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Synthesis of TiO_2 and TiN nanosize powders by intense light ion-beam evaporation

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Ultrafine nanosized powders of TiO_2 and TiN have been synthesized by the reactive ion-beam evaporation technique. In an oxygen or nitrogen atmosphere (1–10 Torr), a high-power-density ion beam (about 0.4 GW cm^{-2}) is focused onto a Ti target; as a result of the interaction between ablated particles and gas, fine and ultrafine powders are synthesized. The influence of gas pressure and target–collector distance on the particle composition, size distribution and shape have been studied. At longer target–collector distances and higher pressures, powders in the 4–45 nm range are collected while, at shorter distances and lower pressures, the powders are in the micrometre range. TiO_2 particles are spherical in shape, while TiN particles are cubic.

1. Introduction

The interest in preparing powders is driven largely by the enhanced possibility of commercial-scale processes. Generally, the new synthetic routes to advanced powders are more expensive than currently established powder-manufacturing methods. Therefore, increasing knowledge in the area of advanced synthesis methods will improve the production reliability and lower their cost.

Intense light ion beams promise to yield exciting results in the applications which usually involve rapidly melting, evaporation or ablation of a target material surface. Applications as beam–matter interactions and materials processing continue to be explored, e.g., alloy mixing, thin-flim deposition or powder production [1–4]. At high intensities (greater than 20 J cm^{-2} and greater than 0.25 GW cm^{-2}), the ion-beam evaporation (IBE) technique can provide rapid ablation of material from targets. If this process takes place in an ambient gas, it will be followed by fast reaction and cooling by collisions with the gas particles. In this way, fine and ultrafine powders can be synthesized.

IBE seems to be similar to the laser ablation method [5, 6], but the greater efficiency of ion beam sources, the more efficient coupling of energy to the target and the weaker ion-beam–plasma interactions should allow efficient production in comparison with pulsed-laser methods. Our initial results on Al_2O_3 [7] have shown the feasibility of this approach.

In this paper we present investigations on the synthesis by reactive IBE of TiO_2 and TiN powders. A detailed study of the influence of the major operating conditions on the powder characteristics is reported.

2. Experimental procedure

The powder production by the reactive IBE method is depicted schematically in Fig. 1. A target is irradiated by an intense ion beam. The ablated material expands in a plume normal to the target surface and collides with the ambient gas. As a result of the interaction, fine and ultrafine powders are synthesized. The powders are collected on a mesh collector placed at a given distance from the target.

Experiments currently under way here utilize a light ion-beam generator, ETIGO-II [8, 9]. The ions are provided by a magnetically insulated diode in extraction geometry. This configuration can produce a focusable light ion beam with a high efficiency. The relevant operational parameters for the pulsed ion-beam system and experimental characteristics are presented in Table I. Because the magnetically insulated diode and the reaction chamber are operating in vacuum, about 10^{-4} Torr, and 1–10 Torr pressure, respectively, a Mylar film 2 μm thick has to be placed between them. A view of the experimental set-up is illustrated in Fig. 2. Powders of TiO_2 and TiN have been prepared in the same way; only the gases were oxygen and nitrogen, respectively.

The powders collected on a stainless steel mesh (400 meshes) were observed and characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and transmission electron diffraction (TED).

3. Results and discussion

In Fig. 3 we present the SEM photographs of TiO_2 powders produced in oxygen at 10 Torr from a Ti target and collected at different distances. Powders collected at 100 mm distance from the target have

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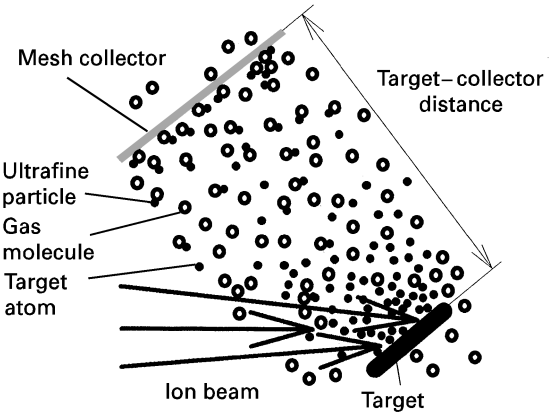


Figure 1 Schematic diagram of powder production.

TABLE I Ion beam characteristics and main experimental characteristics

Pulsed ion-beam system parameters	
Diode voltage	1.1 MV
Diode current	80 kA
Ion current density	0.5 kA cm^{-2}
Pulse width	70 ns
Fluence on target	30 J cm^{-2}
Power density on target	0.4 GW cm^{-2}
Beam composition	80% protons
Experimental characteristics	
Target	Ti
Ambient gas	O_2, N_2
Gas pressure	1, 10 Torr
Target–collector distance	100–330 mm
Beam–target angle	45°
Beam area on target	5 cm^2

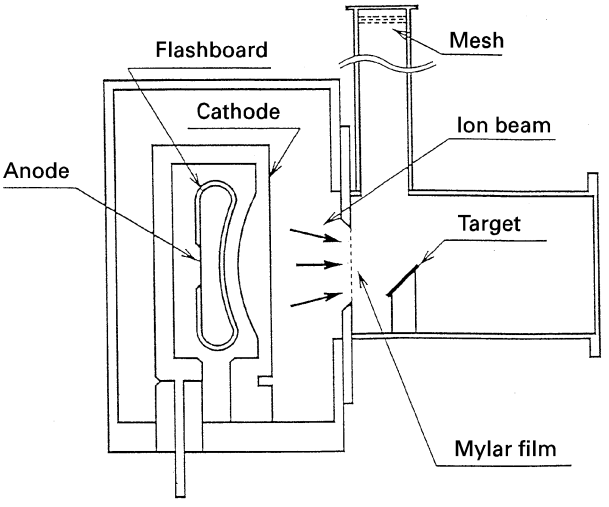
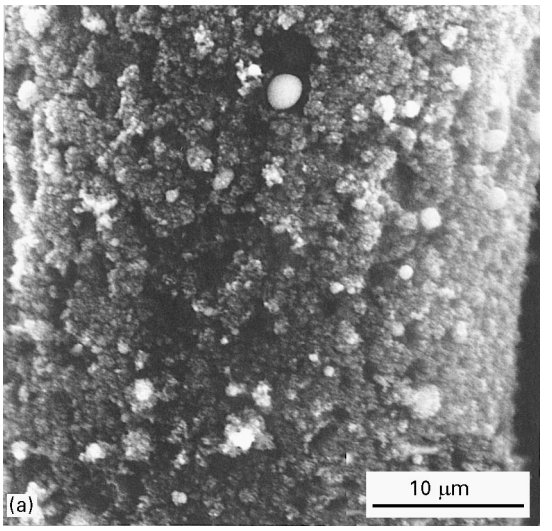
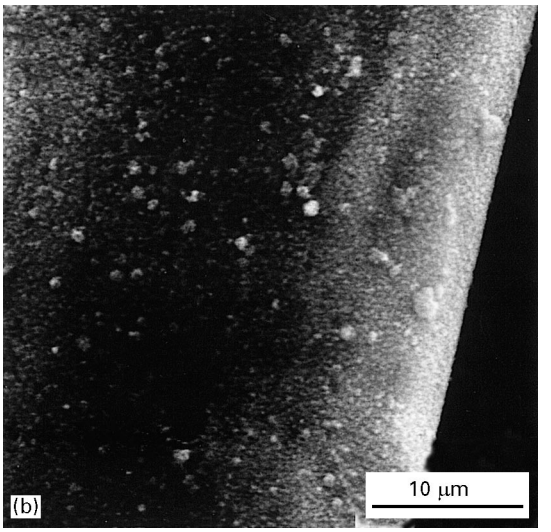


Figure 2 Experimental set-up.





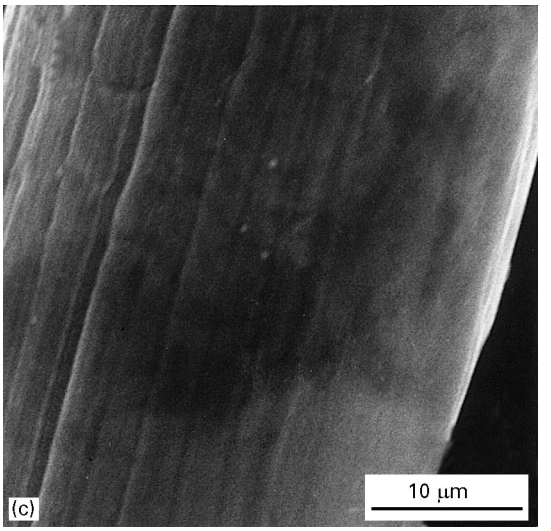


Figure 3 SEM photographs of the powders deposited on stainless steal mesh in an oxygen atmosphere (10 Torr) with a Ti target: (a) collected at 100 mm; (b) collected at 200 mm; (c) collected at 330 mm.

relatively large diameters (micrometre range). TEM investigations have shown that the microsized particles are covered with nanosized particles. By increasing the collecting distance, the particle diameter decreases and hence at 330 mm they are in the nanometre range. In addition, the quantity decreases at longer distances.

Fig. 4a shows the TEM photograph of TiO_2 powder prepared in oxygen from a Ti target and collected at 330 mm. The particles are in globular shape. Fig. 4b is a TEM photograph of TiN nanosized powders. In this case the particles are no longer of spherical form, TiN being nanocrystallites with typical cubic form.

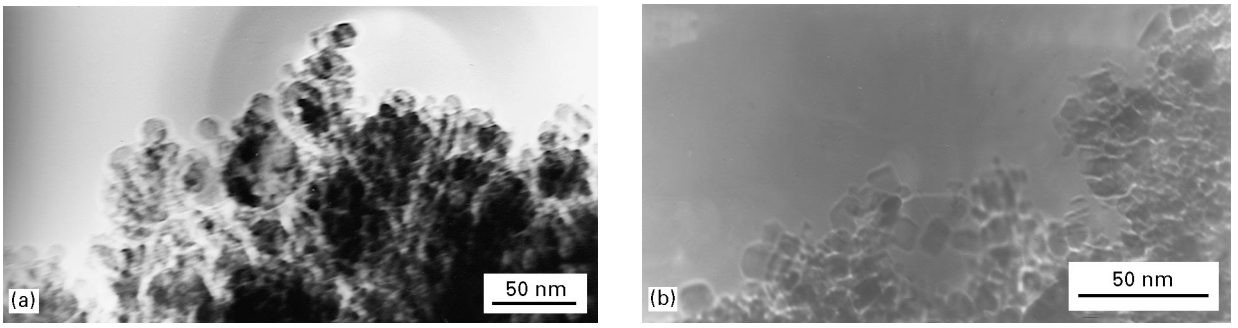


Figure 4 TEM photographs of TiO_2 powders and TiN nanosized powders produced by IBE and collected at 330 mm with a Ti target: (a) oxygen at 10 Torr; (b) nitrogen at 10 Torr.

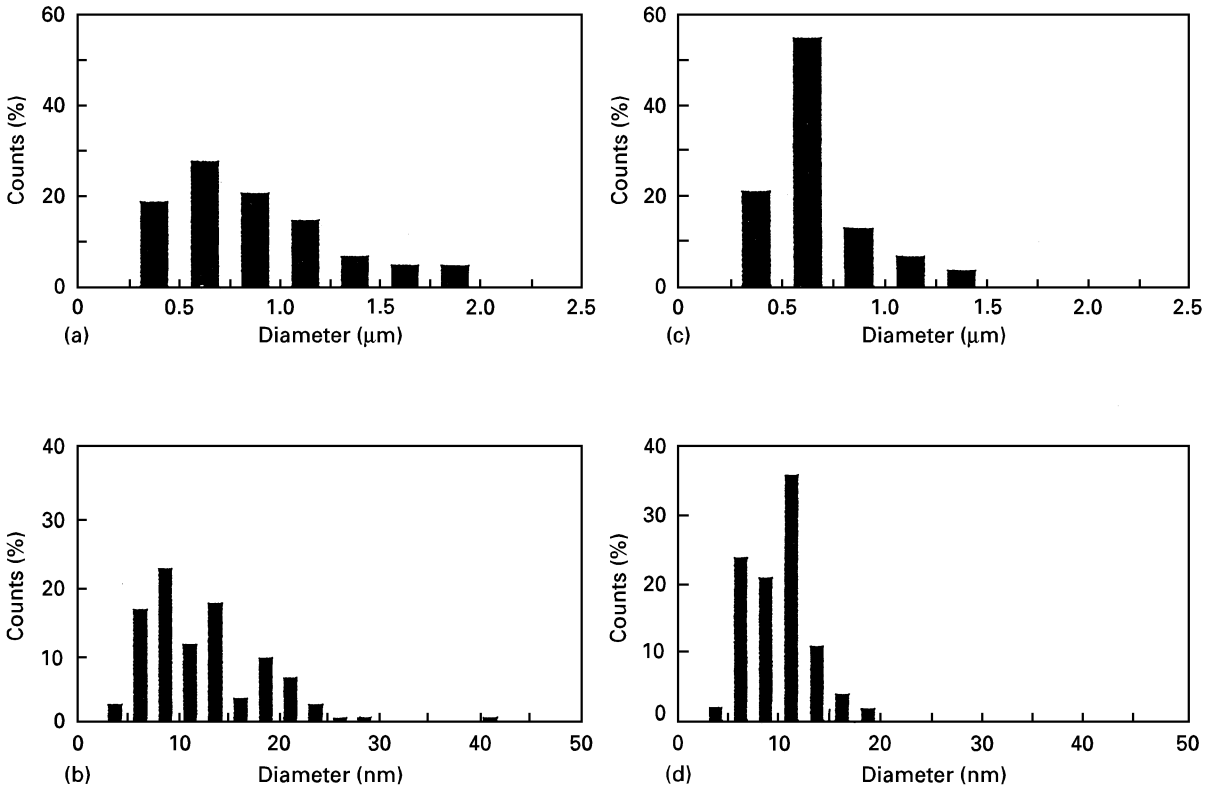


Figure 5 Typical size distribution of the powders prepared by reactive IBE with a Ti target (20 shots): (a) in oxygen at 10 Torr, collecting distance $l = 100$ mm; (b) in oxygen at 10 Torr, collecting distance $l = 330$ mm; (c) in nitrogen at 10 Torr, collecting distance $l = 100$ mm; (d) in nitrogen at 10 Torr, collecting distance $l = 330$ mm.

The size distributions of the TiO_2 particles synthesized in oxygen at 10 Torr and collected at 100 mm and 330 mm are shown in Fig. 5a and b, respectively. At 100 mm the TiO_2 powder is represented by larger particles, which have diameters in the 0.3–2 μm range. It is obvious that ultrafine powders with diameters of 4–45 nm could be collected only at 330 mm distance. In Fig. 5c and d are given the size distributions of TiN produced in nitrogen at 10 Torr for two collecting distances. Also, in this case, the ultrafine powders were collected at longer distances, while at short distances they are in the micrometre range.

Regarding the composition of the nanosized powders prepared in oxygen, in Fig. 6 are shown the electron diffraction patterns. At lower oxygen pressures, we notice that, besides TiO_2, TiO is formed as well; this suggests that oxygen at 1 Torr is not sufficient for complete reaction of all ablated Ti particles.

From Fig. 7a we observed another interesting aspect; in the case of nitrogen at 1 Torr, besides TiN, TiO has been identified too. Similar components have also been noticed in XRD patterns. This can be explained by two possible processes: (a) because of the lack of nitrogen, not all Ti particles react, causing pure Ti particles to remain; when TiN and Ti powders are taken from the reaction chamber, because nanosize powders are very reactive, Ti atoms will react with atmospheric oxygen; (b) it is possible that adsorbed oxygen on the chamber walls is responsible for TiO.

In Table II we present an overview of the powders produced by reactive IBE from a Ti target irradiated in an oxygen or nitrogen atmosphere.

From Table II, one can see that the collector–target distance and the gas pressure are two important parameters. The powders collected at smaller distances

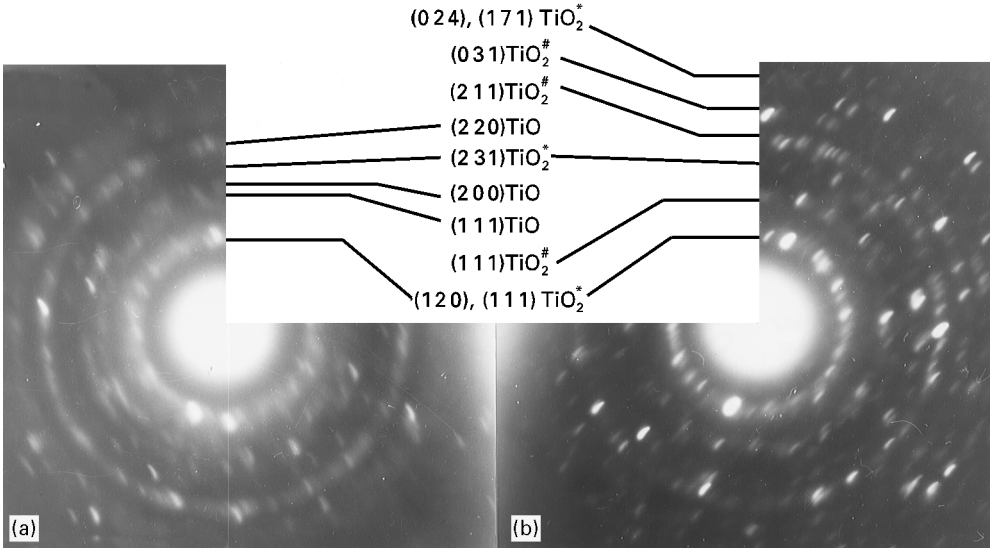


Figure 6 Electron diffraction patterns of TiO_2 powders prepared in oxygen from a Ti target and collected at 330 mm (Joint Committee on Powder Diffraction Standards [10] data: * Card 29-1360; # Cards 21-1276 and 29-1361): (a) 1 Torr; (b) 10 Torr.

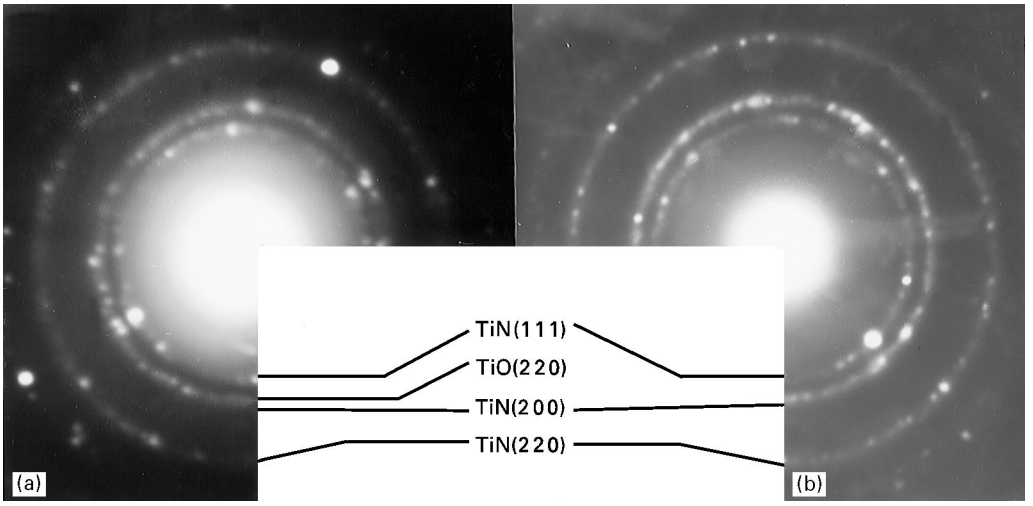


Figure 7 Electron diffraction patterns of TiN powders prepared in nitrogen from a Ti target and collected at 330 mm (Joint Committee on Powder Diffraction Standards [10] data: Cards 29-1361 and 38-1420): (a) 1 Torr; (b) 10 Torr.

TABLE II Characteristics of powders produced by the reactive IBE method

Target material	Ambient gas	Gas pressure (Torr)	Target–collector distance (mm)	Particles	Particle size minimum–maximum (nm)
Ti (99.5%)	O_2 (99.5%)	1	100	TiO + TiO_2 (XRD)	380–2410 (SEM)
			330	TiO + TiO_2 (TED)	4–40 (TEM)
		10	100	TiO_2 (XRD)	320–2000 (SEM)
			330	TiO_2 (TED)	4–45 (TEM)
	N_2 (99.5%)	1	100	TiO + TiN (XRD)	180–1800 (SEM)
			330	TiO + TiN (TED)	5–38 (TEM)
		10	100	TiN (XRD)	380–1420 (SEM)
			330	TiN (TED)	5–23 (TEM)

have larger diameters. This could be useful for powder preparation with a controlled particle distribution.

4. Conclusions

From the above experimental studies we have drawn the following conclusions.

1. TiO_2 and TiN nanosized powders have been prepared by the IBE reactive method.

2. Powders collected at longer distances are nanosized particles, 4–45 nm in diameter, while powders collected at shorter distances are mostly in the micrometre range.

3. At higher pressures and longer target–collector distances, the particles of the plume react completely with the ambient gas.

4. TiO_2 nanosized particles are spherical, while TiN particles are cubic.

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