

PREPARATION AND MORPHOLOGY OF NIOBIUM OXIDE FIBERS

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Abstract. Niobium oxide/poly(vinyl acetate) composite nanofibers have been prepared by electrospinning method. Pure ceramic niobium oxide fibers were obtained by high temperature calcination of the organic-inorganic composite nanofibers. The materials have been characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and infra-red (IR) spectroscopy. It has been observed that both the morphology and the crystallinity of the fibers depend on the calcination temperature.

1. INTRODUCTION

Niobium oxide has a wide variety of applications ranging from capacitors [1], to wave guides [2], and oxygen sensors [3]. It is an important component in many alloys improving corrosion resistance [4]. Importantly, niobium oxide is used as high refractive index layers in optical interference filters [5]. These consist of a multilayer stack of high and low refractive index materials. In recent years, niobium oxide has attracted considerable interest as a promising material for electrochromic devices [6-8]. Transparent electrochromic device materials are receiving growing interest because of applications such as energy efficient windows and switchable mirrors in automobiles [9]. Niobium oxide also attracts attention due to its presence as a constituent of different compound oxides such as lead, barium and lithium niobate, which are used in optical waveguides and modulators [10,11].

Most of the previous work in synthesis of niobium oxide has focused on the preparation of niobium oxide in the form of films by different methods such as thermal evaporation [12], anodization [13], sputtering [14] and sol-gel processes [15]. In a large

number of possible applications it may be advantageous to prepare particles of controlled dimensionality. In this work, we have prepared niobium oxide in the form of nanofibres by an electrospinning method using niobium oxide sol combined with poly(vinyl acetate) (PVAC). This technique [16-18] is attractive since it enables fibers to be prepared with nanometer dimensionality, high aspect ratio and a high surface area to volume ratio.

2. EXPERIMENTAL

The PVAC (14 wt%) solution was prepared using acetone as solvent. The niobium oxide (50 wt%) sol solution was obtained from a niobium ethoxide molecular precursor based on conventional sol-gel procedures [19]. Briefly, 2.0 g niobium ethoxide was dissolved in 2.0 g ethanol and 0.006 g acetic acid added, whilst stirring. A clear pale yellow solution was obtained after stirring for 2 h. Addition of acetic acid was important not only as a hydrolysis/condensation catalyst but also because it reacts with the alkoxide forming reasonable complexes which effectively retard hydrolysis during sol synthesis so preventing precipitation. The electrospinning solu-

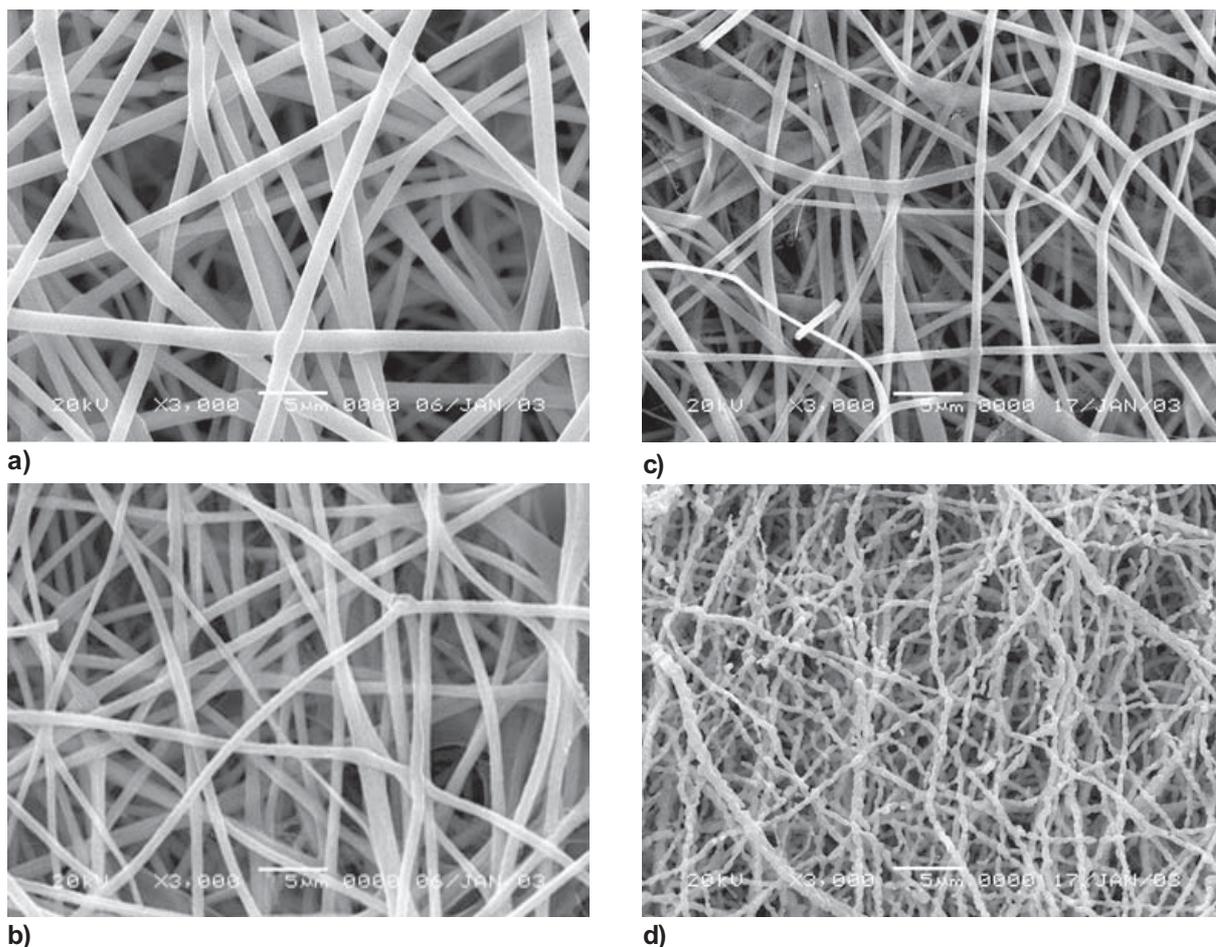


Fig. 1. SEM images of the 50 wt% niobium oxide/PVAC fibers: (a) as-synthesized material; (b) calcined at 500 °C; (c) calcined at 700 °C; (d) calcined at 1000 °C.

tion was prepared by mixing the PVAC (14 wt%) solution with niobium oxide sol solution (1.5 : 0.8 by wt. ratio) under stirring for 5 h. The PVAC/niobium oxide fibers were prepared by subjecting the solution to a high electrical potential. The solution was placed in a hypodermic syringe at a fixed distance (15–17 cm) from a metal cathode electrode such as aluminum foil. The positive (anode) terminal of a variable high voltage transformer capable of delivering 30 kV was attached to a copper wire inserted into the polymer solution in the hypodermic syringe, the negative terminal was attached to the aluminum foil target electrode. The tip of the syringe was placed at an angle 15° to the horizontal in order to maintain a uniform flow of the solution. When the voltage applied between the anode and cathode reached 15 kV, dry, centimeter long fibers accumulate on the surface of the cathode resulting in a non-woven mesh of nano to micron diameter organic-inorganic composite fibers. The as-prepared com-

posite fibers were subjected to high temperature calcination to obtain pure niobium oxide fibers. Scanning electron microscopy (SEM) images of the products were collected using a JOEL GSM-5900 scanning electron microscope. Atomic force microscopy (AFM) images were recorded in noncontact mode with a XE-100 (PSIA, Korea) atomic force microscope. Powder X-ray diffraction (XRD) patterns of the fibers were obtained with a Shimadzu Lab-X 600 X-ray diffractometer using Cu-K α irradiation. The infrared spectra (IR) were recorded using a Bio-Rad Win FT-IR spectrophotometer.

3. RESULTS AND DISCUSSION

SEM photographs in Fig. 1 summarizes results on material prepared using 50 wt% of Nb₂O₅ in as-prepared and calcined form. These micrographs show the general morphology of niobium oxide fibers. It can be seen that the surface of the fibers is smooth

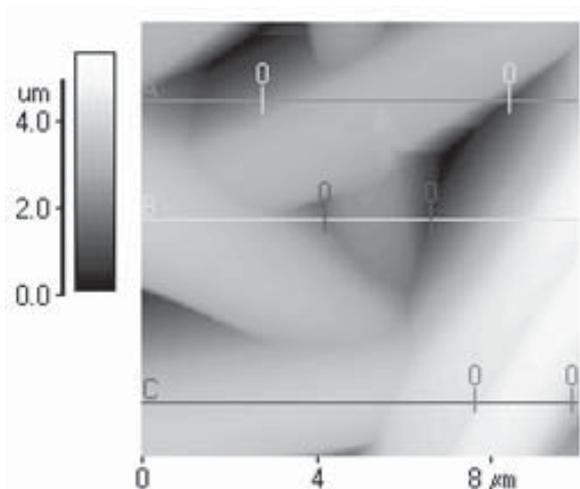


Fig. 2. AFM image of 50 wt% niobium oxide/PVAC composite fibers.

and uniform. The fibers obtained after calcination at 500 °C exhibit shrinkages and diameters are reduced by about 50% due to the decomposition of the PVAC component. After calcination at 700 °C, any shrinkage is minimal, but the fibers can be seen to have porous surfaces. It is thought that this is due to the complete decomposition of PVAC components. The fiber structure is retained with polymorphic structures even at higher calcination temperature (1000 °C). However, it can be seen that the material surface is now much smoother and the particle morphology has changed to one where the fibers appear to consist of linked particles or crystallites. The fibrous nature of the niobium oxide is further confirmed by the AFM studies. Data is shown in Fig. 2. The AFM image indicates that the fibers have cylindrical-like geometries.

The fibers were also characterized by XRD. Fig. 3 shows diffractograms of the 50 wt% Nb₂O₅ samples as a function of calcination temperature. The as-synthesized PVAC/niobium oxide composite fibers are essentially x-ray amorphous (i.e. any crystallinity is over dimensions too small to coherently scatter x-rays) in the as-synthesized form. Following calcination at 500 °C well-defined features appear due to the crystallization of niobium oxide. The structural chemistry of niobium oxide is complex and several stoichiometric and nonstoichiometric phases exist and coexist [20]. The diffractogram of the material calcined at 500 °C has a major phase described by a monoclinic structure of Nb₂O₅ (JCPDS data file set 27-1312). There

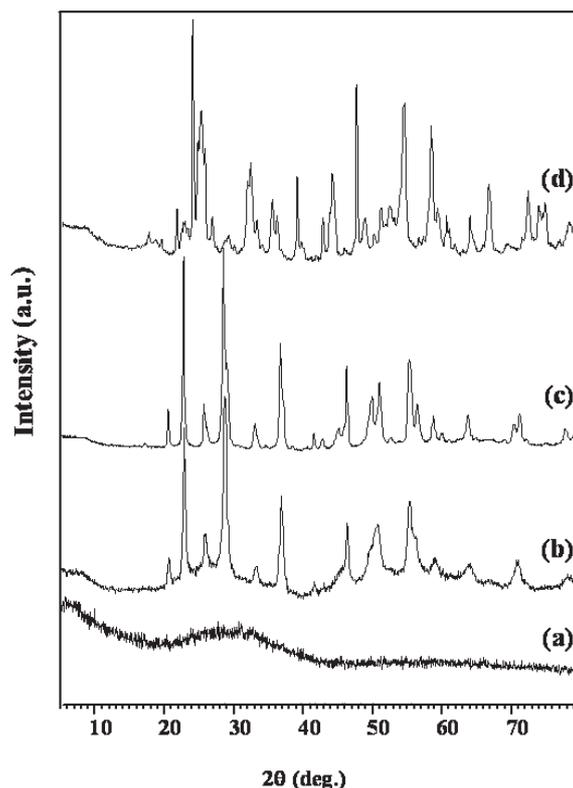


Fig. 3. X-ray diffraction patterns of the 50 wt% niobium oxide fibers: (a) as-synthesized material; (b) calcined at 500 °C; (c) calcined at 700 °C; (d) calcined at 1000 °C.

are also weaker features not assignable to this phase around 21, 26, 33, 42 degrees 2θ. These are more difficult to assign but are likely to be due to an NbO₂ phase with tetragonal structure [20]. Following calcination at 700 °C the features become sharper and well defined although position and relative intensity do not alter significantly. This would suggest a higher degree of crystallinity and larger particle sizes.

The higher resolution afforded by this heat treatment allows us to confirm the assignment of the major phase. Although, niobium oxide is well known to have a number of different modifications this basic structure consists of an anion defective unit cell with six or seven oxygen atoms coordinated to the niobium atom [21]. It is also apparent from this diffractogram that the lower intensity features can not be assigned to one single phase. The data here is fitted to reveal the presence of an NbO₂ (JCPDS 85-0379) and another Nb₂O₅ phase (JCPDS 15-0493). As was suggested by the dramatic change of morphology observed after calcination at 1000 °C, there is a very sudden change in crystal structure also observed. Finally, the sample calcined at

1000 °C crystallizes in a new monoclinic system (JCPDS 15-0493) [22, 23]. It is also likely that some NbO₂ remains as a minor phase. However, it appears to have formed a new structure. This is rutile-like (JCPDS 08-0215) consistent with the simplification of the NbO₂ structure at high temperature that is well known [24].

The formation of pure niobium oxide fiber is further supported by IR spectra. In the as-synthesized form, strong bands are absorbed between 1000 and 2000 cm⁻¹ which can be assigned to bend and stretching frequencies of the PVAC. After calcination at 700 °C all these strong features are removed. No sign of adsorbed water or hydroxy, carbonate or hydrocarbon impurity can be observed. Instead, the only significant features are Nb-O bands at low wave numbers (500-1000 cm⁻¹) [8].

4. CONCLUSIONS

In conclusion, niobium oxide fibers have been successfully prepared using an electrospinning method. The morphology and crystallinity of the fibers were determined by the calcination temperature. The diameter of the fibers was determined by the inorganic content of the precursor material.

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