

## CHAPTER 2

### ANALYTICAL METHODS FOR TUNGSTEN CARBIDE POWDERS

#### 2.1 INTRODUCTION

A considerable amount of work has been done on the physical properties of hardmetals (Brookes, 1979; Fry, 1982; internet: <http://www.infim.ro/1/190/result.htm>; Luckyx, 1997), such as density, hardness, transverse rupture stress, etc. Whole volumes have been issued on the microstructure of tungsten carbide (internet: <http://www.infim.ro/1/190/result.htm>) but very little has to date been published on the chemical analysis of the metallic elements in hardmetals.

#### 2.2 SAMPLE PREPARATION

In most of the published work (ISO, 1983, 1985; Piippanen et al, 1997a, 1997b), hardmetal powders are dissolved in nitric and hydrofluoric acids. When hydrofluoric acid is used it is necessary to complex it with boric acid before analysis to avoid etching the glass parts of the analytical instrumentation. The addition of a metallic element like boron to the already complex matrix necessitates an investigation into its effect on the measurement of the elements of interest, in addition to the effects of the other elements already present in the matrix. Piippanen et al (1997a, 1997b) experimented with phosphoric acid as a complexing agent for tungsten. The main difficulty with both these dissolution methods is that tungsten trioxide ( $WO_{3,x}H_2O$ ) is easily precipitated from the solution at  $pH < 1.5$  (Townshend et al, 1995). It has been found by Piippanen et al (1997a) that some co-precipitation of the analyte elements can occur. The dissolution procedure is also lengthy (longer than 45 minutes per sample) and difficult.

Older methods of dissolution were based on the fusion of powdered samples with potassium nitrate, extraction of the melt with hot water and acid dissolution of the insoluble fraction (Naish et al, 1953).  $WO_3$  and  $SiO_2$  were removed by filtration. This method takes several hours to perform, and co-precipitation is a serious problem.

### 2.3 ANALYTICAL TECHNIQUES

Techniques which have been used for the chemical measurement of metals in tungsten carbides include spark emission spectrometry (Thomson, 1995), x-ray diffraction spectrometry (Chen et al, 1986), titrimetry (Vasilescu et al, 1980), x-ray fluorescence (Kinson et al, 1976), neutron activation (Kubsch et al, 1975) and atomic absorption spectrometry (ISO, 1983, 1985; Piippanen et al, 1997b). Only one published account of analysis by ICP-OES could be found (Piippanen et al, 1997a).

### 2.4 COMPARISON OF TECHNIQUES

#### 3.4.1 Spark Emission

Spark excitation sources use a current pulse (spark) between two electrodes to vaporise and excite analyte atoms (Tissue, 1995-2000). The electrodes are either metal or graphite. If the sample to be analysed is a metal, it can be used as one electrode. Non-conducting samples are ground together with a graphite powder and placed in a cup-shaped lower electrode. Spark sources can excite atoms for atomic emission spectrometry or ionise atoms for mass spectrometry. According to Townshend et al, (1995), spark sources have been largely phased out in favour of plasma and laser sources but are still widely used in the metals industry.

#### 2.4.2 X-Ray Diffraction (XRD)

The wavelengths of x-rays are of the same order of magnitude as the distances between atoms or ions in a molecule or crystal,  $10^{-10}$  m (Tissue, 1995-2000). A crystal diffracts an x-ray beam passing through it to produce specific angles depending on the x-ray wavelength, the crystal orientation and the structure of the crystal. X-rays are predominantly diffracted by electron density and analysis of the diffraction angles produces an electron density map of the crystal. Since hydrogen atoms have very little electron density, determining their positions requires extensive refinement of the diffraction pattern (Tissue, 1995-2000; Townshend et al, 1995). Electron diffraction and neutron diffraction are sensitive to nuclei and are often used to determine hydrogen positions. X-ray tubes generate x-rays by bombarding a metal target with high-energy (10–100 keV) electrons that knock out core electrons. An electron in an outer shell fills the hole in the inner shell and emits an x-ray photon. These sources produce a continuous spectrum of x-rays and require a crystal monochromator to select a single wavelength.

#### 2.4.3 Titrimetry

Titrimetry is defined as the “process of determining the quantity of a substance, A, by adding measured increments of substance B, the titrant, with which it reacts until exact equivalence is achieved” (Townshend et al, 1995). The detection of the equivalence point can be achieved in two ways: visually, if an indicator is present, or by measuring a physical property of the solution being titrated (pH, conductivity, absorbance). Titrimetry is one of the oldest analytical techniques but continues to be used today because of its

high accuracy and precision, and relatively low costs. It has in fact been recognised as a primary method of analysis (Milton, Quinn, 2001). The equipment used ranges from a simple graduated burette, operated manually, to complex automated systems. Titrations are classified according to the nature of the end-point measurement. For the analysis of cobalt, for example, Vasilescu et al (1980) used a complexometric titration, with EDTA as the complexing agent in the presence of murexide. The same authors measured iron, after extraction by hydrochloric acid, by photocalorimetric titration. Iron can also be measured by redox titration (Basset, Denney, Jeffery, Mendham, 1978).

#### **2.4.4 X-Ray Fluorescence**

X-ray fluorescence (XRF) is a spectroscopic method that is commonly used for solids in which secondary x-ray emission is generated by excitation of a sample with x-rays (Tissue, 1995-2000; Townshend et al, 1995). The x-rays eject inner-shell electrons. Outer-shell electrons take their place and emit photons in the process. The wavelength of the photons depends on the energy difference between the outer and inner shell electron orbitals. The amount of the x-ray fluorescence is very sample-dependent and quantitative analysis requires calibration with standards that are similar to the sample matrix.

Solid samples are usually powdered and pressed into a wafer or fused in a borate glass. The sample is then placed in the sample chamber of an XRF spectrometer and irradiated with a primary x-ray beam. The x-ray fluorescence is recorded with either an x-ray detector after wavelength dispersion or with an energy-dispersive detector. According to Tissue (1995-2000) and Townshend et al (1995) very high precision can be achieved with XRF, even in routine operation.

#### 2.4.5 Neutron Activation

Neutron activation is a powerful nondestructive multielement technique (Townshend, 1995). It can be applied to over sixty elements in a broad range of matrices and no sample dissolution is required. The sample is activated in a source of neutrons, followed by  $\gamma$ -ray spectrometry to identify and quantify the induced activity. The basis of this method is the fact that most elements have one or more stable isotopes that can be made radioactive on interaction with neutrons. A neutron source is required, the most commonly used one is the nuclear reactor (a core of uranium enriched in  $^{235}\text{U}$ ). A 14 MeV neutron generator, or a  $^{252}\text{Cf}$  or Am/Be source may also be used.

#### 2.4.6 Atomic Absorption Spectrometry (AAS)

Matter can capture electromagnetic radiation and convert the energy of a photon to internal energy. This process is called absorption. Energy is transferred from the radiation field to the absorbing species. The energy change of the absorber is described as an excitation from a lower energy level to a higher energy level. Since the energy levels of matter are quantized, only light of energy that can cause transitions from one level to another will be absorbed. The type of excitation depends on the wavelength of the light. In atomic absorption, as used in analytical chemistry, the absorption spectrum is that of light and is a function of wavelength (Tissue, 1995-2000).

Several methods of atomisation are in use, the most common being a flame, using air/acetylene or nitrous oxide/acetylene. A light source of a specific wavelength is required and the most widely used source is the hollow-cathode lamp (HCL), in which the cathode

is lined with the element to be determined (Haswell, 1991). Electrons are released from the cathode when a striking potential is applied. The electrons cause impact ionisation of the background noble gas, and acceleration of the noble gas cations to the cathode causes vaporisation of the cathode lining. An atomic vapour is produced and excitation occurs. Emission from the lamp passes as a beam through the flame. The beam then passes through a monochromator to a photomultiplier tube, and the photons are converted to an electrical signal. A readout in absorbance units is obtained. Atoms in the flame absorb energy, provided it is of a suitable wavelength, from the beam, which registers as an increase in absorbance units (the logarithmic function of transmission). The technique is quantitative since the absorbance of an absorbing species is proportional to its concentration (Beer's law).

#### **2.4.7 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)**

The electrons in atoms, ions or molecules that are excited to high energy levels can decay to lower energy levels by emitting radiation (emission or luminescence). For atoms excited by a high-temperature energy source this light emission is called atomic or optical emission. The emission intensity of an emitting substance is linearly proportional to analyte concentration, provided that all other parameters stay constant, and is used to quantify emitting species (Kawaguchi, 1995; Moore, 1989; Thompson & Walsh, 1983; Tissue, 1995-2000; Townshend et al, 1995).

A full description of inductively coupled plasma-optical emission spectroscopy is included

under Section 5.2.

## 2.5 CONCLUSIONS

Although a minimum of sample preparation is needed, the XRD technique cannot be considered a quantitative method. XRD spectrometry is primarily used to characterise a material and to study internal defects in the atomic arrangement in crystalline material (Townshend, 1995).

With spark emission, the amount of sample introduced into the spectrometer cannot be easily controlled, necessitating the use of an internal standard. The detection limit is generally poor and strong matrix effects require that a large library of solid reference materials is available (Tissue, 1995-2000; Townshend, 1995).

The use of titrimetry for the measurement of metals in tungsten carbide solutions is rather limited. Although titrimetry is a highly accurate and specific method and requires relatively inexpensive equipment, conditions such as pH may have a large influence. Essentially, only one element can be measured at a time, making this a time-consuming method if a number of elements are to be measured. Vasilescu et al (1980) applied titrimetric analysis only to cobalt and iron, which were present as impurities due to machining and sintering. The preparation method was an extraction procedure with hydrochloric acid, rather than a complete dissolution of the metal carbide matrix.

Neutron activation is a sensitive method which can produce very accurate results if properly applied. It is also rapid, since no sample preparation is required and it is very useful for the

analysis of substances that do not dissolve easily. However, this technique is not as well used as most of the others mentioned, possibly because the most common neutron source is a nuclear reactor (Tissue, 1995-2000). It is relatively expensive to buy and access to a reactor is needed. It also requires a high level of operator skill.

XRF spectrometry, AAS and ICP-OES can all be used as quantitative techniques. However, as already mentioned, quantitative XRF analysis requires a reference material of known composition that is close to that of the sample. These standards are not always available and may be relatively expensive if they can be obtained. Another disadvantage of the method when applied to hardmetal samples, is that the samples must be fused with Li-La tetraborate and then briquetted with graphite (Kinson et al, 1976).

Atomic absorption spectrometry (AAS) has been shown to be very accurate but in most cases, only one element (one wavelength) can be measured at a time, after which the hollow cathode lamp must be changed. On older instruments the operating parameters should be re-optimised. This makes the technique very time consuming. With AAS the ability to compensate for interferences is limited and in some cases the method of standard additions must be applied, which makes the method more time-consuming (ISO 1983, 1985). In general the calibration curves are linear at low absorbance values but exhibit an increased curvature at higher concentrations (Haswell, 1991). The sample concentrations must therefore fit a much narrower measurement range than for ICP-OES.

ICP-OES is a technique which can measure multiple elements in the same solution, either





sequentially or simultaneously. This is a great advantage over AAS. The same element can be measured at several different wavelengths, which is helpful in eliminating interferences. The linear range of ICP-OES is also over several orders of magnitude. This means that elements present in different concentrations in the solution can be measured without the need to make several dilutions (Moore, 1989).