciprocal lattice vector of CrN/NbN superlattice having a period \(\lambda=5.0\) nm. XTEM image in fig.4 shows the layered structure, and the [200] preferred orientation (SAD image in the small frame) of the film. The period thickness do not vary considerably and the average value, measured to be \(4.7\pm0.5\) nm, it is in good agreement with the value predicted by growth conditions and XRD measurement.

### 3.2 Surface and defects

Optical and scanning electron images of (a), (b) and (c)-type coatings are shown in fig. 5. All the three kind contain droplet growth defects, craters and dish-like growth defects, with size varying from less than a \(1\mu m^2\) up to \(100\mu m^2\) with the (a) and (b)-type coating having an overall defects amount visibly lower but an evident less flat defect-free surface. In order to compare in a semi-quantitative
way number and features of these defects, images acquired by Optical Microscopy (2,048x1,536 pixel resolution) have been processed using a cascade of filters according to the following procedure: mean ranking, shading correction, threshold, binarize, morphological closing, ranking. Detected particles are classified on the basis of their area; for each class, number of particles, defects area fraction and mean shape factor have been calculated, together with a total defects area percentage for each type of coating. Results are showed in fig. 6, where data are averaged on 5 different analysis frames, resulting in about $10^5 \mu m^2$ surface area investigated for each sample. In all three diagrams, fraction of overall defect area (i.e. percentage amount of the whole defected area due to defect belonging to each class) and averaged shape factor are plotted vs. each class (the measured defects area).

Fig. 5. Surface morphology of (a) on top, (b) middle and (c)-type coatings (OM: DF, Objective 50X, 10.000x, SE, tilt 25°)
Fig. 6. Image analysis of coatings surface; features reported versus class of macroparticle (defects area, $\mu m^2$); see text for details.
Circle dimension is proportional to the number of defects populating that class (reported near each circle). It is evident that (a)-type coating shows a more rounded defects with the most part of defected area occupied by few large defects (more than 20 μm²). There are noticeable very small droplets (below 1 μm²) and clustering effect is very poor. (b)-type coating shows that defected area is produced mainly by mid-size defects (about 50% having area in the range of 6 μm² to 10 μm²) and the clustering effect is evident in defects having area greater than 10 μm² (mean shape factor below 0.6). Same behaviour is noticeable for (c)-type coating, were clustering is more evident, especially for very large particles. Finally, total defects area for the (a)-type coating is 40% lower that (b)-type coating and less than one half with respect to the (c)-type coating. The difference on defect density and clustering observed by the comparison of the two CrN samples, deposited in continuous or switching reactive CAE, can be related to a prevention of cathode overheating by the alternation of the evaporators sets. This effect can be enhanced when using Nb cathode due to the lower thermal capacity and higher melting temperature. Fig. 7 shows the details of a typical Nb macroparticle, that is found in superlattice coating, with EDS line analysis on the corresponding droplet profile. Strong differences in composition and structure around the defect are evident: line compositional profiles reveal that the droplet has a niobium core enriched in nitrogen in the periphery area:

Fig. 7 (a)-type coating, typical Nb droplet defect and its surroundings; (12kV, 60000x, BSE)
Fig. 8. (a)-type coating, Nb droplet: film crack due to residual stresses between shell and coating (120kV, 88,000x, BF)

Fig. 9 detail of left image: columnar growth shell and rims (120kV, 380,000x, BF)

Fig. 10. AFM detail of a droplet defect on (a)-type surface, clearly separated from the adjacent coating matrix.

the metal droplet formed at the cathode surface appears to be incompletely reacted with the reactive gas during its flight to the substrate. Thin layer of condensed Fe all around the droplet is also visible where a chromium rich shell has grown equiaxially with a radial crystal orientation. TEM images reported in fig. 8 and fig. 9 reveal that the droplet is surrounded by several narrow rims upon whom coating grows radially, forming a shell. Further investigation of the same sample with TEM (fig. 8) allow to determine dimensions of shell grains and display coating failure in the inner part of the shell suggesting very high residual stresses in this region. Fig. 10 shows an AFM image of a droplet defect on superlattice sample surface. At the interface between the defect shell and adjoining coatings there is a void zone where the physical bonding of the defect to the coating matrix is obviously poor. This effect is known in literature to be caused by relative shrinkage [9] and alteration of normal crystal growth in the droplet surroundings.
4 Conclusions

CrN/NbN superlattice coatings with a superlattice period $\lambda=5$ nm have been produced by a reactive arc cathodic deposition technique. The deposition of superlattices were carried out using interrupted deposition by alternatively triggering on two cathodes (Cr, Nb) in order to obtain sharp interfaces. In the same way two different CrN coating samples were produced using continuous and switching CAE in order to better understand the improvements in superlattice surface morphology. X-ray diffraction in low-angle configuration and XTEM analysis confirmed the formation of a superlattice structure. First of all it was confirmed that the method of alternatively triggering cathodes is not only an original process to obtain desired superlattice multilayer with designed period, but that this method is also able to reduce the typical defects (droplets) usually found in standard reactive CAE coatings. Moreover defects on superlattice surface appear to be reduced if compared with defects density on SRCAE CrN surface mainly because of lower thermal capacity and higher melting temperature of Nb.

Acknowledgment

Part of this work was supported by MURST under Project n° 66649 “START- Sviluppo di Tecnologie Avanzate per Rivestimenti Tribologici”. Morphological and compositional analysis have been carried out at the “Interdepartmental Laboratory of Electron Microscopy - LIME”, University of Rome “ROMA TRE”, Via Vasca Navale, 79 00146 – Rome, Italy (http://www.lime.uniroma3.it).

References

[8] S600 (Böhler designation), hardened and tempered at 550°C