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Sintering behaviour of ultrafine NbC and TaC powders

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Compositional and microstructural changes upon firing ultrafine (300 to 400 Å) stoichiometric NbC and TaC powder lots have been studied up to a temperature of 1600°C. Substantial amounts of oxygen impurities, mostly oxide particles or layers are eliminated by reductions with hydrogen, free carbon or the carbides themselves. TGA showed these reactions to take place at 700 to 1400°C with maxima around 1000 to 1100°C. Low temperature sintering is inhibited by this impurity and its removal is thus essential. Other impurities (Ni, Cr, Fe) were also found in the starting powders in total concentration 0.5 to 1%. They give rise to a liquid phase located at grain edges at temperatures as low as 1100°C which then controls microstructure development. It dissolves to some extent in the carbide matrix at high temperature, and has a tendency to rise to the free surface of the samples. Compositional and structural heterogeneities are thus produced between bulk and surface at high temperatures. Owing to these impurity effects, it was not possible to clearly evaluate the influence of powder granulometry.

1. Introduction

Because of the technological importance of transition metal carbides, most studies about the shaping and fabrication of these materials have been concerned with sintering in the presence of sizable amounts of a liquid phase. Some general goals have been to reach theoretical density while maintaining a small, uniform grain size in the final products. Other problems, however, arising in the processing of presumably purer powders seem to have been less extensively considered, except for special materials such as the nuclear carbides.

Interest also has sometimes been expressed in recent years in powders of very high surface area which can be prepared more or less industrially by such methods as chemical reaction of methane and metal chlorides in an arc plasma [1]. It was hoped, by using such raw materials, that finer microstructures and, hence, improved mechanical properties, could be achieved under less stringent firing conditions than for coarser powders. To our knowledge, however, relatively few studies have been published about the processing of ultrafine transition metal carbides or nitrides [2, 3]. From these studies no general conclusion may be drawn as to their sinterability: titanium nitride was reported to be readily densified to about 95% theoretical at temperatures as low as 1400°C. Similarly prepared and fired submicronic titanium carbide on the other hand, could not be densified, presumably because of the presence of free carbon in the starting powders [3].

The present paper reports on the sintering behaviour of niobium and tantalum carbide powders having particle sizes of the order of 300 to 400 Å. The exploratory study which we chose to conduct was designed as a survey of those systems, and an identification of specific problems to be considered further. It is, therefore, not our purpose to present a fully substantiated account of any phenomenon in particular. Rather, we hope to give a precise feeling for the overall compositional and microstructural changes of compacts made from as-prepared powders. Because of the very high specific areas involved, oxygen contamination is obviously of particular importance. Similarly, residual metallic impurities, especially those of the iron group, deserve close consideration. The paper will thus be centred around the influence of

TABLE I Characteristics of starting powders.

Property and measuring technique	Niobium carbide powder	Tantalum carbide powder
Particle size		
BET	320 ± 30 Å	420 ± 40 Å
Line broadening	350 ± 50 Å	400 ± 50 Å
Observed lattice parameter [4]	4.467 ± 0.002 Å	4.454 ± 0.002 Å
Theoretical density and lattice parameter [5]	$\rho = 7.74$ g cm^{-3} $a = 4.465$ Å	$\rho = 14.45$ g cm^{-3} $a = 4.452$ Å
Composition (wt. %)		
Total carbon	11 ± 0.1	6.7 ± 0.1
Free carbon (supplier)	0.8	0.35
Oxygen (neutron activation)	> 3	> 1
Nitrogen (neutron activation)	$\gtrsim 0.5$	$\gtrsim 0.05$
Chemical formula	$NbC_{0.90}$	$TaC_{0.98}$
Metallic impurities (u.v. spectrometry) in wt. %		
Nickel	0.20 ± 0.04	0.5 ± 0.1
Iron	0.05 ± 0.01	0.05 ± 0.01
Chromium	0.20 ± 0.04	0.25 ± 0.05
Aluminium	0.010 ± 0.002	0.025 ± 0.005
Cobalt	<0.002	< 0.005
Copper	<0.003	< 0.005

oxygen elimination and liquid phase formation during heat-treatment of both carbides.

2. Experimental

The physico-chemical characteristics of the powders* studied are given in Table I. They concern the two particular lots used for present work: variability was recorded for a given carbide from one lot to another, particularly in the nature and amount of metallic impurities. These powders were prepared via the arc plasma route [1]. They have a tendency to oxidize slowly upon storage. Oxygen and nitrogen contents were determined by neutron activation analysis of the powders and of some heat-treated samples described below. Minor amounts of oxygen and/or nitrogen may be dissolved in the lattice of niobium carbide as suggested by the observed lattice parameter, compared with the theoretical value [5]. Two weak peaks corresponding to niobium monoxide have been observed on the X-ray powder pattern of NbC.

The as-received powders (Fig. 1) were stored and handled in a glove box filled with argon. They were isostatically pressed to 2000 bar without any lubricant or additive. Green densities of the compacts reached 45% of theoretical but packing heterogeneities were frequently noted after the samples had been sintered and the corresponding areas had to be discarded before microstructural evaluation was made. Heat-treatments were conducted either in a furnace with silicon carbide heating elements, or in a hydrogen protected molybdenum wound furnace. Recrystallized high purity alumina† was used for laboratory tubes. Temperatures were stabilized to ± 5 to 10°C. The firing atmosphere used for most of the work was hydrogen (dew point −40°C). Argon was also used as indicated in the next paragraph. The samples were contained in molybdenum boats with molybdenum covers. High purity graphite pellets were placed in the boats, together with the samples. It was observed during occasional runs above 1600°C that the laboratory tube would react with the atmosphere

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*Supplied by H. C. Starck GmbH, Goslar, Fed. Germany.
†Morgan and Co.

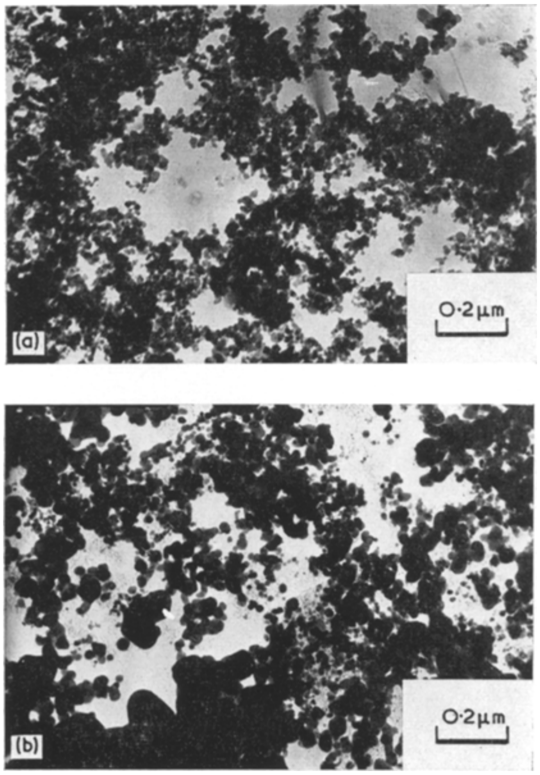

Figure 1 TEM of as-received NbC and TaC powders (a) NbC, (b) TaC.

and alumina wool be deposited in a colder part of the tube. This effect was not observable in the absence of graphite or at lower temperatures up to our longest annealing periods. Within the analytical uncertainties, aluminium was not more abundant in the sintered samples than in the starting powders. For the study of microstructural evolutions in the time and temperature ranges: 5 min to 15 h at 1300 to 1600° C, specific heating and prefiring schedules were developed as a result of the work to be reported in the next paragraph. It is sufficient here to note that heating the samples from 1100 to $\geqslant$ 1300° C was as rapid as possible by quick introduction in the hot zone at the origin of times. Temperature equilibration was reached within tens of seconds. After firing, the samples were similarly rapidly quenched to 1000° C then slowly cooled to room temperature.

Sintered microstructures were characterized on diamond polished surfaces etched approximately 10 sec in HNO_3. 20% HF at room temperature. Grain sizes were determined by the classical linear intercept method [6]. The average grain diameter is taken as: $D = 1.5L/(NG)$ where L is the length of the test line, G the optical magnification, N the number of grain boundary intercepts. More than 100 intercepts were counted in each sample with a magnification set at × 1000 or × 1500 depending upon grain size. Bulk densities were determined by toluene displacement. Other particular experimental techniques have been used and will be mentioned below when applicable.

3. Results and discussion

3.1. Weight loss during prefiring

Preliminary sintering trials yielded defective samples exhibiting evidence of substantial gas evolution during firing. Thermogravimetric analyses were thus carried on compacts of both carbides at constant heating rates = 270° C h^{-1} from room temperature to 1400° C. Fig. 2 shows the rate of weight change $\Delta m/(m\Delta t)$ normalized to the final mass, for NbC samples heated in argon and hydrogen. For the latter

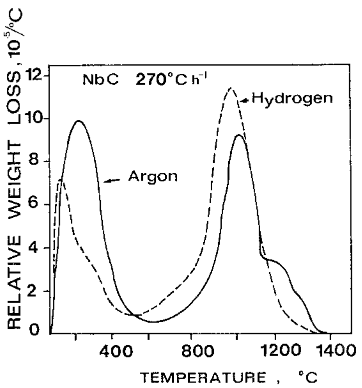

Figure 2 Weight change rates in NbC compacts upon heating.

atmosphere, correction has been made for reaction between hydrogen and the graphite pellets by subtracting the curve obtained during a blank trial. Both curves on Fig. 2 are roughly similar and subsequent runs were carried in argon for both carbides as this gas facilitates the weight loss experiments. Fig. 3 similarly shows the rate of weight change in TaC. The low temperature peaks on these TGA curves correspond to the usual drying and outgassing of the compacts. Above 700° C, chromatographic analysis showed significant amounts of carbon monoxide to be present in the argon flowing out of the furnace. In hydrogen, small amounts of water were also present. Peak heights were

TABLE II Weight loss upon constant heating rate.

Experimental conditions	Final mass of sample (g)	% of final mass lost in temperature interval (°C)										Total loss (%)
			700		1100		1200		1300			
TaC; argon	0.742	0.5		0.4		0.4		0.5		0		1.8
NbC; argon 270°C h⁻¹	0.370	1.7		1.9		0.5		0.7		0		4.8
NbC; argon 270°C h⁻¹ after storage	0.435	3.4		3.0		0.6		0.4		0		7.4
NbC; hydrogen 270°C h⁻¹	0.773	3.2		1.6		0.5		0.5		0		5.8
NbC; argon 590°C h⁻¹ after storage	0.375	3.7		3.0		0.5		0.4		0		7.6
Residual oxygen (wt. %)			2.25		1.75		1.25		0.50		0.05	
Lattice parameter (Å)			4.467						4.463		4.462	

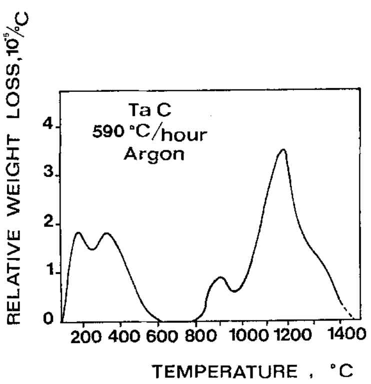

Figure 3 Weight change rate in TaC compacts upon heating.

recorded every 4 min on the chromatograph. It was observed that the corresponding gaseous impurity concentration in the atmosphere, qualitatively matched the TGA curves. Increasing the heating rate to 590°C h^{-1} made no great difference: the TGA recordings closely paralleled those obtained at 270°C h^{-1} heating rate. However, similar experiments performed at 3 or 4 month intervals, clearly indicated that weight loss upon heating older powders was higher, both in the 300 to 400°C range and at higher temperatures.

The preceding results which are quantitatively summarized in Table II suggest that oxygen impurities present in the system are extracted from the compacts as H_2O or carbon monoxide. Further proof was obtained by direct oxygen determination in samples whose heating had been discontinued at various temperatures. It was also observed (Table II) that the lattice parameter of NbC heated in argon was essentially constant up to about 1200°C. It decreased slightly at higher temperatures. The lattice parameters of NbC heated in hydrogen and of TaC, remained constant within experimental error (± 0.002 Å).

Oxygen impurities are present in the carbides mostly as oxide particles or layers. Minor amounts may also be dissolved in the NbC lattice as previously mentioned. For experiments carried in argon, direct reference may be made to the thermodynamic analysis of Worrell and Chipman [7] of the Ta–C–O and Nb–C–O systems. Pourbaix-Ellingham diagrams published by these authors show that the CO partial pressures are always markedly higher than those of CO_2 in the temperature range of the present work, and indeed detectable at 700°C. At low temperatures, oxide reduction proceeds thanks to free carbon present in the starting powder. The knees observed in the TGA curves (1100 to

1200°C for NbC and 1250°C for TaC) correspond to consumption of this element. At higher temperatures reduction must and can be effected by the carbides themselves, with the corresponding modifications of the stoichometries. This is more readily observable in NbC than in TaC. Worrell and Chipman's data further show that at any given temperature, the equilibrium CO partial pressure in the Ta–C–O system, is somewhat smaller than in Nb–C–O. Thus the TGA curves for the former carbide are displaced towards higher temperatures (Figs. 2 and 3) if the corresponding reaction kinetics may be assumed equivalent. Several oxides may *a priori* be present in the starting powders which might possibly account for the small 900°C peak of Fig. 3. This point has not been checked further.

When heating is carried in hydrogen on the other hand, deoxidation is effected mostly by carbon. At low temperatures, this species is present as such in the compacts (free carbon of the starting powders). At higher temperatures when it has been consumed, reaction between hydrogen and the graphite pellets present next to the samples, produces methane. The latter thus may permeate the compacts and provide more carbon for deoxidation to proceed. Stoichiometry therefore can be maintained in the carbides as is confirmed by the constancy of the lattice parameters and the absence of knees in the TGA curves (Fig. 2).

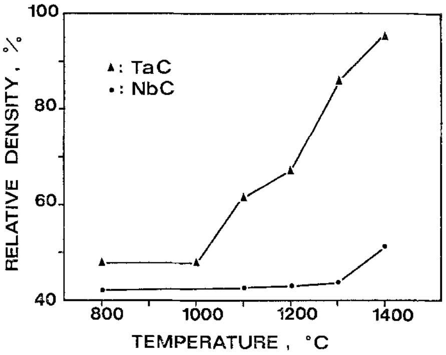

Figure 4 Densification upon heating compacted NbC and TaC.

Oxygen elimination and the corresponding chemical purification bears an influence upon densification of both carbides. Fig. 4 shows the bulk densities of compacts on first heating at 590°C h^{-1}. Similar results were obtained in argon and hydrogen. A substantial difference is apparent between NbC and TaC. The former does not start densifying until temperatures of 1300°C are reached, whereas the latter does as low as 1000 to 1100°C. From available information about diffusivities in both carbides [8], specific surface energies [9] or eutectic temperatures between the carbides and metallic impurities (cf. next paragraph), such a difference is not to be expected *a priori*. It then seems likely that oxygen impurities play a definite role in this matter. Indeed, making the assumptions that initial compact densities are equivalent for both carbides and that powder particles, all spherical (Fig. 1) and of the same sizes (Table I) are randomly packed, then a unit volume of compact offers approximately the same area for matter exchanges with the atmosphere in either carbides. Making use of previous results (Table II), the following numbers may be computed for gas evolution in the temperature range 700 to 1400°C:

mass of gas = compact density × amount of weight change

i.e. in NbC:

$$(0.45 \times 7.8) \times (3.9 \times 10^{-2}) \simeq 0.14 \text{ g cm}^{-3}$$

in TaC:

$$(0.45 \times 14.5) \times (1.3 \times 10^{-2}) \simeq 0.09 \text{ g cm}^{-3}$$

The specific amount of oxygen to be eliminated from the compacts thus appears higher in NbC than in TaC. Potter [10] and Harrison *et al* [11] have shown that oxygen elimination was essential in the densification of UC and (U, Pu)C powders by doing a systematic study of the inhibiting influence of that impurity. Our experimental evidence points to the same conclusions for NbC and TaC.

It will be seen below that, due to the presence of metallic impurities in the starting powders, a liquid phase may be present in the compacts at temperatures as low as 1100°C. In order to avoid difficulties with simultaneous deoxydation and liquid formation in NbC, a presintering treatment was given to all niobium carbide samples to be mentioned in the next section. This treatment of 24 h at 1100°C in a hydrogen atmosphere, also had the advantage of bringing similarity back between NbC and TaC compacts. Fig. 5 shows the bulk density of as-compacted and presintered NbC upon heating at 590 to 600°C h^{-1}. The difference between the two curves gives further evidence for the inhibiting effect of oxygen. Comparison between

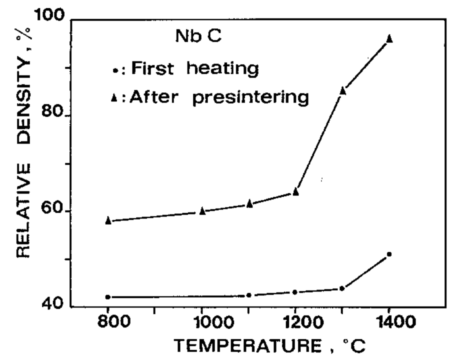

Figure 5 Densification of compacted and presintered NbC.

Figs. 4 and 5 also shows the near identity of the densification profiles of TaC and presintered NbC. Other characteristics of both carbides in the "intermediate" state are given in Table III together with corresponding values for a typical "final" state, the attainment of which will now be described.

3.2. Microstructure development

Tantalum and niobium carbide samples, preheated as has been described, were sintered in hydrogen at temperatures 1300 to 1600° C, for times up to 15 h. Figs. 6 to 8 give an idea of the densification and grain growth kinetics that were observed. Grain growth in tantalum carbide seems to be well represented by the classical law: $D^3 - D_0^3 = Kt$ where the initial mean diameter D_0 may be neglected. Final densities obtained with this carbide are somewhat lower than with NbC and it may be pointed out that deoxydation

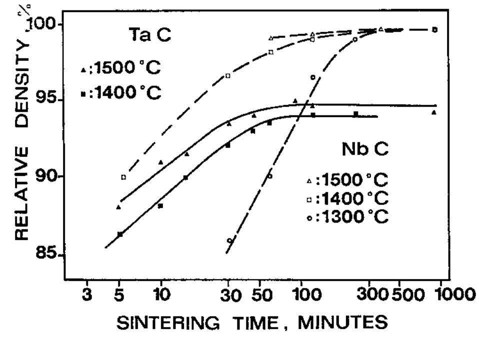

Figure 6 Isothermal densification of NbC and TaC.

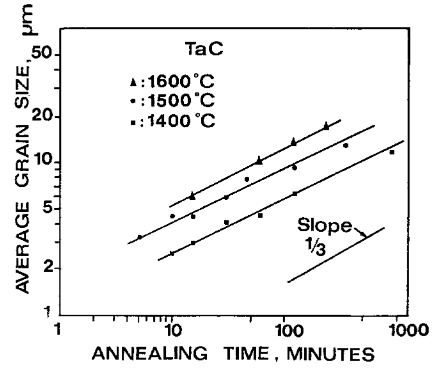

Figure 7 Isothermal grain growth in TaC.

TABLE III Characteristics of NbC and TaC at various stages of processing.

	Initial state: isostatic pressing 2000 bar	Intermediate state: NbC: (a) TaC: (b)	Final state: (a) or (b) + 1 h; 1500° C hydrogen
Stoichiometry (x =) NbC$_x$	0.90	0.89	0.89
TaC$_x$	0.98	0.97	0.97
Wt % oxygen			
NbC	3	0.5	0.015
TaC	1	0.5	0.033
Lattice parameter a/a_{theor}			
NbC	1.003	0.998	0.998
TaC	1.001	1.000	1.000
Density ρ/ρ_{theor}	0.42 to 0.48	0.6	0.95 to 0.98
Particle and grain size (µm)	0.03 to 0.05	0.1 to 0.2	6 to 8

(a) 24 h prefiring in hydrogen at 1100° C.
(b) Argon or hydrogen heating at 600° C/h to 1100° C.

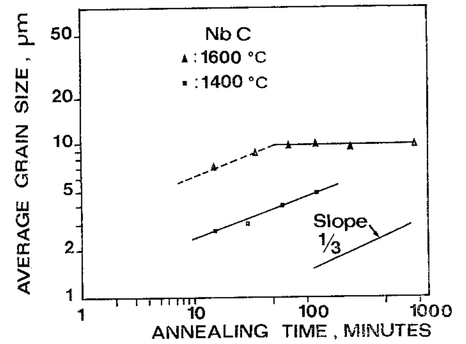

Figure 8 Isothermal grain growth in NbC.

was not as complete (Table III). It is also important to note that grain sizes reported on Figs. 7 and 8 have been obtained in the hearts of the samples, after cutting and polishing. A peculiarity appears on Fig. 8: at lower temperatures (1400° C) grain growth kinetics in NbC are similar to those of TaC. At 1600° C, however, a limiting grain size of about 10 μm is recorded in the former carbide. Such an inhibition may be due to grain boundary pinning by pores or inclusions [12] or to the occurrence of another process resulting in the arrest of grain-boundary migration. Evidence to be given below points to the latter possibility. Available information on grain growth in presumably pure carbides [13, 14] shows it to be negligible at temperatures $\lesssim$ 1600° C.

Typical microstructures of the samples are shown on Figs. 9 for TaC and 10 for NbC. No evidence of the presence of a grain-boundary liquid phase is obviously seen in NbC. Intergranular pores in TaC show a tendency to grow with time as has been observed in other ceramic systems [15]. In niobium carbide, however, residual pores are mostly intragranular and clustered approximately at grain centres. Such situations have also been observed in the final densification of oxide systems [16]. Individual pore sizes and interpore spacings suggest that both spherodization and grain-boundary unpinning took place at an early time during sintering, earlier in any case than that necessary for the grains to reach their limiting size. Pore pinning, therefore, cannot account for the occurrence of this limiting size.

Chemical analyses of the starting powders (Table I) show that 0.5 to 1 % metallic impurities (mostly Ni, Cr, Fe) are present in either carbide, pointing to the possible presence of a liquid phase at the sintering and annealing temperatures of this study. Such a phase was directly observed in two ways, and its influence upon the development of microstructures has been qualitatively assessed. Thermal etching polished samples at 1400° C for times of the order of a minute brought liquid drops to the free surfaces from the interior of the polycrystals (Fig. 11). Longer etching times yielded more copious exudation in NbC as well as TaC. Coalescence of such drops took place mostly in the centres of the grains with a small contact angle indicative of good wetting of the carbides by the corresponding liquids. Substantial amounts of nickel, chromium and iron were detected with an electron microprobe in these drops. Owing to their small diameters and thicknesses, however, no quantitative evaluations could be made. Similar etching treatments were made at lower temperatures in other samples. Liquid exudation by capillary rise along the grain boundaries to the free surface could be detected as low as 1100° C in both carbides. Such a temperature approximately corresponds to the binary eutectics between niobium carbide and chromium or nickel [17]. It was further checked that the liquid phases were intergranular at least initially. Indeed, scanning electron microscopy showed them as thin cylindrical shapes along grain edges in the bulk of the samples (Fig. 12). Such liquid cylinders were hardly observable if at all, in niobium carbide samples held for more than 1 h at 1600° C. By then, the grains in that material had reached their limiting size.

It is our feeling that grain growth in NbC stopped because of the disappearance of the liquid phase at higher temperature. This conclusion was reached in view of the preceding and following experimental evidence. Exudation was checked by repeated etchings and polishings and by SEM observations, to affect a zone of at most 100 to 200 μm thick near the free surface of the samples. Such a process, therefore, cannot account for the disappearance of the liquid phase in the bulk of the samples, i.e. 2 to 3 mm below the free surface. The only other possibility then seems to be a dissolution of the liquid phase into the carbide matrix, which is not contradicted by solubility limits of the order of 2 to 3 wt. % at the eutectic temperatures [17]. It thus appears that in the absence of the liquid phase, boundary migration necessitates solid state diffusional processes which are comparatively slower. As for tantalum carbide, abnormal grain growth

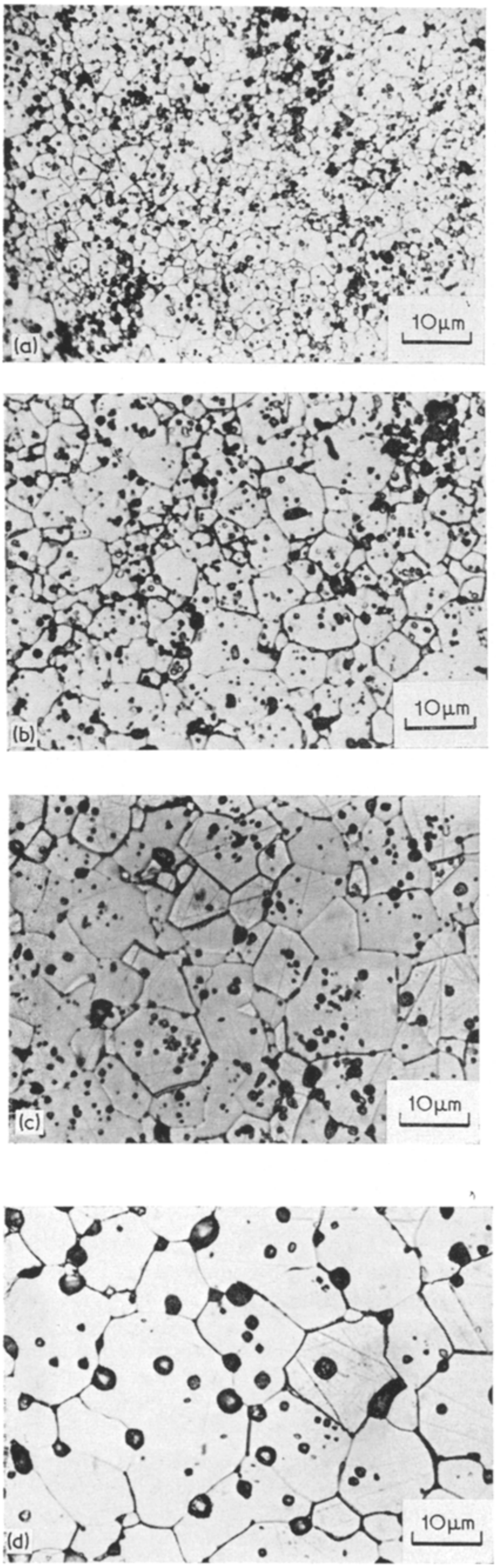

Figure 9 Microstructures of sintered tantalum carbide. (a) 15 min at 1400°C; (b) 2 h at 1400°C; (c) 15 min at 1600°C; (d) 2 h at 1600°C.

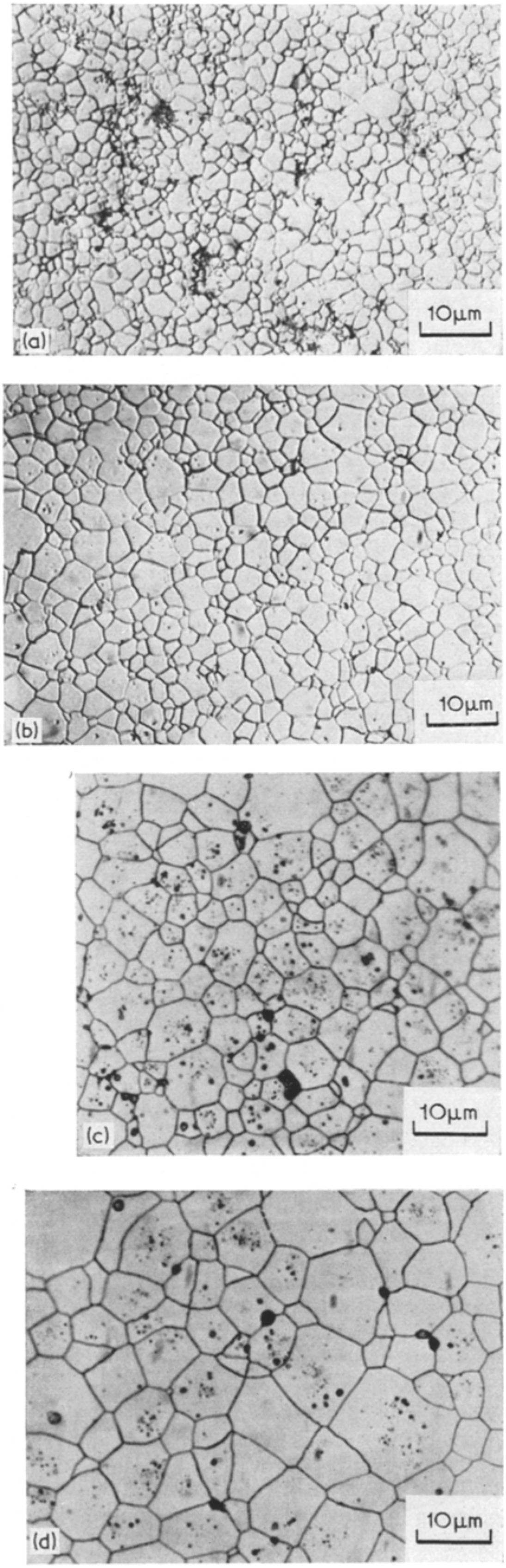

Figure 10 Microstructures of sintered niobium carbide. (a) 15 min at 1400°C; (b) 2 h at 1400°C; (c) 15 min at 1600°C; (d) 2 h at 1600°C.

takes place systematically near the free surface of the samples: large cubic grains develop in the small grain matrix towards the end of the sintering periods, i.e. 10 to 15 h depending on temperature. These grains are usually 10 to 20 times larger than individual grains in the matrix. Their special positions and apperance after some time has elapsed suggest that a minimum volume fraction of liquid must be present for them to develop. Similar observations of abnormal grain growth in oxide systems showed that the corresponding volume fraction of liquid is of the order of 1% [18].

It is hardly possible to unequivocally determine which is the rate controlling mechanism from the mere observation of the time dependence of grain coarsening in a two phase system [15]. Exner, in a recent study on the TaC-Ni and TaC-Co binaries [19], gave convincing evidence of the difficulties involved in interpreting Ostwald ripening of the carbide when a high volume fraction of liquid is present. The problem is undoubtedly more complex in our case where only a very small amount of second phase having a peculiar morphology was detected. It should also be borne in mind that porosity effects are probably superimposed to those originating from the liquid metallic impurities. This is suggested in Fig. 9 where a number of pores are seen to remain intergranular during grain growth. They must, therefore, be migrating together with the grain boundaries. As there is apparently no independent driving force for this migration, it can only be effected at the expense of a slowing down of the overall grain growth rate. These arguments suggest that not a single mechanism, amenable to a simple analytical model, may be expected to account for grain growth in the bulk of our TaC samples.

4. Conclusion

In our ultrafine nearly stoichiometric niobium and tantalum carbides, the early stages of sintering in hydrogen or argon are markedly influenced by oxygen impurities. These are present in the starting powders, mostly as oxide inclusions or layers, with a definite tendency to augment upon storage. Their elimination, which may be studied in particular by thermogravimetry, is achieved by reaction with hydrogen, free carbon or the carbides themselves (with the corresponding slight modifications of stoichiometries). Purification from oxygen may be obtained by heat-treating at 1000 to 1100°C

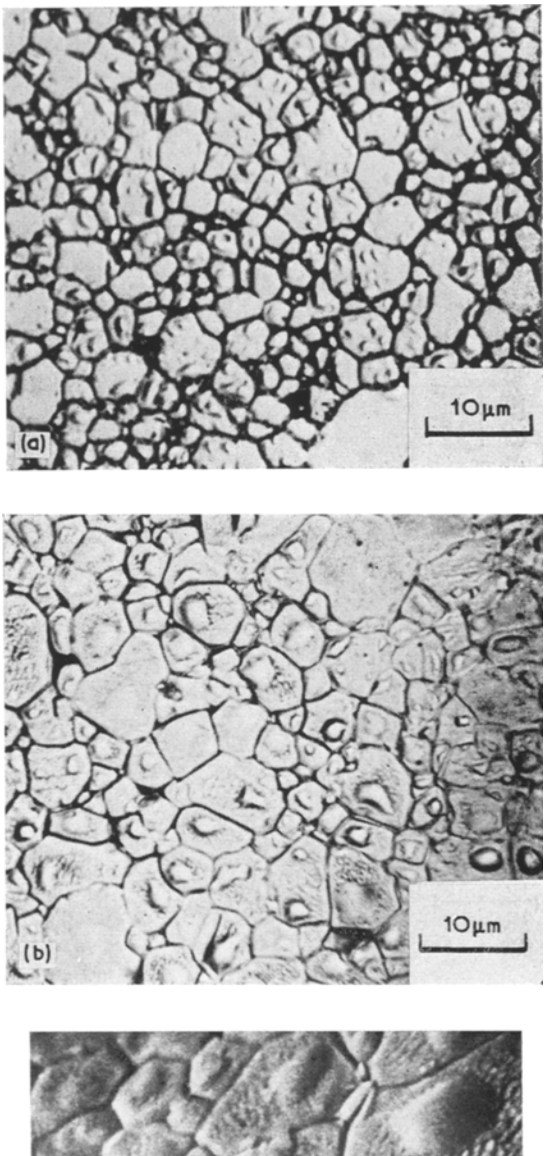

Figure 11 Thermally etched polished surfaces showing liquid exudation. (a) NbC: optical micrograph; (b) TaC: optical micrograph; (c) TaC: SEM.

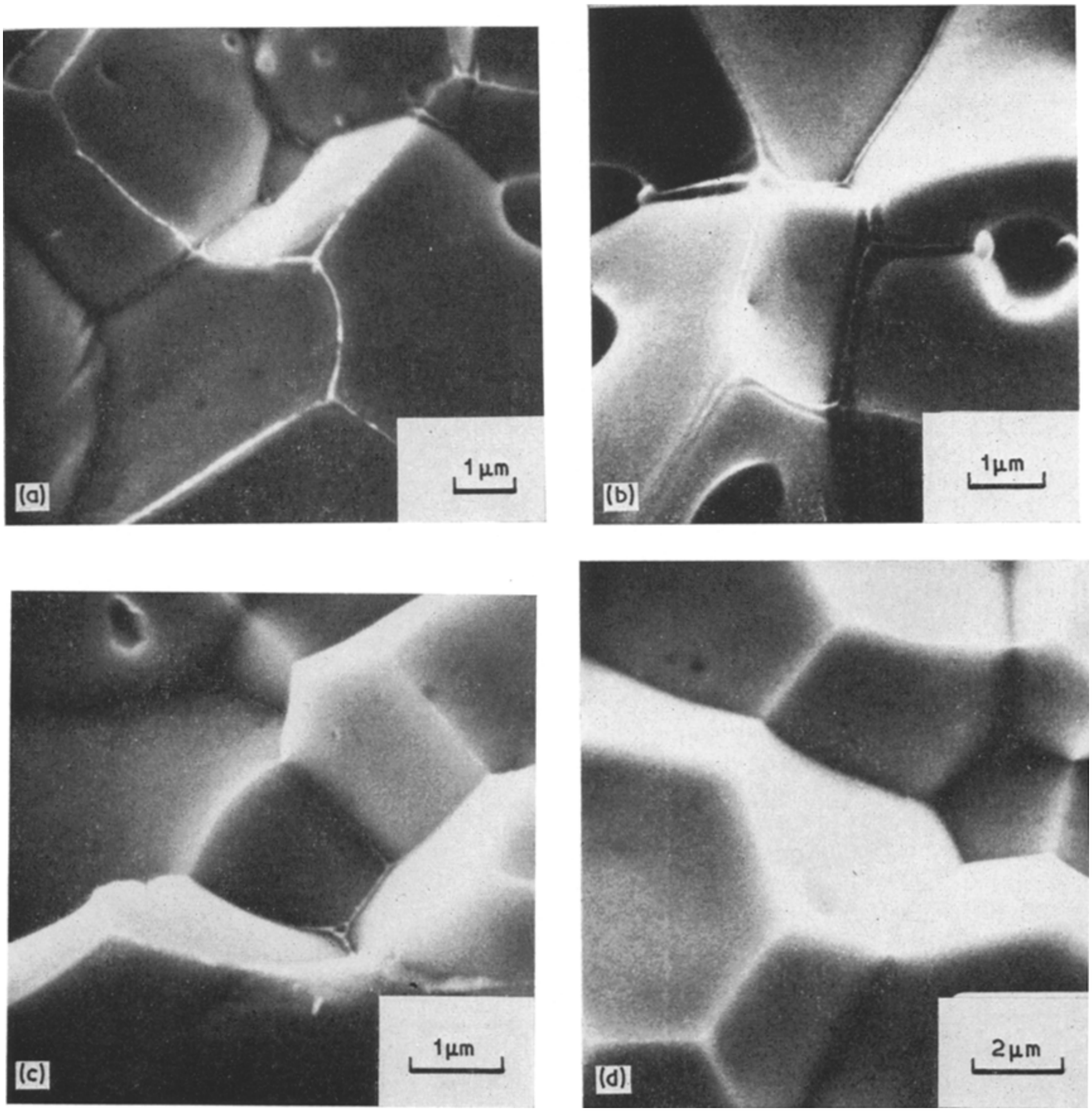

Figure 12 Intergranular fracture surfaces showing liquid phase along grain edges. (a) TaC: 2 h at 1500°C; (b) TaC: 2 h at 1600°C; (c) NbC: ¼ h at 1600°C; (d) NbC: 4 h at 1600°C.

during practical periods of time. This is essential from the point of view of densification at low temperatures, short times and satisfactory microstructural regularity. Incomplete oxygen elimination yields structurally defective samples, or inhibits densification in direct relation to the residual concentration of this species. Oxygen levels satisfactory for further high temperature sintering are of the order of several thousand parts per million. The corresponding compacts then are approximately 60% dense with crystal sizes of the order of 0.1 to 0.2 μm. It thus appears that necessary chemical purification brings the systems to a state quite similar to that which can be obtained with more common powders thus casting some doubt on the practical interest of using ultrafine particles for conventional sintering of transition metal carbides.

A rapid study of microstructure development upon firing such deoxidized compacts in hydrogen at 1300 to 1600°C showed it to be controlled by 0.5 to 1% metallic impurities (Ni, Fe, Cr) also present in the starting powders. It may be that these kinds of impurity are difficult to eliminate or maintain at reproduceable levels during fabrication. They have been observed to be present as a wetting liquid phase located along grain edges at temperatures as low as 1100° C in the sintered compacts. They are at least partly soluble in niobium carbide at the temperatures of this study. During heat-treatment, the liquid phases in both matrices have a tendency to rise by capillarity to the free surface of the samples thus producing compositional and marked structural heterogeneities between bulk and cortical zones. As a result, it must be concluded that the ultrafine powders that have been studied were not of sufficient chemical purity for the influence of granulometry to be satisfactorily assessed.

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