

# Ambient temperature formation of (Ta, Nb)C and (Ta, Nb)N

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A tantalum/niobium concentrate has been mechanically milled with magnesium and either graphite or nitrogen for 100 h. Directly after milling the formation of MgO was evident in both systems, a mixed metal carbide (Ta, Nb)C was also present in the carbon system. A cubic phase, close to that expected for the mixed metal nitride, was found in the powder milled under nitrogen. Annealing of the powders showed the reaction was incomplete with reduced oxide phases present. The carbide/nitride phases were readily separated from the MgO by acid leaching which left powders  $<5 \mu\text{m}$  in size. The leaching preferentially dissolved the smaller, more highly strained crystallites in both cases. © 1999 Kluwer Academic Publishers

## 1. Introduction

Transition metal carbides and nitrides are increasingly important materials due to their hardness, high melting point and chemical resistance. In commercial practice, they are made by two routes: reaction between the refined metal and either carbon or nitrogen or reduction carburisation/nitridation of a purified oxide. Tantalum and niobium carbides and nitrides are used in many areas, e.g., refractories, low electron emissivity parts, crucibles for molten metals and high temperature heating elements [1]. The largest application of the carbides is as an additive to tungsten carbide and titanium carbide based hard materials where they improve the rupture strength [2], presumably by improving the bonding between the binder and carbide grains [3]. The carbothermic reduction of the pentoxides of tantalum and niobium takes place at temperatures around  $1500^\circ\text{C}$  [4], although the use of hydrogen as the reductant decreases the temperature to  $1250^\circ\text{C}$  [5]. Carburisation of  $\text{Nb}_2\text{O}_5$  using hydrogen and methane required temperatures in excess of  $1100^\circ\text{C}$  and formed  $\text{NbO}_2$  as an intermediate phase [6], although a different starting material of higher surface area could be carburised at  $900^\circ\text{C}$  [7]. A temperature of  $>800^\circ\text{C}$  was used to decompose a mixture of an organometallic niobium compound and polyacrylonitrile to form niobium carbide [8]. Niobium carbide can also be formed by a self-propagating high temperature reaction of an intimately mixed pellet composed of the elements [9, 10]. Very little has been published on novel methods of formation of tantalum carbide, but the chemical similarity between tantalum and niobium would suggest that the methods for NbC formation would also apply to TaC.

The carbothermic reduction of a mineral concentrate showed that complete reduction of columbite

$\text{Fe}(\text{Nb}, \text{Ta})_2\text{O}_6$  occurred in 45 min using coal and 100 min using graphite at  $1400^\circ\text{C}$  [11]. The iron in the mineral acted as a binder for the carbide phases, although the final solid showed residual porosity even after sintering above the melting point of iron [12]. The grain size of the carbides was  $>10 \mu\text{m}$ , which is larger than the  $<1 \mu\text{m}$  typically used in cemented carbides for cutting tools [2]. The porosity and large grains size implies that this route was unable to produce a suitable product for cutting tools.

The metal nitrides can be formed at  $400^\circ\text{C}$  by reacting the metal with the nitrogen radicals from the thermal decomposition of hydrazine [13], although the product was always contaminated by oxide. Direct reaction between metal and nitrogen to form layers of NbN occurs at  $>500^\circ\text{C}$ , although higher temperatures ( $>1000^\circ\text{C}$ ) are required for bulk NbN or TaN [5]. The direct reaction between metal and nitrogen can also be achieved by high energy ball milling, the reaction apparently going to completion after 200 h [14]. Thermal reduction/nitridation of niobium pentoxide can also be performed using carbon as the reductant, the analogous reaction with tantalum pentoxide has been reported to produce a mixture of TaC and TaN at  $1200^\circ\text{C}$  [5]. Thermodynamic assessment of the stability of TaN in the presence of C indicates that the carbide is more stable at temperatures  $>1140^\circ\text{C}$ , thus the use of a lower temperature should allow exclusive formation of the nitride. Lower temperature nitridation of  $\text{Nb}_2\text{O}_5$  sol-gel derived fibres can be performed using ammonia at  $800^\circ\text{C}$  [15].

Previous work on the mechanical activation of minerals has demonstrated that reduction/carburisation (or nitridation) reactions can be induced to occur at room temperature which otherwise require a significant

thermal input [16–23]. This method of processing can form phases which are difficult to make by more conventional routes (e.g.,  $W_2C$  [22]) and leads to nanocrystalline powders (<10 nm crystallite size) which form particles which are typically <5  $\mu m$ . Careful selection of the reaction can lead to the formation of ultrafine composites of hard materials (TiC, Ti(C, N), TiN) dispersed in an alumina ceramic, both with and without a metallic phase present [17–19, 23]. Changing the reductant from aluminium to magnesium allows simple, selective leaching of the oxide (and metal) product leaving a powder consisting of the insoluble carbide or nitride [20–22]. This route is simpler than the more conventional processes, produces fine powders of carbides and nitrides directly from mineral concentrates at room temperature and may prove to be a less expensive route.

This paper examines the mechanochemical carburisation/nitridation of a tantalum/niobium concentrate by high energy ball-milling of concentrate with magnesium and either carbon or nitrogen. The separation of the hard phases from the unwanted phases is also examined by means of a simple acid leach.

## 2. Experimental

The tantalum-niobium concentrate was obtained from a commercial concentrator and had a particle size  $\sim 100 \mu m$ . X-ray fluorescence revealed that it contained 66%  $(Ta, Nb)_2O_5$ , 21%  $(Fe, Mn)O$  and 6%  $TiO_2$ , the remaining 7% was predominantly  $SiO_2$  and  $Al_2O_3$ . X-ray diffraction of a powdered sample showed that all of the peaks present were due to phases with the general formula  $AB_2O_6$ , where  $A = Fe$  or  $Mn$  and  $B = Nb$  or  $Ta$ , although a small peak around  $31^\circ$  may have been due to quartz.

The graphite powders had a particle size of <20  $\mu m$ , the magnesium was in the form of  $\sim 5 \times 2 \times 0.5$  mm shavings, both were nominally >99% pure. The feed powder consisted of 63.6 wt % concentrate, 33.0 wt % Mg and 3.4 wt % graphite, this was calculated from the composition of the concentrate to give a 50% magnesium excess over the required amount for reduction to  $(Ta, Nb, Ti)C$ , Mn and Fe.

The mixture was sealed in a laboratory-scale ball mill with five 25.4 mm  $\phi$  stainless steel balls giving a ball: powder mass ratio of 43 : 1. The mill was evacuated to  $\approx 10^{-2}$  Pa, sealed and rotated at 165 rpm for 100 h, using magnets to control the motion of the balls within the mill chamber [24]. After milling, there was no pressure change in the mill, indicating that gas was neither evolved nor leaked into the system. A second mixture (65.8 wt % concentrate, 34.2 wt % Mg) was also milled for 100 h, but under an initial pressure of 550 kPa of nitrogen. The pressure in this mill after 100 h milling was 310 kPa, clearly nitrogen had either been consumed or leaked out of the system.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on the milled powder. Samples were loaded into an alumina crucible and heated up in an inert argon atmosphere to 1200  $^\circ C$  at 20  $^\circ C/min$  using either a Shimadzu DTA-50

or TGA-50 instrument. Selected powders were subjected to an agitated leach for 4 h at 1% slurry density in azeotropic HCl ( $\sim 20\%$ ) at room temperature to remove any soluble products. The suspended solids were settled by centrifugation, the supernatant was decanted and deionised water added to wash the solids. After the second wash the settled solids were dried for 24 h at 110  $^\circ C$  in air and then weighed.

The products were analysed by X-ray diffraction (XRD) using monochromatised  $CoK_\alpha$  radiation ( $\lambda = 0.178896$  nm), traces were obtained over the range 10–130 $^\circ$  using a count time of 2 s per 0.02 $^\circ$  step. The unit cell sizes were calculated using the relationship between the measured  $d$ -spacing and the Miller indices for a cubic unit cell [25].

Selected powders were imaged using a Jeol 2600 scanning electron microscope incorporating energy dispersive X-ray (EDX) elemental analysis. The samples were coated with carbon to enhance conductivity whilst allowing analysis, consequently, this element could not be quantified.

## 3. Results

The TGA traces of the as-milled powders are shown in Fig. 1. The powder milled with carbon shows a mass loss event starting at  $\sim 820^\circ C$ , this mass loss has been associated with the carbothermic reduction of the  $AB_2O_6$  phase [21]. There is also a small mass loss for the sample milled under nitrogen, the reason for this loss is uncertain, with the expected reaction not forming volatile compounds (i.e., Fe,  $(Ta, Nb, Ti)N$  and  $MgO$ ).

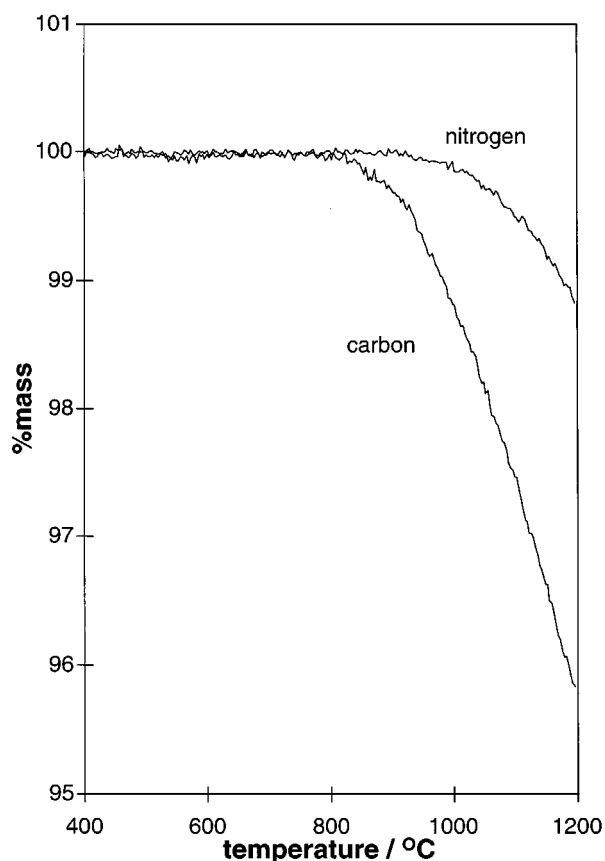


Figure 1 TGA trace for the powder milled with carbon.

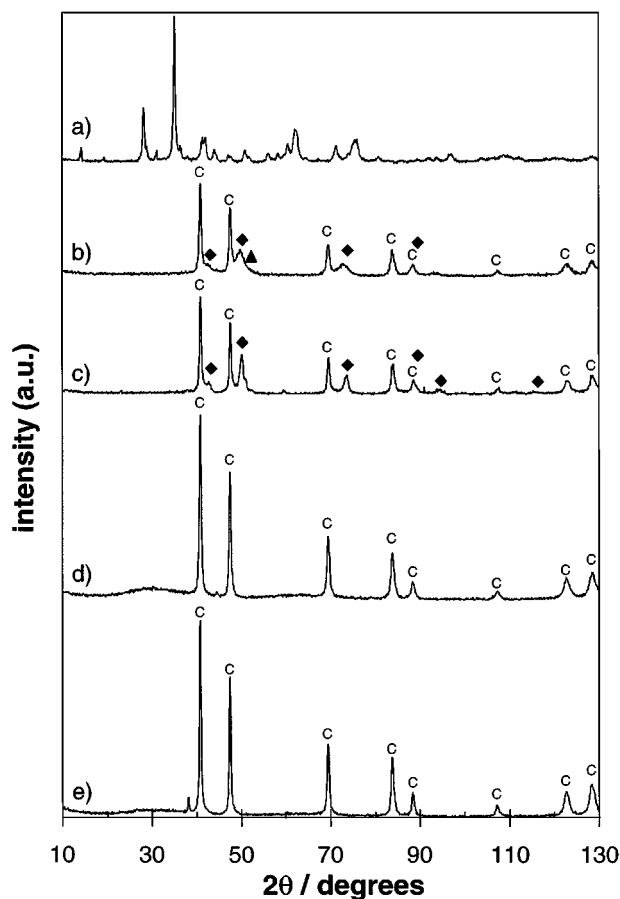


Figure 2 Intensity –  $2\theta$  traces for powders milled with carbon: (a) ore milled for 1 h under vacuum, (b) as-milled, (c) sample b heated for 1 h at  $1000\text{ }^{\circ}\text{C}$  in argon, (d) sample b leached for 1 h in 20% HCl, (e) sample c leached for 1 h in 20% HCl (▲: Fe, ◆: MgO and C: cubic carbide phase).

There may have been some unreacted nitrogen present in the powder after milling which was only released on heating, but this cannot be confirmed at present.

DTA showed no thermal reactions during either heating to  $1200\text{ }^{\circ}\text{C}$  or cooling to  $400\text{ }^{\circ}\text{C}$ . The absence of the expected endotherm for magnesium melting around  $650\text{ }^{\circ}\text{C}$  would indicate that it was completely consumed during milling, despite the apparent 50% excess. This may imply that there was insufficient magnesium to complete reduction within the system, which could explain the mass loss due to carbothermic reduction.

The XRD traces of the 100 h milled powder is shown in Fig. 2b, clearly there has been substantial reaction with no evidence of the original ore (XRD trace shown in Fig. 2a) remaining. Peaks are present for MgO, although at slightly lower  $2\theta$  than the standard sample [26], this may be due to partial substitution of iron for magnesium but evidence is lacking. Elemental iron could not be confirmed as present, with only a weak shoulder evident on the peak at  $51^{\circ}$  possibly due to Fe. The major peaks evident were all due to a cubic phase which has a calculated unit cell size of  $0.44430 \pm 0.00028\text{ nm}$ . On heating this sample, Fig. 2c, no new phases became apparent, the peaks for MgO narrowed and intensified and had moved closer to the expected  $2\theta$ , clearly, annealing the system decreased the MgO cell size slightly. The unit cell of the cubic phase decreased slightly to  $0.44394 \pm 0.00029\text{ nm}$ .

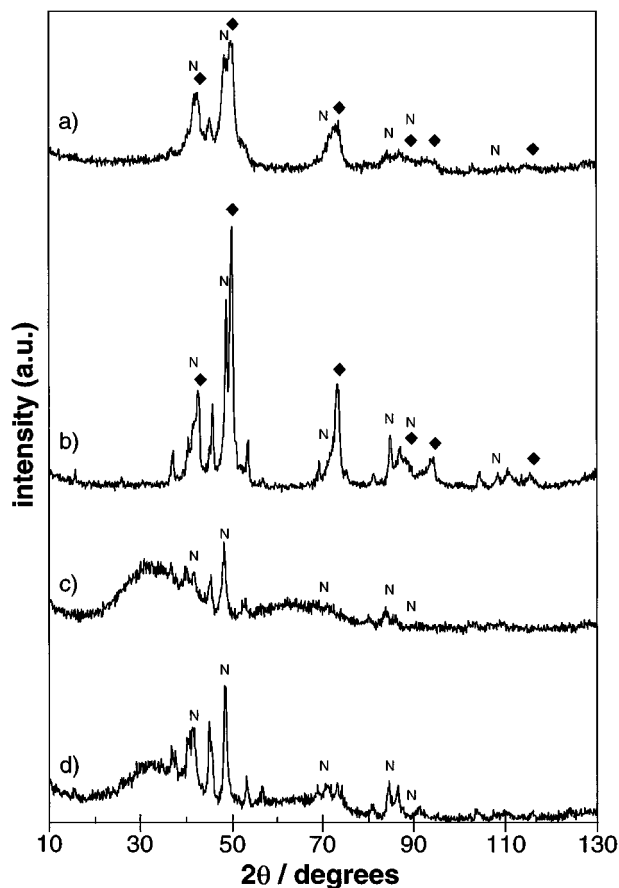


Figure 3 Intensity –  $2\theta$  traces for powders milled under nitrogen: (a) as-milled, (b) sample a heated for 1 h at  $1000\text{ }^{\circ}\text{C}$  in argon, (c) sample b leached for 1 h in 20% HCl, (d) sample c leached for 1 h in 20% HCl (◆: MgO and N: calculated positions of peaks for nitride phase).

The samples milled under nitrogen, Fig. 3, proved to have more complex XRD traces. Magnesium oxide was certainly present directly after milling, (a), there also seemed to be peaks coincident with those predicted for the multinitrile. Unlike the carbon system, the peaks of the cubic MgO and MN phases overlap somewhat and the weaker peaks for the nitride make peak fitting, and subsequent calculation of unit cell parameters, prone to potentially large errors. Consequently, no attempt has been made to calculate cell parameters for this system. There is a peak at  $\sim 45^{\circ}$  not associated with either the starting material or the expected product phases, the absence of other peaks makes attribution difficult, but both tantalum and niobium metal have their major peak at  $45^{\circ}$ .

On annealing the system to  $1000\text{ }^{\circ}\text{C}$  under argon trace (b) was obtained. The peaks for the nitride and MgO phases have narrowed, but still overlap somewhat, several peaks have become more obvious due to crystallite growth. The peak at  $45^{\circ}$  has narrowed and intensified and a new peak at  $83^{\circ}$  adds weight to the presence of elemental Ta and/or Nb. The remaining peaks are difficult to assign to specific phases due to a different composition to the standard phases [26]. However, possible phases present are  $(A, B)\text{O}_2$ ,  $B_2\text{N}$  and/or  $\text{ABO}_4$  ( $A = \text{Fe, Mn}$  and  $B = \text{Ta, Nb, Ti}$ ).

On adding the acid to the powders, it was noted that the as-milled powders reacted very vigorously for several seconds with the evolution of gas, gas was also

TABLE I Values of the unit cell size, crystallite size and lattice strain for the cubic carbide phase calculated from the XRD traces shown in Fig. 2. The errors given are those corresponding for  $2\sigma$  of the data derived from the eight evident peaks

|   | Sample                   | Unit cell size (nm)   | Crystallite size (nm) | Lattice strain (%) |
|---|--------------------------|-----------------------|-----------------------|--------------------|
| a | As-milled                | $0.44430 \pm 0.00028$ | $13.7 \pm 6.9$        | $0.485 \pm 0.123$  |
| b | As-milled, 1 h @ 1000 °C | $0.44394 \pm 0.00029$ | $16.9 \pm 8.3$        | $0.401 \pm 0.165$  |
| c | Sample a leached         | $0.44458 \pm 0.00017$ | $15.0 \pm 5.7$        | $0.444 \pm 0.155$  |
| d | Sample b leached         | $0.44483 \pm 0.00029$ | $22.7 \pm 8.4$        | $0.295 \pm 0.115$  |

evolved from the annealed powders but at a much lower rate with bubbles still evident after five minutes.

The expected mass loss in the carbon system was estimated from the composition, assuming the reactions went to completion, at  $\sim 60\%$ . The experimental values were 67 and 58% for the as-milled and annealed samples respectively. The XRD traces for the leached powders are shown in Fig. 2 as traces (d) and (e) for as-milled and annealed respectively. In both cases the peaks for MgO are not present, confirming that the leach removed the MgO. The peaks for the carbide phase have intensified due to their increased concentration in the solids. Peaks not evident in the unleached samples have appeared in both of the leached samples. The peak at  $44.5^\circ$  in (d) was probably due to  $(\text{Ta}, \text{Nb})_2\text{C}$  and the peak which emerged at  $38^\circ$  in (e) may be due to one, or more, of  $(\text{Ta}, \text{Nb})_2\text{O}$ ,  $(\text{Ta}, \text{Nb})\text{O}$  or  $(\text{Ta}, \text{Nb})\text{O}_2$ , however, these attributions are only tentative with no other peaks for any of these phases evident. For both of the leached powders, a broad peak is evident around  $30^\circ$  which is typically due to amorphous material.

The mass loss in the nitride system was expected to be  $\sim 60\%$ , the actual values were found to be 62% for the milled and 52% for the annealed powder. After leaching the XRD traces in (c) and (d) were measured for as-milled and annealed powders respectively. The peaks for MgO have gone, as expected, leaving the peaks for nitride, Ta/Nb and the same phases as present in the unleached samples. A very broad peak around  $30^\circ$  has emerged and this is typical of a material which was amorphous or of very small crystallite size. The absence of this peak in the unleached powders implies that the phase was derived from the solution processing, presumably by a dissolution/precipitation process.

Elemental analysis of the powders before and after leaching was made using EDX in the SEM. From these analyses, and the observed mass loss during leaching, the fraction of each major element leached was calculated and these are shown in Table II. In general, the

fraction of metal leached from the annealed powders was less than from the as-milled powders. The removal of the major soluble product, MgO, was  $>99.5\%$  for all powders. Both iron and manganese were  $\sim 95\%$  solubilised, regardless of annealing in the carbon system. Under nitrogen, these metals were slightly less soluble which would imply that they had either formed a less soluble phase during milling or remained unreacted in an insoluble form. The similarity between the iron and manganese solubilities would suggest that they were probably present in the same phase, XRD showed peaks for elemental iron which were absent after leaching, suggesting that a solid-solution between these metals was present. The solubility in the nitride system was lower and this was probably due to a lesser extent of reaction, as indicated by the presence of unattributed peaks in the XRD traces of the leached powders shown in Fig. 3.

Niobium and tantalum had similar solubilities which were considerably lower after annealing, clearly, the annealing step reduced the solubility of the Ta/Nb phases. The solubility of titanium was greater than that of Ta/Nb, but showed a similar decrease after annealing. These three elements are the primary constituents of the carbide and nitride phases and their decrease in solubility after annealing may be related to the increase in crystallinity and decreased lattice strain after annealing. Although the continued solubility after annealing, particularly for Ti, would seem to be as a consequence of the remaining lattice strain and small crystallite size. The greater solubility of titanium would suggest that there may have been more than one stoichiometry of carbide present, the phase with a high titanium content being more soluble than that with a low content. However, a second more soluble titanium phase may also have been present which was partially converted to another less-soluble phase during annealing. These possibilities cannot be distinguished due to the absence of conclusive XRD data.

Scanning electron micrographs of the leach products for the as-milled powders are shown in Fig. 4. The annealed powders showed little difference in morphology and particle size. For the carbon powder (a) the particle size range is  $<1\text{--}80 \mu\text{m}$ , the large particle in the centre left of image is clearly very porous with a large open area where MgO and Fe/Mn were removed during leaching. A more detailed image is shown in (b) where the particle is clearly an aggregate of particles  $<1 \mu\text{m}$  in size. The nitride particles (c) show a similar morphology, although the minimum particle size was somewhat larger at  $\sim 5 \mu\text{m}$ , although the more detailed view (d) suggests there were a number of rounded

TABLE II Fraction of metal leached, calculated from the EDX analysis of particles in the SEM and the experimental mass loss

| % metal leached | Milled with carbon |          | Milled under nitrogen |          |
|-----------------|--------------------|----------|-----------------------|----------|
|                 | As-milled          | Annealed | As-milled             | Annealed |
| Mg              | $>99.5$            | $>99.5$  | $>99.5$               | $>99.5$  |
| Ti              | 58                 | 31       | 75                    | 29       |
| Mn              | 97                 | 93       | 78                    | 79       |
| Fe              | 98                 | 98       | 79                    | 73       |
| Nb              | 31                 | 8        | 28                    | 6        |
| Ta              | 28                 | 11       | 25                    | 8        |

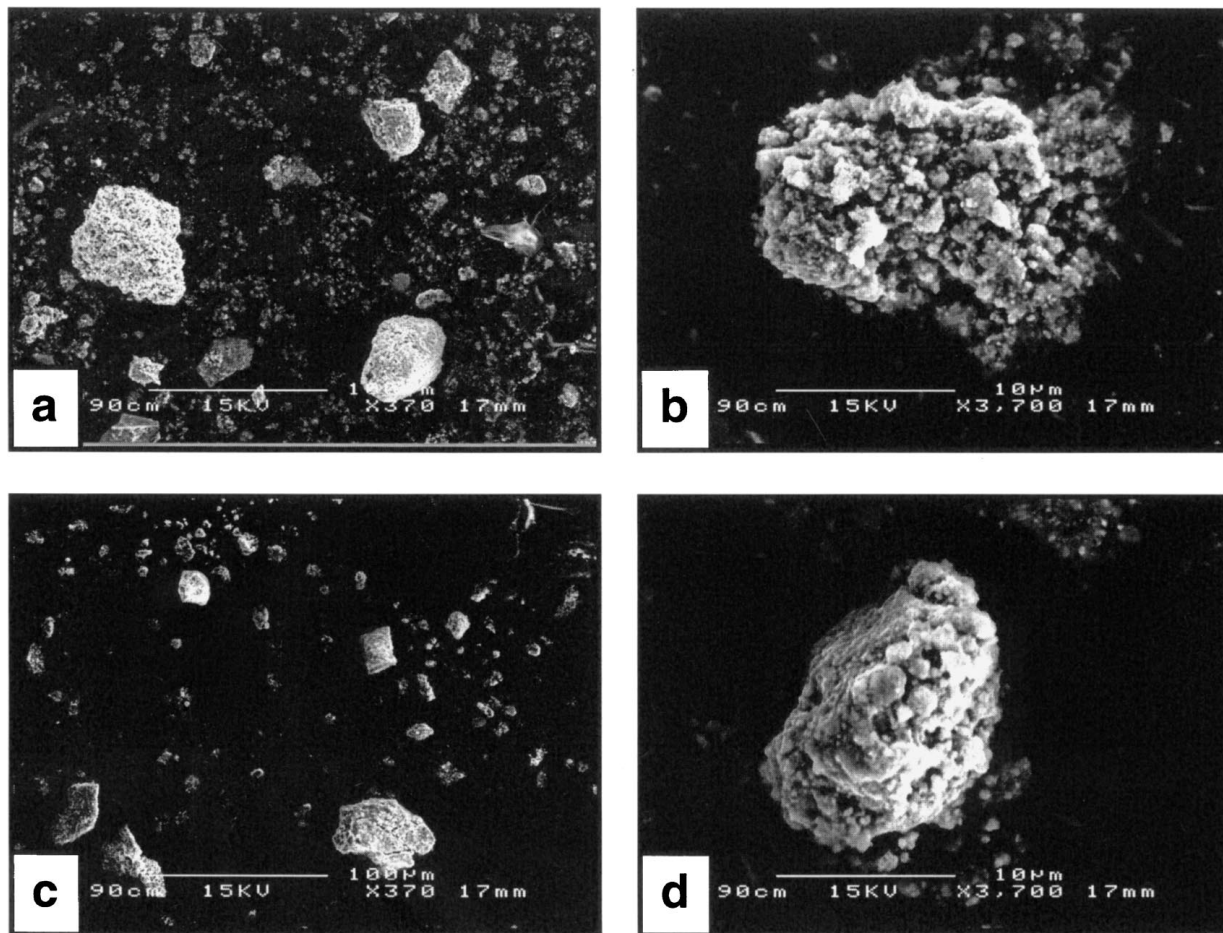


Figure 4 Scanning electron micrographs of leached powders: (a) milled with carbon, (b) detail of single particle of carbon product, (c) milled under nitrogen, (d) detail of single particle of nitrogen product.

particles  $< 1 \mu\text{m}$ . The minimum estimated size of the particles in both of these powders was  $< 0.2 \mu\text{m}$ , most of the unagglomerated particles were rounded. The high degree of porosity evident in these particles is due to the removal of  $\sim 65\%$  of the as-milled mass during leaching, the higher density of (Ta,Nb)C compared with that of the leached phases ( $\rho_{(\text{Ta,Nb})\text{C}} = 10.8 \text{ g cm}^{-3}$ ,  $\rho_{\text{Fe}} = 7.86 \text{ g cm}^{-3}$ ,  $\rho_{\text{Mg}} = 3.58 \text{ g cm}^{-3}$ ) means that a volumetric loss of  $> 80\%$  would occur during the leaching. Thus, the leached aggregate particles are probably extremely porous and a further short milling would break them down into the sub-micron constituent particles.

#### 4. Discussion

The absence of magnesium melting peaks during DTA would indicate that all of the magnesium had reacted, despite a 50% molar excess was used. There are two possible explanations: the oxide on the surface of the shavings was much more extensive than thought or, the magnesium was completely consumed by reaction. Preliminary work on this system, using highly oxidised magnesium powder, showed that milling and heating to  $1000^\circ\text{C}$  formed  $\text{Mg}_4(\text{Ta,Nb})_2\text{O}_9$  as a major phase. This was thought to be due to non-reductive replacement of the iron/manganese in the  $\text{AB}_2\text{O}_6$  phase by MgO with only minor amounts of (Ta,Nb)C detected by XRD. Had more Mg been present then more extensive re-

duction would have occurred preventing formation of  $\text{Mg}_4(\text{Ta,Nb})_2\text{O}_9$  by reducing Ta and Nb. The absence of this phase, after milling and heating with excess Mg, would indicate that there was sufficient magnesium to perform the reduction. Thus, either there was an almost exact stoichiometric quantity of Mg (i.e., 33 wt% of the shavings was oxide) or another reaction consumed the remaining magnesium. The mills were unloaded in air and, although there was no heating evident due to reaction with air ( $\Delta H_{298} = -601 \text{ kJ mol}^{-1} \text{ MgO}$ ), it may be that aerial reaction decreased the residual magnesium metal content to near zero by formation of MgO and/or  $\text{Mg}_3\text{N}_2$ .

Magnesium nitride has been reported [27] to undergo decomposition around  $800^\circ\text{C}$ , approximately where the mass loss in the carbon system starts. This phase has been reportedly formed during the milling of magnesium in ammonia [28]. Were  $\text{Mg}_3\text{N}_2$  formed, it would be more likely to do so during milling (when the pressure of nitrogen was  $> 500 \text{ kPa}$  and fresh Mg surfaces were being exposed) than during exposure to  $\sim 80 \text{ kPa N}_2$  in air. This was not the case, as the mass loss from the sample milled in nitrogen was much smaller and occurs at higher temperature. Thus, it would seem that the mass loss cannot be due to nitrogen loss and must be due to another reaction. The lack of a mass loss in the nitrogen milled system would seem to confirm that only oxide formed on exposure to air.

Reaction could occur between the carbide and residual oxide phase evolving carbon monoxide which

would cause a mass loss. This would remove carbon from the carbide rendering it even more sub-stoichiometric and decreasing the unit cell size, as was observed on annealing. A similar decrease in the stoichiometry, due to oxidative mass loss by solid-state reaction has been observed for titanium carbide [29].

The crystalline parameters calculated from profile fitting of the XRD traces are shown in Table II. The cubic unit cell for the main phase in the milled and annealed powders was smaller than those of both TaC (0.44547 nm) and NbC (0.44698 nm) but larger than that of TiC (0.43274 nm). Vegard's rule has been shown [5] to apply for all of the binary compositions of these carbides and, assuming it applies in this three component system, the unit cell size predicted from the known composition is 0.44413 nm. The measured values were both slightly lower than that predicted, this could be due to several factors, deviation from Vegard's rule, incorporation of adventitious nitrogen into the carbide or formation of non-stoichiometric carbide. All three elements form cubic nitrides which have smaller unit cells and the incorporation of nitrogen into the lattice could account for this difference. The single element carbides all show a range of stoichiometry between  $MC_x$  ( $x \sim 0.5$  for Ti, 0.7 for Nb and Ta) and MC [4, 5] with a concomitant increase in the unit cell with carbon content. The formation of carbides by solid-state diffusion of carbon has been shown to be slow, even in intimately mixed powders [29], with sub-stoichiometric carbides forming prior to the filling of the vacancies in the carbon lattice.

However, the incorporation of nitrogen into the lattice could only have occurred during milling as no thermal treatment was made under  $N_2$ , the mill showed no evidence of leakage, maintaining the same pressure throughout the 100 h. The absence of the expected increase in the unit cell during annealing, as carbon filled up vacancies in the lattice, would seem to rule out the formation of sub-stoichiometric carbide. However, the graphite used has been shown [30] to contain adsorbed gas and the mass of graphite added to the mill did not account for this, providing insufficient carbon within the mill for the formation of a stoichiometric carbide.

Leaching of the powders showed a greater solubility in the as-milled powders than in the annealed powders, in both systems the difference was around 10%. The greater solubility for the as-milled powder was not unexpected as phases with a small crystallite size tend to solubilise more readily than phases with larger crystallites. The elements which were most affected by annealing were Ta, Nb and Ti and the 10% difference in mass loss was probably due to these elements becoming less soluble.

After leaching of the carbon system, the calculated unit cell for both as-milled and annealed powders increased slightly compared with the unleached material. This may be related to the large fraction of titanium leached, a titanium rich carbide would be expected to have a smaller unit cell than a titanium poor phase, assuming Vegard's rule applies. The large loss of Ti compared with that of Ta and Nb would imply that the surface of the particles may have been titanium rich,

however, a soluble non-carbide titanium phase could also have been present directly after milling and was converted to a less soluble phase during annealing.

The mean crystallite size and lattice strain were also noted to increase and decrease respectively after leaching. This would imply that smaller, more strained crystallites were leached preferentially compared with the larger, less strained crystallites. This same effect has been shown to occur in ilmenite powders milled for up to 200 h [31, 32] and in tungsten powders formed by mechanochemically induced reaction [22].

Directly after leaching there were large ( $> 10 \mu\text{m}$ ) aggregates which were observed to have high porosity and small ( $< 1 \mu\text{m}$ ) unaggregated particles. It is probable that a further short period of milling would reduce the mean particle size to below  $1 \mu\text{m}$  by breaking the aggregates. These particles would then be the optimum size for use in cutting tools [2].

In any commercial use of this process it is imperative to minimise the milling time as this will be the greatest expense. The particular mill used in these investigations is known to be extremely inefficient, other mills (e.g. vibratory, planetary, tower) are considerably more intensive than tumbling mills [33] and their practical application would be expected to reduce the milling time considerably. Indeed, it has been suggested that vibratory mills may achieve in 15 min the same result as 11000 min in a ball mill [34], making this method considerably more attractive.

## 5. Conclusions

Formation of a mixed tantalum/niobium carbide has been shown to occur during high energy milling of a mixture of an oxide mineral concentrate, graphite and magnesium. The formation of a nitride phase was observed when milled under nitrogen in the absence of graphite. The carbide was readily separated from the MgO product by acid leaching, with most of the iron and manganese also removed. The nitride reaction seemed to be less extensive with several unattributed XRD peaks present after leaching. The unit cell size of the carbide was calculated to be 0.444 nm which was close to that expected from the composition. Leaching was observed to preferentially dissolve the smaller, more highly strained crystallites of the carbide phase. The simplicity of the milling process to form the carbide and the ease of separation from unwanted products makes this a potentially attractive route for the formation of carbide from concentrate.

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