

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the early 1900's, 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 (Brookes, 1979). 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 rockdrilling bits for geological purposes. Tungsten carbide compounds are also known as hardmetals.

The properties of hardmetals are affected by the cobalt concentration and the impurities present in the material (Luyckx, 1997). Other metals, such as tantalum, titanium, vanadium and chromium are added to the tungsten carbide for various reasons, but mainly to inhibit grain growth (Brookes, 2001). Grain growth describes the merging of the tungsten carbide particles during sintering of the pressed product. Grain growth is undesirable because it may weaken the product, especially that of cutting tools (Luyckx, 1997). According to Piippanen (1997a), used materials are also recycled and the composition 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.

Various analytical methods have been used for the measurement of metallic elements in tungsten carbide (Brookes, 1979; Chen, Shao, 1986; ISO 1983, 1985; Kinson, Knott, Belcher 1976;

Kubsch, Herman, Stahlberger, Goerner, 1975; Piippanen, Jaatinen, Piirjeta and Tummavuori, 1997a, 1997b; Thomsen, Baker, 1995; Vasilescou, Abraham and Maruntu, 1980). Most are time-consuming and some may be outside the scope of commercial laboratories. A faster method that still produces reliable, high-quality results was investigated.

1.2 FIELD OF RESEARCH

For the measurement of metallic elements in tungsten carbide, the most frequently used method is x-ray fluorescence spectrometry (XRF) as discussed by Brookes (1979), Kinson et al. (1976) and Townshend, Worsfeld, Haswell, Werner, Wilson (1995) but it may not be sensitive enough for some applications. In general, XRF analysis requires prior fusion of the sample, a task requiring considerable practice (Naish, Clennel, Kingwood, 1953). Atomic absorption methods have been published by ISO (1983, 1985) and Piippanen et al. (1997b). Emission measurement methods have been used by Thomson (1995) and Piippanen et al. (1997a) but these are the only published methods found.

Tungsten carbide powder is highly resistant to acid attack and the dissolution process is lengthy, even when hydrofluoric acid is added. The published dissolution methods by ISO (1983, 1985) and Piippanen et al. (1997b) all have the drawback of being fairly time-consuming (from 45 to 75 minutes per sample) and employ undesirable reagents such as hydrofluoric acid, boric acid and phosphoric acid. Hydrofluoric acid in an analytical solution may etch glassware and instrument components. It may be complexed with boric acid but then research into the possible interference of boric acid on the analysis must be done. It has been proved by Kawaguchi (1995) that the presence of 'heavy' acids, such as phosphoric and sulphuric acid, in a solution for ICP analysis tends to give rise to nebulization (physical) interferences unless strict matrix

matching techniques are applied. Another problem with the dissolution method is a tendency for tungsten oxides to precipitate out of the acid solution and co-precipitation of the elements under investigation (Piippanen et al, 1997a).

The official method of chemical analysis of metallic elements in hardmetal powders is by dissolution in nitric acid and hydrofluoric acid and measurement by flame atomic absorption spectrometry (FAAS), using the method of standard additions (ISO, 1983, 1985). This method is very time-consuming, involving instrument set-up for each element and measurement of five different solutions of each sample. If replicate dissolutions are done, five different solutions of each replicate must be measured.

1.3 HYPOTHESIS

The purpose of the study was to provide an alternative, faster and less expensive method of dissolving tungsten carbide-cobalt powder by the use of nitric acid, hydrochloric acid, hydrogen peroxide and tartaric acid. In this manner, no additional metallic elements would be introduced into the sample matrix and the use of hydrofluoric acid will be avoided.

An efficient way to prevent the precipitation of tungsten oxides will also be investigated. The effect of tartaric acid, instead of phosphoric acid, as a stabilising agent was studied. This research differs from previous published methods for the chemical analysis of tungsten carbide mainly in the dissolution procedure for the tungsten carbide-cobalt powder prior to analysis by ICP-OES.

The experimental work included the investigation of the most efficient measurement procedure

for cobalt, tantalum, titanium, vanadium and chromium by inductively coupled plasma-optical emission spectrometry (ICP-OES). 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 could be found. Investigation of the interference effects in the sample was essential for accurate results which are comparable to other published analytical methods.

1.4 OBJECTIVES

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 measurement of cobalt, tantalum, titanium, vanadium and chromium in a tungsten carbide solution, and
- c) accurate and precise results can be obtained with such a technique.

1.5 SPECIFIC AIMS

This treatise investigates the dissolution of tungsten carbide powder in a solution of 5% aqua regia (1 part nitric acid and 3 parts hydrochloric acid, v/v) in hydrogen peroxide. The efficiency of the dissolution procedure was evaluated by the use of certified or secondary reference materials and by matrix spiking. A visual examination of the solution to determine the effectiveness of the solvent is not always conclusive, since a slight precipitate which is invisible to the eye may result in significant error. Further, there are often particles of free carbon present which may lead to false conclusions. The only practical way to evaluate the effectiveness of the dissolution procedure was to compare the results of the ICP-OES measurement to the certified or theoretical concentrations of cobalt, tantalum, titanium, vanadium and chromium.

Further research on the most suitable ICP-OES analytical wavelengths and the effect of the complex sample matrix on the measurement of the elements of interest was undertaken. These effects are not very well described in the literature (Piippanen et al., 1997a; Thompson and Walsh, 1983; Townshend et al, 1995) and not at all for vanadium in tungsten carbide by ICP-OES. The only study of the measurement of some of the metallic elements in tungsten carbide by ICP-OES was published by Piippanen (1997a).

In order to investigate the effect of each of the elements that may be found in a solution of tungsten carbide on each other, acidic solutions containing each element, in the concentration range expected for actual samples, were prepared and the ICP emission measured at the chosen analytical wavelengths. These elements were tungsten, cobalt, tantalum, titanium, vanadium and chromium. Since tungsten was not assigned as an analyte, it was evaluated purely as a potential interferent. Each of the potentially interfering elements were added in turn to a solution of the element under investigation and the change in emission at the same wavelength recorded. In this manner, it could be determined which of the chosen analytical lines were suitable for quantitative analysis. If no interference-free wavelengths for some of the analyte elements could be found, the need for matrix-matching of the calibration reference solutions with the interfering element could also be evaluated.

In addition to being faster and less expensive, the results must be shown to be accurate. In order to properly evaluate the results, certified reference materials and/ or secondary reference materials were dissolved and the solutions analysed by ICP-OES. In certain cases, materials of the appropriate composition were not available. Spiking of a tungsten carbide solution in which



the specific element was not present was employed, and the recoveries calculated to ensure accuracy.