Pergamon

Materials Research Bulletin, Vol. 32, No. 5, pp. 491-499, 1997

0025-5408/97 $17.00 +.00

PII S0025-5408(97)00019-6

THE REDUCTION OF Co^{2+} BY POLYALCOHOLS IN THE PRESENCE OF WC SURFACES STUDIED BY XPS

G. Eriksson and H. Siegbahn*
Department of Physics, University of Uppsala, Box 530,
S 751 21 Uppsala, Sweden

S. Andersson, T. Turkki and M. Muhammed
Department of Chemistry, Inorganic Chemistry,
Royal Institute of Technology, S 100 44 Stockholm, Sweden

(Refereed)
(Received October 14, 1996; Accepted October 14, 1996)

ABSTRACT

Cemented carbides, widely used in cutting tools, are made by sintering fine particles of WC and Co. So far the production of the sintering material has utilized a time and energy consuming grinding and mixing step. An alternative process to chemically precipitate Co metal directly onto WC particles in solution has been investigated by one of the author groups. A Co salt is dissolved in a suspension of ethylene glycol and WC powder and boiled under vigorous stirring. In the present work, surfaces of WC were studied with X-ray photoelectron spectroscopy (XPS), with Al Kα radiation and synchrotron radiation, before and after various reaction times. These studies were undertaken to further clarify the reaction mechanism in particular the possible existence of a Co^{2+} complex specifically adsorbed on the WC-surface. The morphology of the surfaces was examined with scanning electron microscopy (SEM). The Co precipitation seems to proceed through ordinary heterogeneous nucleation. WO_3 on the surface was reduced by hot glycol. No evidence for Co-complex binding to the surface could be found. This lends support to the use of the developed process for coating other substrate surfaces. *Copyright © 1997 Elsevier Science Ltd*

---

*To whom correspondence should be addressed.

KEYWORDS: A. carbides; C. photoelectron spectroscopy, C. electron microscopy

INTRODUCTION

Cemented carbides are widely used in cutting and abrading tools as well as for wear resistant coatings due to their exceptional combined properties of hardness, toughness, and wear resistance (1–7). These hard materials consist of two separate phases. One is a hard and high melting phase which consists mostly of pure WC or mixed carbides such as (W–Ti)C, (W–Ti–Ta)C. The other phase consists of a ductile binder phase with a lower melting point; mainly cobalt metal is used due to its outstanding wetting, adhesion, and mechanical properties. Nickel metal is also used sometimes. In these composite materials the positive properties of the two phases are superimposed, the carbide phase providing hardness and wear resistance, while the ductile binder phase contributes toughness.

Different grades of cemented carbides are obtained by varying the cobalt content, the ratio of different carbides, and the grain size of the carbide particles. The commercially available grades of these cemented carbides contain binder phase in a concentration range between 3 and 30 percent, while the size of the carbide particles varies between 1 and 10 µm. Depending on the application, hard materials with higher cobalt content or coarser carbide grains lead to increased toughness but decreased hardness. On the other hand, the more complex carbides are harder, exhibit less wear, and are chemically more resistant than WC-based alloys but have decreased toughness.

In the conventional production of hard materials, the starting materials WC or (W–Ti)C and cobalt or nickel metal are prepared and reduced in two separate streams. The compounds are then mixed by grinding with ethylene glycol used as a solvent binder. This is a time-consuming and costly process. The thus prepared powder is then spray-dried, pressed, and sintered.

A new process which circumvents the grinding and mixing step has been investigated (8). WC and (W–Ti)C are coated with cobalt and nickel metal in solution by reducing the metals from a suitable salt with ethylene glycol while keeping the solid in suspension. The ethylene glycol plays the role of a solvent and a reducing agent at the same time. This process is based on the so-called polyol process, described in the literature by Fievet, Figlarz, and others (9–15). The polyol process is used for the fabrication of cobalt and nickel metal powders with small particle size. These metal powders can be used, for example, in the production of hard materials.

The polyol process can be used to reduce cations of a number of transition metals such as Co, Ni, Cd, Pb to the metallic state, as well as of more easily reducible metals such as Cu and precious metals. The reducing agent is a polyalcohol such as ethylene glycol, diethylene glycol, or propylene glycol. The reaction proceeds in two steps (9), which in the case of reduction from $Co(OH)_2$ can be sketched as follows:

Step 1: Crystalline hydroxide → Intermediate phase

- Progressive dissolution of the hydroxide.
- Precipitation of the intermediate phase.
- Formation of water.

Step 2: Intermediate phase → Metal

- Dissolution of the intermediate phase.
- Reduction in solution.
- Formation of volatile byproducts.
- Homogeneous nucleation and growth of metal particles.

In the first step, ethylene glycol is dehydrated to acetaldehyde by heating. This reaction is catalyzed by the presence of Co2^{+} ions. The acetaldehyde then acts as a reducing agent by reducing Co^{2+} to cobalt metal. The main oxidation product in this step is diacetyl ((2,3)butadion). The overall reaction is then summarized as

$$2CH_2OH–CH_2OH\text{----}(–2H_2O)\rightarrow 2CH_3CHO\text{----}(+CO^{2+})\rightarrow$$
$$CH_3–CO–CO–CH_3 + H_2O + Co$$

According to Fievet et al. (9), two intermediate phases form during the reaction. They have a lamellar structure with intercalated organic molecules, but are not fully understand. The first phase is believed to consist of layers of $Co(OH)_2$ with intercalated molecules of ethylene glycol and is present during the heating. The second phase, occurring at 195°C, is modelled ethylene glycolate sharing an oxygen atom with the cobalt hydroxide.

Experiments showed that WC or (W–Ti)C powder suspended in the glycol promoted the kinetics of the Co reduction. It was completed in a shorter time, 5 h, compared to 24 h without the powder. Also, the reduction rate of Ni was enhanced. Metal precipitation occurred on the carbide grains (8). This indicated a possibility for another reaction mechanism, where the carbide surface could participate in the reaction, for instance, with a Co-complex directly bonding to the surface.

Further clarification of the role of the carbide surface in the reaction mechanism is important in order to optimize the process and also to assess its potential applicability to other surfaces, and the possibilities to reduce the amount of ethylene glycol and/or to recycle solvent. The WC surfaces were thus studied with XPS and SEM. A Co^{2+}-complex binding to the WC surface would be expected to lead to observable chemical shifts, primarily in the W4f core spectrum. A Co^{2+} bound directly to surface tungsten atoms would withdraw charge yielding a W4f peak shifted towards higher binding energy with respect to the WC peak.

EXPERIMENTAL

Discs of WC were used as substrates and the coating process was carried out in a 2-liter glass reactor. Heating and temperature control was accomplished with an electric mantle heater and a thermocouple. An air-cooled condenser allowed the removal of water and volatile byproducts while the ethylene glycol was refluxed back to the reactor. The discs were hung from the central neck on stainless steel wires, so that the liquid could circulate and the concentration would be homogenous around the discs. Prior to the reaction, the discs were cleaned and etched in 65% HNO_3 for 15 min, 7 M KOH for 15 min, and rinsed in high purity water (MQ), to remove any surface contaminants.

To the 2-liter glass reactor, 400 ml of ethylene glycol and 3.15 g of $Co(OH)_2$, corresponding a glycol/Co molar ratio of 210, were added. Ten discs were hung as described earlier, and the reactor was heated to 195°C. After 1 min, and then after every 20 min, a disc was removed and immediately put in cold glycol to quench the reaction and then kept in glycol. Another disc was put in glycol directly, as a reference sample.

In a second experimental series, the discs were subjected to three alternative treatments: boiled in pure glycol (1, 10, 30 min), glycol + $CoAc_2$ (1, 10, 30 min; glycol/Co molar ratio 500), or glycol + $Co(OH)_2$ (1, 10, 30 min; glycol/Co molar ratio 200). The reacted discs were quenched in cold glycol and dipped in MQ water just before XPS analysis. Prior to the reaction, four of these discs had been etched and also had been oxidized in an oven at 110°C for 18 h, to promote the formation of an oxide layer.

All the discs were examined with XPS prior to and after each experiment. Al Kα radiation (hn = 1487 eV) was used to excite spectra over the binding energy regions of W4f (45–28 eV), C1s (296–278 eV), and Co2p (795–775 eV). Total scans (1000–0 eV) were also recorded. In addition, spectra were run at MAX-lab, Lund, using synchrotron radiation at hn = 157 eV. The chosen low photon energy yielded photoelectrons with a very short mean free path in the solid, resulting in extreme surface sensitivity.

The morphology of the surfaces was investigated with SEM. To facilitate pump-down, the discs were rinsed in a small amount of ethanol to remove glycol and then blown dry with argon. Emitted X-rays were analyzed by energy-dispersive spectroscopy (EDS) for one disc.

RESULTS AND DISCUSSION

The spectra prior to the reaction were found to be identical except for minor variations of the relative intensity of the C1s hydrocarbon contamination peak for some specimens. In the spectra obtained after the reaction, the Co signal (Co2p, Co3p) intensity increased with increasing reaction time (i.e., the time the discs were kept in the reactor). There was a corresponding decrease of the C1s carbide signal and the W4f signal intensity. This illustrates the WC surface being gradually coverd by cobalt metal. The development of scan spectra (650–0 eV) with reaction time (normalized to the O1s peaks) is shown in Figure 1. The Co2p lines (not shown) showed the presence of Co metal as well as divalent species, which we interpret as due to an oxidized overlayer on the precipitated metal. The relative weights of these two Co-states varied in an irregular way with reaction time, and a natural interpretation is thus that this simply reflects a statistical fluctuation in exposed Co metal beneath an oxidized overlayer. In view of this as well as the comparatively broad features observed which made resolution into component peaks difficult, no further attempts were made to identify possible additional states in the Co-spectra. Instead, attention was focused on the W4f lines, the general appearance of which made identification in terms of different chemical states more straightforward.

The upper panel in Figure 2 shows Al Kα-excited W4f spectra, the major feature of which is a spin-orbit-split doublet ($j = 5/2$ and $j = 7/2$) due to WC. The low intensity peak at 38 eV is assigned to the $j = 5/2$ component of WO_3, the other component being partially hidden under the WC $j = 5/2$ peak. In this excitation mode, the WC W4f lineshapes remained the same, independent of reaction time, however at decreasing relative intensity as shown in Figure 1. The only noticeable difference is that the WO_3 peaks decrease slightly in intensity compared to the WC peaks after reaction (cf. inset in Fig. 2 after 40-min reaction).

The lower panel of Figure 2 shows spectra recorded at MAX-lab using synchrotron radiation at hn = 157 eV. These spectra are substantially different from those excited with Al Kα radiation shown in the top panel. First, the increase in surface sensitivity at lower photon energy leads to enhancement of the oxide states in the outermost surface layers. Two oxide

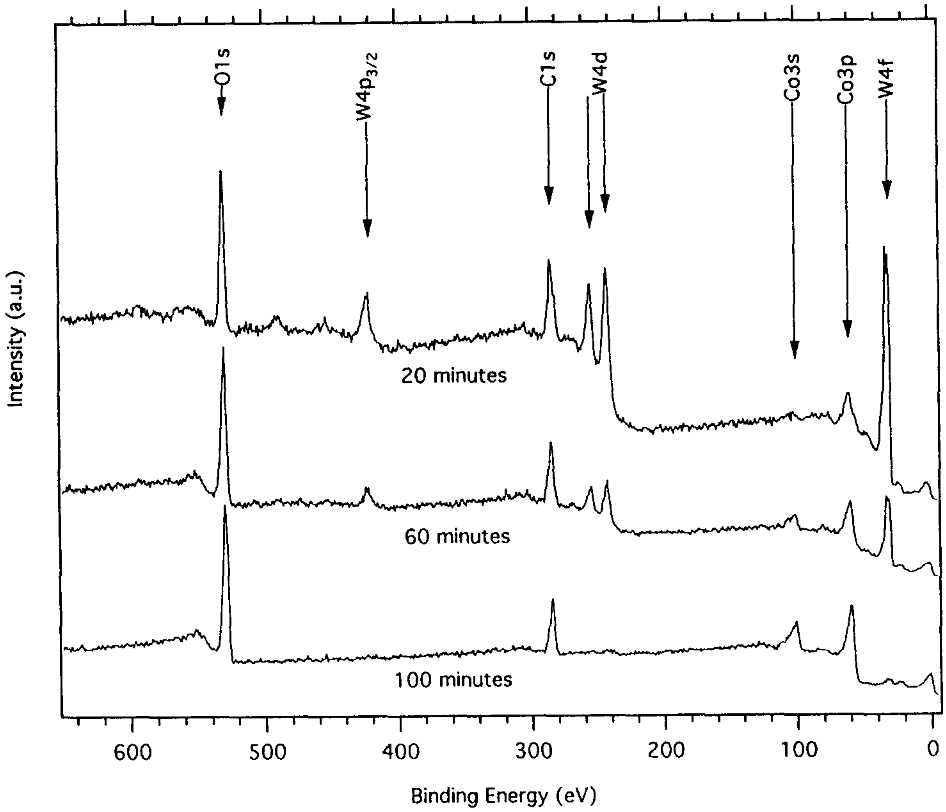

FIG. 1

XPS scans (hn = 1487 eV) of discs reacted 20, 60, and 100 min in $Co(OH)_2$ and glycol. The spectra are normalized to the O1s signal.

states are now clearly apparent, one corresponding to WO_3, also seen in the upper-panel spectra, as well as another intermediate state which we interpret as a WO_2-like state. This fits with previous studies of W oxides (16). This latter state cannot be easily resolved using Al Kα excitation, but it is seen only as a minor asymmetry of the WC peaks. Second, the experimental resolution is significantly improved (FWHM = 0.3 eV for the WC peaks, compared to 0.9 eV in the upper-panel spectra).

The reduction of the surface is even more clearly demonstrated in the spectra (Fig. 3, upper panel) of a disc which was preoxidized in an oven at 110°C for 18 h prior to the recording of the spectra. These spectra amplify the effect of reduction of the WO_3 state due to the reaction. It can be noted that the ratio between the WO_2 and WC peaks remains approximately the same after reaction; however, no new W4f peaks due to the reaction are observed. We thus interpret the general behavior at the WC surface/solution interface during the reaction process as follows: the WO_3 outermost layers are successively dissolved, uncovering the WC bulk with a thin terminating layer of partly oxidized W. The WO_2 peaks are likely, then, to originate from this terminating layer (on the order of one to two atomic layers), which explains their constant relative intensity with respect to the WC peaks.

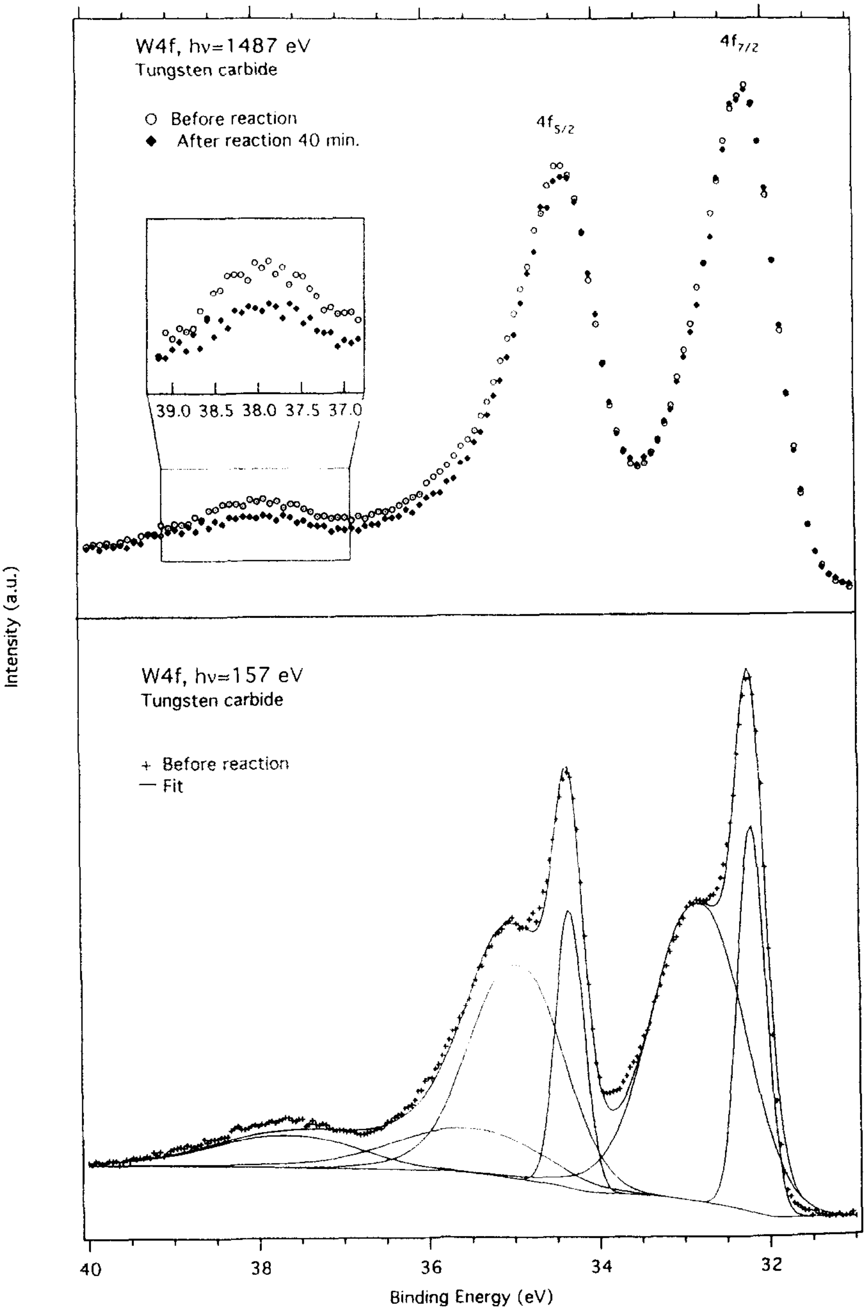

FIG. 2

(upper) XPS spectra of a disc prior to the reaction, and the same disc after 40-min reaction (hn = 1487 eV, take-off angle = 90°). (lower) Spectrum of an etched surface recorded with hn = 157 eV and take-off angle = 60°. Three spin-orbit doublets are fitted.

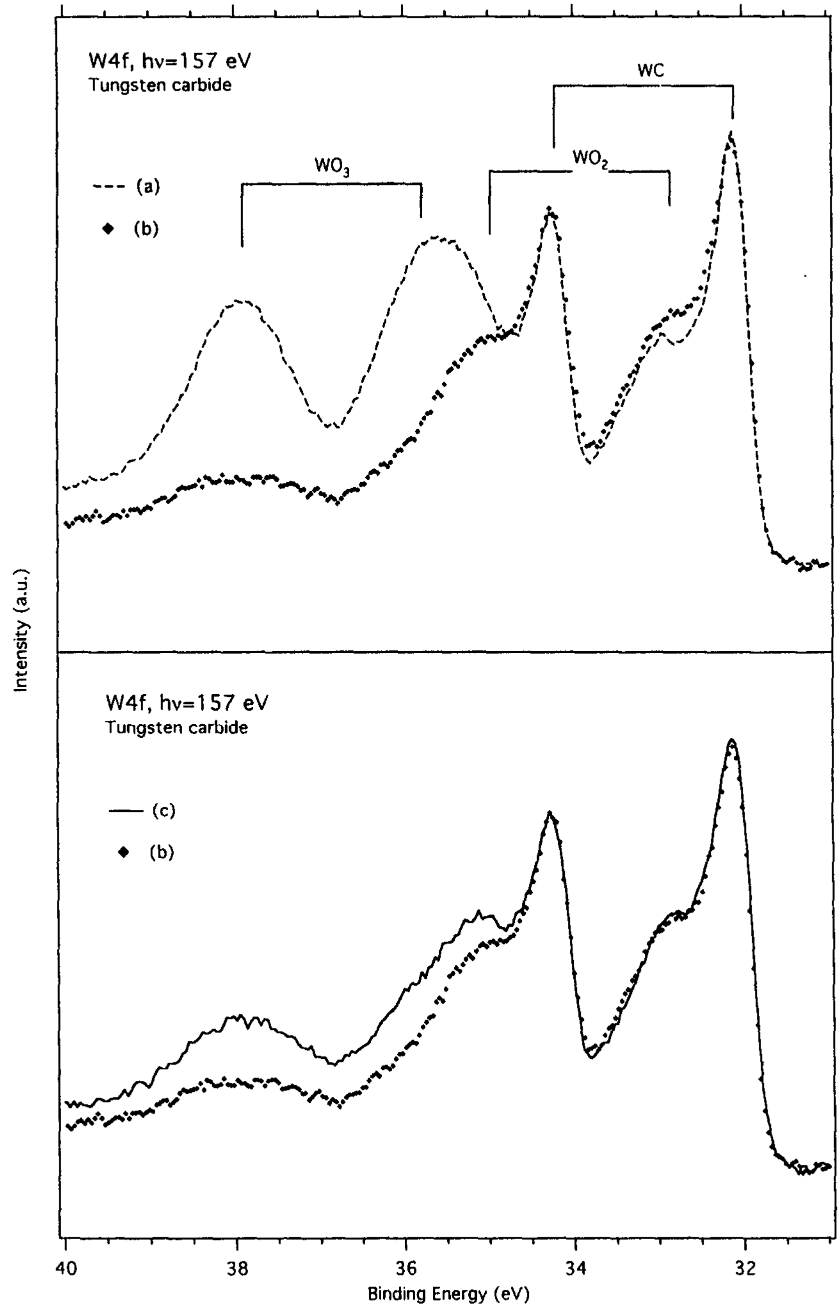

FIG. 3

(upper) Spectra for a heat-treated disc (a) before and (b) after reaction 1 min with pure glycol (b). (lower) Spectra (b) is the same as (b) in upper panel, and spectra (c) is obtained from a heat-treated disc reacted in Co(OH)$_2$ for 1 min.

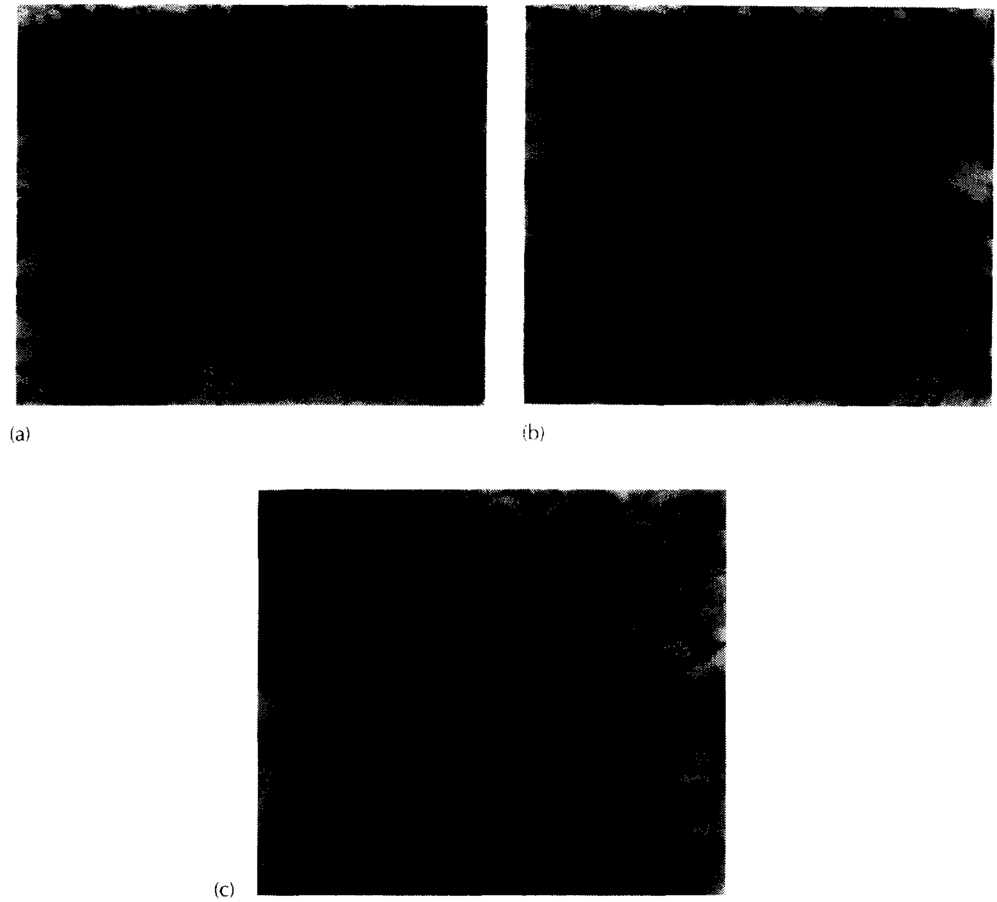

FIG. 4
SEM pictures of discs reacted (a) 40, (b) 60, and (c) 120 min in a glycol solution of $Co(OH)_2$. Nuclei of cobalt metal are seen to form and coalesce at a size of about 1 μm.

With access to the extreme surface sensitivity provided by the synchrotron radiation excitation, it is natural to use the W4f spectra as fingerprints of the surface condition for different reactions. In order to investigate the possibility of catalytic activity involving direct Co^{2+}/surface bonding, W4f spectra obtained after various reaction conditions were compared. Two of the resulting W4f spectra are shown in Figure 3 (lower). If the WC particles were to act catalytically, one would expect to observe spectral changes specifically associated to the states derived from the WC surface, viz. the two components of lowest binding energy. As can be seen, the spectra are virtually identical in this energy range for the two reaction conditions. We thus conclude that the WC surface most likely is not specifically involved via catalytic states in the reduction of Co. This conclusion is supported by earlier experiments (8), in which coating of an insulator, γ-Al_2O_3 with cobalt, was studied. The reaction time in this case was about 5 h, similar to that for WC, but the yield was somewhat lower, 78% compared to 94% in the case of tungsten carbide.

The conclusion is further corroborated by SEM pictures at different reaction times (cf. Fig. 4). The Co metal growth on the WC surfaces is seen in these pictures to proceed from nuclei which grow in size with reaction time. The density of nuclei seems to be related to substrate topology (scratches in the WC surface lead to lower density of nuclei). After 2 h reaction time, the average size of the nuclei was ≈1 μm and coalescence had occurred over most of the surface.

CONCLUSIONS

We have studied the reduction of Co^{2+} by polyalcohols in the presence of WC surfaces by means of XPS at high surface sensitivity using synchrotron radiation excitation. Two oxide states have been identified on the WC surface which vary in relative magnitude with reaction time. WO_3 states are found to be rapidly reduced by reaction with hot glycol. The metal precipitation seems to be assisted by heterogeneous nucleation and not a catalytic action by the WC surface. This should enable the process to be used for a greater variety of substrate and coating materials. The process is promising, and future work should be directed toward quality control of the coated powder.

ACKNOWLEDGMENT

This work was supported by the Swedish Board of Technical Development (NUTEK).

REFERENCES

1. H.E Boyer, T.L. Gall, *Metals Handbook*, American Society for Metals, Metals Park, OH (1985).
2. R.E. Kirk and D.F. Othmer, *Encyclopedia of Chemical Technology*, Vol. 23, Wiley–Interscience (1971).
3. S.W.H. Yih and C.T. Wang, Tungsten, *Sources, Metallurgy, Properties and Applications*, Plenum, New York (1979).
4. P. Schwarzkopf and R. Kieffer, *Refractory Hard Materials*, Macmillian, New York, (1953).
5. H.E. Exner, *Int. Metals Rev.* **4**, 149 (1979).
6. B.H. Kear and L.E. McCandlish, *Nanostr. Mater.* **3**, 19 (1993).
7. B.H. Kear and L.E. McCandlish, *Nanostr. Mater.* **1**, 119 (1992).
8. S. Andersson and M. Muhammed, unpublished results.
9. F. Fievet, J.P. Lagier and M. Figlarz, *MRS Bull.* **14**(12), 29 (1989).
10. B. Beaudoin and M. Figlarz, *Solid State Ionics* **32/33**, 198 (1989).
11. M. Figlarz, F. Fievet and J.P. Lagier, in *Proc. MRS International Meeting on Advanced Materials*, Vol. 3, p. 125, Materials Research Society, Pittsburgh, PA (1988).
12. B. Blin and F. Fievet, *New J. Chem.* **13**, 67 (1989).
13. M. Figlarz et al., U.S. Patent 4539041.
14. F. Fievet, J.P. Lagier, M. Figlarz, B. Blin, M. Bonneau and H. Pastor, *Informations Chimie* **294**, 247 (1988).
15. B. Blin, Thèse de Docteur Ingénieur, L'Université Paris VII, 1987.
16. R.J. Colton and J.W. Rabalais, *Inorg. Chem.* **15**, 236 (1976).