

Influence of Induction Plasma Treatment on Compositional Modification of Titanium Carbide Powders

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The in-flight compositional modification of titanium carbide powders was carried out in an R.F. inductively coupled plasma. The treatment in Ar-H₂ plasmas induced the formation of carbon site vacancies. The mixing of NH₃ to Ar-H₂ plasma at the bottom of the plasma torch resulted in the substitution of carbon by nitrogen. The dependence of nitrogen substitution on reactor pressure is discussed comparing with the predictions by a theoretical model.

1. INTRODUCTION

The thermal plasma is characterized by very high temperature and the presence of reactive chemical species. Powders injected into a plasma are subjected, in-flight, to modifications of their morphology, chemical composition and crystal structure in a short time, i.e., of the order of tens of milliseconds. With the growing interest in the processing of powders under plasma conditions, it is becoming increasingly important to know of the interaction between the plasma and the powder particles. The variation of shape, morphology, chemical composition, and crystal structure in plasma treated powders reflects the history of powder through the powder processing [1,2].

Titanium carbide with very high melting temperature, ~3290 K, has excellent properties, such as high electric conductivity, high hardness, and good corrosion resistance and high-temperature strength. The non-stoichiometric range of x in TiC _{x} is very large, i.e., $0.5 < x < 1$, and carbon atoms can be substituted by nitrogen and oxygen atoms, that is, the formation of TiC _{x} N _{y} O _{z} , while its crystal structure of NaCl-type remains unchanged[3]. It is known that the properties varies depending on nonstoichiometry. In this paper, both experimental and theoretical studies are carried out of the in-flight compositional modification of titanium carbide powders in an RF induction plasma.

2. EXPERIMENTAL

A schematic diagram of the induction plasma torch used in this work is shown in Fig. 1. The plasma was generated using a radiofrequency power supply with a nominal oscillator frequency of 2 MHz and a maximum plate power of 70 KW. Three gas streams, the powder carrier gas, the plasma gas and the sheath gas

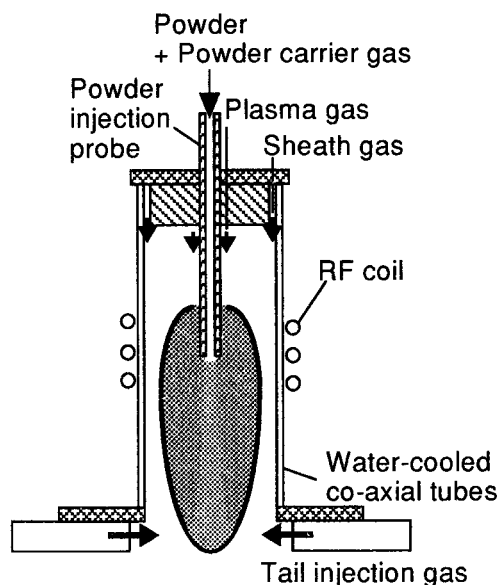


Figure 1. A schematic diagram of plasma torch.

gases were introduced into the torch. The operating conditions are summarized in Table 1. The plasma is confined in a 46 mm ID water-cooled quartz tube. At the tail of plasma, a tail injection gas was radially injected through 8 slots of 0.8 mm ID. The plasma discharges into a water-cooled stainless steel chamber in which the absolute pressure was maintained over the range of 400~600 Torr.

Titanium carbide powders were axially injected into the center of the discharge through a powder-injection probe with carrier gas. The powder, supplied by Hermann C. Stark TiC c.a.s., has a average particle size of 1.3 μm and the chemical composition of $\text{TiC}_{0.96}\text{O}_{0.01}$.

The plasma-treated powders were collected on the quartz wall of 150 mm ID set below the plasma torch. The crystal phase was identified using an X-ray diffractometer. For the determination of lattice constant of titanium carbide, silicon(Johnson-Matthey, purity 5N+) was used as an internal standard substance. The contents of carbon, nitrogen and oxygen in an initial powder and plasma-treated powders were determined by using a carbon analyzer[Horiba, EMIA-511] and an oxygen/nitrogen determinator[LECO, TC-136], respectively. The treated powders was observed with a scanning electron microscopy(SEM).

Table 1. Plasma generating and powder feeding conditions.

	[A]	[B]	[C]
Sheath gas(1):	Ar	Ar	Ar
[l/min]:	30	30	30
Sheath gas(2):	H ₂	H ₂	H ₂
[l/min]:	3.5	3.5	3.5
Plasma gas:	Ar	Ar	Ar
[l/min]:	6	6	6
Powder carrier gas:	Ar	H ₂	H ₂
[l/min]:	4	4	4
Tail injection gas(1):	Ar	Ar	Ar
[l/min]:	15	10	10
Tail injection gas(2):		NH ₃	H ₂
[l/min]:		5	5
R.F. frequency[MHz]:	2		2
Plate power[kW]:	50		25*
Reactor pressure[Torr]:	400-700		
Powder feed rate[g/min]:	1-10		0

*Power input to plasma.

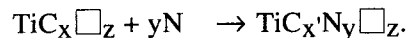
3. RESULTS AND DISCUSSION

X-ray diffractometry showed that no other crystal phase but titanium carbide was formed in the collected powders. The melting and evaporation of the particles was partially achieved, since the plasma-treated powder consists of spheroidized particles, and fumes deposited on them. For the same plasma composition and reactor pressure, the number fraction of spheroidized particles increased with the decrease in powder feed rate. This is explained by the increase in heat transfer from plasma to a particle.

The lattice constant and the nitrogen and oxygen contents of plasma-treated titanium carbide powders are shown in Fig. 2. The lattice constant in the Ar-H₂ plasma treated powders increases with the decrease in powder feed rate. It is known that the lattice constant depends on the nonstoichiometric composition, TiC_x , and that, in the region of $x > 0.8$, the lattice constant increases with the increase in carbon deficiency[3]. The increase in lattice constant by the Ar-H₂ plasma treatment[A] corresponds to the formation of carbon-site vacancy. The oxygen incorporated into the vacancy after the experiment,



In the Ar-H₂-NH₃ treatment, the oxygen content is almost the same as that in Ar-H₂ plasma powders. The amounts of plasma induced carbon-site vacancy are almost equal in the both treatments. The lattice constant remains unchanged in spite of the formation carbon-site vacancy. This is due to the substitution of carbon atoms by nitrogen atoms[3]. The substitution occurred in the tail plasma region,



The nitrogen contents increases with the decrease in powder feed rate.

Figure 3 shows the variation of nitrogen contents in the Ar-H₂-NH₃ treatment. The dependence of nitrogen contents on reactor pressure is as follows,

$$400 \text{ Torr} > 500, 600 \text{ Torr}.$$

Equilibrated compositions were calculated for the system, Ti(C,N) in Ar-H₂-NH₃, by minimization of Gibbs free energy[4]. The re-

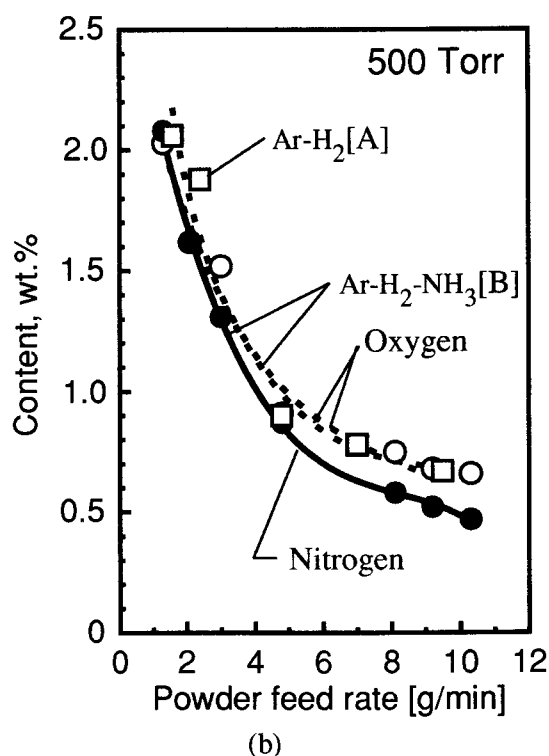
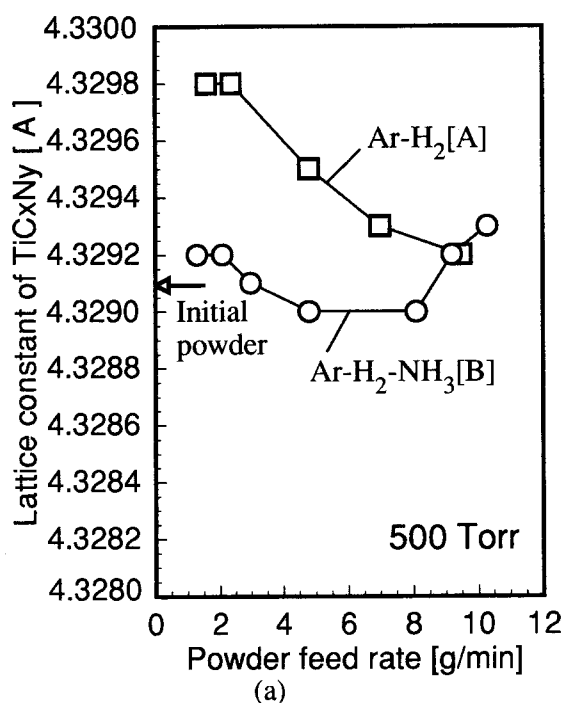


Figure 2. Change of (a) lattice constant and (b) contents of nitrogen and oxygen.

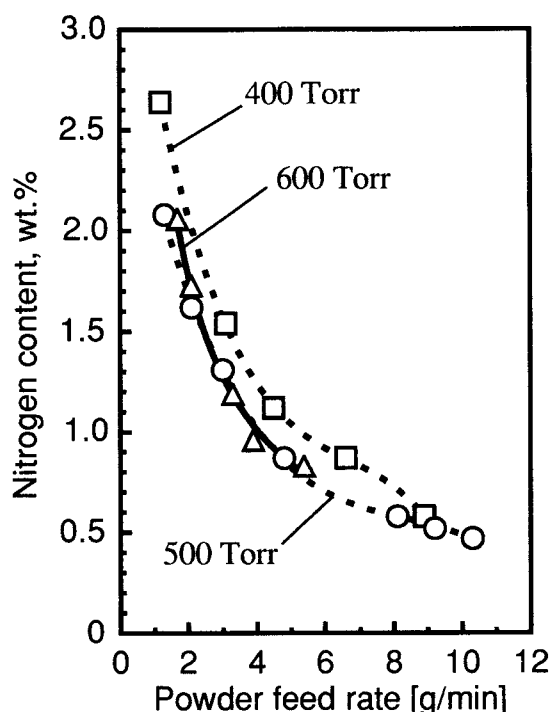


Figure 3. Variation of nitrogen content with the reactor pressure.

sults suggested that, in the temperature region of 2000-3000 K, the rising temperature of particles leads to the higher nitrogen content in Ti(C,N) . Therefore, the substitution by nitrogen needs the well heating of powder.

If all particles go along the centerline of plasma torch and reactor chamber, the present pressure dependence of nitrogen content is not explained, because the heat transfer from plasma to a particle becomes smaller and the residence time in the plasma and tail flame region along the centerline becomes shorter at the reduced pressure. The Knudsen effect reduces the heat flux from plasma to a particles, when the mean free path-length in the plasma is comparable to the dimension of a particle at the reduced pressure[5]. As the particle size of the present powders is relatively small, the Knudsen effect would be superior to the contribution by the elevated thermal conductivity of plasma, which is attribute to the increase in the dissociation of hydrogen and the ionization at the reduced pressure. The reduced pressure gives rise to the higher velocity of plasma, which results in

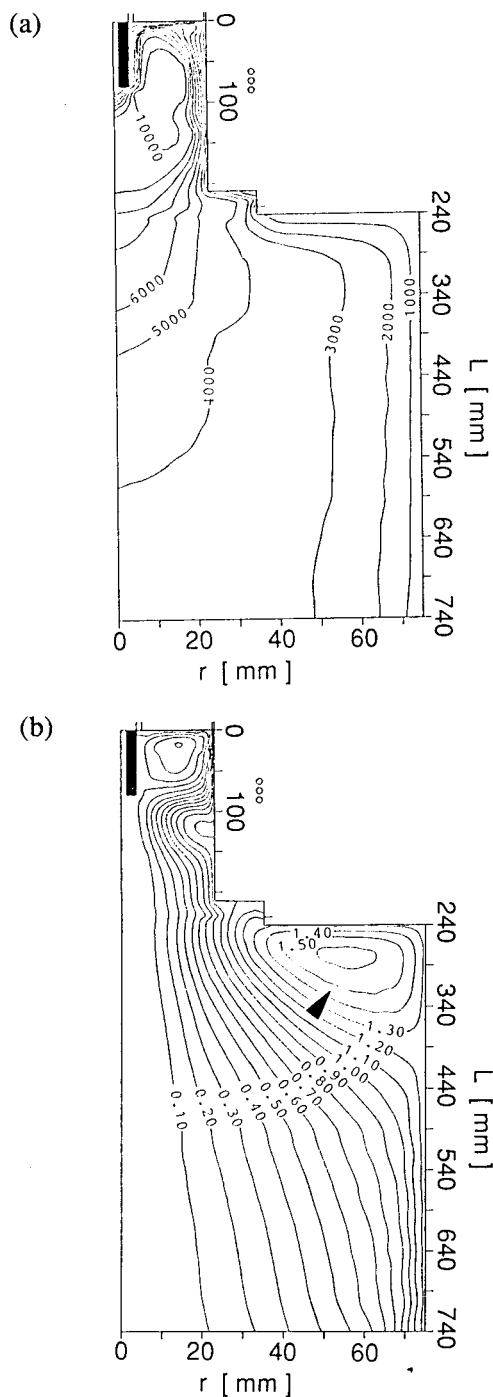


Figure 4. Calculated (a) isotherms and (b) streamlines at 500 Torr. (Plasma condition; [C] in Table 1.)

the shorter residence time of particles immersed into the plasma along the centerline.

Numerical calculation was performed for the condition [C] of Table 1 to simulate the distribution of temperature, flow and concentration of chemical species [6]. Although H_2 was mixed into the tail injection gas instead of NH_3 and no powder feeding was taken into account in the calculation, the result would give the first approximation. In Fig. 4, the (a) isotherms and (b) streamlines are shown at the pressure of 500 Torr. In the flow field (b), there are three recirculations, above the RF coil, below the coil and in the reaction chamber. The second and third ones affect on the powder trajectory. Comparing the flow fields at the variable pressures, the second recirculation below the coil became larger and the boundary between the third recirculation and the down stream shifted to the direction indicated by an arrow in the figure, when the reactor pressure increased.

And so, the powder flying at the off-center would be easy to go to the outer part, i.e. the lower temperature region, and reach to the quartz wall at the elevated pressure, which agrees with the experimental result that most of powders were collected on the inner quartz wall. It is thought that the resultant shorter residence time in the region, where the nitrogen substitution should occur, gives the lower nitrogen content at the higher reactor pressure.

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