Influence of Chemical Pretreatment of Hard Metal Substrates for Diamond Deposition

Volker Buck, Friederike Deuerler[*], Holger Kluwe, Bernd Schmiler

Universitaet GH Essen, Essen, Germany
[*]Bergische Universitaet GH Wuppertal, Wuppertal, Germany

Summary

Diamond coated cutting tools are of increasing importance in the fields of high speed cutting, dry machining or machining of special materials such as Metal-Matrix-Composites. A well known problem is the poor adhesion of diamond films on hard metals due to the Co- or Ni-binder that catalyzes the formation of graphite. Several methods − such as the application of intermediate layers or mechanical or chemical pretreatment of the hard metal substrate − have been developed to overcome this effect. Usually chemical pretreatment is used in order to reduce the concentration of binder phase on the surface that is to be coated. Surprisingly pretreatment with agents such as Murakami's solution result in improved adhesion and nucleation of diamond films while the concentration of the binder phase on the surface is enhanced. This "contradiction" can be explained by proving that the surface is converted into a very thin oxide/hydroxide film.

Keywords:

Diamond coatings, pretreatment, Murakami's solution

1. Introduction

In recent years considerable progress has been achieved in the coating of hard metal cutting tools with diamond films. Apart from several other aspects (see e.g. /1,2/), problems due to the difference in thermal expansion coefficients of diamond and hard metal as well as the detrimental effect of the binde phase - usually Co - on the formation of diamond films /3/ had to be solved. Several solutions using mechanical or chemical pretreatment of the substrate or special interlayers have been reported (see e.g. [4-22]); common

to all these approaches is the aim to reduce the Co-content on the substrate surface. However, one of the well established and successful methods, the pretreatment of the substrate with Murakami's solution [20-22], turned out to enhance the Co-concentration on the surface [20,23]. This appears to be a contradiction to existing models.

1.   Experimental Details

Commercial hard metal cutting tool inserts (THM SNMQ 120 408 containing 6 % Co-binder) were chosen as sample for the basic experiments. After the usual cleaning procedures these samples were etched with Murakami's solution for different periods of time. Thereafter the cutting tool inserts were coated with diamond, and the nucleation or adhesion of the diamond coatings was determined.

In addition model experiments on hard metal cutting tool inserts as well as on pure Co samples have been carried out. Apart from etching with Murakami's solution electrolytic etching has been applied as well.

The Co content was determined by energy dispersive X-ray analysis (EDX) within the probing depth typical for this technique (a few micrometers). Apart from this, especially surface modifications were investigated by X-ray photoelectron spectroscopy (XPS) using Al K_α-radiation. Additionally the etchant was analyzed by ICP-mass-spectroscopy in order to monitor possible reaction products.

2.   Results

3.1   Treatment of WC/Co with Murakami's solution

Hard metal cutting tool inserts were – after the usual precleaning – etched with Murakami's solution. Subsequently the samples were investigated by means of a scanning electron microscope (SEM) to characterize the morphology of the surface; additionally the Co content was determined using quantitative energy dispersive X-ray analysis (EDX). The results are shown in Fig. 1; one finds a nominal Co-concentration of 6 % in the untreated sample and an enhanced Co-content of 8.2 % after treatment with Murakami's solution.
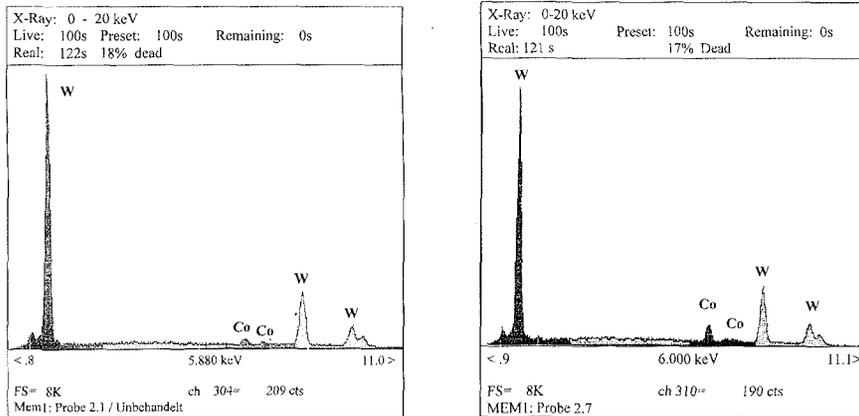
Fig. 1: EDX - analysis of a treated and an untreated sample

The XPS spectrum of a typical sample after 20 s etching (and subsequent cleaning in distilled water) is given in Fig. 2. Apart from a significant contamination of the surface (the O peak at 531 eV and the C peak at 287 eV) one finds as the main peaks the 4d and 4f peaks of W at 257/245 eV and 36/34 eV respectively, the Co $2p_{1/2}/2p_{3/2}$ at 794/778 eV and the Co 3s/3p at
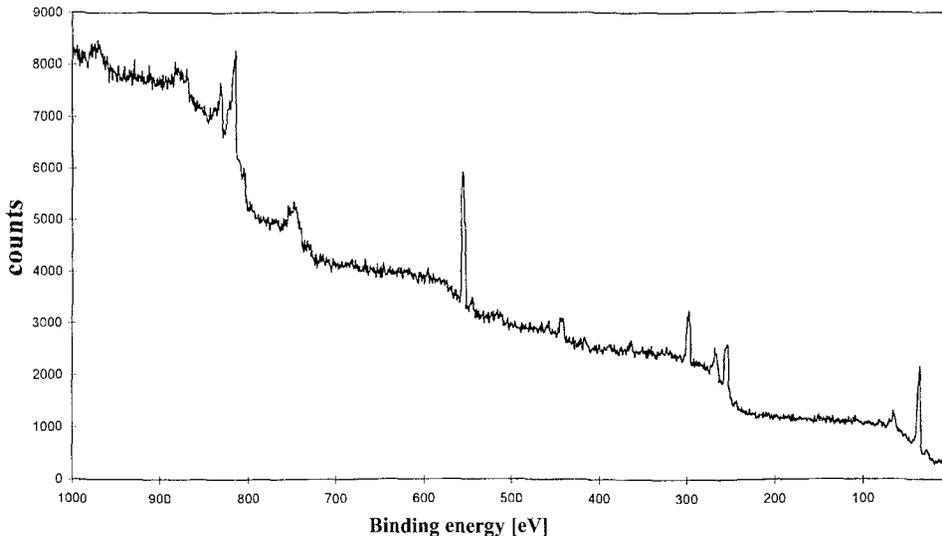
Fig. 2: XPS-Spectrum of a sample after 20s of etching

103/63 eV, but it should be mentioned that the positions of the Co-peaks are shifted to higher energies by 2 eV with respect to the pure metal reference spectra [24]. The oxygen is adsorbed and not chemically bound; this can be proved by heating the sample (inside the XPS equipment) to a temperature of 573 K where the oxygen reacts with the Co to form Co O, as the XPS spectra show.

Although it has been stated that Murakami's solution does not influence the Co [22], in the following especially the Co peaks will be investigated.

A comparison of the Co 2p peaks of the sample before and after etching shows a chemical shift of about 1 eV towards lower energies after etching, additionally the left peak has broadened, Fig. 3:
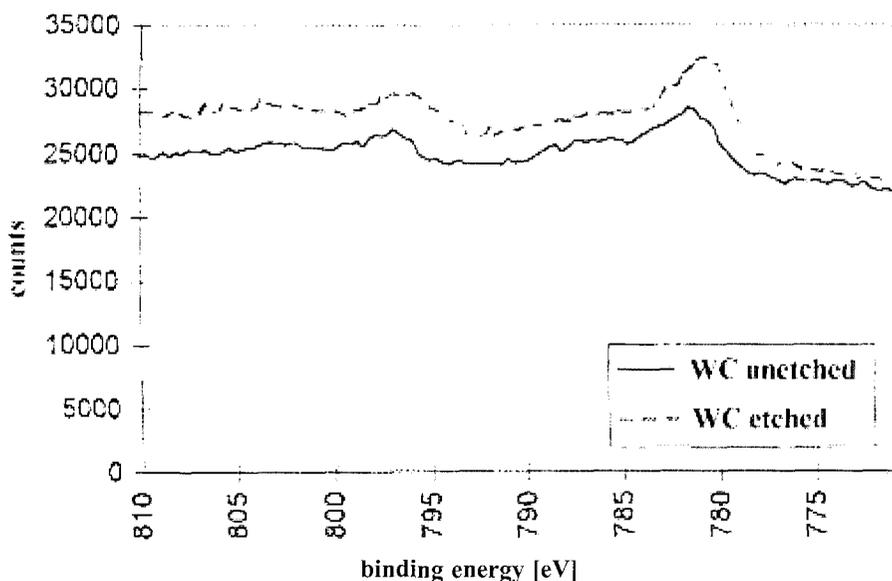

Fig. 3: Spectra of an etched and an unetched WC - samples

Since the peaks of W and C did not shift but remain in the same position, it can be excluded that these elements are partners of chemical reaction. Thus it can be concluded that Co is influenced by Murakami's solution, but the question for the nature of the chemical reaction remains. Consequently the following experiments concentrate on the behavior of cobalt.

3.2 Treatment of Co with Murakami's solution

First Co-films ca. 100 nm thick were sputtered onto glass substrates and treated with Murakami's solution for 10 sec, 30 min and 23 h. No enhancement of the Co signal in the remaining solution could be detected by ICP-mass spectroscopy and no reduction of the thickness of the Co film by optical spectroscopy. To exclude an influence of film structure, the residual gas pressure of the sputtering equipment was systematically varied between $3,5*10^{-7}$ mbar and $1,5*10^{-5}$ mbar, but no difference between these samples could be observed.

Secondly Co films were deposited on Si substrates and their surfaces were investigated by XPS.

Fig. 4 shows the spectrum of a Co film as deposited; one finds the dominating Co 2p peak as well as the 3s and $3p_{1/2}$ peaks in accordance with the reference
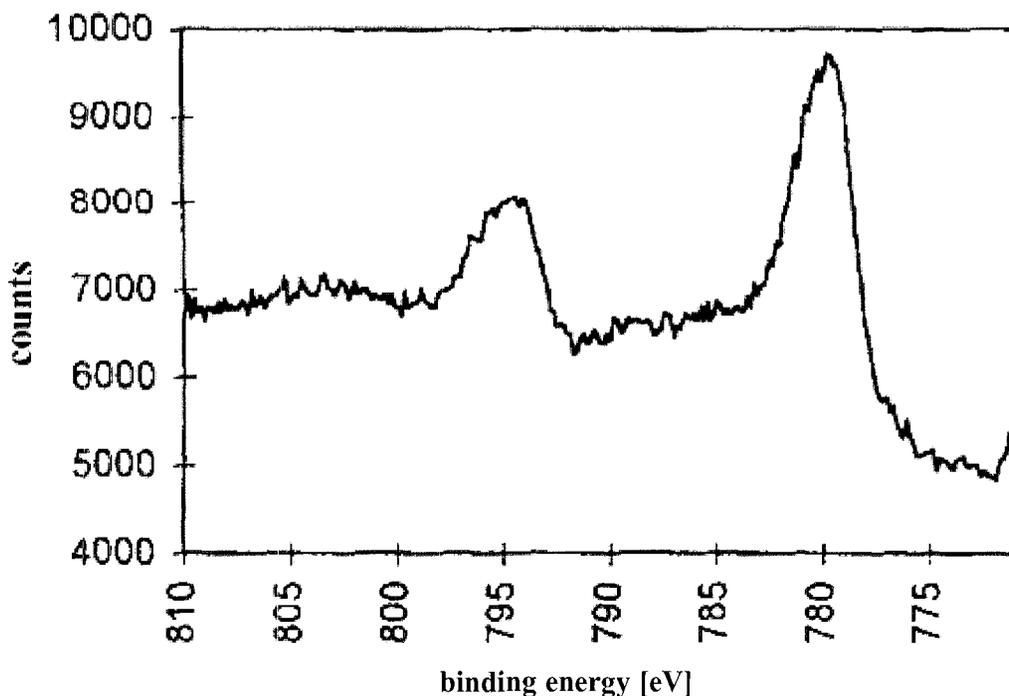
Fig. 4: Spectrum of a Co-film

data /24/. In the following the structure of the 2p peaks will be considered in detail. In Fig. 5 a sample treated 18 h with Murakami's solution is depicted and can be compared to the untreated one. Even here no chemical shift is detectable, the same result is obtained when the 3s and 3p peaks are considered. The untreated Co-sample as well as a sample treated with Murakami's solution for one day were then coated in a hot filament reactor at the usual conditions, but no diamond film could be deposited. Thus it has to be concluded that the surface of the Co has not been modified by Murakami's solution - in contrast to the findings on WC-Co samples.

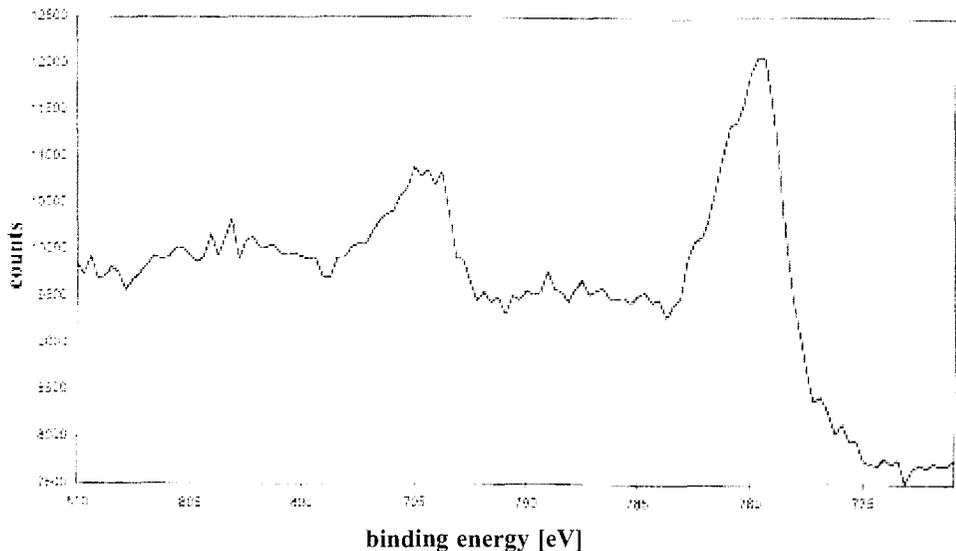## 3.3   Etching of Co in presence of other materials

Fig. 5: Spectrum of a sample etched for 18 h in Murakami's solution

To solve this puzzle, a Co film (on a glass substrate) was etched together with a hard metal sample. The effect could be observed with bare eyes: the Co film peeled of at points of contact with the cutting insert (after 24 h etching) and a bulk Co sample changed its color at that part of the surface which was in contact with the cutting tool insert. To elucidate which component of the cutting tool insert was responsible for this effect, the experiment was repeated with pieces of W and C; only the W led to the same result as the WC-Co.

The XPS spectra of the Co2p-peaks are compared in Fig. 6.
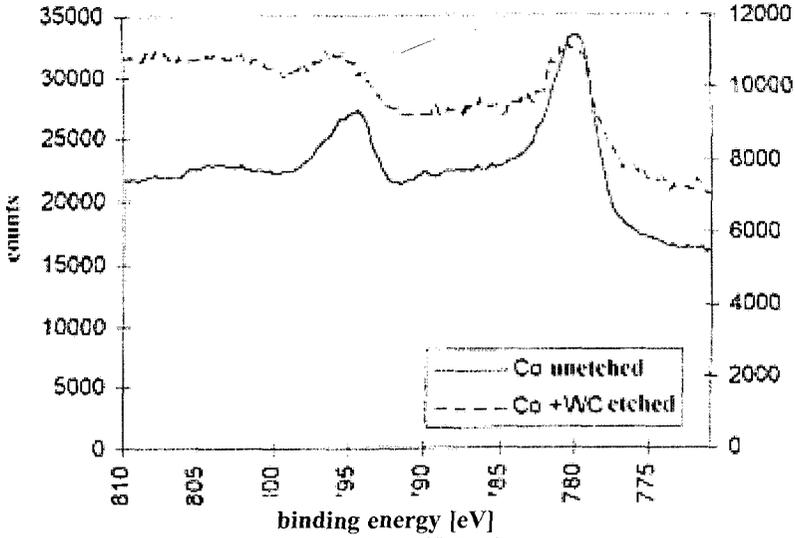After etching the peaks are shifted about 1 eV towards lower energies

Fig. 6:Spectra of Co sample unetched and Co + WC etched

compared to pure Co, but due to the 2 eV shift to higher energies - with respect to pure Co - of the untreated hard metal, this is the same effect as occurs when the hard metal has been etched; Fig. 7 summarizes this result.
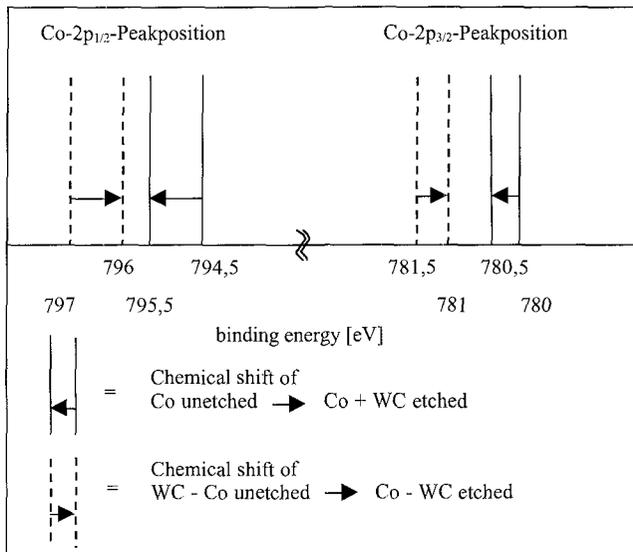

Fig. 7: Co-peak shift of the binding energy

To prove this effect, a Co coated Si substrate was etched with Murakami's solution having only one half of its area in contact to WC then (after rinsing with distilled water) it was coated with diamond (in a hot filament reactor at the usual conditions). The results are shown in Fig. 8: the upper part shows significantly less nuclei than the lower pretreated part.

3.4   Electrolytic etching

To elucidate the influence of W on the etching process, electrolytic etching has been applied; in addition to Murakami's solution (10 g KOH + 10 g K_3 [Fe(CN)$_6$] + 100 ml H_2O), $Na_2 CO_3$ (5g Na_2CO_3 +100 ml H_2O) and KOH + $Na_2 CO_3$ (10 g KOH + 6 g $Na_2 CO_3$ + 100 ml H_2O) were used.
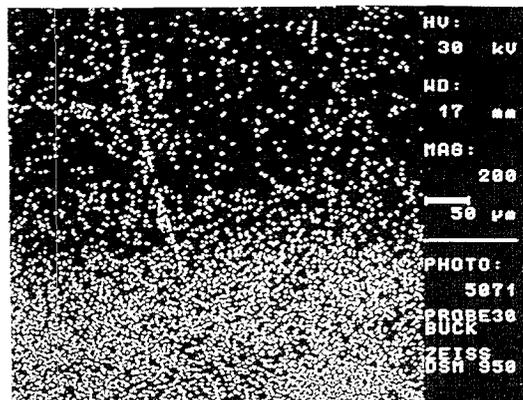

Fig. 8 SEM Image of a diamond coated Si sample

First of all it could be observed, that Murakami's solution etches significantly the WC-phase not only without applied potential (as is well known), but even when a voltage is applied. But the essential fact is, that at a potential of about 1.45 eV passive films on the Co have been obtained - similar to the usual etching with Murakami's solution.

Especially the performance of diamond coatings after electrolytic etching was similar to that after etching with Murakami's solution.

3.   Discussion

An unusual behavior of passive Co has already been reported by HEUSLER [25]. It is due to a thin film – only existing at positive potentials - consisting of an inner Co (II) oxide-phase and an outer spinel-phase. There is no evidence for a similar duplex layer on any other passive metal.

Cobalt is active at potentials below $U = 0.15$ V. At potentials between $U = 0.15$ V and $U = 0.7$ V in the region of primary passivity a layer is formed which - for thermodynamic reasons - can only consist of Co (II) oxide or the respective hydroxide. The film thickness increases only slightly from 2.0 nm at $U = 0.45$ V to 2.5 nm at $U = 0.86$ V. Above $U = 0.9$ V a layer is formed on top of the first layer showing strong optical absorption. It consists of a spinel phase Co_2O_4 [26] with a composition that can vary between Co_3O_4 and Co_2O_3; the change occurs at a voltage of $U = 1.22$ V. At even higher potentials the formation of Co OOH and CoO_2 would be thermodynamically possible. The thickness of the outer layer increases proportionally to the applied voltage up to 37 nm at $U = 1.65$ V. The dependence of film thickness on the pH-value is shown in Fig. 9.
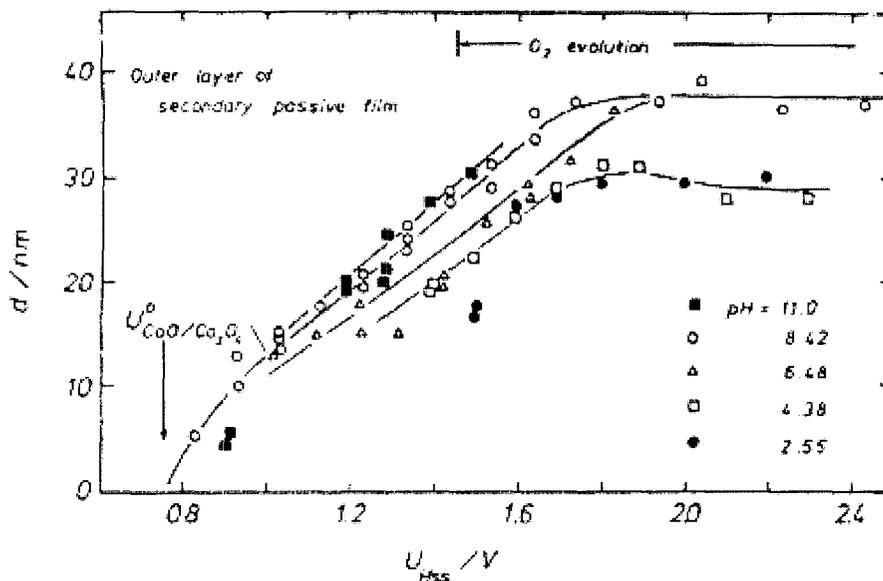

Fig. 9: Dependence of film thickness on the ph-value (after /25/)

Electrolytes containing complexing ligands with metal-ions produce a significantly more negative potential (for example, Cu in cyanid-solutions produces a negative potential to the hydrogen-electrode instead of producing the usual positive value because a complex-ion $[Cu(CN)_2]$ is formed). Murakami's solution contains a complexing ligand, too, namely the $Fe(III)(CN)_6$. A simple measurement of the potential of a Co-W-element and a Co-Murakami-W-element shows a difference greater than 0.7 V, this is sufficient for an anodic oxydation of Co. Thus it has to be concluded that Co is covered by a protective layer after treatment with Murakami's solution.

4. Acknowledgements

References

1. R. Haubner: Int. J. Refract. Metals & Hard Materials 16 (1998)167

2. R. Haubner, B. Lux in Hartstoffe, Hartstoffschichten, Werkzeuge, Verschleißschutz, Pulvermetallurgie in Wissenschaft und Praxis, Ed.: R. Ruthardt, Werkstoff-Informationsgesellschaft, Frankfurt, 1977, p. 89 – 116 (in German)

3. S. Kubelka, R. Haubner, B. Lux, R. Steiner, G. Stingeder, M. Grasserbauer: Diamond Films and Technology 5 (1995) 105 – 120

4. M. Nesladek, C. Asinan, J. Spinnewyn, R. Lebout, R. Lorent, M. D. Olieslaeger: Diamond Relat. Mater. 3 (1994) 912 - 916

5. J. Spinnewyn, M. Nesladek, C. Asinari: Diamond Relat. Mater. 2 (1993) 361 - 364

6. H. Schachner, B. Lux, K. G. Stjernberg, A. G. Thellin, H. Tippmann: EP 0166708 A2 (1986)

7. M. Tsubokawa, N. Hayashi: EP 0413834 A1 (1991)

8. K. Shibuki, K. Sasaki, M. Yagi, T. Suzuki, and Y. Ikuhara, Surface & Coatings Technol. 68/69 (1994) 369 - 373

9. M. Murakawa S. Takeuchi, H. Miyazawa, and Y. Hirose, Surface & Coatings Technol. 36 (1988) 303 - 310

10. Y. Saito, K. Sato, S. Matuda, and H. Koinuma, J. Mater. Sci. 26 (1991) 2937 - 2940

11. T.-Y. Yen, C. T. Kuo, and S. E. Hsu, Mater. Res. Soc. Symp. Proc. 168 (1990) 207 - 212

12. T. H. Huang, C. T. Kuo, and T. S. Lin, Surface & Coatings Technol. 56 (1993) 105 - 108

13. K. J. Grannen, F. Xiong, and R. P. H. Chang, Surface & Coatings Technol. 57 (1993) 155 - 162

14. H. Itoh, T. Nakamura, H. Iwahara, and H. Sakamoto, J. Mater. Sci. 29 (1994) 1404 - 1410

15. T. Isozaki, Y. Aito, A. Masuda, K. Fukumoto, M. Chosa, T. Ito, E. J. Oles, A. Inspector, and C. E. Bauer, Diamond Relat. Mater 2 (1993) 1156 - 1159

16. E. R. Kupp, W. R. Drawl, and K. E. Spear, Surface & Coatings Technol. 68/69 (1994) 378 - 383

17. M. Kawarada, K. Kurihara, and K. Sasaki, Diamond Relat. Mater. 2(1993) 1083 – 1089

18. S. Takatsu, K. Saijo, M. Yagi, K. Shibuki, and J. Echigoya, Mater. Sci. Eng. A 140 (1991) 747 -752

19. Y. Saijo, T. Isozaki, A. Fukumoto, M. Chosa, T. Ito, E. Bauer, A. Inspector, and E. J. Oles, Diamond Relat. Mater 2 (1993) 1391

20. F. Deuerler, M. Pies, H. van den Berg, R. Tabersky, V. Buck: phys. stat. sol. (a) 154 (1996) 403 - 422

21. R. Haubner, S. Kubelka, B. Lux, M. Griesser, M. Grasserbauer: J. Physique C5 (1995) 753 - 760

22.   M. G. Peters, R. H. Cummings: EP 0519587 A: (1992)

23.   V. Buck, F. Deuerler: Diamond Relat. Mater. 7 (1998)1544 – 1552

24.   C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder: Handbook of X-ray photoelectron spectroscopy, Perkin Elmer Corporation, Eden Prairie, Minnesota

25.   K.E. Heusler: Passivity and Breakdown of Passivity of Nickel, Cobalt, and Chromium in (Eds.):
R. P. Frankenthal, J. Krüger: Passivity of Metals, The Electrochemical Society 1978, 771-801

26.   P. Petzow: Metallographisches Ätzen, Gebr. Bornträger, 1976, p. 8 ff (in German)