Journal of the European Ceramic Society 18 (1998) 1513–1519

PII: S0955-2219(98)00076-4
0955-2219/98/$—see front matter

Synthesis and Characterisation of $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ Whiskers

Niklas Ahlén, Mats Johnsson* and Mats Nygren

Department of Inorganic Chemistry, Stockholm University, S-106 91 Stockholm, Sweden

(Received 12 September 1997; accepted 16 February 1998)

Abstract

$Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers have been synthesised via a carbothermal vapour–liquid–solid (VLS) growth mechanism in the temperature region 1250–1400°C, in argon and nitrogen atmospheres, respectively. The starting materials consisted of Ta_2O_5, TiO_2, C, Ni and NaCl. Carbon was added to reduce the oxides, and nickel to catalyse the whisker growth. NaCl was used as a source of Cl for vapour phase transportation of Ta-oxochlorides and Ti-chlorides to the catalyst. The yield of whiskers was about 80 vol%, with a length of 10–30 μm and a diameter varying from about 0·25 μm for TaC to about 0·55 μm for TiC. The whiskers were straight and had smooth surfaces. TEM studies showed that they were monocrystalline. The average x*-value of the formed whiskers could be controlled by varying the weighed-in ratio of Ta_2O_5 to TiO_2 and the synthesis temperature. The maximum nitrogen content decreased with increasing* x *value in $Ta_xTi_{1-x}C_yN_{1-y}$. The residual oxygen content in the whiskers decreased with increasing synthesis temperature and increasing* x*-value. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Whiskers of transition metal carbides, carbonitrides and nitrides are highly interesting as reinforcing materials in ceramics for cutting tools and other wear-resistant applications. In this article we present a preparation route for $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers. The method used is based on a carbothermal vapour–liquid–solid (VLS) growth mechanism which has been described in some detail in three recent articles concerning the synthesis of TaC, TiC and TiN_xC_{1-x} whiskers.[1–3] By changing the metal and/or carbon and nitrogen content in the whiskers, the thermal expansion coefficient, chemical properties and the diameter of the whiskers can be varied, which in turn ought to increase the usefulness of these whiskers as reinforcing materials. The solid solutions $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ have NaCl-type structure with the *a*-axis ranging from 4·4547 Å for TaC to 4·327 Å for TiC, while that of TiN is 4·242 Å.

The VLS growth mechanism involves a vapour phase transport of one or more of the reacting species to a droplet of a metal catalyst where they are decomposed and the components dissolved in the catalyst, and the desired whisker grows out of the droplet. The VLS-mechanism is only operative at temperatures exceeding the melting temperature of the catalyst, and its melting point thus constitutes the lower temperature limit for the whisker synthesis. The catalyst must also be able to dissolve the whisker components, i.e. Ta, Ti, C, and N in our case, lowering its melting point. Nickel has proved to be a good catalyst and is known to dissolve Ta, Ti, C, and N.[4] For successful whisker growth, appropriate gas species have to be formed and transported to the catalyst at a sufficient rate. Equilibrium calculations[13] show that Ta and Ti are transported mainly as $TaO_xCl_y(g)$ and $TiCl_y(g)$ in our experiments. The overall chemical reaction is a straightforward carbothermal reduction/nitridation of Ta_2O_5 and TiO_2, respectively, but the reactions that actually take place are much more difficult to predict and thus also to study. According to the experience obtained in connection with preparing TiC, TaC and other transition metal carbide and carbonitride whiskers, the following or very similar reactions most probably represent the actual mechanism. For simplicity the formulas below are not scaled against each other.

Formation of Ti- and Ta-gas species using Cl as volatilising element.

*To whom correspondence should be addressed.

$$NaCl(l) \rightarrow Na(g) + Cl(g) \quad (1)$$

$$TiO_2(s) + 3Cl(g) + 2C(s) \rightarrow TiCl_3(g) + 2CO(g) \quad (2)$$

$$Ta_2O_5(s) + 6Cl(g) + 3C(s) \rightarrow 2TaOCl_3(g) + 3CO(g) \quad (3)$$

The following reactions are expected to occur at the catalyst (Ni–C, Ni–N–C, Ni–Ti–N–C, etc., denote that C, N and C, Ti, N and C, etc., are dissolved in the Ni-catalyst).

$$C(s) + Ni(s) \rightarrow Ni-C(l) \quad (4)$$

$$1/2N_2(g) + Ni-C(l) \rightarrow Ni-N-C(l) \quad (5)$$

$$TiCl_3(g) + Ni-N-C(l) \rightarrow Ni-Ti-N-C(l) + 3Cl(g) \quad (6)$$

$$TaOCl_3(g) + C(s) + Ni-Ti-N-C(l) \rightarrow Ni-Ta-Ti-N-C(l) + CO(g) + 3Cl(g) \quad (7)$$

$$Ni-Ta-Ti-N-C(l) \rightarrow Ta_xTi_{1-x}C_yN_{1-y}(s) + Ni(s) \quad (8)$$

If $Ta_xTi_{1-x}C$ whiskers are to be synthesised, the reactions given above have to be performed in argon instead of nitrogen.

2 Experimental

2.1 Precursor materials

The starting materials used in the preparation of $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers are listed in Table 1. The precursor materials are the same as those which gave the highest yield of TiC, TiN_xC_{1-x}, and TaC whiskers.[1–3] The carbon source used contained 21 wt% volatile components which are burned off during the heating-up period. The choice of carbon source has a strong influence on the whisker yield. It has thus previously been shown that carbon black with a volatile part retains its fluffy consistency after the 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. The weighed-in molar ratio of TiO_2/Ta_2O_5 can be varied in order to obtain whiskers with different x-values. The used molar ratios of the different precursor materials in relation to the Ta_2O_5 and TiO_2 content for some selected $Ta_xTi_{1-x}C$ compositions with $0 \leq x \leq 1$ are listed in Table 2.

Table 1. Precursor materials used

Substance	*Purity (wt%)*	*Manufacturer*	*Particle size*	*Comment*
Ta_2O_5	99·9	Starck	≈1 μm	Ceramic grade
TiO_2	99·9	Aldrich	0·2–0·6 μm	
C	—	Degussa FW200	13 nm	Channel black (containing 21 wt% volatiles)
NaCl	99·5	Akzo	< 5 μm	
Ni	99·9	Cerac	325 mesh	

2.2 Synthesis route

The starting materials were homogenously mixed in a blender. Portions of about 10–20 g were placed in a graphite crucible covered with a lid having a number of holes to allow a controlled gas exchange between the reactor chamber and the surrounding atmosphere. The mixture was then heated in a graphite furnace (Thermal Technology) at a rate of $1000°C\,h^{-1}$ to the synthesis temperature and was held there for 4 h, in an Ar or N_2 atmosphere depending on whether $Ta_xTi_{1-x}C$ or $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers were to be produced. All experiments were conducted at atmospheric pressure and at synthesis temperatures in the range 1250–1400°C. Previous studies have revealed the optimum temperature for growth of TaC whiskers to be 1250°C[3] and for TiC whiskers 1400°C.[1] For $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers with $0 < x < 1$ the optimum yield was found between those temperatures.

2.3 Characterisation

The morphology and composition of the $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers were investigated with a light microscope and a scanning electron microscope (SEM, JEOL 880) equipped with an energy-dispersive spectrometer (EDS, LINK *ISIS*). The Ta and Ti contents were determined by taking an average of 100 EDS measurements from different whiskers for each nominal composition. The whisker product was blended before analysing to ensure a random distribution.

Transmission electron microscopy (TEM, JEM-2010) was used for detailed studies of the surface morphology of whiskers and to verify their monocrystalline nature.

The formed phases were characterised by their X-ray powder diffraction patterns (XRD) obtained in a Guinier–Hägg focusing camera with Cu-$K_{\alpha 1}$ radiation ($\lambda = 1{\cdot}5405981$ Å). Finely powdered silicon was used as internal standard. The recorded

Table 2. Molar ratios in relation to the sum of Ta_2O_5 and TiO_2, and weighed-in masses within brackets, for some selected precursor materials used for preparation of whiskers of the compositions $Ta_xTi_{1-x}C$ with $0 \leq x \leq 1$

Precursor	x = 1	x = 0·85	x = 0·5	x = 0·15	x = 0
Ta_2O_5	1 (60·00 g)	0·425 (50·00 g)	0·25 (30·00 g)	0·075 (9·76 g)	—
TiO_2	—	0·15 (3·19 g)	0·5 (10·85 g)	0·85 (20·00 g)	1 (20·00 g)
C	7·2 (14·86 g)	3·54 (11·32 g)	3·4 (14·24 g)	3·26 (11·53 g)	3·2 (12·56 g)
NaCl	0·5 (3·97 g)	0·288 (4·48 g)	0·375 (5·95 g)	0·4625 (7·96 g)	0·5 (7·31 g)
Ni	0·05 (0·40 g)	0·0288 (0·45 g)	0·0375 (0·60 g)	0·0463 (0·80 g)	0·05 (0·73 g)

films were evaluated in an automatic film scanner.[5] The XRD peaks were identified by matching them to JCPDF data base cards of TaC (card no. 35-801), TiC (32-1383) and TiN (38-1420).

The C, N, and O contents of the prepared materials were analysed by a standard combustion technique. The overall Ti and Ta contents were determined from spectrometric data and plasma emission lines, respectively.

The average whisker diameter was determined from 100 arbitrarily chosen whiskers depicted in SEM-micrographs.

3 Results and Discussion

3.1 The $Ta_xTi_{1-x}C$ whisker product

The whisker yield is dependent on both the synthesis temperature and the composition. Generally temperatures below 1200°C resulted in a low whisker yield and also somewhat curved whiskers. Temperatures higher than 1300°C lowered the whisker yield except for compositions close to TiC, which is in agreement with our previous findings concerning the optimum synthesis temperature for TiC and TaC-whiskers, respectively.[1–3] The highest whisker yield was obtained at 1250°C for $Ta_xTi_{1-x}C$ with $0 \leq x \leq 1$. For the $Ta_{0.5}Ti_{0.5}C$ composition we obtained a whisker yield of ~80%, while carbide particles, having a slightly different metal content than the formed whiskers (see below), constituted the remaining 20%. The whisker diameter was 0·3–0·5 μm and the length 10–30 μm as seen in Fig. 1. The whiskers mainly showed smooth surfaces as shown by the TEM micrograph in Fig. 2(a) and the monocrystalline nature of the whisker is verified by its electron diffraction pattern in Fig. 2(b). Some whiskers had protuberances on their surfaces [see Fig. 2(c)], of unknown origin; one possible explanation being that growth in new active directions has ceased due to lack of Ni and/or C.

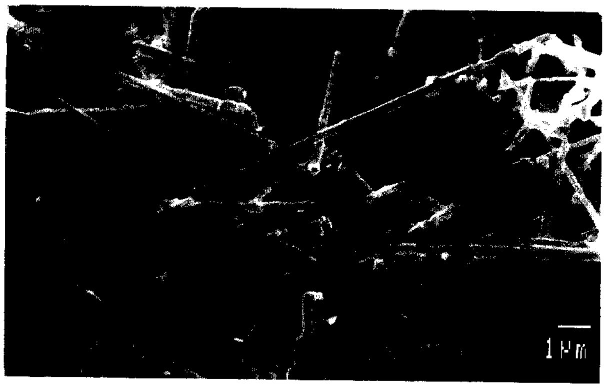

Fig. 1. An SEM micrograph of $Ta_{0.5}Ti_{0.5}C$ whiskers prepared at 1250°C.

3.1.1 Characterisation of obtained $Ta_xTi_{1-x}C$ whiskers

The results of overall chemical analysis and EDS-analysis of whiskers prepared at 1250 and 1400°C are given in Table 3. These measurements thus yield information on both the overall composition of the prepared samples and on the metal content of individual whiskers.

The bulk analyses of Ta and Ti are in good agreement with the nominal composition for all samples (see Table 3). It is well known that oxygen can replace carbon in TiC and TaC. The oxygen content in the whiskers prepared at 1250 and 1400°C decreased with increasing Ta-content. The oxygen content was also substantially lower in the whiskers prepared at 1400°C than in those prepared at 1250°C. However, increasing the synthesis temperature reduced the whisker yield, i.e. there is a balance between whisker yield and residual oxygen content.

A plot of the results from the EDS-analysis of whiskers from three different $Ta_xTi_{1-x}C$ compositions is given in Fig. 3. Element mapping of Ta and Ti indicated that those elements are homogeneously distributed within the whiskers. The x-values obtained from the EDS-studies of whiskers are higher than the nominal values of the starting materials and thus also higher than those obtained from the bulk chemical analysis, and this tendency is more pronounced for whiskers prepared at 1250°C with low nominal x-values than for those with high x-values, as seen in Fig. 4. Thermodynamic calculations with the program package HSC[6] have shown that the formation temperature of TaC is substantially lower than 1250°C, while TiC just barely forms at this temperature (see Fig. 5). This observation might explain why especially the whiskers prepared at 1250°C from mixtures having high nominal x-values have higher x-values than expected.

Figures 4 and 5 suggest that the whisker products essentially are monomodal with respect to

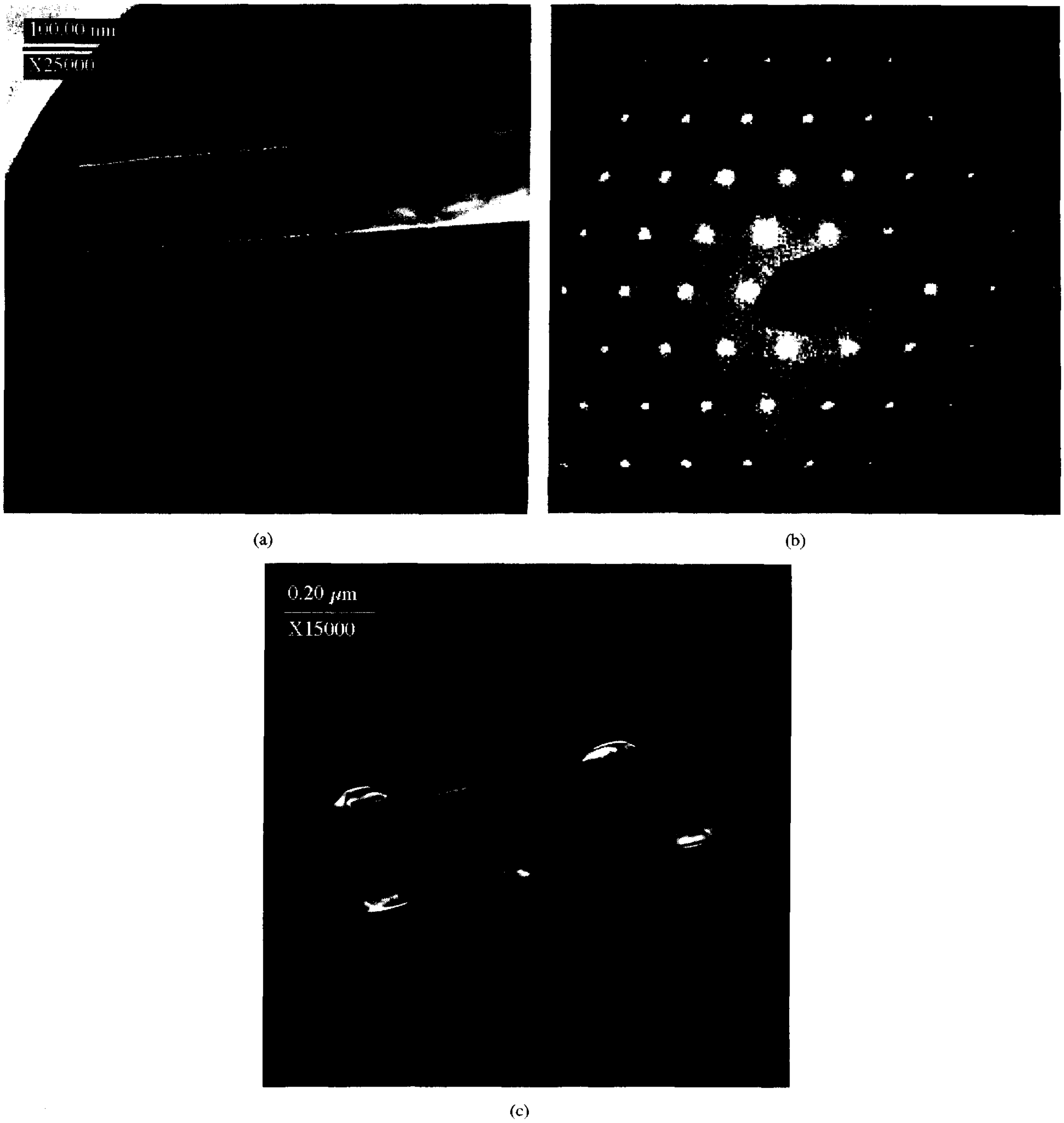

Fig. 2. (a) A TEM dark-field image of one whisker with uniform diameter and smooth surfaces; (b) diffraction pattern obtained from the same whisker; (c) dark-field image of a whisker with protuberances on the surface.

Table 3. Chemical and EDS element analysis of prepared $Ta_xTi_{1-x}C$ samples and of individual whiskers, respectively. The excess carbon used (see text) was not removed prior to the chemical analysis

Nominal composition	*Synthesis temperature (°C)*	*Ta (wt%)*	*Ti (wt%)*	*C (wt%)*	*O (wt%)*	*x-value Chem. anal.*	*x-value EDS anal.*
$Ta_{0.95}Ti_{0.05}C$	1250	88	1·5	7·2	0·11	0·94	0·96 ± 0·03
$Ta_{0.85}Ti_{0.15}C$	1250	83	4·2	7·7	0·17	0·84	—
$Ta_{0.8}Ti_{0.2}C$	1250	84	5·5	7·8	0·27	0·80	0·86 ± 0·08
$Ta_{0.67}Ti_{0.33}C$	1250	77	10·1	8·3	1·32	0·67	0·7 ± 0·05
$Ta_{0.5}Ti_{0.5}C$	1250	65	17·8	10·5	1·08	0·49	0·58 ± 0·08
$Ta_{0.33}Ti_{0.67}C$	1250	53	27·8	13·2	2·27	0·34	0·43 ± 0·09
$Ta_{0.15}Ti_{0.85}C$	1250	29	44·0	17·4	4·3	0·15	0·31 ± 0·14
$Ta_{0.05}Ti_{0.95}C$	1250	11	56·2	21·0	7·0	0·049	0·3 ± 0·14
$Ta_{0.95}Ti_{0.05}C$	1400	89	1·3	6·98	0·04	0·95	0·96 ± 0·01
$Ta_{0.85}Ti_{0.15}C$	1400	85	4·0	7·7	0·04	0·85	—
$Ta_{0.8}Ti_{0.2}C$	1400	84	5·6	7·8	0·06	0·80	0·86 ± 0·06
$Ta_{0.67}Ti_{0.33}C$	1400	79	10·3	7·8	0·17	0·67	0·77 ± 0·08
$Ta_{0.5}Ti_{0.5}C$	1400	66	18·0	10·3	0·4	0·49	0·58 ± 0·06
$Ta_{0.33}Ti_{0.67}C$	1400	54	28·7	12·4	0·78	0·33	0·45 ± 0·07
$Ta_{0.15}Ti_{0.85}C$	1400	—	—	—	—	—	0·25 ± 0·14
$Ta_{0.05}Ti_{0.95}C$	1400	12	59·6	19·8	3·8	0·05	0·051 ± 0·07

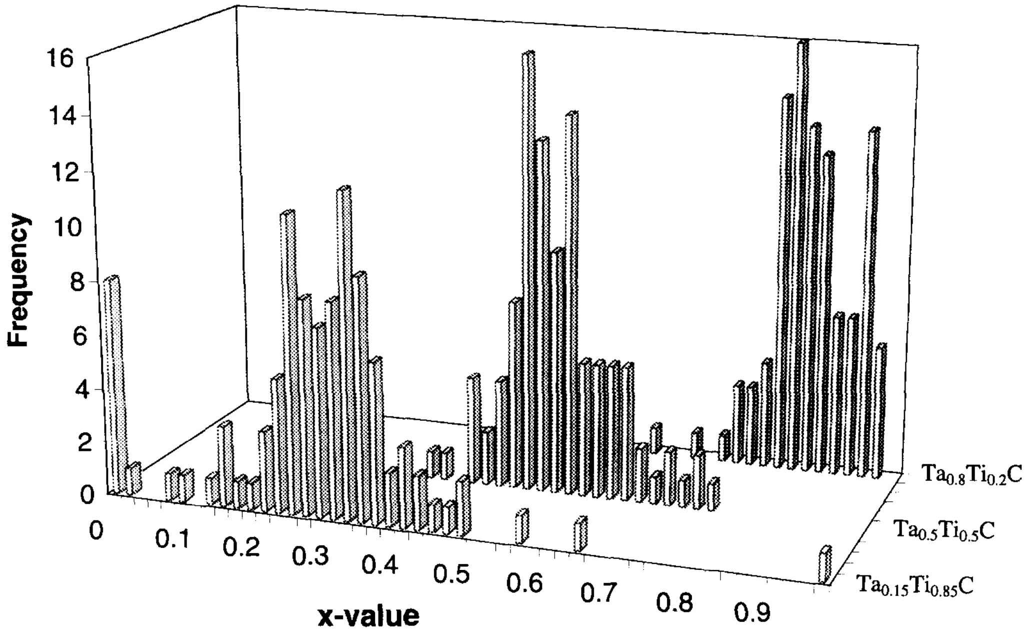

Fig. 3. Typical spread in the x-value of individual whiskers in three $Ta_xTi_{1-x}C$ batches with different nominal compositions. Within each batch 100 whiskers have been analysed with respect to their Ta and Ti contents. Each bar represents a step length of 0·02 in x.

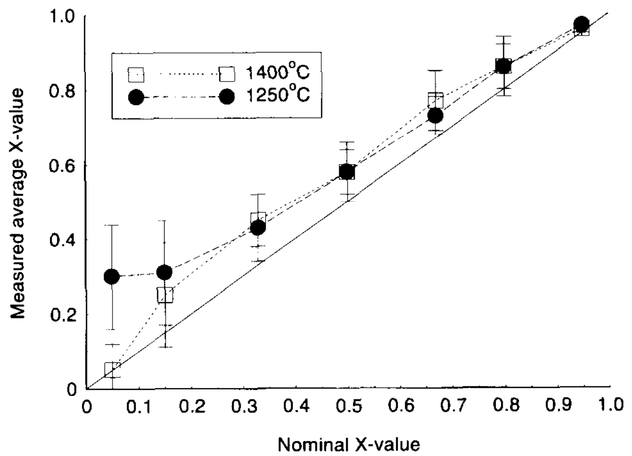

Fig. 4. EDS-measured x-value plotted versus the nominal one for $Ta_xTi_{1-x}C$ whiskers prepared at 1250 and 1400°C.

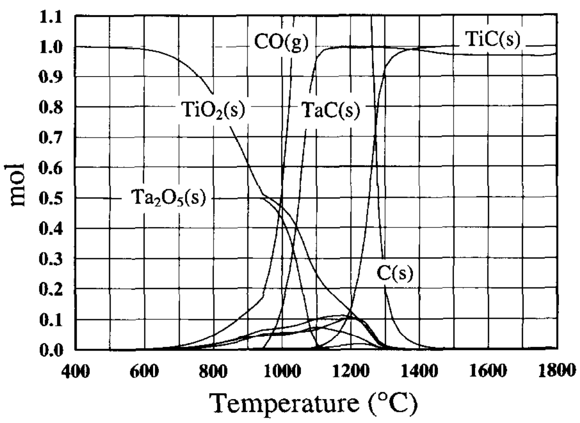

Fig. 5. Equilibrium calculation of phase stability of TaC and TiC for a starting mixture of 0·5 mol Ta_2O_5 + 1 mol TiO_2 + 0·5 mol NaCl + 6·5 mol C + 0·05 mol Ni + 3 mol Ar.

their x-value. However, the XRD studies of the bulk products indicate actually that all products with $0 < x < 1$ have a bimodal composition distribution. The normalised (200) XRD diffraction peak for $Ta_xTi_{1-x}C$ whiskers with nominal x-values of 0, 0·15 and 1·0 is shown in Fig. 6. The intensity of the TaC peak is substantially higher than that of TiC because the former has a much higher X-ray scattering power. The $Ta_{0\cdot15}Ti_{0\cdot85}C$ product yields two peaks, i.e. the sample seems to be bimodal with respect to its composition. This can be explained as follows. Because the whiskers have a higher Ta-content than the nominal one, the formed particles must have a lower than nominal content, since the chemical analysis of overall Ta and Ti content was in agreement with the nominal composition. All diffraction patterns of the whisker products with $0 < x < 1$ contained doublets, but the splitting of

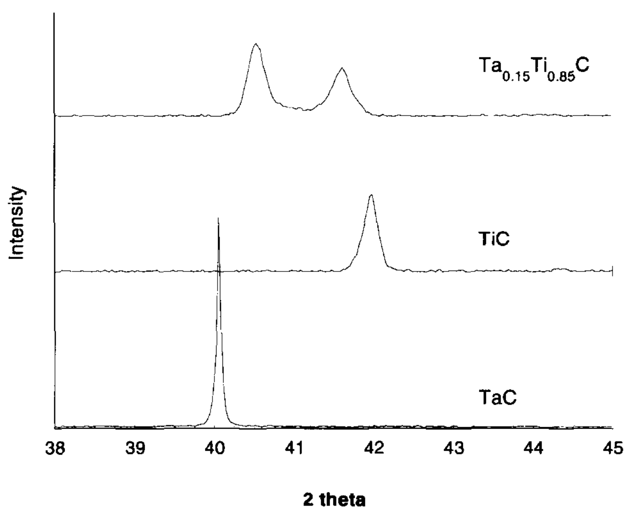

Fig. 6. The (200) X-ray diffraction peaks obtained for samples of the nominal compositions TaC, TiC and $Ta_{0\cdot15}Ti_{0\cdot85}C$.

the reflections decreased with increasing x-value, in agreement with the observation that the difference between the nominal and observed x-value decreased with increasing x (see Fig. 4). It should be possible to determine the x-values of the two fractions by applying Vegard's law, i.e. using the linear relation between the lattice parameters and x in $Ta_xTi_{1-x}C$. However, we have refrained from doing so, because these values must have large errors due to: (i) the oxygen content of the whiskers varies with x in $Ta_xTi_{1-x}C$ (see above), and it is well known that the lattice parameter also varies with the oxygen content of the product; (ii) the X-ray reflections for the $Ta_xTi_{1-x}C$ products being broad, which in turn makes it difficult to obtain lattice parameters of sufficient accuracy.

3.1.2 Influence of composition on the whisker diameter

The average whisker diameter was found to vary with x in $Ta_xTi_{1-x}C$ from (0·25 μm for TaC to $\approx$0·55 μm for TiC (see Fig. 7), while the whisker length was confined to 10–30 μm in all compositions. We do not know why all batches contain whiskers with similar diameters or why the whisker diameter varies with the metal content. If we replace the Ni catalyst by Co or Fe we normally obtain substantially smaller whisker yields, but we do obtain whiskers with somewhat different diameters whereas the whisker length remains almost constant. The size and surface tension of the droplet of the catalyst must most probably play a role in this process. The variation of the whisker diameter with the composition might thus be related to a variation of surface tension of the catalyst droplet as different amounts of Ta and Ti are dissolved in the droplet for different overall compositions. On the other hand, we have not observed any variation of the whisker diameters with y for fixed x-values in $Ta_xTi_{1-x}C_yN_{1-y}$.

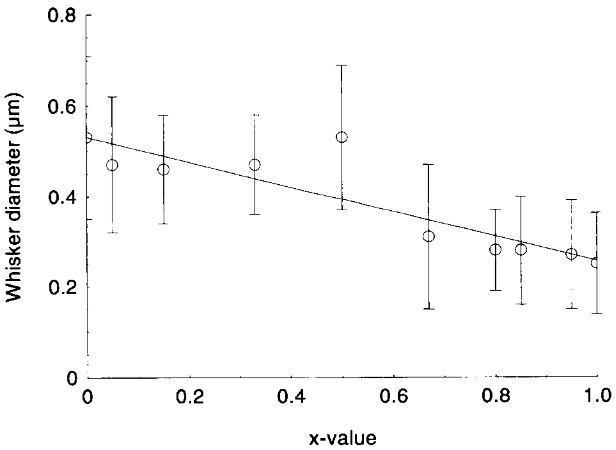

Fig. 7. A plot of the diameter as a function of the nominal composition of $Ta_xTi_{1-x}C$ whiskers.

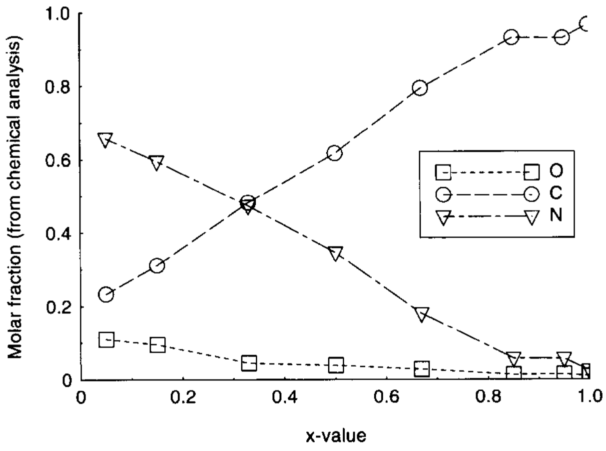

Fig. 8. Carbon, nitrogen and oxygen content in $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers prepared at 1250°C plotted as function of the nominal x-value. The excess added carbon has been removed before the element analysis was performed.

3.2 Characterisation of obtained $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers

Using the same overall compositions as above, whiskers of the composition $Ta_xTi_{1-x}C_yN_{1-y}$ have been prepared at 1250°C. After removal of excess carbon, the C, N and oxygen content in these whiskers was determined and is plotted versus the overall x-value in Fig. 8. The nitrogen and carbon content varied significantly with the x-value, i.e. the Ti-rich whiskers had the highest nitrogen content and lowest carbon content, and vice versa for the Ta-rich whiskers. These observations are consistent with our previous findings that TaN does not form in the presence of carbon at 1250°C[3] and that the maximum nitrogen content in TiN_yC_{1-y} whiskers at 1250°C is around $y = 0{\cdot}7$.[2] The oxygen content in the whisker product decreased also with increasing x-value. It can also be noted that the Ta/Ti ratio in the $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers of the same nominal composition was the same, i.e. EDS-analysis of whiskers with an overall composition of $Ta_{0{\cdot}5}Ti_{0{\cdot}5}C_yN_{1-y}$ yielded an average x-value of 0·57 ± 0·09 while for $Ta_{0{\cdot}5}Ti_{0{\cdot}5}C$ it was found to be 0·58 ± 0·08.

4 Conclusions

Whiskers of the compositions $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ have been prepared in yields of 80 vol% at 1250°C via a carbothermal VLS-growth mechanism. The whisker diameter varies with the Ta/Ti content from ~0·25 μm for TaC to ~0·55 μm for TiC, while all whiskers had a length in the range 10–30 μm, independent of the Ta/Ti content. The whiskers exhibited smooth surfaces, and TEM diffraction patterns indicate that they were monocrystalline. The temperature range for whisker growth was found to be 1250–1400°C. The residual oxygen content decreased with increasing synthesis temperature, but the tendency to form particles instead of whiskers increased. For a given nominal x-value one obtain whiskers which have somewhat different x-values. Typically the spread in the x-values at 1250°C is of the order $\pm 10\%$ of the average one for x-values larger than 0·5 while for $x < 0{\cdot}25$ the spread is somewhat larger. Increasing synthesis temperatures seem to give more confined compositions. The nitrogen content of the $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers is strongly dependent on the x-value, i.e. low x-values yield whiskers with low y-values and vice versa.

Acknowledgements

The authors are grateful to Dr Viveka Alfredsson for her assistance with the TEM studies. This work was financially supported by the Swedish Board for Industrial and Technical Development.

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