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Point of zero charge of different carbides

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Abstract

Points of zero charge, pH_{pzc}, of various samples of NbC, WC, SiC and TiC powders were investigated using a batch equilibration method. The examined powders were both laboratory prepared (NbC and WC via plasma-chemical method (PCM), while SiC was sol–gel derived) and commercial ones (WC, TiC, and laser derived SiC). The applied solid/liquid ratio ranged from 0.1 to 0.3 g/20 ml. The aqueous solution of KNO_3 (10^{-3} to 10^{-1} mol/l) was used as a background electrolyte. The points of zero charge for all investigated carbides were found to be between 3.2 and 5.0. They were not affected by the concentration of KNO_3, indicating its nonspecific nature vis-à-vis studied carbides. The pH_{pzc} values were correlated with the physicochemical properties of investigated powders.

Keywords: Carbides; Surface properties; Point of zero charge; Boehm titration

1. Introduction

Metal carbides are important ceramic materials used for various applications, due to their superior mechanical and electrical properties at elevated temperatures. These materials exhibit high strength, good chemical, corrosion and oxidation resistance, as well as good thermal and shock resistance, and as such can be widely used in the future.

Numerous books and review papers devoted to the preparation and properties of these materials have been published recently [1–5]. However, colloidal chemical properties of aqueous dispersions of various solids continue to be the subject of intensive academic and industrial research. The dispersion behavior is dictated by interfacial chemistry of solids and suspending media. The particles of these solids in aqueous solutions develop their surface charge through acid–base surface reactions.

The point of zero charge, pH_{pzc}, and the number of acidic and basic groups on carbide surfaces are important guides to these interfacial properties. Only a few papers [6–20] on the surface properties of carbide powders have been reported. The majority of cited articles [6–18] have been devoted to the study of surface properties of silicon carbide particles in aqueous solutions.

2. Experimental

2.1. Materials

Carbide powders chosen for this study were both laboratory prepared (NbC and WC via plasma-chemical method (PCM), described previously [21], while SiC was sol–gel derived [22] from a colloidal silica dispersion and saccharose) and commercial ones (WC, TiC, and laser-derived SiC).

All chemicals, used to synthesize the powders and to determine the point of zero charge, pH_{pzc}, and the number of acidic and basic groups on the powder surfaces, were of A.R. quality and applied as received.

2.2. Methods

The specific surface areas of carbide powders were determined by BET nitrogen adsorption method. A Siemens-D 500 diffractometer with Cu Kα Ni-filtered radiation was used for the X-ray structure analysis of studied powders.

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The point of zero charge of powders was determined by the batch equilibration technique [23]. The technique is founded on the assumption that the protons, H^+, and hydroxyl groups, OH^-, are potential determining ions. The particles of powders in an aqueous medium adsorb H^+ or OH^-. The net surface charge on each particle depends on the pH of the solution. The surface groups can dissociate or associate an additional proton from the solution depending on the properties of the powder and the pH of the solution. Thus, the surface becomes positively charged by reacting with protons from the solution under acid conditions or negatively charged due to loss of protons under alkaline conditions. The pH at which the surface has zero net charge, known as pH_{pzc}, is characteristic of amphoteric surfaces and is determined by the type of surface sites on solids and their structures. The adopted technique was as follows: the samples of powders (0.100 g) with 20 ml KNO_3 solution were shaken in PVC vials. Preliminary experiments were carried out to determine the time required for the adsorption of H^+ and OH^- ions from aqueous solutions on various carbides to reach equilibrium. The equilibrium was reached after about 4 h. For the sake of convenience, the equilibration of 24 h was chosen. The initial pH values were adjusted (in the pH range from 2 to 12) by adding a small amount of HNO_3 or KOH solution (concentration 0.1 mol dm^{-3}) keeping the ionic strength constant. The pH_{pzc} was determined in 0.001, 0.01 and 0.1 mol dm^{-3} KNO_3 solutions. In order to examine the extent to which the washing of samples with distilled water influences the pH_{pzc} values, the following experiment was conducted. A certain amount of the as-received powder was thoroughly washed with distilled water, dried at 383 K overnight, and reused in further pH_{pzc} experiments.

The Boehm titration method [24], originally developed for studying the acidic properties of activated carbons, was applied to evaluate the number of acidic and basic groups on all carbide surfaces. It is based on the reaction of these groups on carbide surfaces by sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), and hydrochloric acid (HCl). The number of acidic sites was calculated assuming that NaOH neutralizes carboxyl, phenolic, and lactonic groups, Na_2CO_3 neutralizes carbonyl and lactonic groups, while $NaHCO_3$ neutralizes carboxyl groups only. The number of surface basic sites was calculated from the amount of hydrochloric acid reacting with the carbide sample. To the best of our knowledge, this is the first report on the direct use of the Boehm titration method for determination of the number of acidic and basic groups on metal carbide surfaces. Recently, this method has been successfully applied to determine the amount of acidic groups on the surface of ultradispersed diamonds [25].

The procedure was as follows: 0.5 g of carbide sample was added into PVC vials with 25 ml of 0.05 mol dm^{-3} NaOH, Na_2CO_3, $NaHCO_3$, or HCl solution. The vials were sealed and shaken for 24 h, and then 5 ml of each filtrate was pipetted, and the excess of base and acid was titrated with 0.05 mol dm^{-3} HCl and NaOH solution, respectively.

Determination of the point of zero charge and the number of acidic and basic groups on all carbides was performed in duplicate. In the case of determination of the point of zero charge, the discrepancy between the two results is ±0.1 pH unit. The overall acidic and basic group measurements error was estimated to be not greater than ±3%.

All experiments were conducted at room temperature of $22 \pm 2\,^{\circ}C$.

3. Results and discussion

Physicochemical characteristics of the used carbide powders are summarized in Table 1, while their XRD patterns are shown in Fig. 1. As can be seen, all the carbide powders are well crystallized.

The determination of pH_{pzc} of the NbC powder is illustrated in Fig. 2. It is given as pH values of filtered solutions, after their equilibration (pH_f) with NbC, as a function of initial pH values (pH_i) of solutions. It can be seen that the pzc of NbC, in aqueous KNO_3 solutions, is at pH 3.6 (the pH_f level where a common plateau was obtained). As evident, NbC (like other carbides) exhibits amphoteric properties, and acts as a buffer. The plateau of the pH_i–pH_f plot corresponds to the pH range where the buffering effect of the carbide surface takes place, i.e. where for all pH_i in this range the pH_f is almost the same and corresponds to pH_{pzc}. The pH region where NbC buffers the solution is from ∼4 to ∼8. It means that for all values of pH_i, in this range, the pH_f is the same and equal to pH_{pzc}. The pH_{pzc} determined in KNO_3 solutions of different concentrations is the same. This leads to the conclusion that pH_{pzc} is independent of the ionic strength of KNO_3 solutions, i.e. that KNO_3 is an indifferent electrolyte. This is valid, as can be seen later, for all other investigated carbides. To our knowledge, there is no report on the pH_{pzc} value for NbC in literature.

Fig. 3 illustrates the determination of pH_{pzc} of TiC in the presence of KNO_3 as a background electrolyte. Also, in this figure, the influence of various powder/liquid ratios on the pH_{pzc} value of TiC was presented. The obtained common plateau corresponds to pH_{pzc} 5.0. It is evident that the increase in TiC/solution ratio up to 0.3 g/20 ml does not change the pH_{pzc} value. The same results were obtained for all investigated carbides. Zhang et al. [19] determined the zeta potential of commercially available

Table 1
Characteristics of carbide powders

Powder	NbC	WC		TiC	β-SiC	
Supplier	Laboratory	Laboratory	VOKSAL	STARCK	Laboratory	MarkeTech Intern.
Preparation	PCM	PCM	Electrochemical	–	Sol–gel	Laser
Particle size (μm)	0.01–0.02	0.1–0.52	0.75	–	<0.05	0.02
Specific surface area ($m^2\,g^{-1}$)	30	6	6	17	7	75