

# On the Preparation of Fine $V_8C_7$ -WC and $V_4C_3$ -WC Powders

C. Osborne, L. Cornish

Department of Metallurgy, University of the Witwatersrand, Johannesburg, South Africa

&

S. Luyckx

Mattek, CSIR, Pretoria and Schonland Research Centre, University of the Witwatersrand, Johannesburg, South Africa

(Received 24 October 1995; accepted 15 November 1995)

**Abstract:** The aim of this work was to produce  $V_8C_7$ -WC and  $V_4C_3$ -WC powders with grain size between 1 and 2  $\mu\text{m}$ , as a first stage of the preparation of fine grained WC-VC-Co hardmetal.

$V_8C_7$ -WC powder was produced via two routes: starting from preformed  $V_8C_7$  and WC, and starting from  $V_2O_5$ , WC and carbon black. The  $V_4C_3$ -WC powder was not produced because all attempts led to the formation of  $W_2C$  or  $V_8C_7$ . © 1997 Elsevier Science Limited

## 1 INTRODUCTION

During the last few years attempts have been made to partially replace the tungsten carbide (WC) in cemented tungsten carbide (WC-Co) with vanadium carbide (VC).<sup>1</sup> These attempts have produced a hardmetal which is harder, but less tough than WC-Co of equal cobalt content.

The lower toughness of the VC-WC-Co hardmetal has been found to be due to the low toughness of the VC grains. These offer an easy path to fracture propagation. It is reasonable to assume that the toughness of VC-WC-Co could be improved by reducing the VC grains to a size below the critical crack length of the hardmetal, so that even if the grains do crack, the cracks do not cause catastrophic failure.

This paper describes the first stage in the preparation of fine grained VC-WC-Co, i.e. the preparation of fine  $V_8C_7$ -WC or  $V_4C_3$ -WC powders. The final aim is to produce a VC-WC-Co hardmetal where the VC grain size is of the order of 1–2  $\mu\text{m}$ , instead of the 10–15  $\mu\text{m}$  achieved in previous attempts.<sup>1</sup>

## 2 MATERIALS AND METHODS

In order to produce fine VC-WC powders ( $V_8C_7$ -WC or  $V_4C_3$ -WC) attention had to be paid to the following points:

- characterization of the powders at all stages of the process;
- mixing and milling of the powders;
- carburization of the milled powders (where necessary).

The initial powders were tungsten carbide,  $V_8C_7$  or  $V_2O_5$  (depending on the preparation route) and carbon black. Powders were supplied by Boart International, with the exception of  $V_8C_7$  from Metallurg and  $V_2O_5$  from Highveld Steel and Vanadium. The characterization of the powders consists of the following:

- chemical analysis (to ensure that the impurity levels were within acceptable limits);
- analysis by X-ray diffraction;

- analysis of particle size and particle size distribution.

The chemical analysis was performed by means of ICP-mass spectroscopy and gave impurity contents down to ppm. X-ray diffraction was carried out using Cu radiation (wavelength=0.15418 nm). The analysis of particle size and particle size distribution was performed by means of the Malvern Laser method. The choice of this method was determined by availability and speed, which were important in a project involving the measurement of the particle size of a large number of powders.

The mixing and milling was carried out in a laboratory mill consisting of either 250 or 500 ml Pyrex bottles resting on rolling cylinders. The bottles contained cylindrical stainless steel 'rods' of length 11 mm, diameter 8 mm and mass 3.8 g. The milling liquid was alcohol. The charge mass varied from 25 to 100 g, and was made up of varying ratios of tungsten carbide, vanadium oxide or preformed vanadium carbide, and carbon black when necessary.

The carburization experiments were carried out in a Lenton laboratory tube furnace. An alumina tube was placed through the furnace leaving 750 mm of tubing protruding at each end (Fig. 1). This was done in order to allow the insertion of the rubber stoppers into the cooler ends of the tube. An argon atmosphere was used when heating the furnace up to temperature, and upon cooling. Once the furnace was at temperature, either an argon or hydrogen atmosphere was used.

The  $V_8C_7$ -WC powders were produced via two routes:

- starting from a preformed  $V_8C_7$  powder and a preformed tungsten carbide powder, which were mixed and milled together with a 0.5 wt% cobalt addition, and heat treated;
- starting from  $V_2O_5$ , which was mixed with tungsten carbide and carbon black, milled and carburized under hydrogen.

The  $V_4C_3$ -WC powder was supposed to be produced starting from  $V_2O_5$ , which was mixed with tungsten carbide and carbon black, milled and carburized. Atmospheres of hydrogen or argon were used.

The particle size and composition of the powders were analysed after each stage of the process.

### 3 RESULTS AND DISCUSSION

#### 3.1 Characterization of the starting powders

The commercial tungsten carbide powder had a nominal average particle size of 1  $\mu\text{m}$ . The powder was measured by the Malvern Laser method to give the Sauter Mean Diameter (SMD) which is defined as:

$$\text{SMD} = \frac{\int_{D1}^{D2} D^3 n(D) dD}{\int_{D1}^{D2} D^2 n(D) dD} \quad (1)$$

where  $n(D)$  is the number distribution and  $D$  is the particle diameter from  $D1$  (minimum) to  $D2$  (maximum), and the span which is a measure of the range of the distribution and is defined as:

$$\text{Span} = \frac{D(v, 0.9) - D(v, 0.1)}{D(v, 0.5)} \quad (2)$$

where  $D(v, x)$  is the diameter, below which  $x$  volume fraction of the particles lie. The Sauter Mean Diameter of the tungsten carbide powder was found to be 6.45  $\mu\text{m}$  with a span of 4.3  $\mu\text{m}$ . A plot of the particle size distribution exhibited a double peak, which indicated some agglomeration and explained the discrepancy between nominal particle size and Sauter Mean Diameter.

The commercial  $V_8C_7$  powder had Sauter Mean Diameter of 4.25  $\mu\text{m}$  with a span of

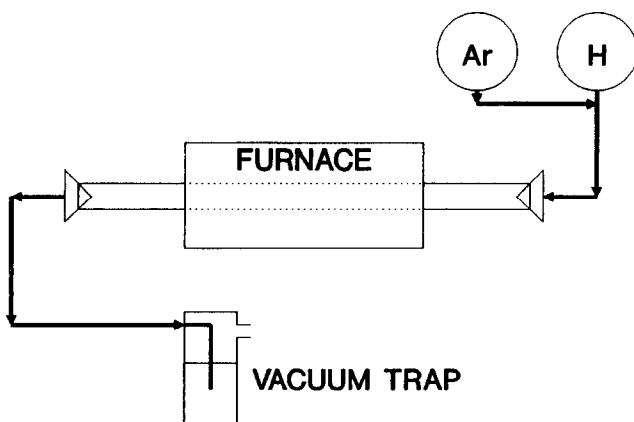


Fig. 1. Schematic of the carburization apparatus.

1.5  $\mu\text{m}$ . The  $V_2O_5$  powder had a Sauter Mean Diameter of 22.55  $\mu\text{m}$  with a span of 1.9  $\mu\text{m}$ .

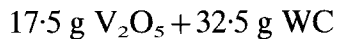
The impurity level in the tungsten carbide,  $V_8C_7$  and carbon black powders was within limits acceptable by the hardmetal industry. The impurity level in the  $V_2O_5$  powder was generally low ( $10^1$ – $10^2$  ppm), except for sodium ( $3 \times 10^3$  ppm), calcium ( $8 \times 10^2$  ppm) and aluminium ( $5 \times 10^2$  ppm).

The  $V_2O_3$  powder was prepared by partial reduction of  $V_2O_5$  at 600°C for 3 h, under a 0.2 litre/min hydrogen gas stream. The resulting powder had a Sauter Mean Diameter of 27.94  $\mu\text{m}$  and a span of 2.4  $\mu\text{m}$ .

### 3.2 Mixing and milling

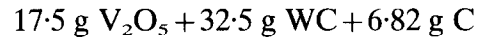
#### 3.2.1 The $V_2O_5 + WC$ powder

The first experiment consisted of mixing  $V_2O_5$  and tungsten carbide powders in the following proportion:



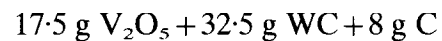
The mixture was milled in a 500 ml Pyrex bottle, with 20 stainless steel cylinders of a total mass 76 g, and 100 ml of alcohol. This mixture was milled for 336 h, taking samples at various time intervals for particle size analysis. Figure 2 shows that the particle size decreased rapidly during the first 48 h, remained almost constant for the next 200 h, and then started to increase. Plots of the particle size distribution showed that after 240 h of milling the tendency towards agglomeration became stronger than the tendency towards comminution, as illustrated by the formation and growth of a double peak (Fig. 3).

A second experiment consisted of mixing  $V_2O_5$ , tungsten carbide and carbon black in the following proportion:



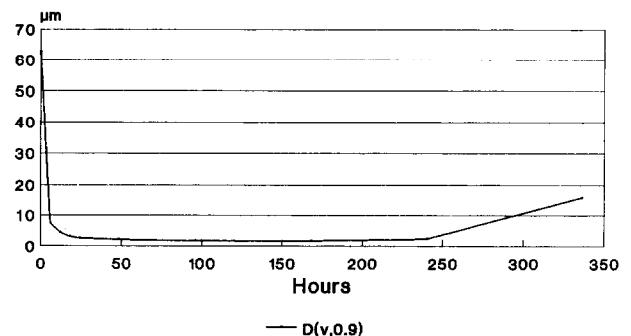
This mixture was milled under the same conditions used in the first experiment and was also milled for 336 h. It was found to be less prone to agglomeration, since no second peak was observed in the particle size distribution plots. Figure 4 shows that the tendencies towards agglomeration and comminution balance, even after 336 h of milling.

An optimum milling time of 48 h was selected on the basis of Fig. 4 (since very little change in size occurs after this time), and a charge consisting of:



was milled in a 500 ml Pyrex bottle, with 20 stainless steel cylinders of a total mass 76 g, and 100 ml of alcohol for 48 h. The resultant pow-

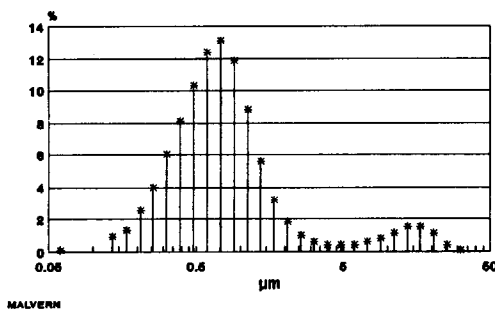
#### No Carbon Added MALVERN



$D(v,0.9)$  = The diameter by volume, below which 90% of the particles lie.

Fig. 2. Plot of the upper limit of the diameter of 90% of the particles of a vanadium pentoxide-tungsten carbide powder, versus milling time.

#### Particle Size Distribution at 240 Hours



#### Particle Size Distribution at 336 Hours

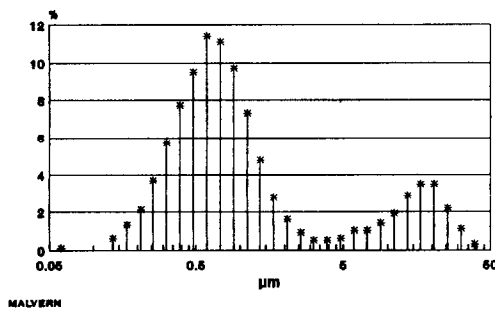
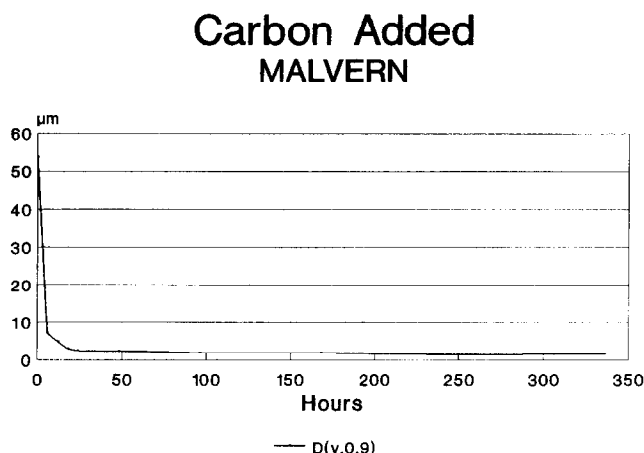


Fig. 3. The particle size distribution of the vanadium pentoxide-tungsten carbide powder, at 240 and 336 h.



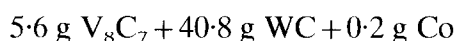
D(v,0.9) = The diameter by volume, below which 90% of the particles lie.

Fig. 4. Plot of the upper limit of the diameter of 90% of the particles of a vanadium pentoxide–tungsten carbide–carbon black powder, versus milling time.

der mixture had a Sauter Mean Diameter of  $0.87 \mu\text{m}$  and a span of  $1.3 \mu\text{m}$ .

### 3.2.2 The $V_8C_7$ +WC powder

The preformed  $V_8C_7$  powder was mixed with the tungsten carbide powder and 0.5 wt% Co, in the following proportion:



The mixture was milled in 500 ml Pyrex bottles, with 20 stainless steel cylinders of a total mass 76 g, and 100 ml of alcohol. Milling was continued for 48 h and the Sauter Mean Diameter of the final powder mixture was  $1.35 \mu\text{m}$  with a span of  $1.3 \mu\text{m}$ . A 48 h milling period was selected for comparison with the  $17.5 \text{ g } V_2O_5 + 32.5 \text{ g WC} + 8 \text{ g C}$  powder mixture described in Section 3.2.1.

After milling, the powder was heated to  $1200^\circ\text{C}$  and held for 3 h, in order to promote the formation of the (V,W)C mixed carbide. The heat treated powder consisted of  $V_8C_7$ , WC and (V,W)C, as shown in Fig. 5, and had a Sauter Mean Diameter of  $1.42 \mu\text{m}$ . Cobalt peaks were not identified, as was expected due to the low amount of cobalt added.

### 3.2.3 The $V_2O_3$ +WC+C powder

The  $V_2O_3$  powder was mixed with tungsten carbide and carbon black in the following proportion:

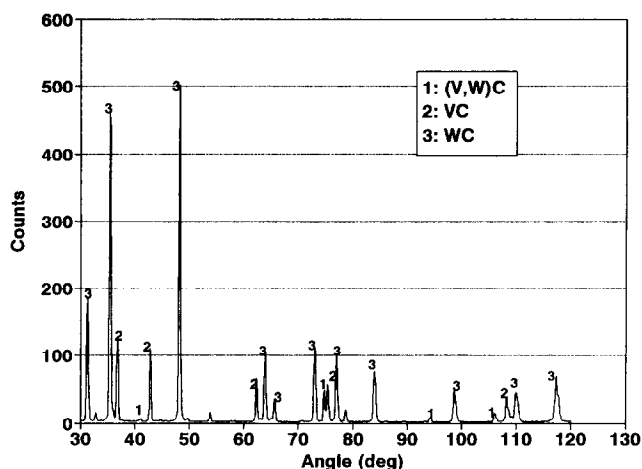
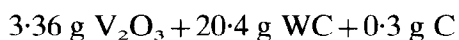


Fig. 5. X-ray diffraction spectrum of the VC–WC–(V,W)C powder produced in process 3.2.2.

The mixture was milled for 310 h in a 250 ml Pyrex bottle containing 10 stainless steel cylinders of a total mass of 38 g, and 50 ml of alcohol. Samples were taken at various time intervals for particle size analysis. The final Sauter Mean Diameter of the powder was  $0.79 \mu\text{m}$  with a span of  $1.3 \mu\text{m}$ .

## 3.3 Carburization

### 3.3.1 Carburization of the $V_2O_5$ -WC-C powder mixture

The carburization conditions were selected on the basis of the following experiments, taking into consideration that the carburization time had to be kept as low as possible in order to minimize particle growth. Powder mixtures consisting of the initial  $V_2O_5$ /WC ratios:

Powders 1 and 2: 1 g  $V_2O_5$  to 5.03 g WC

Powders 3 and 4: 1 g  $V_2O_5$  to 2.63 g WC

were heated in a hydrogen atmosphere to temperatures ranging from  $800$  to  $1200^\circ\text{C}$ , and kept at the temperature for 2 h.

At each temperature,  $V_2O_5$  was completely reduced to  $V_2O_3$ . However, the reduction and subsequent carburization of the  $V_2O_3$  was found to be incomplete at all temperatures except  $1200^\circ\text{C}$ . The amount of residual  $V_2O_3$  in powders 1–4 at each temperature has been reported in Table 1. These values were obtained using X-ray diffraction.

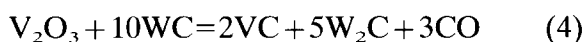
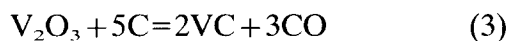
Since the  $1200^\circ\text{C}$  temperature was the lowest temperature without residual  $V_2O_3$ , this temperature was selected for carburization. The carburization time was determined by heating

**Table 1.** Effect of temperature on residual  $V_2O_3$  in powders 1–4

Temp. (°C)	Powder	Powder	Powder	Powder
	1	2	3	4
	$V_2O_3$ (%)	$V_2O_3$ (%)	$V_2O_3$ (%)	$V_2O_3$ (%)
800	3.42	2.96	4.94	5.80
900	2.53	2.61	4.58	5.20
950	2.51	2.62	4.08	4.79
1000	2.97	2.37	3.78	3.70
1050	1.77	1.92	3.14	3.23
1100	1.55	1.97	2.54	2.59
1125	1.23	1.77	2.40	2.61
1150	1.51	1.57	2.99	2.46
1175	0.86	0.97	1.90	1.76
1200	0.00	0.00	0.00	0.00

the powder mixture (which, as described in Section 3.2.1, consisted of 17.5 g  $V_2O_5$ +32.5 g WC+8 g C, and was milled for 48 h) under hydrogen to 1200°C, holding for different times, and then analyzing the powder for residual  $V_2O_3$ . The results are summarized in Table 2. In this experiment (Test 2) unlike the initial trial (Test 1), some residual  $V_2O_3$  was found after 2 h at 1200°C, so the carburization time was set at 3 h to ensure complete carburization.

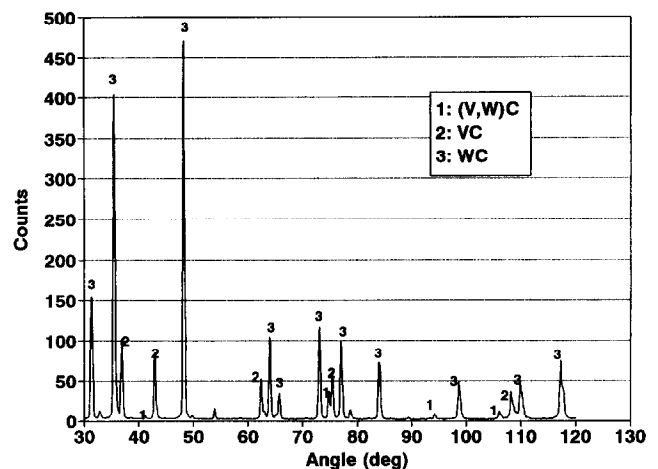
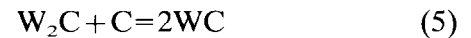
The different results obtained from Test 1 and Test 2 were due to the differences in the  $V_2O_5$ :WC ratio of the powder mixtures. The reduction rate of the vanadium oxide is dependent on the amount of tungsten carbide powder added,<sup>2</sup> when the carburization temperature used is above 1160°C [the temperature above which eqn (4) below becomes thermodynamically possible]. The additional presence of WC, rather than C alone, increases the rate of reaction, because both C and WC are reducing and carburizing  $V_2O_3$ :



The  $W_2C$  produced in eqn (4) is subsequently recarburized:

**Table 2.** Effect of time on residual  $V_2O_3$  on carburizing at 1200°C under hydrogen

Time (min)	60	90	120	150
$V_2O_3$ (%)	0.88	0.70	0.48	0.00

**Fig. 6.** X-ray diffraction spectrum of the VC-WC-(V,W)C powder prepared in process 4.1.

The  $V_2O_5$ :WC ratio in Test 2 was 1:1.86 compared to 1:5.03 for powders 1 and 2, and 1:2.63 for powders 3 and 4, explaining the presence of residual  $V_2O_3$  found after 2 h at 1200°C.

The X-ray diffraction spectrum of the VC-WC powder obtained from the final carburization conditions is shown in Fig. 6. The powder consists of  $V_8C_7$ , WC and (V,W)C. The Sauter Mean Diameter of the powder prior to milling with cobalt was 1.84  $\mu\text{m}$  and the span 1.3  $\mu\text{m}$ .

### 3.3.2 Carburization of the $V_2O_3$ +WC+C powder mixture

In Section 3.3.1, excess carbon was used to ensure complete carburization to a  $V_8C_7$ -WC powder, and in order to reduce the residual oxide in the powder. By contrast, in this method, at the carburization temperature of 1200°C nearly all oxygen from  $V_2O_3$  is removed as  $CO_3$ , which should enable one to calculate accurately the intermediate amount of carbon required for reduction and carburization, to produce a  $V_4C_3$ -WC carbide powder. The  $V_2O_3$ -WC-C mixture (Section 3.2.3) was carburized at 1200°C for 3 h, but X-ray diffraction analysis showed the presence of  $W_2C$  after carburization in both hydrogen and argon atmospheres. By adding excess carbon,  $W_2C$  was no longer produced, but  $V_8C_7$  was obtained instead of  $V_4C_3$ .

Since the  $W_2C$  phase was observed after carburization under both hydrogen and argon atmospheres, decarburization through hydrogen formation is an unlikely explanation for its

presence. Obviously there is an intermediate amount of carbon that would give  $V_4C_3$  without  $W_2C$ . The difficulty in assessing the amount of carbon required lies in accounting for carbon lost due to reaction with residue  $WO_3$ .

#### 4 CONCLUSIONS

The experiments described above showed that a  $V_8C_7$ -WC powder of mean particle size between 1 and 2  $\mu\text{m}$  can be produced from at least two routes:

- by milling a mixture of coarse  $V_8C_7$  and tungsten carbide powders, with a 0.5 wt% Co addition for 48 h, followed by a 3 h heat treatment at 1200°C;
- by milling a mixture of coarse  $V_2O_5$ , tungsten carbide and carbon black powders for 48 h, which is then carburized at 1200°C for 3 h.

The second route is more economical, because the  $V_2O_5$  oxide is cheaper than the preformed  $V_8C_7$ . However, the most effective route for the

production of fine  $V_8C_7$ -WC powder for VC-WC-Co hardmetal can only be assessed after sintering.

The production of a fully carburized  $V_4C_3$ -WC powder starting from a mixture of  $V_2O_5$ , tungsten carbide and carbon black has not been successful because all attempts have led to the formation of  $W_2C$  or  $V_8C_7$ .

#### ACKNOWLEDGEMENTS

The authors are grateful to MINTEK and VANITEC (UK) for their financial support, and to Highveld Steel and Vanadium for supplying the  $V_2O_5$  powder.

#### REFERENCES

1. Luyckx, S., *Proceed. Powd. Met. World Congress, PM '94*, Paris 6–9 June, Vol. 1, p. 169.
2. Schwarzkopf, P. & Kieffer, R., *Cemented Carbides*, The Macmillan Company.
3. Gupta, C. K. & Krishnamurthy, N., *Extractive Metallurgy of Vanadium*, Elsevier, 1992.