

CHAPTER 3

THE PRODUCTION OF TUNGSTEN CARBIDE

3.1 INTRODUCTION

To understand why the analysis of certain metals in tungsten carbide is important, it is necessary to briefly describe the process of tungsten carbide production.

Prior to 1945, tungsten carbide was prepared by melting tungsten, carbon black and metal oxides at a temperature of 2000 °C but the tools made from this metal were found to be far too brittle for industrial use. Today, tungsten carbide tools are made by pressing the tungsten carbide powder in a die to produce a green compact, which is then sintered in a vacuum oven. The process, known as powder metallurgy, was introduced by Karl Schröter in 1914 (Brookes, 1979; Luyckx, 1997) and is used because:

- Tungsten carbide decomposes before melting
- The component materials retain their original properties
- It can be used to produce a large number of small parts (for example bolts) which require close tolerances and minimum finishing, and is economical
- There are no stresses on the finished product (so that they are shock-resistant), in contrast to brazed tools which suffer from stresses left by the process and which can cause fractures

The technique has certain limitations:

- design
- requires a high press capacity
- the powders must have certain properties or the density will not be uniform

3.2 COMPOSITION OF HARDMETALS

Different combinations of tungsten carbide, cobalt and metal carbides produce products with different mechanical properties. As an example, the typical composition of some grades of tungsten carbide for use in tool tips are illustrated in Table 3.1. The full table with the historical development from 1923 to 1975 is given in Appendix 2. Today most of these combinations are still in use, together with more advanced materials (Brookes, 1979, 2001; Luyckx, 1997).

Table 3.1: Standards for hardmetal tools tips (Brookes, 1979)

Composition (%)				
WC	TiC	TaC	VC	Co
34.5	60	-	-	5.6
69	25	-	-	-
78	16	-	-	-
78	14	-	-	-
85	-	-	-	-
88	5	-	-	-
89	-	-	-	-
91.5	-	1	0.5	-
94	-	-	-	-
94	-	-	-	-

It can be seen in Table 3.1 that the composition of hardmetals may vary widely. The exact cobalt content, for example, affects factors such as density, hardness, transverse rupture strength, tensile strength and thermal expansion of the sintered product (Brookes, 1979, 2001). The properties of the product may be similarly affected by the concentration of titanium, tantalum and vanadium. These and other physical properties are usually measured to control the quality of the material (Luyckx, 1997). In order to link the measured physical properties with

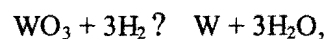
composition, it is important to measure the concentrations of the elements that affect these properties.

Appendix 1 contains a table detailing the changes in the properties of sintered tungsten carbide with changing cobalt concentration (Brookes, 1979).

3.3 PRODUCTION OF TUNGSTEN METAL

Tungsten occurs in nature as wolframite, FeMnWO_4 , and scheelite, CaWO_4 (Brookes, 1979; Luyckx, 1997; Townshend et al, 1995). The ore is digested in hydrochloric acid to remove the calcium and to precipitate tungstic acid, H_2WO_4 , which is then dissolved in ammonia and crystallized as ammonium tungstate, $(\text{NH}_4)_2\text{WO}_4$. Ammonium tungstate is evaporated by boiling to give ammonium paratungstate, or APT, $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$. At temperatures below 50°C , fine APT is obtained. By calcining APT or tungstic acid, tungsten oxide, WO_3 , is obtained. The lower the temperature, finer the WO_3 produced (Luyckx, 1997).

When WO_3 is reduced in hydrogen, tungsten, W, is produced:



because oxygen forms a more stable bond with hydrogen than with tungsten (Brookes, 1979; Luyckx, 1997; Townshend et al, 1995). In this procedure, the tungsten oxide is spread in thin layers in nickel boats and passed through a small push- or rotary-type furnace at 800 to 1100°C in the opposite direction to the hydrogen flow. The water vapour is condensed in drying towers and the purified hydrogen re-circulated. To obtain a uniform product, the oxide particles must all be at the same temperature and in the same atmosphere. This is where the rotary

furnace has the advantage by exposing all the particles to the hydrogen atmosphere. If the tungsten oxide is too coarse, layers of tungsten will form around the particles and prevent reduction of the oxide in the centre.

Several changes may take place during the reduction process. These are summarized in Table 3.2. The changes are due to changes in the stability of the oxides, relative to the stability of the water with changing temperature (Luyckx, 1997).

Table 3.2: Changes occurring during the reduction of tungsten oxide (Luyckx, 1997)

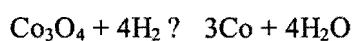
Temperature (°C)	Appearance	Approximate composition
400	Green-blue	WO ₄ + W ₄ O ₁₁
500	Intense blue	WO ₄ + W ₄ O ₁₁
550	Violet	W ₄ O ₁₁
575	Purple-brown	W ₄ O ₁₁ + WO ₂
600	Chocolate brown	WO ₂
650	Brown-black	WO ₂ + W
700	Grey-black	W
800	Grey	W
900	Metallic grey	W
1000	Coarse metallic	W

3.4 CARBON POWDER

The carbon used in hardmetals is usually pressed lampblack, of which the ash content should not exceed 0.2%.

3.5 COBALT POWDER

Cobalt metal powder is obtained by the reduction of cobalt oxide in hydrogen, at temperatures of between 600 and 700°C, according to the following reaction:



Generally, the lower the reduction temperature, the finer the particle size of the powder produced (Luyckx, 1997). Powders with a particle size of less than 5 μm do not require milling (a source of contamination) before addition to the tungsten carbide powder but the coarser powders are milled for 24 hours. Cobalt liquidizes during the sintering process and acts as a glue to bond the WC particles. Some of the desirable properties of tungsten carbide tools are undermined with increasing cobalt concentration. According to Luyckx (1997), these include:

- high impact resistance,
- high modulus of elasticity,
- high compressive strength,
- low tensile strength,
- low impact strength,
- low coefficient of thermal expansion, and
- high thermal conductivity

Charts of the changes in the properties with changes in the cobalt concentration are included under Appendix 1. Carbide particles are 'cemented' by a binder metal, such as cobalt, which is liquid at sintering temperature (Brookes, 1979; Luyckx, 1997).

3.6 OTHER ADDITIVES

In more than 98% of all carbide production, cobalt is the binder. Nickel is sometimes used as a binder and the carbides of tantalum, titanium, molybdenum, vanadium, chromium and niobium may be alloyed with the tungsten carbide as grain growth inhibitors (Brookes, 2001; Luyckx, 1997).

Chromium, as Cr_3C_2 , or vanadium, as VC, are added as grain growth inhibitors. TaC, NbC and TiC are also used as grain growth inhibitors but as the nominal grain size of the powder becomes smaller, only VC and Cr_3C_2 are effective (Brookes, 1979, 2001; Luyckx, 1997; Fry, 1982). These authors hold that VC also imparts high hardness resulting from a very fine microstructure.

TiC is used to resist diffusion attack during sintering that causes 'cratering', a structural defect in the product that reduces strength. TiC-based tools are considerably more brittle than tungsten carbide tools, so the TiC content is kept as low as possible (Brookes, 1979).

Tantalum also helps to resist 'cratering' but at a considerably higher cost. In addition, it improves the shock-resistant properties of the hardmetal. Niobium has a similar effect to tantalum but to a lesser degree. Although the complete separation of tantalum and niobium when used in hardmetal production is difficult (they have similar properties) and not really necessary, both the niobium and tantalum content of a powder are usually measured. If the raw materials already contain one of these elements, then the added concentration of the other must be adjusted to be able to predict the effect on the product properties. Similarly, if only one of the elements (niobium or tantalum) is measured during the quality control procedure, a false indication of the properties is obtained if the other element is also present undetected (Luyckx, 1997).

In research environments, a knowledge of the exact additive concentration in the tungsten carbide powder is required to determine how the physical properties of the product are affected. For example, Figure 3.1 shows the classification of crater resistance as a function of

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tantalum or titanium concentration in carbide materials.

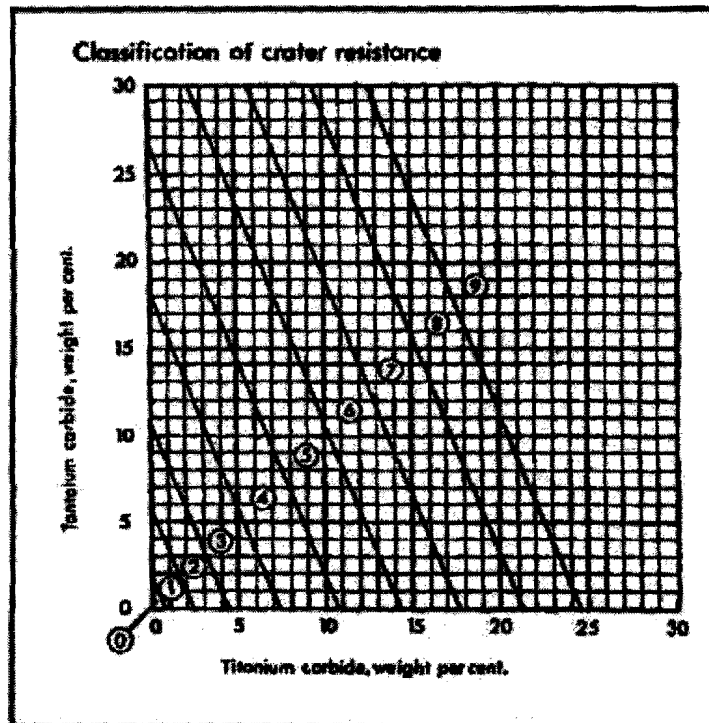
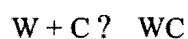


Figure 3.1: British Hard Metal Association (BHMA) numerical coding system for hardmetal properties. A three-digit code serves to classify the crater resistance property of the hardmetal (Brookes, 1979)

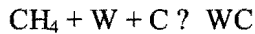
Although the coding system is hardly of interest here, Table 3.1 does show that the properties of the product change with change in the titanium or tantalum concentration.

3.7 TUNGSTEN CARBIDE POWDER (WC)

Tungsten carbide is produced by blending dry tungsten powder with carbon black and the required metal oxides, then firing this in a hydrogen atmosphere at temperatures of between 1400 and 2650°C (Luyckx, 1997). The chosen temperature depends on the particle size desired, again with smaller particle sizes being produced at the lower temperatures. The reaction, known as carburisation, proceeds as follows:



In the process, gaseous hydrocarbons are formed:



and these combine with the tungsten to form W_2C , also known as “eta phase” tungsten carbide nuclei. As additional carbon is absorbed, polycrystalline WC particles are formed (Luyckx, 1997).

To obtain a 1:1 ratio of W:C, the amounts are calculated as follows:

$$\text{Mass of carbon in WC} = \frac{12 * 100}{184 + 12} = 6.12 \text{ g / 100 g,}$$

but in practice a 3 to 10% excess of carbon is added, since a slight excess of carbon in the product has little effect on the properties. However, if the carbon content is too low, W_2C , is formed, which is undesirable. Figure 3.2 presents a flow chart for the production of tungsten carbide powder from the raw materials described above.

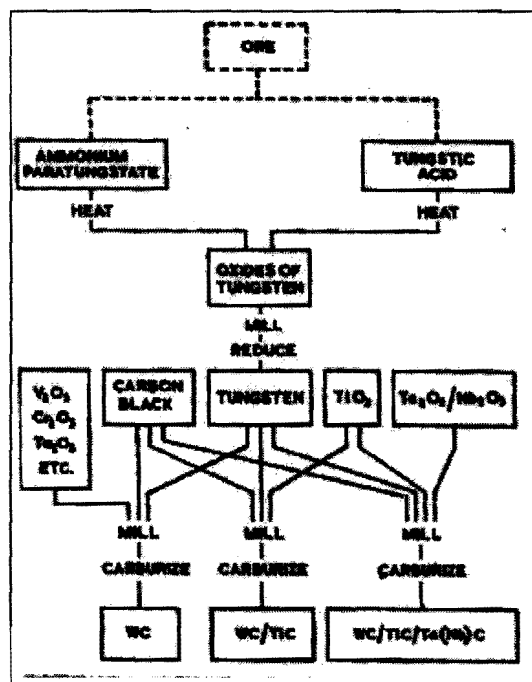


Figure 3.2: Simplified flow chart for the production of carbide powders (Brookes, 1979)

3.8 IMPURITIES AND QUALITY CONTROL

There are many sources of impurities and the quality of the raw materials is strictly controlled by testing before blending. According to Luyckx (1997), the presence of impurities and trace elements may lead to serious defects in the product, including pores, large crystals, weak interfaces, unwanted phases and inclusions. Tungsten carbide tools are used under extreme conditions (Brookes, 1979, 2001), for example in rock drilling and cutting of very hard materials, and the use of weakened products may have serious and expensive consequences. Table 3.3 (Luyckx, 1997) gives the desired characteristics of the starting materials and intermediate products.

In Table 3.4 (Luyckx, 1997) the maximum limits of impurities have been tabulated. The potassium and sodium content of coarse grain powders tend to be higher than in finer grades. The oxygen content of fine grain powders, however, tends to be higher (Luyckx, 1997).



Table 3.3: European data for the characteristics of starting materials and intermediate products (Luyckx, 1997)

Material	Particle size range(μm)	Weight increase on annealing in air (%)	Approximate chemical analysis (%)
Ammonium paratungstate	0.5-65	-	W: 70.2 Si: 0.04 Fe: 0.01 Alkalies: C: 0.01 0.03 S: 0.01
Tungstic acid	0.5-11	-	W: 73.5 Si: 0.04 Fe: 0.05 Alkalies: C: 0.01 0.05 S: 0.01
Tungsten trioxide	0.5-15	-	W: 78.6 Si: 0.03 Fe: 0.05 Alkalies: 0.1 C: 0.01 S: 0.06
Tungsten from tungstic acid	0.5-3	350°C for 5 min: 18-21	O ₂ : 0.2-0.4 Impurities: approx. as above
Tungsten from tungsten trioxide	0.5-5	350°C for 5 min: 18-21	O ₂ : 0.1-0.35 Impurities: approx. as above
Carbon, reduced	0.5-10	400°C for 30 min: 2.3	W: 99.2 S: 0.01 Fe: 0.09 O ₂ : 0.4 C: 0.06
Cobalt	1-3	400°C for 30 min: 28	Co: 98.6 Zn: 0.05 Fe: 0.08 O ₂ : 0.6 C: 0.1 Alkalies: Mn: 0.1 0.08 Si: 0.05 Ni: 0.1
Graphite (milled)	-	-	C: 98.2 Ash: 0.6 Moisture 0.2 Volatiles: 0.9
Carbon black	-	-	C: 97.9 Ash: 0.05 Moisture: 0.1-2 S: 0.3-0.5 Volatiles: 1
Sugar charcoal	-	-	C: 94.7 Ash: 0.7 Moisture: 1.4 S: 0.3 Volatiles: 2.6



Table 3.4: Limits of impurities in raw materials (Luyckx, 1997)

Element	Tungsten carbide (WC) powder (mg/kg)	Cobalt powders (mg/kg)
Aluminium (Al)	<20	<50
Arsenic (As)	<5	-
Calcium (Ca)	<20	<100
Cobalt (Co)	<300	-
Chromium (Cr)	<30	-
Carbon (C)	-	<500
Copper (Cu)	<10	<20
Iron (Fe)	<200	<100
Lead (Pb)	<10	<10
Magnesium (Mg)	<10	<100
Manganese (Mn)	<10	<100
Molybdenum (Mo)	<90	-
Nickel (Ni)	<20	<500
Oxygen (O ₂)	<500	-
Phosphorus (P)	<30	<10
Potassium (K)	<50	<50
Silicon (Si)	<40	<40
Sodium (Na)	<30	<50
Sulphur (S)	<30	<50
Tantalum (Ta)	<30	-
Tin (Sn)	<10	-
Vanadium (V)	<5	-
Zinc (Zn)	-	<50