Fabrication of Te Micro-Tubes and TeO_2 Micro-Wires From Powders by Cold Spray

Dr. Mohammed S. Hamza
Materials Engineering Department, University of Technology/Baghdad
Dr. Alaa A. Abdul alhameed
Materials Engineering Department, University of Technology/Baghdad
Email:adr.aLaa@yahoo.com
Sinan salman Hamdi
Materials Engineering Department, University of Technology/Baghdad

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ABSTRACT

A one-dimensional micro-structured tellurium (Te) microtube and tellurium dioxide (TeO_2) microwire were successfully prepared by cold spray process in large scale by a facile approach of sprayed (Te), (TeO_2) dry powder in an inert atmosphere using helium gas onto glass substrate. Tellurium and Tellurium dioxide were sprayed by heating carrier gas at (200,300,400 and 500 °C) and 2 MPa pressure on the glass substrate (100°C). Heat treatment was done under vacuum (0.0133mbar) for (30 min) at (200°C) for Te and (400°C) for TeO_2.The prepared microtubes and microwire was examined by XRD, AFM and SEM. The result showed that the obtained microtubes and microwire were highly pure.

Keywords: Cold Spray Process, Microtube, Tellurium, Tellurium Dioxide, Microwire.

تصنيع أنابيب التيليريوم المايكروية وأسلاك أوكسيد التيليريوم المايكروية من المساحيق بواسطة الرش على البارد

الخلاصة

تم في هذا البحث تحضير تراكيب مايكروية أحادية البعد من التيليريوم (Te) كأنابيب مايكروية و أوكسيد التيليريوم (TeO_2) كأسلاك مايكروية بنجاح بتقنية الرش على البارد بمدىواسعٍ عن طريق الرش الجاف للمساحيق (TeO_2 ،Te) في جو خامل باستعمال غاز الهيليوم على قواعد من شرائح زجاجيةِ. تم رش التليريوم وثاني أوكسيد التليريوم بتسخين الغازِ الحامل عند درجة 500 (200,300,400, °C) وضغط 2 MPa على قواعد زجاجيةِ بدرجة (100°C). تم أجراء المعاملة الحرارية باستخدام فرن تلدين بالفراغ (0.0133 mbar) ولمدة (30 min) وبدرجات حرارة (200oC) لعنصر (Te) بينما استعمل درجة حرارة (400°C) لمادة (TeO_2). الأنابيب االمايكروية المصنعة و الأسلاك المايكروية المصنعة تم فحصها بواسطة XRD وFM وSEM. بينت النتائج أن هذه الأنابيب الرقيقة و الأسلاك الرقيقة كانت ذات نقاوة عالية.

INTRODUCTION

The discovery of carbon nano-tubes (CNTs) in 1991 by Iijima [1], which was attracted wide attention to investigating one-dimensional nanostructures materials. One-dimensional (1D) nanostructures, such as nanowires, nanorods, nanobelts, and nanotubes. Nanostructured materials in general, tend to have properties, which may differ substantially from those observed from normal structure in bulk materials [1]. Much attention has recently been focused on the synthesis of nanowires, microrods and microtubes due to their potential in many applications. Among these 1D micro and nano structured materials, (Te, Se) represent a class of interesting elements, in which anisotropic crystal structure gives a strong tendency toward 1D growth [2]. Trigonal tellurium (t-Te), as well as trigonal selenium (t-Se) and Se-Te alloys, have a highly anisotropic crystal structure, consisting of helical chains of covalently bound atoms, which are in turn bound together through van der Waals interactions into a hexagonal lattice [2, 3]. This inherent anisotropy makes these materials ideal candidates for generating 1D nanostructures even though without the need for templates or surfactants to induce their anisotropic growth. Elemental tellurium is a narrow band gap (direct band gap energy of 0.35 eV) semiconducting material [2, 3]. As a p-type semiconductor, trigonal tellurium exhibits many useful and interesting properties, for example, photoconductivity, and catalytic activity toward some reactions, high piezoelectricity, thermoelectricity, and nonlinear optical responses [2]. In addition, (Te) can react readily with the other elements to generate many functional materials such as ZnTe, CdTe, Nd_3Te_4, and Bi_2Te_3.1D tellurium nanocrystals, including Te nanotubes, nanorods, nanowires, and nanobelts, have been synthesized through different routes, such as refluxing process, solvothermal or hydrothermal methods, microwave-assisted method, biomolecule- assisted routes, chemical (physical) vapor deposition, visible-light-assisted technique and thermal evaporation method [2], while the crystal structure of TeO_2 1-D tellurium oxide nanocrystals were tetragonal, Tellurium dioxide (TeO_2), a versatile wide band gap semiconductor material, is a significant acousto-optical and electro-optical material with a variety of desirable characteristics including elastic behavior, a high refractive index, and good optical quality [4]. Accordingly, TeO_2 has wide applications in active devices such as deflectors, modulators, dosimeters, optical storage material, laser devices, and gas sensors [5]. TeO_2 nanocrystals have been synthesized by a range of techniques such as thermal evaporation of Te powders, laser ablation of Te, and thermal oxidation of Te in a flow of O_2 with no use of catalyst, Huriet et al [5].

The aim of this work is preparation of tellurium (Te) micro-tubes and tellurium dioxide (TeO_2) microwires from powders onto glass substrates by using the cold spray process is the newest member of the thermal spray family.

EXPERIMENTAL PART

Materials and Equipment

The materials and substrates used in this work, are shown in Table 1.

The substrate used is a microscope glass slide (25× 70 × 1mm) which was cut into small pieces(1×2×1mm) and degreased in ethanol, washed with distilled water(non ionized) followed by drying in air. The substrates were placed and fixed on the electric heater with temperature control.

Cold spray Apparatus

The cold spray apparatus was designed and built by the author as shown in Figure 1.the main parts of the apparatus are:-

1. Powder feeder.
2. Two electric valves.
3. Heater. (To heat the carrier gas).
4. De Laval-type nozzle.
5. Control module.
6. Gas regulator.

The operating parameters are shown in Table(2).

Spray Process

After substrates are prepared and fixed onto electric heater, the powder of Tellurium and Tellurium oxide was sprayed in a powders under inert atmosphere (Helium gas) at a feed rate (0.2 g/s) and temperature (300°C) onto glass substrate at substrate temperature (100°C) and at pressure of (2 MPa). The nozzle is kept at a short distance (50 mm) from the substrate, and subsequently develops a nanocrystalline layer.

Heat Treatment

The samples were put in a vacuum furnace (IVOCLAR type Programat X1,Germany) at the college of Dentistry/the University of Baghdad , and were annealed to (200°C) for Te samples, and (400°C) for TeO_2 samples for 30 min at a rate of 30 °C/min under high vacuum of (0.0133 mbar).

Characterization of Structure

X-Ray Diffraction (XRD) of type (XRD 6000 SHIMADZU, Japan) at the Nanotechnology and Advanced Materials Research Center / the University of Technology was used to characterize the Te and TeO_2 samples. An X-ray diffraction (XRD) pattern of the specimen was recorded on a Rigaku D/max-rc (12 kW) diffractometer operated at 40 kV voltage and 30 mA current with filtered wave length (0.154060 °A) $Cu_{K\alpha}$ radiation. The X-ray diffraction data were collected at a scanning rate of 0.02 degrees per second in 2θ ranging from 10 to 80°. Atomic Force Microscopy (AFM) of type (CSPM-AA3000, Angstrom Advanced Inc. USA) at the Nanotechnology and Advanced Materials Research Center / the University of Technology, was used to characterize the Te and TeO_2, and give Information on the structural morphology of the Te and TeO_2 nanotubes that can be revealed by AFM. Scanning electron microscopy exam to the samples was done using SEM type (S-4160 Hitachi, Japan) at University of Tehran/Iran.

Results and Discussion

Figures (3) and (4) show XRD patterns for Te and TeO_2 deposited onto glass substrate in the 2θ range (10-80°). Figure (3) represents the XRD pattern of the Tellurium micro-tubes which indicated that there are three strong and sharp reflection peaks (100), (101), and (102) at 23.043°, 27.562°, and 38.26° respectively. The (100) peak was attributed to t-Te micro or nano-tubes. The hexagonal structure was matched with the standards peaks (ASTM - Card file No. 36-1452) in Table 3, with lattice constants ($a = 0.4519$ nm and $c = 0.6025$ nm). The peaks (111), (003), (202) are characteristics of a hexagonal cross section of micro or nano-tube, which were in agreement with other published research [6]. Figuer (4) shows the XRD pattern for TeO_2 microwires. All the reflection peaks in the patterns match very well to those of tetragonal TeO_2 (ASTM card No. 42-1365) which are explained in Table (4), with lattice constants (a = 0.481 nm and c = 0.761 nm). The strong diffraction peak due to the reflection from the (102) crystal plane reveals that (α-TeO_2) nano-wires have grown with a strong preferred orientation, and also the peaks at (200), (212) indicated crystalline simple tetragonal TeO_2 which were in agreement with other published results [7], [8].

Figures (5) and (6) show the three dimensional (3D) image of Te microtubes and TeO_2 microwires using AFM. The Tellurium microtubes were found to have an average diameter of (107.86 nm). This is in agreement with SEM images, which was formed on a glass substrate. The Tellurium oxide micro-wires have an average diameter of (82.60 nm). This is in agreement with our findings using SEM where the diameter of TeO_2 MWs was formed on a glass substrate.

Figure (7 (a, b)) show images of SEM for prepared Te micro-tubes and TeO_2 micro-wires. It is clear from these images the Te microtubes and TeO_2 microwires have different dimensions of different temperature parameter onto glass substrate after annealing, with other parameters fixed. The SEM images show the diameter of the micro-tubes and micro-wires changed after annealing. In general the diameter and the length of the Te MTs and TeO_2 MWs increased with increasing the temperature of the process, because it is likely that the effect of the collision of Te andTeO_2 atoms with helium atoms at low temperature could reduce the amount of Te and TeO_2 atoms available for the growth. So, there were not enough atoms (under saturation) for the growth of micro-tubes and micro-wires [9, 10]. As heating proceeded, the groove-like microstructures gradually developed into micro-tubes or micro-wires which often exhibited unclosed segments at the ends of Te or nano-wires of TeO_2 [9, 10]. The experimental results observed that the optimum growth was obtained at (500°C) after annealing.

CONCLUSIONS

The following conclusions can be obtained from this study:

Tellurium micro-tubes (Te MTs) crystals with a hexagonal cross-section, and Tellurium oxide micro-wires (TeO_2 MWs) with a tetragonal structure were successfully synthesized by cold spray process. The XRD results of the Te microtubes crystals were very pure as only Te metal, while TeO_2 microwires are consistent with the structure of the tetragonal α-TeO_2 phase, and no template or catalyst was used. Tellurium micro-tubes crystals with a hexagonal cross-section and Tellurium oxide micro-wires with a tetragonal structure were successfully synthesized by cold spray process. The diameter and the length of the Te microtubes and TeO_2 microwires increased with increasing temperature of the process.

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Table (1) Powder were used in this work.

Chemical formula	*Purity %*	*Grain size µm*	*Melting point °C*	*origin*	*substrate*
Te	*99.9*	*23.913*	*449.6*	*Fluka co.*	*glass*
TeO_2	*99.9*	*21.210*	*733*	*Fluka co.*	*glass*

Table (2) Gas-jet parameters for cold spray process.

Parameters	*Range*
Operation gases	Oxygen (O_2) or Helium (He).
Gas pressure Mpa	2
Gas temperature °C	200,300,400,500
Spray distance mm	50
Power consumption(for heat gas) Kw	3
Powder feed rate g/s	0.2

Table (3) XRD results for the Te Micro-tubes.

$2\theta_{ASTM}$	$2\theta_M$	I_{ASTM}	I_M	*hkl*
23.043	23.1	16	21	100
27.562	28.2	100	100	101
38.26	38.5	36	40	102
40.445	40.01	25	23	110
43.331	43.47	8	---	111
45.900	45.3	9	4	003
49.629	50.01	14	15	201
56.876	56. 0	8	21	202

Table (4) XRD results for the TeO_2 Micro-wires.

$2\theta_{ASTM}$	$2\theta_M$	I_{ASTM}	I_M	*hkl*
21.845	21.11	8	21	101
26.185	25.6	95	65	110
28.738	27.9	14	15	111
29.933	28.4	100	100	102
37.358	37	15	6	200
48.585	48.3	47	28	212
55.274	55.1	19	14	114

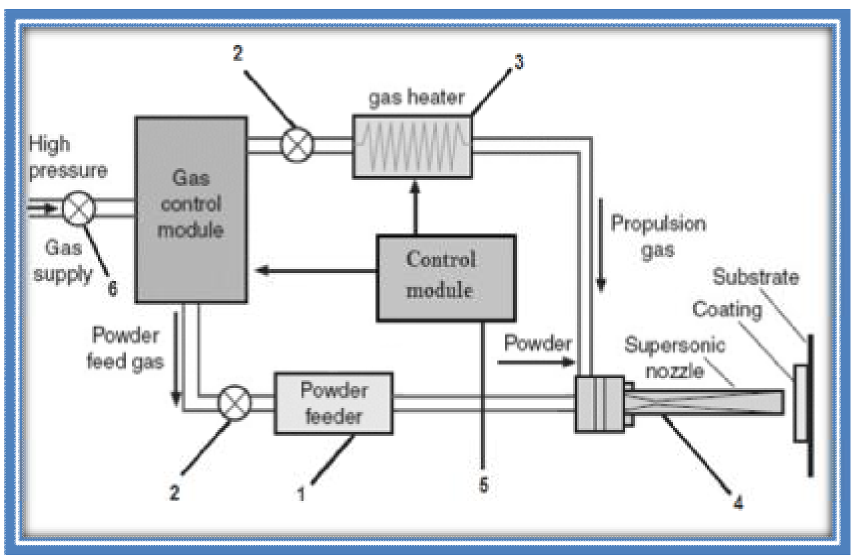


Figure.(1) Schematic diagram of cold spray system: 1. Powder feeder; 2.Two electric valves; 3. Heater. (To heat the carrier gas); 4. De Laval-type nozzle; 5. **Control module; 6. Gas regulator**.

Figure.(2) Images explain the interior and external parts of the apparatus.

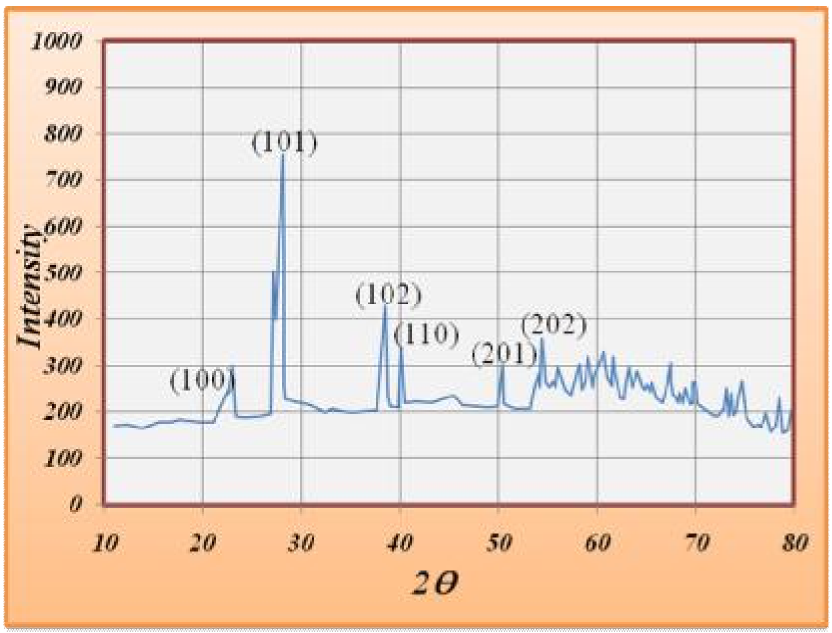


Figure.(3) The XRD patterns of the Te microtubes.

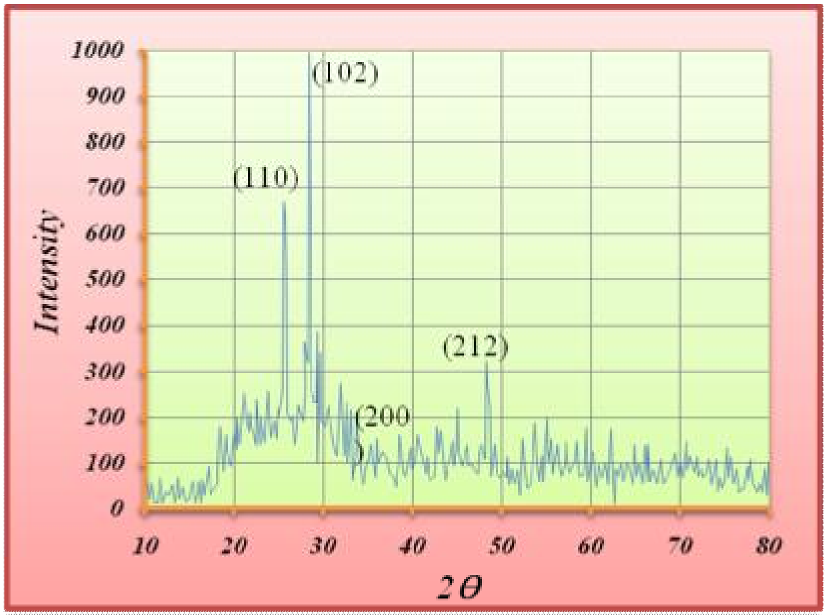


Figure.(4) The XRD patterns of the TeO_2 microwires.

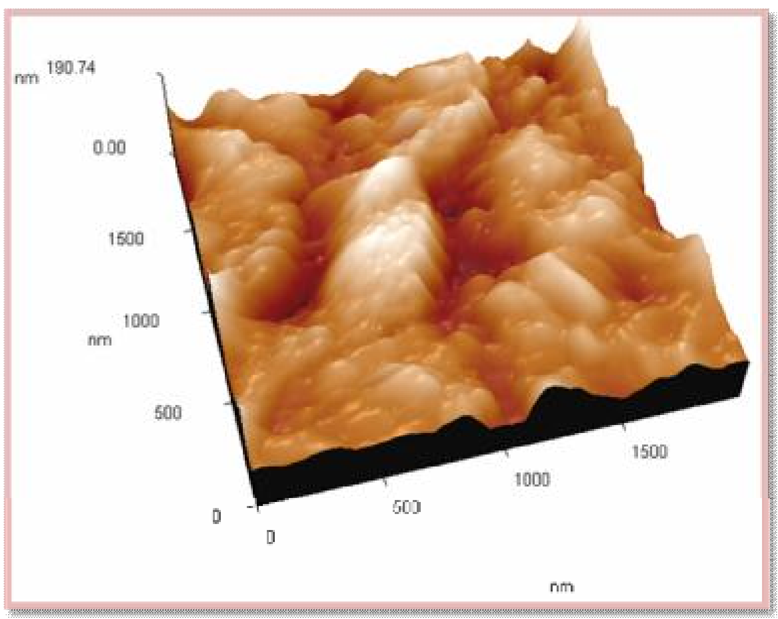


Figure.(5) AFM image of Te microtubes onto glass substrate at 200°C.

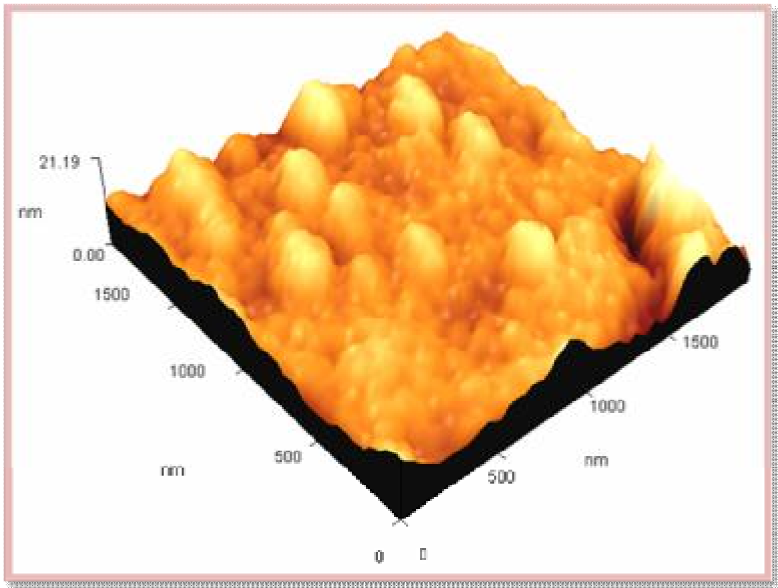
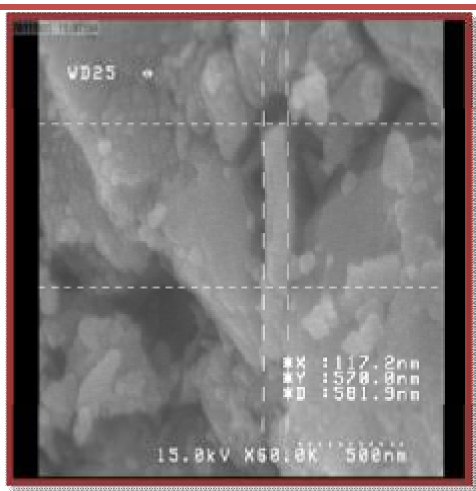
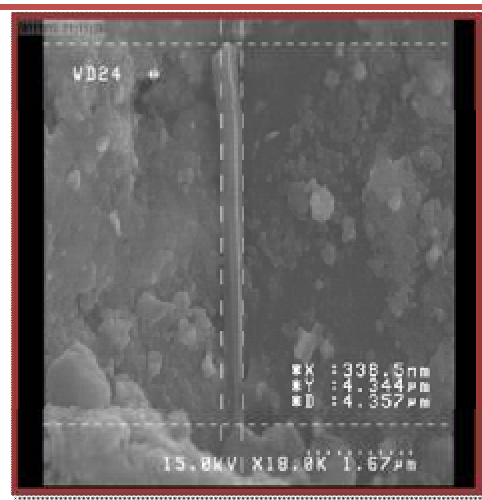
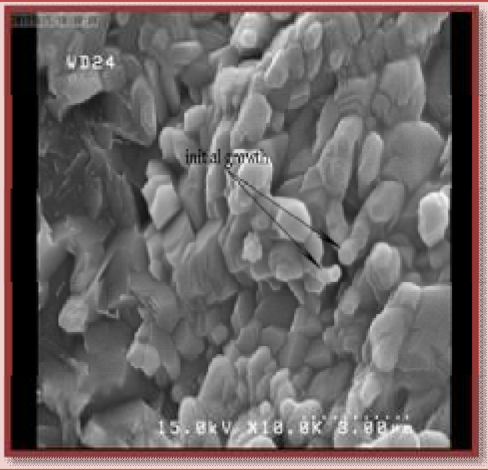
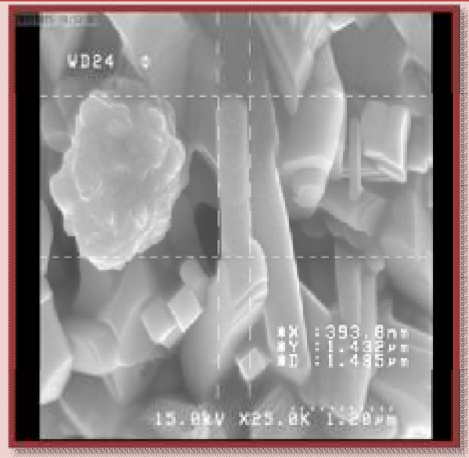


Figure.(6) AFM images of TeO_2 microtubes onto glass substrate at 200°C.

	
200°C (initial growth)	500°C (complete growth)
(a)Te microtubes onto glass substrate.	



200°C (nucleation)



500°C (longitudinal growth)

(b) TeO_2 microwires onto glass substrate.

Figure.(7) SEM images of Te microtubes and TeO_2 microwires onto glass substrate.