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A co-reduction synthesis of superconducting NbC nanorods

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Abstract

NbC nanorods with diameters of 50–150 nm were successfully synthesized through a new chemical route by using $NbCl_5$ and hexachlorobutadiene (C_4Cl_6) as Nb and C sources, and Na metal as the reductant at 600 °C in an autoclave. This reaction temperature is much lower than that used in traditional methods. The as-prepared NbC nanorods were characterized by x-ray powder diffraction, transmission electron microscopy and x-ray photoelectron spectra. Magnetization measurement indicated that the NbC nanorods have a superconducting transition at 12.3 K.

1. Introduction

Niobium carbide (NbC) is a very important non-oxide ceramic on account of its high melting point (3610 °C), outstanding hardness, excellent chemical stability and good wear resistance. NbC also exhibits high conductivity with a normal electrical resistance of 4.6 mΩ and superconductivity at about 11 K [1]. Due to these attractive properties, NbC has extensive applications and potential applications in mechanical industry, chemistry and microelectronics.

It is a well-known fact that the shape and size of nanocrystals have an important influence on their physical properties and applications. As a specific nanomorphology, one-dimensional nanorods can be used as building blocks for many functional materials, which have many potential applications in electronic and optoelectronic devices. As for NbC, the effect of dimensionality and size on its superconductivity is interesting for many researchers. Furthermore, superconducting NbC nanorods can serve as the building blocks in superconducting nanodevices.

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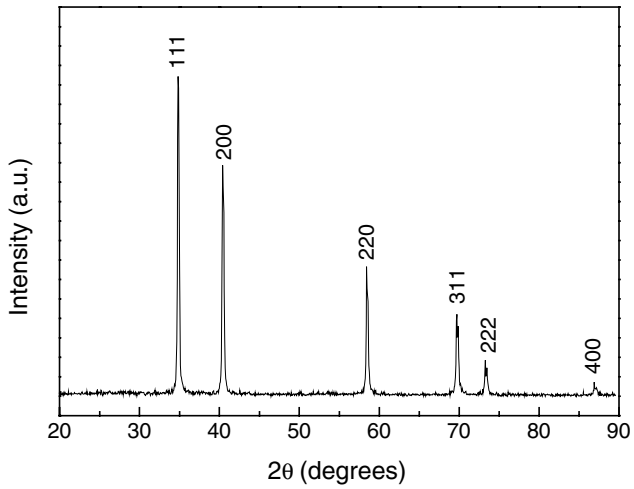

Figure 1. XRD pattern of the NbC sample at room temperature and all the peaks can be indexed as cubic NbC (JCPDS card, no. 38-1364).

Previously, NbC has been prepared by various high-temperature reactions above 1000 °C, such as the direct combination of niobium metal with carbon [2], gas-phase reaction of $NbCl_5$ with hydrocarbon [3] and carburization of the oxides by carbon or methane–hydrogen mixtures [4, 5]. However, these methods cannot produce nanocrystalline NbC. Recently, much effort has been made to develop a new low-temperature route to synthesize NbC or assemble for its desired nanostructures [6–8].

Here, we report a simple low-temperature chemical route to synthesize NbC nanorods. In the present study, NbC nanorods were synthesized at 600 °C by using hexachlorobutadiene (C_4Cl_6), $NbCl_5$ and Na as the reactants. The reaction was carried out in an autoclave and can be described as follows:

$$C_4Cl_6 + 4NbCl_5 + 26Na \rightarrow 4NbC\ (\text{nanorods}) + 26NaCl.$$

2. Experimental procedure

All manipulations were carried out in a dry glove box with an Ar flow. In a typical procedure, an appropriate amount of anhydrous $NbCl_5$ (0.02 mol), C_4Cl_6 (0.005 mol), and Na metal (0.13 mol) was placed in a glass-lined stainless autoclave of about 50 ml capacity. The autoclave was sealed and maintained at 600 °C for 8 h and then cooled to room temperature. The product was washed with absolute ethanol, dilute hydrochloric acid and distilled water, respectively, to remove NaCl and other impurities. After drying in vacuum at 60 °C for 4 h, the final black powder was obtained as product.

3. Results and discussion

Evidence for phase structure of the products was obtained by x-ray powder diffraction (XRD) pattern, which was carried out on a Rigaku Dmax-γA x-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). Figure 1 shows the XRD pattern of the as-prepared NbC sample and all the

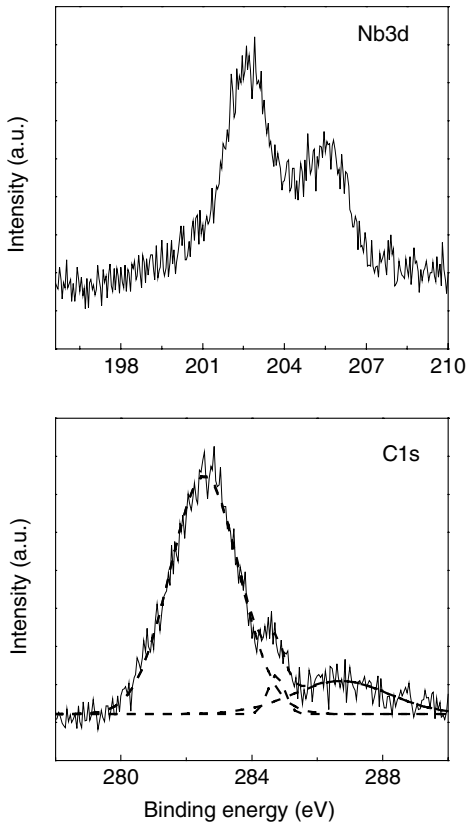

Figure 2. XPS of the Nb 3d and C 1s core-level regions for the as-prepared NbC sample.

peaks can be indexed as cubic NbC (JCPDS card, no. 38-1364). After refinement, the lattice constant $a = 4.472$ Å. The ratio of (C/Nb) was estimated to be 1.03 by using the relationship between lattice constant and the C/Nb ratio [9]:

$$a\,(\text{Å}) = 4.09847 + 0.71820(\text{C/Nb}) - 0.34570(\text{C/Nb})^2.$$

The composition details of the NbC sample can be obtained from the x-ray photoelectron spectra (XPS). XPS spectra were recorded on a VG ESCALAB MKII x-ray photoelectron spectrometer, using non-monochromatized Mg Kα x-ray as the excitation source. As shown in figure 2, the Nb 3d and C 1s core-level regions were examined. The peak at 202.6 eV corresponds to Nb 3d 5/2 binding energy and the C 1s in NbC is found at 282.6 eV, which agree well with the reported value for NbC [10]. Two other C 1s peaks, at 284.4 and 286.1 eV, were also found, which could be attributed to a small amount of residual carbon and absorbed CO_2 on the powder surface, respectively.

The morphology of the as-prepared NbC sample was studied by transmission electron microscopy (TEM) using a Hitachi H-800 transmission electron microscope. Figure 3 shows TEM images of the NbC sample. It is seen from figures 3(a) and (b) that NbC nanorods are straight with diameters in the range 50–150 nm. The average length of the nanorods is about 5 μm. Some NbC nanoparticles can also be observed in the TEM images. The yield of NbC nanorods is estimated to be 40–60% in the product based on the TEM view. Figure 3(c)

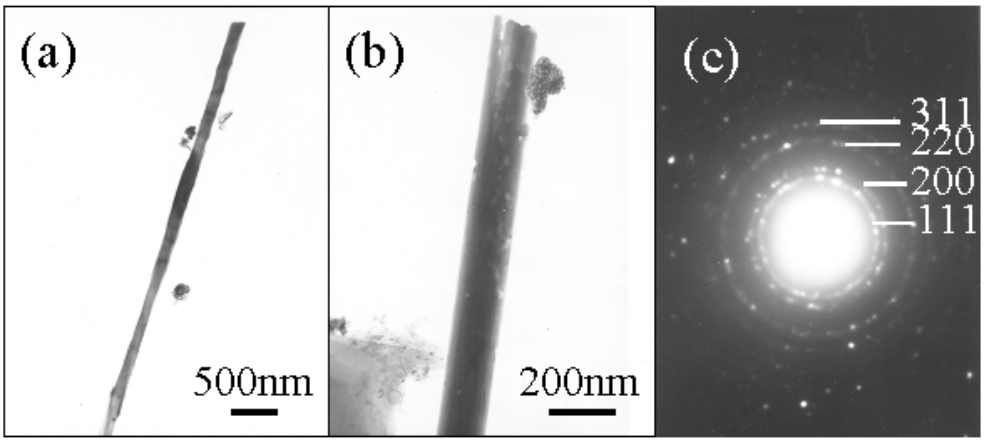

Figure 3. (a, b) TEM images of NbC nanorods with diameters in the range 50–150 nm and an average length of about 5 μm and (c) selected-area electron diffraction pattern of the NbC sample.

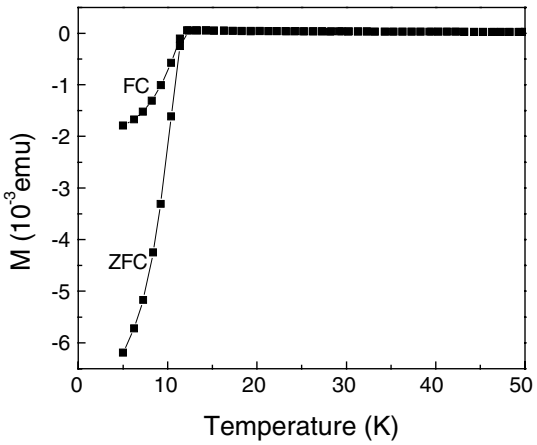

Figure 4. Temperature dependence of magnetization for the NbC sample. Data are shown for measurements under conditions of ZFC and FC at 50 Oe; $T_c = 12.3$ K.

shows the selected-area electron diffraction pattern of the as-prepared NbC sample, which is consistent with the high crystallinity of the sample and reveals four clear diffraction rings in accordance with the (111), (200), (220) and (311) crystal planes of cubic NbC.

Magnetization on the as-prepared NbC sample was measured with a superconducting quantum interference device (SQUID) magnetometer (MPMSXL-5T, Quantum Design). Magnetization as a function of temperature is plotted in figure 4, under conditions of zero field cooling (ZFC) and field cooling (FC) at 50 Oe. The clear onset of a strong Meissner effect can be observed, which indicates that the superconducting transition temperature T_c for the NbC sample is 12.3 K. It is also found that the diamagnetism observed in the ZFC is obviously larger than that under FC conditions. This may result from the existence of flux trapping in the superconductor under FC, which causes the irreversibility of the magnetization curve [11]. This T_c is a little higher than that of stoichiometric bulk NbC ($T_c = 11.1$ K [1]), which may originate from the higher carbon stoichiometry (1.03) in the as-prepared NbC

sample. It has been reported that the T_c varies with carbon stoichiometry in NbCx [12], and a higher value of T_c corresponds to higher x for NbCx. The additional carbon above the equiatomic stoichiometry could increase the electronic density of states at the Fermi level and result in a higher T_c when compared with the ideal bulk stoichiometric NbC [13].

In our experiments, growth of the NbC nanorods may be attributed to the in-site formation mechanism. According to free energy calculations, our synthetic route is highly exothermic ($\Delta H^{\circ} = -2009.3\,\mathrm{kJ\,mol^{-1}}$). During the reaction process, with increase in temperature, C_4Cl_6 will be reduced by Na through dechlorination to free C_4 chains. $NbCl_5$ will also be reduced by Na to activated Nb particles. The co-reduction of $NbCl_5$ and C_4Cl_6 generates a great deal of heat and results in a high local temperature, which may be sufficient to melt the reaction by-product, NaCl (melting point, 801 °C). The free C_4 chains in the molten NaCl may join with each other to produce long carbon chain clusters. The newly formed activated Nb particles disperse in the molten NaCl and diffuse easily to the surface of carbon chain clusters, where Nb reacts with carbon in-site to form TaC nanorods. Meanwhile, the vaporization of $NbCl_5$ (boiling point, 254 °C) and C_4Cl_6 (boiling point, 215 °C) during the reaction process can bring about high pressure in the autoclave (according to the ideal gas law, the highest pressure can be about 3.6 MPa), which may favour the formation of NbC nanorods.

The effects of reaction temperature and time on the formation of NbC nanorods were investigated. It is found that the reaction temperature plays a key role in the formation of NbC nanorods. If the temperature is below 400 °C, the main product is amorphous carbon and metal Nb. Heating at 550 °C could produce NbC, but the product is mainly nanoparticles, and little NbC nanorods can be found. Temperatures higher than 700 °C cause the diameters of the NbC nanorods to increase obviously. The optimum temperature for NbC nanorods is about 600 °C. At 600 °C, the reaction time must be longer than 8 h to ensure the completion of the reduction and growth process of the NbC nanorods.

4. Conclusions

In summary, NbC nanorods were successfully synthesized at 600 °C in an autoclave by co-reduction of $NbCl_5$ and C_4Cl_6 with Na. The atomic ratio of C to Nb was determined to be 1.03 : 1.0 from the calculation of the lattice parameter of NbC. The superconducting transition temperature of the as-prepared NbC nanorods was found to be 12.3 K.

Acknowledgments

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