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Materials

Fabrication and formation mechanism of NbC_x-C three-dimensional netted fibers

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Abstract: Micrometer NbC_x-C three-dimensional netted fibers were synthesized by the carbothermal method under 0.1 MPa of N_2 ambient atmosphere at a relatively low temperature. Raw materials were commercial powders of Nb_2O_5 (99.95%), reactive carbon (99.99%), NaCl (99.95%) and sucrose (99.94%). The relationship of the fabrication processing with the composition, crystal structure and morphology of fibers was investigated. The formation mechanism was also proposed and discussed.

Key words: NbC_x-C three-dimensional netted fibers; fabrication; morphology; formation mechanism

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The successful synthesis of three-dimensional (3-D) netted fibers of any kind of useful materials is a very important technology because it might take the place of the 3-D weaving technology of long fibers that is costly but plays a very important part in aviation, spaceflight *etc.* or might result in some materials with more important or particular properties in the future.

Niobium carbide with NaCl structure is of special interest in the fields of the high temperature technology and electrical industry due to its good structural and electrical properties, such as high melting point (>3500℃), hardness, resistance to chemical attack and thermal shock, and good electronic conductivity and superconductivity at low temperatures [1,2]. Therefore, for over 30 years, several methods have been used to synthesize NbC powder, or particles including: (1) direct reaction of niobium metal with carbon [3], (2) gas phase reaction of $NbCl_5$ with hydrocarbon [4], (3) solid-state reaction of niobium oxide (Nb_2O_5) with carbon [5], and (4) reaction of Nb_2O_5 with polyacrylonitrile composites at 1000℃ [6]. The flux method [7], floating zone technology [8], and low temperature electrosynthesis [4] were used for preparation of NbC_x single crystals. Except results in reference [9] there is no reports about preparation of NbC_x-C 3-D netted fibers until now.

In this paper, NbC_x-C 3-D netted fibers were synthesized by the carbothermal method at relatively low temperatures under 0.1 MPa of N_2 ambient atmosphere. The relationship of the synthesis processing with the compositions, crystal structure and morphology of fibers was investigated in detail. Besides, the formation mechanism was discussed.

1 Experimental

The experimental processing consisted of several steps [9]. Raw materials were commercial powders of Nb_2O_5 (99.95%), reactive carbon (99.99%), NaCl (99.95%) and sucrose (99.94%). It was expected that NaCl and sucrose as additives could excite reduction of Nb_2O_5 and supply an active carbon source. The carbon added was excessive to obtain a near monocarbide NbC. Three groups of experiments were performed to investigate the effect of the composition of starting mixture, reducing temperature and time, and carbon powder, such as its addition way and particle size *et al.*, on the formation of NbC_x-C 3-D netted fibers. All experimental conditions are listed in **table 1**.

In the first group, samples 1-7 were the same in initial composition and addition way of carbon powder with the same particle size. The objective of this group was to investigate the function of reducing temperature and time, which meant that the samples were reduced at different temperatures and for different time under 0.1 MPa of N_2 ambient atmospheres.

In the second group, samples 8-10 were different in

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initial composition from the samples of group 1 to understand functions of the additives of NaCl and sucrose.

In the third one, samples 11-13, different addition way and particle size of carbon powder were adopted to investigate functions of carbon powder.

Table 1 fabricating conditions of NbC_x-C 3-D netted fibers

Sample No.	Molar ratio				t / ℃	τ / h	Size of carbon / μm	Adding way of carbon powders
	Nb_2O_5	C	NaCl	sucrose				
1	1	4	2	2	970	0.5	5-30	A
2	1	4	2	2	1020	0.5	5-30	A
3	1	4	2	2	1070	0.5	5-30	A
4	1	4	2	2	1120	0.5	5-30	A
5	1	4	2	2	1120	1.0	5-30	A
6	1	4	2	2	1120	1.5	5-30	A
7	1	4	2	2	1120	2.0	5-30	A
8	1	4	—	2	1120	0.5	5-30	A
9	1	4	4	—	1120	0.5	5-30	A
10	1	4	2	—	1120	0.5	5-30	A
11	1	0	2	2	1120	0.5	5-30	A
12	1	4	2	2	1120	0.5	0.5-1.5	A
13	1	4	2	2	1120	0.5	5-30	B

Note: A denotes carbon powder was separated from the mixture of others; B denotes carbon powder was mixed with others.

The reducing temperature and time for samples 8-13 were the same as sample 4.

The composition, crystal structure and unit cell constant were determined by the powder X-ray diffraction (XRD) method (nickel-filtered CuK_α radiation, scan step 0.25°/min.). The morphology was observed by a scanning electron microscope (SEM; CAMBRIDGE, S-360). The surface impurities were analyzed by an X-ray photoelectron spectroscope (XPS).

The carbon content was determined by mass gain or mass loss of samples in isothermal oxidation. The samples used for oxidation experiments were washed repeatedly to get accurate results. The initial mass of the samples was 10 g. Isothermal oxidation was performed at 500℃ for 3 h in air.

2 Results and discussion

2.1 Preparation of NbC_x-C 3-D netted fibers

In the first group, there are 3-D netted fibers produced over the entire fabrication conditions. Powder XRD patterns of the netted fibers reduced at different temperatures for 0.5 h are shown in **figure 1**. It can be seen that there are no peaks of carbon since it is amorphous, the 3-D netted fibers are NbC_x with NaCl crystal structure at temperatures higher than 1070℃ and are the mixture of NbC_x, NbO_2, $NaNbO_3$ and NaCl at temperatures lower than 1020℃. As the temperature increases from 970 to 1020℃, the $NaNbO_3$ content in the mixture increases, while the NbO_2 content decreases. They all disappear and are reduced into

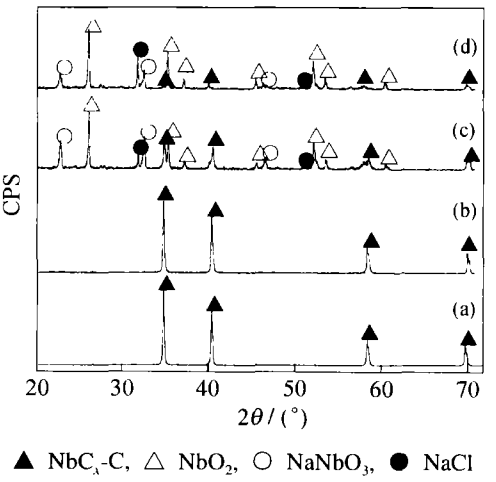


Figure 1 X-ray powder diffraction patterns of 3-D fibers obtained at (a) 1120, (b) 1070, (c) 1020, and (d) 970℃.

NbC_x at temperatures higher than 1070℃ in a short time. These results mean that NbO_2 might be produced at lower temperatures, chemical active increased and turned into $NaNbO_3$ later.

In the second group, there is no 3-D netted fibers formed. Determined by XRD analysis, as shown in **figure 2**(a-c), it is known that the product of sample 8 is NbC_x porous solid, the products of samples 9 and 10 are hard solid mixtures consisting of NbC_x, $NaNbO_3$ and NaCl, and NbC_x, $NaNbO_3$ and NbO_2, respectively. These results mean that neither NaCl nor sucrose is added there is no NbC_x-C 3-D netted fibers formed, and the composition of the products varies with the amount of NaCl added.

In the third group, there is no netted fibers formed

either. According to the results of XRD analysis, as shown in figure 2(d-f), the following results were obtained. The products of samples 11 and 12 are porous mixture consisting of NbC_x, $NaNbO_3$ and NbO_2, and porous solid of NbC_x respectively, which means that when carbon powder is not added, and the particle size of carbon powder is too large, 3-D netted fibers can not be obtained. The product of sample 13 is NbC_x powder, which means that the addition way of carbon powder is a very important factor to formation of the netted fibers too.

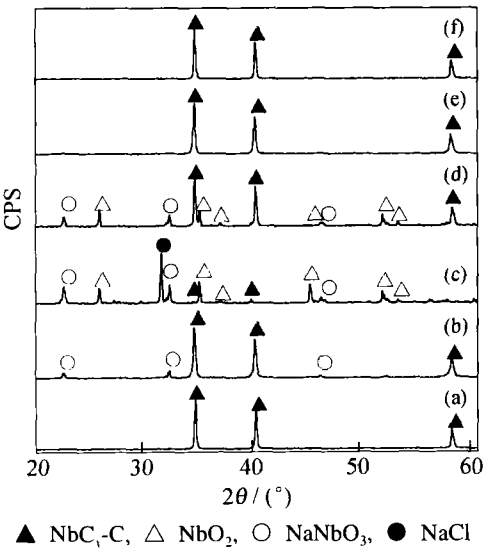


Figure 2 X-ray powder diffraction patterns of (a) sample 8, (b) sample 9, (c) sample 10, (d) sample 11, (e) sample 12, and (f) sample 13 at 1200℃ for 0.5 h.

2.2 Determination of carbon content

Since the carbon exists in amorphous state, there are no obvious peaks of carbon in the XRD patterns of samples, as shown in figures 1 and 2. The carbon contents of samples 3-7 were determined by the isothermal oxidation method.

According to the theoretical mass gain and the practical mass gain or mass loss of a sample before and after isothermal oxidation experiments were performed, and the carbon content was determined.

On the assumption that the initial mass of a sample be m in g, the carbon content x in % (mass fraction), the practical mass gain y in % (mass fraction), and the relative molecular masses of Nb_2O_5 and $NbC_{0.98}$ be $M_{Nb_2O_5}$ and $M_{NbC_{0.98}}$ respectively, there should be the following equation:

$$y = \frac{(1-x)(0.5M_{Nb_2O_5} - M_{NbC_{0.98}})}{M_{NbC_{0.98}}} - x,$$

where, as described above, the x value of NbC_x is 0.98. When 1 mol of $NbC_{0.98}$ is oxidized into Nb_2O_5, the mass gain should be 26.97% in mass fraction, which is equal to the value of $(0.5M_{Nb_2O_5} - M_{NbC_{0.98}})/M_{NbC_{0.98}}$ and is the theoretical value of mass gain. After isothermal oxidation experiments, it was known that the values of the practical mass gain of samples 3-7 were about (6.5 ± 0.03)% in mass fraction, among which there was not great difference. The carbon content was then calculated to be 16.12%. Furthermore, the molar ratio of NbC_x to carbon in the NbC_x-C netted fibers was determined to be 1:1.98.

2.3 Morphology of NbC_x-C 3-D netted fibers

After the graphite crucible was opened, it could be found that there was a thin mushroom film of NbC_x-C on the top of NbC_x-C 3-D netted fibers, namely, NbC_x-C 3-D netted fibers are under the thin film of NbC_x-C mushroom. Their color was brown at temperatures higher than 1070℃ and grey at temperatures lower than 1020℃ depending on their composition. The scanning electron micrographs of samples 1-4 reduced at 970, 1020, 1070, and 1120℃ for 0.5 h and those of samples 4-7 reduced at 1120℃ for 0.5, 1.0, 1.5, and 2.0 h are shown in **figures 3 and 4**, respectively. It can be observed that the shape of the netted holes can be round, pentagon or tetragonal whose morphology, diameter and circumference vary with the reaction temperature and reaction time.

Having been observed, analyzed and measured by SEM, the fiber diameter D_f and the hole circumference L_h of different 3-D netted fibers were determined. By calculation of L_h/D_f, the ratio of the hole circumference to the fiber diameter was obtained. The hole diameter D_h was determined by the formula of $L_h = \pi D_h$. All of these results are shown in **table 2**.

From table 2, it can be observed that with the increase of reducing temperature and time, the fiber diameter decreases but the hole circumference increases. When the reducing temperature increases from 970 to 1120℃ and the isothermal time 0.5 to 2.0 h, they vary in the range from 8 to 47 μm and 0.12 to 2.2 mm respectively, the ratio of hole circumference to fiber diameter is 12.0-62.0, the hole diameter varies in the range from 38 to 701 μm.

The microstructure of fractographs and the knot of the 3-D netted fibers have been described [10]. It is known that their cross-sections are triangle and many white spots on the surface of the netted fibers are convexity upwards of the foamed structure. It means that some netted fibers are porous although some are a little dense. The foamed structure is the reason that the netted fibers are fragile.

2.4 Surface impurities

In order to determine the surface impurities of ini-

tial products (unwashed), XPS analysis was used. Results show that the surface impurities are composed of 1.84% NbO_2, 5.90% NaCl, and 92.26% free carbon in molar number fraction. It can be found that there is much amount of free carbon, little of NbO_2 and NaCl on the surface of NbC_x-C 3-D netted fibers. The content of free carbon on the surface impurities is much greater than that of others. This free carbon might come from the flowing carbon powder moved by gas flow and plays an important part in the formation of networks. The oxygen content may be due to the absorption of oxygen by NbC_x-C 3-D netted fibers as reported [10], which may be the reason that the color of NbC_x-C 3-D netted fibers is brown. The NaCl content may result from its condensation when cooled down from high temperatures.

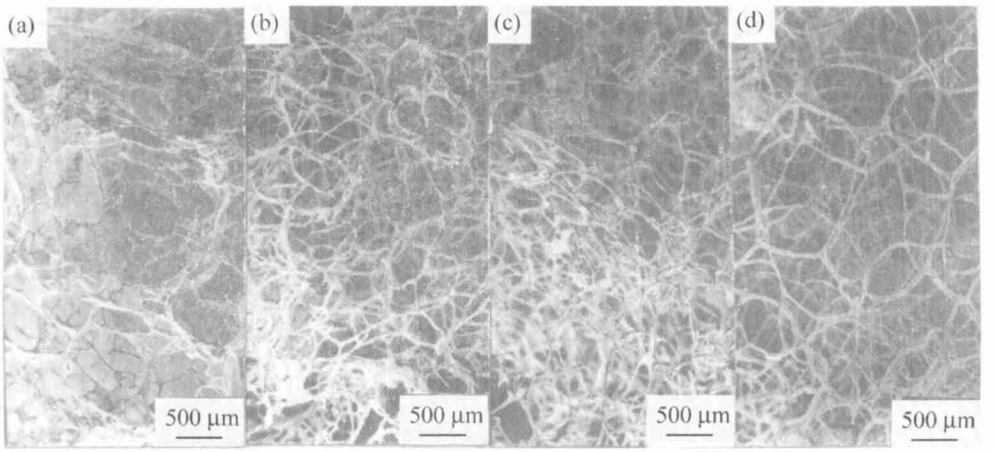


Figure 3 Scanning electron micrographs of NbC_x-C 3-D netted fibers reduced at (a) 970, (b) 1020, (c) 1070, and (d) 1120℃ for 1.0 h.

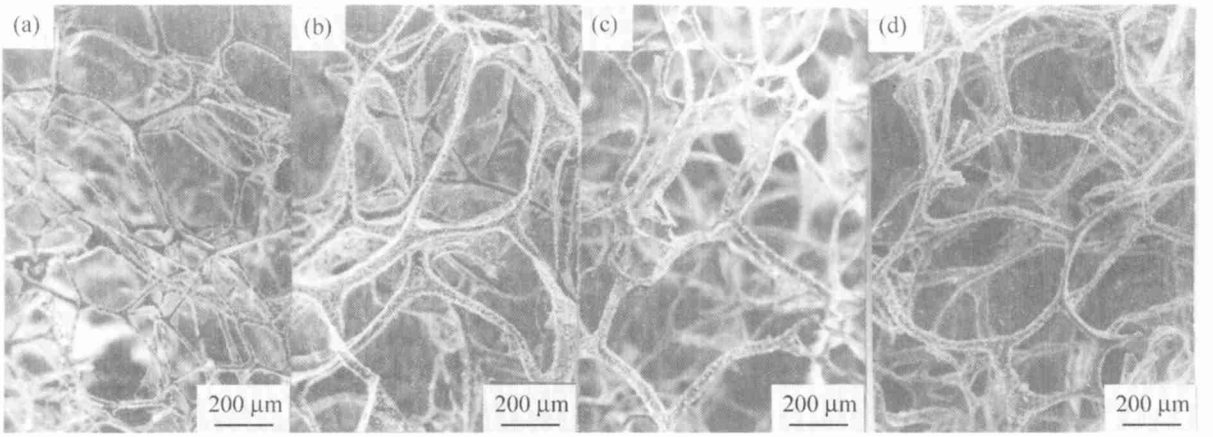


Figure 4 Scanning electron micrographs of NbC_x-C 3-D netted fibers reduced at 1120℃ for (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 h.

Table 2 Fiber diameters, hole circumferences and hole diameters at various temperatures for different time

t / ℃	τ / h	D_f / μm	L_h / mm	D_h / μm	L_h / D_f
970	0.5	10-47	0.12-0.74	38-236	12.0-15.8
1020	0.5	8-40	0.20-0.95	64-303	25.0-28.0
1070	0.5	18-38	0.22-1.00	70-318	12.2-26.3
1120	0.5	18-36	0.50-2.20	159-701	28.5-62.0
1120	1.0	17-33	0.48-1.60	153-520	28.2-48.5
1120	1.5	16-29	0.45-1.50	143-478	28.1-51.7
1120	2.0	12-20	0.40-0.90	127-287	33.0-45.0

3 Reaction mechanism

According to XRD analytical results, as shown in figure 1, it is known that with the increasing of reaction temperature, the $NaNbO_3$ content in the products increases, the NbO_2 content decreases, and they disappear when the temperature is not lower than 1070℃. These results indicate that Nb_2O_5 is reduced into

$NbO_{2(s)}$ by sucrose at a relatively low temperature through the reaction

$$24Nb_2O_5+C_2(H_2O)_{11} = 48NbO_{2(s)}+12CO_{2(g)}+11H_2O_{(g)} \quad (1)$$

Gas CO_2 and H_2 formed in the reaction above is reduced into CO according to the reaction

$$CO_{2(g)} + C_{(s)} = 2CO_{(g)} \quad (2)$$

$$H_2O_{(g)} + C_{(s)} = 2CO_{(g)} + H_2 \quad (3)$$

Then, $CO_{(g)}$ takes part in a series of chemical reactions as follows. Firstly, NbO_2 is converted into $NaNbO_3$ through the reaction

$$NbO_{2(s)} + NaCl_{(l)} + CO_{(g)} = NaNbO_{3(l)} + 2CCl_{(g)} \quad (4)$$

Secondly, in the reducing atmosphere of CO, $NaNbO_3$ formed is thought to be reduced into $NbO_{(l)}$ through the reaction

$$NaNbO_{3(l)} + CCl_{(g)} + CO_{(g)} = NbO_{(l)} + NaCl_{(g)} + CO_2 \quad (5)$$

Because there is no $NbO_{(s)}$ found from 970 to 1120℃, the product, $NbO_{(l)}$ in liquid state, is reduced further into NbC_x according to the reaction

$$NbO_{(l)} + CO_{(g)} = NbC_{(l)} + CO_2 \quad (6)$$

or

$$NbO_{(l)} + C_{(s)} = NbC_{(l)} + CO_{(g)} \quad (7)$$

Because the temperature is lower than the melting point of NbC, $NbC_{(l)}$ is condensed into $NbC_{(s)}$ quickly according to the reaction

$$NbC_{(l)} = NbC_{(s)} \quad (8)$$

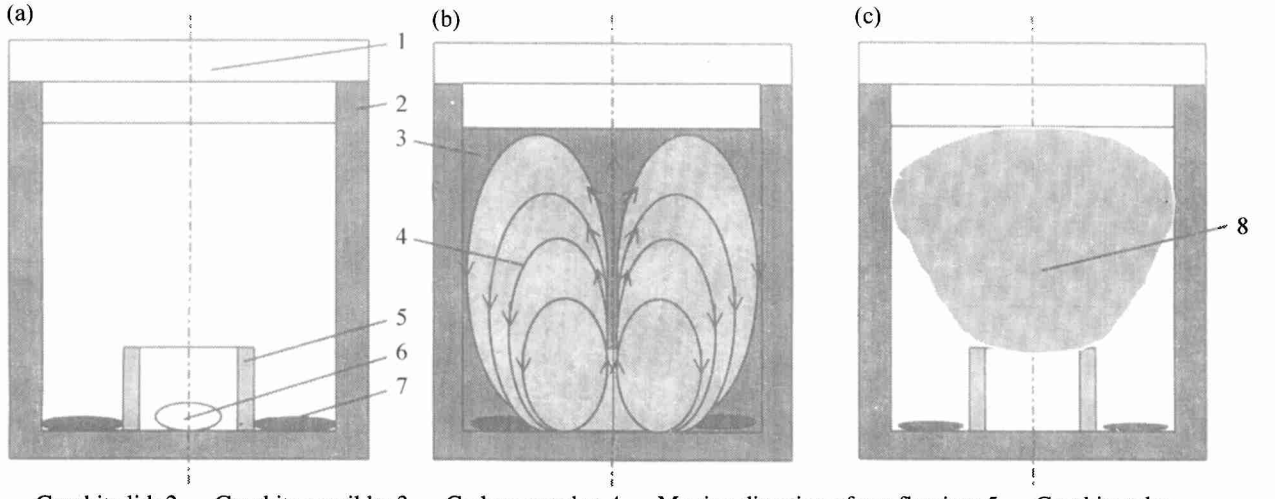
where, $C_{(s)}$ may come from the flowing gas containing carbon, and the subscripts of (s), (l) and (g) represent that the substance is in the states of solid, liquid and gas respectively.

Reaction equations (4) and (5) describe the function of NaCl as a catalyst, which is demonstrated by the experimental results of samples 9 and 10. Namely, when more amount of NaCl was added, more $NaNbO_3$ and less NbO_2 were detected by XRD and there was no other sodium compound found.

4 Formation mechanism

Whether it is process biomimetic approaches or traditional methods used for the fabrication of porous materials, of which many researches about the formation mechanism of porous structure have been done [11-12]. The main formation mechanism of NbC_x-C 3-D netted fibers should belong to the later one. It is similar to but not the same as the fabrication of porous materials by traditional methods [13-14], from which the main difference is the function of carbon powder.

A rough sketch for the formation mechanism of 3-D netted fibers is shown in **figure 5**. As discussed above, it is known that the amounts and the addition way of NaCl and sucrose and the particle size of carbon powder are very important to the formation of NbC_x-C netted fibers. Among the mixture of Nb_2O_5, NaCl and sucrose, sucrose with the lowest melting point melts at lower temperatures and reacts with Nb_2O_5 according to equation (1). The products of gases CO_2 and H_2O will react with carbon according to equations (2) and (3) and a lot of gases, such as CO, H_2 and CO_2 are produced. These gases make strenuous whirlpool movement, take along carbon powder with particles of certain size outside the mixture, and turn



1 — Graphite lid; 2 — Graphite crucible; 3 — Carbon powder; 4 — Moving direction of gas flowing; 5 — Graphite tube; 6 — Mixture; 7 — Carbon powder; 8 — 3-D netted fibers

Figure 5 Rough sketch of formation mechanism of NbC_x-C 3-D netted fibers. (a) initial state of sample. (b) Moving directions of gas flow. (c) Rough position of 3-D netted fibers.

the mixture into foamed melt containing powders of NbO_2, NaCl and Carbon. With the temperature increasing, NaCl melts and reacts with NbO_2 according to equation (4) and is finally reduced to NaCl gas according to equation (5), and much more gases, such as NaCl, CCl and NbO *etc.*, are produced. During these processes, carbon powder contained in gas flow passes through and destroys the thin films in the foamed melt and makes the formation of the 3-D netted fibers become true. This point is particularly important to the formation of the 3-D netted fibers and is the difference from the traditional formation mechanism of the porous or foamed structure. This last conclusion comes from the experimental results of samples 11, 12 and 13, namely, when there is no carbon powder added, or the particle size of carbon powder is too large and/or carbon powder is mixed with others, there is no 3-D netted fibers formed. Besides, it has been known that there is much carbon powder on the surface of the initial products.

It is proposed that the pressure in the system and the kinematic viscosity of the melt are very important factors. In general, when the pressure and the kinematic viscosity are too high, the product might be sound solid. On the contrast, the product might be porous solid. In order to get significant results, the appropriate processing parameters should be investigated in detail.

5 Conclusions

(1) NbC_x-C 3-D netted fibers can be fabricated by the carbothermal method with NaCl and sucrose as additives. When there is no NaCl or sucrose as additives, the 3-D netted fibers can not be formed.

(2) The addition way and the particle size of carbon powder are essential to the formation of NbC_x-C 3-D netted fibers.

(3) The composition of the 3-D netted fibers is dependent on the fabrication temperature. When the temperature is not lower than 1070℃, NbC_x-C 3-D netted fibers can be obtained.

(4) Determined by isothermal oxidation method, the carbon content of samples 3-7 is about 16.12% in mass fraction. The molar ratio of NbC_x to carbon in NbC_x-C 3-D netted fibers are 1:1.98.

(5) The fiber diameter and the hole circumference of the 3-D netted fibers vary with the reaction temperature and time. With the increase of temperature and time, the fiber diameter decreases but the hole circumference increases.

(6) The formation mechanism was proposed and discussed. It is similar to the traditional formation mechanism of the foamed structure, from which the most important difference is the addition way and the function of carbon powder with suitable particle size.

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