

# Vapour–liquid–solid growth of TiB<sub>2</sub> whiskers

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Whiskers of TiB<sub>2</sub> have been synthesised via a carbothermal vapour–liquid–solid (VLS) growth mechanism. The whisker growth was investigated in the temperature region 1100–1800°C in argon. The best result was obtained with a starting mixture of TiO<sub>2</sub>:B<sub>2</sub>O<sub>3</sub>:C:NaCl:Ni in the molar ratios 1:1:6:0.25:0.1 at 1500°C. Thermogravimetric analyses and mass-spectroscopy measurements were used in studying the whisker growth. The obtained TiB<sub>2</sub> whiskers are 0.5–2 μm in diameter and 10–50 μm in length. TEM studies of the whiskers showed that the dominating growth direction is temperature dependent. © 2002 Kluwer Academic Publishers

## 1. Introduction

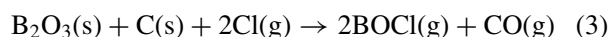
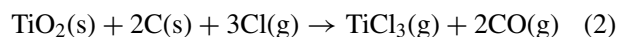
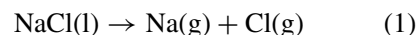
SiC whiskers are used commercially as reinforcing material in ceramic cutting tools. During recent years, attempts have been made to develop other whisker materials, more chemically stable than SiC, for cutting e.g., stainless steel. The development of new whisker materials has been focused mainly on carbides, nitrides and carbonitride phases, and the growth mechanisms of e.g., TiC, TaC, NbC, (Ti,Ta) C,N and (Ti,Ta,Nb) C,N with cubic NaCl structures (*Fm3m*) have been discussed [1–6]. However, less attention has been paid to boride phases in the form of whiskers. TiB<sub>2</sub>, with the hexagonal structure (*P6/mmm*), is a potential reinforcing material, because it has a high melting point, a low thermal expansion coefficient, and a high E-modulus. Chemical vapour deposition (CVD) synthesis of TiB<sub>2</sub> whiskers by a vapour–liquid–solid (VLS) growth mechanism has been described in a review [7]. The VLS mechanism have been thoroughly described in e.g., [8–10].

The aim of the present project was to investigate if TiB<sub>2</sub> whiskers can be produced by a carbothermal VLS growth mechanism. The mechanism is complicated to control, and whiskers of TiC may form in addition to TiB<sub>2</sub> if the reaction is not carefully governed. The mechanism involves carbothermal reduction of oxides and subsequent transport of Ti and B as gas-phase species to a liquid catalyst metal in which the whisker constituents dissolve. When the catalyst becomes supersaturated, TiB<sub>2</sub> whiskers precipitate out of the metal droplets. The whisker growth terminates when the concentrations of reacting gas species near the droplets diminish below a certain level.

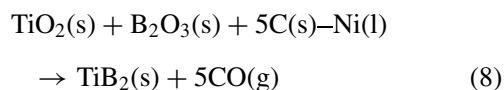
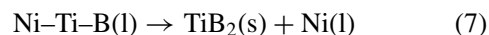
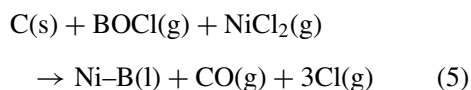
Equilibrium calculations by means of the computer program HSC [11], taking 134 phases into consideration for the system Ti–B–C(amorphous)–O–Na–Cl–Ni–Ar, indicate that TiC should form in the temperature interval 950–1300°C and TiB<sub>2</sub> above 1100°C. In order to form only TiB<sub>2</sub> as the product phase, the temperature must thus be above 1300°C (see Fig. 1a). Calculations also suggest that if local boron concentrations become

too low, then TiC may form even above 1300°C. Ti is transported mainly as TiCl<sub>3</sub>(g), B mainly as BOCl(g), and the catalyst Ni mainly as NiCl<sub>2</sub>(g) at the reaction temperature according to the calculations, see Fig. 1b–d.

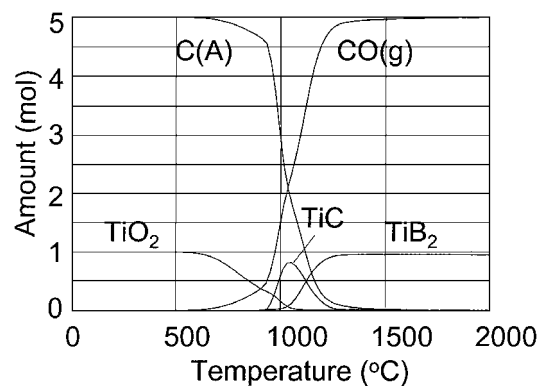
Our experience, obtained in preparing different carbide and carbonitride whiskers, shows that the following reactions or very similar ones represent the actual mechanism when the reactions take place in a flowing Ar atmosphere, using Cl as volatilising element.



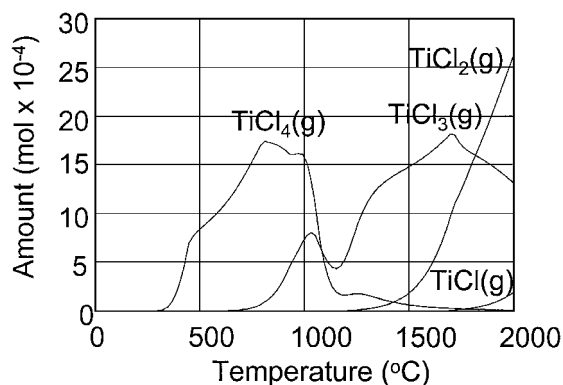
Nickel is transported and recycled by reacting with chlorine gas to form NiCl<sub>2</sub>(g), which in turn reacts with BOCl(g) and TiCl<sub>3</sub>(g), forming an Ni–B–Ti alloy. The reactions are not balanced with respect to the Ni alloy formation



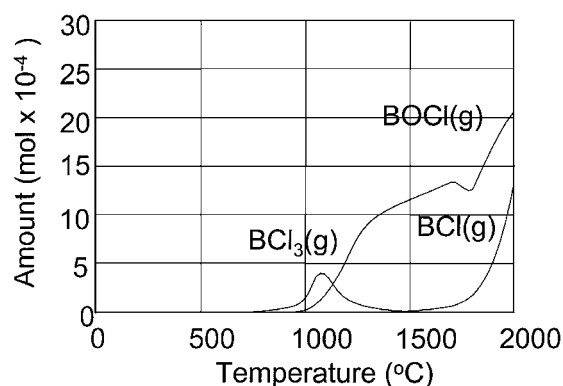
A principal requirement for VLS growth is that the carbothermal reduction process (reaction 8) should be thermodynamically possible, yet kinetically retarded.



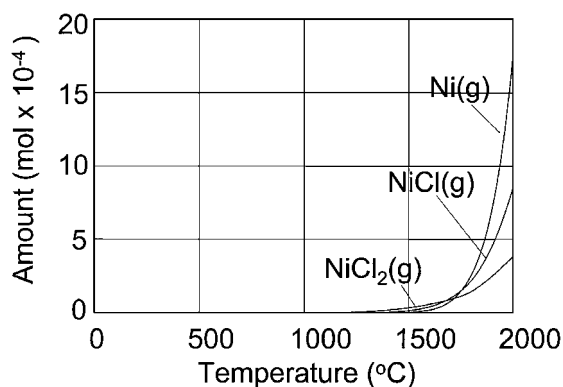
(a)



(b)



(c)



(d)

Figure 1 Gibbs energy minimisation calculation for a starting mixture with the following molar ratios:  $\text{TiO}_2\text{:B}_2\text{O}_3\text{:C:NaCl:Ni} = 1\text{:}1\text{:}5\text{:}0.25\text{:}0.1$ . Amorphous carbon was used in the calculations. (a)  $\text{TiB}_2$  is the product phase above  $1300^\circ\text{C}$ . In the temperature range  $950\text{--}1300^\circ\text{C}$ ,  $\text{TiC}$  can also form. It is thus important to use a high heating rate up to the temperatures where only  $\text{TiB}_2$  will form. (b) Titanium is mainly transported as  $\text{TiCl}_3(\text{g})$  at the reaction temperatures. (c) Boron is mainly transported as  $\text{BOCl}(\text{g})$  at the reaction temperatures. (d) The catalyst metal nickel is transported mainly as  $\text{NiCl}_2(\text{g})$ .

## 2. Experimental

### 2.1. Synthesis

A number of commercially available precursor materials have been tested, and their origin, purity and particle size are given in Table I. The starting materials were first mixed in a high-speed blender and then put into a graphite reactor and heated in flowing argon ( $0.7 \text{ dm}^3/\text{min}$ ) in a graphite furnace (Thermal Technology, Inc., Santa Rosa, CA). Various plateau temperatures in the range  $1100\text{--}1800^\circ\text{C}$  were tried, with a temperature increase rate of  $1500^\circ\text{C/h}$  and a plateau holding time of 3 h.

The reactor, designed for  $10\text{--}15 \text{ g}$  of starting mixture, consisted of a simple graphite crucible covered by a perforated lid allowing gas exchange between the interior of the crucible and the furnace chamber. An excess of carbon powder was used in the starting mixture in order to allow the whiskers to grow separated from each other and thus to avoid formation of agglomerates. The  $\text{TiB}_2$  product was separated from excess carbon by adding water/surfactant, treating the mixture with ultrasound and letting the  $\text{TiB}_2$  phase settle.

### 2.2. Characterisation of the whisker product

The solid phases formed were characterised by their X-ray powder diffraction (XRD) patterns, obtained with a Guinier-Hägg focusing camera in subtraction geometry.  $\text{Cu-K}\alpha_1$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) was used, and finely powdered silicon ( $a = 5.43088(4) \text{ \AA}$ ) was added as an internal standard. The recorded films were evaluated in an automatic film scanner [12]. The XRD peaks were identified by matching them to JCPDS-ICDD data cards of  $\text{TiB}_2$  (No. 35-0741) and  $\text{TiC}$  (No. 32-1383).

A quantitative XRD study of the  $\text{TiC}$  and  $\text{TiB}_2$  content in the product was performed by comparison with XRD patterns from a series of standards of  $\text{TiC}$  (H.C. Starck, STD 120) and  $\text{TiB}_2$  (Johnson Matthey 99.5%). Mixtures with  $\text{TiC}/(\text{TiC} + \text{TiB}_2)$  molar ratios of 0, 0.05, 0.1, 0.15, 0.25, 0.5, 0.75 and 1 were used as standards.

Intensity ratios of eleven combinations of diffraction peaks covering most of the  $2\theta$  scale were plotted versus the  $\text{TiC}$  content, and power functions were then fitted. The fractions of  $\text{TiB}_2$  in the synthesis products were then averaged from those eleven calibration curves.

The whisker morphology was investigated by both light microscopy and SEM. The whisker yield was

TABLE I Starting materials used

Substance	Particle size	Purity (wt%)	Manufacturer	Comment
$\text{TiO}_2$		99.9	Aldrich	
$\text{B}_2\text{O}_3$		99	Aldrich	
$\text{Na}_2\text{B}_4\text{O}_7$		99	ABCRC	
$\text{NaCl}$		–	Akzo	Pretzel, coarse
$\text{NaCl}$		–	Akzo	Microsalt
$\text{Ni}$	$<40 \mu\text{m}$	–	Cerac	
$\text{Ni-20at\%Cu}$	$<45 \mu\text{m}$	–	–	Gas atomised alloy
$\text{Cu}$	$<40 \mu\text{m}$	99	J and M	
$\text{Co}$	$<40 \mu\text{m}$	–	Cerac	
$\text{Fe}$	$<40 \mu\text{m}$	97	Aldrich	
$\text{C}$	13 nm	–	Degussa	FW200, 21 wt% volatiles

estimated from SEM micrographs, and is expressed in vol%.

A transmission electron microscope (JEOL TEM 3010, Japan) was used for the high-resolution transmission electron microscopy (HREM) and electron diffraction (ED) experiments. The accelerating voltage was 300 kV, and the microscope was equipped with a double-tilt holder with a maximum tilting angle of  $\pm 20^\circ$ .

The bulk composition of the prepared materials was analysed by a standard combustion technique (LECO) for O.

### 2.3. Reaction studies

Reaction kinetics and mechanisms were investigated with a thermogravimetry (TG) arrangement mounted on the graphite furnace. A special set-up was designed where the same large crucible as for the syntheses could be used. It was suspended via a tungsten wire from a clamp mounted on a balance (AND Electronic Balance, FX 2000, Japan), see Fig. 2. This set-up was necessary in order to follow the synthesis conditions. Commercially available TG-equipments are only designed for samples in the milligram range and were found not to be suitable for those studies.

The gas species CO(g), CO<sub>2</sub>(g) and H<sub>2</sub>O(g) were analysed and recorded on-line with a quadrupole mass spectrometer (MS) (Baltzers, QMG 420, Switzerland) connected to a computer, see Fig. 2. The time delay for detection due to the furnace volume, atmosphere flux and the MS pump capacity was measured to be about 60 seconds. The level away of gaseous species formed, e.g., CO(g), filling the furnace chamber during reactions was found to be much dependent on the amount of starting mixture used in each experiment. In order to compare different experiments therefore only the rise of a MS-peak was taken into account and not the whole time lapse during which a certain gas species could be detected.

TG and MS studies were performed on the carbon-black powder as well as two different starting mixtures: (#1) the optimum whisker synthesis mixture and (#2) a mixture without NaCl and Ni (see Table II).

Two different temperature profiles were used for the TG and MS experiments. One temperature profile mimicked the optimum synthesis conditions with a heating

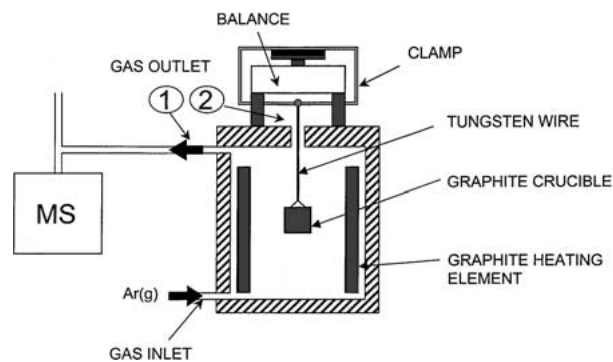


Figure 2 Sketch showing how the mass spectrometer (MS) and the thermogravimeter (TG) are connected to the graphite furnace. During MS-experiments gas outlet (1) was used, while during TG-experiments gas outlet (2) was used.

TABLE II Starting mixture (#1) resulting in the highest whisker yield, and a starting mixture without presence of NaCl and Ni (#2). The carbon source contained 21 wt% volatiles, which have been compensated for

Raw material	Weighed-in mass (g)	Weighed-in amount (mol)	Molar ratios #1	Molar ratios #2
TiO <sub>2</sub>	10.00	0.1252	1	1
B <sub>2</sub> O <sub>3</sub>	8.71	0.1252	1	1
Ni	0.73	0.01252	0.1	–
NaCl	1.83	0.0313	0.25	–
C	11.42	0.7512	6	6

time of 1 h up to 1500°C and a plateau holding time of 3 h. The other temperature setting was a constant heating rate up to 1800°C in 3 h, with zero holding time.

Evolution of gases containing e.g., Na, Cl, Ni, Ti and B could not be detected with the mass spectrometer, because gas species containing those elements condense at room temperature and therefore never reached the spectrometer. However, condensing evolved gases onto chilled copper plates provided a qualitative measure of gases containing those elements, except for boron. The chemical composition of the deposits on those plates was analysed in a high-resolution scanning electron microscope (SEM, JEOL 880, Japan) equipped with an energy-dispersive spectrometer (EDS, LINK *ISIS*). The copper plates were changed every 10 minutes during synthesis in order to follow the evolved gas composition.

## 3. Results and discussion

### 3.1. The TiB<sub>2</sub> whisker product

TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> were used as sources of Ti and B, respectively, amorphous carbon powder to reduce the oxides, and NaCl was added as a chlorine source for formation of TiCl<sub>3</sub>(g) and BOCl(g). Ni was used as catalyst metal. The weighed-in amounts and molar ratios in the starting mixture that gave the highest TiB<sub>2</sub>-whisker yield (#1) are given in Table II.

The following synthesis route was used: The starting mixture was put in a graphite crucible and heated, up to the synthesis temperature, in a graphite furnace with flowing argon. The highest TiB<sub>2</sub> whisker yield was obtained in the temperature range 1400–1500°C.

The starting mixture contained excess carbon, which was added in order to make the whiskers to grow separated from each other. After carbon removal, the TiB<sub>2</sub> phase was found to consist of about 50 vol% whiskers and 50 vol% particles. The obtained whiskers had smooth rounded surfaces and were 10–50 μm in length and 0.5–2 μm in diameter (see Fig. 3).

### 3.2. Synthesis temperature

Different reaction temperatures in the range 1100–1800°C were tested in order to optimise the synthesis. From XRD it was clear that 1100°C was a too low temperature for the reaction to take place and that only reduced oxides were formed. TiC was found in the temperature range 1200–1300°C, and this is also supported by equilibrium calculations (see Fig. 1a). TiB<sub>2</sub> was formed at temperatures from 1300°C and up, and in the temperature range 1400–1500°C it was the only product

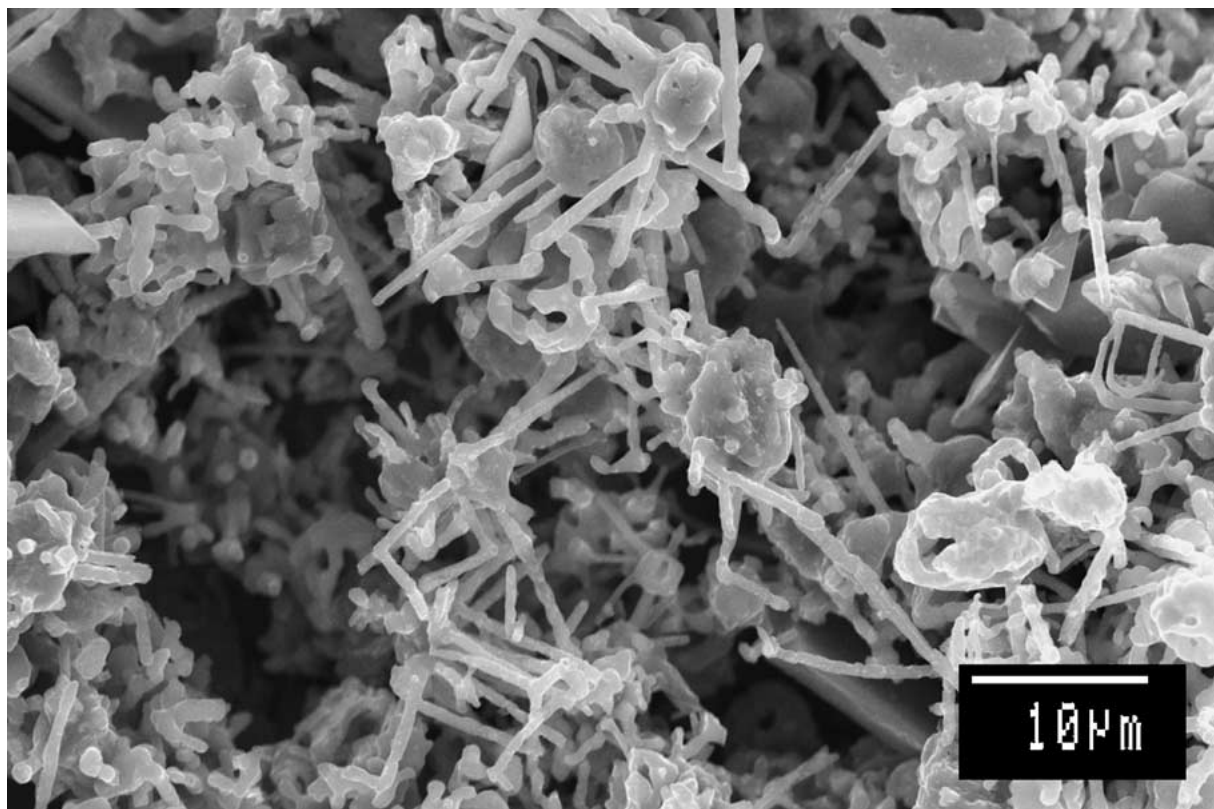


Figure 3 SEM micrograph of  $\text{TiB}_2$  whiskers synthesised at  $1500^\circ\text{C}$  in an estimated yield of 50 vol%.

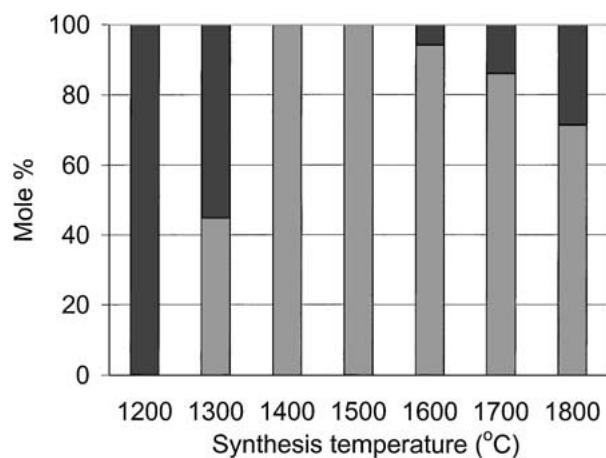


Figure 4 XRD quantification of the fractions of  $\text{TiB}_2$  (light grey) and  $\text{TiC}$  (dark grey) in the synthesis product.

phase. It is thus evident that a fast heating rate is required up to  $1400^\circ\text{C}$  in order to avoid formation of  $\text{TiC}$ .

At  $1600^\circ\text{C}$  and higher temperatures,  $\text{TiC}$  was again observed, in increasing proportion with increasing temperature, see Fig. 4. A reason that  $\text{TiC}$  reappear at the highest temperatures is most likely due to some boron evaporating as  $\text{BOCl}(\text{g})$  from the reactor before the reaction to form  $\text{TiB}_2$  has had time to take place. This gives possibilities instead for  $\text{Ti}$  to react with carbon to form  $\text{TiC}$ . Chemical analyses of oxygen in the as-synthesised product show that the oxygen content decreases with increasing synthesis temperature, reaching a level below 1 wt% at  $1500^\circ\text{C}$ , see Fig. 5.

From TEM and SEM-EDS analyses it appears that both  $\text{TiB}_2$  and  $\text{TiC}$  grow in the form of whiskers. The total whisker yield observed was about 50% at all temperatures above  $1100^\circ\text{C}$ .

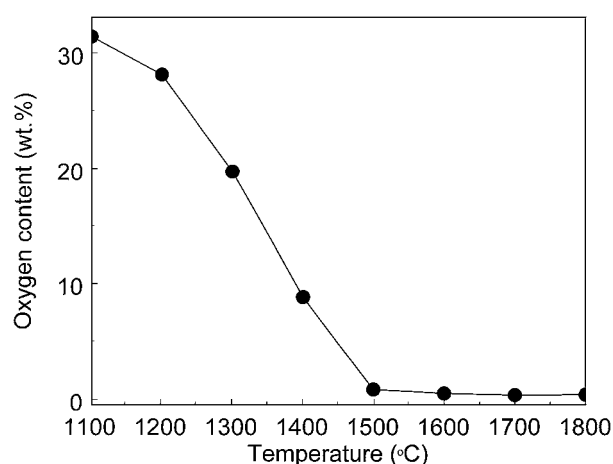


Figure 5 Chemical analyses of residual oxygen in the synthesis products.

### 3.3. Selection of starting materials

#### 3.3.1. Boron source

Both  $\text{Na}_2\text{B}_4\text{O}_7$  and  $\text{B}_2\text{O}_3$  were tested as boron sources. Equilibrium calculations and experimental results from XRD indicate that the addition of  $\text{Na}$  from  $\text{Na}_2\text{B}_4\text{O}_7$  leads to formation of stable  $\text{Na-B-O}$  phases at the reaction temperature, thus suppressing the formation of  $\text{TiB}_2$  and instead favouring the formation of  $\text{TiC}$ .

#### 3.3.2. Catalyst metal

The presence of a catalyst metal is a requirement for  $\text{TiB}_2$  whisker formation. Tests of a reaction mixture without catalyst metal easily showed that only  $\text{TiB}_2$  particles and no whiskers were formed in the product. The catalyst metals tried were  $\text{Ni}$ ,  $\text{Cu}$ ,  $\text{Co}$ ,  $\text{Fe}$ , and an  $\text{Ni-Cu}$  alloy at three different temperatures:  $1400^\circ\text{C}$ ,

1500°C, and 1600°C. Nickel gave the highest whisker yield, as described above.

Iron was tested in both Ar and in N<sub>2</sub>, because the use of nitrogen suppresses the formation of Fe<sub>3</sub>C [1], but almost no whiskers were formed. Copper was tested because it dissolves boron but not carbon [13], so it was expected to work as a catalyst metal for TiB<sub>2</sub> whiskers but not for TiC whiskers. However, Cu was completely ineffective as a catalyst metal. The Ni–Cu alloy gave about 15 vol% whiskers; it is thus better than Cu but inferior to Ni.

### 3.3.3. Halogenide salt

A halogenide salt acts as a precursor for the formation of gaseous titanium and boron species, and the salt is also thought to distribute the catalyst metal in the

reaction. Four halogenide salts (NaCl, KCl, NaI and NaF) were tested in combination with Ni as catalyst at 1400°C, 1500°C and 1600°C. All the salts were effective to some extent, but NaCl gave the highest whisker yield at all the temperatures tested. The formation of gaseous catalyst metal halogenides might be the critical step for the whisker formation.

### 3.4. Reaction studies

Up to 900°C the measured temperature fluctuated around the preset temperature, giving rise to stepwise TG weight loss and multiple MS peaks of CO<sub>2</sub>(g). At higher temperatures the measurements followed the preset values; see Figs 6a and b and 7a and b.

The weight loss during the initial heating period is due to burn-out of the volatile content of the

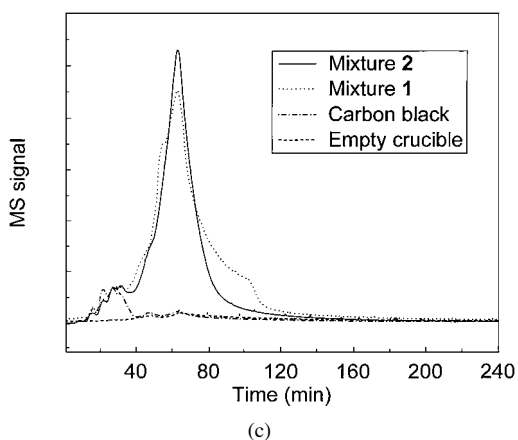
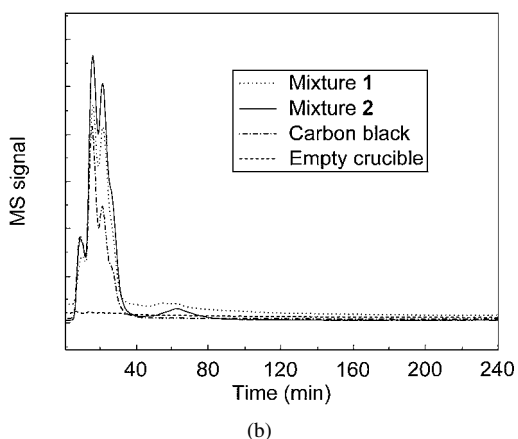
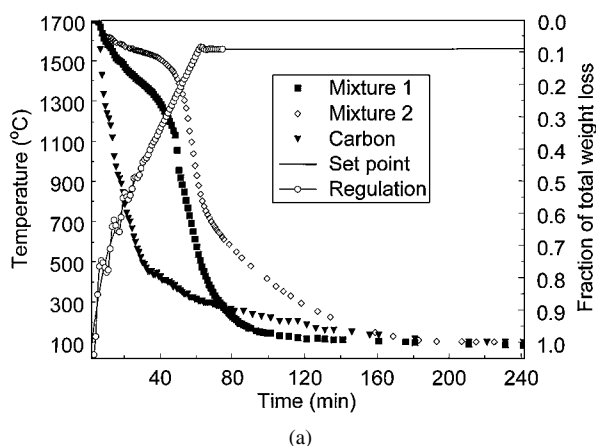


Figure 6 TG and MS measurements, using the same temperature profile as the optimum synthesis, of the carbon-black powder and of the starting mixtures #1 and #2. (a) TG measurements and inserted temperature profile. (b) MS signal from CO<sub>2</sub>(g). (c) MS signal from CO(g).

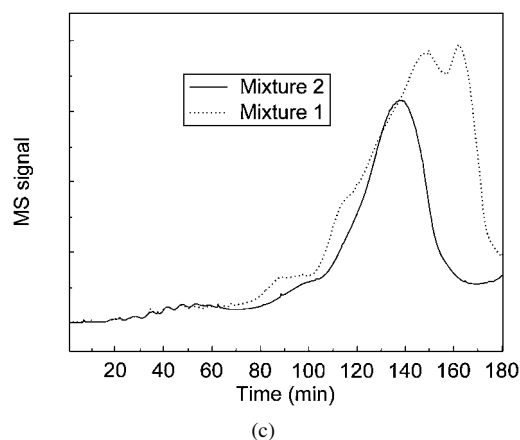
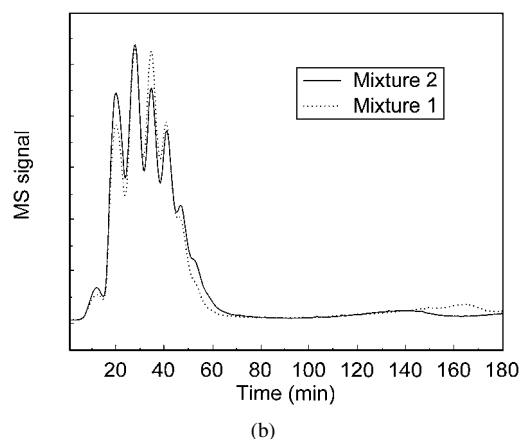
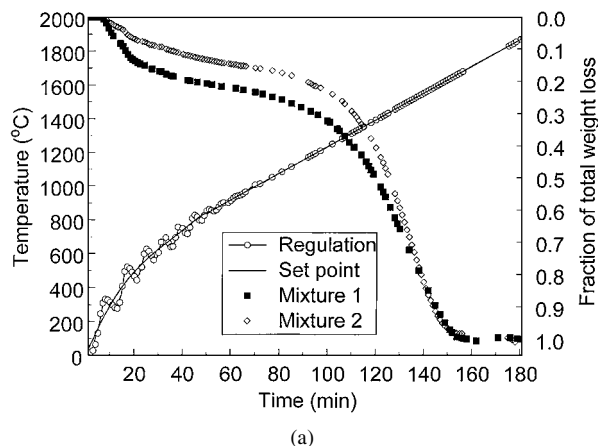


Figure 7 TG and MS measurements, using starting mixtures #1 and #2, with constant heating rate up to 1800°C in 3 h and no holding time. (a) TG measurements and inserted temperature profile. (b) MS signal from CO<sub>2</sub>(g). (c) MS signal from CO(g).

carbon-black powder. From the TG and MS recordings it is clear that the evolution of  $\text{CO}_2(\text{g})$ , mainly in the temperature range 350–1000°C, originates almost only from the heating of the carbon-black powder. The MS signal from  $\text{H}_2\text{O}$  was negligible.

The carbothermal reduction of the precursor oxides started at about 1000°C. Those reactions were associated with evolution of  $\text{CO}(\text{g})$  and at those high temperatures the MS spectra showed no additional evolution of  $\text{CO}_2(\text{g})$ . The start of carbothermal reduction is also indicated by a sudden increase in the slope of the weight loss curve, see Figs 6a–c and 7a–c.

The carbothermal reduction (mixture #2) starts at a somewhat higher temperature than the VLS growth (mixture #1). From the TG curves it is also obvious that the carbothermal reduction process is slower than the VLS mechanism in the initial part; see Figs 6a and 7a. The kinetics of  $\text{TiB}_2$  whisker formation via the carbothermal VLS process is thus faster than formation of  $\text{TiB}_2$  particles via conventional carbothermal reduction of the starting oxides.

EDS analysis of gas species condensed on copper plates gave precipitates of Cl during the whole reaction

time. Na was detected at temperatures above 1000°C. Weak Ni peaks were detected during the heating up to 1200°C. Small amounts of Ti were detected during heating from 1200 to 1500°C. Most Ti reacts to form  $\text{TiB}_2$  and only minor amounts disappear from the reactor during the synthesis. However, the temperature regions where Ni and Ti are observed are supported by the equilibrium calculations showing  $\text{NiCl}_2$  and  $\text{TiCl}_3$  gas formation, see Fig. 1b and d.

### 3.5. Growth directions

Whiskers prepared at temperatures ranging from 1300°C to 1800°C were characterized in the TEM regarding their morphology and crystallographic growth directions. However, the discussion here will focus on whiskers grown in the temperature range 1500–1600°C.

The TEM study showed that the limiting faces, parallel to the growth direction of the whiskers, are normally  $\{011\}$  or  $\{001\}$  planes. In the 1500°C synthesis, whiskers with the  $\{011\}$  planes parallel to the growth direction were the most frequent. These whiskers thus grew in the  $\langle 122 \rangle$  direction (Fig. 8a). As the temperature

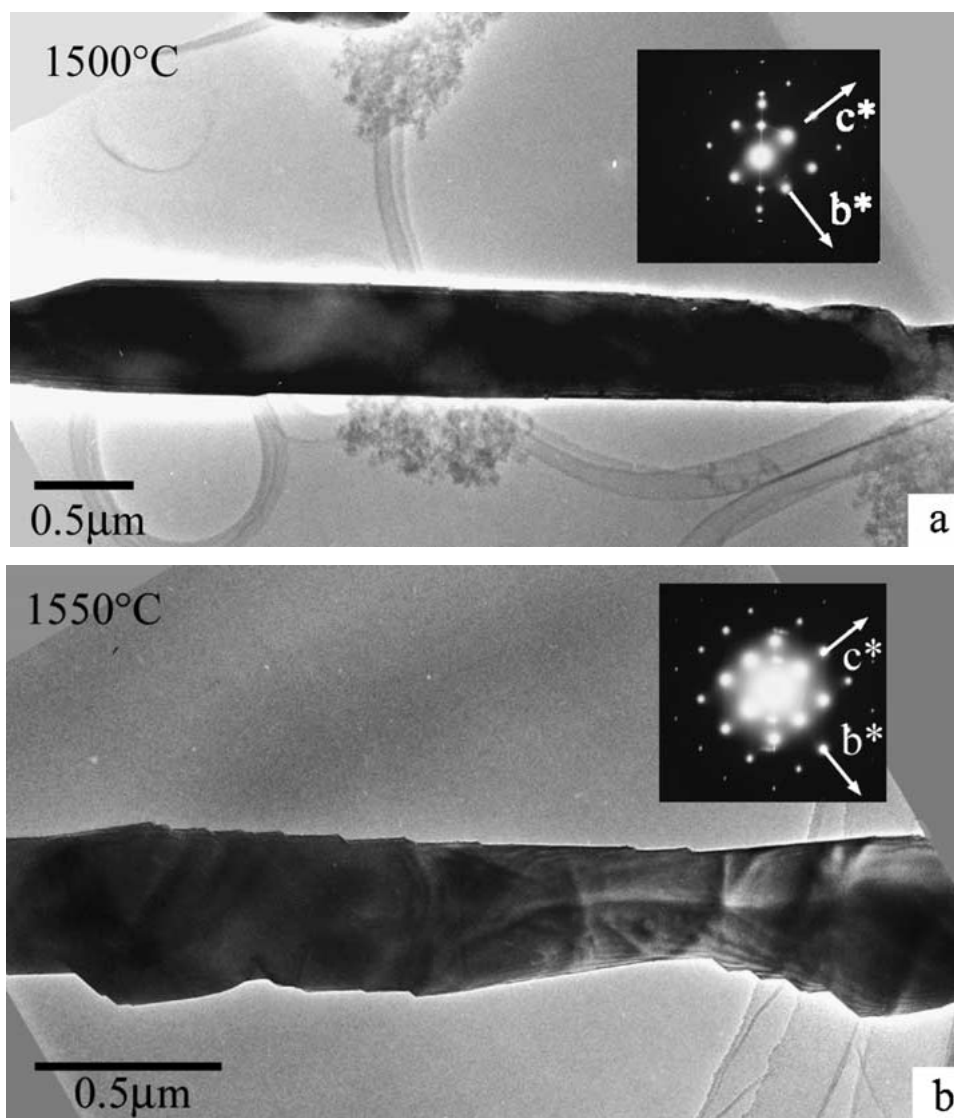


Figure 8 TEM studies of  $\text{TiB}_2$  whisker growth directions. The dominating growth direction was observed to depend on temperature. (a) At 1500°C  $\{011\}$  planes parallel to the  $\langle 122 \rangle$  growth direction dominate. (b, c) At 1600°C the surface was full of steps because  $\{001\}$  planes started to develop as frequently as  $\{011\}$  planes. Both the growth directions  $\langle 122 \rangle$  and  $\langle 120 \rangle$  were observed. (d) At 1550°C some whiskers showed the “high temperature morphology,”  $\{001\}$  limiting planes, and they grew in the  $\langle 120 \rangle$  direction. (Continued)

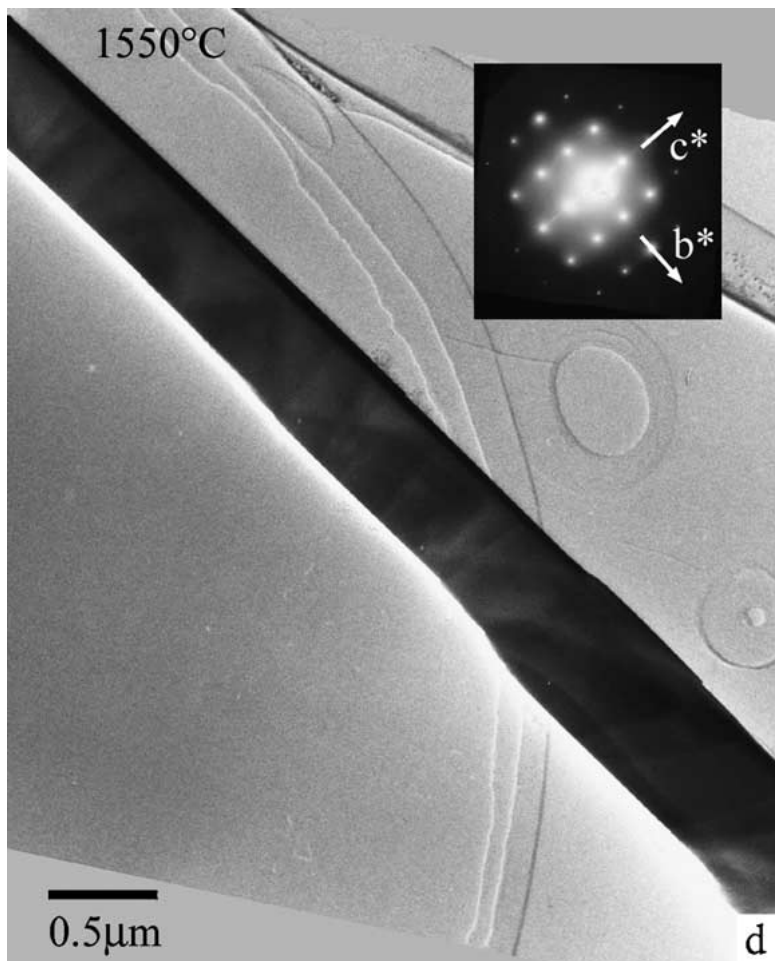
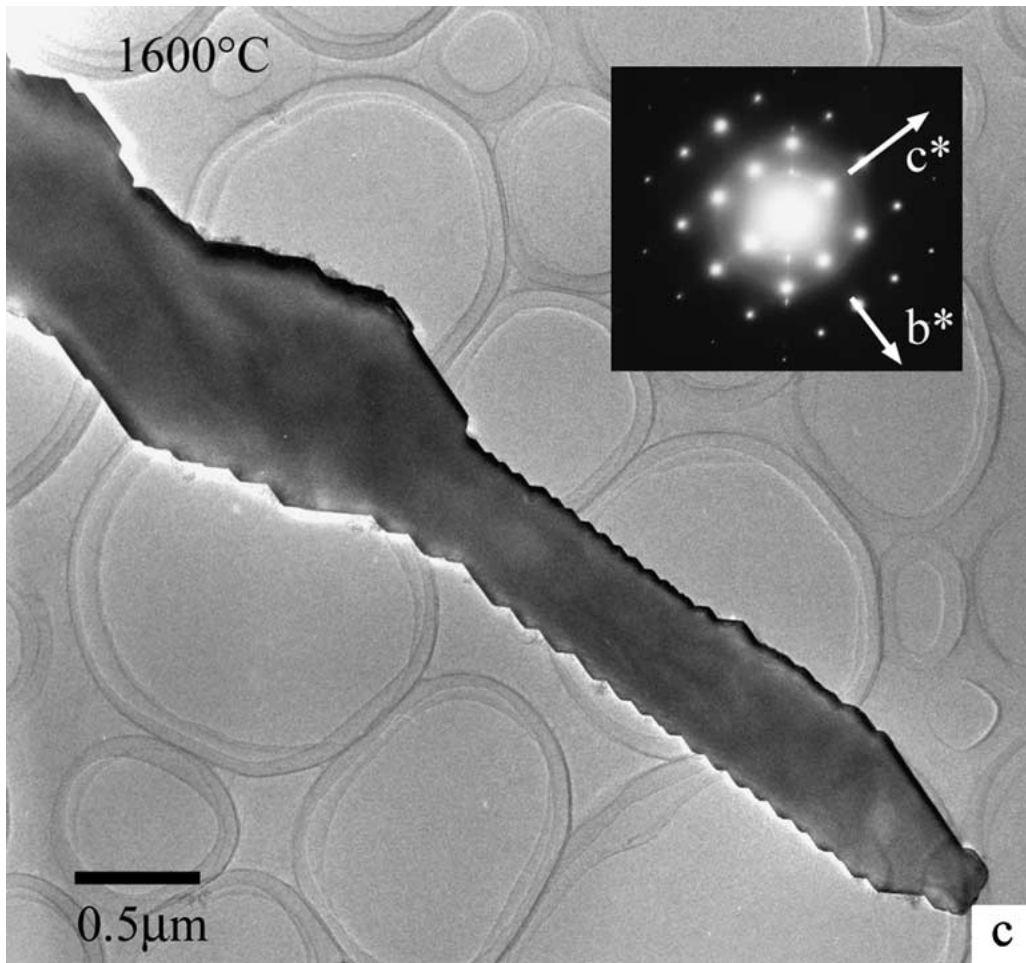


Figure 8 (continued.)

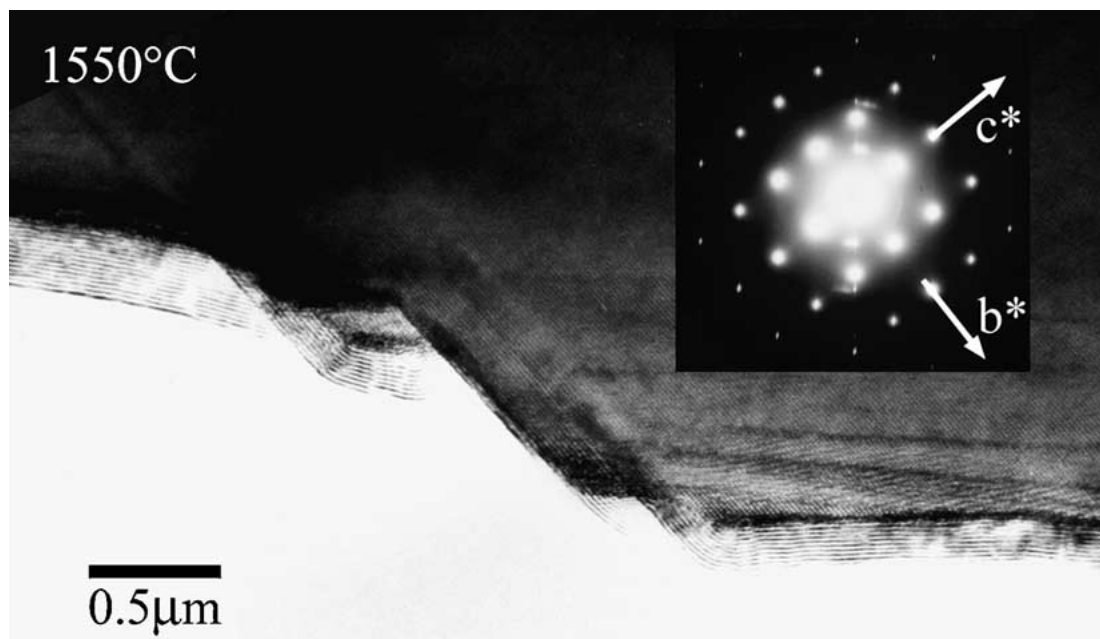


Figure 9 In the temperature region 1500–1600°C graphite was observed growing in close contact with the {011} surfaces of the whiskers.

of the synthesis was increased, {001} surface planes started to develop. In the 1600°C preparation they were almost as frequent as the {011} planes, giving a limiting surface full of steps (Fig. 8b and c). Whiskers prepared at 1800°C grew in the  $\langle 120 \rangle$  direction and showed almost exclusively {001} limiting planes without steps. This confirms the observed trend that the {001} surfaces tend to dominate the surfaces of the whiskers prepared at higher temperatures. The “high-temperature morphology” was sometimes observed in the 1500–1600°C syntheses as well (Fig. 8d). This can be explained by the fact that the reaction is exothermal and may create hot spots, warm enough to generate the “high temperature morphology”.

It should be stressed that the TEM images presented in Fig. 8a–d were all recorded with the zone axis parallel to the  $\langle 100 \rangle$  direction. No characterisation of surfaces perpendicular to the viewing direction was possible, due to the limiting tilting angles of the specimen holder. However, considering whiskers characterised with zone axes parallel to other directions, it is plausible that these surfaces consisted of {100} planes.

In the ED patterns, showed as insets in Fig. 8a–c, there are extra spots in the  $\langle 011 \rangle$  directions (vertical in the ED patterns), which are not possible to index using the basic vectors in the  $\text{TiB}_2$  diffraction pattern. These rows of extra spots correspond to diffraction from graphite. The extra spots can be indexed as (00l) reflections of graphite with the expected interplanar distance 3.35 Å. Since the graphite reflections extend in the  $\langle 011 \rangle$  ( $\text{TiB}_2$ ) directions in the ED patterns, graphite appears to have grown with the  $a$ - $b$  plane parallel to the {011} planes of the  $\text{TiB}_2$  whisker. This assumption was confirmed in HREM micrographs of  $\text{TiB}_2$  prepared at 1550°C, where the graphite planes are seen growing in close contact with the {011} whisker surface the (Fig. 9). Graphite was observed growing almost exclusively on {011} surfaces, and only in the temperature interval 1500–1600°C. The graphite may have formed

from the mixture of  $\text{CO}(\text{g})$  and  $\text{CO}_2(\text{g})$  present in the reactor during synthesis.

#### 4. Conclusions

$\text{TiB}_2$  whiskers can be grown by a carbothermal vapour–liquid–solid (VLS) mechanism at 1500°C. If the reaction is not fully controlled, TiC may also form during the process. In the VLS growth mechanism used, Ti and B in form of gaseous chloride and oxochloride species are transported to liquid–metal catalyst droplets that become supersaturated, resulting in the precipitation of  $\text{TiB}_2$  as whiskers. The reaction terminates when the concentrations of reacting gases near the catalyst droplets have reached a certain lower limit. The best result was obtained with a mixture of  $\text{TiO}_2:\text{B}_2\text{O}_3:\text{C}:\text{NaCl}:\text{Ni}$  in the molar ratios 1:1:6:0.25:0.1 in argon atmosphere. The obtained  $\text{TiB}_2$  whiskers are 0.5–2 μm in diameter and 10–50 μm in length. Reaction studies by use of thermogravimetry and mass-spectroscopy show that the VLS reaction is faster than a direct carbothermal reduction reaction between the oxides and carbon.

The dominating growth direction was observed to depend on the synthesis temperature. At 1500°C, {011} planes parallel to the growth direction  $\langle 122 \rangle$  dominated. At 1600°C, the surface was full of steps because {001} planes started to develop as frequently as {011} planes. Both the growth directions  $\langle 122 \rangle$  and  $\langle 120 \rangle$  were observed. At 1800°C, the whiskers almost exclusively showed {001} limiting planes, and they grew in the  $\langle 120 \rangle$  direction. In the temperature range 1500–1600°C, graphite was observed growing in close contact with the {011} surfaces of the  $\text{TiB}_2$  whiskers.

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