

On the carbothermal vapour–liquid–solid (VLS) mechanism for TaC, TiC, and Ta_xTi_{1-x}C whisker growth

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Received 9 December 1999; received in revised form 10 April 2000; accepted 13 April 2000

Abstract

The growth of TaC, TiC and Ta_xTi_{1-x}C whiskers has been studied in some detail. The whiskers were synthesised via a vapour–liquid–solid (VLS) growth mechanism in the temperature range 1220–1400°C. The starting materials were Ta₂O₅, TiO₂, C, NaCl, and a catalyst metal (Ni, Co, Fe, and Cu were tested). The main reaction during synthesis was a carbothermal reduction of Ta₂O₅ and TiO₂, and NaCl was added to form the oxochlorides and chlorides of Ta and Ti that account for the transport to the catalyst metal. The syntheses were made in a protecting Ar atmosphere. From experiments interrupted after different times at the synthesis temperature it is clear that sodium tantalates form as intermediate products, whereas sodium titanates cannot be identified. Only metals that are able to dissolve the elements building up the whiskers work as catalysts. Whisker growth starts either from a catalyst droplet in contact with carbon or from an oxide particle in contact with both catalyst metal and carbon. For TaC and Ta_xTi_{1-x}C the only growth direction observed is [100], while TiC may grow either along [100] or along [111]. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbides; TaC; TiC; VLS process; Whiskers

1. Introduction

This article presents a study of the carbothermal vapour–liquid–solid (VLS) mechanism for whisker growth. The whisker materials we have studied are TaC, TiC and Ta_xTi_{1-x}C. The VLS growth mechanism involves all three aggregation states: a vapour phase transport of one or more of the whisker components to a melted catalyst droplet where the desired whisker grows. The catalyst must be able to dissolve the whisker components and the VLS mechanism is only operative at temperatures above the melting point of the catalyst (i.e. the eutectic temperature of the multi-component system catalyst-whisker), which therefore constitutes the lower temperature limit for whisker synthesis via this growth mechanism. The catalyst metal must also be able to dissolve the whisker components. There are two competing reactions taking place at the synthesis temperature: the VLS growth of whiskers and the direct reaction between carbon and the transition metal oxides resulting in carbide particles. The VLS growth mechanism

can be favoured by optimising the molar ratios, the particle sizes of the precursor materials and the reaction temperature. The temperature should be raised as high as possible in order to reduce the residual amount of oxygen. There is a compromise to be achieved, however, because at a too high synthesis temperature the solid-state reaction between the oxide precursor and carbon may dominate over the VLS growth process. Furthermore, at high temperatures the gaseous chloride and oxochloride species that are responsible for transport of Ta and/or Ti show a tendency to escape from the reaction chamber before reacting at the catalyst. Another problem at too high synthesis temperatures is that whiskers may start to sinter together, forming agglomerates.

Two main types of VLS growth mechanisms can be defined in general: (i) all mass transport takes place in the vapour phase to the vapour–liquid interface (characteristic for growth of whiskers via chemical vapour deposition, CVD),¹ and (ii) as in the present case solid carbon dissolves into the catalyst at the droplet interface, while the other whisker component are transported in the vapour phase to the catalysts (characteristic for the carbothermal VLS mechanism).^{2,3}

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The carbothermal VLS mechanism thus involves four main steps: (1) dissolution of carbon at the interface between the catalyst droplet and solid carbon, (2) mass transport of whisker elements in the vapour phase to the vapour–liquid interface (3) chemical reaction at the vapour–liquid interface, (4) dissolution into and diffusion through the liquid alloy phase, and (5) precipitation at the liquid–solid interface.

The overall chemical reaction for the synthesis of $Ta_xTi_{1-x}C$ from TiO_2 and Ta_2O_5 is a straightforward carbothermal reduction of the oxides.

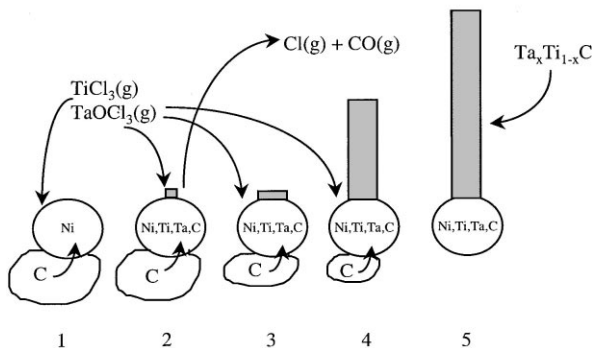
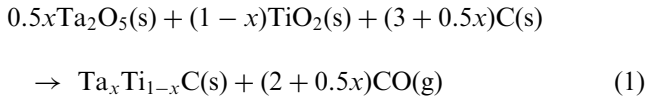


Fig. 1. A simplified sequence for the carbothermal VLS growth mechanism. The reactions at the catalyst droplet can be described as follows: (1) the catalyst particle (Ni) in contact with carbon start to dissolve the whisker constituents: C, Ta, and Ti. (2) The droplet is supersaturated and a $Ta_xTi_{1-x}C$ whisker is nucleated. (3) The surface tension balance at the interface between the whisker and the catalyst droplet determines the whisker diameter. (4) As the reactants are continuously being dissolved into the catalyst, the whisker grows, and the carbon particles are consumed. (5) When all carbon in contact with the catalyst droplet has been consumed, the whisker growth terminates.

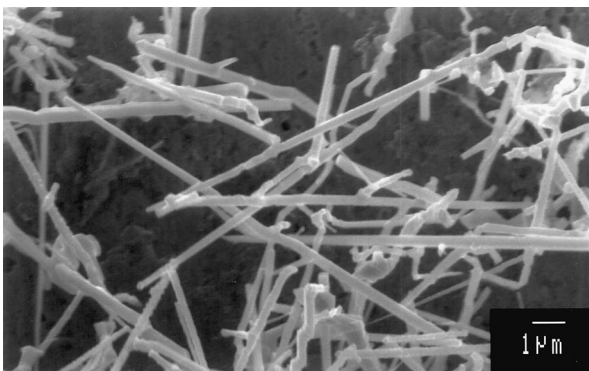


Fig. 2. An SEM micrograph of $Ta_{0.5}Ti_{0.5}C$ whiskers. The yield is estimated to be 80 vol.%. The whisker diameter is 0.2–0.6 μm and the length 10–30 μm .

Within a certain temperature range, however, this direct carbothermal reaction is not kinetically favoured in the presence of NaCl and Ni. The reactions that actually take place in the carbothermal VLS mechanism are complicated to study.

There must be a gas phase transport of Ta and Ti to the catalyst metal. Thermodynamic calculations with the computer program HSC⁴ that uses the Gibbs energy minimisation method suggest the following reactions to take place at the synthesis temperature:

Table 1
Raw materials used in the synthesis

Substance	Purity (wt.%)	Manufacturer	Particle size	Comment
Ta_2O_5	99.9	Cerac	<325 mesh	Ceramic grade
TiO_2	99.9	Aldrich	0.2–0.6 μm	Anatase
C	–	Degussa (FW200)	13 nm forming flocculent agglomerates	Carbon black (containing 21 wt.% volatiles)
NaCl	99.5	Akzo	< 5 μm	
Ni	99.9	Cerac	< 325 mesh	
Co	99.9	Cerac	< 325 mesh	
Fe	97	Aldrich	< 325 mesh	
Cu	99.5	Aldrich	< 150 mesh	
P(red)	99	Kebo		

Table 2
The molar ratios in the starting mixtures that were found to give the highest whisker yield for TaC, TiC and $Ta_{0.5}Ti_{0.5}C$ ^a

	TaC	TiC	$Ta_{0.5}Ti_{0.5}C$
Ta_2O_5	1 (60.00 g)	–	1 (30.00 g)
TiO_2	–	1 (20.00 g)	2 (10.85 g)
C	7.2 (14.86 g)	3.3 (12.56 g)	13 (14.24 g)
NaCl	0.5 (3.97 g)	0.5 (7.31 g)	1.5 (5.95 g)
Ni	0.05 (0.40 g)	0.075 (1.13 g)	0.15 (0.60 g)

^a Weighed-in amounts are given within parentheses.

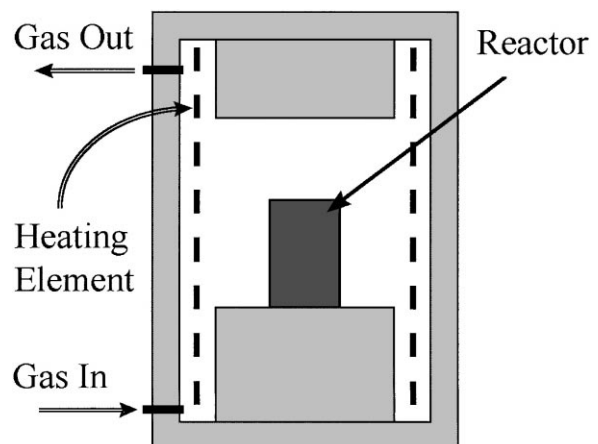
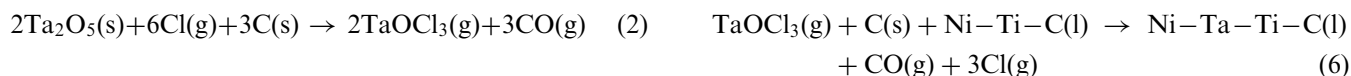
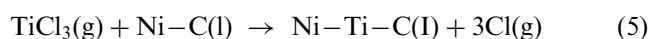


Fig. 3. The furnace set-up with the gas flow around the reactor.



Other gas-phase species that also form by similar reactions but in lower concentrations are $\text{TaO}_2\text{Cl}(\text{g})$, $\text{TaCl}_5(\text{g})$, and $\text{TiCl}_4(\text{g})$, and these may also to some extent be responsible for the transport of Ta and Ti.

The melting temperature of the catalyst metal must match the temperature range where $\text{TiCl}_3(\text{g})$ and $\text{TaOCl}_3(\text{g})$ form in high concentrations. If a catalyst metal with a too high melting point is chosen, then a direct carbothermal reaction, resulting in particles, may dominate over the whisker formation by the VLS mechanism. The following reactions are expected to occur at the catalyst (Ni-C, etc., denote that C, Ta, and Ti are dissolved in the Ni catalyst).



A simplified sequence for the carbothermal VLS growth mechanism is outlined in Fig. 1.

For some years, we have been studying growth of different transition-metal carbide and carbonitride whiskers.^{2,3,5-7} We have achieved control of the synthesis so as to gain a high whisker yield (see Fig. 2), but we have not obtained a detailed understanding of the growth mechanism. In the present article we have performed a detailed study of the growth mechanisms of $\text{Ta}_x\text{Ti}_{1-x}\text{C}$ whiskers with $0 \leq x \leq 1$ designed to explore some essential features of the VLS mechanism.

2. Experimental

2.1. Synthesis

The starting materials used in the preparation of $\text{Ta}_x\text{Ti}_{1-x}\text{C}$ whiskers are listed in Table 1. The carbon

Table 3
Chemical analysis data and measured weight loss for the series with interrupted TaC synthesis experiments^a

	Weight loss (wt.%)	O (wt.%)	C (wt.%)	Na (wt.%)	Ni (wt.%)	N (wt.%)	Ta + Cl (wt.%)
Analysis method		LECO	LECO	AAS	AAS	LECO	Balance
Starting mixture	0	16.2	15.0	2.4	0.8	0.2	65.1
0	6.8	13.7	14.3	1.9	0.8	0.2	69.1
5	8.6	13.2	14.0	1.6	0.9	0.1	70.2
15	12.2	12.3	13.4	1.3	0.9	0.1	72.0
25	16.7	10.8	12.6	0.8	0.7	0.1	74.9
45	21.2	8.4	11.3	0.3	1.3	0.2	78.5
60	23.5	7.3	10.7	0.2	1.1	0.1	80.6
90	25.8	5.5	9.7	0.2	1.0	0.2	83.5
120	28.1	3.7	8.6	0.2	1.1	0.3	86.2
150	30.6	2.0	8.6	0.2	1.1	0.2	88.0
180	33.0	0.4	6.5	0.2	1.1	0.2	91.6
210	33.0	0.09	6.3	0.02	1.2	0.2	92.2
240	33.3	0.1	6.4	0.01	1.2	0.2	92.1

^a The experiments were quenched after different holding times, from 0 to 240 min, at the synthesis temperature 1220°C. Ta and Cl were not analysed. No information on the number of vacancies is available.

Table 4
Phases present according to powder X-ray diffraction data (XRD) after different reaction times for the series of interrupted TaC-whisker syntheses^a

	Starting mixture	0	5	15	25	45	60	90	120	150	180	210	240
Ta ₂ O ₅	×	×	×	×	×	×	×	×	×	×	×	–	–
Na ₂ Ta ₄ O ₁₁	–	–	–	×	×	×	×	×	×	×	–	–	–
NaTaO ₃	–	–	–	–	×	×	×	×	×	×	×	–	–
TaC	–	×	×	×	×	×	×	×	×	×	×	×	×

^a The experiments were interrupted after different holding times, from 0 to 240 min, at the synthesis temperature 1220°C. NaCl, Ni, and C could not be detected.

source contained 21 wt.% volatile components that were burned off during the heating-up period. The choice of carbon source has a strong influence on the whisker yield. It has been shown in earlier studies that carbon black with a volatile part retains its fluffy consistency after heat treatment, in contrast to carbon powder without volatiles, and we believe that this is essential in improving the ease with which the volatile Ta and Ti species reach the catalyst.^{2,3} The weighed-in $\text{TiO}_2/\text{Ta}_2\text{O}_5$ molar ratio can be varied in order to yield whiskers with different x -values. The molar ratios of the different precursor materials used in this study for preparation of TaC, TiC and $\text{Ta}_{0.5}\text{Ti}_{0.5}\text{C}$ are listed in Table 2.

The starting materials were mixed to homogeneity in a blender. Portions of about 10–20 g were placed in a graphite crucible covered with a lid with a number of holes to allow controlled gas exchange between the reactor chamber and the surrounding atmosphere (see Fig. 3). The mixture was then heated in a graphite fur-

nace (Thermal Technology) at a rate of $1000^\circ\text{C}/\text{h}$ to the synthesis temperature in an Ar atmosphere. All experiments were conducted at atmospheric pressure and at temperatures in the range 1220 – 1400°C . Previous studies have revealed the optimum temperature for TaC and $\text{Ta}_x\text{Ti}_{1-x}\text{C}$ whisker growth to be 1220 – 1250°C ^{3,5} and 1400°C for TiC whiskers.² The whiskers obtained were 0.2 – $0.6\ \mu\text{m}$ in diameter and 5 – $30\ \mu\text{m}$ in length. The

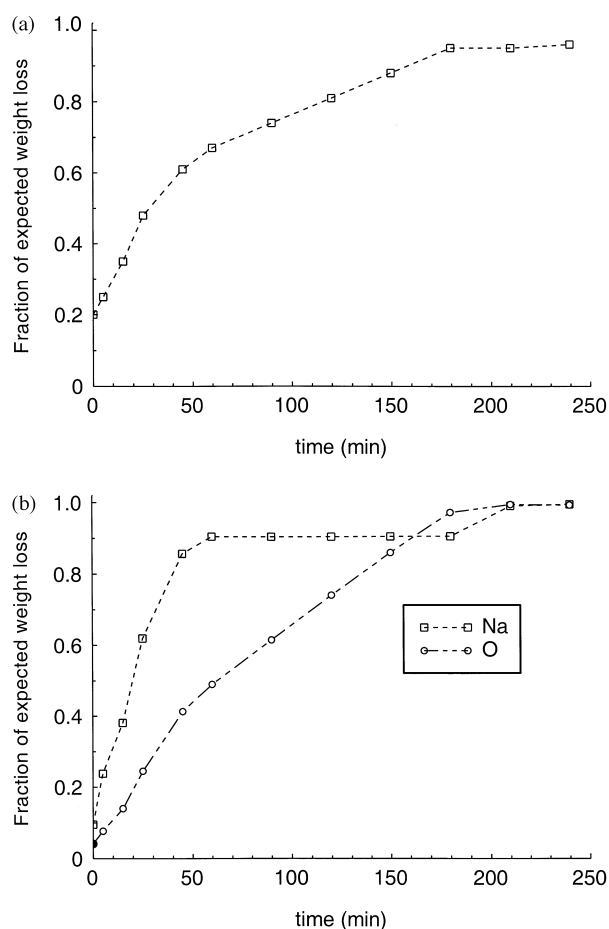


Fig. 4. (a) Observed weight change as a fraction of the expected vs. reaction time for the series of interrupted TaC whisker synthesis experiments at 1220°C ; (b) observed weight change of the different elements as a fraction of the expected vs. reaction time. Based on the assumption that the starting mixture transforms to TaC and that all O, Na, Cl, and Ni disappear from the reactor during synthesis.

Table 5

Chemical analysis data for the series of interrupted TiC synthesis experiments^a

Analysis method	Total weight loss (wt.%)	O (wt.%)	C (wt.%)	Na (wt.%)	Ni (wt.%)	Cl (wt.%)	Ti (wt.%)
Starting mixture	20.9	25.9	7.5	2.9	11.6	31.3	
0	12.5	19.3	24.7	7.6	3.2	12.3	33.1
30	23.4	18.3	25.0	6.2	3.6	9.9	38.1
60	34.2	16.7	25.3	4.1	4.0	6.9	44.3
90	43.1	14.2	25.8	2.2	4.8	3.8	50.8
120	48.1	12.2	26.0	0.4	5.3	2.2	55.0
180	50.8	9.7	25.3	0.08	5.3	0.01	58.9
240	52.5	8.2	24.6	0.05	5.5	0	60.7
960	55.7	5.0	22.8	0	6.5	0	64.4

^a The experiments were quenched after different holding times, from 0 to 960 min, at the synthesis temperature 1250°C . The composition of the starting mixture is not analysed it is calculated from the weight in amounts of the different starting materials.

Table 6

Chemical analysis data for the series of interrupted TiC synthesis experiments^a

Analysis method	Total weight loss (wt.%)	O (wt.%)	C (wt.%)	Na (wt.%)	Ni (wt.%)	Cl (wt.%)	Ti (wt.%)
Starting mixture	–	20.9	25.9	7.5	2.9	11.6	31.3
0	23.7	17.7	23.8	6.5	3.5	10.9	37.5
10	39.5	13.8	24.5	4.3	4.5	8.7	47.0
20	47.3	11.0	25.0	1.7	5.2	3.9	55.0
30	51.3	9.2	24.8	0.4	5.5	1.6	58.8
40	53.2	7.6	24.3	0.08	5.6	1.8	61.2
60	53.8	6.6	23.8	0.02	6.2	1.0	62.5
120	55.1	5.3	23.7	0.01	6.4	1.1	64.0
180	56.1	4.6	23.6	0.01	6.0	0.02	65.2
240	56.3	3.7	23.1	0.009	6.2	0.01	65.8
960	57.5	2.1	23.1	0.006	6.2	0	68.3

^a The experiments were quenched after different holding times, from 0 to 960 min, at the synthesis temperature 1400°C . The composition of the starting mixture is not analysed it is calculated from the weight in amounts of the different starting materials.

reactions were completed after 4 h at the respective optimum synthesis temperature. Three series with experiments interrupted after different times from 0 to 960 min were performed in order to study how the chemical

composition and the phase composition changes during synthesis; one series with TaC whisker synthesis at 1220°C and two series with TiC whisker synthesis at 1250 and 1400°C, respectively.

Only a few whiskers terminated with a catalyst droplet after completed reaction, indicating that there is a rapid redistribution of Ni in the reactor after a whisker has grown to full length. The search for droplets in experiments interrupted before completed whisker growth was a time-consuming task. It was observed that small additions of red phosphorus to the starting mixture increased the occurrence of nickel droplets. After solidification of the droplets small nickel phosphide particles were found to have precipitated on the droplet surface. No effect on the whisker yield was observed, however. Therefore, experiments were done where red phosphorous was added to the starting mixture in order to increase the possibility to find whiskers terminated with a catalyst droplet.

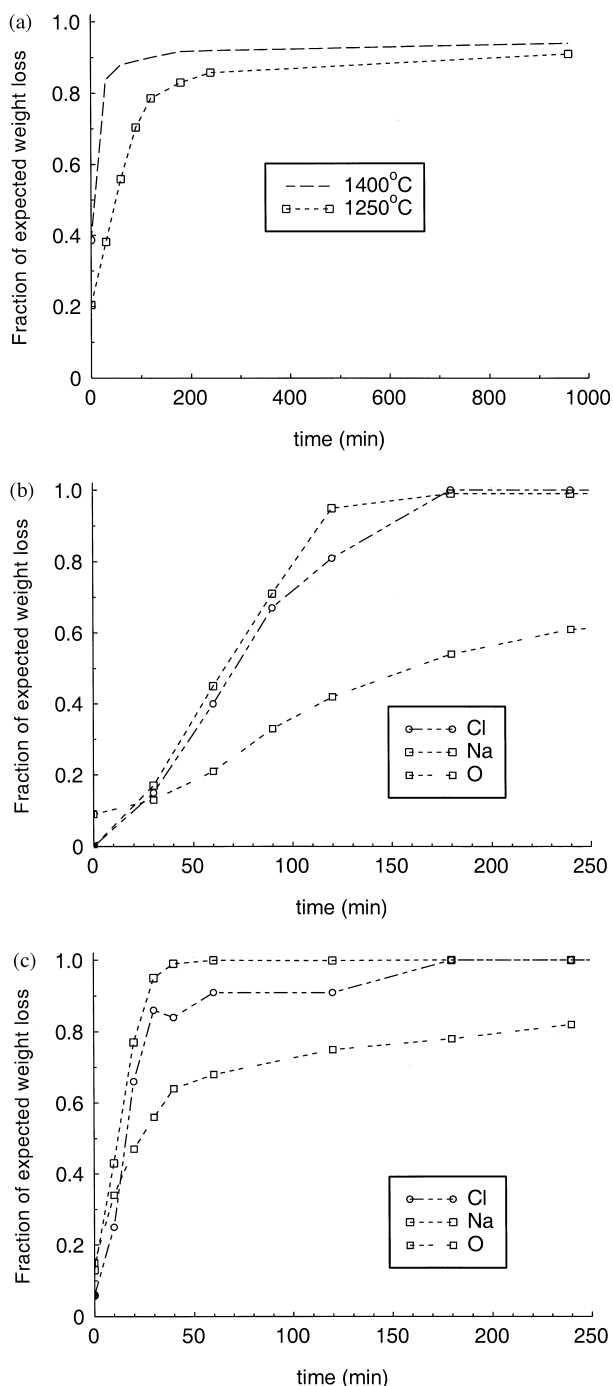


Fig. 5. (a) Observed weight change as a fraction of the expected vs. reaction time for the two temperature series (1250 and 1400°C) of interrupted TiC whisker synthesis experiments; (b) observed weight change of the different elements as a fraction of the expected vs. reaction time for TiC whisker synthesis at 1250°C. Based on the assumption that the starting mixture transforms to TiC and that all O, Na, Cl, and Ni disappear from the reactor during synthesis; (c) same as (b) but for TiC whisker synthesis at 1400°C.

2.2. Characterisation

The products were characterised by their X-ray powder diffraction patterns (XRD), obtained with a Guinier-Hägg focusing camera. $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54060 \text{ \AA}$) was used, and finely powdered silicon [$a = 5.430880(35) \text{ \AA}$] was added as an internal standard. The recorded films were evaluated in an automatic film scanner.⁸

The morphology and composition of the whiskers and catalyst droplets were investigated using a high-resolution scanning electron microscope (SEM, JEOL 880) equipped with an energy-dispersive spectrometer (LINK *ISIS*), which allows detection of boron and heavier elements. A high-resolution transmission electron microscope (TEM, JEOL 3010) and a TEM (JEOL 2000FX) equipped with EDS (LINK AN10000) were used for the electron diffraction work to determine whisker growth directions and for studies of the catalyst droplets.

Table 7
Phases present, according to powder X-ray diffraction data (XRD), after different reaction times for the 1250°C series of interrupted TiC whisker synthesis experiments^a

	Starting mixture	0	30	60	120	180	240
TiC	–	×	×	×	×	×	×
TiO ₂ (rutile)	–	×	×	×	×	×	–
TiO ₂ (anatase)	×	×	×	×	×	×	–
Ti ₂ O ₃	–	×	×	×	–	–	–
Ti ₃ O ₅	–	×	×	–	–	–	–
NaCl	×	×	×	×	–	–	–

^a The experiments were interrupted after different holding times from 0 to 240 min. Ni and C could not be detected from XRD data.

3. Results and Discussion

3.1. Interrupted experiments

3.1.1. TaC

We followed the reaction forming TaC whiskers at the optimum synthesis temperature, 1220°C. TaC whiskers were found as soon as the synthesis temperature had been reached, with the same length and diameter as those present after completed carbothermal VLS growth. This indicates that, once a whisker has nucleated,

it grows to full length very rapidly. The rate-determining step should then be the formation of supersaturated catalyst droplets from which whiskers can grow. The time dependence of the TaC formation is extracted from the data given in Tables 3 and 4. The fraction of expected weight loss is thus plotted versus reaction time (see Fig. 4a). These data show that the reaction is complete after 210 min and that TaC is then the only phase that can be identified. The change in chemical composition during synthesis can be followed in a graph showing the observed weight change as a fraction of expected vs. reaction time for the different elements, assuming that the starting mixture will transform to TaC during the reaction (see Fig. 4b). The sodium level rapidly dropped to about 10% of the initial amount, but stayed at this level during the remaining TaC whisker growth period, just until the reaction came to completion after 210 min. According to XRD analysis, this is due to that sodium tantalates (NaTaO_3 and $\text{Na}_2\text{Ta}_4\text{O}_{11}$) are formed as intermediate phases during synthesis (see Table 4). As the last reduction step during synthesis (see Table 4), the main impurity in the synthesis product, found from chemical analysis, is remnants of the Ni catalyst (see Table 3) that, however, is too low to be detected by use of XRD.

3.1.2. TiC

Two series of experiments interrupted after different reaction times were performed, one at 1250°C and one at 1400°C. At 1400°C the TiC whisker yield is slightly higher and the residual level of oxygen is lower than at 1250°C. Primary chemical analysis data are given in Tables 5 and 6.

The reaction time required to form TiC whiskers at 1250°C is about the same as for TaC, deduced both from weight loss curves and from chemical analysis data (Fig. 5a–c). Just as for TaC synthesis, a few TiC whiskers had already formed when the synthesis temperature was reached. No sodium titanates were found as intermediates during the reaction, according to the XRD studies, and neither did chemical analysis show any plateau in the Na content (see Fig. 5b and c), which was the case for TaC synthesis. Traces of reduced titanium oxides (e.g. Ti_3O_5 and Ti_2O_3) were, however, found in some of the interrupted experiments (see Table 7).

3.2. The catalyst metal

Ni has proved to be the best catalyst metal for synthesis of TiC and TaC whiskers.^{2,3} After completed whisker growth, however, only a minor fraction of the whiskers terminate with a Ni droplet (<5%), and even those droplets are found at different levels of erosion (see Fig. 6). An attempt was made to study the catalyst droplets that terminate some of the whiskers. Phosphorous additions to the reaction mixture were found to increase the possibility for finding whiskers terminated with a

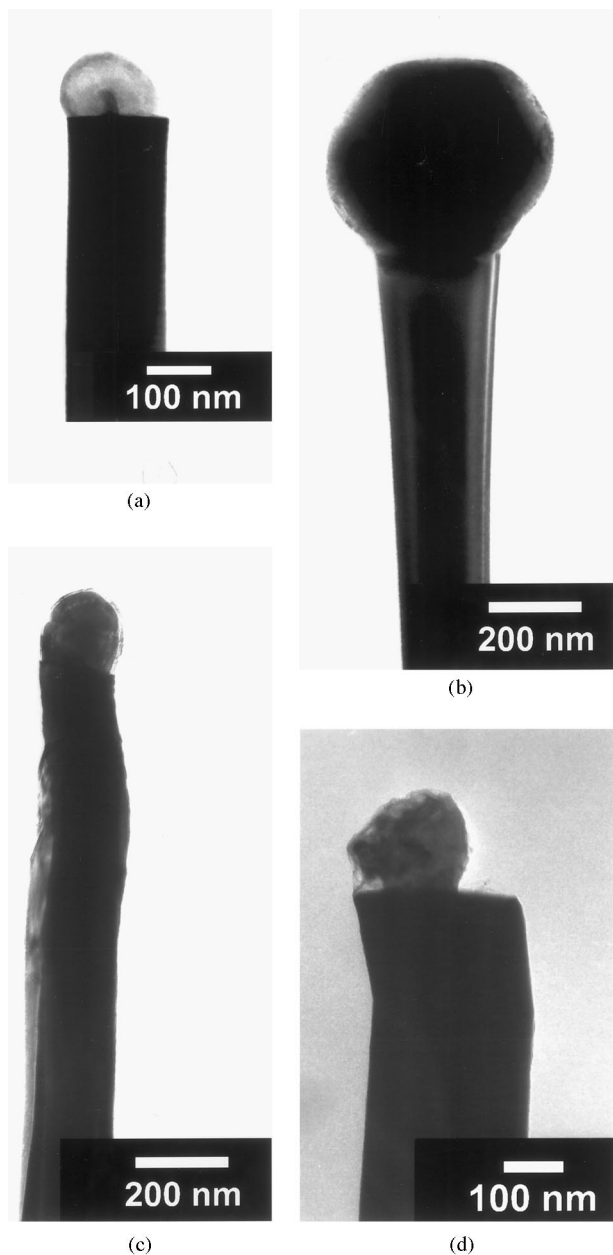


Fig. 6. (a) TEM micrograph of a TiC whisker terminated by a Ni droplet. The interface between the whisker and the droplet is very sharp, indicating that the whisker has nucleated on the surface of the droplet; (b–d) droplets terminating whiskers in different degrees of erosion.

Table 8
EDS-TEM analyses of Ni droplets terminating Ta_xTi_{1-x}C whiskers and Fe-droplets terminating TiC_xNi_{1-x} whiskers^a

Whisker composition	Droplet no.	Ni (at.%)	Fe (at.%)	Ti (at.%)	Ta (at.%)	Na (at.%)	Cl (at.%)	P (at.%)
Ta _x Ti _{1-x} C	1	99.1	–	0.1	0	0.5	0.3	0
Ta _x Ti _{1-x} C	2	97.5	–	0.6	0.4	1.5	0	0
Ta _x Ti _{1-x} C	3	92.7	–	0.3	0.4	2.8	1.4	2.4
Ta _x Ti _{1-x} C	4	94.3	–	0.3	0.2	1.0	0	4.2
Ta _x Ti _{1-x} C	5	86.1	–	0.4	0	0.4	0	13.1
Ta _x Ti _{1-x} C	6	96.4	–	1.0	0.5	0.3	0.5	1.3
Ta _x Ti _{1-x} C	6	77.9	–	0.2	0	0.3	0	21.6
Ta _x Ti _{1-x} C	6	78.8	–	0.2	0	0	0	21.0
TiC	7	77.7	–	1.0	–	–	–	21.3
TiC	8	73.7	–	0	–	–	–	26.3
TiC	8	73.1	–	0.4	–	–	–	26.5
TiC	8	73.8	–	1.0	–	–	–	25.2
TiC	9	70.6	–	1.0	–	–	–	28.4
TiC	9	71.9	–	1.0	–	–	–	27.1
TiC	10	69.4	–	0.6	–	–	–	30.0
TiC	10	73.9	–	2.6	–	–	–	23.5
TiC	11	77.6	–	1.0	–	–	–	21.4
TiC _x Ni _{1-x}	12	–	98.0	0.6	–	–	–	1.4
TiC _x Ni _{1-x}	12	–	97.4	0.2	–	–	–	2.4
TiC _x Ni _{1-x}	12	–	78.3	0.8	–	–	–	20.9
TiC _x Ni _{1-x}	12	–	85.8	0	–	–	–	14.2
TiC _x Ni _{1-x}	12	–	91.1	0.3	–	–	–	8.6
TiC _x Ni _{1-x}	12	–	97.2	1.1	–	–	–	1.7
TiC _x Ni _{1-x}	13	–	82.0	1.1	–	–	–	16.9
TiC _x Ni _{1-x}	13	–	84.6	1.2	–	–	–	14.2
TiC _x Ni _{1-x}	13	–	86.6	1.0	–	–	–	12.4
TiC _x Ni _{1-x}	13	–	97.9	2.0	–	–	–	1.1
TiC _x Ni _{1-x}	14	–	99.0	0.9	–	–	–	0.1
TiC _x Ni _{1-x}	14	–	81.5	0.6	–	–	–	17.9
TiC _x Ni _{1-x}	14	–	99.5	0.5	–	–	–	0
TiC _x Ni _{1-x}	14	–	84.2	0.2	–	–	–	15.6
TiC _x Ni _{1-x}	14	–	99.5	0.5	–	–	–	0
TiC _x Ni _{1-x}	14	–	93.8	0.7	–	–	–	5.5

^a Red phosphorus was added to the starting mixtures in order to enhance the possibility of finding droplets. Different spot analysis on the same droplet may give a wide spread in the phosphorous content due to that it is present in small discrete Ni- or Fe-phosphide particles.

Ni-droplet in the product. TEM-EDS point analyses of Ni droplets terminating whiskers show very little Ti and/or Ta left in the Ni catalyst after solidification (see Table 8). A SEM-EDS line scan over a Ni droplet terminating a TiC whisker shows that there is no Ni dissolved into the structural framework of the carbide whisker (see Fig. 7). The experimental results do not contradict that Ti and/or Ta dissolve in the droplet at the synthesis temperature.

Equilibrium calculations with the program ThermoCalc⁹ using data from “the Hard Materials Thermodynamic Database”¹⁰ gives for hand that both C and Ti/Ta are soluble in liquid Ni (see Table 9). The carbide phase thus seems to have precipitated from a super-saturated Ni droplet. The eutectic temperatures found from the equilibrium calculations are, however, a bit higher than the temperatures that are working for the synthesis. The fact that the catalyst metal forms a melt at the synthesis temperature may be due to that other

elements also being present, e.g. O and Na, are lowering the eutectic temperature.

Cobalt also works as catalyst metal for whisker growth, but the whisker yield is not as good as when Ni is used. According to calculations with the computer program ThermoCalc, cobalt behaves similarly to nickel and can dissolve both Ti and Ta, but in much lower concentrations (Table 9). The reason why cobalt is not as efficient a catalyst as nickel is unclear but may be due to the lower solubility of Ta (a factor of 8), especially considering that both Ni and Co can form gaseous oxochlorides and chlorides at the synthesis temperature, which may account for transport during the synthesis.

In our studies we have found that iron does not function as a catalyst for Ta_xTi_{1-x}C whiskers, which is most likely due to poisoning of the catalytic effect by formation of Fe₃C as observed by Wokulski and Wokulska^{11,12} in a CVD study of TiC whisker synthesis. However, iron catalyses growth of TiC_yNi_{1-y} whiskers

(see Fig. 8), most likely due to that the presence of nitrogen suppresses the formation of Fe_3C at the synthesis temperature. The whisker diameter is generally larger with Fe than with Ni catalysts, indicating a difference in the surface tension between the droplet and the solid whisker phase. EDS analysis of Fe droplets also gives very low contents of Ti (< 1 at.%). Copper does not work as catalyst metal. It has no solubility for carbon at the synthesis temperature.

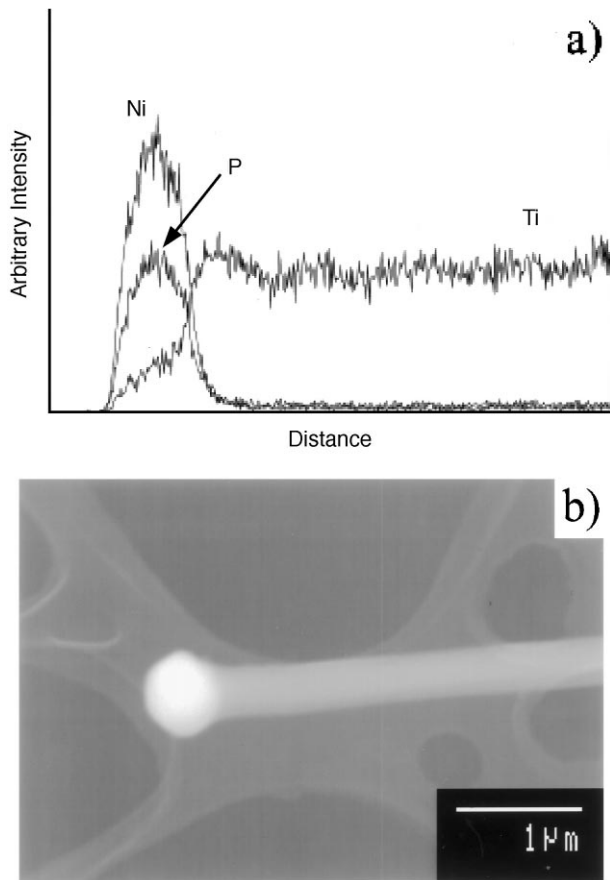


Fig. 7. (a) SEM micrograph of a TiC whisker terminated by a Ni droplet; (b) linescan of the whisker in (a) showing that no Ni is incorporated in its structural framework and that very little Ti remains dissolved in the Ni droplet after solidification. The Ti level is the same as the background level.

Table 9

Composition of the liquid phase at the eutectic temperature to indicate the solubility of the whisker constituents in some catalyst metals tested^a

System	Eutectic temperature (°C)	Composition of the liquid phase at the eutectic temperature
Ni-Ta-C	1347	Ni-6.7 at.% Ta-7.8 at.%C
Ni-Ti-C	1257	Ni-9.0 at.% Ti-5.6 at.%C
Co-Ta-C	1311	Co-0.8 at.% Ta-11.8 at.%C
Co-Ti-C	1284	Co-3.9 at.% Ti-15.5 at.%C
Fe-Ti-C	1151	Fe-0.2 at.% T-17.5 at.%C

^a The eutectic temperature given is the lowest temperature where liquid is in contact with carbide phase, e.g. TiC or TaC.

3.3. Whisker growth

Most observations indicate that whisker growth starts from where nickel is in contact with carbon.² Both SEM and TEM micrographs of interrupted experiments show that whisker growth occasionally also may start on oxide particles that are in contact with both carbon and nickel, giving very short transport distances (see Fig. 9a). Such oxide particles were found in interrupted experiments for all types of whiskers studied. They were detected by giving a distinct EDS peak for oxygen in the SEM. For $\text{Ta}_{0.5}\text{Ti}_{0.5}\text{C}$ the oxide phase found contained both Ta and Ti, which showed it to be a secondary precipitate. Whiskers also frequently terminate in a carbide particle that is actually a part of the same crystal as the whisker itself (see Fig. 9b). Such a carbide particle can be the result of direct carbothermal reduction of oxide remnants.

Some whiskers are thick at one end and much thinner at the other (see Fig. 10). Some narrowing whiskers terminated in a small Ni droplet at the thinnest end. This narrowing may be explained by that the catalyst droplet has been eroded during whisker growth by reacting with chlorine gas, giving a progressively smaller diameter, and since the surface tension balance with the solid whisker must be retained, this also leads to a progressively thinner whisker.

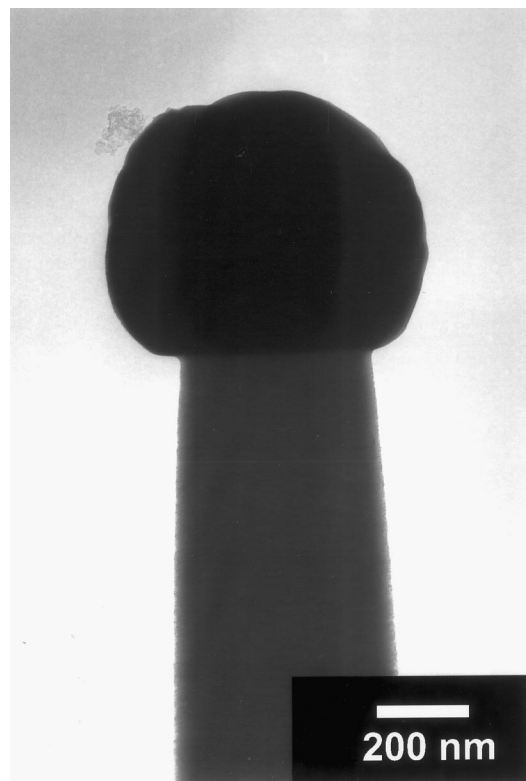
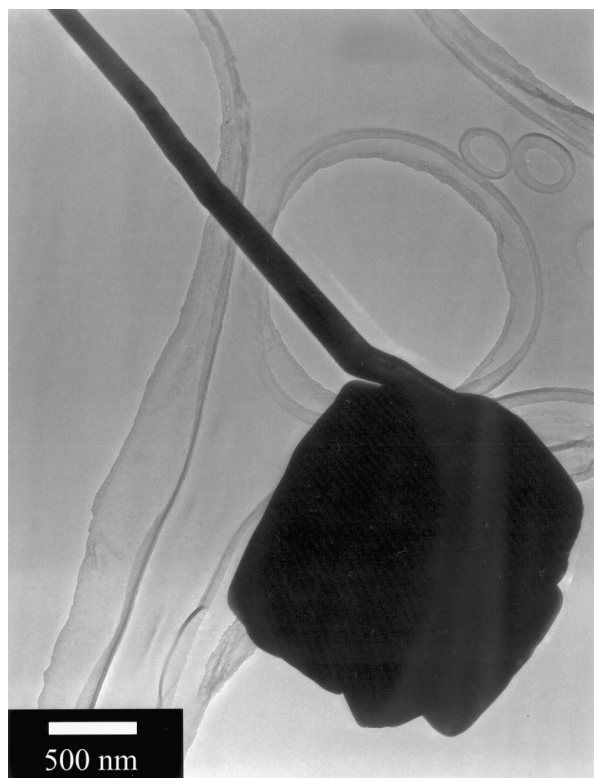


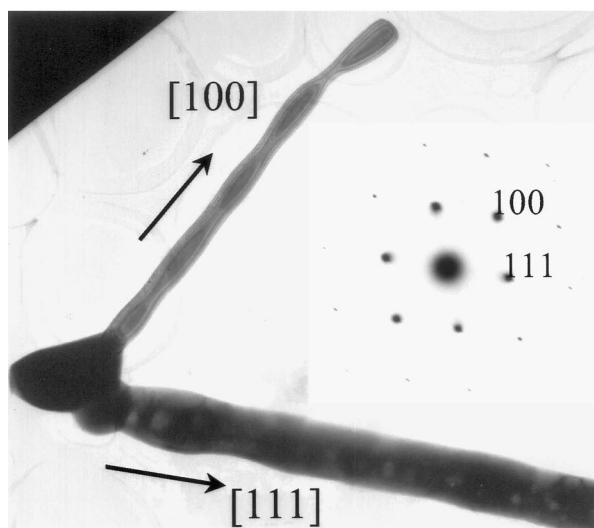
Fig. 8. $\text{TiC}_y\text{Ni}_{1-y}$ whisker terminated by a Fe droplet. Those whiskers generally have larger diameters than those grown with Ni as catalyst metal.

3.3.1. Growth directions

The growth directions of the whiskers were identified by electron diffraction. In TaC whisker samples (synthesised at 1250°C) only the growth direction [100] was found. The TaC whiskers are generally well shaped — straight



(a)



(b)

Fig. 9. (a) Whisker that may have started to grow from the surface of an oxide particle; (b) TiC particle terminating TiC whiskers (1300°C) the whiskers and the particle constitute the same crystal. The carbide particle may be the result of a direct carbothermal reduction of oxide.

and with smooth surfaces. Also in the Ta_{0.5}Ti_{0.5}C sample (1250°C), only the [100] growth direction was found, but the surface shape of these whiskers was quite different. If they are studied at fairly low resolution, or if they are not properly oriented, they may appear to have smooth surfaces, but if the crystals are investigated carefully (aligned perpendicular to the whisker direction) it is clear that the surfaces are wavy. This appearance can be compatible with a screw-like three-dimensional shape of the whisker that was also found for TiC (1275°C) (see Fig. 11a and b). The screw-like shape can be more or less pronounced than in this example.

Studying the appearance of the TiC whiskers as a function of temperature, we found that at low temperatures (around 1150–1200°C) the whiskers were fairly straight. At about 1250°C the screw-like shape were most prominent (see Fig. 12). Samples at moderately high temperatures (1275°C) had screw-like shapes similar to the Ta_{0.5}Ti_{0.5}C (1250°C) sample (see Fig. 13). At 1300°C, the crystals are again straighter, but still not as perfectly shaped as the whiskers grown at lower temperatures (see Fig. 13). At even higher temperatures (1400°C) the shape of the whiskers is again smooth.

The majority (roughly three quarters) of the TiC whiskers obtained at 1250°C were screw-shaped. The growth direction of these “screws” is a crystallographic direction which would be either [100] or [111]. On many occasions there was a sharp bend in the crystals, where the growth changed to another direction, either crystallographically equivalent or the other one possible. For instance, the whisker in Fig. 12b changes growth direction from [100] to [010]. In addition to these screwed whiskers in the TiC (1250°C) sample, slightly thinner, straight whiskers could also be found.

TaC and Ta_xTi_{1-x}C whiskers cannot be prepared in a high yield above about 1250°C. At higher temperatures Ta_xTi_{1-x}C particles are instead formed by a direct carbothermal reduction reaction between the oxide and carbon.

A minor fraction (<5%) of the Ta_xTi_{1-x}C whiskers (1250°C) show a secondary growth of carbide phase out

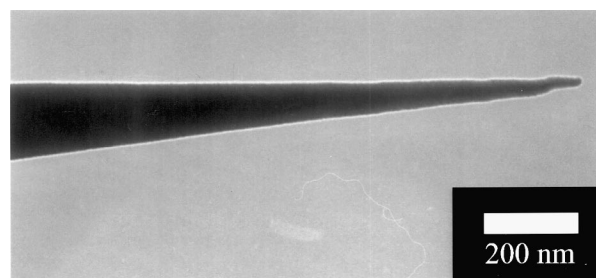
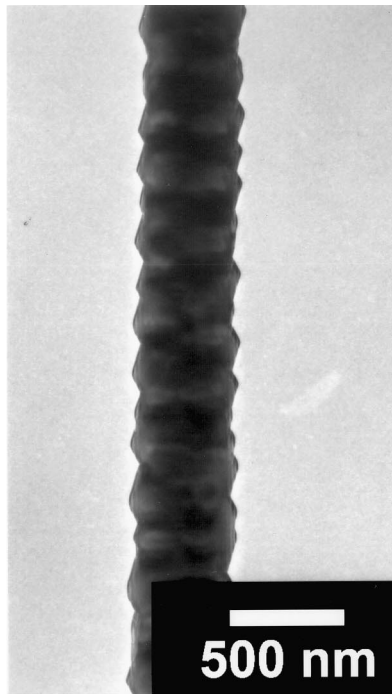
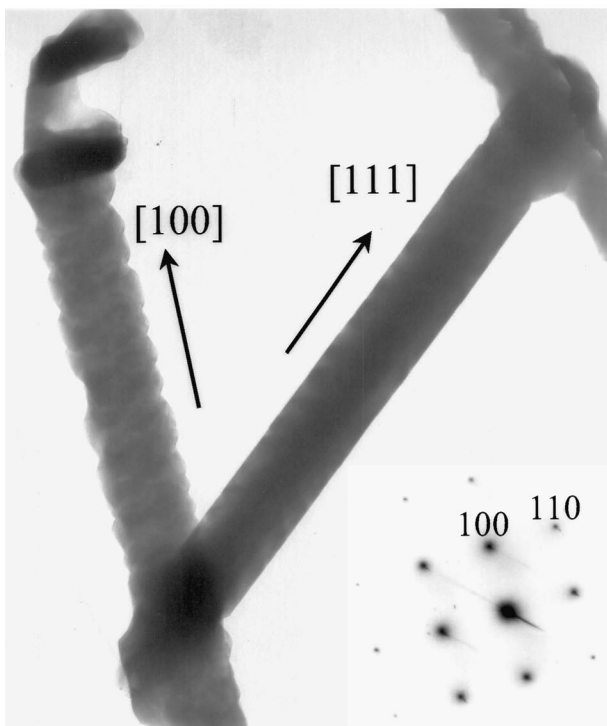


Fig. 10. Narrowing Ta_{0.5}Ti_{0.5}C whisker. At least two mechanisms for the formation of this type of whiskers are possible (see text).

from the whiskers. The whiskers themselves have the same [100] growth direction as the others, and the secondary growth can be described as $\langle 001 \rangle$ terminated slabs with $\langle 110 \rangle$ edges (see Fig. 14). The sec-



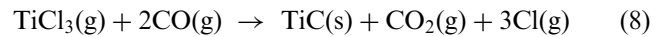
(a)



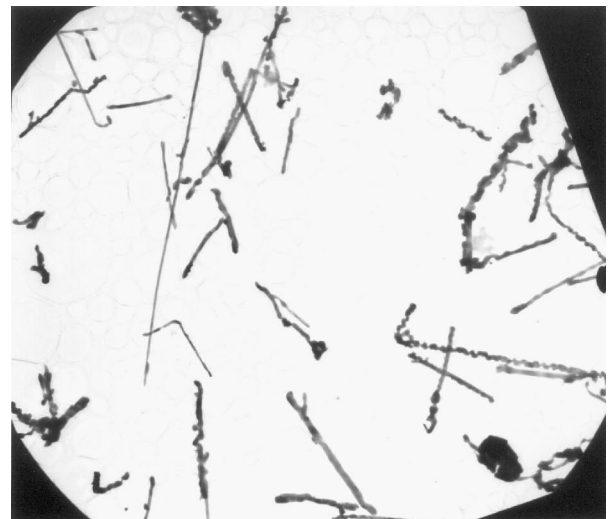
(b)

Fig. 11. (a) TiC (1275°C) whisker with a screw-like shape. $Ta_{0.5}Ti_{0.5}C$ (1250°C) have similar morphology. (b) TiC whiskers (1275°C), the left one grown along [100] and the right one along [111] (note that the right one is not perpendicular to the beam).

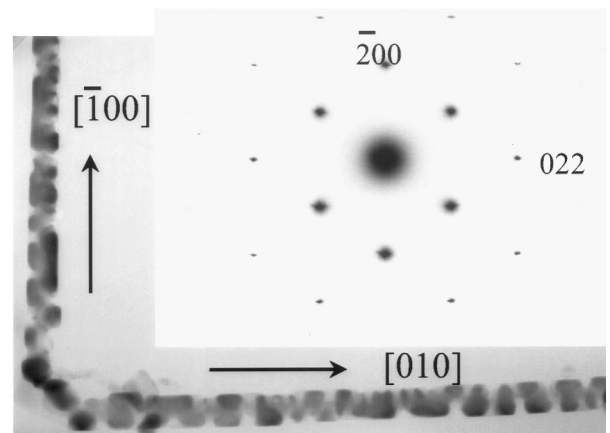
ondary growth is usually flat (the slab thickness is less than the width of the whisker). Viewing crystals like those in Fig. 14 perpendicular to the whisker direction and to the viewing direction of this figure would show a “whisker” with perfect edges. It is obvious that this growth has taken place after the whisker growth was finished. This secondary growth is always more or less pure TiC and may have formed by precipitation directly from the vapour phase.



The $CO_2(g)$ thus produced can then react with carbon to form $CO(g)$



(a)



(b)

Fig. 12. (a) Overview of TiC whiskers (1250°C) showing the frequent screw-like appearance; (b) close up of one screw-like whisker changing growth direction. Growth started along [100] and continued along [010].

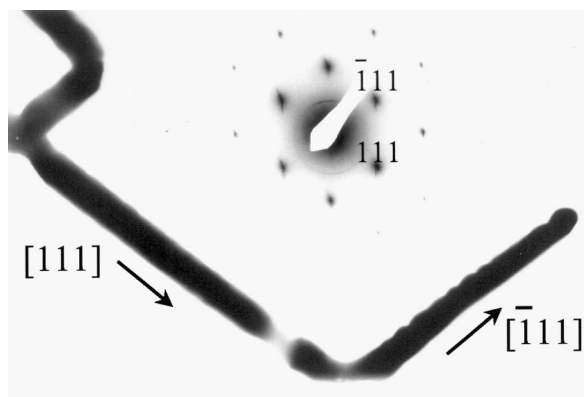


Fig. 13. TiC (1300°C) whisker showing a change in growth direction from [111] to $[-111]$.

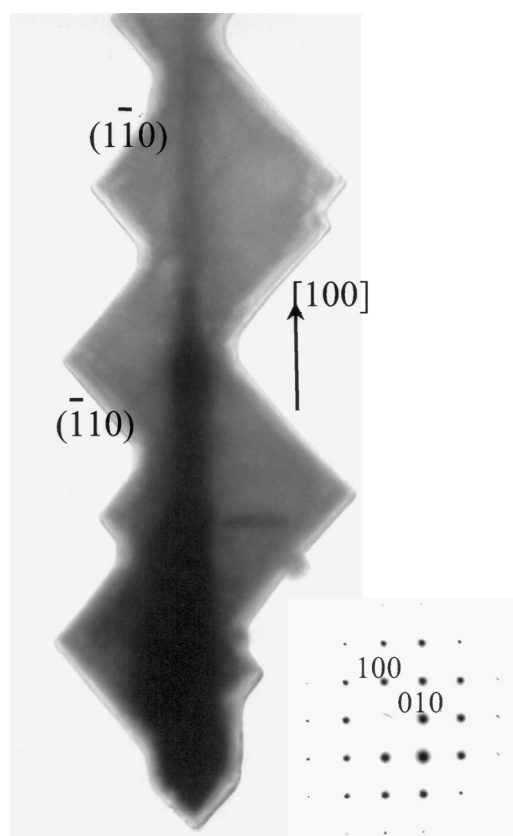


Fig. 14. A minor fraction of the $Ta_{0.5}Ti_{0.5}C$ whiskers (<5%) show a secondary growth of carbide phase in the form of protruding flakes. The [100] growth direction is marked as well as two of the {110} terminating the secondary grown flakes. This secondary growth may have formed by precipitation directly from the vapour phase.

4. Conclusions

The growth of TaC, TiC and $Ta_xTi_{1-x}C$ whiskers has been studied in some detail. The whiskers have been synthesised via a vapour–liquid–solid (VLS) growth mechanism in the temperature range 1220–1400°C. The starting materials were Ta_2O_5 , TiO_2 , C, NaCl, and a

catalyst metal (Ni, Co, and Fe have been tested). The main reaction during synthesis is carbothermal reduction of Ta_2O_5 and TiO_2 . NaCl was added to form oxochlorides and chlorides of Ta and Ti, accomplishing the transport to the catalyst metal. The syntheses were made in a protecting Ar atmosphere.

From experiments interrupted after different times at the synthesis temperature, it is clear that sodium tantalates form as intermediate products, whereas sodium titanates cannot be identified. The reduction of TiO_2 to TiC goes via reduced oxides (e.g. Ti_2O_3 and Ti_3O_5) without formation of sodium titanates.

Experimental observations and phase diagram information show that only metals that are able to dissolve the elements building up the whiskers work as catalysts. Catalyst droplets terminating whiskers in different stages of erosion were found, indicating that the catalyst metal is recirculated during synthesis.

Whisker growth start either from a catalyst droplet in contact with carbon or from an oxide particle in contact with both the catalyst metal and carbon. For TaC and $Ta_xTi_{1-x}C$ the only growth direction observed is [100], whereas TiC may grow either along [100] or along [111]. TaC whiskers show smooth surfaces, but $Ta_xTi_{1-x}C$ and TiC have more wavy surfaces. This appearance can be compatible with a screw-like three-dimensional shape of the whiskers. The shape of the TiC whiskers is temperature-dependent: those synthesised at 1150–1200°C or 1400°C have smooth surfaces whereas those synthesised in the 1250–1300°C range have the screw-like appearance.

This work was in part supported financially by the Swedish Foundation for Strategic Research (SSF) and by the Swedish Research Council for Engineering Sciences (TFR).

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