Analysis of cobalt, tantalum, titanium, vanadium and chromium in tungsten carbide by inductively coupled plasma-optical emission spectrometry

Marcellé Archer,[*a] **Robert I. McCrindle**[b] **and Egmont R. Rohwer**[c]

[a]*National Metrology Laboratory, CSIR, P.O. Box 395, Pretoria 0001, South Africa.*
 E-mail: Marcher@csir.co.za
[b]*Department of Chemistry and Physics, Technikon Pretoria, P.O. Box 56208, Arcadia*
 0007, South Africa. E-mail: McCrindle@techpta.ac.za
[c]*Department of Chemistry, University of Pretoria, Lynnwood Road, Pretoria 0002, South*
 Africa. E-mail: Erohwer@postino.up.ac.za

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the concentrations of cobalt, tantalum, titanium, vanadium and chromium in solutions of tungsten carbide. The main advantage of the method described here lies in the speed, convenience and effectiveness of the dissolution procedure. Aliquots of powdered tungsten carbide were dissolved in a solution of 5% *aqua regia* in 30% hydrogen peroxide. Complete dissolution was usually achieved within 10 min. The accuracy of the method was assessed by the analysis of certified reference materials, secondary reference materials and matrix spiking. The method was successfully applied to commercial type samples with differing compositions. Slightly more emphasis was placed on the measurement of vanadium, since no information on the measurement of this element in solutions of tungsten carbide, by ICP-OES, has been published. Investigation of the interference effects of the elements in the sample matrix on each other was essential for accurate results comparable to other published analytical methods.

Introduction

In the early 1900s, it was found that the outstanding machining properties of high-speed steel were due to the presence of very hard carbide particles, notably tungsten carbide, in the steel matrix.[1] Because tungsten carbide–cobalt, next to diamond, is one of the hardest materials known, it is used in masonry drill bits, saw blades, cutting discs, sanding blocks, files, metal-cutting tools, mining tools and other hand tools. One of the main uses for tungsten carbide–cobalt is in rock drilling bits for geological purposes. Tungsten carbide compounds are also known as hardmetals.

The properties of hardmetals are affected by cobalt concentration and the impurities present in the material.[2] Other metals, such as tantalum, titanium, vanadium and chromium, are added to tungsten carbide for various reasons, but mainly to inhibit grain growth.[3] Grain growth is undesirable because it may weaken the product, especially in the manufacture of cutting tools.[2] Used materials are also recycled[4] and the composition of these is of importance in deciding the most suitable use of the material. In a powder metallurgy research environment, the concentrations of these metals must be accurately known to predict the physical properties of the finished product.

The most frequently used method for the measurement of metallic elements in tungsten carbide is X-ray fluorescence spectrometry (XRF)[1,5,6] but it may not be sensitive enough for some applications. In general, XRF analysis necessitates prior fusion of the sample, a task requiring considerable practice.[7] Atomic absorption methods have been published by ISO[8,9] and Piippanen *et al.*[10] Emission measurement methods have been used by Piippanen *et al.*[4] and Thomson[11] but these are the only published methods which could be found.

Tungsten carbide powder is highly resistant to acid attack and the dissolution process is lengthy, ranging from 45 min to several hours, even when hydrofluoric acid is added. The dissolution methods published by ISO[8,9] and Piippanen *et al.*[10] all have the drawback of being fairly time-consuming and employing undesirable reagents such as hydrofluoric acid, boric acid and phosphoric acid. Hydrofluoric acid in an analytical solution may etch glassware and instrument components. Hydrofluoric acid may be complexed with boric acid but then research into the possible influence of boric acid on the analysis must be done. It has been proved by Kawaguchi[12] that the presence of 'heavy' acids, such as phosphoric and sulfuric acid, in a solution for ICP analysis tends to give rise to nebulization (physical) interferences unless strict matrix matching techniques are used. Another problem with the published dissolution methods is a tendency for tungsten oxides to precipitate out of the acid solution causing co-precipitation of the elements under investigation.[4]

The purpose of the study was to provide an alternative, more rapid and less expensive method of dissolving tungsten carbide–cobalt using only nitric acid, hydrochloric acid, hydrogen peroxide and tartaric acid. In this manner, no additional metallic elements were introduced into the sample matrix and the use of hydrofluoric acid was avoided.

The investigation also covers an efficient way of preventing the precipitation of tungsten oxides. The effect of tartaric acid as a stabilising agent, instead of phosphoric acid, was studied. This research differs from previously published methods for the chemical analysis of tungsten carbide, mainly in the dissolution procedure for the tungsten carbide–cobalt powder before analysis.

This study was undertaken to show whether:

(a) an alternative, rapid dissolution method which avoids the use of reagents that have the potential to complicate the analysis could be found;

(b) the ICP-OES measurement technique is suitable for the

Table 1 Operating conditions for ICP-OES

Monochromator focal length/m	0.64
Monochromator grating/lines mm^{-1}	2400
Radiofrequency/MHz	40.68
Rf power/W	1000
Reflected power/W	<1
Nebulizer argon flow/l min^{-1}	0.3
Sheathing argon flow/l min^{-1}	0.2
Sample uptake rate/ml min^{-1}	2.5

measurement of cobalt, tantalum, titanium, vanadium and chromium in a tungsten carbide solution; and

(c) accurate and precise results can be obtained.

Experimental

Instrumentation

A Jobin–Yvon 24 sequential measuring ICP-OES was employed for this study. The instrumental parameters are listed in Table 1.

Reagents

Certified stock reference solutions of tungsten, cobalt, tantalum, titanium, vanadium and chromium, obtained as 1000 mg l^{-1} solutions from Merck Chemicals, were used to prepare calibration solutions for the ICP-OES. The cobalt solution used to matrix match the calibration solutions was prepared by dissolving pure cobalt sponge (BDH) in dilute hydrochloric acid. To prepare calibration solutions, the stock solutions were diluted with 8.2 MΩ cm deionised water (Milli-Q purification system, Millipore, MA, USA) and analytical reagent (AR) grade hydrochloric acid. The hydrogen peroxide used for the dissolution step was BDH AR grade, and the tartaric acid Merck AR grade. A CRM of cemented carbide–cobalt (NBS 889, obtained from the National Institute for Standards and Technology, USA) was used where possible to evaluate the efficiency of the dissolution procedure and the accuracy of the ICP-OES measurements. Secondary reference materials of cemented carbides were obtained from the Boart Longyear Research Centre, SA, and the University of the Witwatersrand, SA.

Sample preparation

A 0.5000 g aliquot of finely powdered tungsten carbide–cobalt was treated with 30 ml of 5% *aqua regia* (1 part nitric acid and 3 parts hydrochloric acid) in 30% hydrogen peroxide (v/v) in a 150 ml glass beaker covered with a watch glass. The mixture was gently heated on a water bath at 80 °C to start the reaction. At this stage the mixture was removed from the heat, since the hydrogen peroxide tended to bubble vigorously when heated. A 0.6 g portion of solid tartaric acid was added to help complex

the tungsten and prevent it from precipitating. In further tests, differing masses of tartaric acid, from 0.2 g to 1 g, were added to the mixture in order to determine the optimum effective amount.

The solutions were kept covered and occasionally manually swirled during the next 10 min until the sample was completely dissolved. If a tendency to precipitation was observed, a few drops of 30% hydrogen peroxide were added. The solutions were then diluted to 100.00 ml with deionised water.

The vanadium and chromium concentrations in this solution were measured by ICP-OES. The solution was diluted further in order to measure the cobalt, tantalum and titanium concentrations.

Several statistical methods were used during the evaluation of the results and were applied mainly to assess the precision, accuracy and confidence limits, and also to compare the results of two different sets of measurements. The work of Miller and Miller[13] was used as a guide. Each sample was analysed at least five times, usually over a period of several months.

Results and discussion

Spectral lines

Several emission lines for each element were investigated. The lines finally used for quantitative analysis are shown in Table 2. The coefficient of determination (r^2), the limits of detection (LOD) and limits of quantification (LOQ) are also shown, together with the expected concentration ranges for each element in the samples.

Only the wavelengths used for cobalt and vanadium were found to be free of matrix interferences. For the measurement of the remaining three elements of interest, the matrix of the calibration solutions had to be matched with respect to the cobalt and/or tungsten concentrations expected in the sample solutions. In all cases, four point calibration curves were constructed.

It was considered prudent to analyse each element at two emission lines, except for chromium, for which only one suitable emission line was found. Matrix effects do not occur to exactly the same extent at two different wavelengths and any significant differences in the results obtained at the two wavelengths was considered an indication of matrix interferences. The samples analysed differed somewhat in composition and the extra time required for the use of two different analytical lines was justified by the fact that less time was spent on investigating the possible matrix effects in each new sample type.

During the analysis of tantalum, both cobalt and tungsten were found to interfere with quantitative analysis at both the chosen analytical wavelengths. Problems were encountered when attempting to mix cobalt and tungsten in the same solution, since the Merck cobalt solutions were supplied in an

Table 2 Summary of analytical wavelengths and calibration data obtained by ICP-OES measurement

Element	Concentration in sample (% m/m)	Analytical wavelength/nm	LOD^a in solution/mg l^{-1}	LOD in sample (% m/m)	LOQ^b in solution/mg l^{-1}	LOQ in sample (% m/m)	r^2
Co	1–15	228.616	2	0.4	7	1	0.9998
Co	1–15	238.346	1	0.2	4	0.8	0.9999
Ta	0–0.8	240.063	1	0.02	3	0.06	0.9993
Ta	0–0.8	268.517	0.4	0.01	1	0.02	0.9999
Ti	0–4	337.280	0.3	0.01	1	0.02	0.9999
Ti	0–4	368.520	0.2	0.004	0.7	0.01	0.9999
V	0–8	292.402	0.03	0.001	0.1	0.002	1.0000
V	0–8	311.071	0.1	0.002	0.5	0.01	0.9999
Cr	0–0.2	357.869	0.2	0.004	0.6	0.01	1.0000

^{a}LOD: the analyte concentration which gives a signal equal to the blank signal, y_B, plus three standard deviations of the blank, s_B, calculated from the individual calibration curves. ^{b}LOQ: the analyte concentration which gives a signal equal to the blank signal, y_B, plus ten standard deviations of the blank, s_B, calculated from the individual calibration curves.

Table 3 Measurement results after *aqua regia*–hydrogen peroxide dissolution of tungsten carbide–cobalt

Element measured	Certified or expected concentration in reference material [% m/m (g per100 g)][a]	Measured concentration after *aqua regia*–hydrogen peroxide dissolution [% m/m (g per 100 g)][b]
Cobalt	9.50 ± 0.15	9.56 ± 0.19
Tantalum	4.60 ± 0.15	4.48 ± 0.28
Titanium	4.03 ± 0.10	3.96 ± 0.16
Vanadium	0.63	0.59 ± 0.06

[a]The CRM was developed under a cooperative system. According to the certificate of analysis, the estimated uncertainty is based on judgement and represents an evaluation of the combined effects of method imprecision, possible systematic errors among methods (several were used) and material variability. [b]The 95% confidence limits for the measurements were calculated from the formula for small samples: $x \pm t_{n-1} s/\sqrt{n}$, where x is the mean of the measurements, n is the number of sample aliquots analysed and s is the standard deviation of the mean.

acidic matrix and the tungsten solutions were supplied in an alkaline matrix. Mixing of these solutions caused either cobalt or tungsten to precipitate, depending on the pH of the solution. The problem was overcome by matrix-matching the calibration solutions with respect to cobalt only. A separate solution of tungsten, at the concentration expected in the sample solutions, was measured after calibration and its measurement value subtracted from the sample measurement values prior to the calculation of the tantalum in the solution.

Cobalt interfered with the quantitative measurement of titanium at both the analytical wavelengths shown in Table 2. The calibration solutions were matrix-matched with respect to cobalt.

No previous publications that reported the ICP-OES measurement of vanadium in a tungsten carbide matrix could be found. Although preliminary experiments indicated that no matrix interferences affected the results for vanadium, one of the samples was analysed by both the external calibration method and the method of standard additions. This was done because no tungsten carbide reference material containing vanadium was obtainable and there was no available information on the analysis of vanadium by emission spectrometry.

The quantitative measurement of chromium at the 357.869 nm emission line was affected by the cobalt content of the solutions. The calibration solutions were therefore matrix matched with respect to cobalt.

Analysis

The results for the analysis of the cemented carbide CRM, NBS 889, are shown in Table 3. The measurement results for a secondary reference material analysed by XRF at another laboratory only once during a routine measurement run are also shown. The confidence limits for the vanadium secondary reference material were not known. For another sample, a vanadium result of 0.602% (m/m) was obtained by the external calibration method, while a result of 0.599% (m/m) was obtained for the same sample by the method of standard additions. This close agreement between the two sets of results was taken as confirmation of the accuracy of the measurements.

No tungsten carbide reference material containing chromium was available, thus the measurement accuracy was assessed by the addition of chromium to solutions of tungsten carbide. In all cases, a recovery of better than 99% was achieved. One of the samples had been analysed by two other laboratories: they reported chromium values of 0.011 and 0.012% (m/m), respectively. An average chromium concentration of 0.01% (m/m) for this sample was obtained after

dissolution by the *aqua regia*–hydrogen peroxide method and measurement by ICP-OES, using cobalt-matched calibration solutions.

The *aqua regia* was used mainly to improve the solubility of the metallic elements present in the sample. When 5% nitric acid in 30% hydrogen peroxide (v/v) was used instead of *aqua regia*, the sample was completely dissolved but the dissolution time was increased, in some cases by to up to 35 min. It was observed that as the hydrogen peroxide in the solution dissociated, tungstic acid tended to precipitate from the solution. The addition of a few drops of hydrogen peroxide re-dissolved the precipitate. The hydrogen peroxide could thus not be removed from the solutions prior to ICP-OES measurement without causing tungsten compounds to precipitate.

Tartaric acid additions of less than 0.5 g were not effective in preventing precipitation, in spite of the high hydrogen peroxide concentration. This would indicate that hydrogen peroxide alone is not enough to keep the sample in solution. On the other hand, even when 1 g of tartaric acid was added to the solution, precipitation occurred when the hydrogen peroxide was removed. It was found that for all the samples analysed, 0.6 g of tartaric acid added to a solution of 0.5 g of tungsten carbide prevented the precipitation of tungsten compounds while hydrogen peroxide was also present. During ICP-OES measurement, the mandatory presence of hydrogen peroxide in the analytical solutions was found to produce fine bubbles in the nebulizer tubing, with a resultant slight deterioration in precision. However, the RSD of three measurements at a 0.5 mg l^{-1} level was generally less than 7%, and this precision was found to be acceptable.

There is no evidence to suggest that the hydrogen peroxide–*aqua regia* method is not fully effective for the dissolution of cobalt, tantalum, titanium, vanadium and chromium in a matrix of tungsten carbide. The material was usually completely dissolved within 10 min with the hydrogen peroxide–*aqua regia* method, compared with 45 min or more for the alternative nitric acid–hydrofluoric acid method. Precipitation of tungsten complexes from the solution was effectively prevented by the addition of tartaric acid. The traditional use of hydrofluoric acid (caustic and etches glass components) and phosphoric acid (may cause physical nebulizer interferences unless meticulous matrix matching is employed) was thus avoided. The hydrogen peroxide–*aqua regia* method uses less expensive high purity acids and the waste products present fewer problems than with traditional methods. Less expensive equipment is required, since standard laboratory glassware may used instead of PTFE vessels required for use with hydrofluoric acid. The method was found faster and more convenient, as well as less expensive than previous published methods.

Only a few wavelengths were entirely free of interferences, but these could still be used to produce accurate results by the technique of matrix matching. The main advantage of ICP-OES over atomic absorption spectrometry is the fact that several analytical wavelengths may be evaluated during a single run, thus reducing the time required for analyses as well as the amount of work. The use of more than one analytical wavelength is a convenient quality control aid, since interferences seldom occur to exactly the same extent at two different wavelengths. Any differences in analytical results at the different wavelengths may be taken as an indication of a measurement problem.

Another advantage is the multi-element capabilities of ICP-OES. When different elements to be measured are present in the samples in similar concentration ranges, the calibration solutions can be adapted to include them all. An example of this would be the elements tantalum, titanium, vanadium and chromium. These elements were sometimes found together in the same tungsten carbide–cobalt sample and were analysed during the same calibration run, with appropriate modifications

of the matrix matching technique. The expected cobalt concentrations in the samples analysed were always higher than 5% (m/m) and this precluded the co-analysis of cobalt with any of the other elements, since a suitable calibration option was not easily available.

References

1   K. J. A. Brookes, *World Directory and Handbook of Hardmetals*, Engineers' Digest Publications, London, 2nd edn., 1979.
2   S. Luyckx, *The Preparation and Properties of Hardmetals (University of the Witwatersrand Course Literature)*, Sandvik, Benoni, 1997.
3   K. J. A. Brookes, *Metal Powder Report*, 2001, **56**(4), 8–14.
4   T. Piippanen, J. Jaatinen and J. Tummavuori, *Fresenius' J Anal. Chem.*, 1997, **357**(4), 405–410.
5   K. Kinson, A. C. Knott and C. B Belcher, *Talanta*, 1976, **23**, 11–12.
6   *Encyclopedia of Analytical Science*, eds. A. Townshend, P. Worsfold, S. Haswell, H. Werner and I. Wilson, Academic Press, London, 1995, vol. 1–10.
7   W. A. Naish, J. E. Clennel and V. S. Kingswood, *Select Methods of Metallurgical Analysis*, Chapman and Hall, 1953, 2nd edn.
8   International Organization for Standardization, ISO 7627-1, Parts 1–5, Geneva, Switzerland, 1983.
9   International Organization for Standardization, ISO 7627-6, Part 6, Geneva, Switzerland, 1985.
10 T. Piippanen, J. Jaatinen, A. Piirjeta and J. Tummavuori, *Fresenius' J. Anal. Chem.*, 1997, **358**, 771–774.
11 V. B. E. Thomsen and P. J. Baker, *J. Hard Mater.*, 1995, **6**(2), 97–99.
12 H. Kawaguchi, Memoirs of the School of Engineering, Nagoya University, Nagoya, Japan, 1995, **vol. 47(2)**, pp. 145–190.
13 J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood Ltd., Chichester, UK, 1993, 3rd edn.