Interrelation Among Morphology, Mechanical Properties and Oxidation Behavior of \( \text{Nb}_x\text{Al}_y\text{N}_z \) Thin Films

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\( \text{Nb}_x\text{Al}_y\text{N}_z \) thin films were deposited by magnetron sputtering reactive technique with \((y/x+y)\) ratio varying from 0 to 0.4, in order to maintain aluminum atoms inside NbN matrix in solid solution. GAXRD analyses revealed that the crystalline phase obtained for \( \text{Nb}_x\text{Al}_y\text{N}_z \) thin films was \( \text{B1-NbN} \) with a lattice constant shrinkage as Al concentration at these coatings was increased. Due to similarity in electro negativity values between Nb and Al, XPS analyses could not verify pronounced changes among as deposited \( \text{Nb}_x\text{Al}_y\text{N}_z \) coatings. The average hardness values evidenced that solid solution strengthening mechanism did not increase hardness significantly. The oxidation resistance increased with Al content and no oxide phases were registered by GAXRD analyses for coating with more aluminum added. However, SEM images revealed bubbles after oxidation at high temperatures for all samples.

**Keywords:** thin films, magnetron sputtering, niobium nitride, aluminum nitride, \( \text{NbAlN} \), high temperature oxidation.

1. Introduction

Niobium nitride (NbN) has been widely explored as protective coatings mainly due to properties such as high hardness and wear resistance, providing an interesting option for applications that require good mechanical performance\(^{1-2}\). Initially, NbN was used as a component in multilayered thin films along with titanium nitride (TiN)\(^{3-5}\), showing significant improvements regarding hardness and corrosion resistance. Remarkably, when the two nitrides were analyzed separately in those works, NbN showed higher hardness and wear resistance values compared to TiN.

Despite the good mechanical properties, oxidation temperature of NbN is near to 700 K\(^{6}\), which compromises its applicability in high temperature service conditions. One possibility to hinder NbN oxidation process is the addition of a third chemical element, in its matrix, such as aluminum. Al atoms have already been successfully incorporated in Ti(Al)N, Cr(Al)N, Zr(Al)N and Ta(Al)N thin films, improving the oxidation resistance besides good results in coatings mechanical properties\(^{7-11}\). However, as seen in the literature, adding a different element or molecule to coatings matrices is highly prone to result in strong changes on the formed structure and properties\(^{12}\). In particular, when aluminum solubility limit is exceeded, hexagonal AlN phase (B4-AlN) is commonly formed, rendering the ternary coating an improved oxidation resistance but strongly decreasing global mechanical resistance\(^{13,14}\), suggesting the best results for thermal stability and mechanical properties for these nitrides are obtained when aluminum atoms are exclusively in solid solution, without hexagonal AlN grains formation\(^{13,14}\).

Notably, Al solubility in NbN matrix has been reported to be highly dependent on the formed structure. It is relevant to the formation of ternary \( \text{Nb}_x\text{Al}_y\text{N}_z \), given the numerous crystalline structures that pure NbN can manifest, i.e., hexagonal \( \beta-\text{Nb}_2\text{N} \), \( \delta-\text{NbN} \), \( \epsilon-\text{NbN} \) and fcc \( \delta-\text{NbN} \). Earlier works have demonstrated that the latter can accommodate more Al atoms in solid solution compared to the others NbN crystalline structures, retarding therefore B4-AlN or transitions phases formation in \( \text{Nb}_x\text{Al}_y\text{N}_z \) with \((y/x+y)\) ratio value up to 0.45\(^{14,15}\). Thus, a few works reported the thermal stability and tribological behavior for NbAlN cubic structure (B1 phase) with Al in solid solution\(^{14-17}\), however none systematically concerning the influence of aluminum content in B1-NbAlN on crystalline structure, chemical bonds, hardness and oxidation at high temperatures.
Hence, the present work aims to investigate how the morphological and structural characteristics impact hardness and oxidation resistance of Nb$_{x}$Al$_{y}$N$_{z}$ thin films with rock-salt cubic structure, as well as pure NbN and AlN coatings for comparative analyses. Coatings were characterized by Rutherford Backscattering Spectrometry (RBS), Glancing Angle X-ray Diffraction (GAXRD), X-ray photoelectron spectroscopy (XPS), nanohardness, oxidation tests at temperatures up to 873 K and Scanning Electron Microscope (SEM).

2. Material and Methods

Coatings were deposited by reactive magnetron sputtering with an AJA Orion equipment 5-HV Sputtering Systems model. Niobium and aluminum targets with purity of 99.99% were applied on RF and DC power supply, respectively. Polyethylene and silicon wafer substrates were subjected to ultrasonic bath for 20 minutes with distilled water and detergent and then dried. Furthermore, the silicon substrates were subjected to a bath in hydrofluoric acid solution to remove oxides existing on the surface. For Nb$_{x}$Al$_{y}$N$_{z}$ coatings all deposition parameters were kept constant, except for the Al target power which was varied to achieve different aluminum concentrations. Additionally, pure NbN and AlN coatings were deposited with the same basic parameters of Nb$_{x}$Al$_{y}$N$_{z}$ coatings, but using only one target at time. Prior to nitrides deposition, an interlayer of Nb for NbN and Nb$_{x}$Al$_{y}$N$_{z}$ samples and Al for AlN samples were deposited for 5 min. All main deposition parameters can be seen in Table 1.

RBS analysis were performed using a 3 MV Tandetron with alpha particles accelerated up to 2 MeV, with a silicon based detector at an angle of 165° and resolution of 12 keV. The GAXRD analyses were executed on a Shimadzu LabX XRD-6000 model (Cu-Kα radiation; λ = 1.54 Å) with a silicon wafer used in the present work for other characterizations. Similar spectra (not shown) were obtained for other characterizations. Surface morphology after oxidation tests was analyzed by SEM using a JEOL JCM 5700 microscope.

3. Results and Discussion

3.1 Composition characterization

Nb$_{x}$Al$_{y}$N$_{z}$ samples were analyzed by RBS in order to precisely determine chemical composition of the coatings. A typical RBS spectrum is shown in Figure 1, obtained from pure NbN and Nb$_{0.25}$Al$_{0.19}$O$_{0.05}$N$_{0.48}$ samples. Polyethylene substrates were employed for RBS analyses aiming to eliminate high background signal from the silicon wafer used in the present work for other characterizations. Similar spectra (not shown) were obtained for other Nb$_{x}$Al$_{y}$N$_{z}$ samples.

Additionally to the presence of aluminum peak, another noticeable difference between both spectra is the width and intensity in niobium and nitrogen peaks, respectively. The first fact is attributed to the increased thickness associated with aluminum incorporation, given that all parameters is non-monochromatic). The base pressure in the analysis chamber was about 10$^{-8}$ Pa. The anode was operated at 10 W (10 kV, 10 mA) and the analyzer was operated at constant pass energy of 50 eV for survey spectra and 20 eV for selected regions. Before analyzes, all samples were subjected to surface cleaning with Ar$^+$ (1.0 KeV) sputtering procedure for 10 minutes. The ion source IQE12/38 from SPECS was used, which allows the operation at 5 KeV beam energy. The incidence angle is preselected to be 50°, as the sample was not tilted (rotation angle at 0°). The binding energy shifts due to surface charging were corrected using the C 1s level at 284.6 eV, as an internal standard. The spectra were Shirley background-subtracted across the energy region and fitted using CasaXPS Version 2.3.15.

Hardness values were obtained through nanoindentation tests in a Fisherscope HV 100 with a Berkovich indenter. It was performed ten indentations for each analysis, with depth of 40 nm, 10 mN load and 60 seconds for indentation. Oxidation tests on NbN, AlN and Nb$_{x}$Al$_{y}$N$_{z}$ coatings were conducted in a traditional electrical resistance furnace. Samples were annealed in ambient atmosphere at 773 and 873 K for 30 minutes. Thereafter, samples were analyzed again by GAXRD and nanohardness tests using the same parameters mentioned above.

Table 1. Main deposition parameters for NbN, AlN and Nb$_{x}$Al$_{y}$N$_{z}$ coatings.

| Parameter | Value |
|-----------|-------|
| RF power applied to Nb target (W/cm$^2$) | 7.6 |
| (NbN, NbAlN$_{10}$, NbAlN$_{20}$ and NbAlN$_{40}$) |
| DC power applied to Al target (W/cm$^2$) | |
| Base Pressure (Pa) | 1×10$^{-5}$ |
| Working Pressure (Pa) | 3×10$^{-1}$ |
| Flow rates (sccm) | Ar=14; N$_2$=7 |
| (NbN, NbAlN$_{10}$, NbAlN$_{20}$ and NbAlN$_{40}$) | 2 min; 3×10$^{-3}$Pa; 100% Ar; 20 sccm; 7.6 W |

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Figure 1. RBS result for the NbN and Nb$_{0.28}$Al$_{0.19}$O$_{0.05}$N$_{0.48}$ samples.

Regarding NbN were kept constant in all samples. The latter is related to nitrogen raised concentration due to establishment of Al - N bonds.

Using computational simulation software X-rump it was possible to estimate the variation of aluminum concentration for RBS spectra. Table 2 shows the chemical composition obtained for all samples, which nomenclatures are based on Al/(Nb+Al) ratio. Oxygen detected in the samples can be explained as a contaminant derived from reactions between Nb and residual O$_2$/H$_2$O molecules adsorbed in the chamber, though similar oxygen concentrations are frequently found for nitrides deposited by reactive magnetron sputtering.

3.2. Structure analysis

GAXRD obtained from as deposited AlN, NbN, NbAIN$_{10}$, NbAIN$_{20}$ and NbAIN$_{40}$ samples are shown in Figure 2. AlN sample showed a hexagonal wurtzite B4 (JCPDS 65 - 1902) structure while NbN presented a cubic rock-salt B1 (JCPDS 38 - 1155). Nb$_{x}$Al$_{y}$N$_z$ patterns maintained NbN peaks, with no AlN phase identified. The peak at 38.2° is related to the BCC niobium phase from Nb interlayer primarily deposited for all Nb$_{x}$Al$_{y}$N$_z$ samples (JCPDS 35 - 789). The Al interlayer peak was also observed on AlN diffractogram at 44.6° (JCPDS 4 - 787).

Aluminum atoms addition in the ternary nitride coatings promoted a shift of all NbN peaks to larger angles regions, suggesting an interplanar distance shrinkage, from 4.38 Å for pure NbN to 4.28 Å for NbAIN$_{40}$ sample. Such fact is related to the substitution of Nb by Al atoms, since aluminum possess a smaller ionic radius compared to niobium, 0.54 Å and 0.72 Å, respectively.

The average crystallite size was estimated by Debye-Scherrer equation using the FWHM value from XRD diffraction peaks. The values for samples NbN, NbAIN$_{10}$ and NbAIN$_{20}$ were basically the same, varying from 11.7 nm to 11.1 nm. However, for NbAIN$_{40}$ the calculated crystallite size value was 13.1 nm, which is greater than pure NbN and reveals a higher degree of crystallinity when compared to other percentages.

In contrast, it is interesting to observe that this last sample presented a broadening in (200) peak. According to literature, at Al/(Nb+Al) ratio value close to 0.45, NbAIN cubic structure transforms into hexagonal B$_2$ phase, which represents the transition between B1 and B4 phases and possess a similar formation energy to the cubic NbAIN structure. Thus, such broadening probably indicates the start point in a tendency to form the B$_2$ transition phase. That fact, associated with the strong shift of B1-NbN peaks to higher angles, suggests that in sample NbAIN$_{40}$ the aluminum addition induced the disorder of original NbN cubic structure more intensively in order to better accommodate aluminum atoms. In other words, although the highest percentage of Al atoms resulted in the increased grain size for plane (111), the solid solution NbAIN with 40 at.% Al is probably close to its solubility limit.

| Sample        | Nb (at.%) | Al (at.%) | N (at.%) | O (at.%) | (Al/(Nb+Al))*100 |
|---------------|-----------|-----------|----------|----------|------------------|
| NbN           | 47.6      | -         | 47.6     | 4.8      | -                |
| NbAIN$_{10}$  | 40.6      | 4.9       | 49.6     | 4.9      | 10.7             |
| NbAIN$_{20}$  | 37.2      | 9.7       | 48.3     | 4.8      | 20.6             |
| NbAIN$_{40}$  | 28.6      | 19.1      | 47.6     | 4.7      | 40.0             |
For a better understanding of the formed structures, XPS analyses were performed and core-level spectra of Nb 3d, Al 2p and N 1s regions from NbN, AlN and Nb$_{x}$Al$_{y}$N$_{z}$ samples are shown in Figure 3a, 3b and 3c, respectively. Sample NbAIN$_{40}$ spectra for all regions presented very similar results compared to NbAIN$_{40}$ sample and, for better spectra visualization, these analyses will not be shown.

Figure 3a shows Nb 3d photoelectron region from NbN, NbAIN$_{10}$ and NbAIN$_{40}$. The best fit deconvolution yielded three doublets, the component with lower binding energy (203.3 - 206.8 eV) was attributed to Nb 3d$_{5/2}$ - Nb 3d$_{3/2}$ electrons of NbN compound$^{17,20}$. The doublet component at binding energy 204.0 eV (Nb 3d$_{5/2}$) was assigned to Nb-O-N oxynitrides$^{17,20,21}$. It could also be identified a small contribution from Nb-O oxide phases at 206 eV for Nb 3d$_{5/2}$ and 208.8 eV for Nb 3d$_{3/2}$, and these results are in agreement with previous works$^{17,24}$, where oxide compounds are commonly identified in sputtered thin films, and has also been found in RBS analyses. No significant binding energy shift was observed in this region as the Al concentration was raised.

The best fit from N 1s region for NbAIN$_{40}$ samples is shown in Figure 3b. From AlN sample, N 1s spectrum was deconvoluted into two peaks. Peaks identified at 396.3 eV and 397.7 eV were attributed to AlN and Al-O-N oxynitrides, respectively$^{20,26}$. The core-level spectra from NbN sample yielded two peaks at 396.7 and 397.4 eV, attributed to NbN compounds and Nb-O-N oxynitride presence.

The NbAIN$_{10}$ core-level spectra showed a peak centered at 396.9 eV, associated to NbN compounds, a peak at 396.3 eV attributed to Al-N bond$^{17,24}$, and a weak peak centered at 397.6 eV identified as Nb-O-N oxynitride compounds$^{17,27}$. From NbAIN$_{40}$ sample, the N 1s spectrum revealed the presence of characteristic peaks of NbN (396.7 eV) and AlN (395.9 eV) nitrides, in addition to oxynitride presence (394.7 eV). It is possible to observe a tendency of reduction on energy values attributed to Al-N bonds with the increase of aluminum concentration. However, this displacement is lower than 0.5 eV, thus it is not possible to ensure a significant change. From Holec et al.$^{28}$, the charge transfer in a solid solution formed by Nb$_{x}$Al$_{y}$N$_{z}$ with cubic structure presents a greater dispersion for N atoms. The charge transfer is larger from Al to N than from Nb to N, which suggest that the Al-N bond is more ionic than Nb-N one.

In parallel, Al 2p spectrum of AlN and NbAIN$_{40}$ samples (Figure 3c) showed a peak at a binding energy of 73.4 eV, that could be assigned to AlN compounds$^{27,29-31}$. Due to the high background noise caused by low aluminum concentration, the spectrum obtained for samples NbAIN$_{10}$ and NbAIN$_{20}$ will not be shown. No significant binding energy shift was observed between pure AlN and NbAIN$_{40}$ samples. The best fit deconvolution of this band also indicated the presence of a weak peak centered at 74.3 eV, which was attributed to the presence of aluminum oxides$^{29,31,32}$.

From Nb 3d and Al 2p regions it is possible to suggest that the electronic surroundings of both atoms is not affected by the presence of the other. This fact may be associated with the similar electro negativity between Nb and Al atoms, which is 1.6 and 1.5, respectively. From this, no significant change in binding energies could be observed in XPS spectra. Based on these facts, it is possible to suggest that the behavior observed on XPS analyses is in agreement with what was observed by GAXRD analyses, towards the formation of a solid solution and reinforcing that aluminum replaces niobium atoms in the NbN lattice.

### 3.3 Nanohardness analysis

Mechanical behavior of as deposited thin films was verified through nanohardness tests. The hardness values obtained for samples AlN, NbN and Nb$_{x}$Al$_{y}$N$_{z}$ are shown in Figure 4. For AlN sample the hardness value obtained was 18.6 GPa, which has already been reported by others authors$^{11,33,34}$. The hardness value observed for NbN was 23.8 GPa, similar results were observed in previous works for the B1-NbN phase$^{35,36}$.

NbAIN$_{10}$ and NbAIN$_{20}$ samples presented similar results, varying between 25.4 and 26.3 GPa. Although these values are statistically close to NbN hardness value, it is possible to note a slight improvement, possibly due to the solid solution strengthening mechanism derived from the lattice constant shrinkage. Contrarily, the sample NbAIN$_{40}$ presented a tendency of decreasing the hardness value compared to others Nb$_{x}$Al$_{y}$N$_{z}$ and NbN thin films, registering a value of 22.8 GPa. This change in hardness behavior might be attributed to the growth of grain, but the amorphization observed in peak (200) previously discussed in XRD results could also slightly influence the hardness value. Indeed, according to the literature, B1-NbAIN phase
It is a fact that increasing the temperature further facilitates the diffusion of oxygen within the coatings. Oxidation reactions begin at the interface between the surface oxide layer and the thin film, as the amorphous layer thickens, micropores are formed on the surface, favoring oxygen diffusion. In addition, \( N_2 \) gas is released as one of the oxidation reaction products, which generates even more pores and microcracks.

Earlier works\(^{40,41}\) studied the oxidation of NbN thin films, in this case it was found that as the oxygen rate increases after oxidation at 400° C, the nitrogen concentration decreases. \( \text{Nb}_2 \text{O}_5 \) formation over other oxides occurs due to the largest negative Gibbs free energy of \( \text{Nb}_2 \text{O}_5 (\Delta G_{1600K} = -1,215,608 \text{ J/mol Nb}) \) in comparison with \( \text{NbO} (\Delta G_{1600K} = -277,111 \text{ J/mol Nb}) \) and \( \text{NbO}_2 (\Delta G_{1600K} = -515,186 \text{ J/mol Nb}) \), showing a large difference even compared to that reported for NbN (\( \Delta G_{1600K} = -85,208 \text{ J/mol Nb} \)) and \( \text{Nb}_2 \text{N} (\Delta G_{1600K} = -94.715 \text{ J/mol Nb}) \).

As noticed in previous works\(^{17,42}\), in high oxidation temperatures the aluminum atoms present in the NbAlN thin films microstructure diffuse into grain boundary and surface regions, forming amorphous Al\( _2 \)O\( _3 \). In Figure 3c, Al\( _2 \)O\( _3 \) was detected by XPS analysis in AlN and NbAlN\( _{40} \) samples as deposited, but due to its amorphous behavior, cannot be observed in the GAXRD analysis.

GAXRD results after oxidation tests at high temperatures for NbAlN\( _{20} \) and NbAlN\( _{40} \) samples are shown in Figure 6a and 6b, respectively. Differently from samples NbN and NbAlN\( _{10} \), no relevant modification can be observed after exposure to 773 K for sample NbAlN\( _{20} \). At 873 K it is possible to identify the beginning of niobium oxide formation at 22.5°. However, it is still noted the presence of small peaks related to NbN cubic phase and Nb interlayer peak, proving that the coating is not completely oxidized.

For NbAlN\( _{40} \) sample, \( \text{Nb}_2 \text{O}_5 \) formation was not observed in any oxidation temperature and the presence of Nb interlayer is observed even at the highest oxidation test temperature. No considerable modification can be found in
XRD pattern for as deposited sample and when subjected to 873 K or lower.

The behavior of as deposited pure AlN thin film and after oxidation tests at high temperatures can be observed in Figure 7. No modification in AlN patterns or aluminum oxide formation could be found when the coatings were exposed to high temperatures. Similar results were observed earlier, proving the excellent stability at high temperatures for these coatings. Contrary to nanohardness analyses, where aluminum addition in NbN matrix did not modify significantly the Nb\(_x\)Al\(_y\)N\(_z\) coatings hardness, it is possible to observe an expressive and crescent enhancement in oxidation resistance from pure NbN to NbAlN\(_{40}\) sample, proving that incorporation of Al atoms in solid solution reinforce the oxidation resistance of NbN structure.

3.5 Nanohardness and morphological characterization after oxidation tests

Subsequently to oxidation tests, samples were subjected surface SEM analyses and nanohardness tests in order to verify the coatings integrity after exposure to high temperatures. AlN, NbN, NbAlN\(_{10}\) and NbAlN\(_{20}\) coatings showed a drastic reduction in hardness values when exposed to 873 K. Coincidentally, these samples presented a hardness value near to 9 GPa, similar to those found for silicon wafer used as substrate. On the other hand, sample NbAlN\(_{40}\) presented a higher value of 17 GPa, registering a reduction of 20% in relation to the as deposited coating.

Aiming to better elucidate the reduction in coatings hardness after oxidation tests, surface SEM analyses were carried out. All studied as deposited samples presented a regular aspect, without cracks, bubbles or visible defects (not shown).

Figure 8a presents the result for sample AlN after 873 K. It is possible to verify the appearance of many cracks on the sample surface as the oxidation temperature was increased. Thus, although AlN thin films exhibit good resistance to oxidation when exposed to high temperatures (Figure 7), it showed thermal fragile characteristics probably due to cooling from 873 K to ambient temperature, justifying the loss in hardness.

SEM images obtained from NbN, NbAlN\(_{10}\), NbAlN\(_{20}\) and NbAlN\(_{40}\) samples show comparable results. NbN and NbAlN\(_{10}\) coatings after oxidation at 773 K already presented the formation of erupted bubbles on the material surface, as showed in Figure 8b and Figure 8c for samples NbN and NbAlN\(_{10}\), respectively. Such fact is attributed to nitrogen gas release after the transformation of NbN into Nb\(_2\)O\(_5\) by oxidation reactions. Nitrogen molecules formation can lead to the rupture of bubbles, allowing exposure of the substrate. Samples NbAlN\(_{20}\) and NbAlN\(_{40}\) also present bubbles, but none burst. In this context, such surface defects along with regions where the substrate was exposed have a direct influence on the hardness values measurement obtained for these samples.

For sample NbAlN\(_{40}\), despite the maintenance of the NbN cubic phase verified in the GAXRD analysis, it was possible to verify some concentration of defects, represented
by the white agglomerates (Figure 8d). However, they are in lower concentration when compared to other samples. Presence of agglomerates may be caused by the onset of oxide formation on the surface, explaining the reduction in hardness value verified after the oxidation test for this sample. Nevertheless, substrate exposure is not observed, being possible to conclude that NbAlN_40 sample still presents significant value compared to the literature\textsuperscript{15}, showing the best results observed with GAXRD and nanohardness tests. Nonetheless, SEM analyses prove the coating integrity was not maintained after 873 K.

4. Conclusions

The influence of aluminum concentration in Nb_{x}Al_{y}N_{z} solid solution thin films was studied in this work. From GAXRD results it was possible to observe that aluminum addition in the thin films did not change the B1-NbN phase observed in pure NbN. However, peak shifts to larger angles were observed, indicating the shrinkage of lattice constant and the formation of a solid solution, hypotheses ratified by XPS analyses. Nanohardness analyses suggest no significant modification in hardness values among NbN and Nb_{x}Al_{y}N_{z} coatings. On the other hand, GAXRD analyses of oxidized samples showed that aluminum addition improves substantially the oxidation resistance at high temperatures, with further increments as Al content was gradually raised in Nb_{x}Al_{y}N_{z} coatings. Samples AlN, NbN, NbAlN_10 and NbAlN_20 after oxidation tests present hardness values identical to the silicon wafer, suggesting the substrate was exposed, what was confirmed by surface SEM analysis. The images reveal the presence of cracks and bubbles in all coatings. However, GAXRD showed that NbAlN_40 presented the best results against oxidation at high temperatures while hardness value was less affected.

5. Acknowledgements

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6. References

1. Fenker M, Balzer M, Büchi R, Jehn H, Kappl H, Lee JJ. Deposition of NbN thin films onto high-speed steel using reactive magnetron sputtering for corrosion protective applications. \textit{Surface and Coatings Technology}. 2003;163-164:169-75.
2. Cansever N, Danisman M, Kazmanli K. The effect of nitrogen pressure on cathodic arc deposited NbN thin films. *Surface and Coatings Technology*. 2008;202(24):5919-23.

3. Rutherford KL, Hatto PW, Davies C, Hutchings IM. Abrasive wear resistance of TiN/NbN multi-layers: measurement and neural network modelling. *Surface and Coatings Technology*. 1996;86-87(Pt 2):472-9.

4. Selinder T, Sjostrand ME, Larsson M, Ostlund A, Hofmark S. Performance of PVD TiN/TaN and TiN/NbN superlattice coated cemented carbide tools in stainless steel machining. *Surface and Coatings Technology*. 1998;105(1):51-5.

5. Hultman L, Engstrom C, Odem D. Mechanical and thermal stability of TiN/NbN superlattice thin films. *Surface and Coatings Technology*. 2000;133:227-33.

6. Barshilia HC, Rajam KS, Jain A, Gopinadhan K, Chaudhary S. A comparative study on the structure and properties of nanolayered TiN/NbN and TaIN/TiN multilayer coatings prepared by reactive direct current magnetron sputtering. *Thin Solid Films*. 2006;503:158-66.

7. Paldey S, Deevi S. Single layer and multilayer wear resistant coatings of (Ti,Al)N: a review. *Materials Science and Engineering: A*. 2003;342(1-2):58-79.

8. Wang YX, Zhang S, Lee JW, Lew WS, Li B. Influence of bias voltage on the hardness and toughness of CrAIN coatings via magnetron sputtering. *Surface and Coatings Technology*. 2012;206:5103-7.

9. Badini C, Deambrosis SM, Ostrovskaya O, Zin V, Padovano E, Miorin E, et al. Cyclic oxidation in burner rig of NbN films deposited by reactive direct current magnetron sputtering. *Ceramics International*. 2017;43(7):5417-26.

10. Badini C, Deambrosis SM, Ostrovskaya O, Zin V, Padovano E, Miorin E, et al. Cyclic oxidation in burner rig of NbN films deposited by reactive direct current magnetron sputtering. *Ceramics International*. 2017;43(7):5417-26.

11. Barshilia HC, Rajam KS, Jain A, Gopinadhan K, Chaudhary S. A comparative study on the structure and properties of nanolayered TiN/NbN and TaIN/TiN multilayer coatings prepared by reactive direct current magnetron sputtering. *Thin Solid Films*. 2006;503:158-66.

12. Boiko VI, Valyaev AN, Pogrebnyak AD. Metal modification by high-power pulsed particle beams. *Uspekhi Fiz Nauk*. 2008;169:1243-71.

13. Li D, Chen J, Che J, Liu D, Li Y. Effects of Al concentrations on the microstructure and mechanical properties of Ti-Al-N films deposited by RF-ICPIS enhanced magnetron sputtering. *Journal of Alloys and Compounds*. 2014;609:239-43.

14. Franz R, Lechthaler M, Polzer C, Mitterer C. Structure, mechanical properties and oxidation behaviour of arc-evaporated NbAIN hard coatings. *Surface and Coatings Technology*. 2010;204(15):2447-53.

15. Benkahoul M, Zayed MK, Sandu CS, Martinu L, Klemberg-Sapieha JE. Structural, tribo-mechanical, and thermal properties of NbAlN coatings with various Al contents deposited by DC reactive magnetron sputtering. *Surface and Coatings Technology*. 2017;331:172-8.

16. Franz R, Lechthaler M, Polzik P, Figueiredo MR, Mitterer C. Tribological properties of arc-evaporated NbAlN hard coatings. *Tribology Letters*. 2012;45(1):143-52.

17. Barshilia HC, Deepthi B, Rajam KS, Bhatta KP, Chaudhary S. Structure and properties of reactive direct current magnetron sputtered niobium aluminum nitride coatings. *Journal of Materials Research*. 2008;23(5):1258-68.

18. Shannon RD. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallographica*. 1976;A32:751-67.

19. Holec D, Franz R, Mayrhofer PH, Mitterer C. Structure and stability of phases within the NbN - AlN system. *Journal of Physics D: Applied Physics*. 2010;43(14):145403.

20. Liu N, Dong L, Jin S, Wan R, Gu H, Li D. Significant impact of individual surface and modulation structure on mechanical properties of NbN/NbB2 multilayers. *Journal of Alloys and Compounds*. 2017;695:3225-32.

21. Pogrebnyak AD, Bondar OV, Abadhas I, Ivashchenko V, Sobol O V, Jurga S, et al. Structural and mechanical properties of NbN and Nb-Si-N films: Experiment and molecular dynamics simulations. *Ceramics International*. 2016;42(10):11743-56.

22. Ufuktepe Y, Farha AH, Kimura S, Hajiri T, Karadag F, Al Mamun MA, et al. Structural, electronic, and mechanical properties of niobium nitride prepared by thermal diffusion in nitrogen. *Materials Chemistry and Physics*. 2013;141(1):393-400.

23. Alfonso JE, Buitrago J, Torres J, Santos B, Marco JF. Crystallographic structure and surface composition of NbNx thin films grown by RF magnetron sputtering. *Microelectronics Journal*. 2008;39(11):1327-8.

24. Ermolieff A, Giraud M, Raoul C, Duc TM. An XPS comparative study on thermal oxide barrier formation on Nb and NbN thin films. *Applied Surface Science*. 1985;21(1-4):65-79.

25. Ivashchenko VI, Dub SN, Scrynskii PL, Pogrebnyak AD, Sobol’ OV, Tolmacheva GN, et al. Nb-Al-N thin films: Structural transition from nanocrystalline solid solution nc-(Nb,Al)N into nanocomposite nc-(Nb,Al)N/a-AlN. *Journal of Superhard Materials*. 2016;38(2):103-13.

26. Ozgut C, Donmez I, Alevli M, Biyikli N. Self-limiting low-temperature growth of crystalline AlN thin films by plasma-enhanced atomic layer deposition. *Thin Solid Films*. 2012;520(7):2750-5.

27. Wei Q, Zhang X, Liu D, Li J, Zhou K, Zhang D, et al. Effects of sputtering pressure on nanostructure and nanomechanical properties of AlN films prepared by RF reactive sputtering. *Transactions of Nonferrous Metals Society of China*. 2014;24(9):2845-55.

28. Delpeux S, Beguin F, Benoit R, Erre R, Manolova N, Rashkov I. Fullerene core star-like polymers-1. Preparation from fullerenes and monoazidopolyethers. *European Polymer Journal*. 1998;34(7):905-15.

29. Park MH, Kim SH. Thermal conductivity of AlN thin films deposited by RF magnetron sputtering. *Materials Science in Semiconductor Processing*. 2012;15(1):6-10.
30. Ivashchenko VI, Scrynskyy PL, Lytvyn OS, Butenko OO, Sinelnichenko OK, Gorb L, et al. Comparative investigation of NbN and Nb-Si-N films: Experiment and theory. *Journal of Superhard Materials*. 2014;36(6):381-92.

31. Motamedi P, Cadier K. XPS analysis of AlN thin films deposited by plasma enhanced atomic layer deposition. *Applied Surface Science*. 2014;315(1):104-9.

32. Milošev I, Kosec T, Strehblow HH. XPS and EIS study of the passive film formed on orthopaedic Ti-6Al-7Nb alloy in Hank’s physiological solution. *Electrochimica Acta*. 2008;53(9):3547-58.

33. Panda P, Ramaseshan R. Effects of Cr doping on the mechanical properties of AlN films grown by the co-sputtering technique. *Ceramics International*. 2018;45(2)(Pt A):1755-60.

34. Li W, Zhang K, Liu P, Zheng W, Ma F, Chen X, et al. Microstructural characterization and strengthening mechanism of AlN / Y nanocomposite and nanomultilayered films. *Journal of Alloys and Compounds*. 2018;732:414-21.

35. Benkahoul M, Martinez E, Karimi A, Sanjinés R, Lévy F. Structural and mechanical properties of sputtered cubic and hexagonal NbN thin films. *Surface and Coatings Technology*. 2004;180-181:178-83.

36. Fontalvo GA, Terziyska V, Mitterer C. High-temperature tribological behavior of sputtered NbNx thin films. *Surface and Coatings Technology*. 2007;202(4-7):1017-22.

37. Wang L, Zhang G, Wood RJK, Wang SC, Xue Q. Fabrication of CrAlN nanocomposite films with high hardness and excellent anti-wear performance for gear application. *Surface and Coatings Technology*. 2010;204(21-22):3517-24.

38. Xiao X, Yao B. Structure and oxidation resistance of W1 - xAlxN composite films. *Transactions of Nonferrous Metals Society of China*. 2017;27(5):1063-70.

39. Frankenthal RP, Siconolfi DJ, Sinclair WR, Bacon DD. Thermal Oxidation of Niobium Nitride Films at Temperatures from 200-400°C. *Journal of the Electrochemical Society*. 2006;153(10):2056-60.

40. Gallagher PK, Sinclair WR, Bacon DD, Kammlott GW. Oxidation of Sputtered Niobium Nitride Films. *Journal of the Electrochemical Society*. 2006;153(10):2054-56.

41. Oliveira RM, Hoshida L, Oliveira AC, Silva MMNF, Pichon L, Santos NM. Evaluation of the resistance to oxidation of niobium treated by high temperature nitrogen Plasma Based Ion Implantation. *Surface and Coatings Technology*. 2017;312:110-6.

42. Ichimura H, Kawana A. High-temperature oxidation of ion-plated TiN and TiAlN films. *Journal of Materials Research*. 1993;8(5):1093-100.

43. Kar JP, Bose G, Tuli S. Influence of rapid thermal annealing on morphological and electrical properties of RF sputtered AlN films. *Materials Science in Semiconductor Processing*. 2005;8(6):646-51.