Adsorption 6, 213–218, 2000

Adsorption Isotherm Studies on Titanium Carbide Powders

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Received November 1, 1999; Revised April 24, 2000; Accepted May 15, 2000

Abstract. We have used adsorption isotherms to perform a comparative study of the substrate quality of five groups of titanium carbide powder, manufactured following different procedures. The isotherms were measured in an automated setup at 77.3 K using methane and argon as the adsorbates. We determined the specific surface area of each of the powders studied. We also determined whether or not there was evidence of steps (indicative of layer-by-layer adsorption) in each set of adsorption data. The isothermal compressibilities of the adsorbed films were determined from the data measured for each sample. Adsorption measurements were also conducted to determine the effect that heating the powders under vacuum had on the resulting substrate quality.

Keywords: adsorption isotherms, titanium carbide

Introduction

As a promising ceramic for new applications, titanium carbide has received much attention because of its high melting point, extreme hardness and strength, good chemical stability, electrical conductivity and corrosion resistance (Yeh and Hon, 1995). Titanium carbide is currently being used in wear-resistant coatings, high-temperature heat exchangers, magnetic recording heads, and turbine engine seals (Harbuck et al., 1986).

In order to enable the use of ceramic materials in advanced practical applications, it is essential to control all processing steps from the starting raw materials to the finished products. For advanced ceramics, careful attention must be paid to the quality of the starting powders. Also, detailed knowledge of the powder characteristics is required for the control of the microstructure of solids produced by firing. Important powder characteristics are size, size distribution, shape, state of agglomeration, chemical composition and surface structure (Rahaman, 1995). Here, adsorption isotherms were used to conduct a portion of such a characterization study.

Adsorption isotherm studies provide a powerful yet simple method for determining the surface area and porosity of a powder. The number, size, and sharpness of the adsorption isothermal steps provide information on the degree of uniformity of the sample's surface.

A homogeneous powder substrate is one in which there is only a single value of the attractive potential

throughout the sample's surface. On such a substrate, at low temperatures, gas adsorbs one layer at a time. Adsorption takes place essentially at constant chemical potential for each given layer (Dash, 1973). This results in a steep increase in the amount of gas adsorbed at a fixed value of the pressure. For less homogeneous substrates, there is more than one value of the attractive potential on different regions on the surface. As a result, the surface coverage during film growth is not uniform, and the isotherm has no steps in it, even at low temperatures.

We have used Ar and CH_4 adsorption to study a group of different TiC powders. We wanted to compare new, high quality TiC powders (which are relatively homogeneous in chemical composition, and are composed of submicron sized particles), to traditionally produced TiC.

Experimental

Apparatus

An adsorption isotherm is the determination of the amount of gas adsorbed on the surface of a substrate as a function of pressure of the surrounding vapor phase, at a fixed temperature. Our adsorption isotherm setup consists of a set of calibrated volumes separated by high-vacuum valves; a pumping station made of a mechanical and an oil diffusion pump with a liquid nitrogen cold trap; a cryogenic temperature-regulated environment; room-temperature manometers to determine the pressures; and, a computer to control the experiments. The pressures are measured with MKS capacitance gauges which are read with a Keithley voltmeter; the voltmeter is interfaced with an IBM-compatible computer. Electro-pneumatic valves, operated by relays, are controlled by the computer; the valves are opened or closed when equilibrium conditions, preset in the measurement program, are met. The gas is dosed into the system from a high-pressure gas tank via a small dosing volume (of less than 1 cc). The experimental sample cell is attached to the gas-handling system via a 0.159 cm stainless steel capillary. More detailed accounts of the experimental set-up and apparatus have appeared elsewhere (Shrestha et al., 1994). All the measurements were performed at 77.3 K, with the experimental cell in a liquid nitrogen bath.

Ar and CH_4 were used as adsorbates in these studies. These gases provide a convenient range of pressures for us to measure in our setup at the chosen temperature.

Table 1. Analysis and comparison of sample d with commercial TiC.

Property measured	Sample d	H.C. Starck TiC
Surface area by BET (m^2/g)	8.11	2.0–3.5
Total carbon (wt%)	19.9	20–21
Total oxygen (wt%)	1.0–2.0	0.7

In addition, the second and third layers for CH_4 films (on graphite) are below their respective critical points at 77.3 K, while for Ar they are above the critical points at this temperature (Chan, 1990; Hess, 1990). Thus, using these two gases allows us to investigate the response of different types of films (solid or liquid vs. hypercritical fluid, respectively) on the same substrates.

Substrates

Measurements were conducted on four different experimental titanium carbide samples and a commercial grade of TiC. A comparison of the characteristics of a commercial TiC powder and one of the experimental powders (Koc and Folmer, 1997) is given in Table 1. The experimental powders were prepared two processes: a carbon coating process (Koc and Glatzmaier, 1995) and a conventional mixing process. The following labeling was used for the samples: (a) TiC prepared from an initial mixture of TiO_2 and 32 wt% carbon black (Koc, 1997); (b) TiC prepared from TiO_2 coated with 32 wt% carbon following a patented process (Koc and Glatzmaier, 1995), this sample was prepared in a 2 gram batch; (c) TiC prepared from an initial mixture of partially carbon coated TiO_2 and carbon black; (d) a sample prepared as in (b) but in a 50 gram batch (Koc, 1997); and, finally, (e) a sample of commercial TiC from H.C. Starck.

The measurements were made on the as-received powders, and were later repeated following a substrate clean-up step. The purpose of the clean-up step was to attempt to remove surface impurities and ensure a higher quality substrate for adsorption studies. In the clean-up step, the TiC powders used for the Ar adsorption portion of the study were heat-treated under vacuum to 750°C. Since essentially no change was observed on the results obtained before and after the heat treatment at this temperature, the heating temperature was increased to 900°C prior to the methane measurements. In all cases, the vacuum under which the samples were heated was better than 4×10^{-4} Pa during the heating.

Results and Discussion

1. *Argon Adsorption Isotherms on Titanium Carbide Powders*

Our measurements focused on two aspects: a determination of the degree of substrate homogeneity of the different materials and how it is affected by the different treatments; and,—the determination of specific surface area of the different samples of titanium carbide.

Figure 1 shows the adsorption isotherm data taken for all five samples after heat treatment. Samples a) and c) had very similar adsorption isotherm characteristics. Neither of the samples displays step-wise adsorption, indicating for both of them a low degree of binding energy homogeneity.

The data taken at low pressure provide information on the presence of high-energy binding sites on the substrate. When high-energy binding sites are present, the isotherm will be concave, curving towards the coverage axis (Y-axis). If the low pressure portion of the data in Fig. 1 were displayed in an expanded pressure scale (a view which is not shown here), it would show that there is no concave portion, and that, thus, there are no high-energy binding sites in the sample.

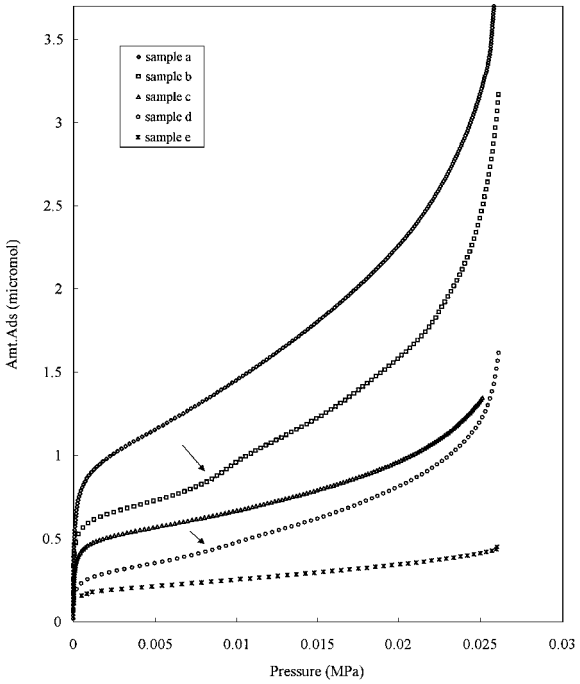

Figure 1. Adsorption isotherm data for Ar on the different titanium carbides used in the measurements. The surface coverage (in the vertical axes) is given in micromoles and the pressure (in the horizontal axes) is given in Pascals. Steps are resolvable for sample b (second one from the top), and for sample d (fourth one from the top). In order to enhance the features of curve d, the adsorption data has been multiplied by a factor 4. Arrows are used to point to the location of the second step in the data for curves b and d. For the sake of clarity the data from the different samples has been displaced upwards in coverage.

The data from samples b) and d), unlike those of samples a) and c), show evidence of the presence of steps. Each step in the adsorption isotherm corresponds, roughly, to the formation of an adsorbed layer of argon on the substrate (Gregg and Sing, 1982).

A clearer signature of the presence of steps in an isotherm can be obtained by calculation of the isothermal compressibility of the adsorbed film. The adsorbed film's isothermal compressibility is defined as (Li et al., 1996);

$$K_T = \frac{1}{n^2 v}\frac{dn}{dP}$$

Here n is the surface coverage, v is specific volume of the vapor, and P is the equilibrium pressure of the vapor. Peaks in the isothermal compressibility correspond to steps in the isotherm. The compressibility peaks are larger for sharper adsorption isotherm steps.

Figure 2 presents the isothermal compressibility of the adsorbed Ar film on the five different samples. In sample (b), there are three peaks in the isothermal compressibility present, in addition to the first one. The first peak, present close to $P = 0$, corresponds to the formation of the first layer on the substrate; the additional peaks correspond to the formation of other layers. Since step-wise adsorption is an indication of substrate quality, this figure provides clear evidence that sample (b) has a more homogeneous surface than the other powders investigated (Taub et al., 1991).

2. *Methane Adsorption Isotherm on Titanium Carbide Powders*

CH_4 isotherms were measured on the same types of substrates as those used for the Ar measurements. These samples were subjected to a more vigorous heat treatment than that used prior to the Ar studies. The samples were heated under vacuum, at 900°C for about 15 hours.

In Fig. 3, we present adsorption isotherm data for methane on the five different samples. While the CH_4 adsorption data are similar to the Ar data, the first

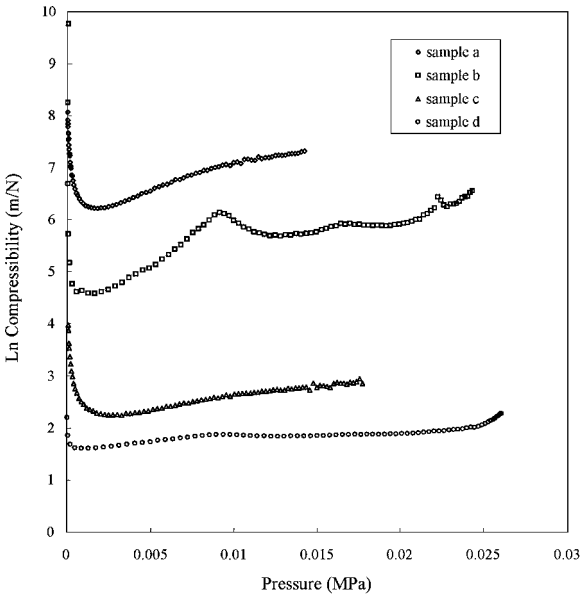

Figure 2. Logarithm of the two-dimensional isothermal compressibility of the Ar films obtained from the adsorption isotherms shown in Fig. 1. The data have been displaced along the *Y* axis for the sake of clarity. The isothermal compressibility for sample b (the second from the top) shows the presence of peaks, which correspond to the steps in Fig. 1. More rounded peaks are also resolvable on the data for sample d.

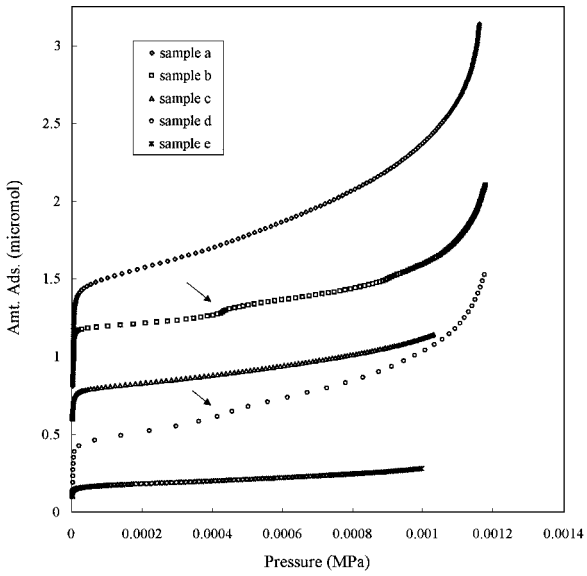

Figure 3. Adsorption isotherm data for CH_4 on the different samples of TiC used in the measurements. The units are the same as those for Fig. 1. Note that now the steps corresponding to the formation of layers are clearly apparent for the data measured on sample b (the second from the top). Starting with the first, low-pressure step, there are at least two additional steps present in the data of curve b. In addition, steps are also resolvable on curve d. For the sake of enhancing the features displayed, adsorption data corresponding to curve d has been multiplied by a factor 5. Arrows are used to point to the location of the second step in the data for curves b and d.

step is sharper than that measured for Ar. Two factors can help explain this:—the heat treatment temperature was increased from 750°C to 900°C for these samples; and, probably more importantly,—the first layer critical temperatures for CH_4 and Ar (on graphite) are, respectively, 67 K and 56 K (Chan, 1990; Hess, 1990). Hence, effectively, at 77.3 K CH_4 is at a lower temperature than Ar.

For sample (b), steps two and three in the isotherm were sharper for CH_4 than for Ar. Correspondingly, the peaks in the isothermal compressibility are more clearly visible for CH_4 than for Ar. This can be readily seen in Fig. 4, which presents the isothermal compressibility of sample (b), for both CH_4 and Ar. While the effect of the lower heat treatment temperature on the substrates used for the Ar measurements cannot be ignored, it is very likely that the difference in the steps' sharpness is due to intrinsic characteristics of both the Ar and CH_4 films. As has already been mentioned, 77.3 K is below the second and third layer critical points for CH_4 on graphite, while it is above these layer critical points for Ar. This difference, which is likely to be maintained in other substrates, would result in broader isotherm steps for Ar than for CH_4.

After the titanium carbide powders were subjected to the heat treatment at 900°C under vacuum, there was some improvement in the quality of the surfaces. Figure 5 shows evidence of the effect of the heating treatment on the TiC powders of sample (c). Prior to clean-up the as-received sample (c) has smooth, featureless isothermal compressibility, while after the clean-up a broad peak appeared in isothermal compressibility. By contrast, the data for sample (b), which was of fairly high quality before the heat-treatment, shows only very minor changes in the isothermal compressibility as a result of the heating (these curves are not shown in the figure).

The specific surface area of a powder can be obtained from an adsorption isotherm by either the BET (Brunauer, Emmett and Teller) method or by the Point-B method (Gregg and Sing, 1982). In the BET method the monolayer capacity is determined by fitting the low pressure data (typically, below $P/P_0 = 0.3$) to the BET equation. In the Point-B method, the monolayer capacity is determined from the coverage at the point where the extrapolated linear section of

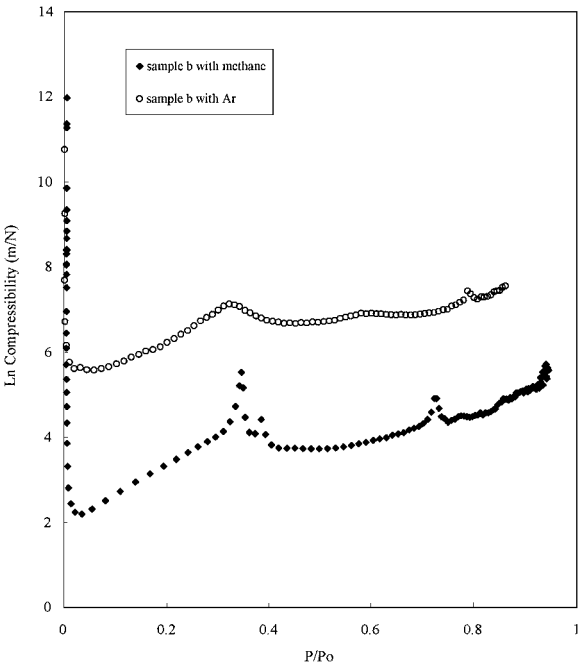

Figure 4. Isothermal compressibilities for the data measured on sample b using CH_4 (lower curve) and Ar (upper curve). The isothermal compressibility peaks appear clearer and sharper in the methane data. This is most likely due to the fact that at the temperature utilized in these measurements, the second and third layers of the methane film are below their respective critical points while those for Ar are above them.

the isotherm below $P/P_0 \sim 0.3$ intersects the adsorption axis. In either case the substrate's area is determined by multiplying the monolayer capacity by the area per molecule for the adsorbate. For CH_4 we used 15.7 A^2/molecule, and for Ar 14.5 A^2/molecule as the specific areas; these values were determined from low temperature monolayer capacity results for these two adsorbates on planar graphite (Mc Tague et al., 1982; Glachant et al., 1979). The values reported here for the specific areas were those obtained from measurements with CH_4, because of the greater sharpness in the steps measured with this adsorbate. The point B method and the BET method yield substantially similar results. In order to make comparisons with other reports easier, the specific surface areas quoted here are those obtained from the BET equation.

There is little increment in the specific surface area of sample (b): from 20.17 m^2/gm to 21.11 m^2/gm after the heat treatment. Sample (c) shows a greater increase: from 52.5 m^2/gm to 57.1 m^2/gm. This is probably because the as-received sample (c) was more heterogeneous than sample (b). The increase in the specific

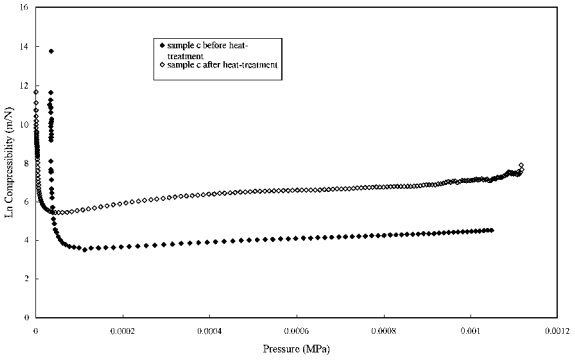

Figure 5. Isothermal compressibility for a methane film obtained from isotherms measured on TiC from sample c (prepared from a mixture of partially carbon-coated TiO_2 and carbon black) before and after heat treatment. The slight improvement in the surface quality of the substrate after the treatment is indicated by the appearance of a broad compressibility peak in data measured after the sample was heat treated.

surface area for sample (c) is most likely due to the removal of impurities from sample's surface as a result of the heating.

Sample (d) was produced in a larger batch (approx. 50 grm.) than sample (b) (produced in an approx. 2 grm. batch). Both powders were produced using the same carbon precursor method. Based on the data reported here, the larger lot size resulted in a more heterogeneous adsorption behavior and a lower specific surface area (8.11 m^2/gm vs. 21.11 m^2/gm, respectively).

Conclusions

We have investigated adsorption of CH_4 and Ar on TiC powders prepared following different processes. Our results show that the surfaces of the resulting TiC powders are significantly different. Sample (b) and (d) show at least 3 steps in the adsorption data for CH_4 and Ar, while sample (a) and (c) show no additional steps beyond the first for either gas. The data measured for CH_4 on samples (b) and (d) show more clearly the presence of steps than the Ar data. This is probably because (just as for the case of films on graphite), 77.3 K is below the critical temperature for the second and third layers for CH_4 but it is above the respective critical temperatures for Ar.

Even though samples (b) and (d) had similar stepwise isotherms, sample (b), (which was produced in a smaller lot than sample (d)), had a more homogeneous surface. This was evidenced by the sharper steps present in adsorption data measured on this sample. In

addition, the specific surface area for sample (b) was higher than that of sample (d),

The clean-up step had little effect on samples (b) and (d), but it had a measurable effect on samples (a) and (c). For samples (a) and (c) a broad peak appeared in isothermal compressibility data after heat treatment.

Acknowledgments

Support for this research has been provided by HECA-IBHE through the grant supporting the X-Ray Collaboration for Illinois Technology and Education, Advanced Photon Source Project and grant funding from the Department of Energy through Oak Ridge National Laboratory.

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