

Progress in thermal plasma deposition of alloys and ceramic fine particles

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Abstract - The recent progress of thermal plasma processes for deposition of fine powder of various metallic and ceramic materials is outlined in this report. R.F. plasma processes for synthesis of ultra fine powder (UFP) of non-oxide ceramic materials such as silicon nitride and silicon carbide are mainly described. Plasma evaporation processes for production of metallic UFP and R.F. plasma processes for synthesis of ceramic UFP which have been developed lately in Japan are explained in detail. The importance of a national research project to be started in order to develop plasma materials processing in this year in Japan is also simply described.

INTRODUCTION

It is very difficult to produce metallic or ceramic fine powder of diameter less than 1000 nm by using spraying techniques with compressed inert gas or liquid and mechanical means such as crushing and grinding.

Lately developmental researches for a large scale production of ultra fine powder (UFP) of metals and ceramic materials are being actively carried out in Japan. UFP of various metals of diameter less than 100 nm can be formed by evaporation and condensation of the metals at reduced pressure in the region of 0.5-50 torr in an inert gas such as Ar. Uyeda and Kimoto (ref. 1) have published such simple method in 1963. This method has been developed in Japan and UFP of several kinds of metals is being produced by melting and evaporation of the metals by R.F. induction heating in a small plant scale. UFP of most of alloys and ceramic materials cannot be easily produced by such method, considering the formation mechanism of UFP during cooling and condensation of metal vapor. A method of UFP production using thermal plasma for evaporation of metals is called "Plasma Evaporation Process". In this case, generally a molten metal pool under high intensity plasma arc is used as an evaporation source of metal, while there is another method in which small particles of metals are injected into thermal plasma and evaporated by heat transfer to the particles from the plasma. When a reactive gas such as nitrogen or methane is mixed into plasma forming gas, UFP of nitride or carbide of evaporated metal can be synthesized by thermal gas phase reaction and rapid cooling of the product. This method is called "Reactive Plasma Evaporation Process". In so-called "Thermal Plasma CVD", a mixture of gaseous reactants are introduced into inert gas plasma for preparation of metallic and ceramic UFP and in some cases the reactants serve as plasma forming gases simultaneously. "Thermal Plasma CVD" seems to be most suitable for synthesis of ceramic UFP.

The recent progress of the above mentioned plasma processes for preparation of UFP is outlined, laying stress on R.F. plasma processes for synthesis of UFP of non-oxide ceramic compounds in this paper.

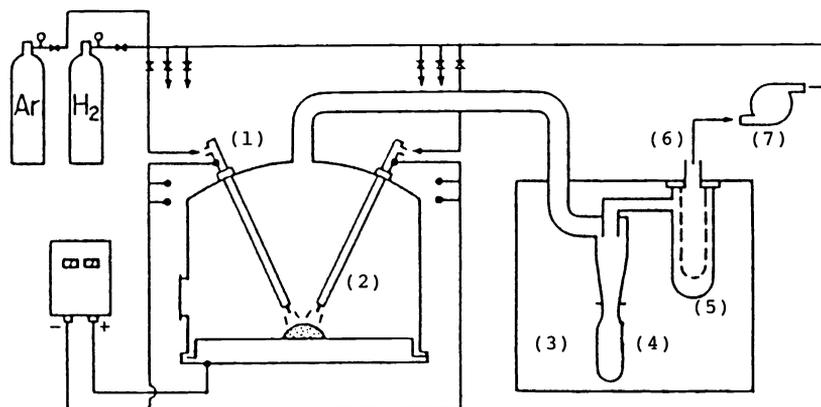
PLASMA EVAPORATION PROCESS

A. EVAPORATION OF MOLTEN METAL POOL

The evaporation and condensation process of anode material overheated under a transferred plasma arc was used for the first time for preparation of UFP of the anode material in 1952 (ref. 2). UFP of many kinds of metals, oxides and carbides was formed by this evaporation process using transferred argon plasma arc. In these both cases, it must be emphasized that a large potential drop at the anode promotes energy transfer of the arc to the anode

material and its vaporization. Horizontally rotating d.c. plasma furnaces have been developed for heating and vaporizing a ceramic material consisting of inside wall of the furnace (ref.3, ref. 4). UFP of the ceramic material are condensed from its vapor at an outlet of the furnace by gas quenching.

A new process for production of UFP of various metals by using d.c. hydrogen plasma arc has been developed recently at National Research Institute for Metals in Japan (ref. 5). A schematic diagram of the apparatus is shown in Fig. 1.



(1):Gas Inlet, (2):Tungsten Electrodes, (3):Globe Box, (4):Cyclon
(5):Filter, (6):Gas Outlet, (7):Gas Circulation Pump

Fig. 1. A schematic diagram of an apparatus using plasma arc for production of metallic UFP developed by Ohno and Uda (ref. 5)

In this process, some drastic changes of physical and chemical properties of hydrogen contacting molten metal at very high temperatures under plasma arc are utilized effectively. The plasma arc between six tungsten electrodes (cathodes) and a massive metal on a copper hearth (anode) is generated under atmospheric pressure in a steady flow of H_2 -Ar mixture (H_2 : 30-70%). Metallic UFP can be efficiently formed by a kind of forced evaporation of molten metal superheated due to the increase of heat transfer from argon-hydrogen plasma arc including a large amount of atomic hydrogen. Such UFP formation can be also promoted by the phenomena that a dissolution rate of hydrogen in a superheated part of molten metal just under the plasma arc is very high and a release rate of hydrogen from non-superheated metal at the circumference of plasma arc root increases remarkably comparing with that from the superheated part. UFP is carried with gas flow into a collector consisted of a cyclon and a cylindrical filter paper. The diameter of UFP produced by this process is in the range of 50 nm - 5000 nm, but 20 nm - 100 nm in some cases. In the case of iron UFP, its production rate (= amount of evaporation per unit area and unit time) is about 3 times as much as that in usual evaporation processes. A typical experimental condition in this process is shown in Table 1.

Table 1. A typical experimental condition in Ar- H_2 plasma evaporation process (ref. 6)

Atmosphere	50% H_2 - Ar
Pressure	101325 Pa
Gas flow rate	$5 \times 10^{-4} m^3/s$
Arc current	260 A
Arc voltage	22-25 V
Reaction time	15-540 s
Sample volume	$3 \times 10^{-6} m^3$

It has been reported that fine spherical iron particles can be obtained by plasma arc evaporation process under nitrogen atmosphere at reduced pressures (~ 1000 Pa), but in this case the nitrogen content in these particles was very high. In view of the present consequence, the productivity of metallic UFP in the above-mentioned hydrogen plasma evaporation process is better than that in other metallic UFP production processes.

B. EVAPORATION OF SMALL PARTICLES OF METALS

Sheer et al (ref. 7, ref. 8) has reported that UFP of several kinds of oxides produced by evaporation of small solid particles of the oxides injected into a d.c. Ar plasma arc. In this case it is very interesting that an electro-magnetic pumping effect arising around a d.c. arc cathode facilitates the introduction of small oxide particles into the plasma arc column.

R.F. plasma evaporation process is also used for metallic UFP formation from small particles of the metal. The possibility of UFP formation of alloy from small particles of its metal components introduced in R.F. Ar plasma under atmospheric pressure was suggested by Gal' (ref. 9). Alpha phase iron or metastable gamma phase iron including a small amount of aluminum was obtained by evaporation of the mixture of iron and aluminum powder in plasma. It was estimated that the quenching velocity by gas injection was 10^4 - 10^5 K/s in this experiment.

Three types of R.F. plasma torches as shown in Fig. 2 are used for UFP synthesis of alloys and ceramic materials in our laboratory.

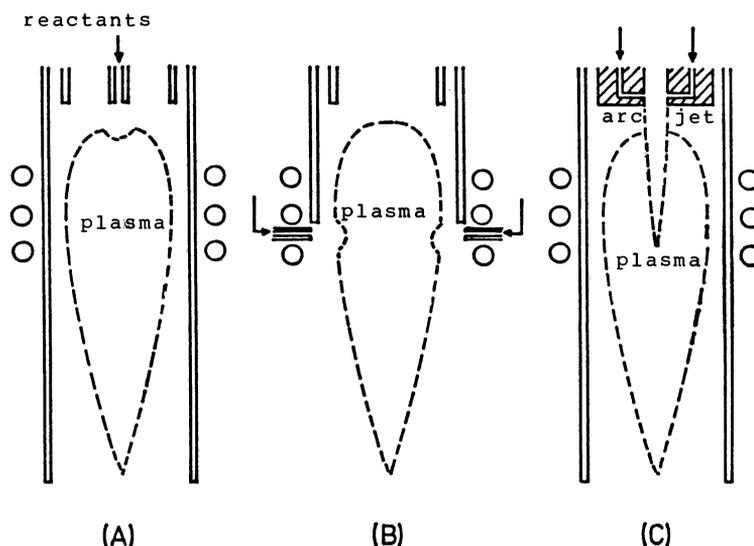


Fig. 2. Schematic drawing of three types of R.F. plasma torches

The type (A) torch (conventional torch) has been used in most of R.F. plasma processes since pioneering works by Reed (ref. 10, ref. 11). In this type (A) torch, the stability of plasma flame is apt to be disturbed with injection of reactants. Therefore reactants are often introduced into the tail flame of plasma, however in most cases the low percentage recovery of products is obtained. In the type (B) torch, reactants are injected into a fire ball zone of plasma flame at the position of R.F. coil for the both purposes of higher percentage recovery of products and stabilization of plasma. In the type (C) torch, a very stable plasma flame can be generated in an R.F. plasma torch in combination with a d.c. plasma jet torch. This type one is often called "hybrid plasma torch" in Japan.

UFP of Nb-Al and Nb-Si alloys has been synthesized by evaporation process of mixed particles of Nb and Al/Si introduced into an R.F. plasma reactor provided with the type (B) plasma torch (ref. 12), but it was impossible to control the composition UFP containing Nb and Al. The outline of this reactor is shown in Fig. 3. UFP of V-Si alloy with a controlled and fixed composition has been synthesized from mixed particles of V and Si by using the same type reactor. The experimental condition and result are summarized in Table 2 (ref. 13).

Plasma modelling is very useful for the estimation of gas velocity distribution and temperature distribution in plasma flow and the analysis of the problems of heterogeneous heat and mass transfer (plasma-wall or plasma-particle). Fauchais et al have published a detailed review on excellent plasma models presented by a few researchers. It is very important to analyse the problems

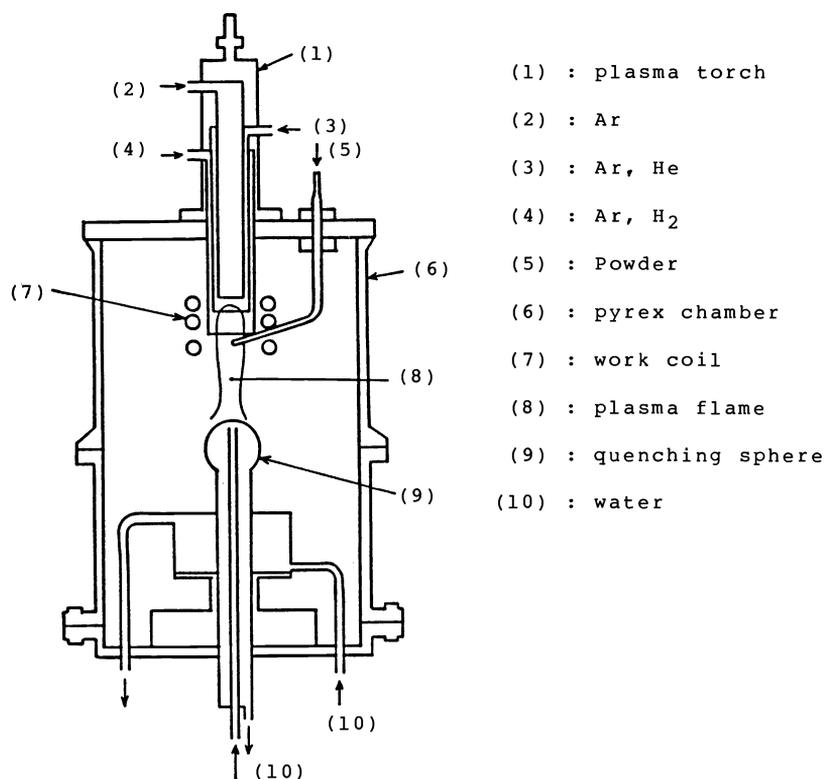
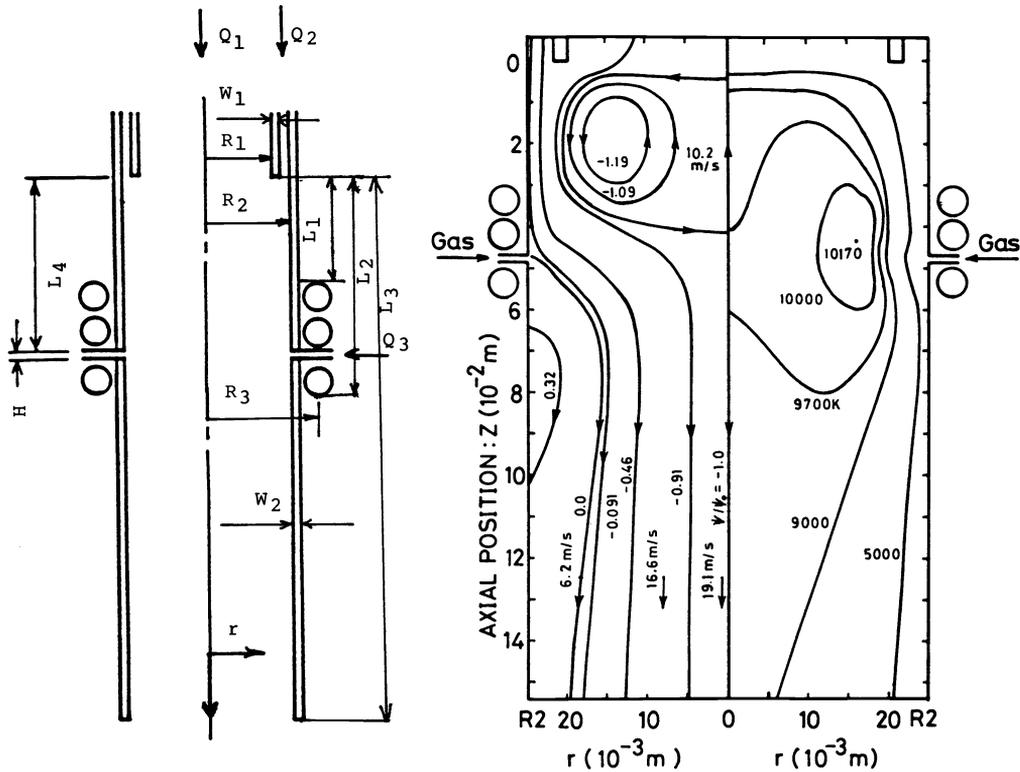


Fig. 3. Plasma flow reactor using type (b) torch (Fig. 1) designed for co-condensation process of high temperature metallic vapors.

Table 2. Experimental condition and phases of V-Si UFP detected by X-ray diffraction analysis

Gas flow rate			
Plasma gas : 10 l/min(Ar) + 5 l/min(He)			
Sheath gas : 40 l/min(Ar) + 4 l min(H ₂)			
Carrier Gas : 4 l/min(Ar)			
Plate power output : 35 kW			
Coil current : 110 A			
Powder feeding rate : 0.5 g/min			
System	Composition of feed powder (at.% Si)	Detected phases	Equilibrium phases
V-Si	67	VSi ₂	VSi ₂
	40	V ₅ Si ₃	V ₅ Si ₃ , VSi ₂
	37.5	V ₅ Si ₃	V ₅ Si ₃
	35	V ₅ Si ₃ , V ₃ Si	V ₅ Si ₃ , V ₃ Si
	25	V ₃ Si	V ₃ Si

of plasma-particle heat transfer, particle velocity, particle temperature, and particle trajectories for explanation of the plasma evaporation mechanism of particles. An example of temperature and flow patterns of Ar plasma under atmospheric pressure estimated in the type (B) torch is shown in Fig. 4. The method for calculation here is based on the model by Boulos (ref. 14), that is, the continuity, momentum, and energy equations are solved simultaneously with the electric field and magnetic field equations making use of the numerical procedure developed by Gosman et al (ref. 15). It can be concluded from this result that eddy flow pattern in the upper part of plasma is not disturbed by



R_1 : 20 mm, R_2 : 25 mm, R_3 : 30 mm, L_1 : 30 mm, L_2 : 60 mm,
 L_3 : 160 mm, L_4 : 48 mm, W_1 : 2 mm, W_2 : 2 mm, H : 1 mm,
 Q_1 : 10 l/min, Q_2 : 20 l/min, Q_3 : 9.5 l/min,
 Oscillator frequency : 4 MHz, R.F. coil current : 110 A, Ψ_0
 = 1.097×10^{-4} kg/sec

Fig. 4. Type (B) torch geometry, dimension, and an example of stream line patterns and temperature distribution in Ar plasmas (ref. 16)

such gas injection through a narrow annular slit of the torch at the lower end of R.F. coil and the stability of plasma can be sustained. An example of the temperature and flow patterns of Ar plasma under atmospheric pressure in the type (C) torch is shown in Fig. 5 (ref. 17). The effect of d.c. plasma jet remains, to some extent, in these patterns.

The nucleation and growth mechanisms of metallic UFP in R.F. Ar plasma tail flame at atmospheric pressure have been discussed in detail by Yoshida and Akashi (ref. 17) and Harada et al (ref. 12). It has been made clear that the growth of UFP occurs at higher temperature in the plasma tail flame than in the inert gas atmosphere in the gas evaporation process at reduced pressures described in INTRODUCTION of this paper, and that the growth of UFP must be under the control of collision and coalescence of particles (clusters) in fog state (so-called "Collision and Coalescence Model"). For example, the relation between number and diameter of each particle included in iron UFP produced by our plasma evaporation process obeys the log-normal distribution function (Gaussian distribution) (ref. 17). This fact supports that collision and coalescence model gives an explanation of UFP formation mechanism in plasma tail flame, as pointed out by Granqvist and Buhrman (ref. 18). The nucleation temperatures of Nb, Si, and Al from those vapor can be estimated by "Rothe-Pound Theory" considering rotation and transition motions of cluster of these elements (ref. 12). From such consideration, it has been deduced that the formation of UFP of Nb-Al or Nb-Si alloy is possible only in the case controlled by collision and coalescence mechanism of clusters in fog state. The calculated value of average diameter of UFP is about 10 nm which is in close agreement with its determined value experimentally.

In conclusion, plasma evaporation process using powder as raw material is very suitable for synthesis of UFP of alloys, if very large cooling velocity of vapor of alloy's components can be attained by newer quenching techniques. But the low productivity of UFP in this process is a problem.

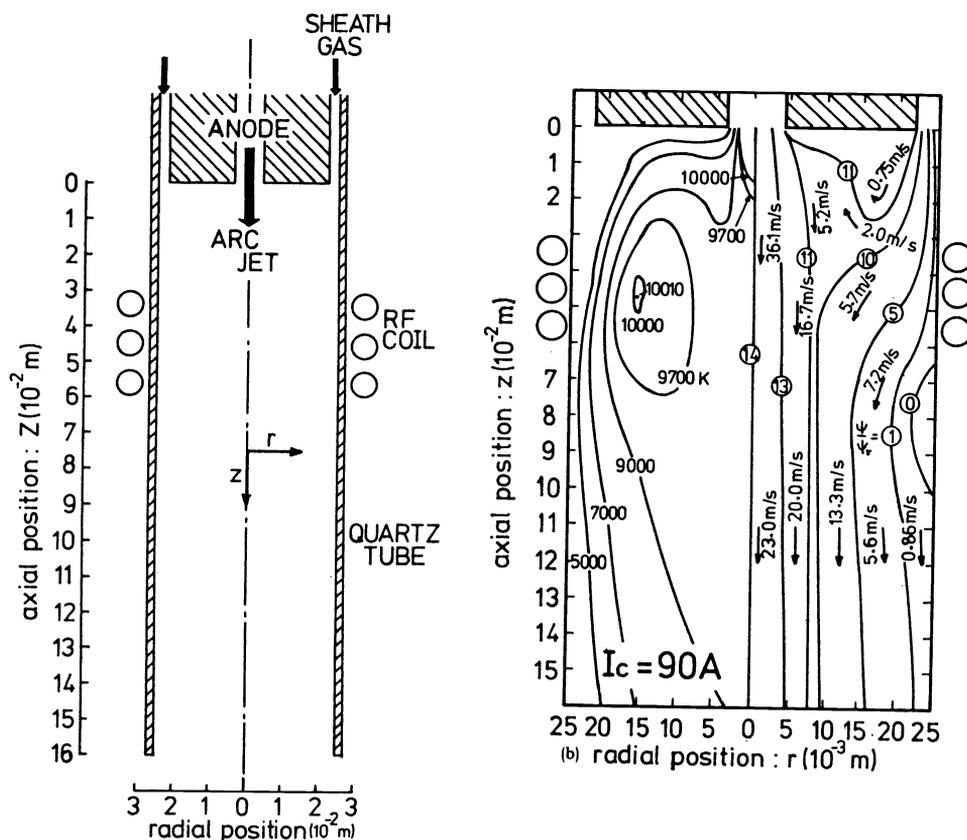


Fig. 5. The type (C) R.F. torch (Fig. 1) geometry used for generation of the hybrid plasma, and temperature distribution and stream-line pattern (oscillator frequency: 4 MHz, gas flow rate of arc jet: 8.8×10^{-5} kg/s, sheath gas flow rate: 6.8×10^{-4} kg/s, R.F. coil current: 90 A). The figure in each open circle shows the value of the stream function normalized by Ψ_r ($= -9.8 \times 10^{-6}$ kg/s).

REACTIVE PLASMA EVAPORATION PROCESS

The most simple process is consisted of evaporation of metal electrode superheated by arc discharge current in a reactive gas atmosphere. The homogeneous reaction between metal vapor and gas reactant proceeds near the the electrode and UFP of compound including metal and gas components can be formed. In some case, a mixture of metal oxide and carbon is used as the electrode for arc discharge (ref. 18).

UFP of metal nitride has been synthesized by superheating metal pool under nitrogen plasma arc of evaporation of metal powder in nitrogen plasma flame. 31 examples of nitrides syntheses by heating powder or lump of metals (or oxide-carbon mixture) in nitrogen plasma atmosphere have been reviewed by Fauchais (ref. 19). 16 examples of carbides syntheses by heating metals in hydrocarbon plasma flame or by heating oxides-carbon mixture in inert gas plasma have been listed in the same review, too. Therefore detailed description of reactive plasma evaporation processes for nitrides and carbides syntheses is neglected here.

It is noticeable that UFP of SiC of high purity can be synthesized from silicon monoxide particles and methane by using a new type d.o. plasma jet reactor with an auxiliary anode (ref. 20). UFP of stoichiometric TiN with a statistical median size of about 10 nm was synthesized by evaporation of Ti powder (average diameter: 0.025 mm) in R.F. Ar-N₂ plasma (ref. 21). Such UFP formation is expected to occur without the appearance of liquid phase during the course of quenching of metal vapor. This estimation can be also supported by thermodynamical consideration of Ti-N system under atmospheric pressure as shown in Fig. 6 (ref. 21). The same thermodynamical diagram of Al-N system was presented

by Bourdin et al (ref. 22) in 1976.

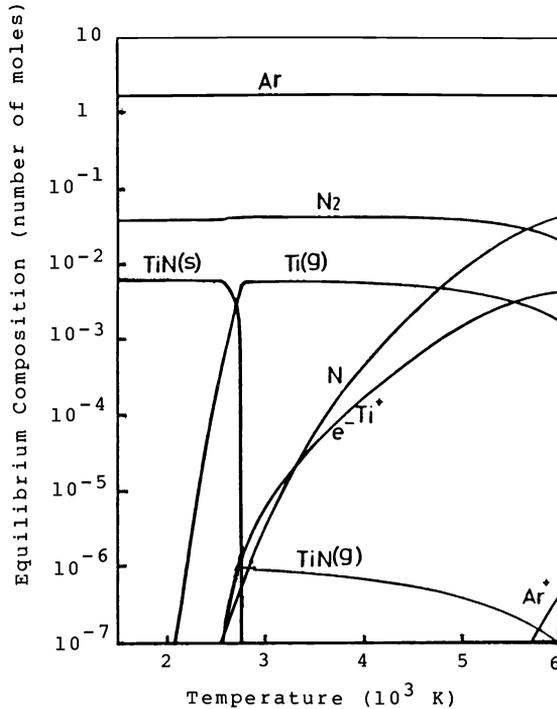


Fig. 6. Thermodynamic equilibrium diagram for the Ar-Ti-N system (ref. 21)

The formation mechanism of such UFP (TiN or AlN) is supposed to be characterized by either collision and coalescence growth in smoke state or heterogeneous nucleation on the surface ultra fine particles. The following conclusions have been deduced from a summary of the experimental results for TiN UFP formation. (1) The $[N_2]/[Ti]$ molar ration affects the composition of the products but has little effect on the shape of the particles. (2) It is possible to control the composition of the products and there appears to be an optimum molar ratio of $[N_2]/[Ti]$ for making stoichiometric TiN. (3) Each particle is a single crystal and the preferential growth form is a cube bounded by (100)-plane. (4) The oxygen level in the product depends to a large extent upon the content of oxygen and water contained as impurities in supplied gases. Most of research works on reactive plasma evaporation processes have been carried out in small laboratory scale. It is questionable whether a high productivity of UFP can be achieved in these processes in the near future.

THERMAL PLASMA CVD PROCESS

Many reserach works of thermal plasma CVD processes for synthesis of various refractory compounds have been put into practice since a success of single crystal growth of several refractory materials by Verneuil method using R.F. argon plasma in 1961 (ref. 10). A complex oxide consisted of Cr_2O_3 and Al_2O_3 was synthesized from a mixture of CrO_2Cl_2 and $AlCl_3$ by thermal plasma CVD using R.F. Ar- O_2 plasma in 1968 (ref. 23). Thereafter almost the same processes have been applied for syntheses of many kinds of simple oxides or complex oxides. For example a success in the synthesis of SiO_2 UFP of high purity by R.F. plasma CVD using silicon tetrachloride and oxygen was reported in 1969 (ref. 24). The successful developments of this process have been taken place to produce quartz glass of ultra high purity as a starting material in fabrication of glass fiber for light communication and other important uses. The outline of these plasma processes for quartz glass formation has been reviewed by Akashi (ref. 24) in 1976. More recently Namikawa (ref. 25, ref. 26) has published interesting papers on preparation of Nd-doped SiO_2 glass by thermal plasma CVD using a new type plasma torch as shown in Fig. 7. The fluorescence properties of this glass have been investigated. Dundas and Thorpe (ref. 27) described the large scale production of titanium dioxide powder by oxidation of the chloride using an R.F. oxygen plasma.

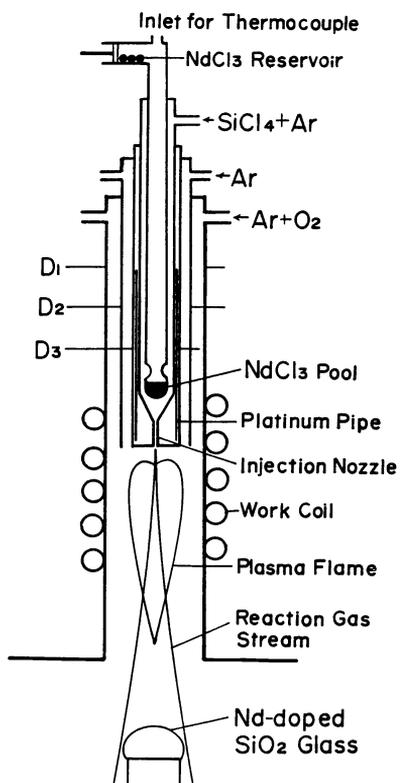


Fig. 7. R.F. plasma torch for preparation of Nd-doped SiO_2 glass from SiCl_4 and NdCl_3 . NdCl_3 gas generator settled in plasma torch (ref. 26).

$$D_1 = 30 \text{ mm}, D_2 = 20 \text{ mm}, \\ D_3 = 13-15 \text{ mm}.$$

The development of the R.F. plasma process for pure silica glass rod with a larger diameter (150 mm) is expected for special uses.

As often pointed out by many people who are engaged in research of plasma materials processing, R.F. plasma provides a very clean system for production of very pure powders of ceramic materials such as nitrides and chlorides. The most general plasma techniques for synthesis of nitride UFP are consisted of reacting a chlorine vapor with nitrogen-hydrogen or ammonia plasma. Winterhager (ref. 28), Harnusch (ref. 29), Neuenschwander (ref. 30), Exell (ref. 31), and Perugini (ref. 32) used d.c. arc plasma jet reactors in their experiments for nitrides syntheses. For example, Exell et al (ref. 31) injected $\text{SiCl}_4 + \text{NH}_3$ (Molar ratio: 3/16, SiCl_4 : 7 mol/h) into the down stream of hydrogen d.c. arc jet and obtained amorphous Si_3N_4 powder in the water cooled reaction chamber together with NH_4Cl powder. Excellent results have not been achieved in these d.c. arc plasma jet processes. But recently it was introduced in CERAMICS JAPAN (Bulletin of the Ceramic Society of Japan, 18, 619, 1983) that amorphous or alpha Si_3N_4 can be efficiently produced by the d.c. arc plasma technique developed at Battelle Geneve Research Center.

The synthesis of Si_3N_4 of high purity has been successfully practiced by using a flow reactor with the hybrid torch as shown in Fig. 2 (C). An example of the reactor is outlined in Fig. 8 (ref. 33, ref. 34, ref. 35, ref. 36, ref. 37). This reactor is consisted of an R.F. generator (5 MHz, 15 KW), a d.c. power supply (5KW), a reactor chamber, reactants (SiCl_4 , NH_3) and gas (Ar , H_2) supplying system, watercooled parts, and an exhausting system. The product is collected on the internal surface of a Pyrex glass cylinder of 10 cm in inside diameter and 60 cm in height. This collector system is set in a steel jacket. The R.F. plasma torch is consisted of a 3-turn induction coil, A watercooled quartz tube of 45mm in inside diameter, a d.c. plasma torch of 40 mm in outside diameter, and a watercooled ring with a slit of very narrow width for NH_3 injection. The upper part of the internal surface of the Pyrex glass tube is heated to the temperature of about 550K and the content of the by-product, i.e., NH_4Cl can be suppressed less than 2-3 %, which is easily removed by a heat treatment in a vacuum or in a N_2 gas flow. Typical operating conditions are shown in Table 3. The prepared powder is soft, fluffy, and pure white. The average particle size is about 20 nm, and the particle range is from 10 to 30 nm, which is estimated from the results observed by TEM. The shape of each particle of the product is almost spherical. X-ray and electron diffraction analyses

revealed that these particles are amorphous and have no internal structure, which were also confirmed by a high voltage electron microscopy.

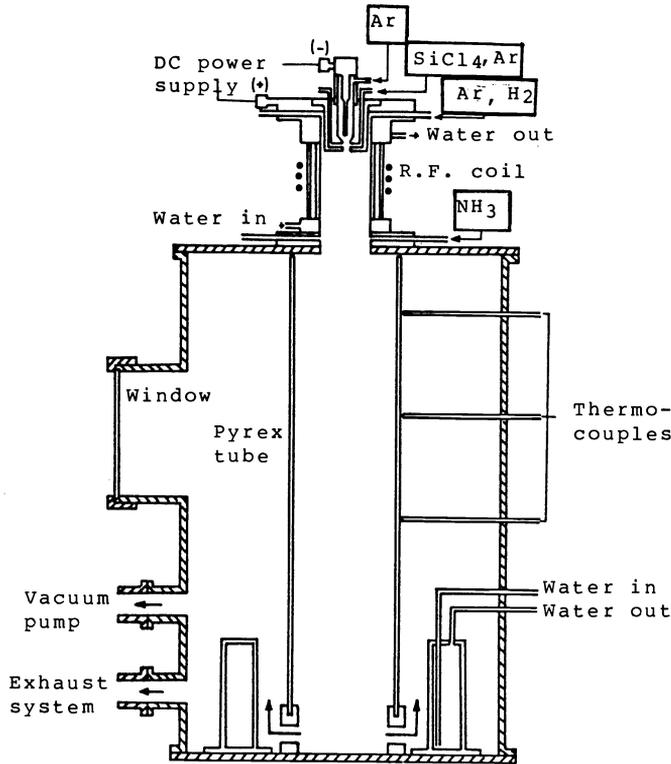


Fig. 8. Hybrid plasma system for preparation of ultrafine Si_3N_4 . (ref. 36)

Table 3. Typical experimental condition for preparation of ultrafine Si_3N_4 by hybrid plasma reactor (ref. 35)

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- (1) Gas flow rate
Arc jet gas : 2.9×10^{-4} kg/s (Ar), Sheath gas :
 $8.7\text{--}10.1 \times 10^{-4}$ kg/s (Ar) + $2.1\text{--}2.8 \times 10^{-6}$ kg/s (H_2),
Carrier gas : $4.3\text{--}5.8 \times 10^{-5}$ kg/s (Ar).
 - (2) Reactants injection rate
 SiCl_4 : 5×10^{-5} kg/s, NH_3 : 2.5×10^{-4} kg/s.
 - (3) R.F. plate power output : 20 KW
 - (4) d.c. power supply : 5 KW
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The chemical analysis revealed that the final product after the heat treatment for removal of NH_4Cl contains 60 ± 2 wt% Si and 37 ± 0.5 wt% N. The high purity of the powder is also verified by the infrared absorption analysis, because there are neither Si-O bond absorption peak nor shift or broadening of the Si-N peak at 940 cm^{-1} toward the Si-O peak at 1070 cm^{-1} . The transition of powder's structure from amorphous state to alpha type does not occur below 1833K. Such high crystallization temperature also gives evidence of high purity of the product. The yield of powder, based on the quantity of the product collected from the upper part of the Pyrex glass collector, is about 30%. This value does not mean the incompleteness of the reaction, but the defectiveness of the collector. It is particularly interesting that such a high pure powder can be prepared by a reaction of NH_3 with SiCl_4 , not with SiH_4 . Thermodynamic equilibrium compositions for the system Ar- SiCl_4 - NH_3 - H_2 system have been calculated up to a temperature of 3500K (ref. 37).

The synthesis of UFP of SiC by the decomposition of CH_3SiCl_3 in R.F. Ar plasma was reported in 1972 (ref. 38). The synthesis of beta-SiC UFP by using d.c. arc plasma jet was carried out at Battelle Geneve Research Center (ref. 39). The success of plasma synthesis of ultrafine SiC from silane and methane at The Los Alamos National Laboratory (ref. 40) has become of major interest lately. A new R.F. plasma system using a quartz plasma tube including several heavy-walled and water-cooled copper fingers has been developed there. Spherical SiC particles with the average diameter of about 5 nm have been synthesized from silane and methane by Kijima at The National Institute for Research in Inorganic Materials

in Japan (ref. 41). A successful result about the synthesis of beta-SiC UFP with a SiC/C ratio of 1, including no free carbon, from SiCl₄, CH₄, and H₂ (quenching gas) using a modified type of hybrid plasma torch, was obtained. The average particle size of SiC UFP can be controlled by injection rate of hydrogen gas for quenching (ref. 42). Sintering behavior and properties of titanium diboride powder synthesized in a plasma arc heater are very interesting (ref. 43). Pure and fine AlN powder will be synthesized by R.F. plasma CVD in the near future. As mentioned above, thermal plasma CVD processes for production of ultrafine ceramic powders or high purity are making great progress. A big national project for development of thermal R.F. plasma processing for chemical syntheses is going to start this year in Japan.

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