Physical, Chemical and Microstructural Modification of Powders by Thermal Plasma Treatment

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Abstract

Two examples are given of thermal plasma treatment of powder, in which chemical and microstructural changes are involved as well as physical shape of particles. In the first, alumina powder is shown to undergo partial vaporization followed by condensation of a fine fume formed of metastable phases. The phase selection was closely related to their microstructure, ultra fine spherical particles or whiskers. In the second example, important modification are noted to take place in the stoichiometry and microstructure of titanium carbide powder through its in-flight melting. The observed loss of carbon and the corresponding increase of the oxygen content of the powder is shown to have an important influence on the sintering properties of powder.

1. Introduction

The plasma processing of powders is generally considered for its modification of the physical shape of the particles through its melting and in-flight solidification. The process known as plasma spheroidization is by now as a well accepted technology that has been used on an industrial scale for many years. Although this can be considered as an intermediate step in the plasma spray coating process which is widely accepted on an industrial scale, little attention has been given to the possibility of introducing subtle chemical and microstructural changes in the powder. Powders injected into a thermal plasma, which is characterized by its high enthalpy and high concentration of chemically active species, are subjected to modifications of their size[1], morphology[2], chemical composition[3] and crystal structure[1, 2].

The evaporation of powder in a plasma is followed by the deposition from a vapor phase. In the growth from a vapor phase, the supersaturation in the vapor phase has an important effect on the nucleation rate and the growth form. It is known that the driving force for condensation from the gas phase at the temperature, T, with the pressure, P, is the free energy difference, $\Delta\mu$,

$$\Delta\mu = - kT \ln(P/P_e) = - kT \ln \alpha \qquad (1)$$

where P_e is the pressure in equilibrium, and α is the saturation ratio (α-1 is the supersaturation). As particles pass through high temperature region exceeding 10000 K, the vapor pressure of evaporated species is very large, and the degree of supersaturation increases considerably when the plasma is cooled, resulting in the homogeneous nucleation in a vapor phase.

Alumina is known to have a wealth of metastable phases. They are generally prepared by the decomposition reactions of aluminum hydroxides,

Gibbsite $\rightarrow \chi \rightarrow \kappa \rightarrow \alpha$
Boehmite $\rightarrow \gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$
Bayerite $\rightarrow \eta \rightarrow \theta \rightarrow \alpha$
Diaspore $\rightarrow \alpha$.

The reported alumina ultra fine powders prepared by thermal plasma methods consisted of γ-, δ- and θ-aliminas, and the phase formation has been discussed in terms of the rapid cooling in the tail flame region.

Ishigaki and his co-investigators[3] have shown that compositional and lattice modifications of nonstoichiometric titanium carbide powders can be achieved by R.F. induction plasma treatment. The process involved the removal of carbon atoms and the subsequent formation of carbon-site vacancies. The vacancies were mostly formed near the surface of the particle resulting in an increased reactivity of the powder and the incorporation of oxygen in its lattice.

In this paper, the thermal plasma modification of alumina and titanium carbide powders were discussed. The deposition from a vapor phase is discussed during the alumina powder treatment. The plasma-treated titanium carbide powder was fired and its sinterability is elucidated. Non-oxide ceramics are known to be difficult to sinter to high density because of small diffusion coefficients of constituent atoms. The sintering of titanium carbide is no exception and requires firing at temperatures above 2000°C, under high pressure, or in the presence of metal as a sintering additive.

2. Deposition from a vapor phase during alumina powder treatment.

2.1 Experimental procedure

The apparatus used in this experiment has been described previously[1]. The operating conditions are shown in [A] and [B] of Table 1. The plasma is confined in a 50 mm ID water-cooled quartz tube. The plasma discharges, at the end of the confinement tube, into a water-cooled stainless steel chamber with an ID of 254 mm and a length of 1020 mm.

α-alumina powder[AMDRY, PWA 1310E] with a mean diameter of 24.5 μm was axially injected into the center of the discharge. The plasma-treated powders were collected separately at the reactor wall, reactor bottom, cyclone and filter.

Table 1 Plasma generating and powder feeding conditions.

	[A]	[B]	[C]
Sheath gas(1) [l/min]:	Ar 82	Ar 82	Ar 82
Sheath gas(2) [l/min]:	H_2 9.6	H_2 9.6	H_2 9.6
Plasma gas [L/min]:	Ar 28	Ar 28	Ar 28
Powder carrier gas [L/min]:	Ar 6.9	Ar 6.9	Ar 6.9
Plate power [kW]:	50		32
Reactor pressure [Torr]:	400		500
Powder feed rate [g/min]:	1-50		3.5
R.F. frequency [MHz]:	3		

2.2 Results and discussion

Particles introduced into the plasma were heated to melt and evaporate. In the Ar/H_2 plasma treatment, and the Ar/N_2 plasma treatment at the lower powder feed rate, the spongy mass was formed on

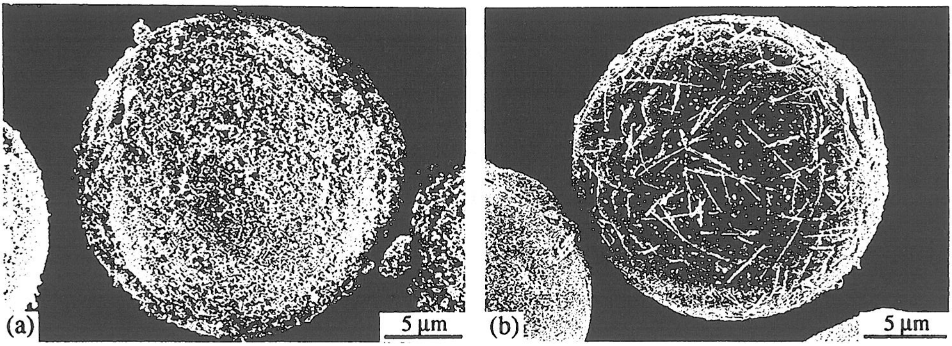

Fig. 1 SEM photographs of Ar/N_2 plasma-treated powders. Powder feed rate: (a) 5 g/min, (b) 50 g/min.

the surface of the spheroidized large particles as shown in Fig. 1(a). The needle-like structure on the particles was observed at the powder feed rate of 10-50 g/min in the Ar/N_2 plasma treatment, in which the amount of evaporation was relatively small. At the higher feed rate, only needles were formed on the large particles(Fig. 1(b)).

TEM showed that the spongy mass consists of fine particles of less than some hundreds of nanometers in diameter. Most of them are spherical but some larger particles showed crystal habits, like as octahedron. An electron diffraction pattern from the fine particles indicated that they consisted of γ-, δ- and θ-aluminas.

As alumina particles pass through high temperature region exceeding 10000 K, the vapor pressures of gas species evaporated from alumina is much greater than the equilibrated ones with liquid alumina, that is, the degree of supersaturation is considerable high. Under the condition with the large value of $\Delta\mu$, the nucleation and the following coalescence of alumina would occur as the liquid phase. And then, the solidification of liquid droplets follows. McPherson analyzed the solidification process and concluded that homogeneous nucleation during the solidification of liquid droplets at considerable undercooling resulted in the formation of γ-alumina rather than α-alumina because of its lower critical free energy of nucleation[4]. The two intermediates, γ and δ, in the transformation series from γ to α are formed during the solidification exotherm in the tail flame region.

The needles were of 0.1-0.3 μm in diameter and 5-15 μm in length. The electron diffraction pattern showed that the crystal structure of needle was similar to those of χ- and κ-aluminas. It is known that both χ- and κ-aluminas have the hexagonal close-packed(h.c.p.) oxygen sublattice like α-alumina. The difference in crystal structure of the aluminas with h.c.p. oxygen lattice comes from that in the stacking sequence in the c-direction. α-alumina has the ABAB... stacking sequence and the unit cell is composed of the six closed-packed planes. To the contrary, κ-aluminas have the ABAC... sequence and the unit cell composed of four close-packed oxygen planes[5, 6]. The occupation of aluminum ions in κ-alumina is the same as that of α-alumina, that is, aluminum cations occupy two thirds of octahedral interstices of h.c.p. oxygen lattice[6].

Figure 2(a) shows the growth of whiskers on the surface of spheroidized particle. The particle was melted and spheroidized in the Ar/N_2 plasma treatment. Figure 2(b) is the surface morphology, where the very fine spherical particles and whiskers were ultrasonically separated in ethanol. It is clearly seen in Fig. 2(b) that the solidified traces develop in the symmetrical form on (0001) of α-alumina, as

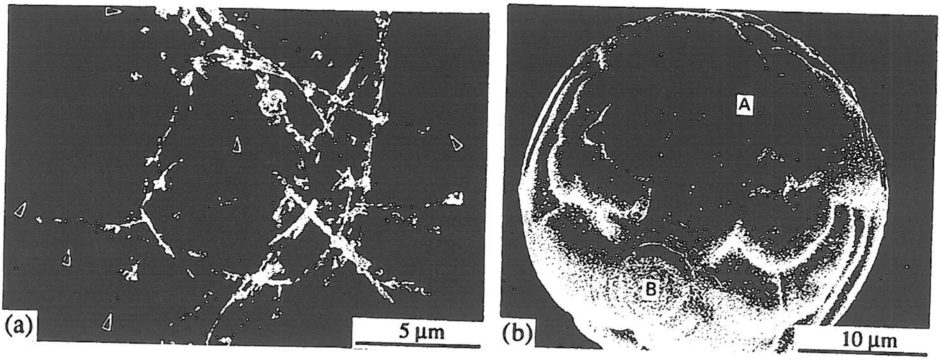

Fig. 2 Surface morphology of spheroidized alumina particle. (a) As is shown by arrows, whiskers grow from the surface of spheroidized particle. (b) The fine spherical particles and whiskers were removed. The solidification feature on the basal plane of hexagonal structure is clearly seen.

indicated by A and B. The surface of α-phase may provide the growth site for the whisker with h.c.p. oxygen sublattice.

3. Plasma-induced formation of carbon-site vacancies in titanium carbide powder and its influence on sintering properties.

3.1 Experimental procedure

The induction plasma torch and reactor chamber used in this work were the same as used in the preceding chapter. The operating conditions are shown in [C] of Table 1. The original TiC powder (TiC c.a., H.C. Stark) had an average particle size of 3.71 µm and a chemical composition of $TiC_{0.96}O_{0.01}$. The plasma-treated powders were collected on the reactor wall. The particle size distribution and the carbon and oxygen contents were determined by a particle size analyzer [Horiba, LA-700] and LECO carbon and oxygen analyzers, respectively.

Both original and plasma-treated powders were uniaxially pressed, followed by isostatic pressing at 200 MPa. Disk specimens with a green density of about 60% of the theoretical density were sintered in a radio-frequency induction heating furnace under an argon gas flow for 1 hour at atmospheric pressure and different temperatures from 1400 to 1800°C. Specimens in a SiC crucible were surrounded by the original TiC powder in order to insure that they are exposed to identical sintering cycles.

3.2 Results and discussion

The plasma treatment gave rise to the melting and partial evaporation of the fed powders, and the formed spherical particles were noted to be covered by a fine fume deposited from a vapor phase during cooling. The plasma treatment resulted in a slight decrease of the particle size distribution, as shown in Fig. 3. Also, the treatment led to the preferential removal of carbon atoms and the formation of chemically active vacancies[3]. The plasma-treated powder had an average particle size of 3.23 µm and a chemical composition of $TiC_{0.90}O_{0.07}$, which clearly shows the decrease in carbon content and the corresponding increase in oxygen content in the plasma-treated powder, compared with the original powder. The fume was formed of ultra fine particles with a particle size of some tens of nm, and the particles had a high concentration of carbon-site vacancies with a value of x in TiC_x, close to 0.5[3].

X-ray diffractometry showed no other crystal phase than titanium carbide in sintered bodies. Careful measurement of the lattice constant is useful for the

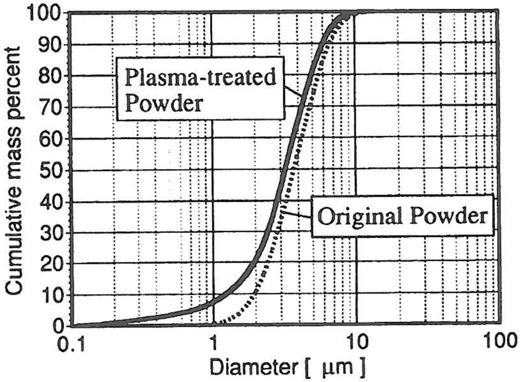

Fig. 3 Particle size distribution of original and plasma-treated titanium carbide powders.

estimation of changes in the chemical composition of $TiC_xO_y(Vac)_z$. During firing, oxygen diffusion took place into the inner parts of the particles giving rise to the observed decrease of the lattice constant in sintered bodies. The change of lattice constant is therefore an indication that the sintering at the initial stage is not controlled by the vapor phase transport, but rather by the solid state diffusion. At the temperature higher than 1600°C, the lattice constant tends to increase. Thermodynamic calculations, carried out in our previous study[3], has shown that the increase is due to the removal of carbon and oxygen atoms as CO molecules.

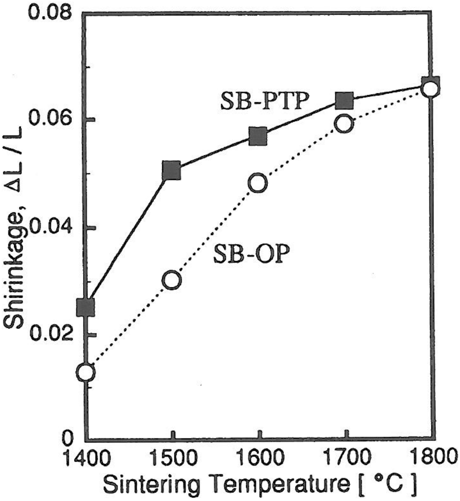

Fig. 4 Shrinkage for sintered bodies(SB) made from the original (OP) and the plasma-treated (PTP) powders.

The compositional discrepancy between the original and plasma-treated powders is reflected by tendencies in the sintering shrinkage, $\Delta L/L$, in Fig. 4. Sintered bodies prepared from the original and the plasma-treated powders show an increase of shrinkage with the increase in firing temperature. Comparing the plasma-treated powder with the original one, the sintered bodies prepared from the plasma-treated powders show a larger shrinkage than those of the other at low temperatures. Since the estimated diffusion coefficient from the sintering rate increased with the decrease of carbon content, x, in TiC_x[7], the sintering of plasma-treated powder would be enhanced by the carbon deficiency near the surface of particles.

When the firing temperature increased, the difference in shrinkage between the two materials becomes smaller and the shrinkage at 1800°C is almost the same regardless of the type of powder used. The variations of lattice constant suggests that the evaporation from the surface of particles retards the sintering shrinkage at temperatures above 1700°C. In a sintered body at 1800°C, the neck growth between the particles proceeded slightly. Chermant and his co-investigators[8] constructed the corresponding sintering diagram, devised by Ashby[9], for titanium carbide. The diagram suggests that the progress of the sintering process necessitates volume or boundary diffusion from grain boundaries. However, at temperatures above 1700°C evaporation increased considerably and the neck growth process was depressed.

4. Summary

The growth form of the deposits from a vapor phase varied depending on the plasma generating and powder feeding conditions. In all treatment with the Ar/H_2 and Ar/N_2 plasmas, very fine spherical particles below 200 nanometers in diameter were formed. The fine particles consisted of metastable γ-, δ- and θ-phases. Whiskers of 0.1-0.3 μm in diameter and 5-15 μm in length were formed in the Ar/N_2 plasma treatment at the powder feed rate exceeding 10 g/min. The structure was very similar to κ- or χ- aluminas with hexagonal close-packed oxygen lattice. The variation is probably related to the difference in supersaturation in the tail flame region.

Considerable changes of chemical composition in titanium carbide powders took place during the treatment of titanium carbide powders. These involved the formation of carbon-site vacancies and the dissolution of oxygen atoms on the surface of particles The compositional modification gave rise to larger shrinkage at the initial stage of the sintering process due to the diffusional transfer of atoms through the vacancies at the temperature lower than 1700°C. Evaporation at temperatures above 1700°C depressed the sintering densification process.

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