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K. SATYANARAYANA MURTHY
Department of Physics,
Nizam College,
Hyderabad–500001, India
K. V. KRISHNA RAO
Department of Physics,
Osmania University,
Hyderabad–500007, India

Ultrafine TaC powders prepared in a high frequency plasma

In recent years, various attempts have been made at preparing ultrafine, i.e. submicron, refractory particles. Stokes *et al.* [1] obtained tantalum and tungsten carbides as a result of reactions in a flame, between the corresponding metal or oxide and methane. The conversion ratios were of the order of 70% and 25%, respectively. Sizable amounts of Ta_2C, or even tantalum metal, could also be detected in the reaction products. Similarly, Neuenschwandter [2] used an arc plasma torch as a heat source to synthesize various transition metal carbides, including TaC. The resulting particle sizes typically ranged between 10 and 100 nm. The vapour-phase reactions involved hydrogen, hydrocarbons and the appropriate metal chloride. A quench then followed and the fine particles were deposited onto a cooled metal substrate, which they impinged with a fairly high velocity. This, together with the presence of chlorinated species such as HCl, is probably responsible for the presence of impurities such as Fe, Ni or Cr, which are usually detected [3] in the condensation products. In an attempt to avoid at least some of these difficulties and obtain as pure an ultrafine TaC powder as possible, a technique has been developed which starts from typical carbide powders, commercially available in the micron range, and uses a radio frequency argon plasma.

Basically, the process, which was previously described in the case of ultrafine nitrides preparation [4], consists in the dissociation–vaporization of the primary powders, followed by a vigorous quench of the resulting vapours in a water-cooled stainless steel chamber, and collection of the condensed products from the walls of this chamber and a cylindrical electrostatic precipitator. Fig. 1 shows a schematic illustration

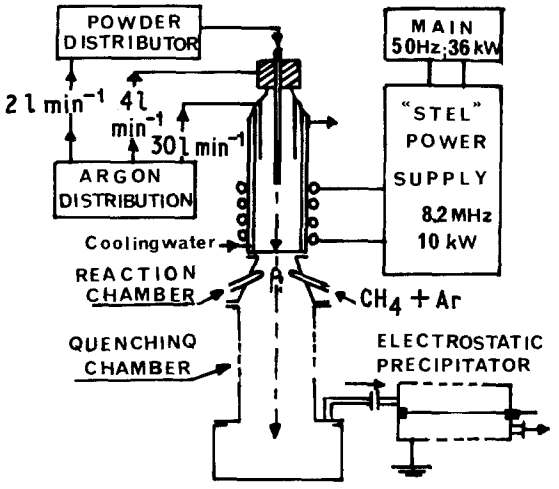

Figure 1 Schematic illustration of the ultrafine powder preparation apparatus.

of the various parts of the experimental apparatus, as well as its principal operating conditions. It will be noticed that gaseous injections can be made radially into the tail of the plasma flame, when the primary powders have been fully vaporized. Methane and argon–CH_4 mixtures have been used in the present case, in order to separately adjust the average carbon potential in the reaction chamber and study its influence on the composition and structure of the reaction products. It was qualitatively observed that both the amount of CH_4 molecules introduced in the reaction chamber (Fig. 1) in the unit of time, and the initial velocity of the reacting gas, bear a strong influence on the course of reactions and the composition of the final products. High methane ratios and/or high initial velocities, the latter allowing improved blending of the reacting species, were found necessary for eliminating Ta_2C from the condensed powders.

The physical and chemical properties of a typi-

TABLE I Emission spectrographic analyses of TaC powders.

Element (ppm)	High frequency powder		Arc plasma [2]
	Starting powder	Ultrafine powder	
Ag	100	10	>1000
Al	10	10	10
As	10	10	0
Co	10	10	1000
Cr	10	10	1000
Cu	1000	1000	100
Fe	1000	1000	1000
In	10	10	0
Mn	5	5	5
Mg	10	10	10
Na	100	50	0
Ni	50	50	1000
Pb	100	10	5
Sb	50	50	10
Si	10	10	100
Sn	10	10	5
Tl	5	0	0
Ti	10	10	0
Zn	1000	1000	10
Total	3500	3300	> 5000

TABLE II Properties of ultrafine powders.

Properties and measuring technique	Arc plasma powder [2]	High frequency plasma powder
Particle size, Å (X-ray line broadening)	400	400
Observed lattice parameter (Å)	4.45	4.45
(1 0 1)Ta_2C/(1 0 1)TaC line intensity ratios	not detected	0.01
Composition, wt% (neutron activation)		
oxygen	2.8	0.12
chlorine	0.22	0.006
total carbon	6.7	8.2

cal sample of tantalum carbide powder, taken from the quenching chamber, are summarized in Tables I and II. The same information, relative to a material prepared via the arc-plasma route [2] is also reported. It is of interest to note that the high frequency plasma technique is non-polluting. On the contrary to that found in the arc-plasma powders [3] no metallic contamination is introduced here as a result of chemical corrosion and/or abrasion of the environment and electrodes

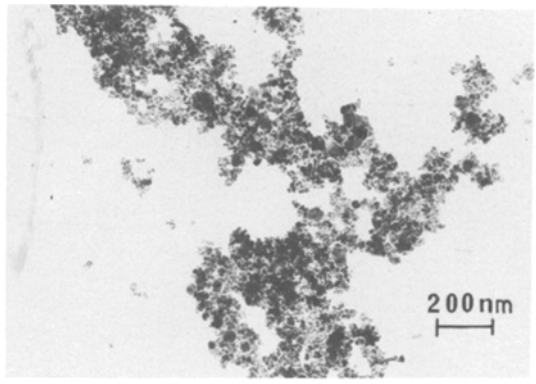

Figure 2 Agglomerates of ultrafine particles.

by the reacting species. It also appears likely that the geometry of the quenching chember (Fig. 1) is responsible for the slight reduction in the Ag and Pb contents in the final products, as it might favour selective transport of some vapours towards the cooled periphery of the main gas flow. Powders collected from the electrostatic precipitator are consistently more carburized than those from the quenching chamber. Ta_2C in particular is easily avoided.

Transmission electron microscopy shows that roughly speaking, two kinds of powder may be obtained, depending upon the carbon potential in the reaction chamber. At low methane injection rates, the condensed products (Fig. 2) consist of agglomerates of more or less faceted mixed TaC and Ta_2C particles, the size distribution curves of which are faily broad. Particle diameters usually range from ~ 5 to ~ 100 nm with a maximum around 40 (Table II). Under high carbon potential

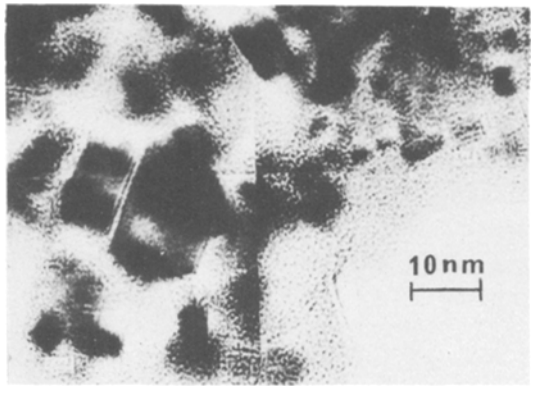

Figure 3 High resolution electron micrograph of TaC particles in a carbon matrix.

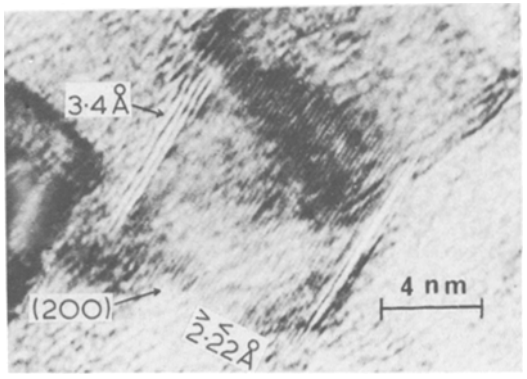

Figure 4 Graphite deposits on (2 0 0) TaC planes.

conditions, on the other hand, Ta_2C can be completely eliminated as mentioned, and the tantalum monocarbide crystals have a tendency to be smaller and more easily identifiable. Fig. 3 shows a typical high resolution electron micrograph of a material prepared under such conditions. The stoichiometric TaC grains are embedded in an amorphous carbon matrix, which probably acts as a protection against oxidation and is thought to be responsible for the rather low oxygen contents recorded here (Table II). On closer examination (Fig. 4), many crystals appear as fairly well formed cubes, the faces of which correspond to the {1 0 0} crystal planes, as indicated by the measured interplanar spacing (Fig. 4). Also, on some of these cube planes, graphite-like deposits a few layers thick, (interplanar spacing: 3.4 Å) are visible.

In summary, the present work is believed to show that ultrafine TaC powders can be prepared under conditions allowing higher purities to be achieved than seems to be commonly possible when arc-plasma or chemical vapour-deposition techniques are used. The presence of sizable amounts of excess carbon appears to be helpful as a protection against oxidation and possibly as a dispersing medium for the carbide particles.

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J. CANTELOUP
A. MOCELLIN
Centre des Matériaux,
Ecole des Mines de Paris,
B.P. 87–91003 Evry-Cedex,
France

Slow surface crack growth during Vickers indentation on glass

The indentation fracture of glass and other brittle materials has been the topic of several recent publications [1–3]. Although cracks have been observed to form beneath the surface of glass during Vickers indentation, the growth of surface cracks during the loading half of the indentation cycle has been a matter of speculation. Almond [4] has observed cracks growing from the corners of Vickers indents in carbides by performing the indentation experiments in a scanning electron microscope, but this technique is not suitable for non-conductors.

A set of indentation experiments performed in these laboratories under unusual conditions has thrown some light on the problem. A bench model Instron testing machine with a Vickers diamond mounted from the cross-head was used to indent a glass block. There was no damping material underneath the Instron, and so the vibration of the motor was transmitted through the frame of the testing machine to the cross-head. Subsequent measurements of the deflection of the cross-head using a displacement transducer indicated that there was a load fluctuation of $\pm\frac{1}{2}\%$ at an applied load of 5 kg.

The Vickers indent formed at 5 kg on glass by this method was very poor (Fig. 1), but it pos-