

Homogeneous WC–Co-Cemented Carbides from a Cobalt-Coated WC Powder Produced by a Novel Solution-Chemical Route

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A solution chemical route to cobalt-coated WC-powder is described that allows for the preparation of WC–Co powders and compacts having a carbon content very close to the desired carbon content even under an inert atmosphere. The microstructural homogeneity in the sintered WC–Co composites when using the Co-coated grains was found to be superior as compared with conventionally mill-mixed powders, and the structural changes in the individual WC-grains were found to be much smaller, which is ascribed mainly to the fact that the coated grains do not require a grinding step leading to the formation of a tail of smaller WC grain sizes.

I. Introduction

THE WC–Co composites are frequently used materials for cutting tools in the machining and drilling of materials ranging from electric circuits boards to rock. The high performance and versatility of the cemented carbides arises from a combination of the very hard WC grains and the tough and well-adhering cobalt binder phase, which is also essential for the sintering process.^{1,2} The composites normally contain 5–10 wt% cobalt as a binder phase between 1- and 10- μm -sized WC-grains. Commercially, a powder-metallurgical route is used in the production of the cemented carbides: the precursor powder mixture is prepared by milling Co and WC powders together with an organic binder in a rotating ball mill. The milled powders are then spray dried into agglomerates, about 100 μm in size, which are then pressed into green bodies of various sizes and shapes. The binder is removed in a hydrogen-containing atmosphere at ca. 400°C, and then follows the sintering process, comprising heating to ca. 1450°C and an isothermal heat treatment at this temperature for typically up to 1 h.^{1–10} The milling procedure has several drawbacks: (i) the wear of the milling bodies may lead to contamination of the milled mixture. (ii) Even after extensive milling, due to crushing of the WC powder, a wide size distribution of the particles is found rather than a narrow size distribution, which implies that larger amounts of Co, higher sintering temperatures, and longer sintering times must be used. (iii) Grain growth during sintering cannot be avoided due to the more rapid dissolution and reprecipitation of the small particles, which makes the microstructure obtained strongly dependent on the milling parameters applied. Therefore, very coarse-grained cemented carbide compacts, needed in the mining applications, or compacts containing grains of a narrow size distribution are difficult or impossible to prepare with conventional techniques.

A way to overcome the problems of the grinding/mixing process and to obtain a higher homogeneity of the WC and Co mixture is to coat the WC powder with the cobalt phase, but in spite of its importance, there are quite a few such routes reported as far as we can find, and most are in the patent literature. Chemical vapor deposition and other gas phase-based routes are of less interest due to the high costs, low flexibility, and low rate of deposition. Solution-based routes have been reported using the polyol precipitation process,^{11,12} electro-less techniques,¹³ and just recently a route based on precipitation by pH adjustment was patented.¹⁴ All of them use thermal treatment under a reducing atmosphere to convert the cobalt compounds to metal and have extra steps introduced to remove different kinds of additives, such as large amounts of organic groups, phosphates, Pd, Sn, and alkali –salts, which are detrimental to the materials' properties even in very small amounts, which makes the processes tedious. It is normally not reported how successfully the additives have been removed and it is difficult to make detailed comparisons, due to the very nature of the patent literature mainly being judicial. The complexity, and in some cases the reduced yields and large volumes of solvents containing complexes that are difficult to purify by precipitation, e.g. in the polyol route, make some of these routes more difficult to apply with environmental restraints, even though water is sometimes put forward as an environmentally benign solvent.

In a patent, we have described an efficient solution-based route to nonagglomerated Co-coated WC.¹⁵ In this case, the precursor solution should preferentially consist of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, triethanolamine (TEA), and methanol to which WC powder is added. The methanol solvent is evaporated under moderate stirring, and the powder lumps thereby obtained are heated to remove the organic residues. The burning-off procedure is carried out under special conditions, in order to ensure that the carbon content of the final compact will not deviate from that set by the chemical composition of the WC powder.

In this article, we will describe the chemistry and microstructure development in some detail but instead of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, a mixture of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is used as a precursor for Co, which permits a more straightforward burning-off procedure of the organic residues, allowing for the production of coated powders with very close to the desired stoichiometric W, Co, and C contents, and very low O (ca. 0.02 wt%) and N (ca. 0.01 wt%) contents. This thus enables a direct formation of Co-coated WC powder without introducing foreign elements and treatment with reducing gases such as H_2/N_2 . This route uses high concentrations of metal salts in the solvent and the yield is very close to 100%. The evaporated methanol can be recycled, and the gases evolved on heat treatment are similar to car exhaust gases such as NO_x , CO_x , and organic molecules and should easily be taken care of with a catalytic converter. There is no strong complex binder that inhibits the easy precipitation of the Co salts from a simple pH adjustment of cleaning solutions, etc., meaning that this route not only produces very controllable metal coatings, but is also very environmentally controllable.

R. Koc—contributing editor

Manuscript No. 22245. Received September 14, 2006; approved June 26, 2007.

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A study comprising carbon content analysis and phase-development studies of Co precursor mixtures with different nitrate-to-acetate ratios was conducted to gain control of the carbon content. The details of the process used for the preparation of nanostructured cobalt was recently described.¹⁶ The microstructure and phase development of the coated powder were investigated. The sintering process to form compacts and their microstructures obtained from cobalt-coated WC powder and ball-milled powder mixtures, respectively, have been compared. The experimental techniques used were scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), transmission electron microscopy-EDS (TEM-EDS), powder-X-ray diffraction (XRD), chemical analysis (W, Co, C, N, O), thermogravimetric analysis, and dilatometry.

II. Experimental Procedure

(1) Equipment and Chemicals Used

The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros Organics, Geel, Belgium; 99%), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (Fluka, Chemie, Buchs, Switzerland; 99+%), methanol (MeOH) (Merck p.a., Darmstadt, Germany), and TEA (Fluka, ca. 99%) were used as purchased. The water contents of the Co salts were determined by a standard thermogravimetric procedure. The WC powder had a main size fraction of 5–8 μm and close to 100% of the particles fell between 3 and 11 μm , according to the analysis supplied (H. C. Starck GmbH & Co. KG, Laufenburg, Germany). The mixed WC+Co powder made for comparison was obtained from Sandvik Coromant (Västberga, Sweden). It was produced by standard milling with the same WC powder source as was used for the coating procedure.

Powder XRD photographs were obtained with a Guiner–Hägg focusing camera (Stockholm University, Stockholm, Sweden), using $\text{CuK}\alpha 1$ radiation and Si as the internal standards. The SEM studies were carried out with JEOL 820 and JEOL 880 microscopes (Tokyo, Japan), equipped with EDS, Link 10000AN, and Link ISIS, respectively, and the TEM imaging was made with a JEOL 2000FX microscope. The thermogravimetric (TG) analyses were performed with a Perkin-Elmer TGA7 apparatus (Waltham, MA), which was thoroughly flushed with nitrogen before the measurements were started. The dilatometer curves were obtained with a Setaram DHT 2050 dilatometer (Caluire, France), in an argon atmosphere. The W, Co, C, N, and O contents were determined by an external analytic laboratory, with the C, N, O contents determined using standard LECO combustion-spectroscopic techniques (Stockport, U.K.), and the W and Co contents using the X-ray fluorescence technique. Small batches of the WC–Co mixtures for the studies of the phase evolution were prepared in the TG apparatus, while the larger batches of ca. 10 g for Co and 50 g for WC–Co dilatometry and chemical analysis were prepared in a closed alumina container in a top-loaded pit furnace with flowing nitrogen gas entering from the bottom. A heating rate of 10°C/min to 700°C was used in both cases.

(2) Preparation of Cobalt Metal

In order to study how cobalt metal with low contents of additional elements, i.e. C, N, and O, could be prepared from the Co salt precursors, a series of samples with varying $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ composition ratios were prepared as outlined in Fig. 1, but without addition of WC powder.¹¹ A more detailed account of the phase development with an aim to prepare nanocrystalline cobalt is published elsewhere.¹⁶ The ratios studied were $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}] = 1:0, 9:1, 4:1, 2:1, 7:6, 1:1, 1:2, \text{ and } 0:1$. The thermal decomposition of these mixtures was studied in the TG unit in a nitrogen atmosphere at a heating rate of 10°C/min. The weight-loss curves are given in Fig. 2. The C, N, and O contents were determined for the larger batches prepared in the top-loaded pit furnace. A graph of the obtained carbon contents plotted versus the $\text{NO}_3:\text{OAc}$ ratio in the

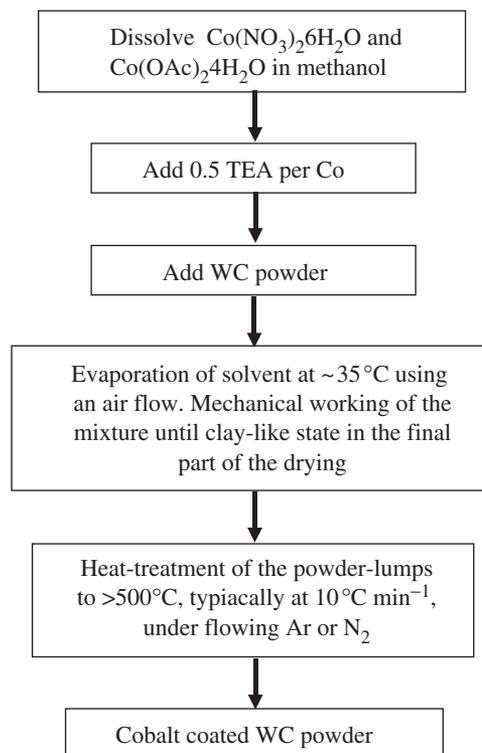


Fig. 1. Preparation scheme for Co-coated WC powder with 6 wt% Co. Table I. The amounts of chemicals used in a normal batch.

Table I. The Amounts of Chemicals Used in a Normal Batch

Chemical	Formula	Amount
Tungsten carbide	WC	18.80 g
Cobalt nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	5.333g
Cobalt acetate	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$	0.507 g
Triethanolamine	$\text{N}(\text{C}_2\text{H}_5\text{OH})_3$	1.35 mL
Methanol	CH_3OH	100 mL

precursor mixture is given in Fig. 3. Powder-XRD patterns were recorded of samples heated to 500°, 700°, and 1000°C in the TG unit, and to 700°C in the furnace. TEM studies were performed on a sample with the $\text{NO}_3:\text{OAc}$ composition 9:1 and heated to 500°C.

(3) Preparation of Co-Coated WC Powder and WC–Co Compacts

Co-coated WC powder (6 wt% Co) was prepared according to the route outlined in Fig. 1, Table I. In order to study how the

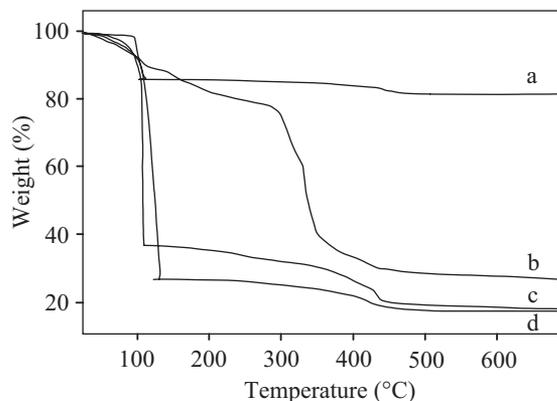


Fig. 2. Thermogravimetry graphs obtained at a heating rate of 10°C/min in a nitrogen atmosphere of a mixture of WC powder and Co concentrate ($\text{NO}_3:\text{OAc}$ ratio of 9:1) for formation of WC–6 wt% Co (a); Pure concentrates of the $\text{NO}_3:\text{OAc}$ ratios 0:1 (b), 9:1 (c), and 1:0 (d).

¹¹Warning: Although we have not observed any tendency toward explosive behavior during the many studies on the cobalt and WC-Co mixtures, any mixture of nitrate and organic compounds should be regarded as potentially hazardous to explosion.

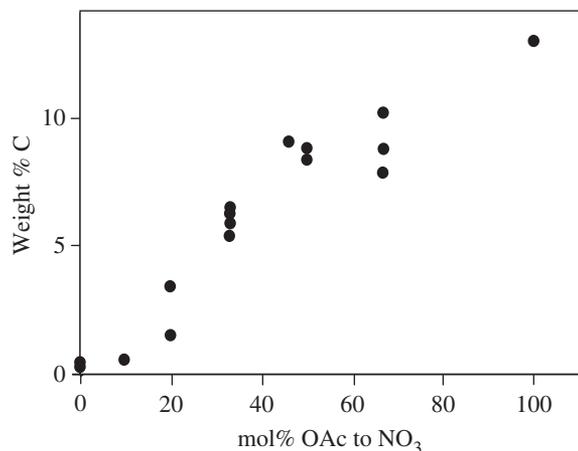


Fig. 3. Carbon content of powders obtained by heating Co precursors with different ratios of acetate to nitrate (mole% OAc in NO₃), to 700°C at 10°C/min, in nitrogen.

morphology and phase contents of the cobalt layer vary with the heat treatment, nonheat-treated powders were heated in the TG apparatus, quenched at 500°, 700°, 800°, 900°, and 1000°C, and subsequently investigated by powder XRD. The XRD peaks, but those of WC are given in Table II. In addition, the samples quenched at 500°, 700°, and 1000°C were studied with SEM-EDS and that from 700°C in the pit furnace also by C, N, and O analysis. A thoroughly ball-milled mixture of Co-metal and WC was prepared for comparison. The coated and ball-milled WC-Co powders were mixed with ethanol and ultrasonically deagglomerated, dried, and then uniaxially pressed under 10 MPa to cylinders with 6-mm diameter and ca. 5-mm length, without a pressing aid. These compacts were studied in a dilatometer using a heating rate of 5°C/min up to 1450°C and isothermal heat treatment at this temperature for 10 min, followed by rapid cooling. The microstructures obtained were investigated with SEM-EDS on polished cross sections.

III. Results and Discussion

(1) Studies on the Co-Metal Formation; Preparation of Cobalt Precursor Mixtures

Cobalt precursor mixtures from TEA, Co(NO₃)₂·6H₂O, and Co(OAc)₂·4H₂O with nitrate-to-acetate ratios from 1:0 to 0:1 were prepared according to the scheme given in Fig. 1, but without addition of WC and heat treatment. The TEA was added in order to inhibit crystallization of the Co precursor, which otherwise easily occurred, especially for the 1:0 nitrate-to-acetate ratio. From IR and TG studies, it was shown that the multidentate TEA is sufficiently strongly bonded to the Co²⁺ ions to remain in the dried concentrates, and the thermal decomposition of the acetate and nitrate groups during drying is believed to be at most very small.

Table II. XRD Peak Maxima for Phases Other than WC in Coated WC-6%Co Powder Heated at 10°C/min

Temperature (°C)	Phase	<i>d</i> -value (Å) (<i>hkl</i>)
500	Co (fcc)	2.04 (111)
700	Co (fcc)	2.04 (111)
800	Co (fcc)	2.05 (111) 1.78 (200)
900	Co (fcc)	2.05 (111) 1.77 (200)
1000	Co (fcc)	2.07 (111)
1000	Co ₆ W ₆ C (η)	2.23 (422) 2.10 (511)

XRD, X-ray diffraction.

(2) Thermal Treatment

The decomposition of organic and nitrate groups to form the Co metal was monitored in the TG unit (see Fig. 2). The decomposition was found to be finished at about 470°C for all NO₃:OAc ratios, but the decomposition patterns changed from high to low NO₃:OAc ratios. The samples with a high ratio of NO₃ groups exhibited a very rapid decomposition step at 130°–150°C, followed by very slow decomposition ending at ca. 470°C. Samples with a high ratio of OAc-groups showed a more complex pattern, without the rapid decomposition found for the nitrate-rich samples. The very rapid reaction of the nitrate-rich concentrates at 130°–150°C is probably due to combustion of the organic parts with the nitrate groups as oxidizers, causing internal heating of the sample to ca. 450°C. This would explain the TG graph plateau found between 150° and 450°C with these samples. At higher OAc concentrations, less net heat should be evolved by the combustion and decomposition, implying that several relatively well-defined decomposition steps can be discerned in the interval 150°–450°C. Above 470°C, the weight loss was almost zero for all samples, and the total weight loss decreased with increasing acetate content. The powder-XRD patterns of all mixtures heat treated to 500°, 700°, and 1000°C contained peaks which could all be ascribed to FCC cobalt.¹⁶

The powder-XRD patterns of the samples heated to 700°C in a furnace showed FCC cobalt to be the only crystalline phase present. Low O and N contents were observed in samples heated to 700°C, ca. 0.23 wt% O, and ca. 0.02 wt% N for the 1:0 sample. If the samples were taken out from the furnace at temperatures of 100°C or more, oxygen contents up to Co:O = 1:1 could be found, i.e. full oxidation to CoO by air-oxygen took place. Likewise, long-time storage or samples heated only to 500°C normally had increased oxygen contents due to air oxidation, and storage should therefore preferably be made in an inert atmosphere. The carbon contents of the samples heated to 700°C decreased from 13 wt% with increased NO₃:OAc ratio, and approached zero close to the 1:0 and 9:1 NO₃:OAc compositions, as shown in Fig. 3. The fact that the oxide was not found even in the 1:0 sample might be explained by the presence of 0.5 equivalents of TEA per Co, implying that TEA is a complexing agent strong enough to remain bound to the cobalt when heated and contains enough reducing components to compensate for the oxidizing power of the NO₃⁻-groups. Considering only the carbon content, the 1:0 mixture seems to be slightly better than the 9:1 and 4:1 mixtures but, as discussed above, crystallization of a Co-nitrate-TEA complex easily occurred at the 1:0 composition, inducing an inhomogeneous distribution of the oxidation and reduction agents in the precursor concentrates, which would lead to an elementally inhomogeneous product. Accordingly, the 9:1 composition was used for the preparation of cobalt-coated WC-Co powders.

(3) Preparation of Co-Coated WC Powder

The TG graph of WC powder coated with an NO₃:OAc (9:1) mixture corresponding to an addition of 6 wt% Co showed a decomposition pattern very similar to that of WC-free NO₃:OAc (9:1 and 1:0) mixtures, as shown in Fig. 2. The studies of pure Co materials thus also seem to be relevant for the WC-Co materials. As discussed above, the TG studies showed the decomposition of the organic and nitrate groups to be finished at temperatures below 470°C.

(A) 500°C: After heating to 500°C, the material consisted of nonagglomerated or loosely agglomerated Co-coated WC grains and a very small amount of isolated, ca. 1-μm sized, clusters of coalesced nano sized Co particles (see Fig. 4). According to the powder-XRD study, the only crystalline phases present were WC¹⁷ and FCC Co.¹⁸ The X-ray intensity from the latter phase was so weak that only the (111) peak could be observed (see Table II). Almost all WC grains were covered with a cobalt coating consisting of coalesced 10–100 nm-sized Co-particles. SEM-EDS studies showed average metal contents of 60 mol% Co and 40 mol% W. The high value of the Co content is due to

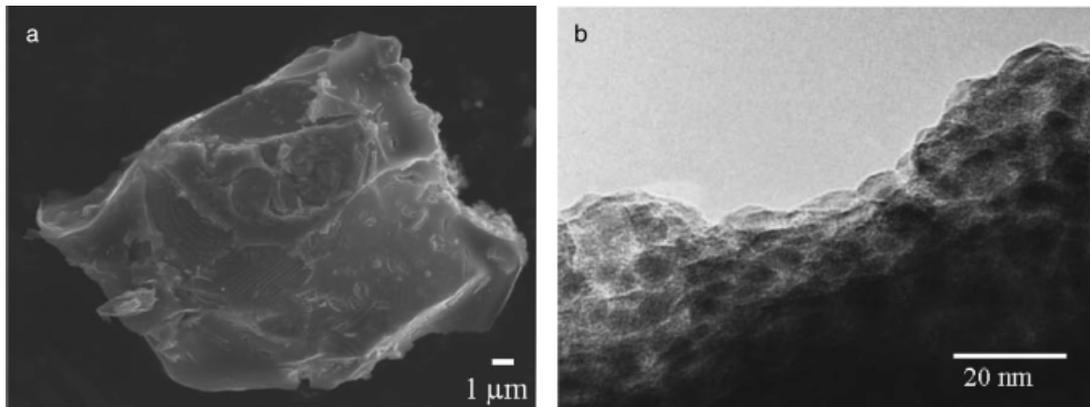


Fig. 4. (a) Scanning electron microscopy image of the WC-6 wt% Co sample heated to 500°C, obtained in secondary-electron imaging mode. (b) Close-up with transmission electron spectroscopy imaging of Co metal obtained at 500°C.

the screening effect from surface cobalt. Approximately the same amount of cobalt was observed in the material that was not burnt off. Spot analyses of the WC-Co grains showed cobalt contents from 11 to 90 mol%, and in no case was a sole tungsten EDS spectrum obtained.

(B) 700°–900°C: Heating to 700°C caused densification of the Co coatings into smoother surfaces, as can be seen in Fig. 5. The grains were still nonagglomerated or loosely agglomerated, and the amount of isolated cobalt clusters was reduced. The powder-XRD studies showed the presence of WC and Co only, the latter through weak peaks assignable to (*hkl*) 111 and 200 (the latter discernable only in the range 800°–900°C as given in Table II). This indicates that no reaction between Co and WC had occurred although, according to the SEM study, the wetting of the Co phase seemed to be good. The average Co and W contents were very similar to those obtained in the EDS studies of the 500°C sample. The spot analyses gave a somewhat lower scatter of Co contents, compared with the 500°C sample, and the lowest values observed were slightly higher, i.e. ca. 17 mol% Co. This indicates that Co in this case is more evenly distributed on the WC surface. From the SEM-EDS studies, it seems that the free cobalt clusters become more and more attached to the WC-coated grains at elevated temperatures. This was also indicated by the surface structure of the coated particles that seemed to have a double coating in some places, although they might also be due to loss of the cobalt coating from weakly attached neighboring coated WC particles. The powder-XRD results remained the same even after heating to 800° and 900°C.

(C) 1000°C: The Co phase sintered to dense, smooth coatings, completely surrounding each WC grain as can be seen in Fig. 6, and very few isolated Co clusters could be found after heating up to 1000°C. The grains were still nonagglomerated or

very loosely agglomerated. Deagglomeration could easily be achieved by gentle hand pressing of the samples or treatment in an ultrasonic bath containing ethanol and coated WC particles. The powder-XRD pattern showed the presence of the η phase, W_6Co_6C ,¹⁹ implying that Co had reacted with the WC grains, although not completely, because the powder-XRD pattern also contained the Co (111) peak. The SEM-EDS analyses yielded a mean surface composition of 21 mol% Co, which is much lower than those found in the 500° and 700°C samples. This lower Co content accords with the powder-XRD studies, which showed the presence of W_6Co_6C through two weak peaks given in Table II.

The larger batches of Co-coated WC powder, prepared in the furnace, showed morphology and phase contents very similar to those of the powder prepared in the TG unit at 700°C. This indicates that the TG study is also relevant for larger batches. The powder heated to 700°C was chosen as a precursor for the preparation of WC-Co compacts, because the Co was relatively smooth but still not alloyed with WC, and had a low surface area reducing its oxidation sensitivity. The carbon content of the sample heated to this temperature was 5.84 wt%, compared with the theoretical value of 5.78 wt% for a mixture of WC and 6 wt% Co. Part of the ca. 1% excess carbon probably stems from the WC powder, which had a slightly higher than stoichiometric carbon content (<0.03% units). If the data of the carbon analyses from the furnace prepared Co metal are used, an excess of 0.03 wt% (using the measured value for the 9:1 composition) to 0.1 wt% (using an imaginary tie line in the plot at the 9:1 composition) carbon stemming from the Co addition is expect-

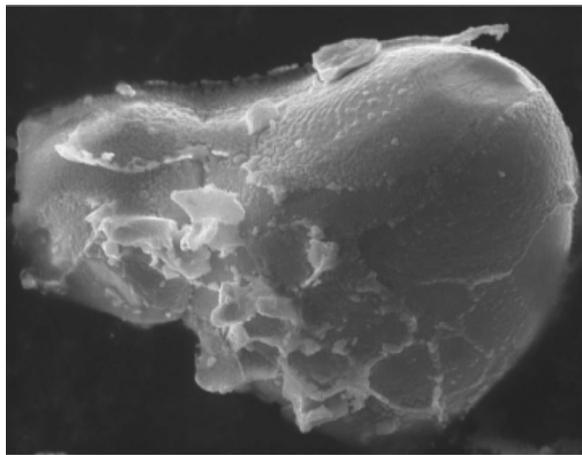


Fig. 5. Scanning electron microscopy image of the WC-6 wt% Co sample heated to 700°C, obtained in secondary-electron imaging mode.

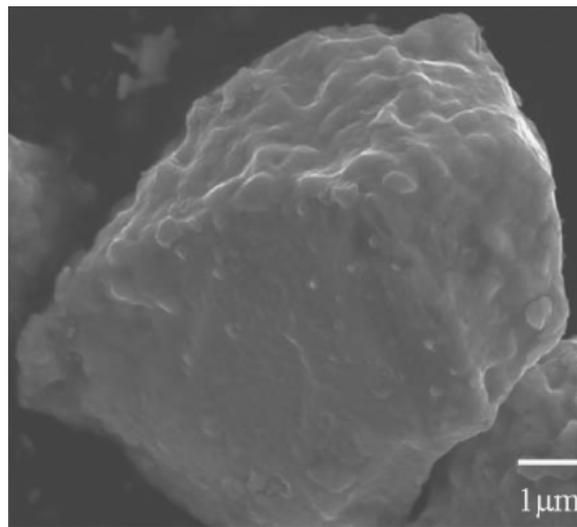


Fig. 6. Scanning electron microscopy image of the WC-6 wt% Co sample heated to 1000°C, obtained in secondary-electron imaging mode.

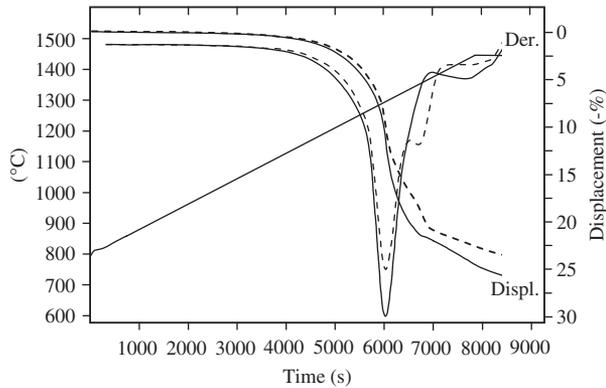


Fig. 7. Shrinkage and time derivative of shrinkage curves of two typical runs of cylinders of a coated WC-6 wt% Co powder: one with a single sintering peak at 1300°C (solid line) and one with an additional sintering peak at 1360°C (dotted line). Heating rate 5°C/min, in an Ar atmosphere.

ed. This shows that it should be possible to adjust the carbon contents of the powder within less than ca. 0.1% unit of the desired value. However, in order to control the carbon contents even further to the exact desired composition, several parameters have to be extremely well controlled, e.g. small oxygen sources reducing the carbon contents and the presence of residual organic decomposition products in the furnace from earlier runs increasing the carbon contents. The final adjustments of the carbon contents are expected to be made during the sintering, making it easier to take care of variations in the WC source and surface oxidation from storage of the powder, but this has not been the aim of the study presented here.

(4) Preparation of Compacts from Co-Coated WC Powder and Ball-Milled WC+Co Powders; Sintering

The sintering process of the solution-processed and ball-milled WC-6wt% Co powders was monitored in a dilatometer, using a heating rate of 5°C/min up to 1450°C, followed by isothermal heat treatment at this temperature for 10 min, and rapid cooling. The selected heating profile is typical for sintering of WC-Co compacts, but has by no means been optimized for the present powders. The shrinkage and its time derivative for the two powders are plotted against temperature in Figs. 7 and 8.

The derivative of the shrinkage curves of the ball-milled powders shows a maximum close to 1360°C, while the corresponding curves of the solution-processed powders show a maximum at 1300°C, and sometimes an additional smaller maximum at ca. 1360°C, as can be seen in Figs. 7 and 8, respectively. Hence, the two powders undergo different sintering processes. It can be noted that 1300°C is close to the lowest liquid-forming eutectic

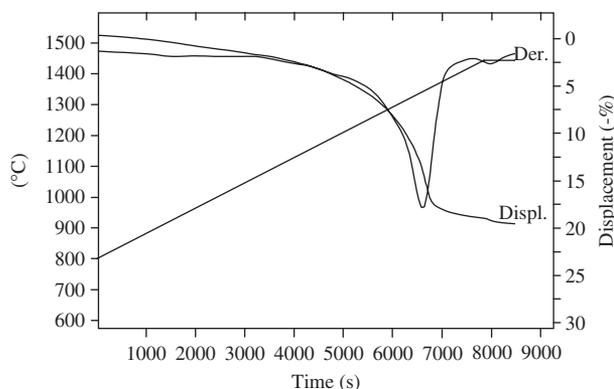


Fig. 8. Shrinkage and time derivative of shrinkage curve of a cylinder of mill-mixed WC+6 wt% Co powders. Heating rate 5°C/min, Ar atmosphere.

at 1275°C found in the Co-WC phase diagram, and 1360°C is close to equilibrium of the Co, WC, graphite, (W,Co)₆C-forming liquid at 1355°C.^{20,21} However, much of the reactions taking place at lower temperatures during the sintering of Co-WC compacts from powders remain unrevealed and kinetic and geometric factors are probably important, making it difficult to give any detailed conclusions on the reactions taking place in the present system.

The difference in sintering behavior between the ball-milled powder and coated powder might stem from the fact that some WC dissolves into the cobalt phase at lower temperatures in the coated powders. The cobalt particles may be expected to have comparatively very small contact areas with the WC grains in the ball-milled powders. This would lead to less diffusion between the WC and Co particles at temperatures up to where the main sintering step starts. The smaller sintering step at 1360°C, found for some of the coated powders, might then be due to the presence of some isolated cobalt particles or due to the circumstance that the diffusion between WC and the Co may have been less complete in some, perhaps thicker parts of the coating. Further studies are needed for more detailed and safe conclusions concerning the presence of different maximum sintering temperatures. The shrinkage was rather similar in the two powders: 20% and 23% for the ball-milled and solution-processed powders, respectively, as averages of three samples each.

(5) Microstructures After Sintering

The microstructures of the compacts after heat treatment at 1450°C for 10 min of the two differently prepared powders are shown in the Figs. 9 and 10. It can be observed that the compact obtained from the solution-processed powder has a much more homogeneous microstructure, i.e. a more narrow distribution of WC grain sizes and a much better distribution of the Co phase, and studies of several compacts clearly show that it contains less pores than that obtained from the ball-milled powder. Another striking difference is that the grains in the compact obtained

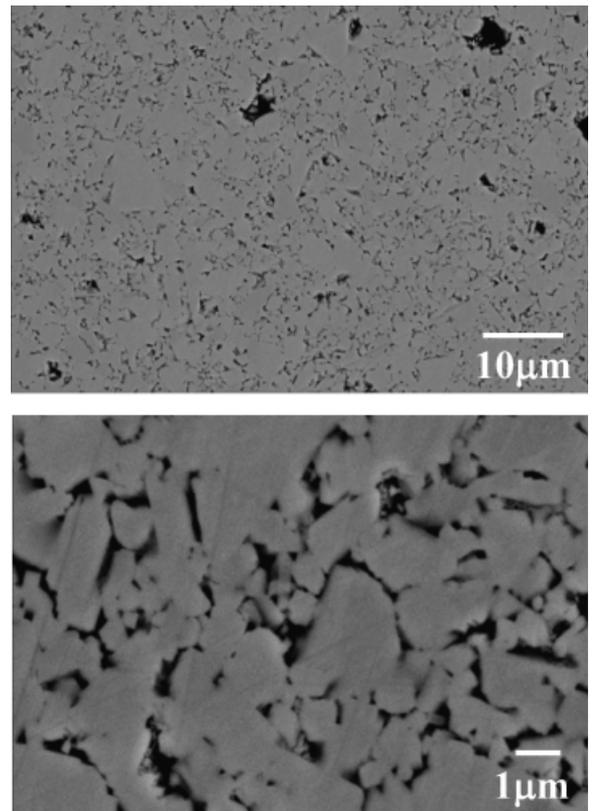


Fig. 9. Microstructure of a compact obtained by sintering a ball-milled powder to 1450°C, and holding at this temperature for 10 min (scanning electron microscopy, backscattered electron imaging).

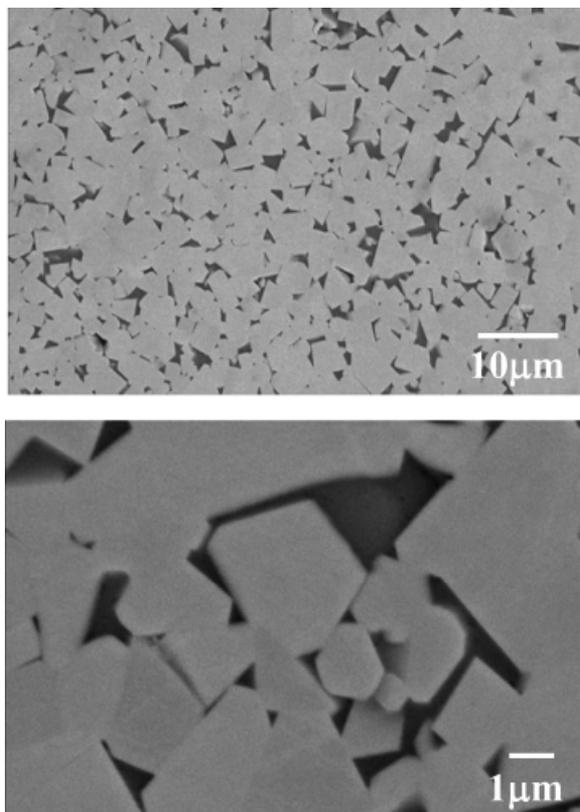


Fig. 10. Microstructure of a compact obtained by sintering a Co-coated WC powder to 1450°C, and holding at this temperature for 10 min (scanning electron microscopy, backscattered electron imaging).

from the solution-processed powder are much more angular and faceted than those in the other compact.

IV. Conclusions

An efficient solution-based process has been developed that produces cobalt-coated WC-powder with an adjustable carbon content from a methanol solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and TEA mixed with WC powder, after drying and heating to 470°C or more under inert gas. The microstructure of the final WC-Co compact produced by sintering of a cobalt-coated WC powder (6 wt% Co) at 1450°C was superior to that obtained from a thoroughly ball-milled mixture, in having less pores, more evenly sized, and more angular WC grains. The improved quality is presumably due to the more homogeneous mixture of WC and cobalt in the Co-coated WC powder allowing for a more homogeneous sintering process and the fact that a ball-milling step, resulting in the formation a tail of smaller WC particles leading to an inhomogeneous sintering process, is avoided. Thus, this novel low-cost route produces superior microstructural homogeneity, removes the need for a ball-milling step, and improves the control of WC grain-size distribution in the preparation of WC-Co compacts. This study describes the coating of large WC grains suitable for preparation of microstructures with large WC grains and low cobalt content, which is highly desired for mining, oil drilling, and tunnel excavation. But the route should also be useful for coating of smaller WC grains allowing for sintering into fine-grained cemented carbides desired in metal machining and fine precision drilling. The even

cobalt coating on the powders should also allow for a more even sintering of the green body and thereby make submicrometer WC-Co composites attainable. This requires, however, that a mono-disperse submicrometer WC powder of a narrow grain size distribution be used. The coating approach should have an advantage compared with routes using highly agglomerated WC-Co-C nanophase powders obtained from solution. Such powders typically sinter firstly within the clusters and make full-dense compacts difficult to achieve without extensive heating, which causes extensive and uneven grain growth. Inhomogeneously distributed surplus carbon that is typical in these processes adds further complications due to the increased sintering activity in these areas, and grain growth inhibitors are typically required. A preliminary study has also shown that it is possible to prepare homogeneous Co-Ni coatings by this route.²²

Acknowledgments

We are grateful to Dr. Kjell Jansson at the Department of Inorganic Chemistry, Stockholm University, for assistance with the dilatometer runs.

All researchers who were involved in this study are affiliated to the Brinell Centre, Inorganic Interfacial Engineering—A competence center financed by VINNOVA, and the BRIIE member companies presently being AB Sandvik Coromant, Höganäs AB, Secotools, Kloster Erasteel AB, and Atlas Copco Secoroc AB.

References

- ¹P. Ettmayer and W. Lengauer, pp. 519–31 in *Encyclopedia of Inorganic Chemistry*, Vol. 2, Edited by R. B. King, John Wiley and Sons, Chichester.
- ²W. M. Stoll and A. T. Santhanam, pp. 841–78 in *Encyclopedia of Chemical Technology*, Vol. 4, 4th edition, Edited by J. I. Kroschwitz and M. Howe-Grant, Wiley-Interscience Publication, John Wiley and Sons, Chichester.
- ³H. E. Exner, "Physical and Chemical Nature of Cemented Carbides," *Int. Metals Rev.*, **24**, 149–73 (1979).
- ⁴B. H. Kear, G. Skandan, and R. Sadangi, "Factors Controlling Decarburization in Hvof Sprayed Nano-WC/Co Hard Coatings," *Scripta Mater.*, **44**, 1703–7 (2001).
- ⁵S. Raghunathan, R. Caron, J. Friederichs, and P. Sandell, "Tungsten Carbide Technologies," *Adv. Mater. Processes*, **4**, 21–3 (1996).
- ⁶M. Christensen, G. Wahnström, C. Alibert, and S. Lay, "Quantitative Analysis of WC Grain Shape in Sintered WC-Co Cemented Carbides," *Phys. Rev. Lett.*, **94**, 066105 (2005).
- ⁷Z. Yao, J. J. Stieglich, and T. S. Sudarshan, "WC-Co Enjoys Proud History and Future."
- ⁸B. Aronsson, *The Origins and Growth of Cemented Carbide*. Ord & Form AB, Uppsala, 2005.
- ⁹R. K. Sadangi, L. E. McCandlish, B. H. Kear, and P. Seegopaul, "Grain Growth Inhibition in Liquid Phase Sintered Nanophase WC/Co Alloys," *Int. J. Powdermet.*, **35**, 27 (1999).
- ¹⁰Z.-H. Xu and J. Ågren, "A Modified Hardness Model for WC-Co Cemented Carbides," *Mater. Sci. Eng.*, **A 386**, 262–8 (2004).
- ¹¹S. Andersson and M. Muhammed, World Intellectual Property Organization Patent: "Method of Making Metal Composite Powder" 9503420-3 (1995).
- ¹²G. Eriksson, H. Siegbahn, S. Andersson, T. Turkki, and M. Muhammed, "The Reduction of Co^{2+} by Polyalcohols in Presence of WC Surfaces by XPS," *Mater. Res. Bull.*, **32**, 491–9 (1997).
- ¹³A. Nakabayashi, "Co-W Coated WC-Powder"; JP Patent 62192501 (1987).
- ¹⁴D. F. Carroll and J. Jarvi, "Methods of Producing Composite Powders"; U.S. Patent 20030097909 (2003).
- ¹⁵U. Fisher, M. Waldenström, S. Ederyd, M. Nygren, G. Westin, and Å. Ekstrand, "Method of Making Metal Composite Materials"; U.S. Patent 5,505,902 (1996).
- ¹⁶A. Ekstrand, K. Jansson, and G. Westin, "A Solution Synthetic Route to Cobalt Film and Sponge," *Chem. Mater.*, **17**, 199–206 (2005).
- ¹⁷JCPDS card No: 25-1047; Bind, McCarty, Pennsylvania State University, University Park, PA, ICDD Grant in Aid, 1973.
- ¹⁸JCPDS card No: 15-806; Natl. Bur. Stand. (U.S.) Monogr. 25, 10, 1965.
- ¹⁹JCPDS card No: 23-939; Pollock, Stadelmayer *Metal Trans.* **1**, 767, 1970.
- ²⁰L. Åkesson, Thesis, Royal Institute of Technology, Stockholm, Sweden, 1982.
- ²¹B. Uhrenius, B. Carlsson, T. Franzen, "A Study of the Cobalt-tungsten-carbon System at Liquidus Temperatures," *Scand. J. Metall.*, 549–56 (1976).
- ²²Å. Ekstrand and G. Westin, "Highly Homogeneous WC-Ni/Co Composites Produced from WC-Powder Coated with a Solution Chemical Route," *Advances in Science and Technology CIMTEC 2002 – 10th International Ceramic Congress [Part C]*, 489 (2002). □