JOURNAL OF MATERIALS SCIENCE 23 (1988) 665–669

Floating-zone crystal growth of WC

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Single crystals of tungsten carbide were grown by the floating-zone technique by adding boron in the molten zone. It is confirmed that WC decomposes into cubic WC_{1-x} and carbon at an elevated temperature and cannot coexist with the liquid which consists of only tungsten and carbon. It was theoretically expected that addition of boron would stabilize the WC structure so that the WC phase could coexist with the liquid. This was proved by the float zoning through the WC rod which contained boron. The WC phase was deposited from the molten zone which consists of tungsten, carbon and boron. The growth of single crystals of WC was carried out under pressurized helium gas atmosphere of 1 MPa. The molten zone, whose temperature was about 2900° C, was inductively heated and driven downwards. The compositions of the molten zone and the feed rod were $[W]/[C]/[B] = 1/0.65/0.06$ and $1/1.08/0.007$ (atomic ratio), respectively. Single crystals with dimensions 9 mm diameter and 5 mm long can be cut out from the zone-passed rod. The boron content in the crystal could be lowered to the order of 100 p.p.m.

1. Introduction

Tungsten carbide (WC) is most widely used in the cemented carbide production, the outstanding properties of which are high hardness and wear resistance. An enormous amount of investigations by powder metallurgy has supported the success of the cemented carbides in technical application. On the other hand, only a restricted amount of investigation of their bulk properties has been carried out because of the difficulties of obtaining single crystals.

Our recent efforts on the floating zone crystal growth of the group IVa and Va transition metal monocarbides [1–6] make it possible to prepare their massive crystals with controlled compositions. These carbides have a cubic structure of NaCl type. Their characteristic is an extremely wide homogeneity range, where they variantly melt except for a certain congruently melting composition definite for each carbide. Thus the floating-zone technique is most appropriate for preparing these crystals with controlled composition because the zone levelling technique can be applied.

On the other hand, WC which is one of the group VIa monocarbides, considerably differs from the group IVa and Va carbides. The crystal structure is simple hexagonal with $a = 0.2906$ nm and $c = 0.2837$ nm [7]. The carbon atoms are located regularly at half the void positions in the simple hexagonal lattice of tungsten atoms (see Fig. 2a). The homogeneity range of WC is very narrow and it is almost a line compound. Its melting behaviour was still ambiguous before the present study began. In previous investigations on single-crystal preparation, WC has been prepared by a flux method using cobalt metal flux [8] and/or a modified Czochralski pulling method from a cobalt flux [9]. In the latter investigation, the WC crystal measuring 1 cm on a side was grown over several days by controlling the temperature precisely at a lowering rate of 3 to 4° C per day.

In order to prepare massive single crystals of WC in fewer hours, we tried to apply the floating zone crystal growth to WC. We began by examining the melting behaviour of WC and found that WC decomposes into two solid phases without melts at high temperatures. Further investigation revealed that addition of boron can stabilize the WC structure so that the WC phase coexists with the liquid. This enabled application of the floating-zone technique to the preparation of WC crystals in which the molten zone consists of tungsten, carbon and boron.

2. Experimental details

We used commercial powders of WC(0.7 μm average, Tokyo Tungsten Co. Ltd), W(0.5 μm, Tokyo Tungsten Co. Ltd), C(graphite of spectroscopic grade, Tokai Carbon Co. Ltd) and B(amorphous, Herman C. Starck Co. Ltd). Before sintering, starting powders were prepared by mixing the raw powders thoroughly with prescribed mixing ratios. A small amount of camphor ethanol solution was added as a binder. The mixture was isostatically pressed into a cylindrical rod at 80 MPa.

The compact rod was sintered in a vacuum using a graphite susceptor inductively heated. The sintering time and temperature were 0.5 h and 1800° C, respectively. The sintered rod had a density of about 95% theoretical.

The float zoning was carried out in a high pressure type furnace (10 MPa, 40 kW max., Arthur D. Little Inc.). The crystals were grown by driving the feed rod and the seed rod upwards through a work coil of inner diameter 18 mm (three turns and two steps). The

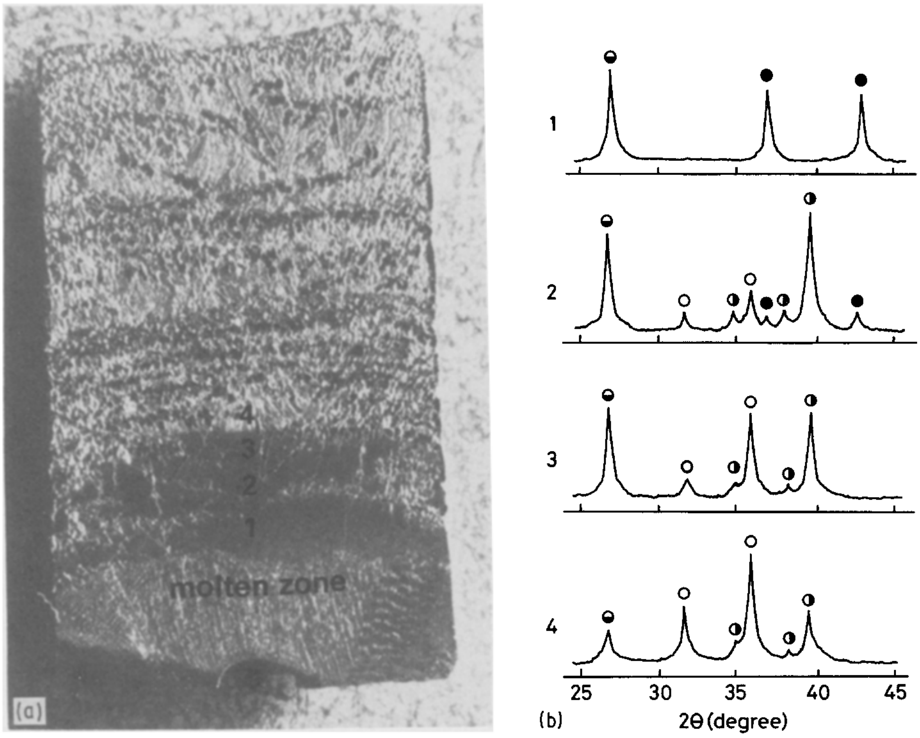

Figure 1 (a) Longitudinal section around the zone quenched during the zone pass of the WC rod. (b) X-ray diffraction pattern for every portion labelled in (a). (●) WC$_{1-x}$, (◒) carbon, (◑) W$_2$C, (○) WC.

furnace was filled with helium at a pressure of 1 MPa. The growth speed was 3 mm h^{-1}. Both drive shafts were counter-rotated at 15 to 20 r.p.m. in order to stir the molten zone.

The carbon content in the sample was determined by the volumetric combustion method using a carbon determinator (WR-12, LECO Corp.). The boron content was analysed by standard methylene blue absorptiometry. The sample was disintegrated by fusion with sodium carbonate and was dissolved in dilute sulphuric acid. The absorbance of the sample solution was measured after colouring the boron by adding methylene blue and fluoric acid.

3. Results and discussion

3.1. Melting behaviour of WC

It is essential to confirm the melting behaviour of WC prior to the floating-zone experiment. There are many phase diagrams of the W–C system, whose outlines coincide with each other. However, there is a serious contradiction with respect to the melting behaviour of WC. Typical examples appear in two phase diagrams reported by Rudy [10] and by Sara [11]. Rudy maintained what WC peritectically decomposes into liquid and carbon at an elevated temperature. On the other hand, Sara reported that WC decomposes into cubic WC$_{1-x}$ and carbon, and then the cubic WC$_{1-x}$ peritectically decomposes into liquid and carbon. If the melting behaviour of WC follows the former phase diagram, floating-zone crystal growth of WC becomes possible. However, if the latter phase diagram is correct, it does not.

In order to examine the above problem, the WC rod was zone passed. After the zone was passed for sufficient time, it was found that the resultant rod consisted of three phases of WC, W$_2$C and C. In a binary system, three phases are not deposited simultaneously from the molten zone because pseudo-equilibrium is achieved at the growth interface. Therefore, at least one compound decomposed after it was deposited from the molten zone. For further confirmation, the molten zone was quenched during the zone pass. The longitudinal section around the zone is shown in Fig. 1a. The zone-passed rod was relatively dense in the range of about 2 mm from the growth interface and became of a rough constitution beyond the range. We carried out X-ray diffraction analysis for every labelled portion in the figure. The results are shown in Fig. 1b. Portion 1, where the compounds are just deposited from the molten zone, consists of cubic WC$_{1-x}$ and C. With decreasing temperature on leaving the molten zone, in Portion 2, most of the cubic WC$_{1-x}$ decomposes into W$_2$C and C. A small amount of WC also appears. In Portion 3, cubic WC$_{1-x}$ diminishes perfectly. A considerable amount of WC is produced by a reaction between W$_2$C and C. This reaction proceeds rapidly around the boundary between Portion 3 and Portion 4. Then, at Portion 4, the rod consists of the dominant component of WC and extra components of W$_2$C and C. This experimental result shows that the melting behaviour of WC is consistent with that represented in Sara's phase diagram.

It was confirmed that the WC phase does not coexist in equilibrium with the liquid which consists of only tungsten and carbon. Therefore, it is impossible to prepare the WC crystal by the zone pass through the WC rod.

3.2. Expectation of coexistence of the WC phase and the liquid

According to Sara's phase diagram, the decomposition temperature of WC is 2755° C. The temperature range where cubic WC_{1-x} coexists with the liquid phase is from 2760 to 2785° C. It is expected that a slight addition of a third element may change the phase relation so that the WC phase coexists with the liquid instead of cubic WC_{1-x}. We searched for a third element on the basis of the following four conditions: (1) the third element should form a compound with tungsten; (2) the crystal structure of the compound should resemble the WC structure, (3) the compound should be stable at sufficiently high temperatures, (4) the melting behaviour of the compound should be congruent.

Boron, silicon and nitrogen were listed from the view point that they can form refractory compounds with tungsten. We selected boron as the third element, because it forms diborides with group IVa and Va transition metals. The AlB_2-type crystal structure of diborides greatly resembles that of WC, as shown in Fig. 2. In WB_2, which is often represented as W_2B_5, the crystal structure is only slightly modified from the AlB_2-type structure. Moreover, WB_2 has been reported [12] to melt congruently at 2365° C for composition of $WB_{\sim 2.3}$. Thus boron satisfies the above four conditions.

The above expectation was readily verified experimentally by the float zoning of the WC rod to which 6 mol % boron was added. It was found that some single phase starts to be deposited from the molten zone after the zone had travelled about 4 to 5 mm. The X-ray diffraction pattern of the single phase was just that of WC, although a very small amount of free carbon was present. Electron probe microanalysis showed that the carbon content in the zone was considerably lower than the stoichiometric value as expected from the phase diagram. Further, the boron content in the WC phase was less than 0.05 wt % and that in the zone was of the order of 0.5 wt %.

3.3. Floating-zone crystal growth

Floating-zone crystal growth of WC had two attendant difficulties. First, it should be noted that the zone pass through the WC rod is technically very difficult. WC has such a high density of 15.8 g cm^{-3} that there is a tendency for the lower part of the molten zone to be extremely swollen in shape. Moreover, the melt which contains boron, is highly wettable for WC. The swollen zone end tends to cover the growing crystal beyond the growth interface if the system is driven downwards. This increases the crystal diameter uncontrollably by consuming the molten zone. After a while the crystal diameter starts to decease as a matter of course. Variation of the volume of the molten zone and the crystal diameter is repeated without reaching a stationary state. Under the incongruent growth conditions where the composition of the molten zone is different from that of the growing crystal, the zone volume and the resultant zone composition must be constant during the zone pass. The above situation is undesirable in the floating-zone crystal growth of WC. Such difficulty was relatively reduced by driving the system upwards. A second problem was that the molten zone covered the feed rod, which occurred especially at the stage of formation of the initial molten zone. There is evidence that the molten zone does not wet carbon. Thus the feed rod was coated with carbon by painting with an emulsion of carbon powder. By these improvements, though a steady zone pass could still not be achieved, the period of cyclic change of crystal diameter was considerably elongated.

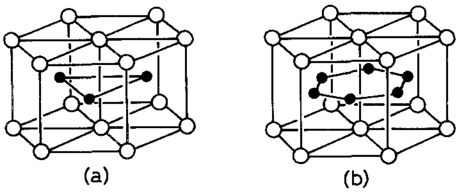

Figure 2 Crystal structure of (a) WC and (b) MB_2.

The second difficulty arose from the fact that the zone composition differed considerably from the crystal composition. The crystals must be prepared under zone levelling conditions. Then, the growth experiments began by determining adequate compositions of the zone and the feed rod. Compared with group IVa and Va carbides, this determination procedure was more troublesome because the present system is ternary. However, the basic concept of the procedure [13] is the same.

In order to determine the optimum carbon contents in the feed rod and the molten zone, the compositions of the final part of the zone-passed rod and the frozen molten zone were analysed after the zone pass through several sintered rods having different chemical compositions. In these experiments, boron contents in the initial molten zone and the feed rod were fixed at 0.4 and 0.05 wt %, respectively. As mentioned above, the float zoning of WC was so difficult that a stable zone pass with a long distance could not be done. The following data, summarized in Table I, were obtained from the zone-pass experiments still on the way to a stationary state. However, the zone was passed through at least three times the zone length. We can consider the above results as an approximation of that at the stationary state.

Judging from the results in Table I, the optimum carbon contents in the feed rod and the molten zone are found to be 6.5 wt % ([C]/[W] = 1.08) and 4.05 wt % ([C]/[W] = 0.65), because the second case achieved the stoichiometric carbon content of 6.13 wt %. It was found that the partition coefficient of boron at the

TABLE I Chemical compositions of the WC crystals after zone pass through the sintered rods having different chemical compositions

Sample	Carbon (wt %)	Boron (wt %)	W:C:B (atomic ratio)	Partition coefficient
S	6.04	0.052	1:0.985:0.0094	
Cry-F	5.80	0.031	0.944:0.0056	
M	3.85	0.42	0.616:0.075	0.074
S	6.52	0.050	1:1.08 :0.0091	
Cry-F	6.14	0.027	1.00 :0.0049	
M	4.06	0.33	0.650:0.060	0.082
S	6.70	0.050	1:1.10 :0.0091	
Cry-F	6.24	0.030	1.02 :0.0055	
M	4.08	0.41	0.655:0.073	0.073

S, feed sintered rod; Cry-F, final portion of crystal; M, molten zone.

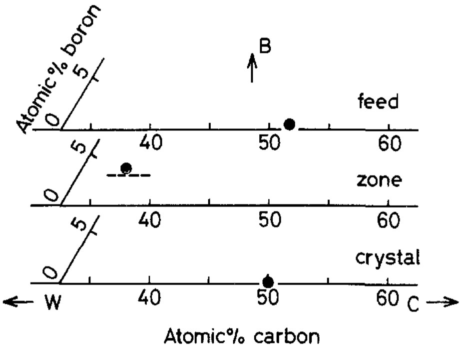

Figure 3 Ternary composition relations for the feed rod, the molten zone and the crystal. The dotted line in the composition relation for the molten zone indicates the lower limit of the boron content necessary to deposit the WC phase.

TABLE II Chemical composition of WC crystals

Sample	Portion	Carbon (wt %)	Boron (wt %)	W : C : B (atomic ratio)
1	S	6.54	0.051	1 : 1.08 : 0.0092
	Cry-1	6.13	0.028	1.00 : 0.0051
	Cry-2	6.14	0.026	1.00 : 0.0047
	Cry-3	6.10	0.027	0.996 : 0.0049
	M	4.10	0.31	0.658 : 0.056
2	S	6.53	0.036	1 : 1.08 : 0.0066
	Cry-1	6.15	0.012	1.00 : 0.0022
	Cry-2	6.11	0.014	0.997 : 0.0025
	Cry-3	6.12	0.013	0.999 : 0.0024
	M	4.00	0.32	0.641 : 0.057

growth interface was 0.07 to 0.08. The boron content in every zone remained almost as it was, i.e. 0.4 wt %. This means that the boron content in the crystals remained constant during the zone pass. Thus the value of 0.03 wt % in the final part of the crystals is also the value through the whole crystal. The difference between the boron content of the feed rod and that of the crystal corresponded to the evaporation loss from the molten zone.

The boron content in the zone was decreased until the WC phase could not be deposited in order to examine its lower limit. The threshold value was 0.27 wt %.

These results are summarized in Fig. 3 as three sheets of ternary composition relation which correspond to the compositions of the feed rod, the molten zone and the crystal. The dotted line in the composition relation for the molten zone indicates the lower limit of the boron content. It is instructive to note that the temperature at the growth interface where the WC phase is just deposited was measured to be 2870° C using a two-colour pyroscope.

According to the above composition relation, many trials of floating-zone crystal growth were carried out. An example of the zone-passed rods is shown in Fig. 4. Dimensions of the rod are about 10 mm diameter and 40 mm long. Because of the difficulties of float zoning mentioned before, the single-crystal region did not cover the whole of the rod, but rather several portions of the rod each about 5 mm long. Longitudinal section of this single-crystal region is shown in Fig. 5a. The growth direction of this crystal was parallel to [1 1 $\bar{2}$ 0]. The whole crystal consisted of a single domain except for a thin peripheral region. Any spots on the back-reflection Laue photograph of this crystal were sharp single spots as shown in Fig. 5b. This shows that the WC crystal of good quality can be grown after the zone experienced instability. Composition of these single-crystal regions cut out from two rods are summarized in Table II. Compared with Rod 1, the boron content in Rod 2 was lowered to the order of 100 p.p.m. by decreasing that in the feed rod. A maximum value of 17 of residual resistance ratio (RRR) was observed for the Cry-2 of Rod 2. However, the RRR value scattered depending on the samples. For example, the value of Cry-3 of the same rod was only 3.6 though both stoichiometry and boron levels are slightly better than those of Cry-2. No metal impurities were detected by fluorescence X-ray analysis for both samples. Thus, scattering of the RRR value may be attributed to the crystallographic quality of the samples.

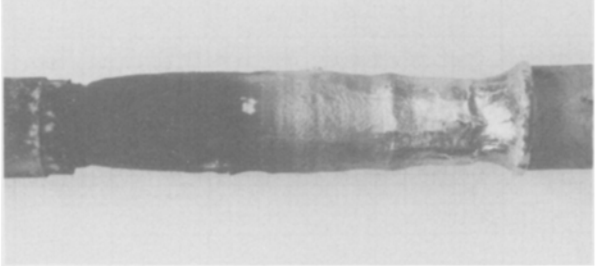

Figure 4 As-grown crystal rod of WC.

As another characterization method, chemical etching was carried out using a solution of hydrofluoric acid and nitric acid ($HF : HNO_3 : H_2O = 1 : 1 : 3$) at 40° C for 1 h. Long thin etch pits whose dimensions were about 1 μm thick and several tens of micrometres long and whose long axis was perpendicular to the [0 0 0 1] direction, appeared on both (1 0 $\bar{1}$ 0) and (1 1 $\bar{2}$ 0) planes of Cry-2 as shown in Fig. 6, but no etch pits appeared on the (0 0 0 1) plane. In Cry-3, similar etch pits appeared also but their dimensions were smaller than Cry-2 by a factor of 3 to 4. The homogeneity range of WC is very narrow and it is almost a line compound. Deviation from the stoichiometry thus appears as an inclusion of W_2C or free carbon. In fact, although the deficiency of carbon from the stoichiometry of Cry-2 and Cry-3 is very little, a trace of W_2C can be detected by X-ray diffraction analysis. By combining this fact with the appearance of the etch pits, it is expected that the etch pits are caused from thin plate-like W_2C inclusions which are included as if in a stacking fault of WC. Unfortunately, electron probe microanalysis of carbon could not verify this expectation. Because the electron beam whose diameter is relatively large in the carbon analysis covers not only the etch pit but also a large area of the WC matrix, it is difficult to distinguish the W_2C phase from the WC matrix in such a narrow region. This has remained a problem.

4. Conclusion

The floating-zone crystal growth of WC is quite characteristic. WC decomposes into other solid phases

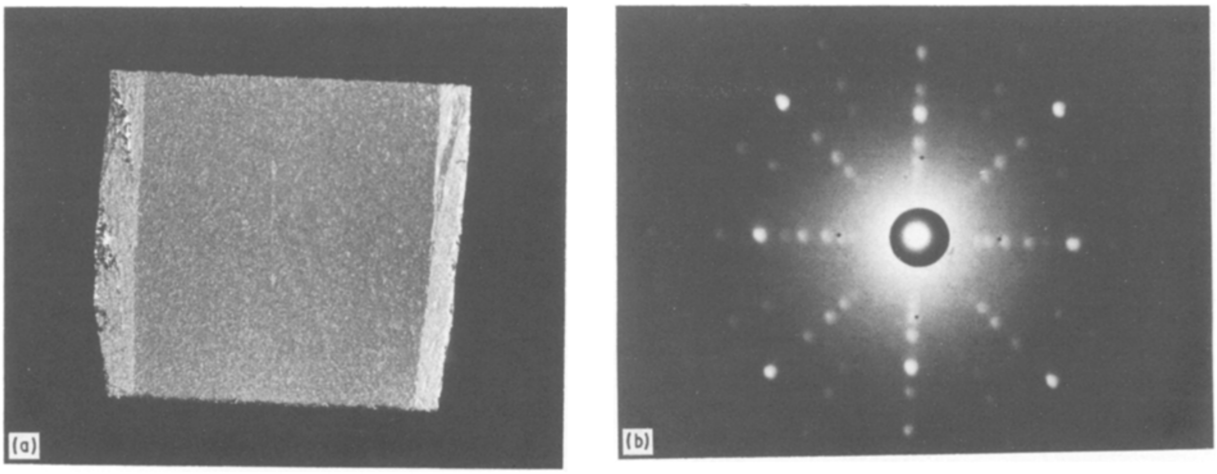

Figure 5 (a) Longitudinal section of the single-crystal region cut from the zone-passed rod. (b) Back-reflection Laue photograph of the crystal.

at an elevated temperature. It is impossible to grow WC crystal from a melt consisting of only tungsten and carbon. However, we found that the addition of boron in the order of impurity level stabilizes the WC structure so that the WC phase coexists with the liquid phase. Thus it renders it possible to apply the floating-zone crystal growth to WC. This concept is first proposed by us and could be applied to other compounds having similar phase relations.

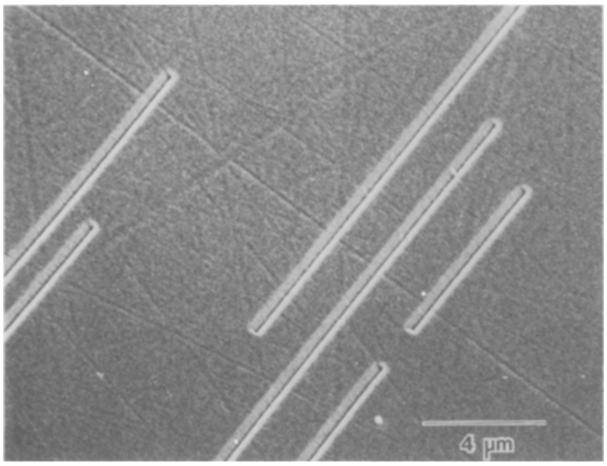

Figure 6 Etch pits on the (1 0 $\bar{1}$ 0) plane of WC. Long axis is perpendicular to the [0 0 0 1] direction of WC.

Acknowledgement

The authors thank Mr Y. Yajima for the chemical analyses.

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Received 13 April
and accepted 29 June 1987