

PRODUCTION BY MECHANICAL ALLOYING AND CHARACTERIZATION OF NANO-SIZE (V, W) C POWDER

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ABSTRACT

Vanadium-tungsten carbide {(V, W) C} nanocrystalline powder has been synthesized by mechanical alloying for the purpose of producing WC-VC-Co alloys of very fine grain size. The starting powders were W, V and C. The V/W mass ratio was selected on the basis of the formula (V_{0.7},W_{0.3}) C, which had been calculated to be the equilibrium formula of (V,W) C. Although milling was carried out in argon, some oxidization occurred leading to the presence of free carbon in the synthesized powder.

INTRODUCTION

In recent years (V, W) C-WC-Co alloys have been produced by powder metallurgy starting from VC, WC and Co powders [1]. The preparation process has involved thorough mixing of the powders, compaction and sintering. After sintering the material has been found to consist of (V, W) C, WC and Co, without any residual VC, even when starting from a large fraction of VC powder [1]. The composition and the lattice parameter of the (V, W) C grains has been found to vary with the overall composition of the alloy, but thermodynamic calculations have indicated that the equilibrium composition should be (V_{0.7}, W_{0.3}) C_{1-x} [2]. (V, W) C has the same NaCl-type crystal structure as VC. Its lattice parameter is ~ 4.21 Å while the lattice parameter of VC is ~ 4.16 Å. Both carbides are never stoichiometric, i.e. they both always have C vacancies. The lattice parameter varies with C content in VC and with W and C content in (V, W) C.

(V, W) C-WC-Co alloys have been found to be possible substitutes for commercial WC-Co alloys in applications requiring high abrasion and erosion resistance [3]. The toughness of the new alloys (as measured by Palmqvist tests [4]) has been found to be comparable to the toughness of WC-Co of equal hardness, but further improvements in toughness have been hindered by the size of the brittle (V, W)C grains which offer an easy path to the propagation of cracks. The size of the (V, W)C grains tends to increase during sintering to many times the size of the VC grains in the starting powder. The finest (V, W)C grain size achieved so far is ± 2 µm as against WC grains of ± 0.5 µm [1].

The ultimate aim of this project is to produce (V,W)C-WC-Co alloys with (V, W)C mean grain size finer than the one produced so far, in order to increase the toughness of the material. To reach this aim we planned to start from the finest possible (V, W) C powder instead of VC powder. Since (V,W) C powder is not available commercially, the first step was to produce the (V,W) C powder. The results of this first step are reported here.

Mechanical alloying was selected as the process most suitable for the production of very fine (V, W) C powder because the process has been used successfully to produce nanocrystalline carbide powders, e.g. TiC [5].

METHOD

The work reported in this paper consisted of synthesizing (V, W) C powder by mechanical alloying starting from W, V and C powders. These were commercial powders of mean particle size 15.4 μm , 44.5 μm and 0.2 μm respectively, as measured by a Malvern Mastersizer 2000. The purity of the powders was analyzed by atomic adsorption spectrometry.

The mechanical alloying was carried out in a PM 400/2 laboratory-scale high energy mill, with one sun disc and two planetary bowls. WC-Co 250 ml vials were used to avoid contamination, with lids designed for milling in inert atmosphere. In this case milling was carried out while flushing argon through the vials to avoid oxidation of the powders. The balls were also of WC-Co and of 10 mm in diameter. During each experiment the milling was interrupted to take small samples of powder for XRD analysis, to monitor the synthesis. XRD was done in a Philips PW 1830 diffractometer (Cu $K\alpha$ radiation, 40 kV, 20 mA) and a Bruker AXS D8 advance diffractometer (Cu $K\alpha$ radiation, 40 kV, 40 mA). The results from the Bruker diffractometer were analyzed by the restricted Rietveld refinement method using the program MAUD with structural data taken from ICSD. The morphology of the powders was examined by scanning electron microscopy using a Jeol JSM-840.

The mechanical alloying process was optimized using only W and C powders, because the V powder was very expensive and in short supply. Different milling speeds, ball-to-powder ratios (BPR) and carbon contents were tested, to determine the conditions at which complete synthesis of the WC powder (without W or C left) would occur in the minimum time. The conditions found to be optimal for the synthesis of WC powder were applied to the synthesis of the (V, W) C powder.

After milling the carbon content of the powders was measured by means of a CS 400 LECO analyzer while the oxygen content was measured at the Fraunhofer Institute in Dresden, Germany, because of lack of local facilities.

RESULTS AND DISCUSSION

1. Optimization of milling conditions

As mentioned above, the optimization of the milling conditions was carried out using only W and C powders (for the synthesis of WC) because of the high cost of V powder. The stoichiometric W/C mass ratio in WC is 93.87/6.13 but it was expected that some C would be lost during milling due to oxidation, despite the argon atmosphere, therefore C contents as high as 23 wt% were tested. The milling speeds tested varied from 250 to 300 rpm and the ball-to-powder ratios (BPR's) from 6.4:1 to 11:1. The BPR was increased by decreasing the powder charge and keeping the ball number constant at 50. The milling conditions that were found to lead to complete synthesis of WC powder in minimum time (as indicated by the disappearance of W peaks in the XRD patterns) are given in Table I.

Figure 1 shows the XRD patterns obtained after 4, 8 and 10 hours of milling W and C powders at the conditions given in Table I. Figure 1 shows that after 8 hours the peaks of W metal had completely disappeared and the synthesis of WC could be considered complete. No C peaks are visible in any of the patterns because the C-black powder used was amorphous.

Table I. Optimal milling conditions for the synthesis of WC powder by mechanical alloying in the equipment available.

Milling speed	300 rpm
Ball-to-powder ratio (BPR)	11:1 in weight
C powder content	6.13 wt%

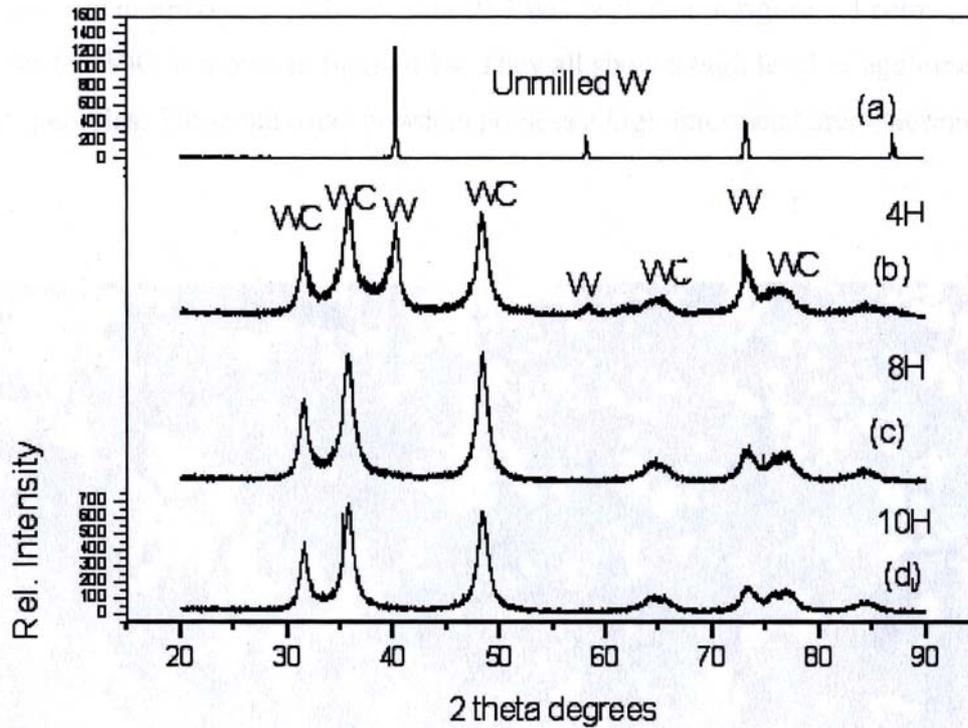


Figure 1: XRD patterns from the phases formed during milling of W and C powders, after 0, 4, 8 and 10 hours.

2. Synthesis of (V, W) C

The milling conditions in Table I were applied also to the synthesis of (V, W) C powder. In the case of the (V, W) C powder it was difficult to predict the required C content of the powder mixture to be milled because it was known that neither VC nor (V, W) C are ever stoichiometric (i.e. their correct formulae are VC_{1-x} and $(V, W)C_{1-x}$, with $0 < x < 1$). The amount of C powder selected was the amount theoretically required to produce stoichiometric $(V,W)C_{1-x}$ with $x = 0$. Since in reality it is $x < 1$, the carbon would be in excess but was thought to compensate for possible carbon losses during milling due to oxidation. As far as the V/W ratio in (V, W) C is concerned, it had been found that the ratio varies with the overall composition of the material [1], but since thermodynamic calculations [2] had predicted the equilibrium formula to be $(V_{0.7}, W_{0.3})C_{1-x}$, the atomic ratio selected was $V/W = 0.7/0.3$ which corresponds to a mass ratio of 35.7/55.2.

Therefore, in order to produce 35 g of (V, W) C powder (which was the aim of the experiments) the powder mixture selected was the one given in Table II.

Table II. Initial composition of the powder mixture used to synthesize 35 g of (V, W) C powder by mechanical alloying 4.09 g of C correspond to 11.69 wt%.

V powder	12.14 g
W powder	18.77 g
C powder	4.09 g

Figure 2 shows the XRD patterns obtained when milling a powder mixture of the composition given in Table 2 under the conditions given in Table I. Figure 2 shows that the W and V peaks disappeared completely only after 40 hours of milling and that the most intense WC peak was present even after 60 hours. Therefore (V, W) C powder was not the only product of the milling process: some WC powder was also produced. The mass fractions of each of the two powders ((V, W) C and WC) are given in Table III, as obtained from Rietveld analysis of the XRD results.

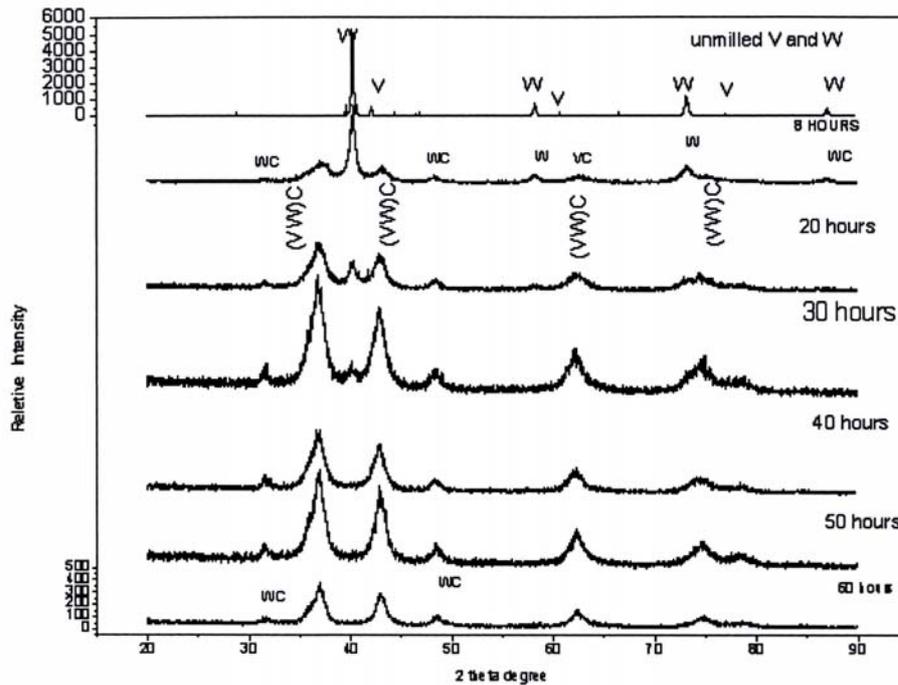


Figure 2. XRD patterns from the phases formed after 0, 20, 30, 40, 50 and 60 hours of milling V, W and C powders.

Table III shows that in case (i) (when the milling was periodically interrupted to take samples for XRD analysis) the synthesized powder was a mixture of (V, W) C and WC and the amount of (V, W) C increased up to 30 hours and then decreased, while the amount of WC kept increasing. This suggests that, although the free energy of formation of (V, W) C is lower than that of WC, V was progressively lost through oxidation (see also Table IV below), leading to the formation of less (V, W) C and more WC. This is confirmed by the results from case (ii) (uninterrupted milling of V, W, C powders) where the vial was not opened during milling: the oxidation was reduced, V was not lost and no WC was produced.

Table III gives also the lattice parameters of the phases, which, however, are expected to be influenced by the stresses induced in the powders through the impacts undergone during milling. The lattice parameter of (V, W) C appears to have generally increased with milling time suggesting an increased W/V ratio.

Table III. Phases obtained from mechanical alloying of V, W and C powder(cases (i) and (ii)) and W and C powders (case (iii)).

Milling time (hours)	Phases obtained	Phase mass percent	Lattice parameters (Å)
(i) Interrupted milling of W,V,C powders			
8	W	5.7	a = 3.1654
	WC	0.4	a = 2.8246 c = 2.8482
	(V,W)C	93.9	a = 4.1965
20	W	2.1	a = 3.1648
	WC	1.1	a = 2.8479 c = 2.8544
	(V,W)C	96.8	a = 4.2152
30	WC	1.4	a = 2.8509 c = 2.8602
	(V,W)C	98.6	a = 4.2106
40	WC	3.3	a = 2.8915 c = 2.8184
	(V,W)C	96.7	a = 4.2288
60	WC	8.1	a = 2.8966 c = 2.8343
	(V,W)C	91.9	a = 4.2155
(ii) Uninterrupted milling of V,W,C powders			
40	(V, W) C	100	a = 4.2155
(iii) Interrupted milling of W, C powders			
4	W	23.2	a = 3.1596
	WC	73.8	a = 2.8873 c = 2.8163
10	WC	100	a = 2.8950 c = 2.8309

Table IV: Carbon and oxygen content of the synthesized powders after 10 hours of milling (in the case of WC) and after 60 hours of milling (in the case of (V, W) C). In both cases the milling had been periodically interrupted.

Element content	in WC powder (wt%)	in (V, W) C powder (wt%)
Total carbon	6.21	9.94
Free carbon	2.05	5.83
Oxygen	2.7 ± 0.3	9.2 ± 0.5

Table IV summarizes the carbon and oxygen content of the synthesized powders. It shows that the total carbon content of the WC powder produced to optimize the milling conditions was approximately the same as the starting content (which was 6.13 wt%) but 2.05 wt %, i.e. approximately one third of the total, was free C, not combined with W. The total carbon in the (V, W) C powder (which was mixed with some WC powder, as shown in Table III) was 9.94 wt % although the starting amount of C was 11.69 wt %. 5.83 wt%, i.e. approximately half of the total, was free carbon. The high amount of free carbon in both powders confirms that oxidation took place during milling. In the case of WC, WO_3 is expected to have formed and in the case of (V,W) C+WC both WO_3 and V_2O_5 (the oxides could not be identified because

no oxide peaks appear in the XRD patterns, which is thought to be due to extremely fine grain sizes). The free carbon is higher in case (i) (V, W) C+WC powder) because the free energy of formation of V_2O_5 is lower than that of WO_3 and because the milling time was longer and so the powders were exposed to oxygen for a longer time. For the same reason the oxygen content in the powders was higher in the case of (V, W) C+WC than in the case of WC alone.

Since most of the oxygen was expected to have been introduced when milling was periodically interrupted to take powder samples for XRD analysis, a powder mixture with the composition indicated in Table II was milled for 40 hours without interruptions at the conditions indicated in Table I. The results are given in Table III (case ii): no WC was formed. Unfortunately neither the free carbon nor the oxygen content of this powder have yet been measured.

The crystallite size of the powders produced was measured from the width at half-height of the XRD peaks. Despite possible errors due to strains induced by milling, it was possible to establish that both in the case of the WC powder and in the case of the (V, W) C powder the crystallite size was of the order of nanometers (approximately 8.5 nm after 60 hours of milling in the case of (V, W) C and approximately 11 nm after 10 hours of milling in the case of WC).

CONCLUSIONS

This work has shown that it is possible to produce nano-size (V, W) C powder by mechanical alloying, starting from V, W and C elemental powders. The new powders are expected to solve the problem of excessively large (V, W) C grain size in (V,W)C-WC-Co alloys, not only because of the initial finer grain size but also because nano-size powders can be sintered at lower temperatures than other powders (grain growth rate is known to increase with increasing sintering temperature). Free carbon and free oxygen, if present, must be removed from the powders before sintering, because they would lead to the formation of graphite and eta-phase respectively, which are both detrimental to the mechanical properties of the sintered material [e.g. 6].

REFERENCES

1. S. Luyckx, "Advantages and disadvantages of the partial substitution of WC with VC in WC-Co alloys", *2006 Int. Conf. on Tungsten, Refractory & Hardmetals VI*, Metal Powder Industries Federation, Orlando, Florida, Feb 7-8, 2006.
2. B. Jansson, 2002, Seco Tools, Sweden, private communication.
3. C.N. Machio, G.Axdogan, M. Witcomb and S. Luyckx, "Performance of WC-VC-Co thermal spray coatings in abrasion and erosion tests", *Wear*, 2005, vol. 254 (1-4), pp. 432-442,
4. D.J. Whitefield, S Luyckx, MJ Witcomb and LA Cornish, "Microstructure and Properties of Fine Grained WC-VC-Co Hardmetal with Cobalt Content Ranging from 10 to 15 wt%", *14th Plansee Seminar*, 1997, vol. 2, pp 477-484.
5. Z Xinkun, Z Kunyu, C Baochang, L Qiushi, Z Xiuqin, C Tieli and S Yunsheng, "Synthesis of nanocrystalline TiC powder by mechanical alloying", *Mater. Sci. Eng. C*, 2001, vol.16, pp.103-105.
6. G.S. Upadhyaya, *Cemented Tungsten Carbides*, 1998, Noyes Publications, USA.