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Crystalline-to-amorphous structure transitions in TiNbN coatings during short-time oxidation

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Background

High temperature nitride coatings are widely used for surface protection of critical components in harsh environments because of their excellent mechanical properties, high melting point, high thermal stability and high temperature oxidation resistance.

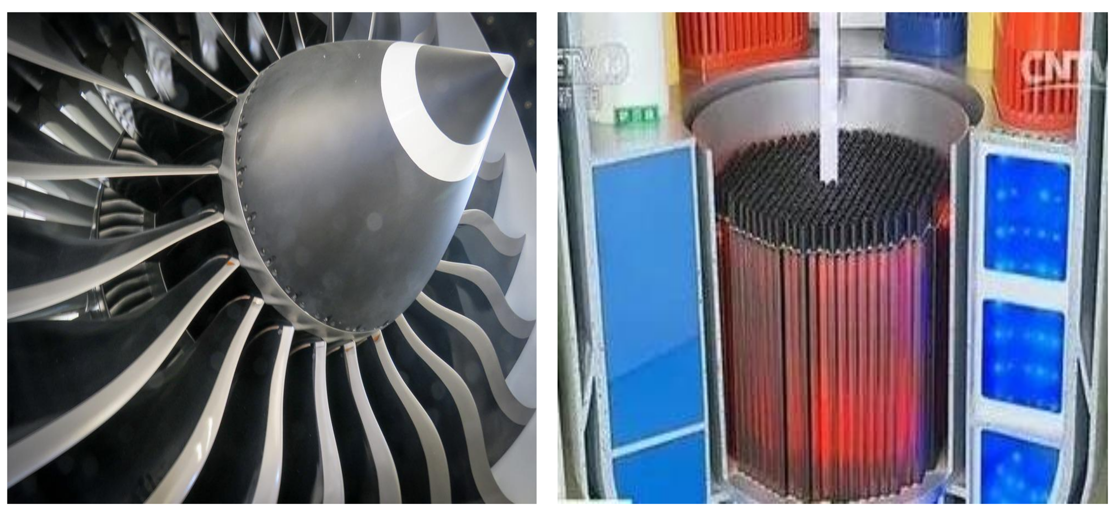

Fig. 1. Applications of nitride coatings.

Methodology

In this work, two types of magnetron sputtered TiNbN coatings with different Ti/Nb atomic ratios were studied using X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and nano-indentation. Aided by the CALPHAD approach, the variations in chemical composition, microstructure and properties in the as-deposited and as-oxidized (at 500 °C up to 300 s) coatings were systematically analyzed to explore their composition-structure-property relationships.

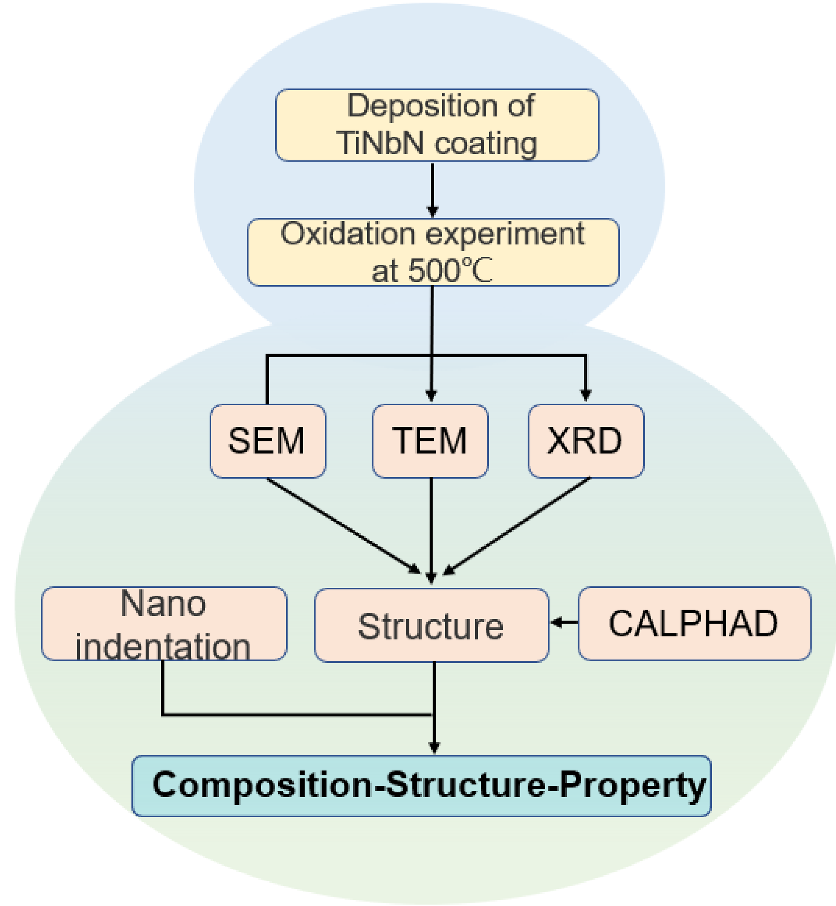

Fig. 2. Workflow chart.

Morphology

Table .1. Composition of coatings (at.%).

Films	Ti	Nb	N
$Ti_{0.5}Nb_{0.5}N$	17.89	15.73	66.38
$Ti_{0.8}Nb_{0.2}N$	38.05	8.92	53.03

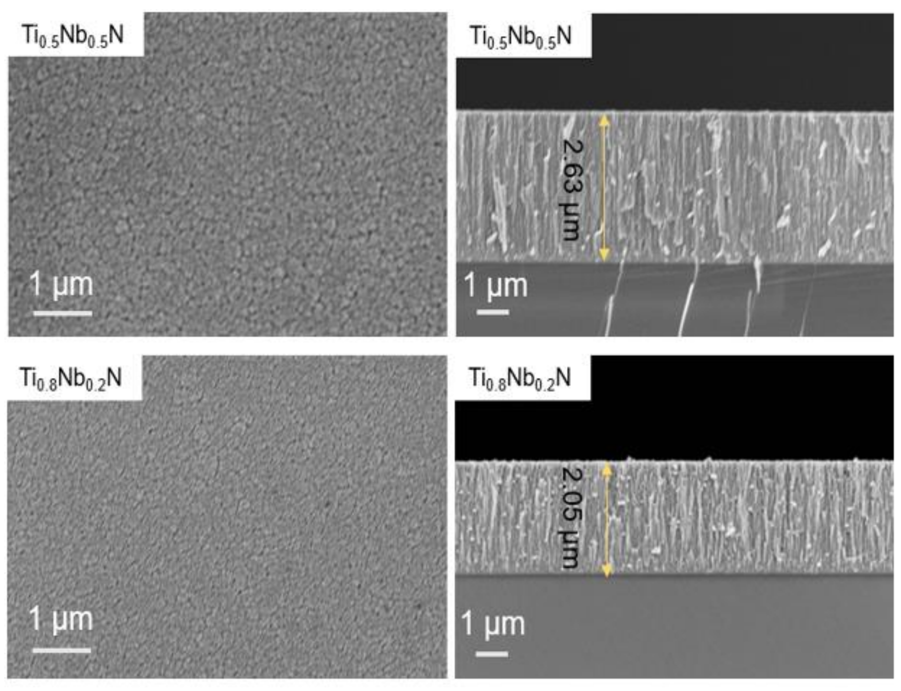

Fig. 3. Surface and cross-sectional morphologies of $Ti_{0.5}Nb_{0.5}N$ and $Ti_{0.8}N_{0.2}N$ coatings.

- The surface of $Ti_{0.8}Nb_{0.2}N$ coating is denser than that of $Ti_{0.5}Nb_{0.5}N$ coating.

Microstructure and mechanical properties

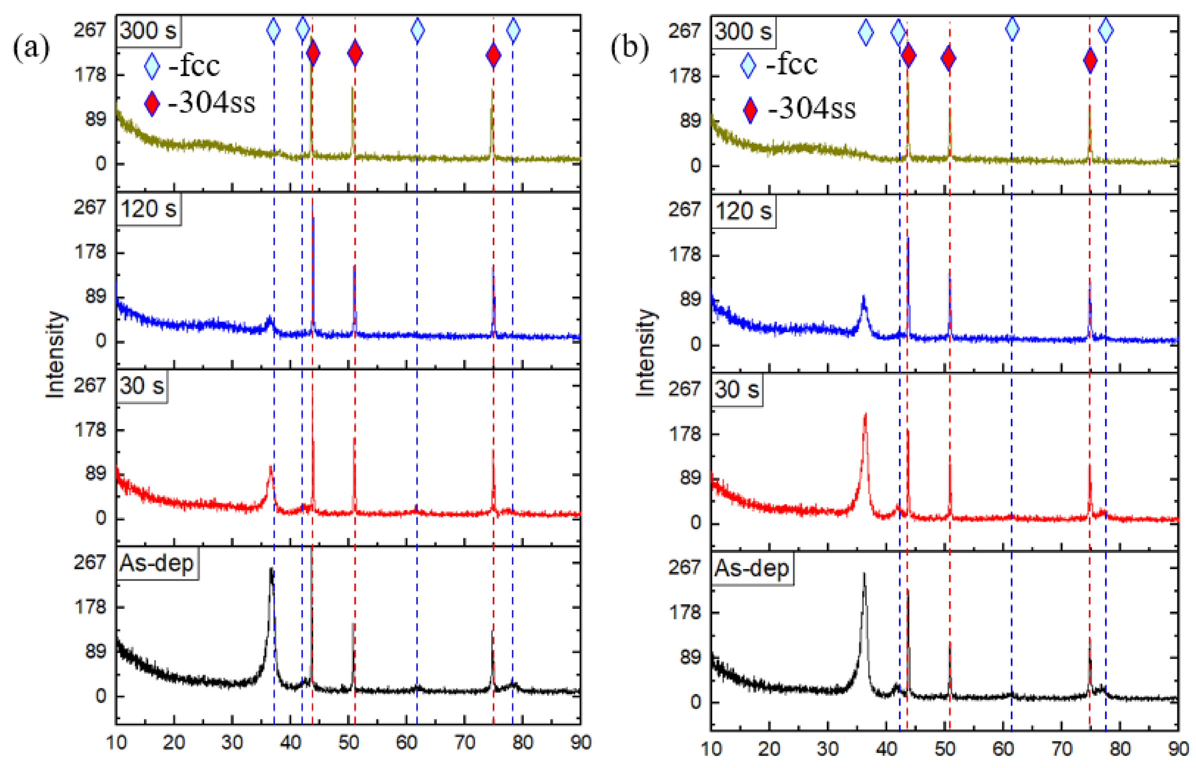

Fig. 4. XRD patterns of the coatings in the as-deposited condition and after oxidation at 500 ℃ for 30, 120 and 300s: (a) $Ti_{0.5}Nb_{0.5}N$ and (b) $Ti_{0.8}Nb_{0.2}N$.

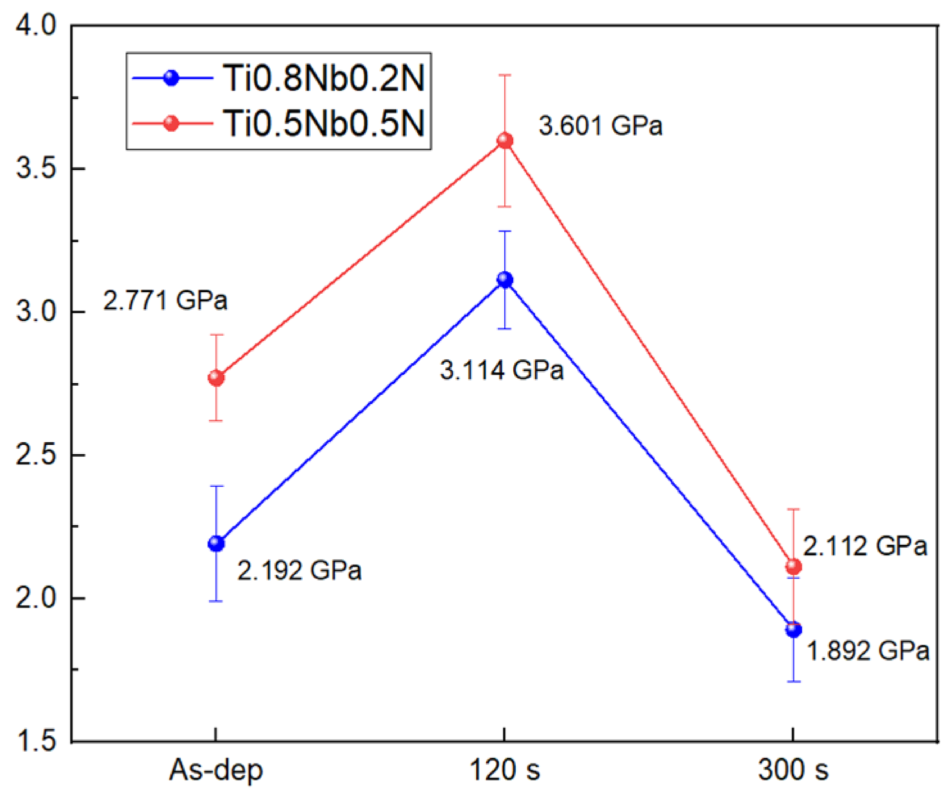

Fig. 5. Hardness of the as-deposited coating and the coatings oxidized at 500 ℃ for 120 and 300s.

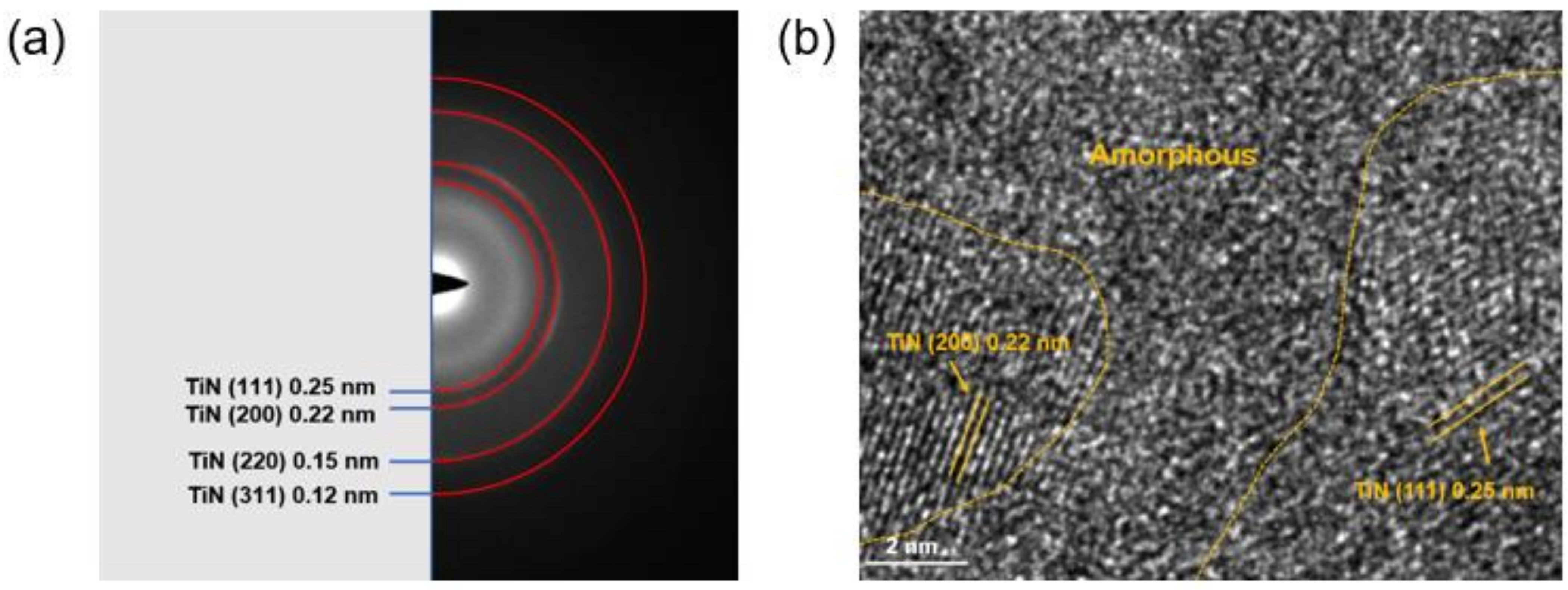

Fig. 6. (a) Fast Fourier transform (FFT) derived diffraction patterns of $Ti_{0.5}Nb_{0.5}N$ coating oxidized at 500℃ for 120 s and high-resolution (HR) TEM image

- The XRD patterns show that with the increase of oxidation time, the characteristic peaks of fcc nitride gradually weakened. After oxidized at 500 ℃ for 300 s, these peaks disappeared completely, and the coating evolved into complete amorphous. The amorphization degree of the $Ti_{0.5}Nb_{0.5}N$ coating is higher than that of $Ti_{0.8}Nb_{0.2}N$ coating in the early stage of oxidation.
- TEM shows the co-existence of amorphous and nanocrystals in the oxidized $Ti_{0.5}Nb_{0.5}N$ coating. According to the nano-indentation test, higher hardness values were recorded on the coatings oxidized for 120 s, as compared to the as-deposited coatings and those oxidized for 300 s. The hardness of the coatings after oxidation for 300 s is the lowest.

Conclusions

In this work, the variations in phase composition and structure of the $Ti_{0.5}Nb_{0.5}N$ and $Ti_{0.8}Nb_{0.2}N$ coatings prior to and after the short-time oxidation (at 500 °C up to 300 s) were systematically studied.

- **The crystalline-amorphous structure transitions are more obvious with a higher Nb/Ti atomic ratio.**
- **The hardness of the TiNbN coatings increases with the precipitation of nanocrystals.**
- **The formation of a mixed structure consisting of nanocrystals embedded in an amorphous matrix may be beneficial to the enhancement of coatings' hardness.**

Expectations

Future work will focus on the following two aspects:

1. Clarify the crystalline-amorphous evolution process of the short-time oxidized TiNbN coatings aided by CALPHAD approach.
2. Study the friction and wear properties of the nanocrystalline and fully amorphous TiNbN coatings.

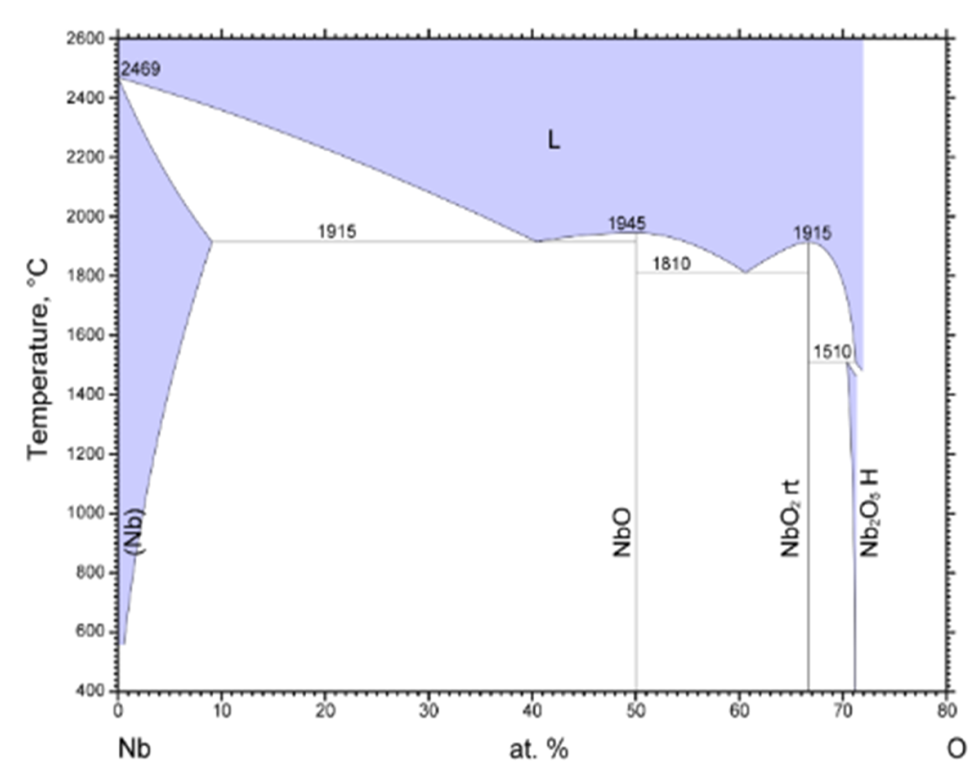

Fig. 7. Nb-O binary phase diagram 0-80 at.% by Okamoto H et al.

Acknowledgment: Financial supports from National Natural Science Foundation of China (51971235), Ningbo 3315 Innovation Team (No. 2019A-18-C) and CAS Pioneer Hundred Talents Program are greatly acknowledged.