

# SYNTHESIS OF ULTRAFINE POWDERS BY MW PLASMA AT ATMOSPHERE PRESSURE

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## ABSTRACT

A microwave thermal plasma reactor system working at atmosphere pressure and oxygen as plasma forming gas has been designed and operated in laboratory. The tests reveal that microwave (MW) thermal plasma working at condition of diatomic gas, such as oxygen, nitrogen or air, can be maintained at lower input power than RF thermal plasma. Furthermore, it has high anti-interference ability to gas flow injected from top of plasma axially. Therefore, it has a great potentialities to be used for synthesizing ultrafine powder by chemical vapor deposition or physical vapor deposition process.

Ultrafine powders of titanium oxide composed of anatase and rutile form and amorphous silicon oxide have been prepared and characterized in this paper. The particle sizes for both of them are in the range of 30-50 nm.

## 1. Introduction

It has been well known that DC and RF thermal plasma techniques are a reliable and prospective method for synthesizing ultrafine powders, which have characteristic physical and chemical properties due to small particle size and large surface area. During last two decades many kinds of these plasma generation methods and various kinds of ultrafine powders have been developed and prepared in laboratory or commercial scale [1,2]. Compared with DC and RF thermal plasma, only a few works were being studied using MW thermal plasma

or MW nonthermal plasma for synthesizing ultrafine powder due to some reasons to be considered, such as smaller diameter of plasma owing to skin effect resulting from ultra high frequency and its hazard of radiation with increasing power level et al [3-6].

The aim of this work is to establish a MW thermal plasma technique and to use it for synthesizing titanium oxide and silicon oxide ultrafine powders by vapor phase reaction of titanium tetrachloride and silicon tetrachloride respectively.

## 2. Experimental set up and procedure

Experimental set up consists mainly of adjustable MW power supply with frequency 2.45 GHz, plasma torch-reactor, reactant evaporator, product collector and exhaust gas scrubber. The MW plasma input power can be adjusted from 0.5-5.0 kw continuously. The plasma output power and efficiency can be maximum by adjusting electric driving tuner to reduce reflection power to lowest for different load. The efficiency of MW plasma from plug to plasma is usually 60-65 %.

Plasma torch-reactor are made up of a 40 mm diameter quartz tube penetrated into E-planes of rectangular waveguide connected to MW power supply. Reactant of  $\text{TiCl}_4$  or  $\text{SiCl}_4$  evaporated and overheated to about  $180^\circ\text{C}$  and  $120^\circ\text{C}$  respectively was injected axially from the top of torch into plasma through a 8 mm diameter quartz tube by means of its pressure. The feeding rate of reactant in the tests was varied from 3 to 12 g/min. The product was separated by a bag filter, and off-gas left from bag filter passes through scrubber for removing chlorine gas before blowing off.

Both of plasma forming gas and sheath gas are injected tangentially from upper torch into plasma.

Based on the results of orthogonal design test with three factors, input power, flow rate of plasma gas and flow rate of  $\text{TiCl}_4$ , and three levels, the optimum operating parameters have been established as follows: input power 3.5 kw, plasma forming gas  $\text{O}_2$   $2.5 \text{ m}^3/\text{h}$ , sheath gas Ar  $1.0 \text{ m}^3/\text{h}$  and flow rate of  $\text{TiCl}_4$  8 g/h. In this case the mean reaction temperature in the reactor is in the range of between  $1200^\circ\text{C}$  and  $1500^\circ\text{C}$  measured by radiation pyrometer.

The powder obtained are characterized by X-ray diffraction, transmission electron micrograph, electron diffraction and BET et al.

### 3. Results and discussion

#### 3.1 MW plasma

Fig. 1 shows the MW thermal plasma which was working at  $O_2$  flow rate of  $3.0 \text{ m}^3/\text{h}$  totally and input power of 5.0 kw. The test indicates that the MW thermal plasma is more stable and smoother than RF thermal plasma, particularly, it is easy to establish a stable plasma using diatomic gas as plasma forming gas at lower input power level than RF plasma. Furthermore, it also has a stronger ability to stand the interference by injected axial gas from top of plasma in any places. In this work  $TiCl_4$  or  $SiCl_4$  was injected into plasma in this form without affecting the plasma stability. It is apparent that the mode with axial injecting reactant into plasma directly has higher reactivity than that with radially injecting reactant into plasma tail region. From these views, therefore, the MW thermal plasma technique might be more suitable to be used for synthesizing ultrafine powder by CVD or PVD process.

Fig. 2 which is a photo of cross section taken from bottom of plasma torch shows obviously that in the case of pure Ar as a plasma forming gas, the plasma has a bright ring and dark core in the quartz tube. But if  $O_2$ , instead of Ar used as a forming gas, it has a full bright ball without dark core. The reason for this is because the Ar plasma has lower thermal conductivity than that of oxygen and the effect of skin effect on plasma form is also to be considered. Therefore, it is expected that MW thermal plasma of diatomic gas has a characteristic of almost homogeneous temperature field.

#### 3.2 Synthesis of $TiO_2$

Pigmentary titanium oxide has been produced in large production scale using DC arc plasma by Tioxide UK Limited for many years [7], But it is being used in many other applications due to its dielectric constant, high refractive index and high chemical stability. In fine particle state it can also be used as magnetic compounds for recording sound and images, thickening and reinforcing agents, fuel pellet powders for nuclear plants, in catalysis, in automobile parts and in piezoelectric materials. The  $TiO_2$  produced by chloride process are usually a mixture of anatase and rutile crystalline structure. In order to produce  $TiO_2$  with only rutile form, the additive for promoting crystal transition to rutile are needed in oxidation reaction process. In this work the product identified by XRD are also a mixture of anatase and rutile, in which rutile content is about 60 %. But the test will be carried out further in order to find the probability of increasing rutile content without adding additives, and just by controlling reaction temperature and duration in reactor. In addition, it is important that the effect of high

electron density in MW thermal plasma on forming rutile  $\text{TiO}_2$  should be studied.

The morphology and particle size of product have been determined by TEM as shown in Fig. 3. From figure it can be seen clearly that the powders consist mostly of single crystalline particles with a few spherical particles. The particle size is about 30-50 nm. The electron diffraction pattern shows some bright spots which fit both anatase and rutile  $\text{TiO}_2$ .

The specific surface area determined by BET method is in the range of 25-35  $\text{m}^2/\text{g}$ .

### 3.3 Synthesis of $\text{SiO}_2$

Silicon oxide has been prepared by RF induction plasma for many years ago [8]. In that paper it has been suggested that  $\text{SiCl}_4$  injected into the tail flame region of plasma by means of radial ports is the satisfactory method. For the axial feeding reactant into the plasma directly, it interferes plasma stability or even extinguishes the plasma. But in this work the  $\text{SiCl}_4$  was injected axially into plasma without any interference to the plasma stability.

It is found in the tests that there is different from  $\text{TiCl}_4$  reaction with  $\text{SiCl}_4$  reaction in reactor. The appearance of  $\text{SiCl}_4$  reacted with oxygen plasma in torch and reactor is almost as same as oxygen plasma itself. that is without any apparent change when reactant was added.

The powder product obtained in this tests are completely amorphous identified by XRD. Fig. 3 shows TEM and electron diffraction pattern which indicates it is amorphous powder with particle size of about 30 nm.

## 4. Conclusions

Microwave thermal plasma using complete oxygen as plasma forming gas at atmospheric pressure has been operated successfully in the input power level from 3 to 5 kw. At that operating condition MW thermal plasma has a excellent stability and efficiency as high as 60-65 %.

The reactant for preparation of ultrafine powder can be added from either plasma tail radially or top of torch axially into reactor without affecting plasma stability. A mixture of rutile and anatase form  $\text{TiO}_2$  and amorphous  $\text{SiO}_2$  with particle size of 30-50 nm have been prepared by injecting evaporated  $\text{TiCl}_4$  or  $\text{SiCl}_4$  from top of torch into plasma axially.

Results of study reveal that MW thermal plasma has a great potentialities to be used for developing the plasma synthesis process of ultrafine powder.

## References

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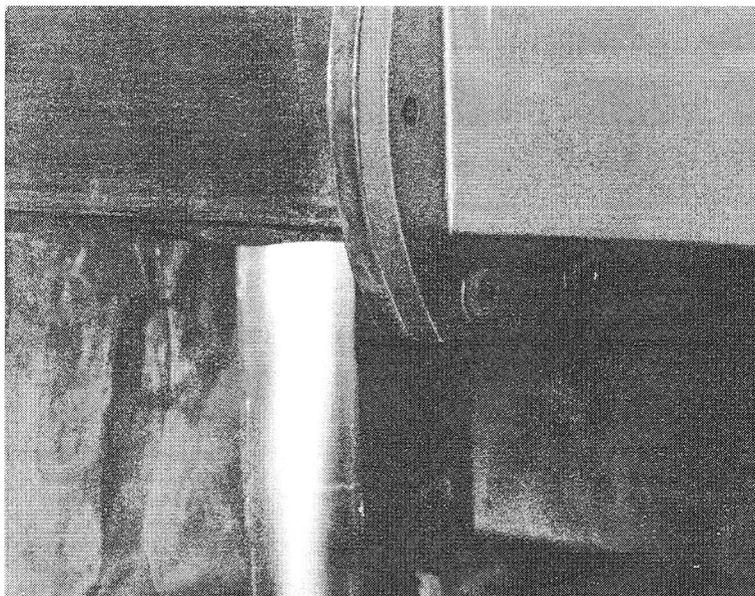


Fig. 1 Photograph of plasma torch

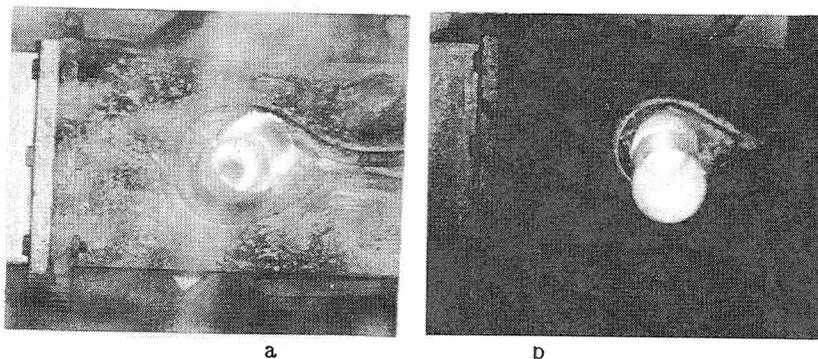


Fig. 2 Photograph of plasma from bottom cross section  
 a. Argon gas;                    b. oxygen gas.

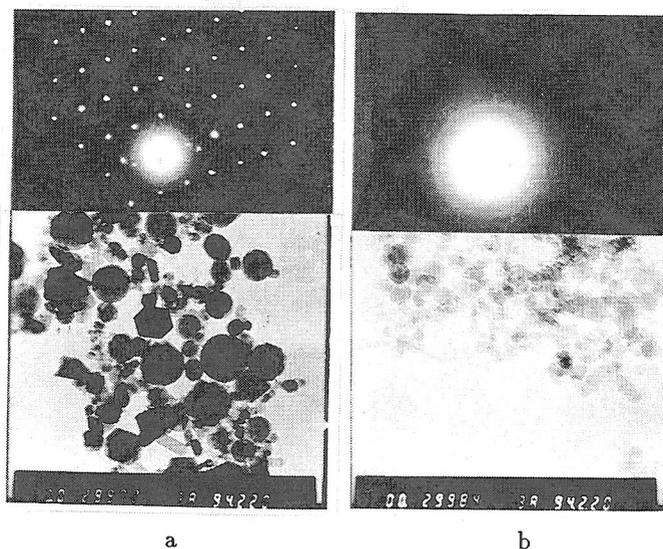


Fig. 3 TEM and electron diffraction of  $\text{TiO}_2$  and  $\text{SiO}_2$  powder  
 a.  $\text{TiO}_2$ ;                    b.  $\text{SiO}_2$