MICROMECHANICAL PROPERTIES OF THE NbC_X MICROSTRUCTURE COATINGS

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Abstract: *Micromechanical properties such as Young's modulus E and hardness HV of the NbCx microstructure coatings were evaluated by microindentation technique (TriboScope).*

The surface morphology, uniformity and homogeneity of the coated samples were examined by (Philips) scanning electron microscopy (SEM) and atomic force microscopy (AFM), and also the coating thickness was measured by cross-section SEM analyses.

The AFM was a MicroScope III, and the indentation time was set to 10 s. The sensor of the transducer recorded the values of normal force and depth. From the analysed load–displacement curves, the Young's modulus of the measured films can be calculated .

In this paper, thin films NbCx was coated by chemical vapour deposition method.

The crystalline structure of the coating was determined by X-ray diffraction (XRD) (using a Dron diffractometer in continuous scanning mode and using Mo, Kα radiation λ =154056 μm) The film composition was determined by X-ray photoelectron spectroscopy (XPS) using monochromatic Al Kα radiation.

Keywords: *microstructure, properties, coating, hardness, Young's modulus, composition.*

1.Introduction

In this paper, thin films NbCx was coated by chemical vapour deposition methods. There are a lot of methods to apply hard alloys coating, including chemical vapour deposition at low pressure (LPCVD), plasma assisted CVD (PACVD) and chemical vapour deposition at normal pressure (NPCVD); however, is an appropriate method for the deposition of wear resistant coatings on temperature sensitive materials [1-4]. Normal presure CVD has the major advantage that coatings of uniform thickness and composition can be produced even on substrates with a complex shape at high temperature[3–8]. Further study has indicated that the properties of niobium carbide are related to its chemical composition and texture and are a result of low adhesion or residual stresses in the thin film [3–10]. In the present paper, we studied the influence of duty cycle on the structure, morphology, chemical composition and tribological behaviour of NbCx. More study showed that the duty ratio and pulse frequency affect the chemical deposition and that the processing rate can be improved [11–13]. Among several parameters with important effect on the properties of the NbCx microstructure coating, duty cycle plays an essential role as a thermodynamic and kinetic parameter.

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2.Materials and Sample Preparations

The alloys WC – Co was used as substrate material. Table 1 illustrates the results of chemical analysis accomplished by spark emission spectroscopy test. The samples of substrate with the dimension 20 x 20 x 5mm was quenched and tempered to a hardness of 14.98 MPa. After being polished to an Ra of 2 μm using Al_2O_3 slurry, the samples were first cleaned with acetone and then cleaned in ethanol and a chemical process in Ar and H_2 before deposition.

Table 1. *Chemical analysis of widia achieved by spectroscopy test*

Composition	WC	Co
Weight per cent	0.94	0.06

The NbCx microstructure coating was deposited by NPCVD in a reactor using a HCl–CH4–H2–Ar gas mixture. The pressure in the reaction chamber amounted to 1 at. For more details concerning the deposition conditions, see Table 2. The substrate temperature was achieved by auxiliary heating system. Three kinds of duty cycles including 20, 35 and 50% were selected for investigating the influence of duty cycle on residual stress and tribology behaviour of NbCx microstructure coating.

Table 2 . *Process parameters for deposition of NbCx*

Parameter	**Value**
Temperature [ºC]	≤ 1068
Process time [h]	4
Ar +H_2 [L/h]	2,5
H_2 + CH_4 + HCl [L/h]	0,5
Duty cycle [%]	20, 35 and 50

In this work niobium tetrachloride is obtained directly in the working chamber of the ferroniobium and concentrated hydrochloric acid at elevated temperature (over 1060 o C) according to the reaction:

$$Nb_s + 4HCl = NbCl_4 + 2H_2 \quad (1)$$

$$NbCl_4 + CH_4 + H_2 = NbC + 4HCl + H_2$$

It is noteworthy that the originality of the paper consists in direct niobium tetrachloride working inside, avoiding the import of these tetrachloride which shows a high toxic.

3.Characterisation of NbC structure coating

The surface morphology, uniformity and homogeneity of the coated samples were examined by (Philips) scanning electron microscopy (SEM) and atomic force microscopy (AFM), and also the coating thickness was measured by cross-section SEM analyses.

Micromechanical properties such as Young's modulus E and hardness HV of the NbCx microstructure coatings were evaluated by microindentation technique (TriboScope). The AFM was a MicroScope III, and the indentation time was set to 10 s. The sensor of the transducer recorded the values of normal force and depth. From the analysed load–displacement curves, the Young's modulus of the measured films can be calculated as follows.

1/Er = 2β/ S (Ac /π)1/2 = (1 – υ2m)/ Em + (1 – υ2i)/ Ei (2)

where Ac, Er, S and β denote the actual contact area, the reduced elastic modulus for each indenter/specimen combination, the measured stiffness and a shape constant of 1 for the Berkovich tip respectively.

The subscripts m and i denote the film and the indenter tip respectively, E is the Young's modulus, and υ is Poisson's ratio. The indenter properties used in this study's calculations are Ei =1120 MPa and υi =0.05, and the assumed Poisson's ratio of NbCx is υm = 0.15[8] .

The film composition was determined by X-ray photoelectron spectroscopy (XPS) using monochromatic Al Kα radiation.

The adhesion of the NbCx microstructure coatings on hot working widia was analysed with a microscratch tester with a diamond tip (radius of 10 μm). The sliding speed was fixed at 15 μm/s. The critical load Lc was defined as the lowest load at which the NbCx microstructure coatings started to delaminate . The delamination of the coatings was confirmed through observation with an optical microscope.

A pin on disc apparatus was carried out on the NbC microstructure coating under loading conditions of maximum 1 MPa pressure with Ø6 mm ball; this is the Hertzian pressure so close to the working condition, such as cutting and forming tools. The load was 5 N, and the sliding speed was 0.1 m /s. All the tests were performed for 1200 cycles. The temperature and relative humidity were 30 oC and 36% respectively. Before the tests, the samples were cleaned with ethanol and dried in hot air.

4.Results and discussion

The crystalline structure of the coating was determined by X-ray diffraction (XRD) (using a Dron diffractometer in continuous scanning mode and using Mo, Kα radiation λ =154056 µm). Figure 1 demonstrates the XRD diffraction patterns for the deposited samples with three different duty cycles, i.e. 20, 35 and 50%

As Fig. 1 shows, the (200) plane is the preferred structure; therefore, this result implies that the NbCx coating was deposited under a thermodynamically stable condition since the (111) structure (or texture) is the common structure of NbC that is observed.

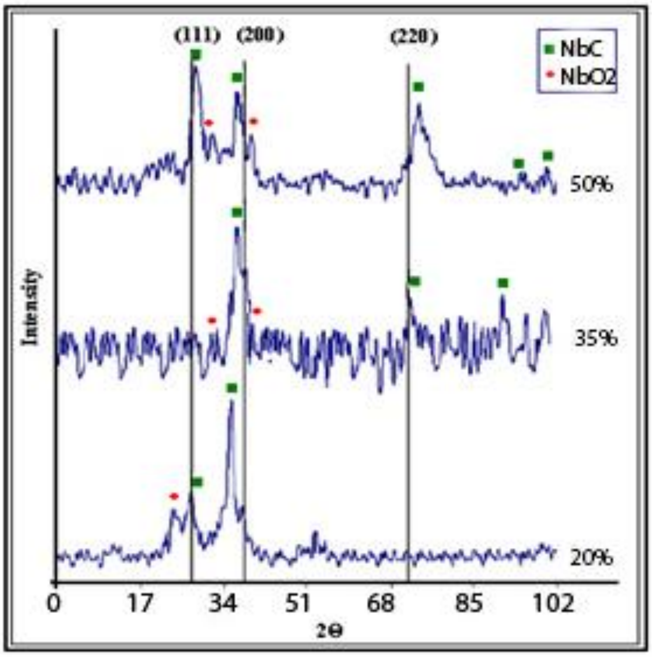

Figure.1. *X-ray diffraction patterns for NbCx microstructure coating at three different duty cycles of 20, 35 and 50%*

The lowest energy surface for the NbCx crystal is the (200) plane, and this is the structure that is expected for coatings deposited under thermodynamic equilibrium . In order to clarify the effects of duty cycle on the chemical composition of NbCx microstructure coatings. In Fig. 1, it can be observed that the increasing duty cycle from 20 to 35% has caused the (200) plane to be the preferred structure, and the NbO_2 phase was detected. It is clear that the detected peak was

increased by rising duty cycles from 20 to 50%; moreover, the (200) and (111) planes are then the preferred structures. The best duty cycle to grow the (200) plane as a preferred orientation is 35%, the crystallite size of the NbC microstructure coating (which was calculated using the Scherrer formula) is 7 µm. An evident change in grain size is observed for changing duty cycle. Actually, the grain size of the NbC was decreased by raising the duty cycle from 20 to 50%, as raising the duty cycle leads to an increase in number of nucleation and cluster on the substrate. Finally, the grain size of the NbC microparticles is decreased accordingly.

A sign of the preferred orientation has been achieved from measurements of the (111) and (200) reflections. As shown in Fig. 1, for all the coatings except for 50% duty cycle, the (200) direction is the preferred one with variations in the (111):(200) ratio ranging from

0 to 0.2. Table 3 shows the properties of NbC microstructure coating at three different duty cycles .

Table 3. *Properties of NbC microstructure coating at three different duty cycles*

Duty cycle [%]	**Grain size** [μm]	**Thickness** [μm]	**Critical load** [mN]	**Hardness** [MPa]
20	8.7	5.8	15	29.10
35	5.6	7.5	34	12.56
50	4.97	9.5	25	14.70

It can be seen that the wear mass loss for both the widia substrate and the NbC microstructure coatings increases with the increase in number of cycles. Compared with the substrate, the NbC microstructure coatings have smaller mass loss, especially for coatings deposited at 35 and 50% duty cycles. In addition, the mass loss of the W–Co pins drastically increases with the increase in number of cycles. It is mentioned that the W–Co pin as the counter body of the NbC microstructure coatings presents less wear mass loss compared to widia substrate.

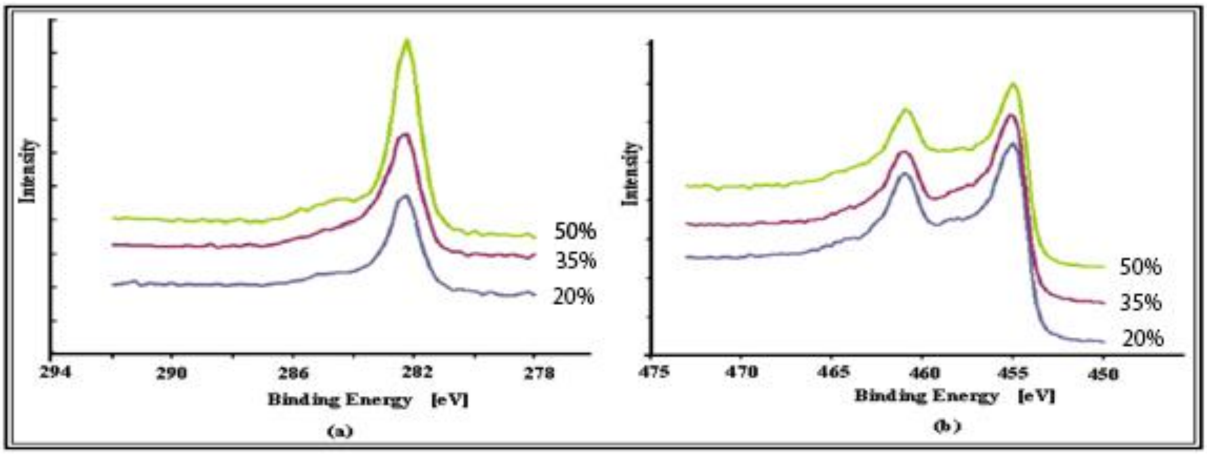

Figure.2. *X-ray photoelectron spectroscopy spectra for surface of NbCx microstructure coatings deposited at three different duty cycles of 20, 35 and 50%: a) C 1s spectra peaks; b) Nb 2p spectra peaks*

Figure 2 displays the C 1s and Nb 2p XPS spectra of the NbCx microstructure coatings deposited at three different duty cycles. The Nb 2p XPS signal is composed of Nb 2p3/2 and Nb 2p1/2 doublets with binding energies of 455 •2 and 460 • 8 eV respectively. These two doublets are separated by 6.0 eV.

The C 1s spectrum shows a peak at 281.6 eV, and NbO_2 is represented by the Nb 2p3/2 peak at 458.4 eV. The existence of the Nb 2p and C 1s peaks indicates that the coating obtained under the deposition conditions (Table 2) is NbC. More over, no significant variation of the surface chemical composition (C/Nb ratio) was observed with the increase in duty cycles. Figure 3 demonstrates the SEM images of the NbC microstructure coating in three kinds of duty cycles, i.e. 20, 35 and 50%. Surface morphology plays an important role in the tribology behaviour of the NbC microstructure coating. It can be seen that the surfaces of the two coatings, which were deposited at 20 and 50%, show similar microstructures (rough surfaces) containing 0.1– 0.2 μm aggregates of 4–10 μm NbC grains, and increasing the duty cycle from 20 to 35% produces relatively smooth and dense surfaces.

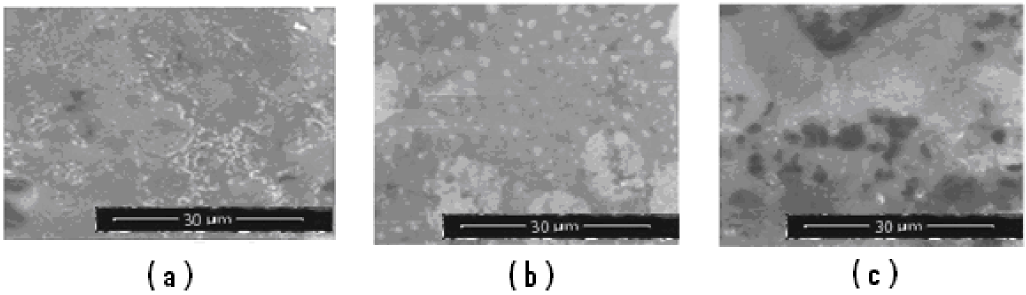

Figure. 3. *Images (SEM) of NbCx microstructure coating deposited at three different duty cycles: a) 20%; b) 35%; c) 50%*

The presence of the dispersed phase in the micro deposited layers was highlighted and map the distribution of elements (Co, Nb) on SEM images of surfaces. EDX is outstanding distribution method elements in microbeads deposited Co and Nb, Figure 4.

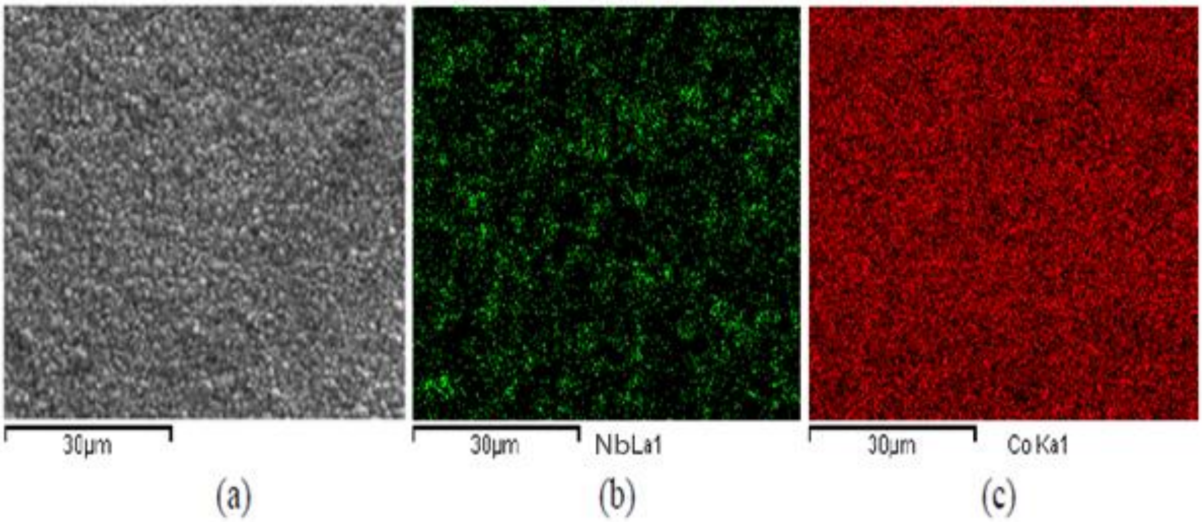

Figure.4. *Images SEM-EDX of NbCx microstructure coating deposited and elements mapping x2000 a) SEM of NbC; b); element mapping of Nb; c) element mapping of Co;*

The surface topographies and roughness plot of the NbC microstructure coating at three different duty cycles, including 20, 35 and 50%, are shown in Fig. 4. This figure depicts that asperities are distributed over a broader range of heights for 50% compared to 20 and 35%.The results of surface roughness are presented in Table 4.

Table 4. *The results of surface roughness at three different duty cycles*

Duty cycles	**20%**	**35%**	**50%**
Ra [µm]	8.992	10.509	14.057
Rrms [µm]	11.668	13.429	18.034

It can be seen from Table 4 that Ra is defined as the mean value of the surface height relative to the centre plane, and Rrms is the root mean square roughness profile of the surface height within the scanned area, and both have been used to explain the surface morphology. This is confirmed by roughness values Rrms of 11.668, 13.429 and 18.034 µm at three different duty cycles, including 20,35 and 50% respectively.

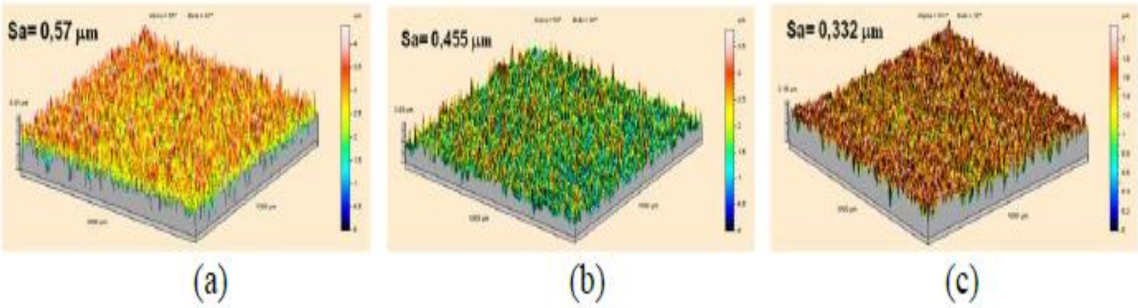

Figure.5. *Images (AFM) and roughness plot of NbCx microstructure at three different duty cycles: a) 20 %; b) 35 %; c) 50 %*

Both the AFM images and the Rrms values prove that increasing duty cycles from 20 to 35 and 50% causes a reduction in overall roughness of the coating. Therefore, the SEM and AFM images of the NbC microstructure coating (Figs.3 and 5) indicated that the growth mechanism of coatings at 20 and 50% are island-like growths, while at 35%, there is a layer growth.

The deposition parameters are responsible for the layer growth, and it can be concluded for the NPCVD process that the chemical deposition conditions ,during deposition, such as duty cycles , determine the nucleation and growth of the layer.

It is noteworthy that increasing the hardness of the NbC microstructure coating is determined by decreases the friction coefficient. In addition, the gradual increase in friction coefficient at 35 and 50% is probably due to the decrease in hardness steadily.

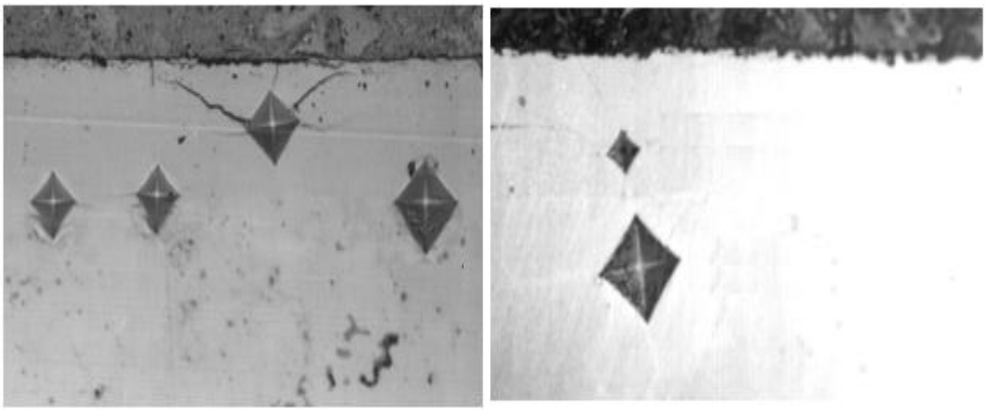

Figure.6. *Hardness of the NbC microstructure coating*

Figure 6 is the front strate layer microhardness. The microhardness tests show a hardness value of the layer NbC, HV0,05 = 29.10 MPa, which value is consistent with data from the literature in relation to the microhardness of the substrate (94% WC 6% Co) that is HV0,05 = 14.58 MPa.

5.Conclusion

The main conclusions are the following.

1.The (200) plane is the preferred structure at lower duty cycle (20%), and an increasing duty cycle from 20 to 50% causes the formation of other planes of NbC, such as (111) and (220) planes.

2.These peaks move to higher angles with increasing duty cycles from 20 to 50%.

3.The grain size of the NbC microstructure coating (~7 µm) was decreased by raising the duty cycle, since the number of nucleation was increased by raising the duty cycle.

References

1.[Man P.,2005] A. Man P. Aubert, F. Mercier, H. Khodja, C. Berthier and P. Houdy - *Surf. Coat. Technol*., (2005), 194, 190–195.

2.[Constantinescu S.,20098] S. Constantinescu - *Nitride coatings on widia substrate for mechanical applications*, Journal Surface Engineering vol. 25, no. 1, , (2009), p .77-81 ,www.ingentaconnect.com

3.[Zang Z.,2016] Z.Zang,Y.Hu,F.Qin,Y.Ding-*Appl.Surf.Sci*.,376,10(2016), https:doi.org/10.1016/j.apsusc.2016.02,155 Google Scholar, CrossRef,CAS

4.[Rai P.,2015] P.Rai,S.M.Majhi,Y.Hu,J.Lee – RSC Adv.5,76229 (2015) https:doi.org/10.1039/C5RA14322E,Google Scholar,CrossRef,CAS

5.[Manandhar K.,2016]. Manandhar K., J.A.Wollmershauser,J.E.Boercher,B.N.Feigelson,J.Vac.Sci.Technol.,A34,021519 (2016) ,https:doi.org/10.1116/1.4941918 Google Scholar Scitation

6.[Xu L.,2014].L.Xu, M.L.Yin, S.Liu – Sci.Rep.4,6745 (2014),https:doi.org/10.1038/srep 06745, Google Scholar, CrossRef,CAS

7.[King D.M. ,2007] D.M.King, J.A.SpencerII, X.Liang,L.F.Hakim,A.W.Weiner-Surf.Coat.Technol.201, 9163 (2007), https:doi.org/10.1016/j.surfcoat.2007.05.002, Google Scholar, CrossRef,CAS

8.[King D.M. ,2012] D.M.King, X.Liang, A.W.Weiner–PowerTechnol.221,13(2012), https:doi.org/10.1016/j.powter.2011.12.020, Google Scholar, CrossRef,CAS

9.[Degai M. ,2012] M.Degai, K.Mamiyama, S.Kubota, K.Hirahana, F.Hirose – Thin Solid Films 525,73 (2012), https:doi.org/10.1016/j.tsf.2012.10.043, Google Scholar, CrossRef,CAS

10.[Kanomata K..,2014] K.Kanomata, P.Pansila,B.Ahmmad,S.Kubota, K.Hirahara,F.Hirose–Appl.Surf.Sci.308,328 (2014), https:doi.org/10.1016/j.apsusc.2014.04.166, Google Scholar, CrossRef,CAS

11.[Kanomata K.,2015] K.Kanomata, P.Pansila,H.Ohba,B.Ahmmad,S.Kubota,K.Hirahara,F.Hirose–IEICE Trans.Electron, E98.C,382 (2015), https:doi.org/10.1587/transele.E98.c382, Google Scholar, CrossRef,CAS

12.[Kanomata K.,2016] K.Kanomata, K.Tokoro,T.Imai,P.Pansila,M.Miura,B.Ahmmad,S.Kubota,K.Hirahara,F.Hirose–Appl.Surf.Sci.387,497 (2016), https:doi.org/10.1016/j.apsusc.2016.06.122, Google Scholar, CrossRef,CAS

13.[Kang H. ,2011] H.Kang, C.Lee,D.Kim,J.Kim, W.Choi,H.Kim–Appl.Catal.B104,328,6(2011), https:doi.org/10.1016/j.apcatb.2011.03.010, Google Scholar, CrossRef,CAS

14.[Hirose F. P.,2014] F.Hirose, K.Kanomata,S.Kubota,B.Ahmmad,,K.Hirahara,–Appl.Mech.Mater.490-491,118 (2014), https:doi.org/10.4028/www.Scientific.net/AMM.490-491.118, Google Scholar, CrossRef,CAS

15.[Bui L.K.,2008] X. L. Bui, Y. T. Pei and J. Th. M. de Hosson - Surf. Coat. Technol., (2008), 202, 4939– 4944.