Oxidation behaviour of $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers

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Abstract

$Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) whiskers have been oxidised under non-isothermal as well as isothermal conditions. The non-isothermal oxidation experiments were carried out in a combined thermogravimetric – differential thermal analysis set-up (TG-DTA), using oxygen atmosphere, with a heating rate of $5°C/min$. It was found that the oxidation onset temperature (T_{on}) increased with increasing x-value within the temperature range 375–550°C for both $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers and also that T_{on} is higher for carbonitrides compared to carbides. Scanning and transmission electron microscopy studies (SEM and TEM) showed that whiskers with a diameter exceeding 0.3 µm were split into two halves along the length of the whisker when oxidised, whereas whiskers with a diameter less than 0.3 µm retained their morphology after oxidation. Isothermal oxidation experiments were performed with $Ta_xTi_{1-x}C$ whiskers in the temperature range 400–1200°C, and it was found that the size of TiO_2 particles formed from mixed transition-metal carbide precursors was substantially smaller compared to the particle size resulting from oxidation of TiC. However, the size of Ta_2O_5 particles were found to be small and of the same size independently if TaC or $Ta_xTi_{1-x}C$ were oxidised. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tantalum carbide (TaC), titanium carbide (TiC) and titanium nitride (TiN) all have material characteristics such as high melting point, favourable mechanical properties and thermodynamic stability that makes them interesting as engineering materials, i.e. as reinforcement materials in high-performance ceramic composites. Characteristic properties such as the thermal expansion coefficient can then be tailored to match the matrix material by varying the chemical composition as outlined by the formula $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$). The oxidation behaviour of those materials is therefore impor-

tant to study, and oxidation studies have been published for several transition metal carbides and nitrides, but there is only one report on the oxidation behaviour of mixed transition-metal carbides [1].

There are investigations of the oxidation behaviour of TiN in the form of thin films [2–4] and compacted monoliths [5], and as composites containing TiN [5–6] as the major component or added as a reinforcing agent. Tampieri et al. [6] have studied the oxidation of Al_2O_3-TiN composites and found a parabolic rate-law behaviour for temperatures exceeding 900°C, while an almost constant oxidation rate was observed for $T < 900°C$ which in turn was ascribed to grain boundary reactions. Gogotsi et al. [5] have performed corresponding studies of Al_2O_3-TiN, Si_3N_4-TiN, AlN-TiN and AlON-TiN composites and found that all the

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oxidation curves could be fitted to a parabolic rate law, independently of the temperature at which the experiments were performed. Shimada and Kozeki [7–8] studied the oxidation behaviour of TiC particles and found that the oxidation process was diffusion controlled. Based on isothermal and non-isothermal oxidation experiments, they divided the process into four steps, I–IV. Step I covered the α-range 0–0.20 (α = degree of oxidation), and within this range a Ti-oxocarbide phase is formed; step II and III occur in the range α = 0.20–0.60 and involve the formation of reduced Ti oxides. The transition from step II to step III could only be discerned in isothermal experiments to take place in the α-range 0.30–0.40. During step IV (0.6 < α ≤ 1.00) TiO_2 is produced in the form of anatase or, at higher temperatures, as rutile. The differential thermal analysis studies performed by Shimada [8] showed a rather broad exothermal DTA peak around 500°C when TiC was exposed to a low partial pressure of oxygen (pO_2); and this peak sharpened and shifted slightly towards lower temperatures with increasing pO_2. At pO_2 ≥ 15 kPa a second and comparatively sharp DTA peak appeared at a temperature about 30°C higher than the first one. The second peak broadened and became less intense with increasing pO_2. Mass spectroscopy measurements showed that CO_2 was evolved in the temperature region where the exothermal DTA peaks appeared.

Voitovich et al. [1] studied the oxidation of hot-pressed TiC compacts and found a parabolic rate-law behaviour. The same authors also oxidised compacts of the composition $Ti_{1−x−y}Zr_xHf_yC$ and found them to exhibit a lower oxidation resistance than pure TiC. They suggest that this is due to the fact that no protecting layer of TiO_2 is formed on the solid solution samples. The oxidation of hot isostatically pressed TaC is reported to proceed by an interfacial reaction [9].

Tampieri et al. [6] oxidised Al_2O_3-TiC composites and reported that the oxidation initially is governed by grain-boundary reactions, but when a continuous rutile layer is formed then the oxidation kinetics change from almost linear to parabolic.

As described above, most oxidation studies of TaC, TiC and TiN have been performed under isothermal conditions, using compacted monoliths of the materials or using composites with particles of TaC, TiC and TiN, respectively, added as a reinforcing material. Our study now presents the non-isothermal oxidation behaviour of mixed transition-metal carbide, $Ta_xTi_{1−x}C$, and carbonitride, $Ta_xTi_{1−x}C_yN_{1−y}$, whiskers with 0 ≤ x ≤ 1, and 0 ≤ y ≤ 1, together with some isothermal oxidation studies of $Ta_xTi_{1−x}C$ whiskers yielding information concerning the phase and morphology evolution with temperature and time.

We have recently synthesised $Ta_xTi_{1−x}C$ and $Ta_xTi_{1−x}C_yN_{1−y}$ whiskers via a carbothermal vapour–liquid–solid (VLS) growth mechanism [10]. The reactions were carried out at 1250°C in argon and nitrogen, 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 source of Cl for vapour-phase transport of Ta as oxochloride and Ti as chloride to the Ni catalyst. Whiskers were obtained in a yield of about 80 vol%, with a length of 10–40 μm and a diameter varying from about 0.25 μm for TaC to about 0.55 μm for TiC. The x-value of the whiskers could be varied by altering the weight in ratio of Ta_2O_5 and TiO_2. The nitrogen content decreased with increasing x-value in $Ta_xTi_{1−x}C_yN_{1−y}$.

The oxidation experiments were performed in a thermogravimetric (TG) apparatus which allows simultaneous recording of the weight change and the heat evolved by the oxidation (DTA). The oxidised samples were characterised by their X-ray powder diffraction patterns and by scanning and transmission electron microscopy (SEM and TEM) studies.

2. Experimental

The starting materials consisted of in-house made $Ta_xTi_{1−x}C$ and $Ta_xTi_{1−x}C_yN_{1−y}$ whiskers, prepared as described briefly above and in detail in [10–14]. The whisker compositions, determined by chemical analysis, are given in Table 1. The C, N, and O contents were analysed by a standard combustion technique. The Ti and Ta contents were determined from spectrometric data and plasma emission lines, respectively, and found to be equal with the nominal ones within experimental errors. The oxidation experiments were performed in oxygen atmosphere (pO_2 = 101 kPa), using a combined TG-DTA apparatus (TAG 24, SETARAM), with a heating rate of 5°C/min from room temperature to 1000°C. From the TG measure-

Table 1
The whiskers used in the TG-DTA measurements and their composition from chemical analysis, the oxidation onset temperature and the degree of oxidation (α)

Nominal composition	Composition from chemical analysis	Results from chemical analysis			Results from TG-DTA	
		C (wt.%)	N (wt.%)	O (wt.%)	Oxidation onset temperature (T_{on})	Degree of oxidation (α)
TiC	$TiC_{0.85}O_{0.15}$	16.7	–	3.7	390	0.97
$Ta_{0.25}Ti_{0.75}C$	$Ta_{0.25}Ti_{0.75}C_{0.92}O_{0.08}$	12.4	–	1.4	375	0.90
$Ta_{0.50}Ti_{0.50}C$	$Ta_{0.50}Ti_{0.50}C_{0.91}O_{0.09}$	9.4	–	1.1	375	0.93
$Ta_{0.75}Ti_{0.25}C$	$Ta_{0.75}Ti_{0.25}C_{0.97}O_{0.03}$	7.8	–	0.3	510	0.95
TaC	$TaC_{0.99}O_{0.01}$	6.7	–	0.1	550	0.96
TiC_yN_{1-y}	$TiC_{0.10}N_{0.71}O_{0.19}$	4.7	15.0	4.5	470	0.95
$Ta_{0.33}Ti_{0.67}C_yN_{1-y}$	$Ta_{0.33}Ti_{0.67}C_{0.44}N_{0.51}O_{0.05}$	6.0	6.8	0.7	460	0.95
$Ta_{0.50}Ti_{0.50}C_yN_{1-y}$	$Ta_{0.50}Ti_{0.50}C_{0.58}N_{0.38}O_{0.04}$	6.4	4.2	0.5	490	0.94
$Ta_{0.67}Ti_{0.33}C_yN_{1-y}$	$Ta_{0.67}Ti_{0.33}C_{0.78}N_{0.19}O_{0.03}$	6.9	1.8	0.3	510	0.96

ments the extrapolated onset temperature of the oxidation (T_{on}) was determined by the standard procedure described by Dodd and Tonge [15]. When calculating the degree of oxidation (α), the chemical composition of the whiskers was taken into account, i.e. their content of titanium, tantalum, carbon, nitrogen and oxygen (see Table 1).

Isothermal oxidation experiments were performed in air with an ordinary high-temperature furnace. TiC and TaC whiskers were oxidised at 400–1200°C for times ranging from 1–100 h, and $Ta_{0.75}Ti_{0.25}C$, $Ta_{0.5}Ti_{0.5}C$, and $Ta_{0.15}Ti_{0.85}C$ whiskers at temperatures between 650 and 1250°C for 10 h. The morphology of these oxidised samples was studied in an SEM (JEOL, 880) and/or in a TEM (JEOL, 2000FX). The oxidised samples were characterised by their X-ray powder diffraction patterns (XRD) obtained in a Guinier-Hägg focusing camera, using Cu Kα_1 radiation (λ = 1.5405981 Å) and silicon (a = 5.430880(35) Å) as internal standard. The recorded films were evaluated in an automatic film scanner [16].

3. Results and discussion

It is well known that TaC, TiC and TiN can dissolve oxygen into their structural frameworks, and this is also the case in the whisker phases investigated (see Table 1). In order to minimise the oxygen content in the whiskers, an excess of carbon was used in the starting reaction mixture. This implies that the product, besides whiskers, will also contain some extra carbon. Most of this carbon was removed by shaking the product with a mixture of water and an organic solvent. The carbon particles are caught in the organic solvent, while the whiskers end up in the water fraction. However, the end product still contains some excess carbon. In calculating the chemical composition of the whiskers from chemical analysis data it was assumed that $y + z + v = 1$ in the formula $Ta_xTi_{1-x}C_yN_zO_v$, and by doing so it was found that the amount of carbon from the analysis was larger than the y-value needed to match the formula. The presence of excess carbon can in part explain why a degree of oxidation of approximately 0.95 (see Table 1) was most often observed rather than the expected 1.00 at the end of the oxidation experiment. Another reason might be that the assumption that $y + z + v = 1$ in the formula $Ta_xTi_{1-x}C_yN_zO_v$ is wrong. It is also well known that TaC, TiC and TiN can easily adopt substoichiometric compositions with respect to their carbon and nitrogen contents. If this is true also in this case, the excess amount of carbon might be substantially higher than given in Table 1. In this connection it should also be noted that the X-ray phase analysis revealed TiO_2 (the rutile and anatase modifications) and Ta_2O_5 to be the only oxides present in all samples. No pseudo-binary compounds were thus found.

3.1. TG and DTA studies of the oxidation of $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers

The experiments on oxidation of $Ta_xTi_{1-x}C$ whiskers resulted in TG curves like those given in Fig. 1,
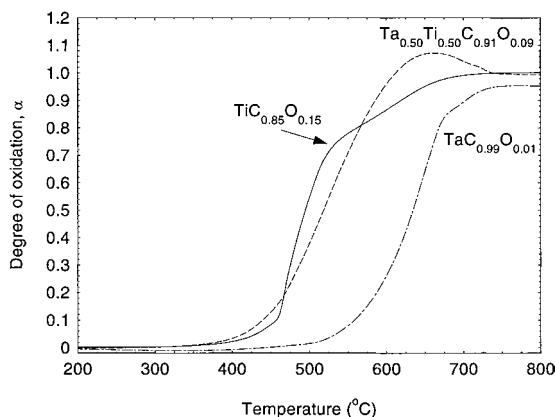
Fig. 1. Non-isothermal oxidation behaviour of $TiC_{0.85}O_{0.15}$, $TaC_{0.99}O_{0.01}$ and $Ta_{0.50}Ti_{0.50}C_{0.91}O_{0.09}$ whiskers from room temperature to $1000°C$ with a heating rate of $5°C/min$ in oxygen.

Fig. 2. Result of DTA-measurements of a selection of $Ta_xTi_{1-x}C$ whiskers, performed with a heating rate of $5°C/min$ from room temperature to $1000°C$ in oxygen. The DTA intensities are given per mol $Ta_xTi_{1-x}C$ whiskers.

where the degree of oxidation α is plotted versus the temperature. From the TG measurements it was found that TiC whiskers had the lowest oxidation resistance ($T_{on} = 390°C$) and TaC the highest ($T_{on} = 550°C$) and that the onset temperature values of the $Ta_xTi_{1-x}C$ whiskers with $0 \leq x \leq 0.5$ were approximately the same as for TiC.

Our oxidation curve for TiC whiskers can be divided into four steps such as those described by Shimada and Kozeki [7–8], but covering different ranges of α. Thus, step I covers the range 0–0.15, steps II, III, and IV 0.15–0.75, 0.75–0.90 and 0.90–0.97, respectively. This discrepancy is not too astonishing if one takes into account that: (i) The TiC particles oxidised by Shimada and Kozeki had an average diameter of $2\,\mu m$, to be compared with the much smaller whisker diameters ($0.55\,\mu m$) used in our experiments; (ii) Pure oxygen was used in our oxidation experiments while Shimada and Kozeki used argon–oxygen gas mixtures; (iii) Different heating rates were used. It can also be noted that the oxidation curve obtained for TaC seems to contain at least two steps.

The oxidation curve of $Ta_{0.5}Ti_{0.5}C$ (see Fig. 1) is quite strange, and so are all curves obtained for $Ta_xTi_{1-x}C$ whiskers. The shape of these TG curves suggest that the sample first becomes fully oxidised and is then reduced. However, X-ray studies of the end products have shown that TiO_2 and Ta_2O_5 are the only phases formed and the sample colours are white to

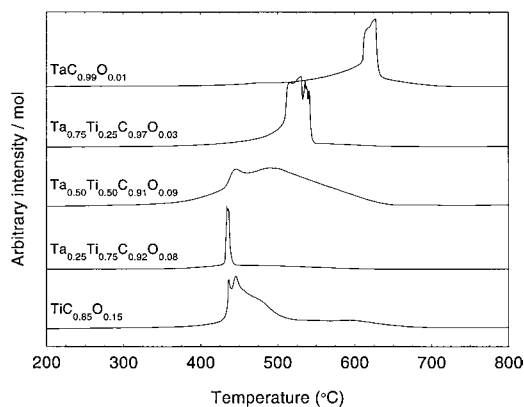pale yellow. These observations suggest that the sample does not contain any reduced phases. We have presently no clear understanding of the origin of the maximum in the weight increase curve. One explanation could be that minor amounts of some metastable compound are formed within this limited temperature range and that this intermediate compound is subsequently decomposed. At present, however, we have no experimental evidence supporting this proposal. This type of oxidation curve is not only obtained for $Ta_xTi_{1-x}C$ whiskers but also for $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers as discussed below.

The DTA curves obtained for the $Ta_xTi_{1-x}C$ whiskers are given in Fig. 2. From this plot it is clear that the peak shape is strongly composition dependent. It can also be noted that the peak onset temperature of the Ti-rich samples is close to that of TiC, whereas for TaC it is substantially higher, in agreement with the TG measurements. The DTA and TG curves from the oxidation of the TiC whiskers are given in Fig. 3. The DTA curve has a large exothermal DTA peak extending between 450 and $650°C$, and containing at least three overlapping peaks. The first one, with a maximum temperature (T_{max}) of $480°C$, correlates fairly well with the end of the oxidation range of step I ($\alpha = 0.15$), and accordingly the DTA peak with a T_{max}-value of $490°C$ is ascribed to reactions occurring during step II, while the shoulder appearing around $520°C$ marks the inception of step III, and finally the T_{max}-value around $630°C$ signals the beginning of the
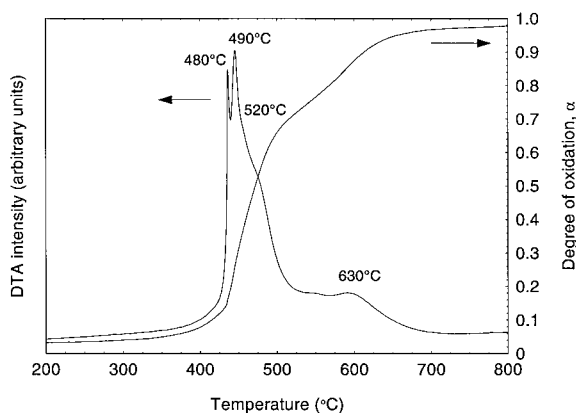
Fig. 3. Detailed TG-DTA plot of the oxidation of TiC whiskers, showing the DTA peaks and the corresponding TG curve. The four oxidation stages (I–IV) can be assigned from these curves. Peak and shoulder temperatures are displayed in the graph.

Fig. 5. Results from DTA measurements of a selection of $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers, performed with a heating rate of 5°C/min from room temperature to 1000°C in oxygen. The DTA intensities are given per mol $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers. In the broken line for $TiC_{0.10}N_{0.71}O_{0.19}$ the intensity is magnified five times in order to show the DTA-peaks more clearly.

last step. The DTA curve obtained for the oxidation of $Ta_{0.5}Ti_{0.5}C$ is also composed of several overlapping peaks, with the first one(s) located in the same temperature range as the two first DTA peaks found for TiC.

The shape of the weight increase curves obtained for oxidation of the carbonitride whiskers, $Ta_xTi_{1-x}C_yN_{1-y}$ (see Fig. 4, increasing x-value implies increasing y-value as seen in Table 1), resembles that observed for the $Ta_xTi_{1-x}C$ whiskers with
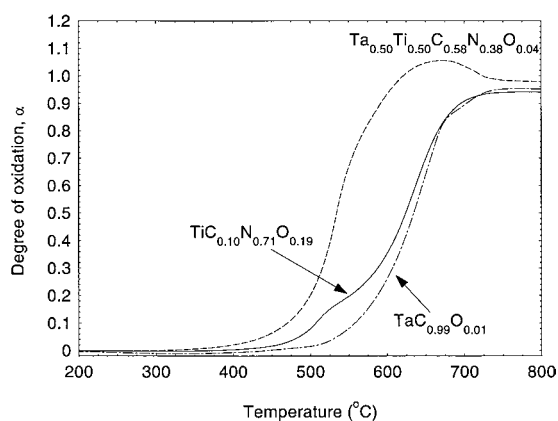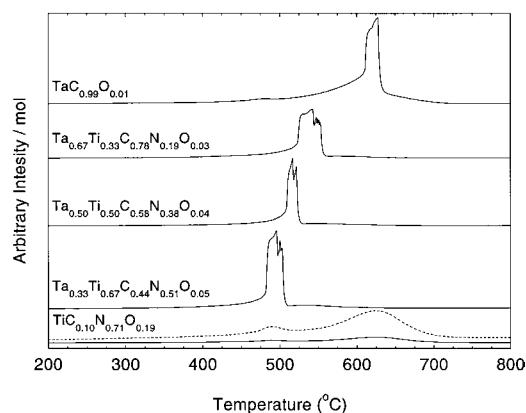

Fig. 4. The non-isothermal oxidation behaviour of $TiC_{0.10}N_{0.71}O_{0.19}$, $TaC_{0.99}O_{0.01}$ and $Ta_{0.50}Ti_{0.50}C_{0.58}N_{0.38}O_{0.04}$ whiskers from room temperature to 1000°C with a heating rate of 5°C/min in oxygen.

$x = 0.5$, i.e. they all exhibit a maximum in the weight increase versus temperature curve. The onset temperature for the oxidation of the TiC_yN_{1-y} whiskers was found to be about the same as that observed for TiC, and the oxidation curve suggest that the process in this case takes place in two steps rather than in four as observed for TiC. The onset temperature for the oxidation of $Ta_xTi_{1-x}C_yN_{1-y}$ increased almost linearly with increasing x-value from $x = 0.33$, as seen in Table 1. This variation of the onset temperature with composition is somewhat different from that observed for the $Ta_xTi_{1-x}C$ whiskers, where the onset temperature remained almost constant for $x \leq 0.5$ and then increased for $x > 0.5$.

The oxidation of $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers yielded the DTA curves given in Fig. 5. Again, the curve shape is strongly composition dependent. The curve obtained for oxidation of TiC_yN_{1-y} whiskers is very different from the other carbonitrides and also different from the ones obtained for the $Ta_xTi_{1-x}C$ whiskers (cf. Figs. 2 and 5). The oxidation of the TiC_yN_{1-y} whiskers thus exhibits two partly overlapping peaks, and both are comparatively very broad. The DTA curves of all the other compositions are composed of several overlapping peaks, but the temperature range within which the main peaks appear is much more restricted. At present we do not have any firm

explanation why the DTA curve obtained for oxidation of TiC_yN_{1-y} whiskers is so different from the others. One hypothesis might be that the first peak can be ascribed to the formation of Ti oxocarbonitrides, while the various reactions involved in the formation of reduced Ti-oxides and their oxidation to TiO_2 (steps II–IV discussed in connection with oxidation of TiC whiskers above) in this case are strongly overlapping and yield a broad DTA peak. Assuming that this is true, it is still difficult to understand why the DTA peaks obtained for oxidation of $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers are comparatively condensed with respect to the temperature in spite of being composed of overlapping maxima.

3.2. SEM and TEM studies of oxidised whiskers

SEM and TEM studies of oxidised whiskers of both $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ compositions revealed that a majority of the whiskers with a composition of $x < 0.5$ were split into two halves along the length of the whisker as seen in Fig. 6. However, according to our findings this behaviour is dependent on the diameter of the individual whisker and not on its composition and the splitting occur for whiskers with a diameter larger than $0.3 \mu m$. Although the average whisker diameter is composition dependent, the splitting has been observed for all compositions because there are always fractions with larger diameters than
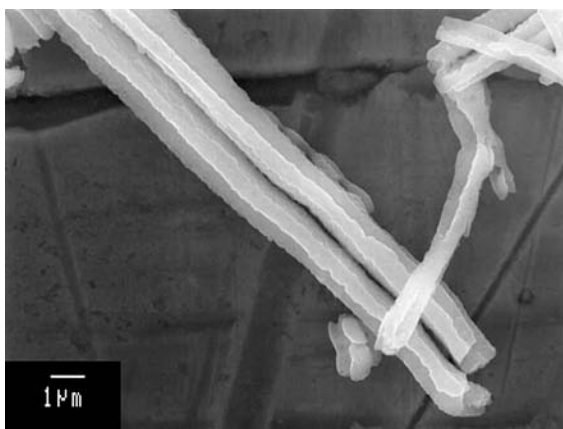

Fig. 6. SEM micrograph of isothermally oxidised TiC whiskers (750°C, 10 h), exemplifying the predominant morphology for whiskers with an x-value < 0.5, were the whisker appears to have been split in half during the oxidation.
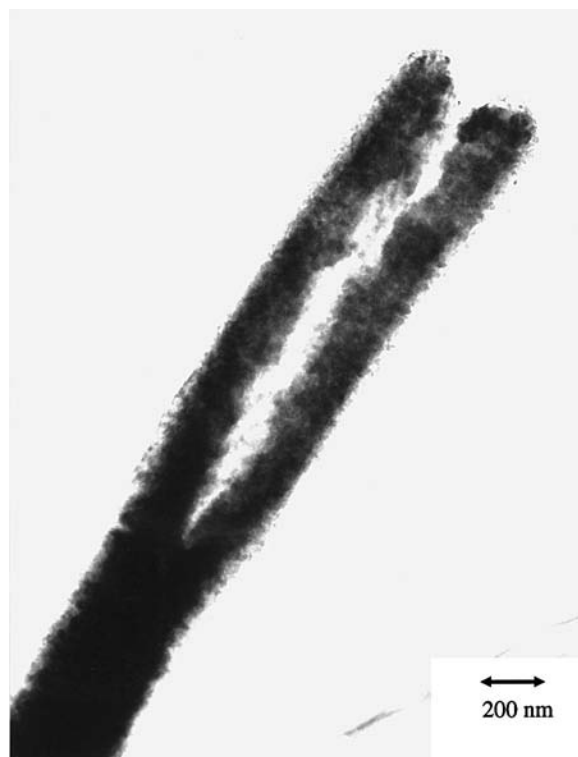

Fig. 7. TEM-micrograph of an oxidised TiC whisker that is partly cracked.

the average. Oxidation causes the diameter to increase substantially for all carbide and carbonitride compositions.

Whiskers with a diameter less than $0.3 \mu m$ are not split, although cracks can be observed, both parallel and perpendicular to the length. The splitting starts at the whisker's ends, as seen in Fig. 7, implying that the oxidation preferentially propagates along these crack paths because it provides unreacted surfaces. This behaviour resembles the findings of Shimada and Kozeki, who reported that oxidised particles of TiC contained several cracks [7]. As the diameters of most of the TaC whiskers are less than $0.3 \mu m$, they do not split into two parts (Fig. 8).

3.3. Isothermal oxidation experiments

The oxidised $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers maintained their high aspect ratio even after being fully oxidised to TiO_2 and Ta_2O_5, respectively. The
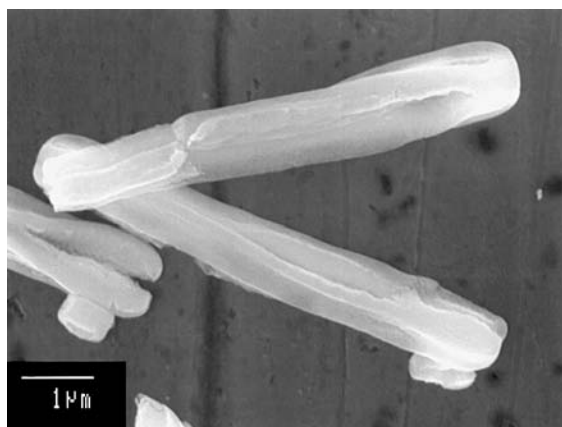
Fig. 8. SEM micrograph of isothermally oxidised TaC whiskers (750°C, 10 h), exemplifying the predominant morphology for whiskers with an *x*-value > 0.5. There is no splitting, although small cracks can be observed both parallel and perpendicular to the whisker length.

X-ray powder diffraction pattern of the oxidised TiC whiskers revealed that the sample was almost completely oxidised already after 1 h at 400°C. Besides reflections which could be ascribed to TiO_2 (mainly the anatase modification), the X-ray diffractogram then contained only a few weak reflections, which could be ascribed to TiC. After 10 h of oxidation at 400°C the phase analysis revealed that the only phases present were anatase and minor amounts of rutile. With increasing oxidation temperature, increasing fractions of the rutile modification of TiO_2 were found, and when the whiskers had been oxidised at temperatures exceeding 800°C only the rutile modification of TiO_2 was present. This is in agreement with previous studies, which have shown that the transformation of anatase to rutile takes place in the temperature range 600–800°C [17].

Titanium carbonitride whiskers required 100 h to be completely oxidised at 400°C, whereas at 500°C the reaction completed in 10 h. Increasing the oxidation temperature to 550°C resulted in a complete oxidation of the TiC_yN_{1-y} whiskers to TiO_2 within 1 h. The tantalum carbide whiskers were much more oxidation resistant than those of TiC and TiC_yN_{1-y}, as expected from the results of TG-DTA experiments. Thus, after oxidation at 400°C for 1 h there was hardly any oxide formed at all, and even after 100 h at 400°C the core of

the whiskers still consisted of TaC, but a Ta-oxide skin was found. Complete oxidation was obtained first after 10 h at 550°C. The results from the isothermal oxidation experiments are in good agreement with findings from the non-isothermal TG and DTA studies described above.

3.4. SEM and TEM studies of isothermally oxidised whiskers

$Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers were isothermally oxidised and subsequently investigated in SEM and/or TEM set-ups to reveal how the morphology of the formed oxide particles varies with the composition and temperature. All of these oxide whiskers are polycrystalline, and the size of the crystallites is in the nanometer range when oxidised at low temperatures (400–500°C), as seen in Fig. 9. Increasing the oxidation temperature yielded larger grains; above 1000°C the grain growth was rapid, and the
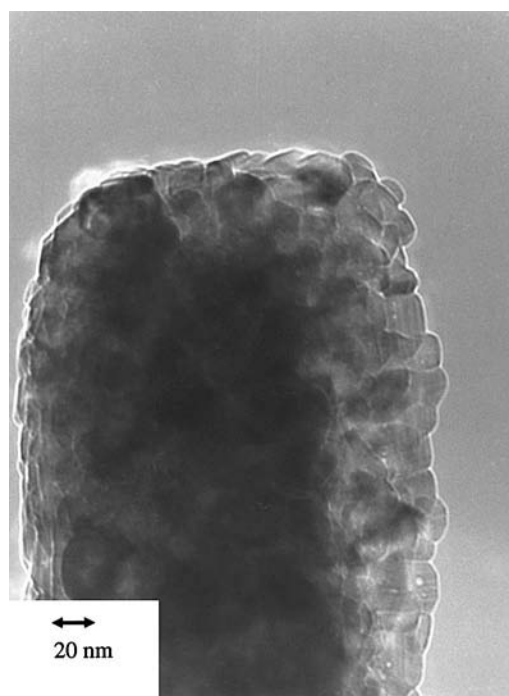

Fig. 9. TEM micrograph of an isothermally oxidised TiC whisker (500°C, 10 h), showing the typical crystallite size of $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers, which is in the nanometer range.
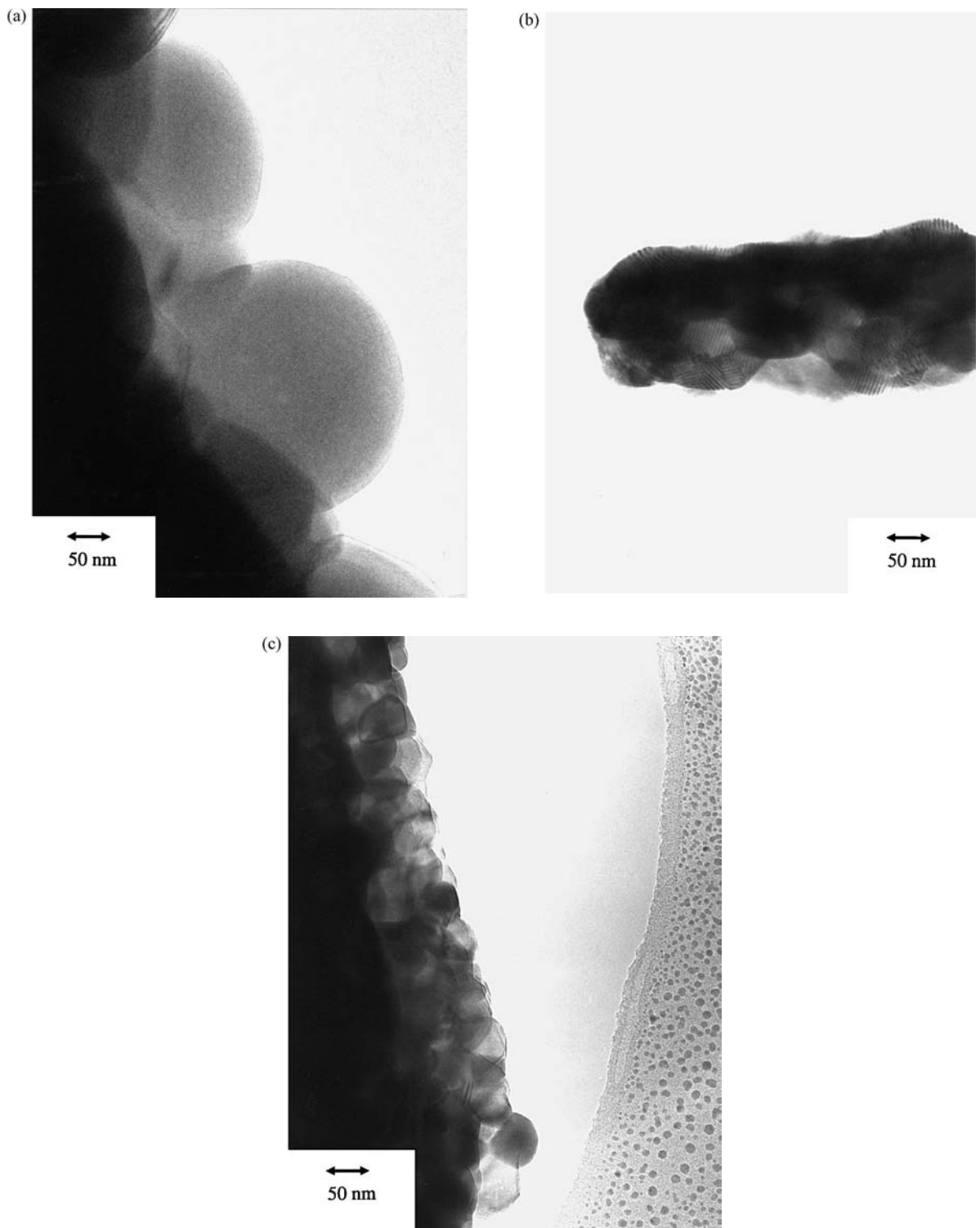
Fig. 10. TEM micrographs of isothermally oxidised (a) TiC, (b) TaC and (c) $Ta_{0.5}Ti_{0.5}C$ whiskers (850°C for 10 h), showing the markedly retarded grain growth of TiO_2 particles when $Ta_xTi_{1-x}C$ whiskers are oxidised compared to TiC. The Ta_2O_5 particle size is similar both after oxidation of TaC and $Ta_{0.5}Ti_{0.5}C$.

oxidised whiskers started to form large hard agglomerates. The Ta_2O_5 particle size formed after oxidation of TaC is in the range 30–50 nm while TiC whiskers gave a TiO_2 particle size in the range 300–500 nm when oxidised at 850°C for 10 h. It was found that the grain growth of TiO_2 particles formed during oxidation of $Ta_{0.50}Ti_{0.50}C$ at the same temperature was markedly retarded compared to that occurring when pure TiC was oxidised. However, the size of the Ta_2O_5 particles were comparable to those found after oxidation of TaC, see Fig. 10.

4. Concluding remarks

The oxidation experiments with TiC whiskers revealed that they had the lowest oxidation resistance of all those studied and that the oxidation of TiC whiskers could be divided into four steps in accordance with the findings by Shimada and Kozeki [7–8]. The oxidation resistance of TiC_yN_{1-y} whiskers was found to be higher than for TiC, but the recorded DTA curve suggests that the oxidation takes place in two steps rather than in four as observed for TiC. TaC whiskers had the highest oxidation resistance ($T_{on} = 550$°C). The DTA curve obtained for TaC whiskers seems to suggest that the oxidation process can be divided into at least two steps. The onset temperature of the oxidation of the $Ta_xTi_{1-x}C$ whiskers with $0 \leq x \leq 0.5$ was approximately the same as that of TiC, but increased markedly for compositions closer to TaC. The onset temperature for oxidation of $Ta_xTi_{1-x}C_yN_{1-y}$ increased almost linearly with x for $x \geq 0.33$. The oxidation curves obtained for $Ta_xTi_{1-x}C$ and $Ta_xTi_{1-x}C_yN_{1-y}$ whiskers are quite strange. Their shapes suggest that the samples first become fully oxidised and are then reduced. However, the X-ray phase analysis revealed that TiO_2 and Ta_2O_5 were the only oxide phases present in all samples and that no pseudo-binary transition-metal oxide compounds were formed.

Whiskers with a diameter exceeding 0.3 μm split into two halves upon oxidation. The oxidised whiskers maintained their high aspect ratio and were polycrystalline. The oxide particle size was in the nanometer range at low experimental temperatures (400–500°C). Increasing oxidation temperature yielded larger grains. It was also found that the

TiO_2 particle size of oxidised $Ta_xTi_{1-x}C$ whiskers is markedly smaller than that obtained from oxidation of TiC whiskers while the Ta_2O_5 particle size was not markedly influenced compared to when TaC was oxidised.

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