NanoTechnology Centre for PVD Research

Novel HIPIMS deposited nanostructured CrN/NbN coatings for environmental protection of steam turbine components.

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National HIPIMS Technology Centre, UK

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MATERIALS AND ENGINEERING RESEARCH INSTITUTE

Motivation

•The main challenges: material failure due to high temperature oxidation, and phenomenon such as creep, erosion and descaling after a stipulated period of time.

•Over the years considerable research has been done in finding solution to the above problems in terms of protective surface layers with limited success.

• Coating technologies investigated are limited to: slurry deposition, pack cementation, sol gel, spray technologies. PVD technology has never been attempted.

Our approach:

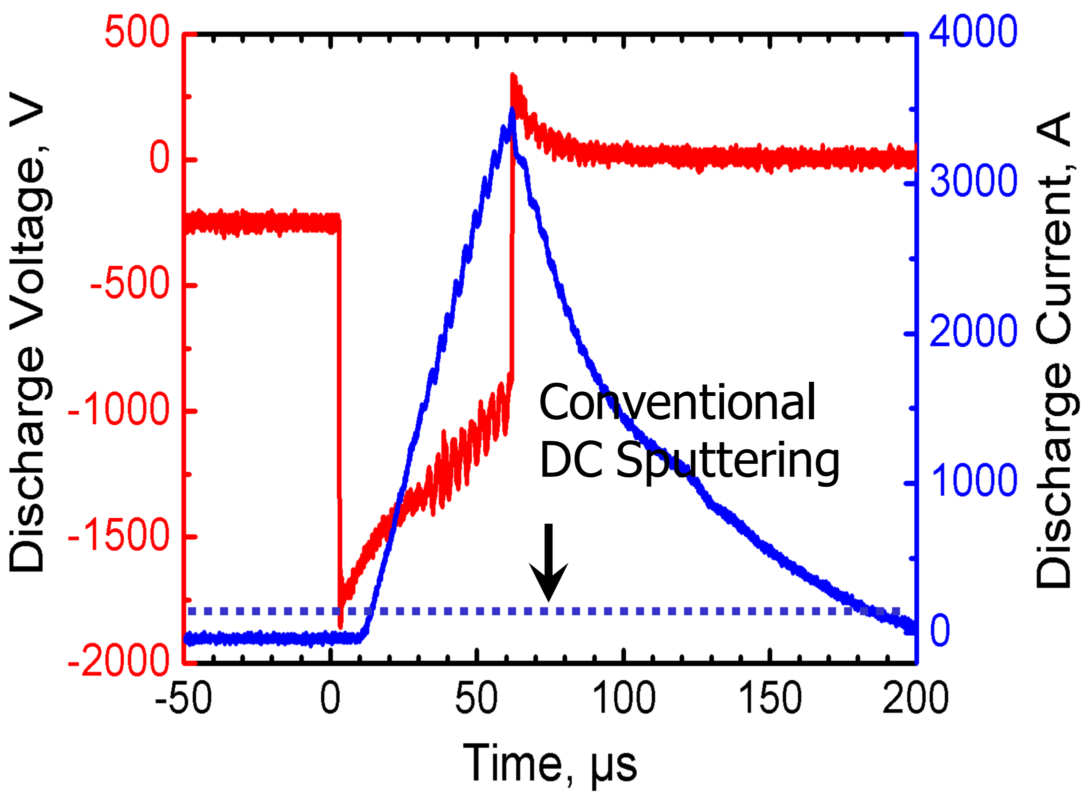
•In the current work, 4 µm thick CrN/NbN coating utilising nanoscale multilayer structure with bi-layer thickness of Δ = 2.9 nm has been used to protect low Cr content P92 steel widely employed in steam power plants.

•The uniquely layered coatings have a combination of nitrides of chromium and niobium which are not only resistant to aqueous corrosion,[1] corrosion erosion, [2] and excellent tribological properties,[3] but also have oxidation resistant in dry air up to a temperature of 850 °C, [4].

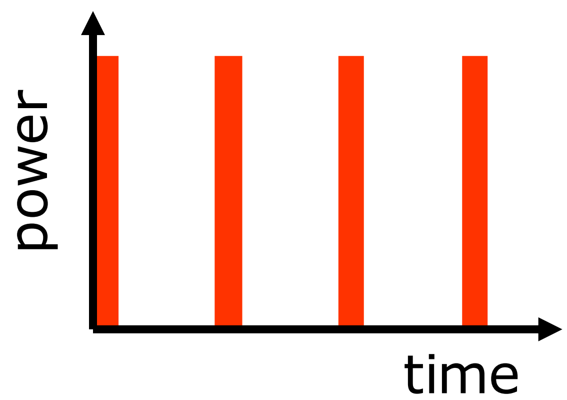
• The novel High Power Impulse Magnetron Sputtering (HIPIMS) deposition technology has been used to deposit CrN/NbN.

[1] P. Eh. Hovsepian et all Surface and Coatings Technology, 120-121 (1999), p. 535-541.
[2] Y.P. Purandare at all, Surface and Coatings Technology 01/2006; 201(1):361-370
[3] P. Eh. Hovsepian et all, Surface and Coatings Technology, 133-134 (2000), p. 166-175
[4] P. Eh. Hovsepian et all,Journal of Surface Engineering, vol. 11.p. 41-46, Edited by H. Dimigen.

6 MW (3000 Wcm^{-2})



Industrial Scale HIPIMS using Huettinger power supplies at SHU



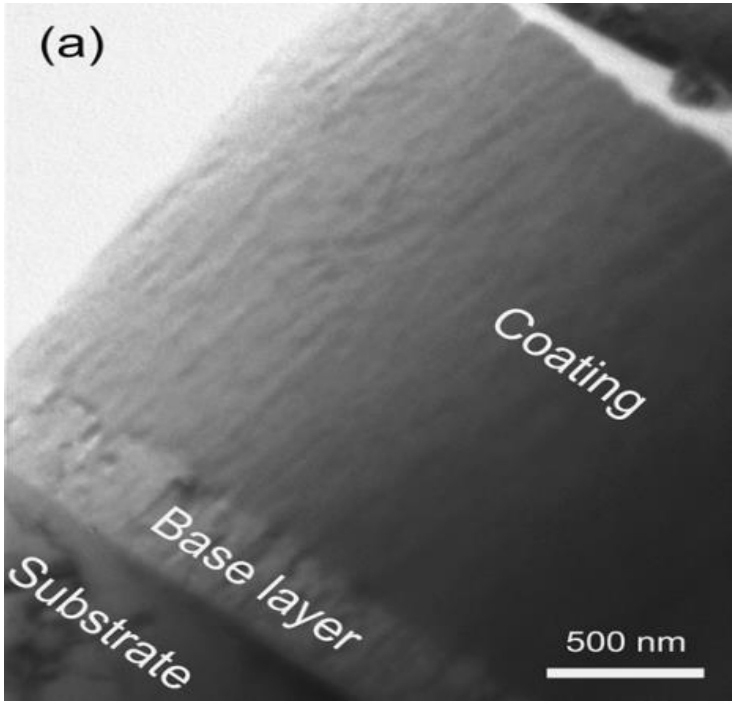
500 Hz

<u>**Target area = 1200 cm^2**</u>

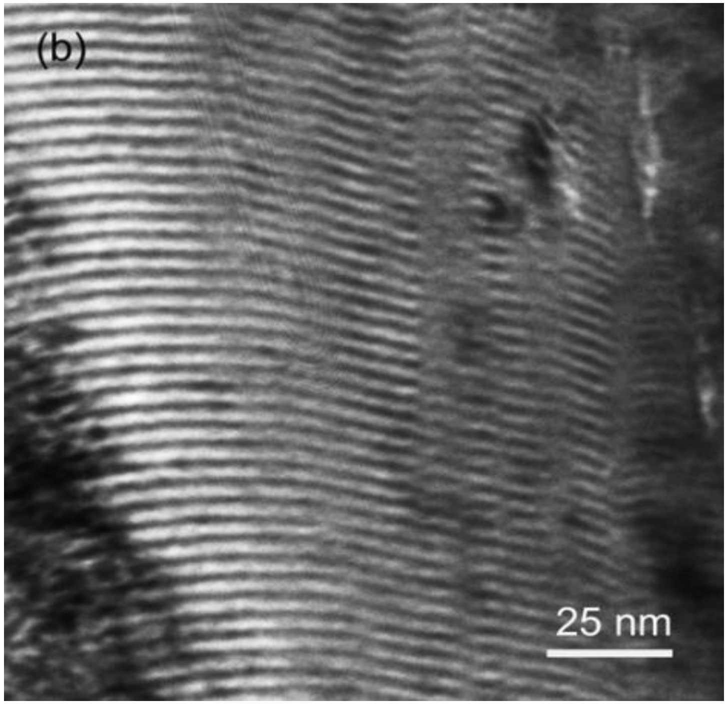
Sample positioning in HTC 1000-4 PVD system to simulate coating deposition on long substrates (turbine blades)

- * T position = Top position
- * M position = Middle position
- * B position = Bottom position

X-TEM showing the nanoscale multilayer structure of CrN/NbN

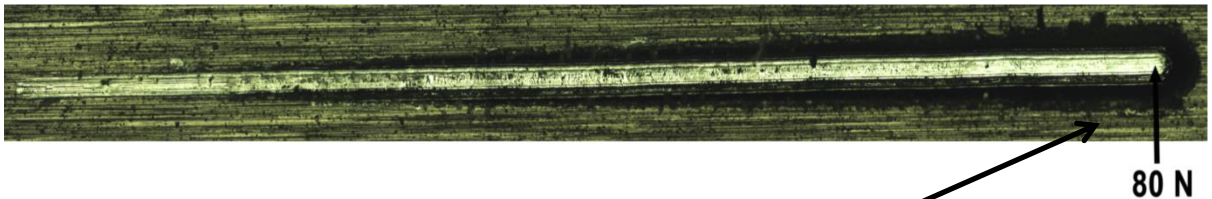


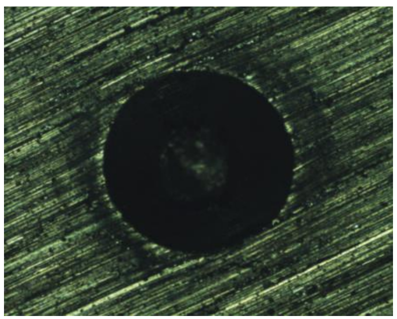
Low magnification image



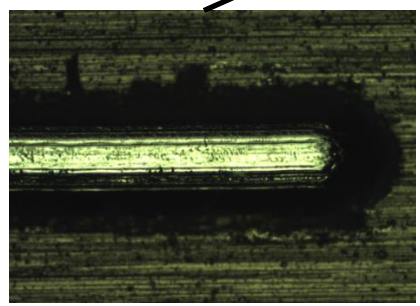
High magnification image

Adhesion and mechanical properties of nanostructured CrN/NbN coating deposited on P92 steel





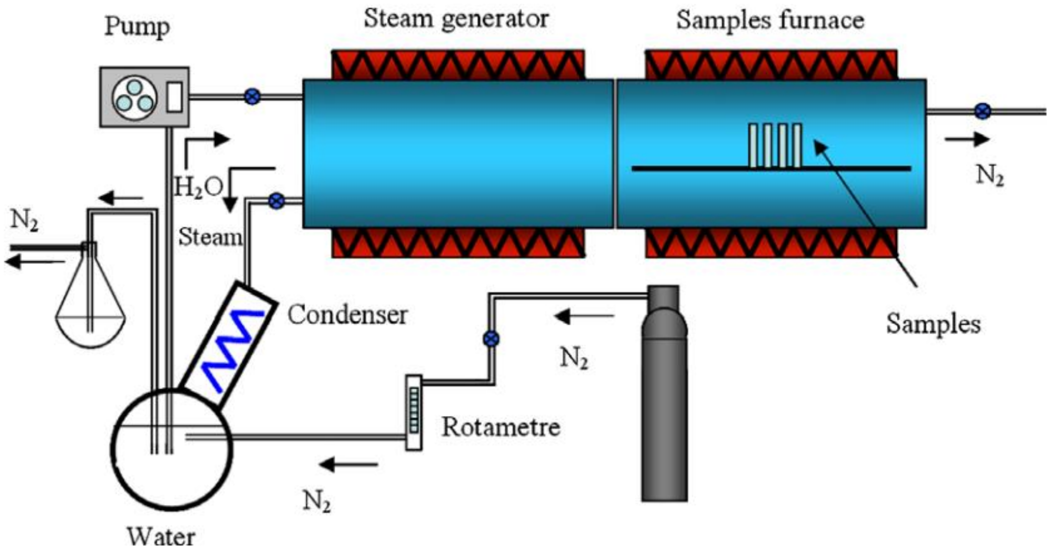
Rockwell C Indentation Test Results



Scratch Test Results

thickness (Si)	Hardness (0.25N)	Roughness uncoated	Roughness coated
4.02 um	3337	0.65 um	0.70 um

Schematics of the laboratory setup used for the steam oxidation tests



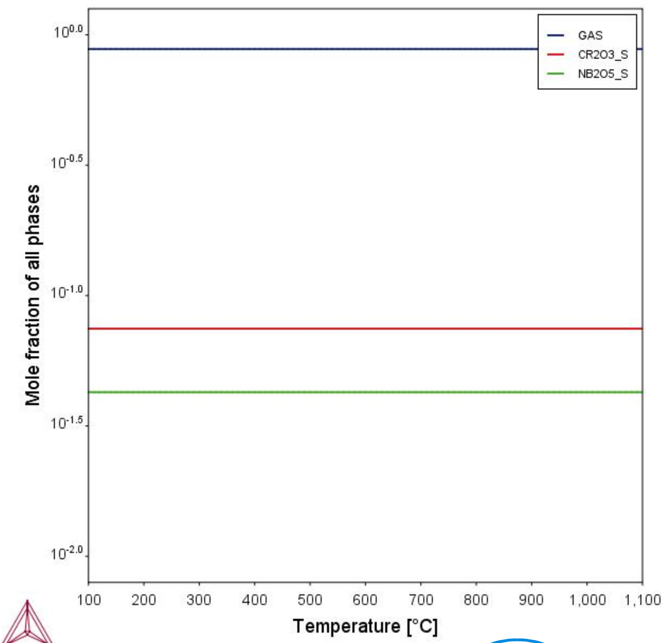
NABERTHERM R 100/750/12
furnace with a ceramic tube reactor

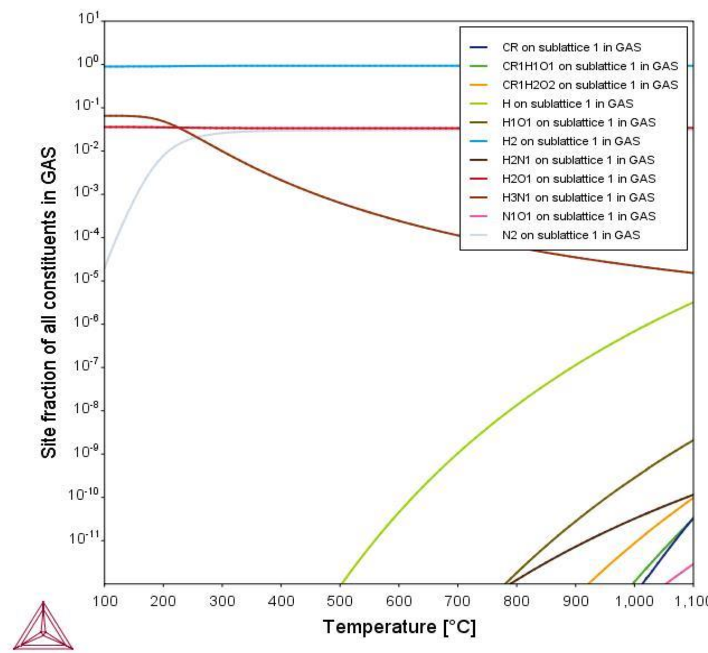
Thermodynamic simulations showing the equilibrium phases formed when CrN/NbN is exposed to steam environment

$$G=\sum_{i=1}^{m}\left(n_i(g)\Delta G_{fi}^{0}(g)+RT\ \ln P+RT\ \ln\frac{n_i(g)}{N(g)}\right)+\sum_{i=1}^{s}n_i(s)\Delta G_{fi}^{0}(s)$$

Gibbs free energy of formation of the various phases

- ***m* , *s*** the number of gaseous and solid species respectively in the system
- $n_{i(g)}$ and $n_{i(s)}$ number of mol of a gaseous and a solid species “i”
- ***N(g)*** total number of mole in gaseous phase
- standard free energy of formation of gaseous and solid species “i”
- ***R*** is the gas constant

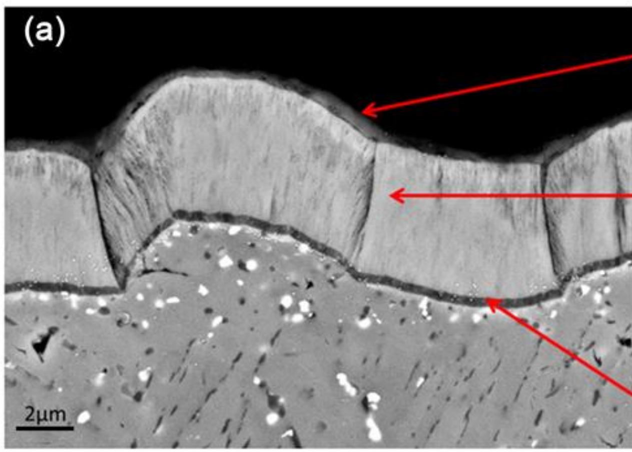




Cross-sectional back scattered SEM analysis of CrN/NbN exposed to steam at 650ºC after 2000 h:

(a) Coating cross-section showing the coating and oxide layers on top

(b) Elemental mapping conducted on the cross-section.

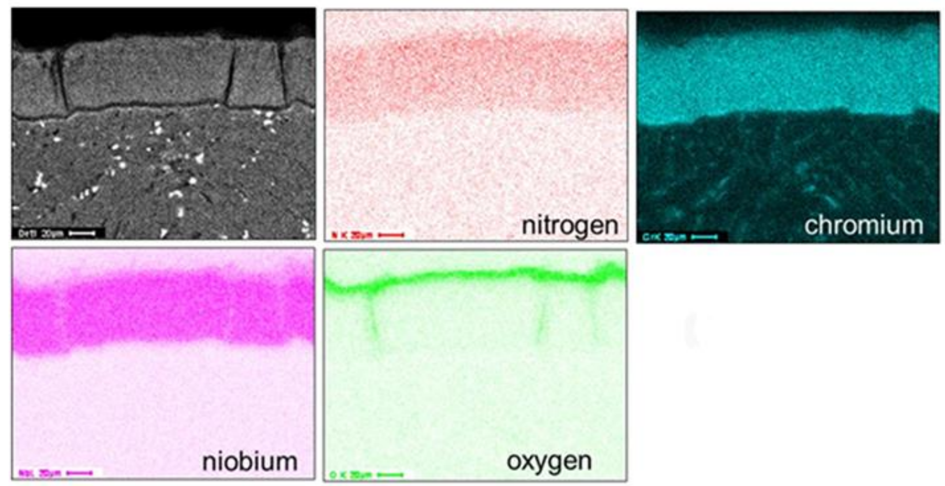


Element	Wt%	At%
OK	38.92	72.02
NbL	27.16	08.66
CrK	33.93	19.32
Matrix	Correction	ZAF

Element	Wt%	At%
NK	23.26	58.52
NbL	35.26	13.37
CrK	41.48	28.11
Matrix	Correction	ZAF

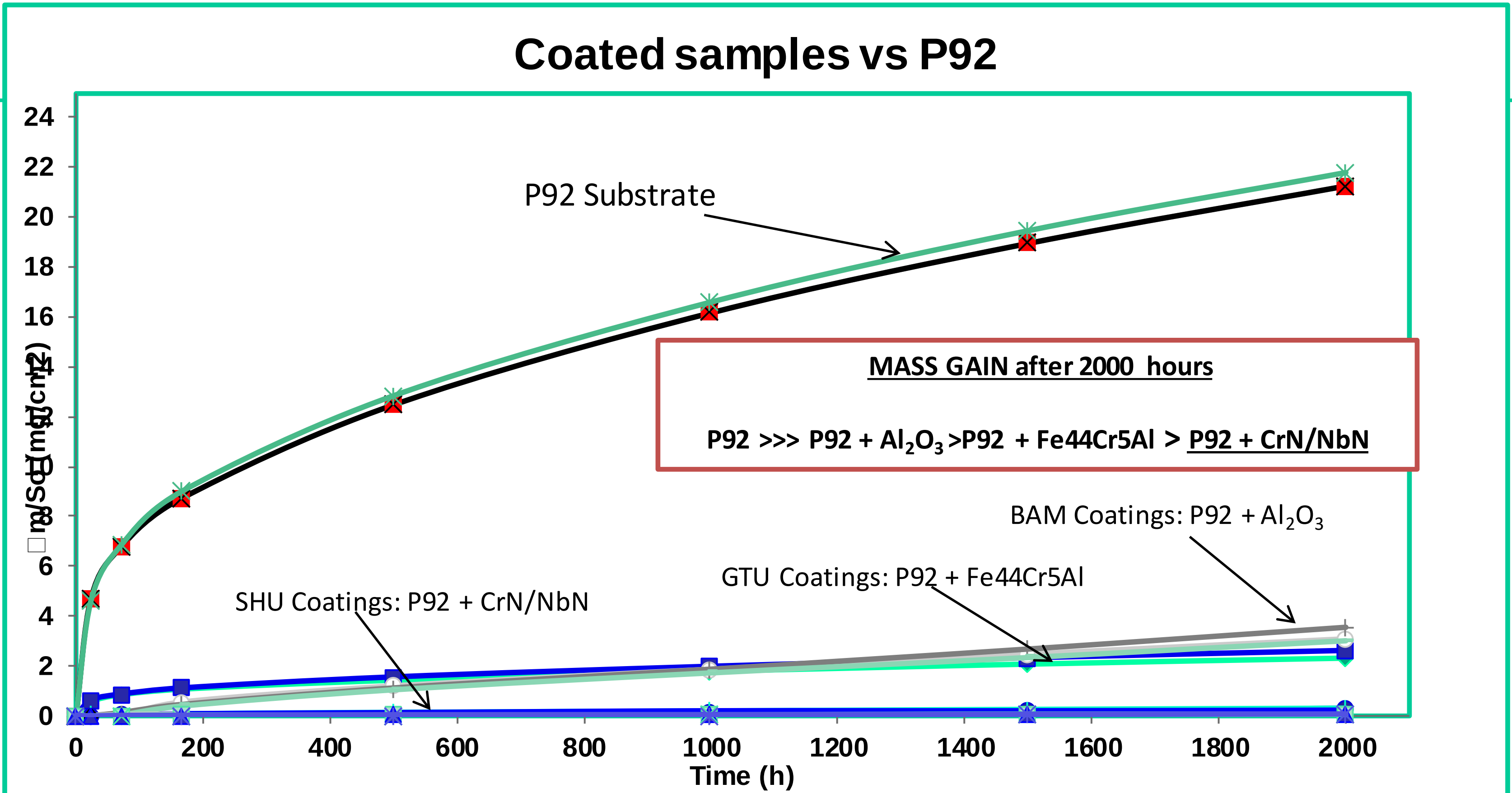
Element	Wt%	At%
NK	16.06	43.71
NbL	12.79	05.25
CrK	49.02	35.93
FeK	22.13	15.11
Matrix	Correction	ZAF

(b)



P. Eh. Hovsepian , A.P. Ehiasarian , Y.P. Purandare, B. Biswas, F.J. Perez, M.I. Lasanta, M.T. de Miguel, A. Illana, M. Juez-Lorenzo, R. Muelas, A. Agüero, Performance of HIPIMS deposited CrN/NbN nanostructured coatings exposed to 650 C in pure steam environment, Materials Chemistry and Physics 179 (2016) 110-119.

Mass gain of various coatings exposed to pure steam at 650ºC after 2000 h.



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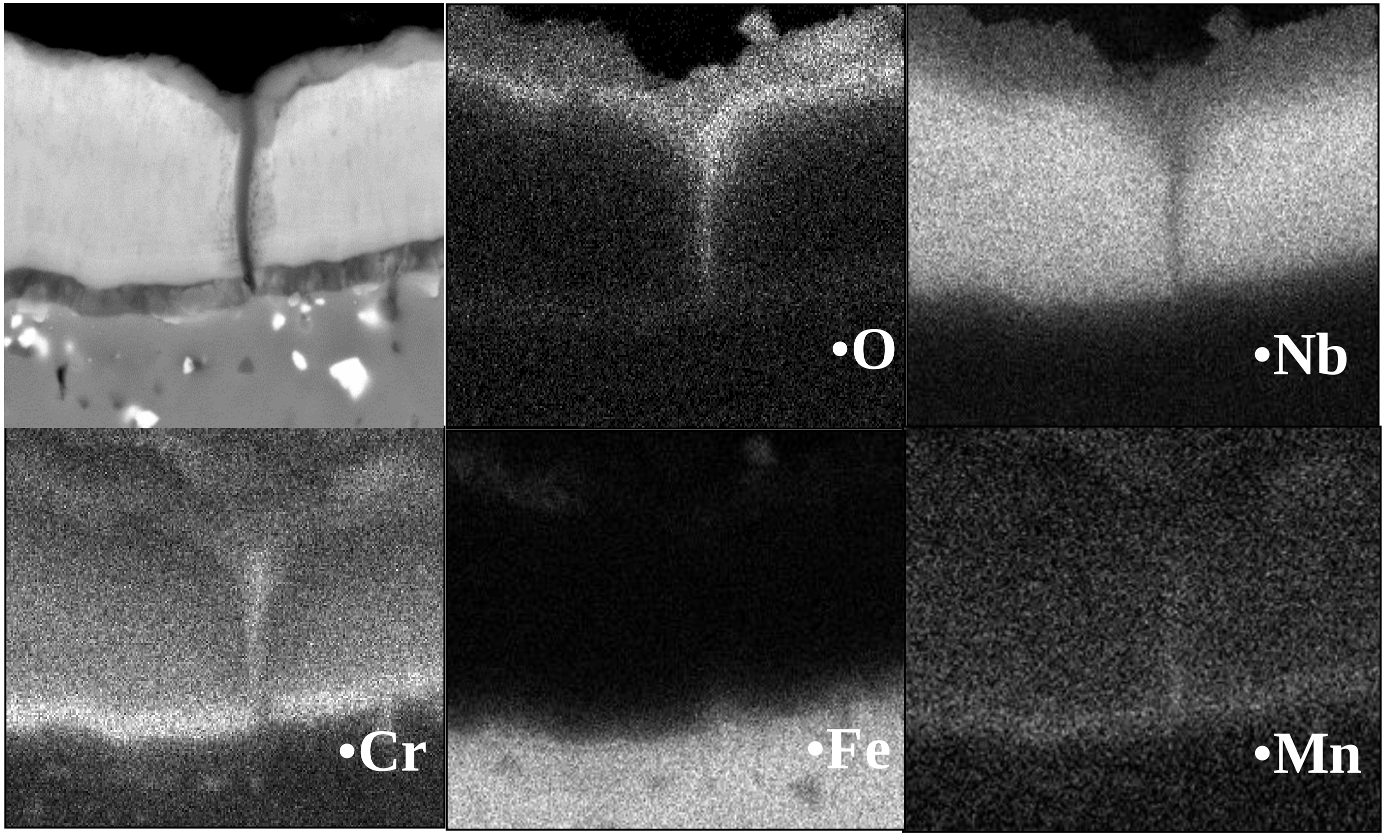
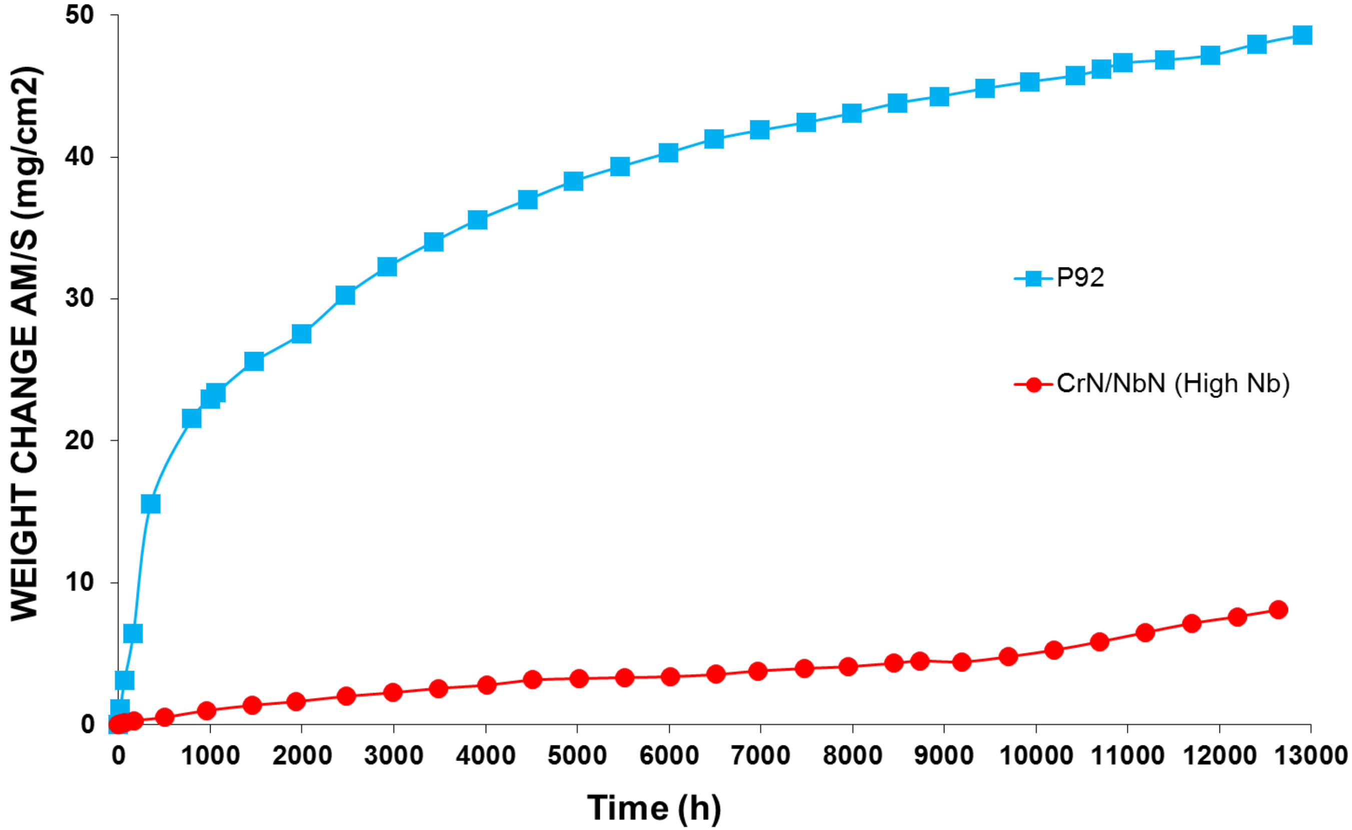
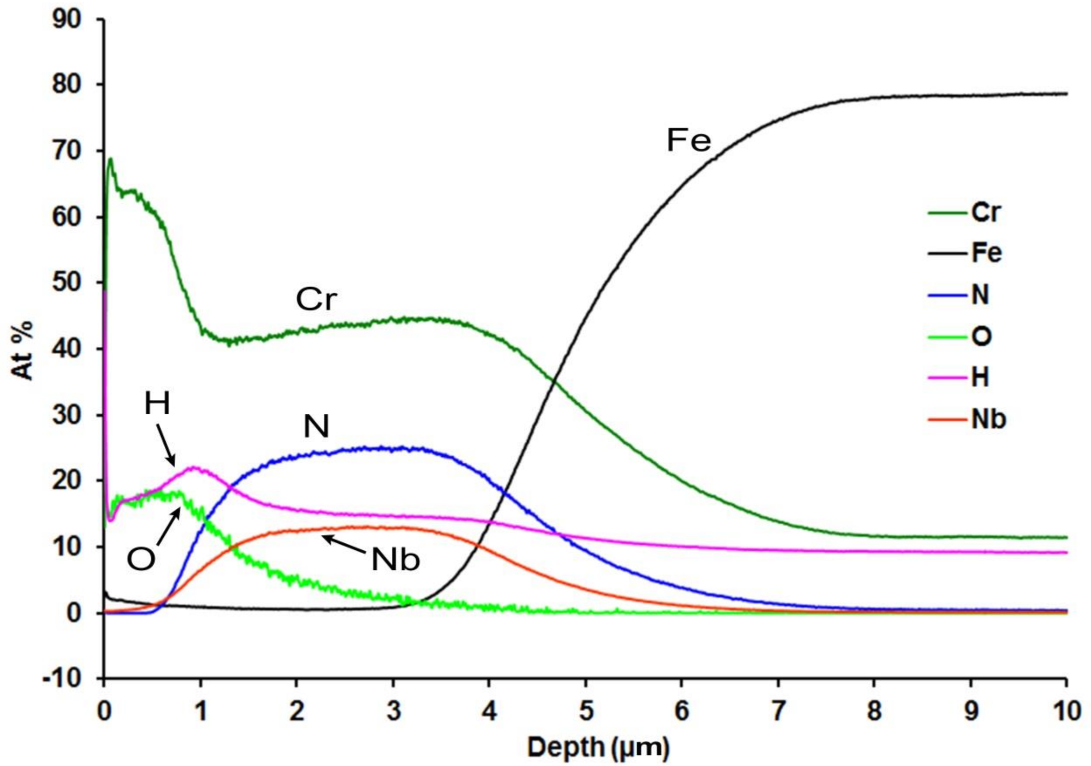
Element EDS mapping of CrN/NbN exposed to pure flowing steam at 650^{o}C after 3,500 h.



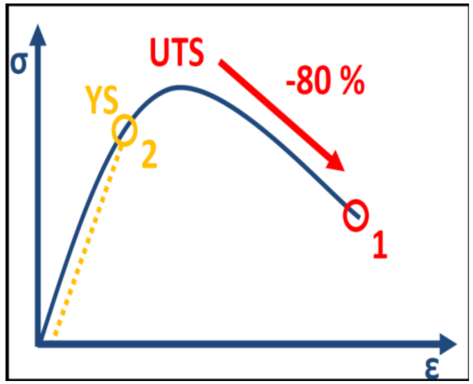
Mass gain of CrN/NbN coating exposed to pure steam at 650^{o}C after 12650 h.

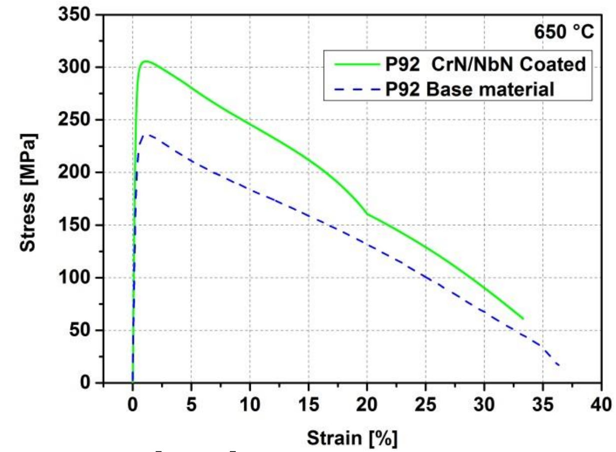


GDOES depth profile of steam oxidised CrN/NbN coating

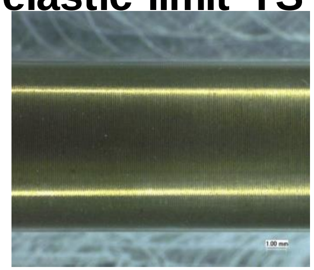


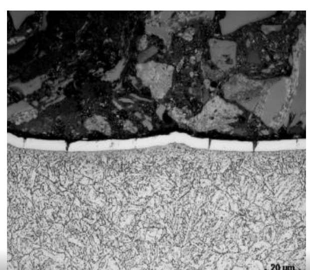
Hot Tensile Test Conditions, T= 650 °C, $\acute{\varepsilon}$ = 1 mm/ min



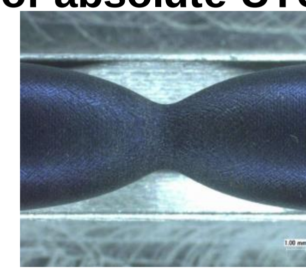


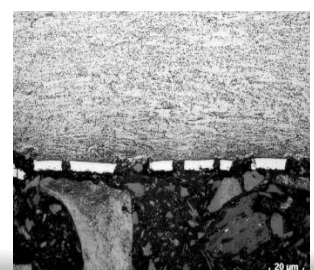
Strained up to elastic limit YS





Strained up to 20 % of absolute UTS

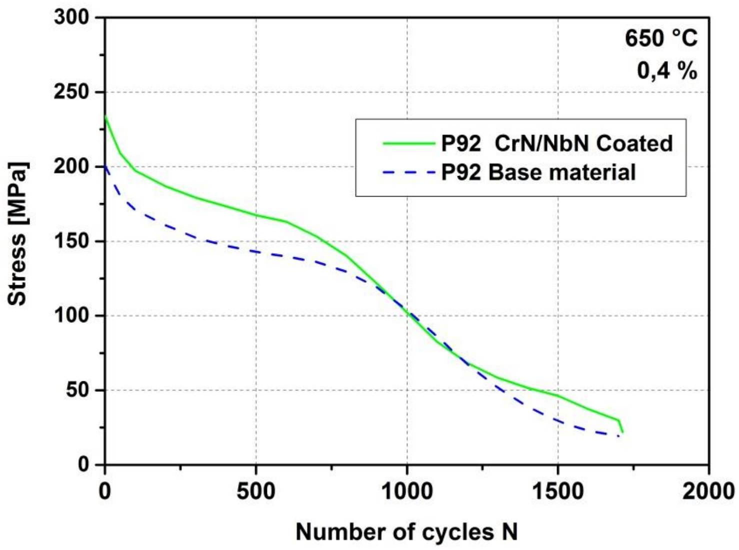




1: Passing Ultimate Tensile Strength, (UTS) with subsequent testing down to 20% UTS absolute value:
pure plastic deformation

2: Up to Yield Strength (YS) value: pure elastic deformation

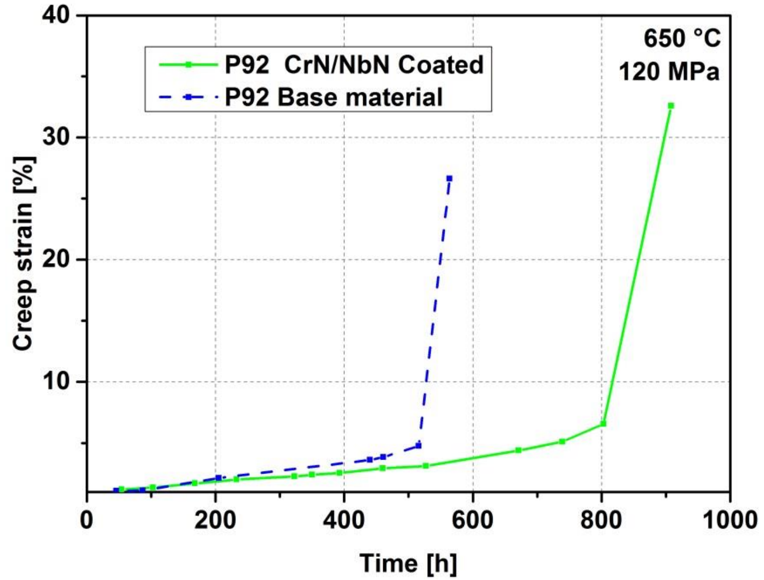
Strain controlled, (0.4% strain) Low Cycle Fatigue tests at 650^{o}C



- Both uncoated and coated specimens failed after similar number of cycles, N_f = 1700 and N_f= 1712 respectively

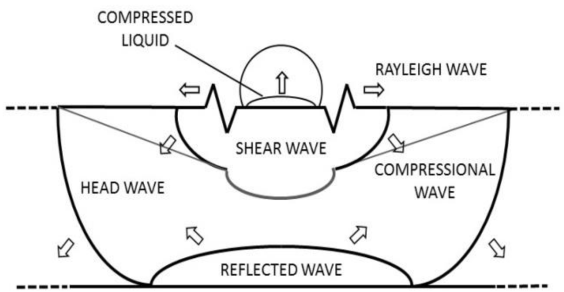
High temperature creep tests at 650ºC, tensile stress of 120 MPa

Creep Lifetime



- HIPIMS coating improved the creep lifetime by almost factor of two from 564 hours to 908 hours.

Schematic of water droplet / solid surface interaction



The pressure during the impact is given by the water hammer equation:

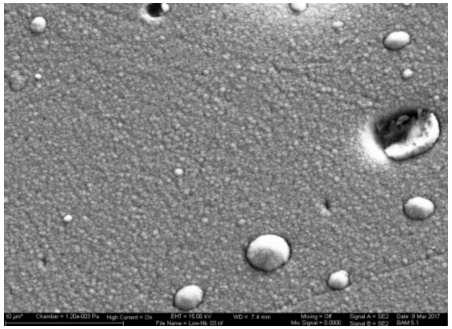
$$P = \rho_0 c_0 V_0$$

$$V_{DT} \approx 1.41 \left(\frac{K_{ic}^2 c_R}{\rho_w^2 c_w^2 d_w} \right)^{1/3}$$

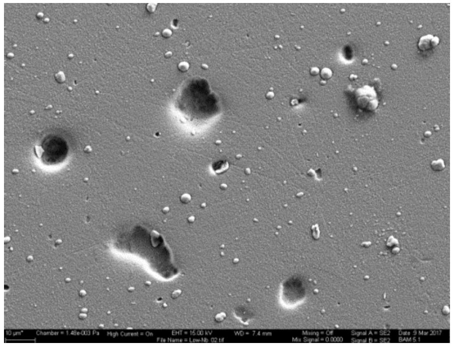
Damage Threshold Velocity, V_{DT} - the lowest velocity, which theoretically could cause surface damage.

- V_{DT} denotes the Damage Threshold Velocity ,*DVT*
- K_{ic}^2 the fracture toughness of the target material

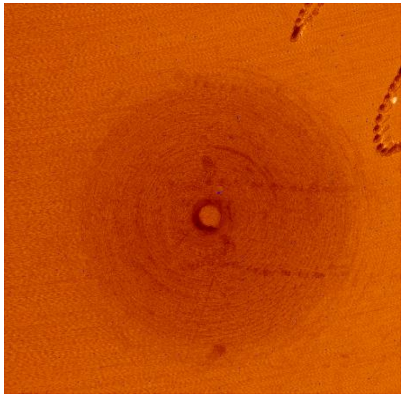
Water droplet erosion test results. Test conditions: *water pressure: 9 bar; impact frequency: 480 min^{-1} ; total number of impacts: 2.4E ^{6}*

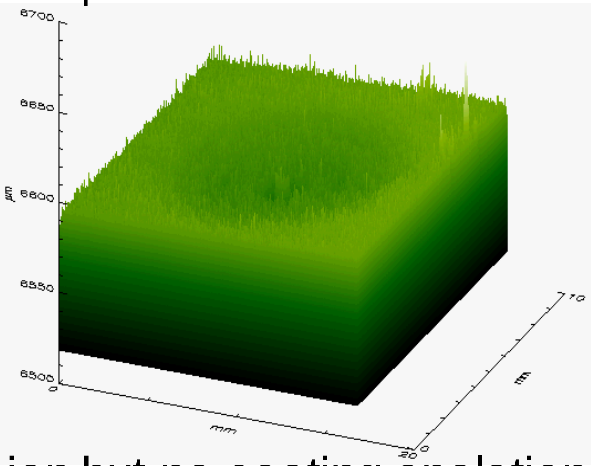


Surface morphology, SEM as deposited CrN/NbN



Surface morphology, SEM after water droplet erosion





2D and 3D profilometry showing 20 µm depression but no coating spalation.

Conclusions

1. The novel High Power Impulse Magnetron Sputtering technology providing highly ionised metal plasma, was successfully employed to deposit high hardness, $HK_{0.25N}$ = 3300 and extremely dense as shown by TEM coatings.

2. High adhesion with scratch test critical load of L_{C2} = 80 N on P92 steel and no spallation in HT tensile test conditions was achieved due to the use of the HIPMS surface pre-treatment.

3. SEM and EDX analyses carried out after exposure to hostile high temperature steam environment showed that the coating developed a protective Cr_2O_3/Nb_2O_5 scale, whilst maintaining its original microstructure and sharp and well defined coating-substrate interface. The results showed that HIPIMS deposited CrN/NbN coatings after long 12,650 hours exposure to 650ºC improved the oxidation resistance of the bare P92 by factor of 10

4. Unlike other state-of -the-art PVD technologies, HIPIMS does not have an adverse effect on the mechanical properties of the substrate material. This was demonstrated in number of high temperature tests at 650ºC such as Tensile Strength, Low Cycle Fatigue and High Temperature Creep test.

5. The coating showed high resistance against water droplet erosion. After $2.4E^{6}$ impacts at a 9 bar pressure no measurable weight loss was detected.

6. The synergy between advanced coating nanostructure and the application of the High Power Impulse Magnetron Sputtering deposition technology produced CrN/NbN as a potential candidate for protection of steam turbine blades as it possesses the whole package of functional properties required for this application.

Acknowledgement

This work has been carried out within FP7 EC funded project "Production of Coatings for New Efficient Clean Coal Power Plant Materials", POEMA, Grant agreement 310436. The financial support of the EC and the intellectual support of all partners are deeply acknowledged.