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Direct production of ultra-fine nitrides (Si_3N_4 and AlN) and carbides (SiC, WC and TiC) powders by the arc plasma method

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A direct method of producing ultra-fine nitride and carbide powders of 20 to 40 nm by arc plasma in a controlled atmosphere (with ammonia or methane gas) is described. The powders produced were SiC, TiC, WC (+W_2C), AlN and Si_3N_4. Other nitrides and carbides may also be produced using this method. Special attention was paid to the production conditions of silicon nitride.

1. Introduction

In recent years, much attention has been given to ultra-fine powders. Physical and chemical property dependence on particle size, which might be different from that of bulk materials, has been a most interesting subject. Ultra-fine powders produced by electric arc plasma are considered to have a low impurity level and they have been successfully applied in powder metallurgy.

In the field of modern ceramics, ultra-fine ceramic powders are useful to obtain materials for new applications as technological advancement demands.

Previously, methods to produce ultra-fine metallic powders by arc plasma [1], and to nitride ultra-fine silicon powders [2] were presented by our group. Uda *et al.* attempted to produce directly ultra-fine nitride powders by the arc plasma method using a nitrogen and argon gas mixture. They could obtain TiN and a mixture of AlN and aluminium powder, but could not produce silicon nitride powder using a nitrogen atmosphere in arc plasma [3]. The possibility of applying ammonia gas in the arc plasma for the production of ultra-fine nitride powders was first reported by our group [4, 5]. The production of a mixture of aluminium and AlN using a gas mixture containing ammonia was later reported by Uda *et al.* [6]. However, in the present work, successful production of silicon nitride and aluminium nitride is reported.

Earlier attempts by us to produce ultra-fine silicon nitride powder, produced crystal growth in a ribbon like shape, and spherical ultra-fine silicon nitride powders could not be obtained [2].

The present work describes a method to produce ultra-fine nitride and carbide powders by controlling the atmosphere inside and outside the arc plasma. Nitride and carbide powders were spherical or cubic in form this time, and not ribbon like. It was also possible to produce directly a mixture of ultra-fine nitride and carbide powders in the case of silicon.

2. Experimental procedure

A homemade arc plasma furnace, that has been previously described [1], was used. In the present work, a different atmosphere control system was applied, as shown schematically in Fig. 1.

The chemical composition (wt %) of the raw materials was as follows: for silicon Si 98.1, C 0.09, P 0.01, S 0.02, Fe 0.62, Al 0.92 and Ca 0.10, for titanium Ti 99.66, C 0.004, N 0.004, H 0.0015, O 0.177 and Fe 0.15, for tungsten W 97.75, Th 1.95, Fe < 0.01 and other elements < 0.01, and for aluminium Al 99.99 and other elements < 0.002.

Experimental conditions are shown in Table I. A 50 vol % argon and 50 vol % nitrogen mixture was used to produce ultra-fine powder at a rate of about 2 mg sec^{-1}. An argon and hydrogen mixture was fixed at 30/70 in order to have the same production rate for all cases. These gas mixtures had been found to give approximately the optimum conditions for powder production [1]. Some other gas mixtures were also employed. Ammonia gas could be mixed up to 30% in volume with argon in the plasma gas without loss of electric arc stability.

Some of the silicon nitride ultra-fine powders were obtained in an amorphous form. They were heat treated at 1623 K for 3600 sec in an argon atmosphere with a small amount of hydrogen in order to crystallize them.

Ultra-fine particles were analysed by X-ray diffractometer and infrared spectrometer. The amount of free carbon was measured by chemical methods. The size and shape of the powders were studied using a transmission electron microscope (TEM).

3. Results and discussion

Ultra-fine nitrides and carbides powders were produced by an electric arc in a controlled atmosphere containing ammonia and methane gas respectively. Table II shows the type of powder produced for each gas mixture applied, and respectively TEM

TABLE I Experimental conditions for the production of ultra-fine nitrides and carbides powders

Metal	Plasma and carrier gas mixture (vol %)		Arc current (A)	Spray gas and flow ($\mathrm{l\,min^{-1}}$)
Si	Ar/N_2	(50/50)	100	–
	Ar/N_2	(50/50)	100	NH_3, 5
	Ar/H_2	(35/65)	100	NH_3, 5
	Ar/NH_3	(70/30)	100	–
	$Ar/N_2/NH_3$	(15–75/20–80/5)	100	–
	Ar/CH_4	(85/15)	100	–
	$Ar/H_2/CH_4$	(85/10/5)	100	–
	$Ar/H_2/CH_4$	(80/10/10)	150	–
	$Ar/H_2/CH_4$	(70/20/10)	150	–
	Ar/H_2	(30/70)	150	CH_4, 8
	$Ar/N_2/NH_3/CH_4$	(48/45/5/2)	150	–
	$Ar/N_2/NH_3/CH_4$	(49.5/45/5/0.5)	150	–
Ti	Ar/CH_4	(85/15)	150	–
	$Ar/H_2/CH_4$	(45/50/5)	150	–
W	Ar/CH_4	(85/15)	150	–
	$Ar/H_2/CH_4$	(45/50/5)	150	–
Al	Ar	(100)	150	NH_3, 5

micrographs (Fig. 2) and X-ray diffractograms (Figs 3, 7, 10 and 11) are indicated.

3.1. Silicon nitride ultra-fine powders

Silicon nitride ultra-fine powders were produced in an amorphous state, and then were heat treated in an argon atmosphere for crystallization. X-ray diffractograms of powders produced with a mixture of argon and nitrogen in the plasma arc, and ammonia gas as the spraying gas, are shown in Figs 3a and b, before and after heat treatment respectively. After heat treatment, the weight percentage of silicon nitride present in the powders was measured by the method of Sawhill and Haggerty [7]. Using a mixture of nitrogen (60%) and argon (40%) in the plasma gas, 71 wt % of crystallized silicon nitride was obtained. However, using a mixture of hydrogen (65%) and argon (35%) in the plasma gas, only 21 wt % of crystallized silicon nitride was obtained. The rest of the material may be silicon and/or amorphous silica. It can also be seen that silicon peaks disappear after the heat treatment (Fig. 3).

When using a nitrogen–argon plasma gas mixture, without applying ammonia, no silicon nitride could be produced. This indicates that only the spraying of ammonia gas provides the necessary nitrogen for the nitridation of the silicon particles to occur. The nitrogen added to the plasma gas has the role of producing the ultra-fine metallic silicon powders, that are subsequently nitrided by the ammonia spray.

A direct result from the changing of the plasma gas composition is obtained in the temperature of the plasma produced. Additions of gases, such as hydrogen and nitrogen, provide a hotter plasma. These gases elevate the plasma arc voltage and thus a higher energy input is necessary to maintain the same current level [8]. Gas thermal conductivity also plays an important role in controlling temperature of the metallic piece. Of the gases used in this work, argon has the lowest thermal conductivity but produces the highest plasma stability because of its higher ionization potential. The high thermal conductivity of the plasma gas raises its heat conduction efficiency and hence the metallic piece becomes hotter [8]. Thermal conductivity is highest in the case of hydrogen, which is ten times that of argon at room temperature. Nitrogen, methane and ammonia gas also have greater thermal conductivities than argon, but the differences are not as great as for hydrogen. Ammonia gas has the strongest effect on the arc stability. It would be thought that a higher plasma temperature produces a better yield of nitride powders, however, that is not

TABLE II Type of ultra fine powder produced, according to gas mixture

Type of ultra-fine powder	Plasma gas	Spraying gas	TEM micrograph Fig. no.	X-ray diffractograph Fig. no.
Si	$Ar + N_2$	–		
Amorphous Si_3N_4	$Ar + N_2$	NH_3		3
	$Ar + H_2$	NH_3		
	$Ar + NH_3$	–	2a	
	$Ar + N_2 + NH_3$	–		
SiC + free C	$Ar + CH_4$	–	2b	7
SiC	$Ar + H_2 + CH_4$	–		
	$Ar + H_2$	CH_4		
Amorphous Si_3N_4 with SiC	$Ar + N_2 + NH_3 + CH_4$	–	2c	10
TiC	$Ar + CH_4$	–		
	$Ar + H_2 + CH_4$	–	2d	
$WC + W_2C$	$Ar + CH_4$	–		
	$Ar + H_2 + CH_4$	–	2e	
AlN	Ar	NH_3	2f	11

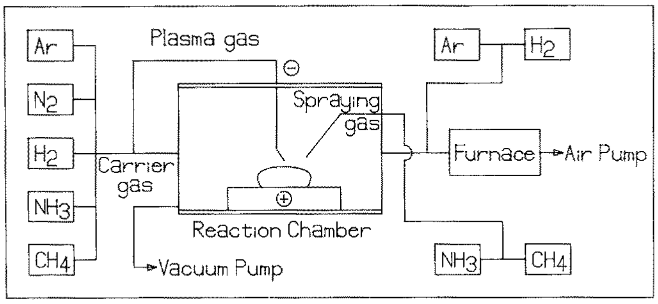

Figure 1 Schematic representation of the new gas distribution system used in the present work. Various kinds of atmosphere may be controlled for carrier, plasma and spraying gas. Possible gas mixtures are argon, nitrogen, hydrogen, ammonia and methane gas. The position of spraying gas was about 20 mm behind the arc.

the case. Using hydrogen, which best elevates the working temperature, instead of nitrogen in the plasma gas, and spraying ammonia gas, produces a difference in the yield of crystallized silicon nitride as indicated before. The presence of nitrogen in the plasma gas mixture, although lowering the plasma temperature with respect to hydrogen, increases the nitrogen partial pressure, leading to higher nitridation efficiency. The presence of hydrogen in the plasma gas mixture, even though it raises the plasma temperature,

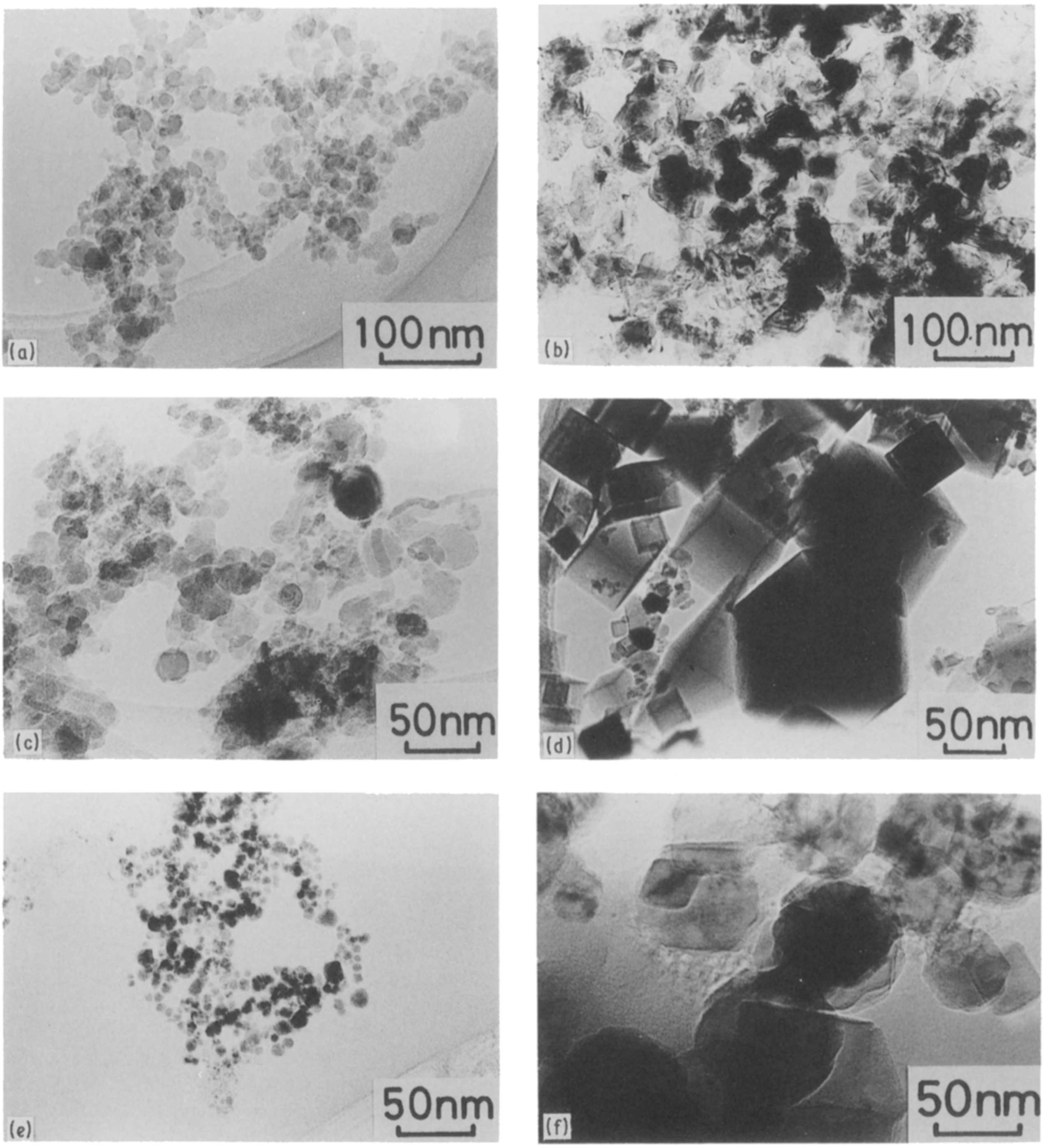

Figure 2 TEM micrographs of powders produced. (a) Amorphous Si_3N_4, (b) SiC with free carbon, (c) SiC with amorphous Si_3N_4, (d) TiC, (e) WC with W_2C, and (f) AlN.

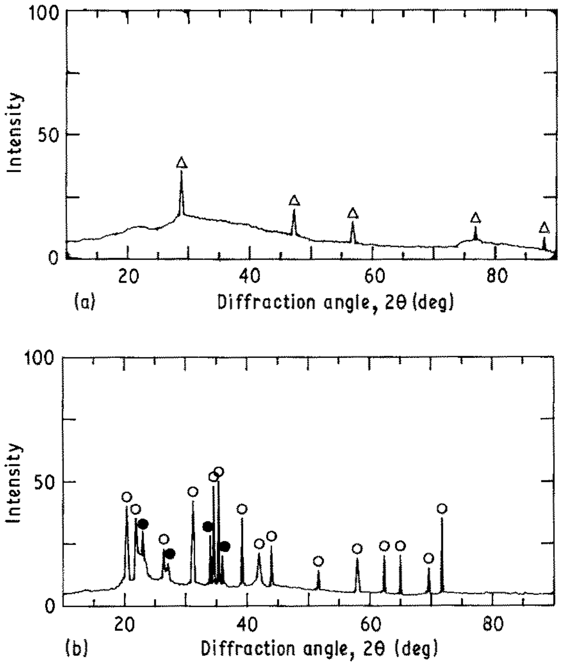

Figure 3 X-ray diffractogram of ultra-fine Si_3N_4 powder. A mixture of nitrogen (60%) and argon (40%) was used for the carrier and plasma gas, and ammonia gas was sprayed on the sample. (a) Before and (b) after heat treatment. (△ silicon, ○ α-Si_3N_4, ● β-Si_3N_4)

increases its partial pressure in the surroundings, and consequently lowers the nitrogen partial pressure, leading to a lower nitridation efficiency.

Amorphous silicon nitride was also produced adding ammonia to the plasma gas mixture. However, the addition of more ammonia to the plasma gas, resulted in a greater silicon residue in the powders, and thus the amorphous silicon nitride amount diminished, as shown in Fig. 4. In this case, the plasma conditions change greatly because ammonia is being added to the plasma gas, instead of being sprayed. Inside the plasma, ammonia gas is ionized and divided in one part of atomic nitrogen to three parts of atomic hydrogen. This may again produce a higher hydrogen partial pressure in the surroundings of the plasma gas that results in a lower nitridation efficiency.

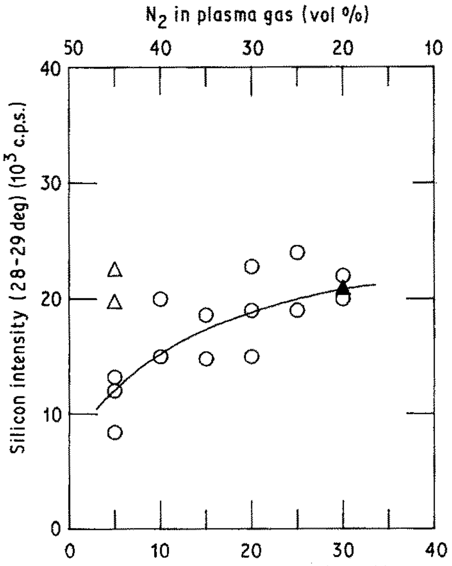

Figure 4 X-ray diffraction intensity of a silicon peak of plane (1 1 1) as a function of nitrogen and ammonia volume percentage in the plasma gas. (○ N_2 + NH_3 50% Ar 50%, ▲ NH_3 30% Ar 70%, △ NH_3 5%, Ar 95%).

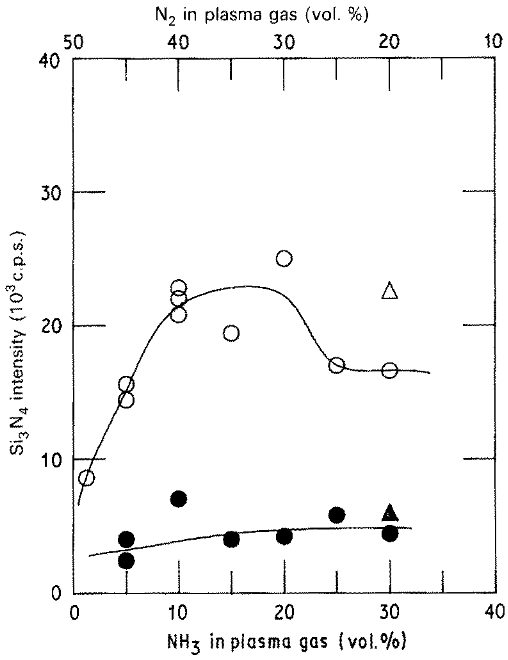

Figure 5 X-ray intensity of α-(△○) and β-(▲●) Si_3N_4 peaks of planes (2 0 1) and (1 0 1) respectively, as a function of nitrogen and ammonia volume percentage in the plasma gas. (○● 50% Ar, △▲ 30% NH_3, 70% Ar).

Results of applying a mixture of only ammonia gas and argon to the plasma gas are also shown in Fig. 4. It can be seen that an argon content of 70% or more in the plasma gas, produces a high, but fairly constant amount of silicon residue. However, as more nitrogen is included in the plasma gas, the silicon residue diminishes, showing the importance of a high nitrogen partial pressure in the surroundings of the plasma for the nitridation to occur effectively.

3.2. Heat treatment of amorphous silicon nitride

The ammonia content in the plasma gas also influences the final crystalline structure of the silicon nitride after heat treatment, as shown in Fig. 5. The crystalline amount is fairly constant in the case of the β phase. However, the α phase yield has a maximum for nitrogen–ammonia gas ratios between 30/20 and 40/10 with 50% of argon content. Silicon nitride weight percentage was calculated for those two plasma gas mixtures: 63.5 wt % for Ar 50%, N_2 30% and NH_3 20%, and 55.1 wt % for Ar 50%, N_2 40% and NH_3 10%. With these combination of gases, the favourable properties of each one of the gases can be successfully applied.

A change in nitrogen content alone, also produces different compositions of α and β phase, as shown in Fig. 6. A constant amount of ammonia gas of 5% was used in the plasma gas, and different mixtures of argon with nitrogen were added. The α phase decreased monotonously by increasing the nitrogen content in the plasma gas. Before the heat treatment for crystallization of the silicon nitride, Fig. 4 indicates a reduction in the amount of silicon residue, hence, an

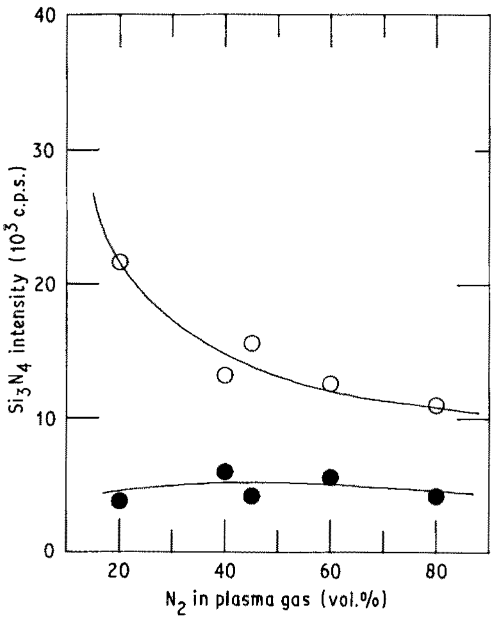

Figure 6 X-ray intensity of α-(○) and β-(●) Si_3N_4 peaks of planes (2 0 1) and (1 0 1) respectively, as a function of nitrogen volume percentage in the plasma gas.

increasing amount of amorphous silicon nitride, with increasing nitrogen content in the plasma gas. However Fig. 6 shows that the degree of crystallization of this amorphous silicon nitride, after heat treatment, is smaller with increasing nitrogen content in the plasma gas. In other words, nitrogen content in the plasma gas, affects crystallization of the amorphous silicon nitride produced. Several parameters may affect the degree of crystallization, such as the presence of defects (porosities, precipitates), and glassy phase energy. Nitrogen, by affecting the thermal conductivity of the gas mixture, may reduce the cooling rate of the powders and hence, reduce the number of defects present and degree of disorder of the amorphous phase. At the moment of heat treatment, low phase energy and a reduced number of nucleation sites, reduces the amount of crystallization.

3.3. Silicon carbide ultra-fine powders

Crystalline silicon carbide ultra-fine powders were directly produced by either including methane gas in the plasma mixture or spraying it. An X-ray diffractogram of the powders produced using argon (85%) and methane (15%) gas in the plasma mixture shown in Fig. 7. The presence of a small amount of silicon powder in the silicon carbide was detected.

The influence of hydrogen content in the plasma gas was also analysed. Fig. 8 shows that the X-ray diffraction intensity of the silicon carbide peak of plane (1 1 1) increases with increasing hydrogen content. The presence of free carbon in the silicon carbide may also be controlled by the amount of hydrogen in the plasma gas mixture, as also shown in Fig. 8. Free carbon content decreases monotonously with increasing hydrogen content. Results of the infrared analysis for the silicon carbide powders produce with and without hydrogen in the plasma gas mixture can be seen in Fig. 9. The amount of silicon in the silicon carbide form, greatly increases when hydrogen is added to the plasma gas mixture.

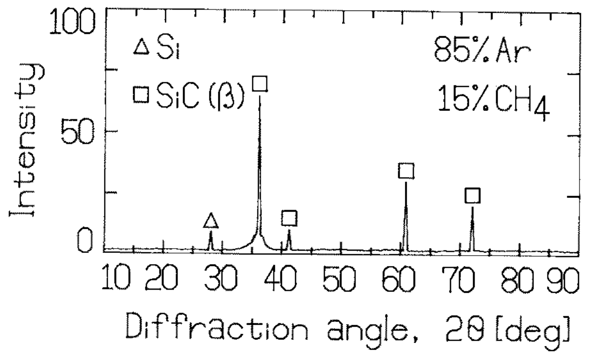

Figure 7 X-ray diffractogram of ultra-fine SiC with silicon powder. A mixture of argon and methane gas was used for the plasma gas.

Hydrogen contributes to the formation of ultra-fine silicon powder that subsequently reacts with methane to produce silicon carbide [5]. At the same time, hydrogen elevates plasma temperature, and hence improves the carburization efficiency of the silicon and reduces the free carbon amount that is present in the powders. The use of methane gas as the spraying gas, requires a high hydrogen content in the plasma gas to produce silicon carbide. The inclusion of methane gas in the plasma gas, provides at the same time of the hydrogen and the carbon necessary for carburization to occur. However, an additional amount of pure hydrogen is always necessary to reduce the amount of free carbon.

3.4. Silicon nitride and carbide ultra-fine powder

A combination of ultra-fine silicon nitride and carbide powder was produced by including ammonia and methane gas in the plasma mixture. The composition of the plasma gas mixture was: NH_3 (5%), CH_4 (2%), N_2 (45%) and Ar (48%). A TEM micrograph can be seen in Fig. 2c. To obtain both nitrides and carbides, the amount and ratio of NH_3 to CH_4 gas should be carefully chosen to control the relative amounts of both nitrides and carbides. X-ray diffractographs of the mixtures produced are shown in Fig. 10. It can be seen that only a small amount of methane gas is enough to produce comparable diffraction patterns of silicon nitride and carbide.

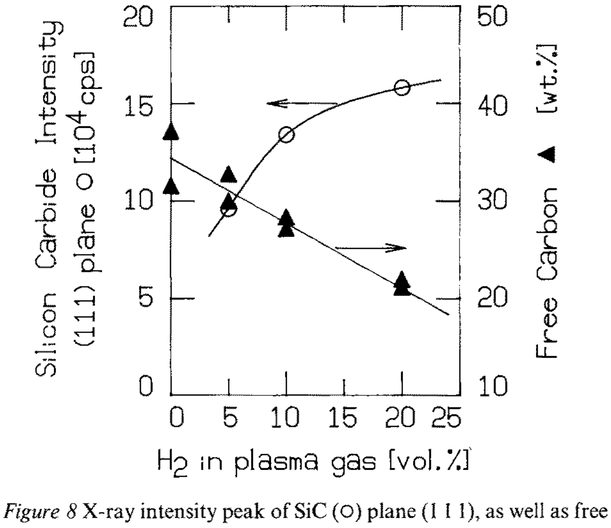

Figure 8 X-ray intensity peak of SiC (○) plane (1 1 1), as well as free carbon (▲) amount present in ultra-fine SiC as a function of hydrogen percentage in the plasma gas.

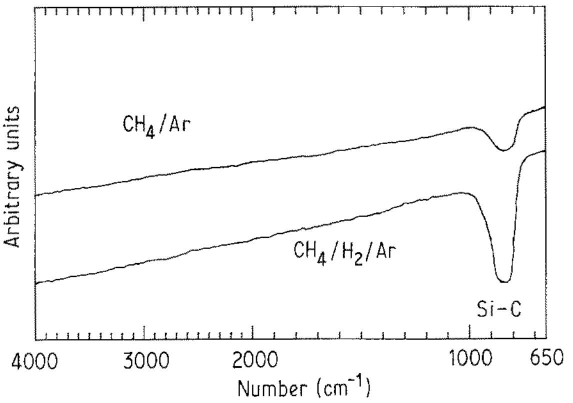

Figure 9 Infrared spectrum of SiC for two different types of plasma gas mixture.

3.5. Other nitrides and carbides ultra-fine powders

Titanium and tungsten carbides were also produced by adding methane gas to the plasma gas. In Figs 2d and e, TEM micrographs are shown. It can be seen that the shape of the titanium carbide crystals is cubic, and that the tungsten carbide crystals are extremely small and spherical in shape.

Aluminium nitride ultra-fine powders were also produced by an argon electric arc plasma in an ammonia atmosphere. The idea of using ammonia gas for the production of ultra-fine nitride powders was first advance by our group [4, 5], and applied for the production of ultra-fine aluminium nitride, by Uda *et al.* [6]. They used ammonia mixed with nitrogen in the plasma gas.

A TEM observation of the powders produced showed that powders of hexagonal crystal like shape with a tendency to be rounded were formed. The particle sizes of this powder were between 20 and 50 nm in diameter, with the smaller ones of rounded shape, forming short chains, and the bigger ones in a more crystal like shape as can be seen in Fig. 2f. An almost full yield of aluminium nitride was produced as seen in the X-ray diffractogram of Fig. 11. The possibility of producing aluminium nitride using only argon as the plasma gas, demonstrates that the main nitriding reaction occurs immediately outside the plasma area. Moreover, unlike in the case of production of silicon nitride, that improves with the presence of nitrogen in the plasma gas, the aluminium nitride yield was as good using only argon gas, as including nitrogen [6]. The lower fusion and boiling points of aluminium may favour the nitridation of aluminium particles away from the plasma. This is not the case for silicon, that requires a high nitrogen partial pressure in the surroundings of the plasma to nitride, as explained before in this work. The spraying of ammonia gas, without using it in the plasma gas, produces a good yield of aluminium nitride.

4. Conclusions

Various kinds of powders were produced by arc plasma in a controlled atmosphere. These are Si_3N_4, AlN, SiC, Si_3N_4 with SiC, TiC, and WC with W_2C. From the obtained results, the following is concluded.

1. Silicon nitride ultra-fine powder can be produced by adding ammonia gas to the arc plasma or to the spraying gas. The highest production rate is obtained when the NH_3 to N_2 ratio in the plasma gas is around 1 to 4. The highest yield of silicon nitride was produced by a mixture of nitrogen and argon in the plasma gas, and ammonia gas as the spraying gas. The presence of hydrogen as well as a high ammonia content in the plasma gas, lowers the amount of silicon nitride produced. Nevertheless, ammonia gas has to be added, mixed in the plasma gas or sprayed in order to obtain silicon nitride.

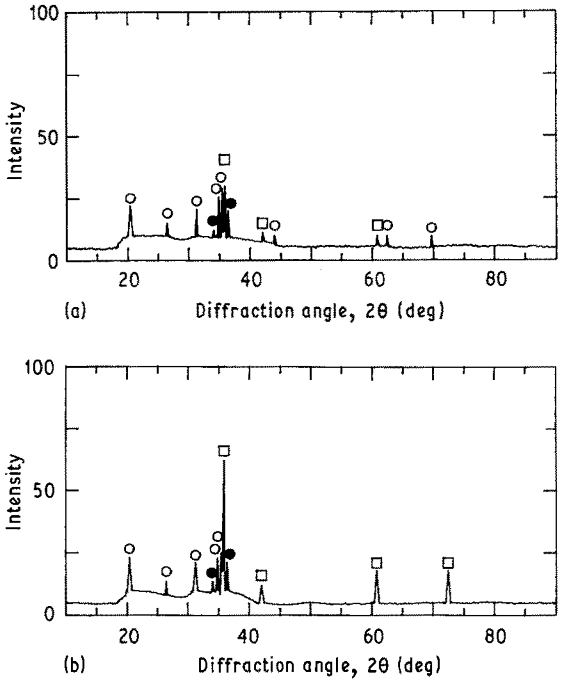

Figure 10 X-ray diffractogram of a mixture of ultra-fine silicon nitride and carbide, produced using ammonia and methane gas in the plasma gas, and subsequently heat treated for crystallization. Plasma gas composition in vol % for (a) Ar 49.5%, N_2 45%, NH_3 5%, CH_4 0.5%, and for (b) Ar 48%, N_2 45%, NH_3 5%, CH_4 2%. (○ α-Si_3N_4, ● β-Si_3N_4, □ SiC).

2. Silicon carbide ultra-fine powders can be produced by including methane gas in the plasma or in the spraying gas mixture. The main product when using silicon, is β-silicon carbide. Addition of hydrogen to the plasma gas mixture, greatly improves silicon carbide formation, and at the same time reduces, the amount of free carbon present in the powder.

3. A combination of ammonia and methane gas added to the plasma gas and to the spraying gas

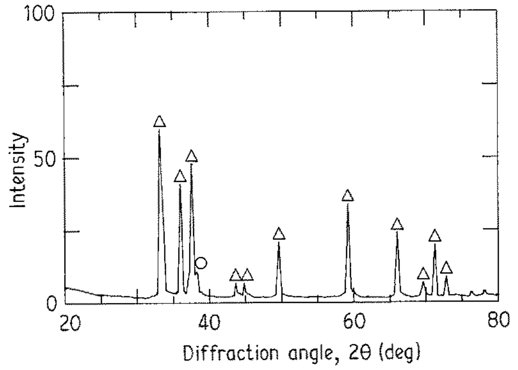

Figure 11 X-ray diffractogram of ultra-fine aluminium nitride with aluminium powder. In an ammonia atmosphere, argon gas was used for the plasma gas. (△ AlN, ○ Al).

produces a mixture of ultra-fine silicon carbide and nitride powders.

4. Tungsten carbide and titanium carbide may also be produced by adding methane gas to the plasma or spraying gas mixture. Titanium carbide crystals were cubic in shape. Tungsten carbide powder was composed of very fine spherical particles of 5 to 10 nm in diameter.

5. Ultra-fine aluminium nitride can be successfully produced in an ammonia atmosphere, by an argon electric arc plasma. Powder particles were rounded crystal like shape, of 20 to 50 nm in diameter.

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