

# Morphology and Texture of Silica Prepared by Sol–Gel Synthesis on the Surface of Fibrous Carbon Materials

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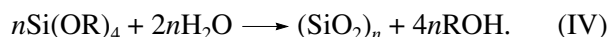
**Abstract**—Silica materials are synthesized by the sol–gel method including the deposition of tetraethoxysilane on various micro- and nanocarbon fibers. The use of nanofibrous carbon as a template makes it possible to prepare thermally stable mesoporous  $\text{SiO}_2$  samples with unusually high surface areas (up to  $1255 \text{ m}^2/\text{g}$ ) and high porosity (up to  $5.6 \text{ cm}^3/\text{g}$ ). These silica materials and aerogels prepared by supercritical drying have comparable pore volumes. It is found by high-resolution electron microscopy that a thin-wall matrix permeated by channels is a prevailing structure of silica materials. When some catalytic fibrous carbons are used as templates, silica nanotubes can be prepared.

## INTRODUCTION

Silica is one of the most frequently used oxide materials and it is widely applied in techniques both alone and in composites. In the past few years, the sol–gel synthesis occupied a special place in the preparation of silica materials such as glass ceramics, various composites, special purity silica gels and aerogels [1–5], synthetic noble opals [6], etc. Alkoxysilanes are most often used as starting silicon-containing organic compounds. From the viewpoint of the transformation of functional groups, the sol–gel synthesis is described by three reactions:



Equation (I) describes hydrolysis, and Eqs. (II) and (III) describe condensation to form an alcohol and water. These processes compete with each other. The complete stoichiometric reaction is described by the following equation:



Note that all these reactions are accelerated by a catalyst (viz., acid or base).

Tetraethoxysilane (TEOS) is most commonly used as a source of high-purity silica in the sol–gel syntheses. Depending on conditions, TEOS is hydrolyzed to form a solution of polyethoxysilane (acid hydrolysis) or a sol consisting of silica particles (alkaline hydrolysis). After drying the hydrolysate, a solid xerogel is formed, whose textural characteristics are determined by the conditions of hydrolysis and drying [7–9].

Porous silica materials are used as adsorbents and supports for catalytically active metals because of their high specific surface areas and easy access to the sur-

face due to the significant transport-pore volume. It is desirable to retain these properties at elevated temperatures. Silica gels prepared by conventional methods are thermally unstable. Their specific surface areas do not exceed  $700 \text{ m}^2/\text{g}$ , and the samples are sintered upon heating at temperatures above  $400^\circ\text{C}$ . This behavior is also typical of the sol–gel prepared silica gels, which are free from alkali ions. According to [10], the specific surface area of silica gel prepared by hydrolysis and the condensation of TEOS was initially  $700 \text{ m}^2/\text{g}$  and decreased to  $450 \text{ m}^2/\text{g}$  upon calcination for 2 h at  $800^\circ\text{C}$ . The sol–gel synthesis provides a unique means for the precipitation of silica-containing particles and polysiloxane molecules on various templates, copying their surface on a nanosized level. Surfactants [11] and carbon materials [12] are used as templates and removed after silica deposition. Extremely fine silica consisting of 2.5–5.0-nm particles and possessing a specific surface area of  $1000 \text{ m}^2/\text{g}$  was prepared by the above method [13]. This material was prepared by the treatment of wet carbon soot with dimethylchlorosilane  $(\text{CH}_3)_2\text{SiCl}_2$  vapors followed by the burn off of the organic substance in air at 773 K. Silica formed in an amount equaling 4% of the initial weight of carbon soot looked as like opalescent powder with spherical particles the same size as soot granules. Hence, the sol–gel synthesis is a promising method for the preparation of oxide materials with novel properties.

This work considers the synthesis of silica materials with an unusual micro- and nanotube structure by the deposition of silica coatings on the surface of various carbon fibers followed by carbon removal.

## EXPERIMENTAL

TEOS hydrolyzed with an understoichiometric amount of water in an acidic medium was used as a

source of silica. The concentration of  $\text{SiO}_2$  in the hydrolysate was 0.147 g per 1 ml of the solution.

A woven carbon material and carbon felt (ANM) were used as microfibrinous carbon matrices. The woven carbon material was a 0.5-mm thick fabric consisting of orderly interlaced long carbon fibers. The carbon felt was a loose thick fabric (4.5-mm thick) consisting of randomly interlaced short carbon fibers.

Catalytic fibrous carbon (CFC) was used as a nanofibrous carbon matrix. This material was prepared by the catalytic decomposition of natural gas on a pilot setup [14]. Highly-dispersed nickel containing 10 wt %  $\text{SiO}_2$  as a textural promoter was used as a catalyst [15]. The reaction was carried out in a vibrofluidized catalyst layer at 550°C and a gas rate of 100 l (g Cat)<sup>-1</sup> h<sup>-1</sup>. The yield of carbon was 150 g/g Cat. CFC was in the form of irregular granules (2–5 mm) consisting of randomly interlaced carbon nanofibers of 10–150 nm.

The textural characteristics of the carbon materials are presented in Table 1.

The carbon matrices were impregnated with an excess hydrolysate for 1 h. Experiments showed that storing the samples in the hydrolysate for a prolonged time (up to 72 h) did not increase their weights after drying. Hence, equilibrium is established in the first hour, and further adsorption from the solution did not occur. The excess hydrolysate was removed, and the samples were dried at room temperature for 24 h, calcined at 300°C for 1 h, and weighed; then, carbon was removed at 600°C in air.

The amount of  $\text{SiO}_2$  supported on carbon was varied by the dilution of the initial hydrolysate with ethanol or by a change in the number of impregnations. When the number of impregnations was greater than one, the whole process, except for the burn off of carbon, was repeated as many times as required. The weight concentration of silica was determined in the grams of  $\text{SiO}_2$  per 1 g of carbon (*viz.*, g  $\text{SiO}_2/\text{C}$ ). The moisture capacity of carbon matrices was determined as follows. The samples were dipped in water that was boiled for 1 h. Then, the samples were cooled and excess water was removed on a nutsch filter. The samples were weighed, dried at room temperature, and weighed again. The water volume was estimated from the difference in weights.

The textural characteristics of the carbon matrices and silica materials after carbon burn off were studied by low-temperature nitrogen adsorption at 77 K on an automatic ASAP-2400 setup.

The concentrations of alkali metals and calcium in the silica samples were determined by ionization spectroscopy on a BAIRD plasma spectrophotometer.

The electron micrographs of samples were obtained on a BS-350 scanning electron microscope and a JEM-2010 transmission electron microscope.

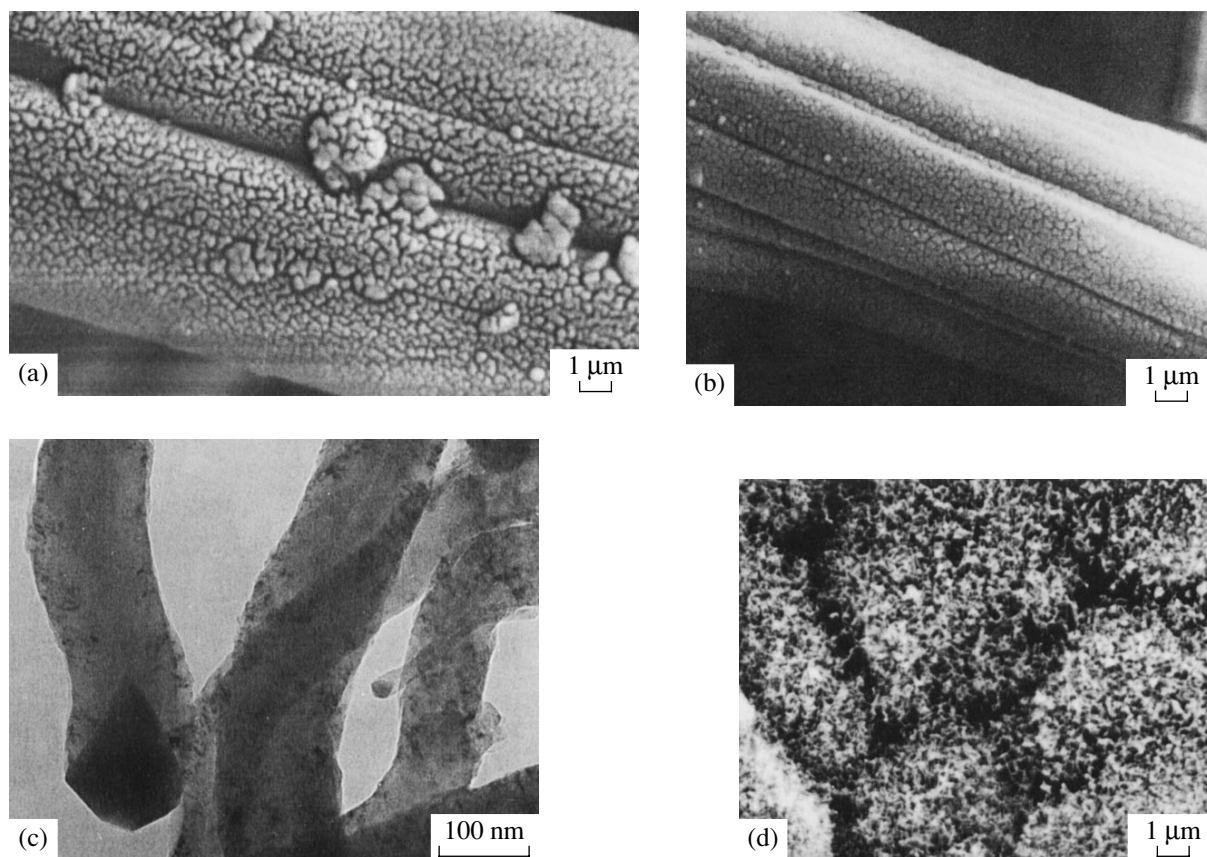
## RESULTS AND DISCUSSION

As can be seen from Table 1, the fibrous carbon materials used as porous matrices differ significantly in their textural characteristics, especially in the specific surface area and porosity. The samples can be categorized as microporous (woven carbon material and carbon felt) and mesoporous (CFC) materials. A typical structure of the fibers is shown on the electron micrographs (Fig. 1).

The carbon-based silica samples are brittle porous materials, which can readily be ground to a fine powder. Their appearance repeated the initial carbons, and their morphology was somewhat stereotypical of the carbon fibers (Fig. 2). As can be seen in Table 2, among three samples after carbon burn off, silica prepared by the sol-gel copying the CFC nanofibers possesses the highest specific surface area. This fact is likely due to the mesoporous texture of this carbon. Probably, the linear polysiloxane molecules more uniformly cover the surface of the most accessible large-pore CFC. In the case of microporous carbons, when the prevailing pore diameter decreases, the polysiloxane molecules cannot penetrate the smallest pores and accumulate on the surface of large pores. The fraction of  $\text{SiO}_2$  molecules that directly contact the carbon surface in the pore volume of the carbon matrices decreases; that is, the silica film becomes thicker. For this reason, the specific surface area of porous silica also decreases after carbon burn off.

In addition to geometric factors, the specific surface area of silica samples depends on the purity of carbon materials used as templates. Particularly, the concentration of alkali metals is of great importance. Alkali metals, which are well known to promote silica sintering, can be introduced into carbon during fiber preparation. After carbon burn off, alkali metals are certainly a part of the silica film. As burn off is carried out at sufficiently high temperatures (500–600°C), sintering due to alkaline admixtures can substantially contribute to a total decrease in the specific surface area of porous silica. As we showed, the sodium and potassium concentrations are the percents of the total weight (2–5% Na and 0.17–1.25% K) in the silica samples prepared by sol-gel copying the carbon fabric and felt, whereas the concentrations of these metals in porous silica prepared with the use of CFC as a template is substantially lower (0.02% Na and 0.03% K). Thus, the high specific surface area of silica prepared by copying CFC is largely due to the high purity of the carbon material. This feature and the absence of micropores in the silica texture explain its high thermal stability. According to the data of Table 3, the calcination of the sample for 2 h even at a temperature of 900°C results in a slight (18%) decrease in the BET specific surface area. The pore volume of the silica sample decreases by at least 9%.

It follows from the above data that the synthetic carbon material CFC is the most promising as a template for the preparation of porous silica materials by sol-gel



**Fig. 1.** Electron micrographs of fibers in (a) carbon fabric, (b) carbon felt, (c) catalytic fibrous carbon, and (d) granules of catalytic fibrous carbon.

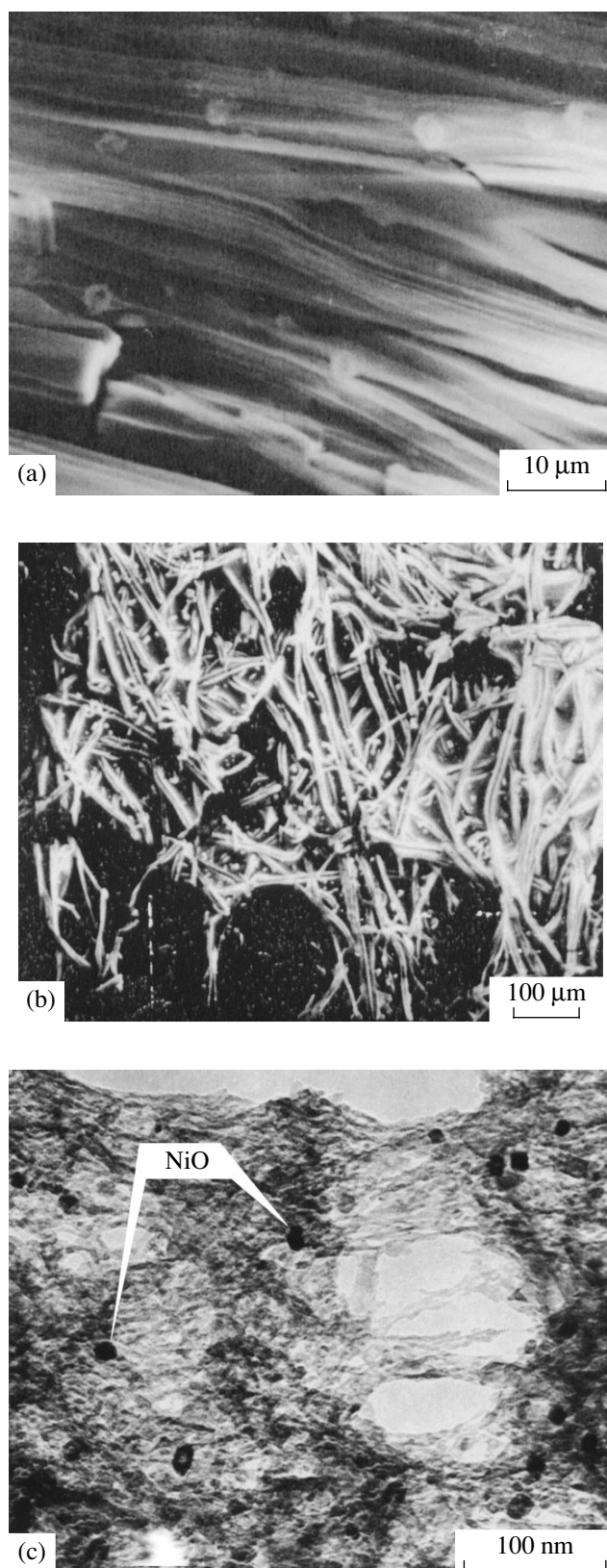
copying. Taking into account this fact, we carried out further studies to elucidate how the CFC texture and the conditions of sol-gel synthesis affect the morphology of porous silica.

Since the specific surface area of the porous silica material prepared by the sol-gel copying of carbon fibers depends on the thickness of the silica film formed on fibers, we assumed that this parameter decreases to a value equivalent to a  $\text{SiO}_2$  tetrahedron size (0.161 nm) with a decrease in the  $\text{SiO}_2$  concentration in the

hydrolysate. Correspondingly, the specific surface area of silica after the burn off of carbon nanofibers should increase until it theoretically reaches  $2000 \text{ m}^2/\text{g}$ . However, this is not the case in practice. Since carbon nanofibers are significantly graphitized and covered by the silica film that protects them from oxidation, they burn off with a noticeable rate at temperatures above  $500^\circ\text{C}$ . At this temperature, the atoms on the silica surface already acquire mobility and the samples lose the narrowest pores. Table 4 presents data on the decrease

**Table 1.** Textural characteristics of the starting carbon matrices

Material	$S_{\text{sp}}, \text{m}^2/\text{g}$	Volume of pores from 0 to 100 nm, $\text{cm}^3/\text{g}$	Micropore volume, $\text{cm}^3/\text{g}$	Average pore diameter, nm	Moisture capacity, ml/g
CFC	94	0.31	0.035	13.27	0.33
Carbon fabric	798	0.47	0.361	4.58	1.88
Carbon felt, ANM	365	0.82	0.166	6.45	9.98



**Fig. 2.** Structure of porous silica prepared by sol-gel copying (a) the surface of the carbon fabric, (b) carbon fiber felt, (c) nanofibers of catalytic fibrous carbon.

in the thickness of the silica coating on the carbon fibers by the decrease in the silica concentration in the hydrolysate. As can be seen from Table 4, the apparent density of silica samples ( $\text{SiO}_2$  amount per 1 g of C) decreases with a decrease in the silica concentration in the hydrolysate. The pore volume in the silica samples corresponds to those in aerogels prepared by the sol-gel method using supercritical drying [16]. Note that the specific surface area increases with a decrease in the  $\text{SiO}_2$  concentration based on the CFC weight in the dried sample, for example, from 867 to 1267  $\text{m}^2/\text{g}$ .

Another way of controlling the morphology of porous silica is to change the morphology and structure of the starting CFC. To evaluate the range of the possible variation in these parameters, it is necessary to examine the growth of carbon nanofibers during catalytic methane decomposition. Note that methane decomposition to produce CFC was carried out in a vibrofluidized catalyst bed. This condition is necessary to avoid the agglutination of growing CFC granules. We have previously considered the growth of the CFC granules in a vibrofluidized bed [17]. The volume of the CFC granules increased in time, and their porosity and accessible surface area decreased due to the growth of carbon fibers with different diameters over the granule bulk. Table 5 shows the findings of textural measurements for three samples of fibrous carbon obtained by methane decomposition on the 90% Ni–10%  $\text{SiO}_2$  catalyst. These samples differ in the carbonization duration (10, 15, and 35 h) and the yield of carbon per 1 g of nickel (100, 150, and 350 g C/g Ni), respectively. It is seen that the more prolonged the carbon growth, the more dense the carbon and the smaller its pore volume. The residual nickel content is also an important factor, along with the textural parameters of carbon, since whole nickel enters the porous silica obtained after carbon burn off. The amount of nickel depends on the duration of the carbonization of the initial catalyst and can vary widely. The carbon obtained with the maximal yield contains a minimal amount of nickel (<0.3%). The nickel content in carbon can be lowered by acidic treatment.

When CFC is impregnated with a hydrolysate solution followed by the removal of a solvent, polyethoxysilane condenses and transforms into a gel, whose volume decreases. This gel forms an elastic film on the surface of the carbon nanofibers. Calcination at 300°C results in the removal of a significant fraction of the organic constituent of the coating and chemisorbed water, but carbon oxidation does not occur. Note that because of high graphitization, there is an insignificant amount of micropores in CFC; that is, there are no sites where polymer molecules cannot penetrate during impregnation. According to adsorption data, the CFC texture does not change after impregnation with a hydrolysate and preliminary calcination, indicating the high uniformity of the carbon surface coating with the

**Table 2.** Textural characteristics of the silica gels prepared by the single impregnation of various carbon matrices with the hydrolysate (0.147 g SiO<sub>2</sub> per 1 ml of solution)

Starting carbon	Amount of supported SiO <sub>2</sub> , g SiO <sub>2</sub> /g C	$S_{sp}$ , m <sup>2</sup> /g	Volume of pores from 0 to 100 nm, cm <sup>3</sup> /g	Micropore volume, cm <sup>3</sup> /g	Average pore diameter, nm
CFC	0.077	1255	5.600	0	17.8
Carbon fabric	0.412	300	0.174	0.0866	2.2
Carbon felt	2.510	9	–	–	–

silica film. Further calcination in air at 600°C for 5–6 h leads to the complete burn off of carbon and fibrous carbon in the silica film. As a result, porous silica with nickel oxide dispersed in its bulk is formed.

Figure 2c shows a typical structure of aerogels prepared by silica deposition on CFC with a high degree of carbonization (>60 g C/g Ni). As can be seen, the aerogel consists of thin-walled prolonged structures which represent the silica shells of carbon nanofibers. It is difficult to separate elements in the aerogel structures, since nanofibers are deeply interlaced in carbon granules (Fig. 1d).

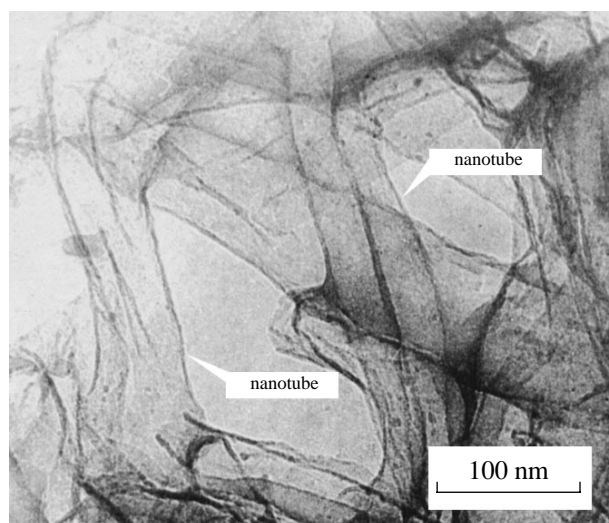
Another picture is observed when the nickel system with particles ~60 nm in diameter is used as a catalyst for CFC growth and the duration of methane decomposition is at most 6 h. Figure 3 distinctly shows the elements in the form of silica nanotubes. The wall thickness of these tubes is 3–5 nm. Such structures have been reported previously in [12]. In this work, silica films were deposited by sol–gel synthesis on short carbon nanotubes that were grown by the plasma technique. Then, the carbon was removed. However, the silica material prepared by this method had a specific surface area of only 550 m<sup>2</sup>/g, probably due to the low density of the initial carbon matrix. After carbon removal, aerogel prepared by our method represents an extremely porous matrix permeated by channels in which the nickel oxide particles were included. The average size of NiO particles was 30–35 nm, because the catalytic nickel particles transform by fusion and dispersion during CFC formation to reach a thermodynamically beneficial size under these conditions [18]. The nickel particles size does not change upon carbon burn off when the nickel concentration is at most 25%. Otherwise, silica cannot stabilize the dispersed NiO particles, and they sinter to larger particles. As was mentioned above, the amount of nickel in the aerogel can be controlled by changing the duration of carbonization of the starting catalyst or by varying the number

**Table 3.** Effect of calcination temperature on the textural characteristics of silica gel prepared by SiO<sub>2</sub> deposition on CFC\*

$T_{cal}$ , °C	$S_{sp}$ , m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g	Average pore diameter, nm
600	1087	4.19	15.84
800	912	3.97	17.40
900	893	3.80	20.00

\* 10% SiO<sub>2</sub> per carbon weight.

of silica deposition cycles on carbon. Since silica films in the aerogels are very thin and contain highly-dispersed active metal, their unusually high performance in the catalytic reactions can be expected.

**Fig. 3.** Silica nanotubes.

**Table 4.** The textural characteristics of the silica gels prepared by SiO<sub>2</sub> deposition on carbon matrices from hydrolysate solutions with various concentrations

SiO <sub>2</sub> concentration in a hydrolysate, g SiO <sub>2</sub> /ml	Amount of deposited SiO <sub>2</sub> , g SiO <sub>2</sub> /g C	$S_{sp}$ , m <sup>2</sup> /g	Volume of 0–100 nm pores, cm <sup>3</sup> /g	Average pore diameter, nm
0.294	0.140	867	3.18	14.7
0.147	0.077	1191	5.60	17.8
0.073	0.043	1255	5.60	19.0
0.036	0.030	1267	5.70	18.0

**Table 5.** Variation in the textural parameters of the CFC samples as a function of the carbon yield over the nickel catalyst

Carbon yield, g C/g Ni	$S_{CFC}$ , m <sup>2</sup> /g	Pore volume, cm <sup>3</sup> /g	Average pore diameter, nm
100	120	0.345	11
150	94	0.310	13
350	70	0.253	15

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