

# FINE-GRAINED WC-VC-Co HARDMETAL

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## ABSTRACT

This paper describes the preparation process and some properties of VC-WC-Co alloys containing approximately 10 wt% VC and 10 wt% Co. The sinterability of the alloys proved to be better than expected and the hardness higher than the hardness of WC-Co alloys of equal cobalt content. The toughness was found to be superior to the toughness of WC-Co alloys of equal hardness.

## 1. INTRODUCTION

It was reported elsewhere<sup>[1]</sup> that VC-WC-Co alloys had been prepared having higher hardness, abrasion resistance and erosion resistance but lower toughness than WC-Co alloys of equal cobalt content. It was also reported that the lower toughness was due to the brittleness of the VC grains, whose average size was not lower than 10  $\mu\text{m}$ . Therefore, attempts have been made to produce the same material with a smaller mean VC grain size, so that cracks forming in VC grains would be much shorter than the critical crack size of the material. Hence effort has been directed towards producing finer grade powders and avoiding grain growth during sintering.

Finer VC-WC-Co grade powders were produced through prolonged milling via two routes<sup>[2]</sup>: from a  $\text{V}_2\text{O}_5$  starting powder, which was mixed with WC, carburized, and mixed with cobalt; and from a preformed  $\text{V}_8\text{C}_7$  starting powder, which was mixed with WC and cobalt. In both cases the grade powder produced had mean grain size smaller than 2  $\mu\text{m}$ . Grain growth in sintering was minimized by keeping the sintering temperature as low as possible.

The present paper describes the material produced so far, problems encountered in its production and some of its properties.

## 2. MATERIALS AND METHODS

The preparation of the two types of grade powder used to produce the samples discussed in this paper has been reported in detail elsewhere<sup>[2]</sup>. The relevant properties of the two types of grade powder (Powder 1 and Powder 2) are given in Table I.

	Powder 1	Powder 2
Starting Powders	$\text{V}_2\text{O}_5$ , WC, C, Co	$\text{V}_8\text{C}_7$ , WC, Co
Approximate Composition* of the Grade Powder (wt%)	10%V, 10%Co, WC	10%VC, 10%Co, WC
Phases Present (from XRD)	VC, WC, (V, W)C	VC, WC, (V, W)C
Mean Particle Size	1.65 $\mu\text{m}$	1.28 $\mu\text{m}$

**TABLE I. Characteristics of the VC-WC-Co Grade powders Used to Prepare the Samples.** (\* The composition is approximate because some (V,W)C was also formed, but its composition is not yet known.)

Table II gives the level of impurities in the  $V_2O_5$  powder, as it is relevant to one of the problems encountered in the preparation of the material.

Li (25), Be (4), B (200), Na (3000), Mg (200), Al (485), Ca (790), Ti (17), Cr (200), Fe (360), Mn (3), Co (5), Ni (30), Cu (3), Zn (100), Ga ( 3), Se (3), Rb (5), Sr (5), Zr (15), Nb (1), Mo (3), Ru (3), Cd ( 3), Sn (3), Te (4), Ba (15), Ce ( 6), W (2), Os (8), Pt (1), Au (3), Pd (3).
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**TABLE II. Impurity Levels in the Starting  $V_2O_5$  Powder in ppm.**

Differential Thermal Analysis (DTA) was used to determine the eutectic point of the VC-WC-Co system, in order to select the lowest possible sintering temperature and minimize grain growth during sintering. The DTA apparatus used was a SETARAM 92-16.18.

Both powders were compacted either uniaxially or isostatically. In either case the maximum green density achieved was  $6.5 \text{ g/cm}^3$ , i.e. approximately 50 % of the theoretical density (the theoretical density could not be calculated with precision on account of the formation of an as yet unknown quantity of (V,W)C).

The green compacts which were compressed uniaxially were sintered at  $1330^\circ\text{C}$  for 1 hour in argon and those which were compressed isostatically were sintered in  $N_2$  up to  $750^\circ\text{C}$ , in vacuum from  $750^\circ\text{C}$  to  $1390^\circ\text{C}$  and hipped at  $1390^\circ\text{C}$  for 30 minutes at 45 bars in argon. Sinterhipping could not be carried out at temperatures lower than  $1390^\circ\text{C}$  because the present samples had to be sinterhipped in industrial facilities together with other samples of different composition.

The sintered samples were polished and analysed for porosity then etched for microstructural analysis. The microstructure and composition were studied by means of SEM, EDS and x-ray diffraction.

The Vickers hardness of the samples was measured in accordance with the ISO Standard 3878, i.e. using a 30 kg load, and the fracture toughness was calculated from the length of the cracks produced by the Vickers indentations, using Shetty et al's formula<sup>[4]</sup>:

$$K_{IC} = 0.0889 (HW)$$

where:

$K_{IC}$  = fracture toughness in  $\text{MPa}\sqrt{\text{m}}$

H = hardness in  $\text{N m}^{-2}$

W = P/L ,

where P (in N) is the load applied to the Vickers indenter, and

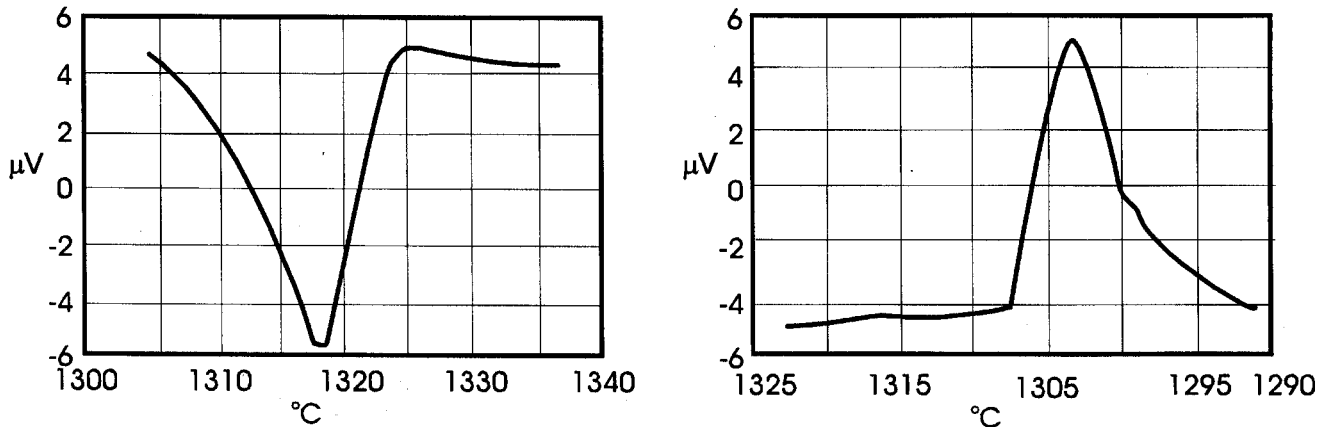
L (in m) is the total length of the cracks produced by the Vickers indentation.

### 3. RESULTS AND DISCUSSION

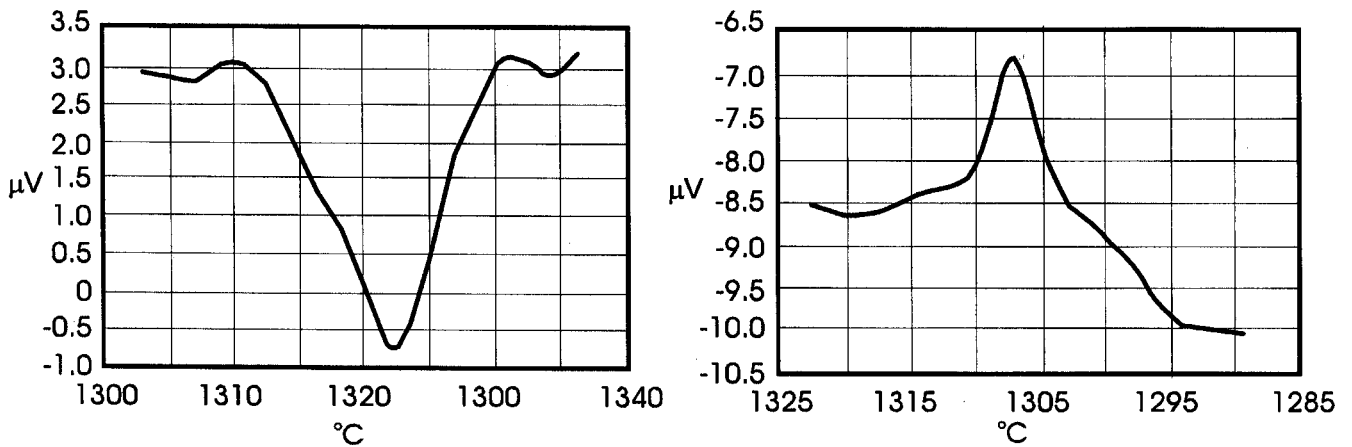
#### 3.1. Differential Thermal Analysis

Figs 1 and 2 show that, on heating, in Powder 1 the onset of the eutectic reaction was below  $1305^\circ\text{C}$  and the reaction peaked at  $1318^\circ\text{C}$ , whereas in Powder 2 the onset was at about  $1310^\circ\text{C}$  and the peak at about  $1322^\circ\text{C}$ . On cooling, the onset and peak temperatures for Powder 1 were about  $1308^\circ\text{C}$  and  $1303^\circ\text{C}$  respectively and for Powder 2 were around  $1317^\circ\text{C}$  and  $1307^\circ\text{C}$  respectively. It can be seen that the trace of Powder 2 is more uneven than that of Powder 1, which could indicate that other reactions also occurred. The difference between the reaction temperatures of Powders 1 and 2 is

likely to be due to slight differences in overall composition and phase content.



**Fig. 1. Heating and Cooling Traces from the DTA of Powder 1 (VC-WC-Co Grade powder Produced Starting from  $V_2O_5$ ).**



**Fig. 2. Heating and Cooling Traces from the DTA of Powder 2 (VC-WC-Co Grade Powder Produced Starting from Preformed  $V_8C_7$ ).**

Fig 3 shows the results of the DTA of a WC-10wt% Co sample (at the same heating and cooling rates as for Powders 1 and 2). The onset of the eutectic reaction was around 1335°C and the peak at about 1363°C. Similarly for cooling, the onset of the reaction was at 1357°C and the peak at 1348°C. These readings are higher than those reported in the literature for WC-Co, which may be due to faster heating and cooling rates. However, what is relevant is that in both Powders 1 and 2 (both containing approximately 10 wt% Co) a liquid phase was present at a lower temperature than in WC-10% Co. This suggested that lower sintering temperatures could be used for VC-WC-Co than for WC-Co of equal cobalt content.

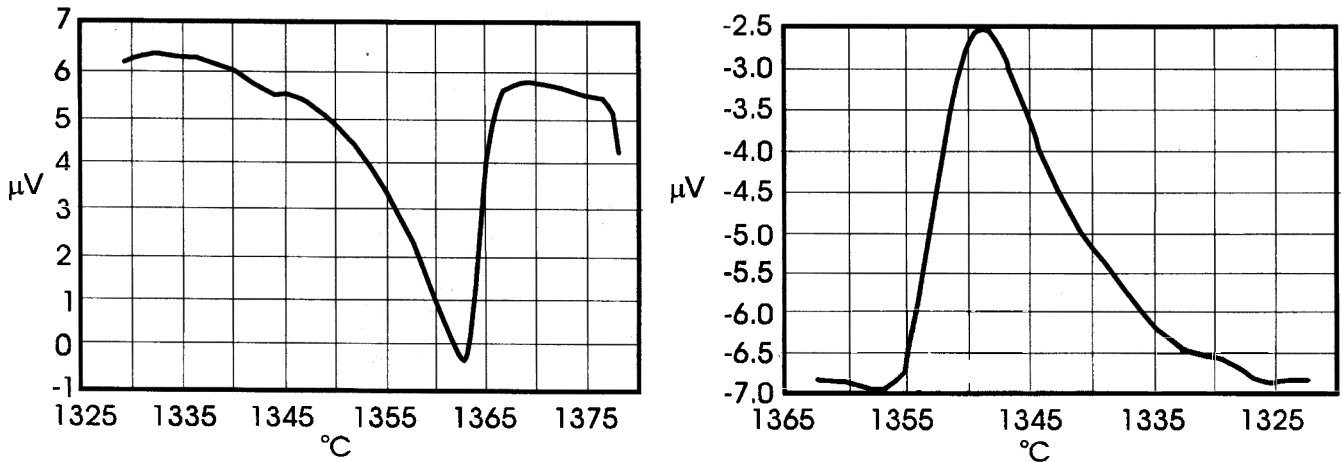
### 3.2. Porosity

The samples prepared from Powder 1 will be called samples "Type 1" and those prepared from Powder 2 will be called samples "Type 2". Both sample types exhibited only A-type porosity, namely pores of approximately 1  $\mu\text{m}$  in size. This was observed both in samples sintered at 1330°C and in samples sinterhipped at 1390°C. It appears, therefore, that the sinterability of the material is good and sinterhipping is not essential. The pore density, however, was higher than the industrially acceptable level, which is attributed to oxidation of the powders.

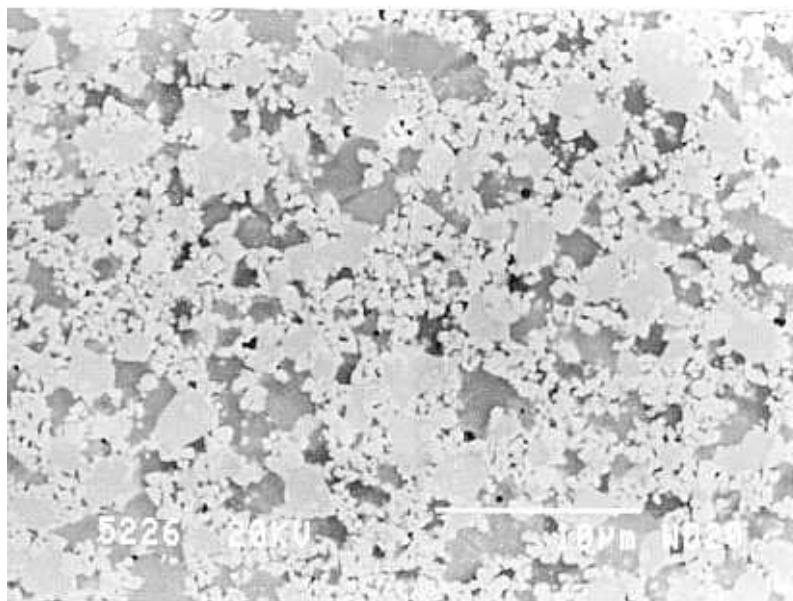
### 3.3. Microstructure and composition

Fig 4 shows the microstructure of a Type 2 sample, which was the closest to the microstructure that was aimed at. The grain size of each phase has not been determined accurately yet, but the carbides

as a whole have a mean grain size lower than 2  $\mu\text{m}$ , although some VC grains are still as large as 5  $\mu\text{m}$ . No significant difference in mean grain size was observed between the samples sintered at 1330°C and those sinterhipped at 1390°C.



**Fig. 3. Heating and Cooling Traces from the DTA of a WC-Co Powder.**



**Fig.4 Microstructure of One of the 10 wt% VC-10 wt% Co-WC Alloys Produced During this Investigation.** The smallest white grains are WC, the grains ranging from light grey to dark grey are (V,W)C of varying composition, and the small black grains are eta phase.

The x-ray diffraction spectra of both sample types showed the presence of WC, (V,W)C, Co and eta phase. SEM and EDS analysis showed that in Type 1 samples the eta phase was present as particles of 1 to 3  $\mu\text{m}$  in size containing up to 2 wt% Ca. Calcium was not present in Type 2 samples, therefore it originated from the  $\text{V}_2\text{O}_5$  powder. Although general quantitative EDS analyses of Type 1 samples showed that the total Ca content was approximately 0.1 wt%, in agreement with the analysis of the  $\text{V}_2\text{O}_5$  powder in Table II, spot analysis showed that the calcium was present only in the eta phase particles.

In Type 2 samples the eta phase was more finely dispersed, as shown in Fig.1. In both sample types

EDS analysis indicated that the eta phase present was closer to  $\text{Co}_4\text{W}_2\text{C}$  than to  $\text{Co}_3\text{W}_3\text{C}$ .

The presence of eta phase is attributed to a high oxygen level in the powders, since no precaution was taken at this stage to avoid oxidation.

Quantitative EDS analysis showed that the composition of both samples was approximately the following: 10 wt% VC, 10 wt% Co, 1 wt% Fe and 79 wt% WC. This composition is only approximate because it was calculated from the EDS elemental analysis assuming that all carbon was combined as  $\text{V}_8\text{C}_7$  and WC, although XRD analysis showed the presence of (V,W)C and eta phase. The high Fe content was due to the use of steel balls in the mills. On account of the Fe present, the binder content of the material was approximately 11 wt%, not subtracting the cobalt combined with W and C in the eta phase.

### 3.4. Hardness and fracture toughness

The average hardness and fracture toughness of the Type 1 and Type 2 samples is given in Table III, together with the hardness and toughness of a WC-Co alloy of similar hardness (tested during this investigation) and of several commercial WC-Co alloys of similar hardness or cobalt content [5].

Hardness and toughness of WC-Co depend on the WC grain size as well as on the cobalt content, therefore an accurate determination of the mean size of the WC and  $\text{V}_8\text{C}_7$  grains would be necessary for an accurate comparison of the properties of WC-VC-Co and WC-Co.

Sample Type	Average Hardness (HV30)	Average Toughness ( $\text{MPa}\sqrt{\text{m}}$ )
VC-WC-Co type 1 (with eta phase particles)	1,512	9.1
VC-WC-Co Type 2 (with fine eta phase)	1,581	11.4
WC-6% Co (without eta phase)	1,574	9.5
WC-6%Co (fine grain size)	1,550	10.4
WC-10%Co (coarse grain size)	1,350	12.6
WC-11%Co (fine grain size)	1,300	13.4

**TABLE III: Comparison of the VC-Wc-Co samples with WC-Co of varying amounts of binder.**

In Table III the presence of eta phase in VC-WC-Co was emphasized because eta phase embrittles cemented carbides and so one can assume that eta-free material would exhibit higher toughness.

It must be noted that the VC-WC-Co samples prepared so far are not perfectly homogeneous. For example, the Type 2 samples (which are closer to the microstructure aimed at) ranged in hardness from 1493 to 1581 HV30 and in toughness from 15.6 to 11.4 MPa m respectively. The value included in Table III is the one corresponding to the highest hardness, although it is not yet clear whether the ideal microstructure is closer to the sample with highest hardness or highest toughness.

The present comparison indicates that the hardness of WC-VC-Co is higher than the hardness of WC-Co of equal Co content, as was reported elsewhere [1], and that the toughness is comparable or superior to the toughness of WC-Co of equal hardness, which is an improvement on previously prepared material<sup>[1]</sup>. The toughness of VC-WC-Co is superior to the toughness of WC-Co of equal hardness, even when eta phase is present.

#### 4. CONCLUSIONS

The Type 1 and Type 2 WC-VC-Co samples, which were prepared starting from  $V_2O_5$  powder and from preformed  $V_8C_7$  powder respectively and which contained approximately 11 wt% binder, were sintered successfully at 1330°C. This sintering temperature is lower than the temperature required to sinter WC-Co of equal binder content. Sinterhipping was not found to be essential. No significant difference in mean carbide grain size was observed between samples sintered at 1330°C and samples sinterhipped at 1390°C.

Both types of samples contained eta phase, which is attributed to a high level of oxygen in the powders. This problem should be solved by the selection of more suitable sintering atmospheres.

Apart from the different eta phase morphology, which appeared to be due to the presence of calcium in Type 1 samples, the two sample types showed similar microstructures, which suggests that the two starting powders ( $V_2O_5$  and  $V_8C_7$ ) produce equivalent materials.

The hardness of the two sample types was similar and significantly higher than the hardness of WC-Co of equal cobalt content. The toughness of Type 2 samples was higher than the toughness of Type 1 samples although they both exhibited eta phase, because the latter were more embrittled by the presence of eta phase particles. The toughness of both sample types was significantly higher than the toughness of WC-Co of equal hardness, in spite of the presence of eta phase.

The above results suggest that VC-WC-Co is a suitable replacement for WC-Co at least in some applications. Work is in progress to improve its preparation process.

#### ACKNOWLEDGEMENTS

The authors wish to thank Mintek and Vanitec for sponsoring the project and Boart Longyear Research Centre for the use of facilities. They also wish to thank Dr CM Stander for the Differential Thermal Analyses and the staff of the Electron Microscope Unit at the University of the Witwatersrand for the quantitative EDS analyses.

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