Journal of the European Ceramic Society 18 (1998) 1011-1015
© 1998 Published by Elsevier Science Limited
Printed in Great Britain. All rights reserved
0955-2219/98/$19.00 + 0.00
PII: S0955-2219(97)00176-3

A New Simple Process for Carbon Coating of Ceramic Particles using Poly(Vinyl Chloride)

Michio Inagaki, Hiroyuki Miura and Hidetaka Konno

Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060, Japan

(Received 18 April 1997; accepted 26 September 1997)

Abstract

Carbon-coated ceramic particles (Al_2O_3, SiO_2, TiO_2, MgO, CaO) were obtained by a simple mechanical mixing of these ceramic particles with poly(vinyl chloride) (PVC) powders and heating at a temperature between 600 and 1200°C in an inert atmosphere. Carbon coating of individual particles was successfully achieved by selecting an appropriate mixing ratio between PVC powders and ceramic particles, γ-Al_2O_3 with high surface area having a wide range of this mixing ratio for coating. The carbon layers coated on the ceramic particles seemed to adhere tightly, but were pervious to air. © 1998 Published by Elsevier Science Limited. All rights reserved

1 Introduction

Poly(vinyl chloride) (PVC) is known to be carbonized through liquid phase with very low viscosity.[1,2] When PVC powders were heated in an alumina crucible to temperatures as high as 1000°C, the wall of the crucible was found to be homogeneously coated by the residue carbon. This experience suggested the use of PVC as the starting materials for carbon to coat the ceramic particles. The intentional coating of ceramic particles by carbon has not been carried out, as the authors concerned. It is supposed to be done by applying chemical vapor deposition (CVD) technique; deposition of carbon by thermal decomposition of some hydrocarbon gases on the surface of ceramic particles. In order to have carbon coating on individual particles with few micron size, however, it is essential to use a fluidized bed during CVD process. If it is possible to coat small ceramic particles by a simple process, such as a simple heating of powder mixtures of ceramic particles and organic precursor at high temperatures, the products are supposed to develop new applications in different fields, such as catalysts and filler of ceramic/carbon composites, etc.

In the present work, carbon coating of fine particles of some ceramics which were stable up to 1200°C in the coexistence with carbon, such as alumina, silica, etc., was found to be successfully carried out by a simple mechanical mixing of ceramic particles with PVC powders and heating up to a high temperature around 1000°C in inert atmosphere to carbonize PVC.

2 Experimental

PVC powders of different polymerization degrees, 500, 700 and 1000 were used. PVC with polymerization degree of 700 was used in most experiments if any remarks were not given.

Ceramic particles used were listed in Table 1, for some of them particle size and specific surface area being listed. Since two alumina samples [γ-Al_2O_3(A) and α-Al_2O_3(A)] were commercially available reagents, their particle size was determined by a scanning electron microscope (SEM), in order to compare the other alumina samples with a limited range of size, and found to be widely distributed. SiO_2, TiO_2, MgO and CaO were also commercially available reagents, their particle size and specific surface area not being determined.

PVC powders and ceramic particles were mechanically mixed in a mortar and heat-treated in an alumina boat up to a temperature between 600 and 1200°C for different periods under argon flow. The heating rate was $500\,K\,h^{-1}$ and the argon flow rate was $40\,cm^3\,min^{-1}$.

Ceramic particles after heating with PVC were observed under optical microscope and SEM to evaluate their color, appearance and size. SEM was operated at an acceleration voltage of 3·0 kV. The amount of carbon residue after heating was measured as the weight loss of thermal analysis in a flow of oxygen up to 1000°C, abrupt weight loss due to burning the residual carbon being detected at about 500°C with an exothermic peak. The crystal structure of ceramics was identified by

Table 1. Ceramic particles used in the present work

Code	*Ceramics*	*Particles size/μm*	*Crystal structure*	*Specific surface area/m^2 g^{-1}*
γ-Al_2O_3(A)	Alumina	50~200	Spinel	95
γ-Al_2O_3(B)	Alumina	40~50	Spinel + γ-AlO(OH)	160
γ-Al_2O_3(C)	Alumina	100~200	Spinel + γ-AlO(OH)	130
α-Al_2O_3(A)	Alumina	30~100	Corundum	1·1
α-Al_2O_3(B)	Alumina	30~45	Corundum	1·1
α-Al_2O_3(C)	Alumina	60~70	Corundum	1·2
SiO_2	Silica	—	Amorphous	—
TiO_2	Titania	—	Anatase	—
MgO	Magnesia	—	Rock salt	—
CaO	Calcia	—	Rock salt	—

X-ray powder diffraction (XRD) with Cu Kα radiation.

3 Results and Discussion

3.1 Carbon coating of alumina particles

Representative SEM micrographs of γ-Al_2O_3(A) and α-Al_2O_3(A) are shown in Fig. 1(a) and (b) on the carbon-coated black particles after simple heating with PVC powders in 33 and 43 wt%, respectively, up to 1000°C. From these micrographs, it was found that there were no differences in the appearance, shape and size between the particles before and after heating with PVC powders, except that the starting alumina particles were white in color but they changed to be completely black after heating with PVC powders. This result reveals that alumina particles seem to be coated with carbon derived from pyrolysis of PVC. In the cases shown in Fig. 1, all particles are separated even after carbon coating, no coagulation of particles by residual carbon being observed. The pyrolysis of PVC is known to occur above 350°C[1] and to give viscous pitch-like materials with a viscosity so low as to wet the surface of crucible, as mentioned before. Therefore, it is reasonably supposed that alumina particles are first coated with a pitch derived from PVC by its pyrolysis on the way of heating and then the pitch is carbonized at higher temperatures.

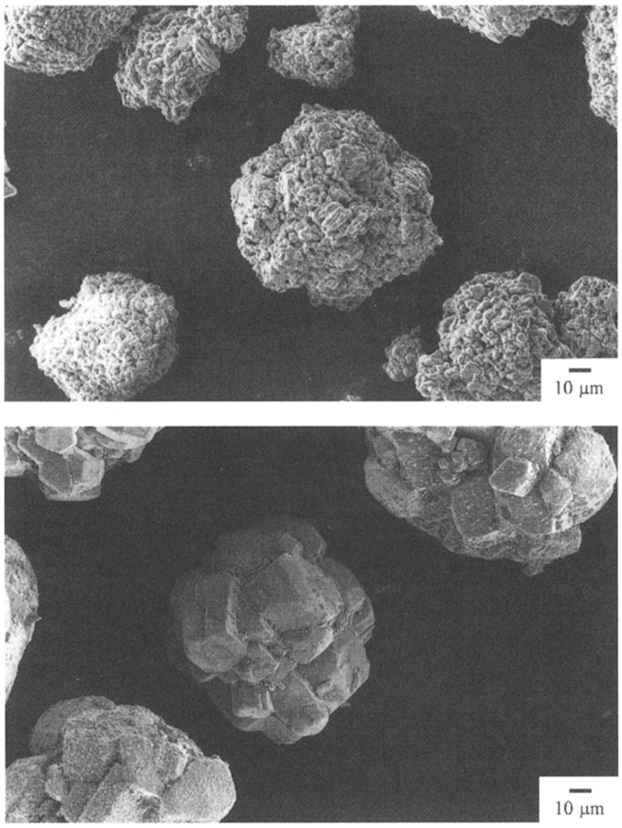

Fig. 1. SEM micrographs of carbon-coated alumina particles: (a) γ-Al_3O_3 (A) and (b) α-Al_2O_3 (A).

It was not essential to mix alumina particles with PVC powders in order to get carbon-coated alumina particles probably because of low viscosity of PVC-derived pitch. Even when the layer of PVC powders was placed on the layer of alumina particles in the crucible, the carbon coating of alumina particles was performed, although there was a little inhomogeneity in carbon coating between particles at the upper part(near PVC before heating) and lower part.

For all six kinds of alumina particles with different particle size and crystal structure (Table 1), carbon coating was successfully achieved by selecting appropriate mixing ratio between PVC powders and alumina particles. From the appearance of these particles, the coated carbon layer on alumina particles seemed to be homogeneous and thin. Even if carbon-coated alumina particles were ground in a mortar, peeling off of the carbon layer from alumina particles was not observed and no white alumina particles were detected. Therefore, the carbon layer seemed to adhere strongly on alumina particles.

XRD patterns of γ-Al_2O_3(B) before and after carbon coating at 600, 800, 1000 and 1200°C are shown in Fig. 2. γ-AlO(OH) which was contained in the starting γ-Al_2O_3(B) sample disappeared and converted to γ-alumina structure after heating up to 600°C. Spinel structure of γ-alumina was kept up to 1000°C and it changed to α-alumina structure

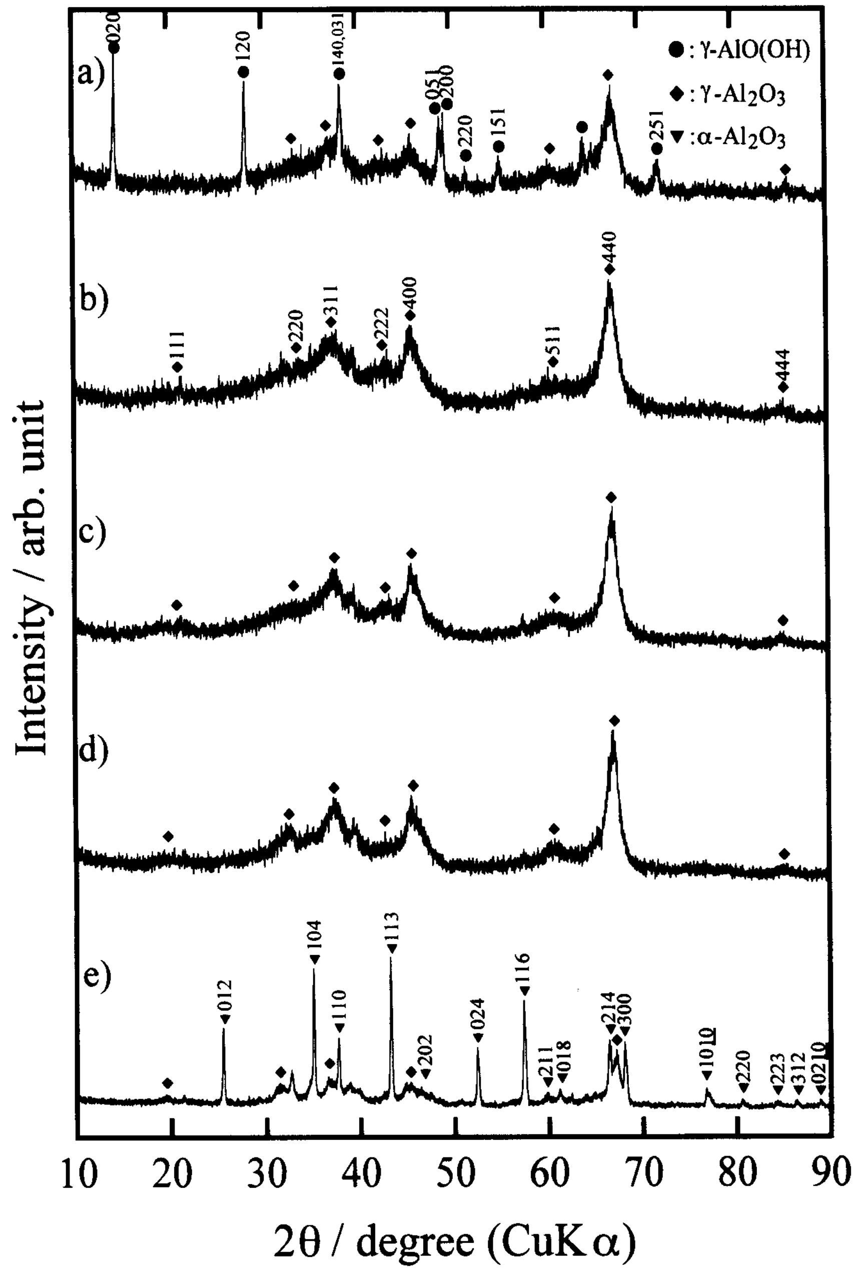

Fig. 2. XRD patterns of γ-Al_2O_3(B): (a) original, (b) carbon-coated at 600°C, (c) at 800°C, (d) at 1000°C and (e) at 1200°C.

though certain amount of γ-alumina remained. The carbon residue after heating up to 1000°C was burned out in a flow of O_2 and the white particles were recovered. However, the particles coated at 1200°C gave gray colored particles even after burning out the residual carbon in oxygen gas flow because a part of it remained inside the particles when γ-Al_2O_3 transformed to α-Al_2O_3. This suggests that carbon derived from PVC was invaded in the pores of γ-alumina particles. High specific surface area of γ-alumina samples was kept after carbon coating, though a little reduction resulted; $95\,m^2 g^{-1}$ for γ-Al_2O_3(A) changed to $58\,m^2 g^{-1}$ after carbon coating at 1000°C. XRD did not show the formation of Al_4C_3,suggesting no reaction between carbon coated and alumina even at 1200°C. If Al_4C_3 were formed at the interface between carbon and alumina, it should be recognized because of its highly hygroscopic nature. The detailed study on the interface between carbon and oxide is needed to understand the mechanism of this carbon coating.

The ranges of weight percentage of PVC in order to get carbon coating on particles of six kinds of alumina are compared in Fig. 3. When a large PVC percentage was used, the coagulation of ceramic particles by residual carbon was observed, and a small PVC percentage led to partial coating, obtaining a mixture of uncoated white particles and carbon-coated black ones. By selecting appropriate PVC percentages, all white ceramic particles changed to black and no coagulation was observed, each coated particle being independent from each other. We called it 'homogeneous' coating in the present work, i.e. homogeneous in particle by particle in carbon coating. Since 'homogeneous' coating was decided only from their appearance under microscope whether there are no coagulation

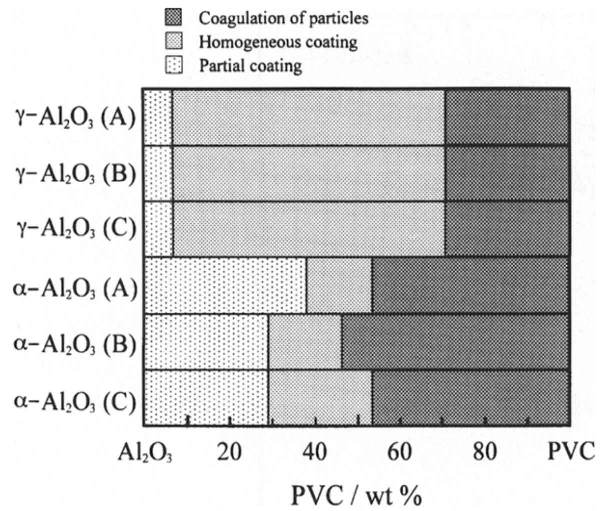

Fig. 3. Ranges of PVC weight percentage in the starting mixtures with different alumina particles for 'homogeneous' carbon coating at 1000°C.

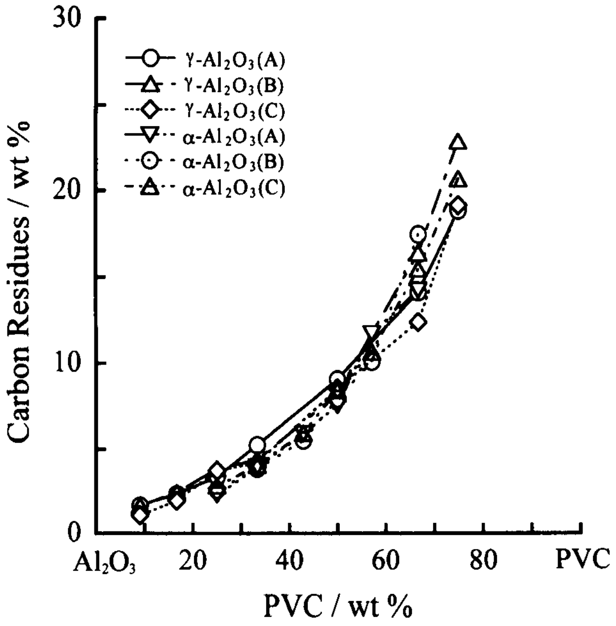

Fig. 4. Amount of carbon residue after heating at 1000°C for 1 h as a function of PVC weight percentage in the starting mixture with different alumina particles.

of particles and whether the color of all particles is completely black, the boundaries of the range for 'homogeneous' coating shown in Fig. 3 are not exact. However, there are pronounced differences in PVC percentage to get 'homogeneous' carbon coating between γ- and α-Al_2O_3 particles; in a wide range of about 10 to 70 wt% PVC for porous γ-Al_2O_3 particles, but a limited range of about 30 to 50 wt% PVC for dense α-Al_2O_3 particles. The wide range for 'homogeneous' carbon coating on γ-alumina particles is reasonably supposed to be due to their high specific surface area and the penetration of carbon residues into the pores located inside the particles. This supposition on γ-Al_2O_3 agrees with the experimental fact that carbon remained in the α-Al_2O_3 particles which is converted from γ-Al_2O_3 during carbon coating at 1200°C, as mentioned before.

In Fig. 4, the amount of carbon residue after heating at 1000°C for 1 h is plotted against PVC weight percentage in the starting mixture. It shows that amount of carbon residue after carbonization at 1000°C was independent of the kind of alumina particles, i.e. independent of crystal structure, particle size and specific surface area of alumina particles. The carbon yield from PVC at 1000°C was calculated on the amount of carbon residue on α-Al_2O_3 samples to be about 8 wt%, which was a little less than the carbon yield of about 12 wt% measured on the present PVC powders and also the reported values.[1,2] From the amount of carbon residue thus determined, it was attempted to calculate the thickness of carbon coated on α-Al_2O_3 particle, but the value obtained was too small (few tens nanometers), in comparison with the one observed on carbon-coated MgO which will be shown in the next section (Fig. 7). For this calculation we assumed the bulk density of carbon residue to be $0{\cdot}1\,g\,cm^{-3}$ because it was reasonably supposed to contain a large amount of hydrogen even after 1200°C heating.

The effects of heating temperature, heating rate up to 1000°C and residence time at 1000°C on the amount of carbon residue were studied on two alumina particles, γ-Al_2O_3(B) and α-Al_2O_3(B), with the mixing ratio of PVC powders which gave the 'homogeneous' carbon coating. The carbon residue in the product decreased as heating temperature increased, residence time increased and heating rate decreased, mainly because of the carbonization kinetics of carbon residues.

When PVC powders with different polymerization degrees of 500 and 1000 were used with γ-Al_2O_3(B) and α-Al_2O_3(B) particles, no appreciable variations in the range of 'homogeneous' carbon coating and the amount of carbon residue were observed.

3.2 Carbon coating of other ceramic particles

Carbon coating of silica, titania and magnesia particles (Table 1) was carried out by various mixing ratios between PVC powders and ceramic particles. Carbon coating of these particles was also successfully achieved by selecting appropriate mixing ratio, as that of alumina particles. The range of weight percentages of PVC mixed in order to get 'homogeneous' carbon coating of SiO_2, TiO_2 and MgO particles are compared in Fig. 5. These oxides have a rather narrow range of PVC percentage to obtain 'homogeneous' coating like α-Al_2O_3 samples, because these do not have so high surface area as γ-Al_2O_3.

The amount of carbon residue after heating at 1000°C for 1 h is plotted against PVC weight percentage in the starting mixture in Fig. 6. The

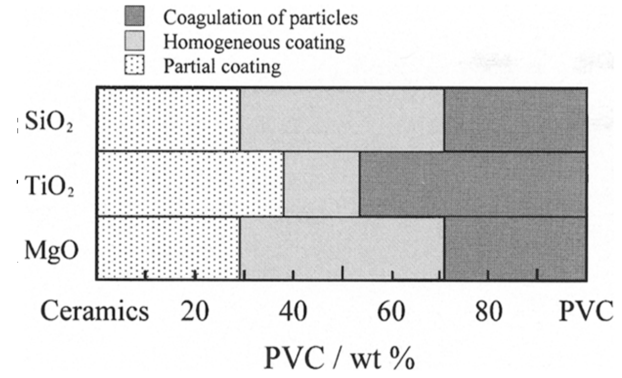

Fig. 5. Ranges of PVC weight percentage in the starting mixture with SiO_2, TiO_2 and MgO for 'homogeneous' carbon coating at 1000°C.

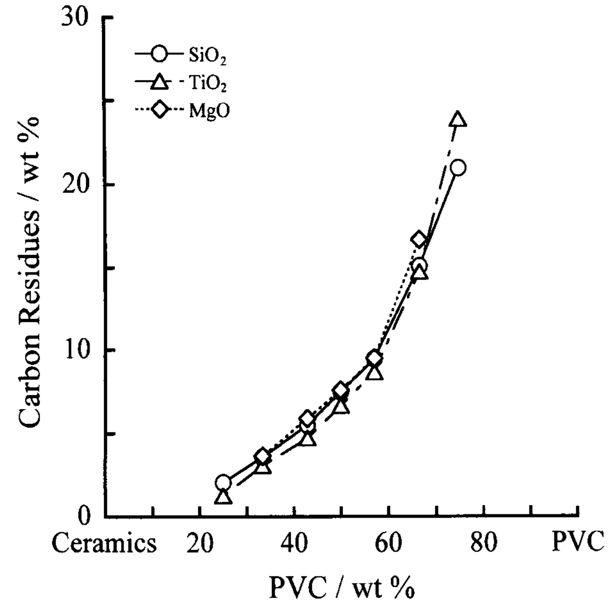

Fig. 6. Amount of carbon residue after heating at 1000°C for 1 h as a function of PVC weight percentage in the starting mixture with SiO_2, TiO_2 and MgO.

relations very similar to alumina particles are observed, showing that the relation is independent of the kind of ceramics.

TiO_2 carbon-coated at 1000°C was partly transformed from anatase to rutile structure. It is known that anatase structure transforms gradually but irreversibly to rutile above 500°C.[3]

Since magnesia is soluble in acid, carbon-coated MgO particles were put into 20% sulfuric acid. After 24 h magnesia was completely dissolved out and hollow carbon shells were obtained, as shown in Fig. 7. This is direct evidence for the carbon coating of ceramic particles. The residues after dissolving magnesia were completely burned out in a flow of oxygen and did not show any peak of magnesia on XRD pattern.

CaO particles were also able to be coated by carbon. Under an atmosphere of 80% humidity at

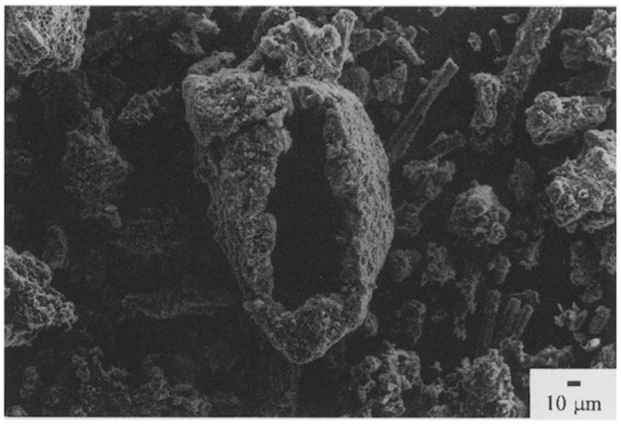

Fig. 7. SEM micrograph of carbon shell after dissolving MgO particle.

25°C for 48 h, calcium oxide thus coated by carbon transformed to a mixture of calcium carbonate and hydroxide by the reaction with carbon dioxide and water in the atmosphere, keeping the black appearance. This result shows that carbon layer formed on the surface of ceramic particles is not impervious, air and water vapor easily passing through it.

4 Conclusion

Carbon-coated ceramic particles were obtained by a simple mechanical mixing and heating of ceramic particles with PVC powders. Carbon coating of individual particles was achieved by selecting mixing ratio between PVC powders and ceramic particles, being very wide range for γ-Al_2O_3 particles with high specific surface area. Amount of carbon residue from PVC was independent of ceramic particles used.

In the present work, the ceramic oxides which did not show any reaction up to 1200°C were selected. If the oxides like Fe_3O_4 were selected, however, we found out the reduction of oxide to metallic iron where not only pyrolysis and carbonization of PVC but also the reduction of oxides at high temperatures were taken into consideration. The details on carbon coating of such oxides as Fe_3O_4 are under investigation.

References

1. Dollimore, D. and Heal, G. R., *Carbon*, 1967, **5**, 65.
2. Winslow, F. H., Baker, W. O. and Yager, W. A., *Proceedings of 1st & 2nd Conference on Carbon*, University of Buffalo, 1956, p. 93.
3. Inagaki, M., Furuhashi, H. and Naka, S., *Bunnko Kennkyu*, 1972, **21**, 202.