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(54) **SOLID CARBON PRODUCTS COMPRISING CARBON NANOTUBES AND METHODS OF FORMING SAME**

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(Continued)

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

1,478,730 A 12/1923 Brownlee  
1,735,925 A 11/1929 Jaeger

(Continued)

**FOREIGN PATENT DOCUMENTS**

EP 0945402 A1 9/1999  
EP 2186931 A1 5/2010

(Continued)

**OTHER PUBLICATIONS**

Bakshi ("Carbon nanotube reinforced metal matrix composites—a review." Intern Mater Rev, 55(1), pp. 41-64, pub 2010).\*

(Continued)

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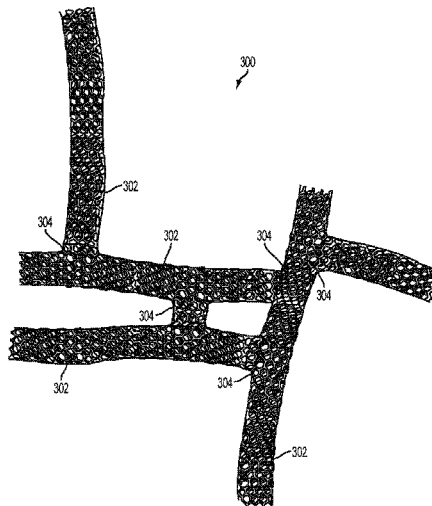
(74) *Attorney, Agent, or Firm* — TraskBritt P.C.

(57)

**ABSTRACT**

Methods of forming solid carbon products include disposing a plurality of nanotubes in a press, and applying heat to the plurality of carbon nanotubes to form the solid carbon product. Further processing may include sintering the solid carbon product to form a plurality of covalently bonded carbon nanotubes. The solid carbon product includes a plurality of voids between the carbon nanotubes having a median minimum dimension of less than about 100 nm. Some methods include compressing a material comprising carbon nanotubes, heating the compressed material in a non-reactive environment to form covalent bonds between adjacent carbon nanotubes to form a sintered solid carbon product, and cooling the sintered solid carbon product to a temperature at which carbon of the carbon nanotubes do not oxidize prior to removing the resulting solid carbon product for further processing, shipping, or use.

**15 Claims, 10 Drawing Sheets**



(51)	<b>Int. Cl.</b>							
	<i>B82Y 30/00</i>	(2011.01)	5,531,424	A	7/1996	Whipp		
	<i>B82Y 40/00</i>	(2011.01)	5,569,635	A	10/1996	Moy et al.		
	<i>C04B 35/645</i>	(2006.01)	5,572,544	A	11/1996	Mathur et al.		
	<i>C04B 35/83</i>	(2006.01)	5,578,543	A	11/1996	Tennent et al.		
	<i>B29C 43/00</i>	(2006.01)	5,589,152	A	12/1996	Tennent et al.		
	<i>B29C 67/24</i>	(2006.01)	5,624,542	A	4/1997	Shen et al.		
	<i>C01B 31/00</i>	(2006.01)	5,641,466	A	6/1997	Ebbesen et al.		
	<i>B29K 105/00</i>	(2006.01)	5,648,056	A	7/1997	Tanaka		
			5,650,370	A	7/1997	Tennent et al.		
			5,691,054	A	11/1997	Tennent et al.		
			5,707,916	A	1/1998	Snyder et al.		
			5,726,116	A	3/1998	Moy et al.		
(52)	<b>U.S. Cl.</b>		5,747,161	A	5/1998	Iijima		
	CPC .....	<i>C01B 31/00</i> (2013.01); <i>C04B 35/645</i>	5,780,101	A	7/1998	Nolan et al.		
		(2013.01); <i>C04B 35/83</i> (2013.01); <i>H01B 1/04</i>	5,859,484	A	1/1999	Mannik et al.		
		(2013.01); <i>B29K 2105/0014</i> (2013.01); <i>B29K</i>	5,877,110	A	3/1999	Snyder et al.		
		<i>2105/251</i> (2013.01); <i>C01P 2006/40</i> (2013.01);	5,910,238	A	6/1999	Cable et al.		
		<i>C01P 2006/90</i> (2013.01); <i>C04B 2235/5288</i>	5,965,267	A	10/1999	Nolan et al.		
		(2013.01); <i>C04B 2235/604</i> (2013.01); <i>C04B</i>	5,997,832	A	12/1999	Lieber et al.		
		<i>2235/6021</i> (2013.01); <i>C04B 2235/656</i>	6,099,965	A	8/2000	Tennent et al.		
		(2013.01); <i>C04B 2235/658</i> (2013.01); <i>C04B</i>	6,159,892	A	12/2000	Moy et al.		
		<i>2235/6562</i> (2013.01); <i>C04B 2235/666</i>	6,183,714	B1	2/2001	Smalley et al.		
		(2013.01); <i>C04B 2235/77</i> (2013.01)	6,203,814	B1	3/2001	Fisher et al.		
(58)	<b>Field of Classification Search</b>		6,221,330	B1	4/2001	Moy et al.		
	USPC .....	252/500–519.1; 423/445 R–448, 445 B;	6,232,706	B1	5/2001	Dai et al.		
		977/742, 745, 842	6,239,057	B1	5/2001	Ichikawa et al.		
	See application file for complete search history.		6,261,532	B1	7/2001	Ono		
			6,262,129	B1	7/2001	Murray et al.		
			6,294,144	B1	9/2001	Moy et al.		
			6,333,016	B1	12/2001	Resasco et al.		
			6,346,189	B1	2/2002	Dai et al.		
(56)	<b>References Cited</b>		6,361,861	B2	3/2002	Gao		
	U.S. PATENT DOCUMENTS		6,375,917	B1	4/2002	Mandeville et al.		
	1,746,464	A 2/1930 Fischer et al.	6,413,487	B1	7/2002	Resasco et al.		
	1,964,744	A 7/1934 Odell	6,423,288	B2	7/2002	Mandeville et al.		
	2,404,869	A 7/1946 Sorrentino	6,426,442	B1	7/2002	Ichikawa et al.		
	2,429,980	A 11/1947 Allinson	6,465,813	B2	10/2002	Ihm		
	2,440,424	A 4/1948 Wiegand et al.	6,518,218	B1	2/2003	Sun et al.		
	2,745,973	A 5/1956 Rappaport	6,596,101	B2	7/2003	Weihls et al.		
	2,796,331	A 6/1957 Kauffman et al.	6,645,455	B2	11/2003	Margrave et al.		
	2,800,616	A 7/1957 Becker	6,683,783	B1	1/2004	Smalley et al.		
	2,811,653	A 10/1957 Moore	6,686,311	B2	2/2004	Sun et al.		
	2,819,414	A 1/1958 Sherwood et al.	6,692,717	B1	2/2004	Smalley et al.		
	2,837,666	A 6/1958 Linder	6,713,519	B2	3/2004	Wang et al.		
	2,976,433	A 3/1961 Rappaport et al.	6,749,827	B2	6/2004	Smalley et al.		
	3,094,634	A 6/1963 Rappaport	6,761,870	B1	7/2004	Smalley et al.		
	3,172,774	A 3/1965 Diefendorf	6,790,425	B1	9/2004	Smalley et al.		
	3,249,830	A 5/1966 Adany	6,800,369	B2	10/2004	Gimzewski et al.		
	3,378,345	A 4/1968 Bourdeau et al.	6,827,918	B2	12/2004	Margrave et al.		
	3,634,999	A 1/1972 Howard et al.	6,827,919	B1	12/2004	Moy et al.		
	3,714,474	A 1/1973 Hoff	6,835,330	B2	12/2004	Nishino et al.		
	3,846,478	A 11/1974 Cummins	6,835,366	B1	12/2004	Margrave et al.		
	3,905,748	A 9/1975 Cairo et al.	6,841,139	B2	1/2005	Margrave et al.		
	4,024,420	A 5/1977 Anthony et al.	6,843,843	B2	1/2005	Takahashi et al.		
	4,126,000	A 11/1978 Funk	6,855,301	B1	2/2005	Rich et al.		
	4,197,281	A 4/1980 Muenger	6,855,593	B2	2/2005	Andoh et al.		
	4,200,554	A 4/1980 Lauder	6,875,412	B2	4/2005	Margrave et al.		
	4,602,477	A 7/1986 Lucadamo	6,890,986	B2	5/2005	Pruett		
	4,628,143	A 12/1986 Brotz	6,899,945	B2	5/2005	Smalley et al.		
	4,663,230	A 5/1987 Tennent	6,905,544	B2	6/2005	Setoguchi et al.		
	4,710,483	A 12/1987 Burk et al.	6,913,740	B2	7/2005	Polverejan et al.		
	4,725,346	A 2/1988 Joshi	6,913,789	B2	7/2005	Smalley et al.		
	4,727,207	A 2/1988 Paparizos et al.	6,916,434	B2	7/2005	Nishino et al.		
	4,746,458	A 5/1988 Brotz	6,919,064	B2	7/2005	Resasco et al.		
	4,900,368	A 2/1990 Brotz	6,936,233	B2	8/2005	Smalley et al.		
	5,008,579	A 4/1991 Conley et al.	6,949,237	B2	9/2005	Smalley et al.		
	5,021,139	A 6/1991 Hartig et al.	6,955,800	B2	10/2005	Resasco et al.		
	5,082,505	A 1/1992 Cota et al.	6,960,389	B2	11/2005	Tennent et al.		
	5,122,332	A 6/1992 Russell	6,962,685	B2	11/2005	Sun		
	5,133,190	A 7/1992 Abdelmalek	6,979,709	B2	12/2005	Smalley et al.		
	5,149,584	A 9/1992 Baker et al.	6,986,876	B2	1/2006	Smalley et al.		
	5,187,030	A 2/1993 Firmin et al.	6,998,358	B2	2/2006	French et al.		
	5,260,621	A 11/1993 Little et al.	7,011,771	B2	3/2006	Gao et al.		
	5,396,141	A 3/1995 Jantz	7,041,620	B2	5/2006	Smalley et al.		
	5,413,866	A 5/1995 Baker et al.	7,045,108	B2	5/2006	Jiang et al.		
	5,456,897	A 10/1995 Moy et al.	7,048,999	B2	5/2006	Smalley et al.		
	5,526,374	A 6/1996 Uebber	7,052,668	B2	5/2006	Smalley et al.		
			7,067,098	B2	6/2006	Colbert et al.		
			7,071,406	B2	7/2006	Smalley et al.		

(56)

References Cited

U.S. PATENT DOCUMENTS

7,074,379 B2	7/2006	Moy et al.	7,883,995 B2	2/2011	Mitchell et al.
7,094,385 B2	8/2006	Beguín et al.	7,887,774 B2	2/2011	Strano et al.
7,094,386 B2	8/2006	Resasco et al.	7,888,543 B2	2/2011	Iaccino et al.
7,094,679 B1	8/2006	Li et al.	7,897,209 B2	3/2011	Shibuya et al.
7,097,820 B2	8/2006	Colbert et al.	7,901,654 B2	3/2011	Harutyunyan
7,105,596 B2	9/2006	Smalley et al.	7,906,095 B2	3/2011	Kawabata
7,125,534 B1	10/2006	Smalley et al.	7,919,065 B2	4/2011	Pedersen et al.
7,132,062 B1	11/2006	Howard	7,923,403 B2	4/2011	Ma et al.
7,135,159 B2	11/2006	Shaffer et al.	7,923,615 B2	4/2011	Silvy et al.
7,135,160 B2	11/2006	Yang et al.	7,932,419 B2	4/2011	Liu et al.
7,150,864 B1	12/2006	Smalley et al.	7,947,245 B2	5/2011	Tada et al.
7,157,068 B2	1/2007	Li et al.	7,951,351 B2	5/2011	Ma et al.
7,160,532 B2	1/2007	Liu et al.	7,964,174 B2	6/2011	Dubin et al.
7,169,329 B2	1/2007	Wong et al.	7,981,396 B2	7/2011	Harutyunyan
7,201,887 B2	4/2007	Smalley et al.	7,988,861 B2	8/2011	Pham-Huu et al.
7,204,970 B2	4/2007	Smalley et al.	7,993,594 B2	8/2011	Wei et al.
7,205,069 B2	4/2007	Smalley et al.	8,012,447 B2	9/2011	Harutyunyan et al.
7,212,147 B2	5/2007	Messano	8,017,282 B2	9/2011	Choi et al.
7,214,360 B2	5/2007	Chen et al.	8,017,892 B2	9/2011	Biris et al.
7,250,148 B2	7/2007	Yang et al.	8,038,908 B2	10/2011	Hirai et al.
7,270,795 B2	9/2007	Kawakami et al.	8,114,518 B2	2/2012	Hata et al.
7,291,318 B2	11/2007	Sakurabayashi et al.	8,138,384 B2	3/2012	Iaccino et al.
7,338,648 B2	3/2008	Harutyunyan et al.	8,173,096 B2	5/2012	Chang et al.
7,365,289 B2	4/2008	Wilkes et al.	8,178,049 B2	5/2012	Shiraki et al.
7,374,793 B2	5/2008	Furukawa et al.	8,226,902 B2	7/2012	Jang et al.
7,390,477 B2	6/2008	Smalley et al.	8,314,044 B2	11/2012	Jangbarwala
7,396,798 B2	7/2008	Ma et al.	2001/0009119 A1	7/2001	Murray et al.
7,408,186 B2	8/2008	Merkulov et al.	2002/0054849 A1	5/2002	Baker et al.
7,410,628 B2	8/2008	Bening et al.	2002/0102193 A1	8/2002	Smalley et al.
7,413,723 B2	8/2008	Niu et al.	2002/0102196 A1	8/2002	Smalley et al.
7,452,828 B2	11/2008	Hirakata et al.	2002/0127169 A1	9/2002	Smalley et al.
7,459,137 B2	12/2008	Tour et al.	2002/0127170 A1	9/2002	Hong et al.
7,459,138 B2	12/2008	Resasco et al.	2002/0172767 A1	11/2002	Grigorian et al.
7,473,873 B2	1/2009	Biris et al.	2003/0059364 A1	3/2003	Prilutskiy
7,510,695 B2	3/2009	Smalley et al.	2003/0147802 A1	8/2003	Smalley et al.
7,527,780 B2	5/2009	Margrave et al.	2004/0053440 A1	3/2004	Lai et al.
7,563,427 B2	7/2009	Wei et al.	2004/0070009 A1	4/2004	Resasco et al.
7,563,428 B2	7/2009	Resasco et al.	2004/0105807 A1	6/2004	Fan et al.
7,569,203 B2	8/2009	Fridman et al.	2004/0111968 A1	6/2004	Day et al.
7,572,426 B2	8/2009	Strano et al.	2004/0151654 A1	8/2004	Wei et al.
7,585,483 B2	9/2009	Edwin et al.	2004/0194705 A1	10/2004	Dai et al.
7,601,322 B2	10/2009	Huang	2004/0197260 A1	10/2004	Resasco et al.
7,611,579 B2	11/2009	Lashmore et al.	2004/0202603 A1	10/2004	Fischer et al.
7,615,204 B2	11/2009	Ajayan et al.	2004/0234445 A1	11/2004	Serp et al.
7,618,599 B2	11/2009	Kim et al.	2004/0247503 A1	12/2004	Hyeon
7,622,059 B2	11/2009	Bordere et al.	2004/0265212 A1	12/2004	Varadan et al.
7,632,569 B2	12/2009	Smalley et al.	2005/0002850 A1	1/2005	Niu et al.
7,645,933 B2	1/2010	Narkis et al.	2005/0002851 A1	1/2005	McElrath et al.
7,655,302 B2	2/2010	Smalley et al.	2005/0025695 A1	2/2005	Pradhan
7,670,510 B2	3/2010	Wong et al.	2005/0042162 A1	2/2005	Resasco et al.
7,700,065 B2	4/2010	Fujioka et al.	2005/0046322 A1	3/2005	Kim et al.
7,704,481 B2	4/2010	Higashi et al.	2005/0074392 A1	4/2005	Yang et al.
7,718,283 B2	5/2010	Raffaella et al.	2005/0079118 A1	4/2005	Maruyama et al.
7,719,265 B2	5/2010	Harutyunyan et al.	2005/0100499 A1	5/2005	Oya et al.
7,731,930 B2	6/2010	Taki et al.	2005/0176990 A1	8/2005	Coleman et al.
7,736,741 B2	6/2010	Maruyama et al.	2005/0244325 A1	11/2005	Nam et al.
7,740,825 B2	6/2010	Tohji et al.	2005/0276743 A1	12/2005	Lacombe et al.
7,749,477 B2	7/2010	Jiang et al.	2006/0013757 A1	1/2006	Edwin et al.
7,754,182 B2	7/2010	Jiang et al.	2006/0032330 A1	2/2006	Sato
7,772,447 B2	8/2010	Iaccino et al.	2006/0045837 A1	3/2006	Nishimura
7,780,939 B2	8/2010	Margrave et al.	2006/0078489 A1	4/2006	Harutyunyan et al.
7,785,558 B2	8/2010	Hikata	2006/0104884 A1	5/2006	Shaffer et al.
7,790,228 B2	9/2010	Suekane et al.	2006/0104886 A1	5/2006	Wilson
7,794,690 B2	9/2010	Abatzoglou et al.	2006/0104887 A1	5/2006	Fujioka et al.
7,794,797 B2	9/2010	Vasenkov	2006/0133990 A1	6/2006	Hyeon et al.
7,799,246 B2	9/2010	Bordere et al.	2006/0141346 A1	6/2006	Gordon et al.
7,811,542 B1	10/2010	McElrath et al.	2006/0165988 A1	7/2006	Chiang et al.
7,824,648 B2	11/2010	Jiang et al.	2006/0191835 A1	8/2006	Petrik et al.
7,837,968 B2	11/2010	Chang et al.	2006/0199770 A1	9/2006	Bianco et al.
7,838,843 B2	11/2010	Kawakami et al.	2006/0204426 A1	9/2006	Akins et al.
7,842,271 B2	11/2010	Petrik	2006/0225534 A1	10/2006	Swihart et al.
7,854,945 B2	12/2010	Fischer et al.	2006/0239890 A1	10/2006	Chang et al.
7,854,991 B2	12/2010	Hata et al.	2006/0239891 A1	10/2006	Niu et al.
7,858,648 B2	12/2010	Bianco et al.	2006/0245996 A1	11/2006	Xie et al.
7,871,591 B2	1/2011	Harutyunyan et al.	2006/0275956 A1	12/2006	Konesky
			2007/0003470 A1	1/2007	Smalley et al.
			2007/0020168 A1	1/2007	Asmussen et al.
			2007/0031320 A1	2/2007	Jiang et al.
			2007/0080605 A1	4/2007	Chandrashekhar et al.

(56)

References Cited

U.S. PATENT DOCUMENTS

2007/0116631 A1 5/2007 Li et al.  
 2007/0148962 A1 6/2007 Kauppinen et al.  
 2007/0149392 A1 6/2007 Ku et al.  
 2007/0183959 A1 8/2007 Charlier et al.  
 2007/0189953 A1 8/2007 Bai et al.  
 2007/0207318 A1 9/2007 Jin et al.  
 2007/0209093 A1 9/2007 Tohji et al.  
 2007/0253886 A1 11/2007 Abatzoglou et al.  
 2007/0264187 A1 11/2007 Harutyunyan et al.  
 2007/0266825 A1\* 11/2007 Ripley et al. .... B82Y 30/00  
 423/445 R  
 2007/0280876 A1 12/2007 Tour et al.  
 2007/0281087 A1 12/2007 Harutyunyan et al.  
 2008/0003170 A1 1/2008 Buchholz et al.  
 2008/0003182 A1 1/2008 Wilson et al.  
 2008/0008760 A1 1/2008 Bianco et al.  
 2008/0014654 A1 1/2008 Weisman et al.  
 2008/0095695 A1 4/2008 Shanov et al.  
 2008/0118426 A1 5/2008 Li et al.  
 2008/0160312 A1 7/2008 Furukawa et al.  
 2008/0169061 A1 7/2008 Tour et al.  
 2008/0176069 A1 7/2008 Ma et al.  
 2008/0182155 A1 7/2008 Choi et al.  
 2008/0193367 A1 8/2008 Kalck et al.  
 2008/0217588 A1 9/2008 Arnold et al.  
 2008/0226538 A1 9/2008 Rumpf et al.  
 2008/0233402 A1 9/2008 Carlson et al.  
 2008/0260618 A1 10/2008 Kawabata  
 2008/0274277 A1 11/2008 Rashidi et al.  
 2008/0279753 A1 11/2008 Harutyunyan  
 2008/0280136 A1 11/2008 Zachariah et al.  
 2008/0296537 A1 12/2008 Gordon et al.  
 2008/0299029 A1 12/2008 Grosboll et al.  
 2008/0305028 A1 12/2008 McKeigue et al.  
 2008/0305029 A1 12/2008 McKeigue et al.  
 2008/0305030 A1 12/2008 McKeigue et al.  
 2008/0318357 A1 12/2008 Raffaele et al.  
 2009/0001326 A1 1/2009 Sato et al.  
 2009/0004075 A1 1/2009 Chung et al.  
 2009/0011128 A1 1/2009 Oshima et al.  
 2009/0035569 A1 2/2009 Gonzalez Moral et al.  
 2009/0056802 A1 3/2009 Rabani  
 2009/0074634 A1 3/2009 Tada et al.  
 2009/0081454 A1 3/2009 Axmann et al.  
 2009/0087371 A1 4/2009 Jang et al.  
 2009/0087622 A1 4/2009 Busnaina et al.  
 2009/0124705 A1 5/2009 Meyer et al.  
 2009/0134363 A1 5/2009 Bordere et al.  
 2009/0136413 A1 5/2009 Li et al.  
 2009/0140215 A1 6/2009 Buchholz et al.  
 2009/0186223 A1 7/2009 Saito et al.  
 2009/0191352 A1 7/2009 DuFaux et al.  
 2009/0203519 A1 8/2009 Abatzoglou et al.  
 2009/0208388 A1 8/2009 McKeigue et al.  
 2009/0208708 A1 8/2009 Wei et al.  
 2009/0220392 A1 9/2009 McKeigue et al.  
 2009/0226704 A1 9/2009 Kauppinen et al.  
 2009/0257945 A1 10/2009 Biris et al.  
 2009/0286084 A1 11/2009 Tennent et al.  
 2009/0286675 A1 11/2009 Wei et al.  
 2009/0294753 A1 12/2009 Hauge et al.  
 2009/0297846 A1 12/2009 Hata et al.  
 2009/0297847 A1 12/2009 Kim et al.  
 2009/0301349 A1 12/2009 Afzali-Ardakani et al.  
 2010/0004468 A1 1/2010 Wong et al.  
 2010/0009204 A1 1/2010 Noguchi et al.  
 2010/0028735 A1 2/2010 Basset et al.  
 2010/0034725 A1 2/2010 Harutyunyan  
 2010/0062229 A1 3/2010 Hata et al.  
 2010/0065776 A1 3/2010 Han et al.  
 2010/0074811 A1 3/2010 McKeigue et al.  
 2010/0081568 A1 4/2010 Bedworth  
 2010/0104808 A1 4/2010 Fan et al.  
 2010/0129654 A1 5/2010 Jiang et al.  
 2010/0132259 A1 6/2010 Haque

2010/0132883 A1 6/2010 Burke et al.  
 2010/0150810 A1 6/2010 Yoshida et al.  
 2010/0158788 A1 6/2010 Kim et al.  
 2010/0159222 A1 6/2010 Hata et al.  
 2010/0160155 A1 6/2010 Liang  
 2010/0167053 A1 7/2010 Sung et al.  
 2010/0173037 A1 7/2010 Jiang et al.  
 2010/0173153 A1 7/2010 Hata et al.  
 2010/0196249 A1 8/2010 Hata et al.  
 2010/0196600 A1 8/2010 Shibuya et al.  
 2010/0209696 A1 8/2010 Seals et al.  
 2010/0213419 A1 8/2010 Jiang et al.  
 2010/0221173 A1 9/2010 Tennent et al.  
 2010/0222432 A1 9/2010 Hua  
 2010/0226848 A1 9/2010 Nakayama et al.  
 2010/0230642 A1 9/2010 Kim et al.  
 2010/0239489 A1 9/2010 Harutyunyan et al.  
 2010/0254860 A1 10/2010 Shiraki et al.  
 2010/0254886 A1 10/2010 McElrath et al.  
 2010/0260927 A1 10/2010 Gordon et al.  
 2010/0278717 A1 11/2010 Suzuki et al.  
 2010/0298125 A1 11/2010 Kim et al.  
 2010/0301278 A1 12/2010 Hirai et al.  
 2010/0303675 A1 12/2010 Suekane et al.  
 2010/0316556 A1 12/2010 Wei et al.  
 2010/0316562 A1 12/2010 Carruthers et al.  
 2010/0317790 A1 12/2010 Jang et al.  
 2010/0320437 A1 12/2010 Gordon et al.  
 2011/0008617 A1 1/2011 Hata et al.  
 2011/0014368 A1 1/2011 Vasenkov  
 2011/0020211 A1 1/2011 Jayatissa  
 2011/0024697 A1 2/2011 Biris et al.  
 2011/0027162 A1 2/2011 Steiner, III et al.  
 2011/0027163 A1 2/2011 Shinohara et al.  
 2011/0033367 A1 2/2011 Riehl et al.  
 2011/0039124 A1 2/2011 Ikeuchi et al.  
 2011/0053020 A1 3/2011 Norton et al.  
 2011/0053050 A1 3/2011 Lim et al.  
 2011/0060087 A1 3/2011 Noguchi et al.  
 2011/0085961 A1 4/2011 Noda et al.  
 2011/0110842 A1 5/2011 Haddon  
 2011/0117365 A1 5/2011 Hata et al.  
 2011/0120138 A1 5/2011 Gaiffi et al.  
 2011/0150746 A1 6/2011 Khodadadi et al.  
 2011/0155964 A1 6/2011 Arnold et al.  
 2011/0158892 A1 6/2011 Yamaki  
 2011/0171109 A1 7/2011 Petrik  
 2011/0174145 A1 7/2011 Ogrin et al.  
 2011/0206469 A1 8/2011 Furuyama et al.  
 2011/0298071 A9 12/2011 Spencer et al.  
 2012/0034150 A1 2/2012 Noyes  
 2012/0083408 A1 4/2012 Sato et al.  
 2012/0093676 A1\* 4/2012 Zoz ..... C22C 49/14  
 419/33  
 2012/0107610 A1 5/2012 Moravsky et al.  
 2012/0137664 A1 6/2012 Shawabkeh et al.  
 2012/0148476 A1 6/2012 Hata et al.  
 2013/0154438 A1 6/2013 Tan Xing Haw  
 2014/0021827 A1 1/2014 Noyes  
 2014/0141248 A1 5/2014 Noyes  
 2014/0348739 A1 11/2014 Denton et al.  
 2015/0059527 A1 3/2015 Noyes  
 2015/0059571 A1 3/2015 Denton et al.  
 2015/0064092 A1 3/2015 Noyes  
 2015/0064096 A1 3/2015 Noyes  
 2015/0064097 A1 3/2015 Noyes  
 2015/0071846 A1 3/2015 Noyes  
 2015/0071848 A1 3/2015 Denton et al.  
 2015/0078982 A1 3/2015 Noyes

FOREIGN PATENT DOCUMENTS

EP 2404869 A1 1/2012  
 JP 339339 B2 10/2002  
 JP 339339 B2 10/2002  
 JP 2004517789 A 6/2004  
 JP 2004360099 A 12/2004  
 JP 2005075725 A 3/2005  
 JP 2005532976 A 11/2005

(56)

## References Cited

## FOREIGN PATENT DOCUMENTS

JP	2007191840	A	8/2007
WO	0230816	A1	4/2002
WO	03018474	A1	3/2003
WO	2004048263	A1	6/2004
WO	2004096704	A3	11/2005
WO	2005103348	A1	11/2005
WO	2006003482	A3	8/2006
WO	2007086909	A3	11/2007
WO	2007139097	A1	12/2007
WO	2007126412	A3	6/2008
WO	2009011984	A1	1/2009
WO	2006130150	A3	4/2009
WO	2009122139	A1	10/2009
WO	2009145959	A1	12/2009
WO	2010047439	A1	4/2010
WO	2010087903	A1	8/2010
WO	2010120581	A1	10/2010
WO	2011009071	A1	1/2011
WO	2011020568	A1	2/2011
WO	2011029144	A1	3/2011
WO	2010146169	A3	4/2011
WO	2010124258	A3	5/2011
WO	2011053192	A2	5/2011
WO	2013090274		6/2013
WO	2013158155		10/2013
WO	2013158155	A1	10/2013
WO	2013158156		10/2013
WO	2013158156	A1	10/2013
WO	2013158157	A1	10/2013
WO	2013158158	A1	10/2013
WO	2013158159	A1	10/2013
WO	2013158160	A1	10/2013
WO	2013158161	A1	10/2013
WO	2013158438		10/2013
WO	2013158439		10/2013
WO	2013158441		10/2013
WO	2013162650	A1	10/2013
WO	2014011206		1/2014
WO	2014011206	A1	1/2014
WO	2014011631		1/2014
WO	2014011631	A1	1/2014
WO	2014085378	A1	6/2014

## OTHER PUBLICATIONS

Li ("Surface graphitization and mechanical properties of hot-pressed bulk carbon nanotubes compacted by spark plasma sintering." *Carbon*, 45, pp. 2636-2642, pub Aug. 23, 2007).\*

Kim ("Improvement of flexure strength and fracture toughness in alumina matrix composites reinforced with carbon nanotubes." *Materials Sc and Eng A*, 517, pp. 293-299, pub 2009).\*

San-Miguel ("Nanomaterials under high-pressure." *Chem Soc Rev*, 35, pp. 876-889, pub 2006).\*

Abatzoglou, Nicolas et al., "The use of catalytic reforming reactions for CO<sub>2</sub> sequestration as carbon nanotubes." *Proceedings of the 2006 IASME/WSEAS International Conference on Energy & Environmental Systems*, Chalkida, Greece, May 8-10, 2006 (pp. 21-26) (available at: [http://www.wseas.us/e-library/conferences/2006evia/papers/516-19\\_3.pdf](http://www.wseas.us/e-library/conferences/2006evia/papers/516-19_3.pdf)).

Abatzoglou, Nicolas et al., "Green Diesel from Fischer-Tropsch Synthesis: Challenges and Hurdles." *Proc. of the 3rd IASME/WSEAS Int. Conf. on Energy, Environment, Ecosystems and Sustainable Development*, Agios Nikolaos, Greece, Jul. 24-26, 2007, pp. 223-232.

Bogue, Robert, *Powering Tomorrow's Sensor: A Review of Technologies—Part 1*, *Sensor Review*, 2010, pp. 182-186, vol. 30, No. 3.

Cha, S. I., et al., "Mechanical and electrical properties of cross-linked carbon nanotubes," *Carbon* 46 (2008) 482-488, Elsevier, Ltd.

Cheng, H.M. et al., "Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocar-

bons," *Applied Physics Letters* 72:3282-3284, Jun. 22, 1998 (available at: [http://carbon.imr.ac.cn/file/journal/1998/98\\_APL\\_72\\_3282-ChengH M.pdf](http://carbon.imr.ac.cn/file/journal/1998/98_APL_72_3282-ChengH M.pdf)).

Chun, Changmin, and Ramanarayanan, Trikur A., "Metal Dusting Corrosion of Metals and Alloys," 2007.

Chung, U.C., and W.S. Chung, "Mechanism on Growth of Carbon Nanotubes Using CO—H<sub>2</sub> Gas Mixture," *Materials Science Forum* vols. 475-479 (2005) pp. 3551-3554.

Dai, et al., "Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide," *Chemical Physics Letters* 260 (1996) 471-475, Elsevier.

Dresselhaus et al., *Carbon Nanotubes Synthesis, Structure, Properties, and Applications*. 2001, pp. 1-9, Springer.

Garmirian, James Edwin, "Carbon Deposition in a Bosch Process Using a Cobalt and Nickel Catalyst," PhD Dissertation, Massachusetts Institute of Technology, Mar. 1980, pp. 14-185.

Grobert, Nicole, "Carbon nanotubes—becoming clean," *Materials Today*, vol. 10, No. 1-2, Jan.-Feb. 2007, Elsevier, pp. 28-35.

Hiraoka, Tatsuki, et al., "Synthesis of Single- and Double-Walled Carbon Nanotube Forests on Conducting Metal Foils," *J. Am. Chem. Soc.* 2006, 128, 13338-13339.

Holmes, et al.; *A Carbon Dioxide Reduction Unit Using Bosch Reaction and Expendable Catalyst Cartridges*; NASA; 1970; available at [https://archive.org/details/nasa\\_techdoc\\_19710002858](https://archive.org/details/nasa_techdoc_19710002858).

Huang, Z.P., et al., "Growth of highly oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition," *Applied Physics Letters* 73:3845-3847, Dec. 28, 1998.

"Inconel® alloy 693—Excellent Resistance to Metal Dusting and High Temperature Corrosion" *Special Metals Product Sheet*, 2005.

Kavetsky et al., Chapter 2, *Radioactive Materials, Ionizing Radiation Sources, and Radioluminescent Light Sources for Nuclear Batteries, Polymers, Phosphors, and Voltaics for Radioisotope Microbatteries*, Edited by Bower et al., 2002, pp. 39-59, CRC Press.

Krestinin, A. V., et al. "Kinetics of Growth of Carbon Fibers on an Iron Catalyst in Methane Pyrolysis: A Measurement Procedure with the Use of an Optical Microscope," *Kinetics and Catalysis*, 2008, vol. 49, No. 1, pp. 68-78.

Lal, Archit, "Effect of Gas Composition and Carbon Activity on the Growth of Carbon Nanotubes," *Masters Thesis*, University of Florida, 2003.

Manasse et al., *Schottky Barrier Betavoltaic Battery*, *IEEE Transactions on Nuclear Science*, vol. NS-23, No. 1, Feb. 1976, pp. 860-870.

Manning, Michael Patrick, "An Investigation of the Bosch Process," PhD Dissertation, Massachusetts Institute of Technology, Jan. 1976.

Muller-Lorenz and Grabke, *Coking by metal dusting of steels*, 1999, *Materials and Corrosion* 50, 614-621 (1999).

Nasibulin, Albert G., et al., "An essential role of CO<sub>2</sub> and H<sub>2</sub>O during single-walled CNT synthesis from carbon monoxide," *Chemical Physics Letters* 417 (2005) 179-184.

Nasibulin, Albert G., et al., "Correlation between catalyst particle and single-walled carbon nanotube diameters," *Carbon* 43 (2005) 2251-2257.

Noordin, Mohamad and Kong Yong Liew, "Synthesis of Alumina Nanofibers and Composites," in *Nanofibers*, pp. 405-418 (Ashok Kumar, ed., 2010) ISBN 978-953-7619-86-2 (available at <http://www.intechopen.com/books/nanofibers/synthesis-of-alumina-nanofibers-and-composites>).

Pender, Mark J., et al., "Molecular and polymeric precursors to boron carbide nanofibers, nanocylinders, and nanoporous ceramics," *Pure Appl. Chem.*, vol. 75, No. 9, pp. 1287-1294, 2003.

Ruckenstein, E. and H.Y. Wang, "Carbon Deposition and Catalytic Deactivation during CO<sub>2</sub> Reforming of CH<sub>4</sub> over Co<sup>0</sup>-Al<sub>2</sub>O<sub>3</sub> Catalysts," *Journal of Catalysis*, vol. 205, Issue 2, Jan. 25, 2002, pp. 289-293.

Sacco, Albert Jr., "An Investigation of the Reactions of Carbon Dioxide, Carbon Monoxide, Methane, Hydrogen, and Water over Iron, Iron Carbides, and Iron Oxides," PhD Dissertation, Massachusetts Institute of Technology, Jul. 1977, pp. 2, 15-234.

SAE 820875 *Utilization of Ruthenium and Ruthenium-Iron Alloys as Bosch Process Catalysts*. Jul. 19-21, 1982.

SAE 911451 *Optimization of Bosch Reaction*, Jul. 15-18, 1991.

(56)

**References Cited**

## OTHER PUBLICATIONS

Singh, Jasprit, *Semiconductor Devices, An Introduction*, 1994, pp. 86-93, 253-269.

Singh, Jasprit, *Semiconductor Devices, Basic Principles*, Chapter 6, *Semiconductor Junctions with Metals and Insulators*, 2001, pp. 224-244, Wiley.

Skulason, Egill, *Metallic and Semiconducting Properties of Carbon Nanotubes*, *Modern Physics*, Nov. 2005, slide presentation, 21 slides, available at <https://notendur.hi.is/egillsk/stuff/annad/Egiii.Slides2.pdf>, last visited Apr. 28, 2014.

Songsasen, Apisit and Paranchai Pairgreethaves, "Preparation of Carbon Nanotubes by Nickel Catalyzed Decomposition of Liquefied Petroleum Gas (LPG)," *Kasetsart J. (Nat. Sci.)* 35 : 354-359 (2001) (available at: [http://kasetsartjournal.ku.ac.th/kuj\\_files/2008/A0804251023348734.pdf](http://kasetsartjournal.ku.ac.th/kuj_files/2008/A0804251023348734.pdf)).

Szkalos, P., "Mechanisms and driving forces of metal dusting," *Materials and Corrosion*, 2003, 54, No. 10, pp. 752-762.

Tsai, Heng-Yi, et al., "A feasibility study of preparing carbon nanotubes by using a metal dusting process," *Diamond & Related Materials* 18 (2009) 324-327, Elsevier.

Tse, Anthony N., *Si—Au Schottky Barrier Nuclear Battery*, A Thesis submitted to the Faculty in partial fulfillment of the requirement for the degree of Doctor of Engineering, Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire, Nov. 1972, pp. 31-57.

Wilson, Richard B., "Fundamental Investigation of the Bosch Reaction," PhD Dissertation, Massachusetts Institute of Technology, Jul. 1977, pp. 12,23, 37, 43, 44, 62, 70, 80, 83-88, 98.

Wei, et al. "The mass production of carbon nanotubes using a nano-agglomerate fluidized bed reactor: A multiscale space-time analysis," *Powder Technology* 183 (2008) 10-20, Elsevier.

Zeng, Z., and Natesan, K., *Relationship between the Growth of Carbon Nanofilaments and Metal Dusting Corrosion*, 2005, *Chem. Mater.* 2005, 17, 3794-3801.

PCT International Search Report and Written Opinion, PCT/US2013/049719, dated Sep. 25, 2013.

Wiegand et al., *Fabrication of High Strength Metal-Carbon Nanotube Composites*, U.S. Army Research and Development, Picatinny, New Jersey, and New Jersey Institute of Technology, Newark, New Jersey, report date Dec. 2008, 6 pages.

\* cited by examiner

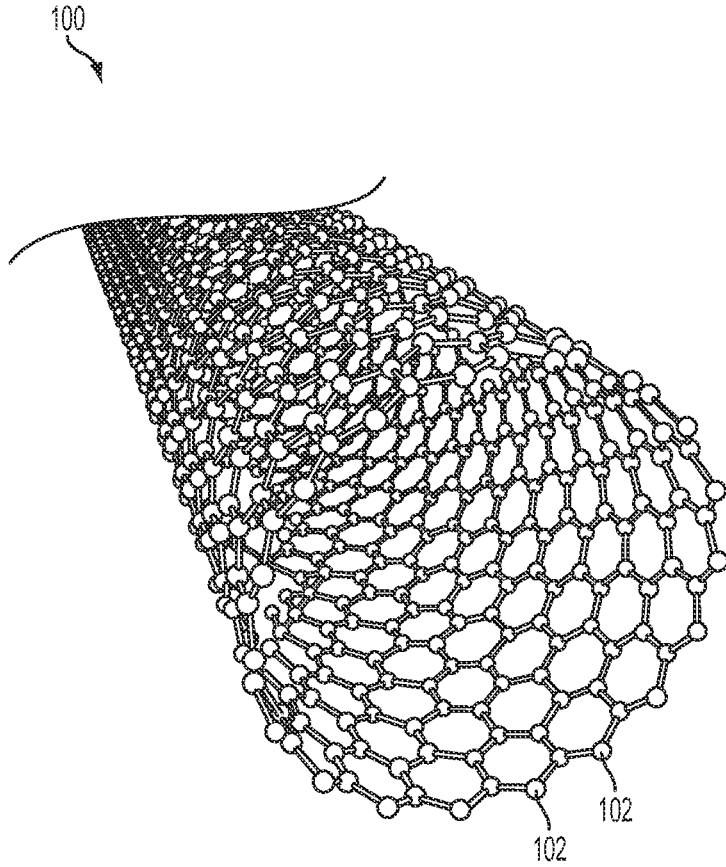


FIG. 1

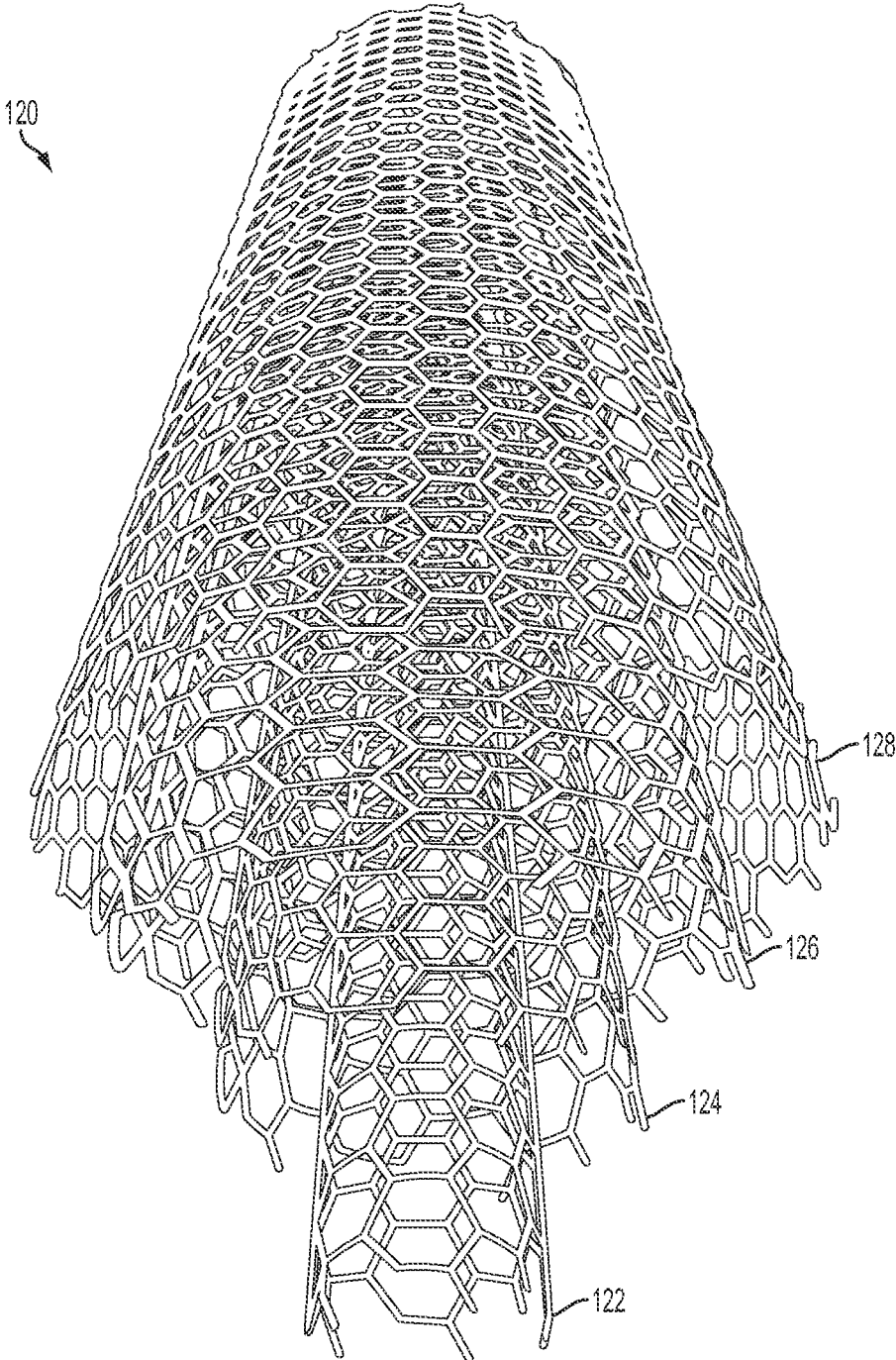


FIG. 2



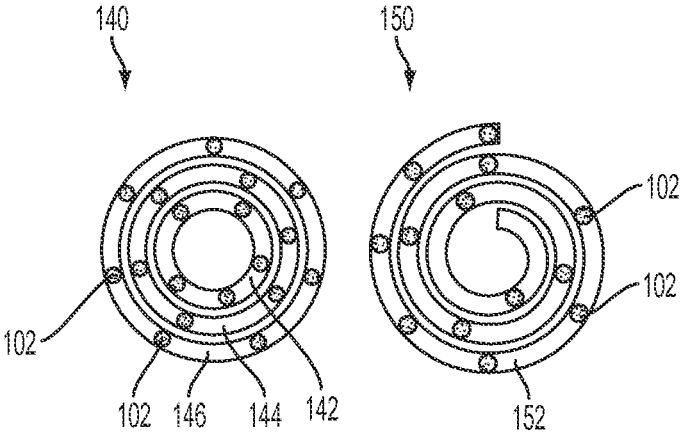


FIG. 3

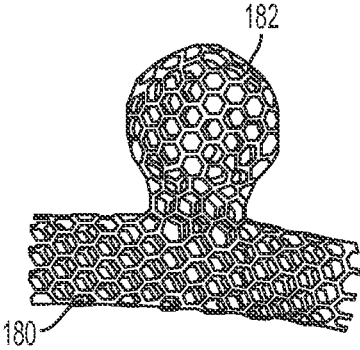


FIG. 4

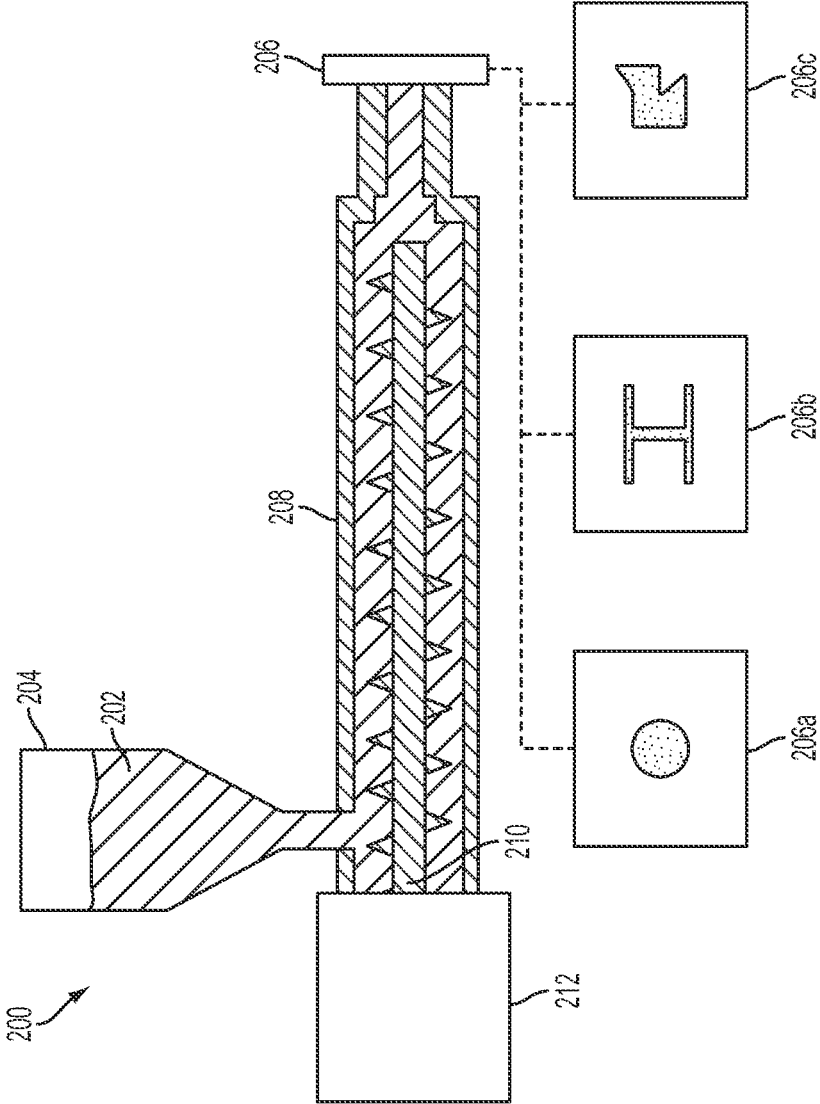


FIG. 5

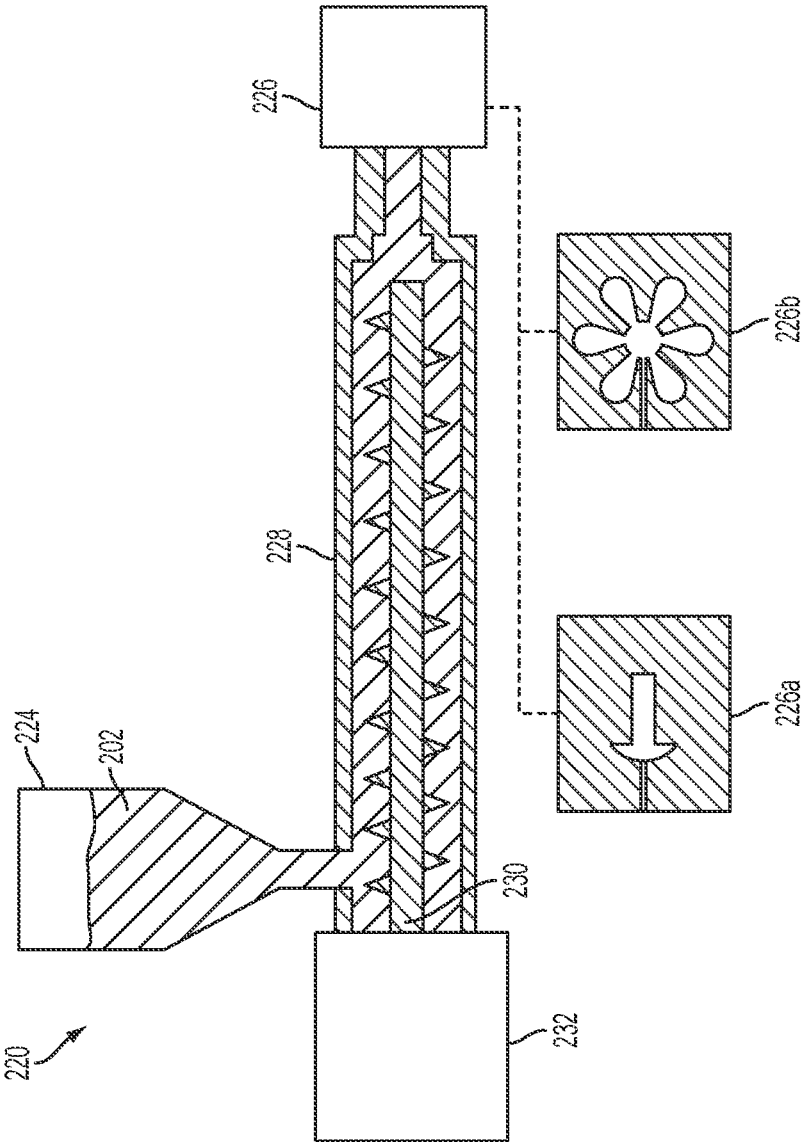


FIG. 6

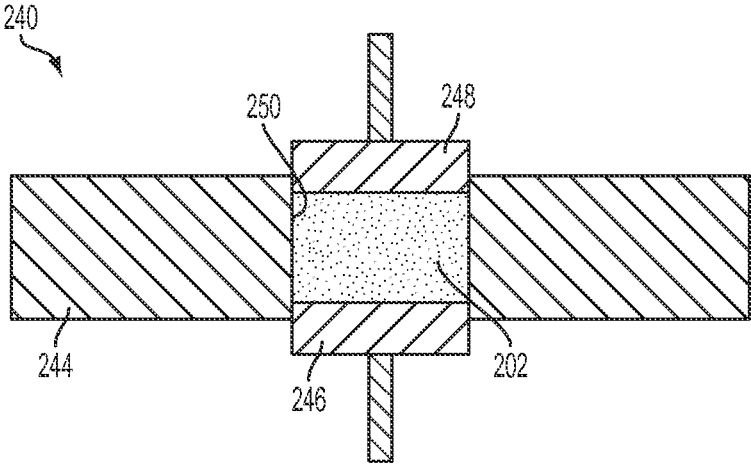


FIG. 7

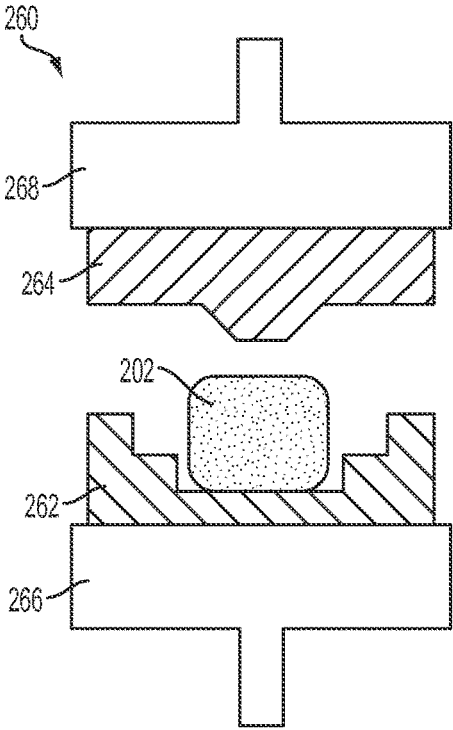


FIG. 8

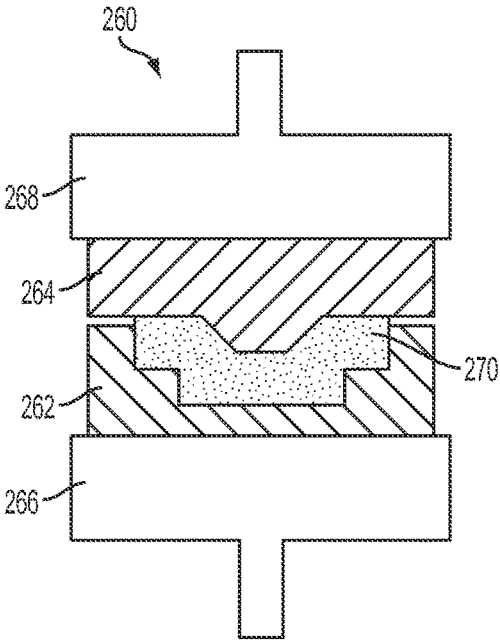


FIG. 9

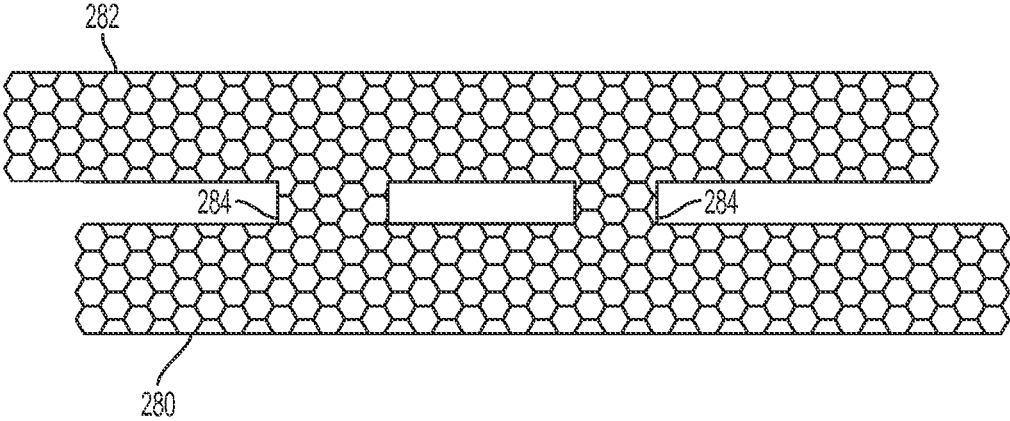


FIG. 10

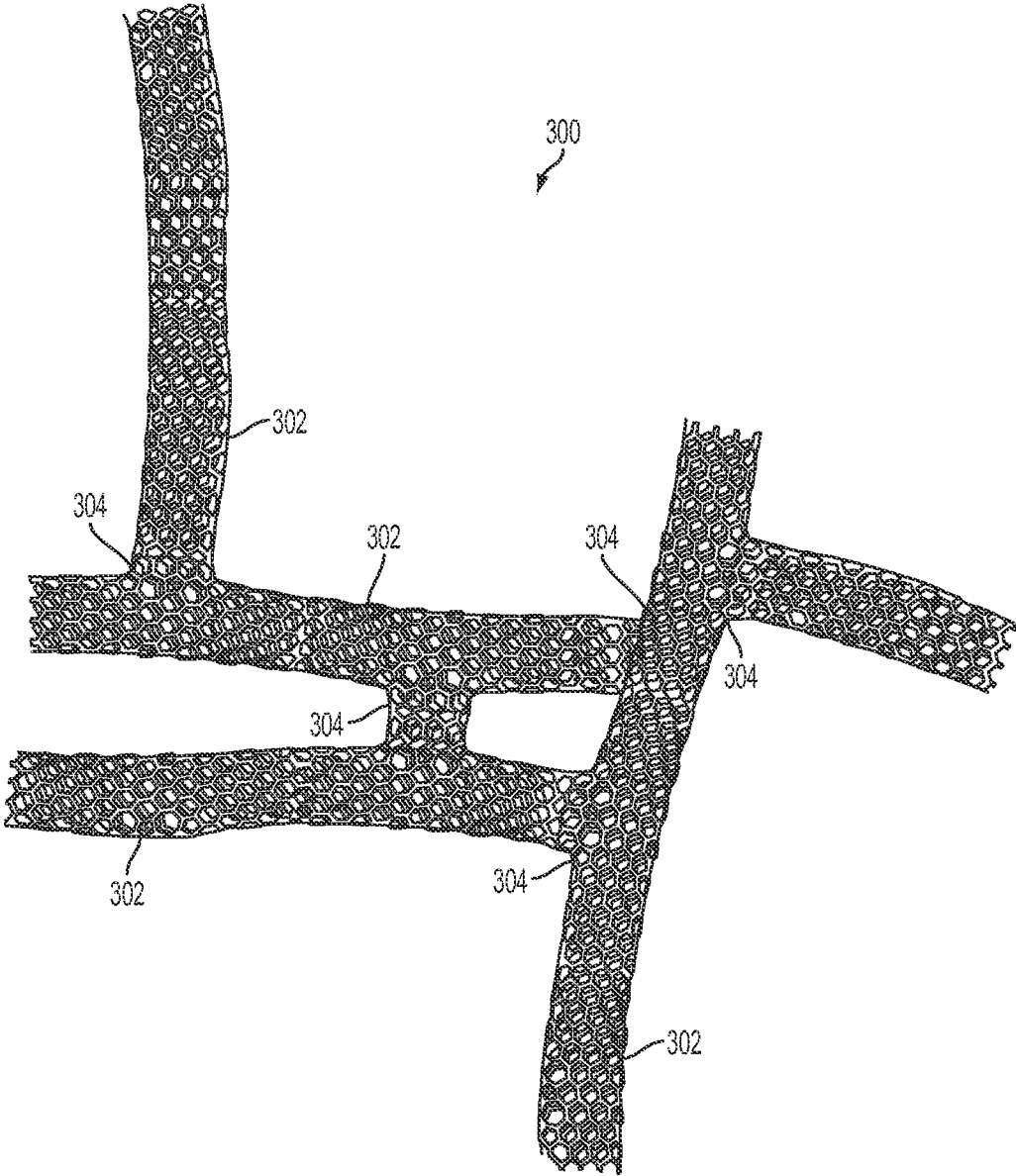


FIG. 11

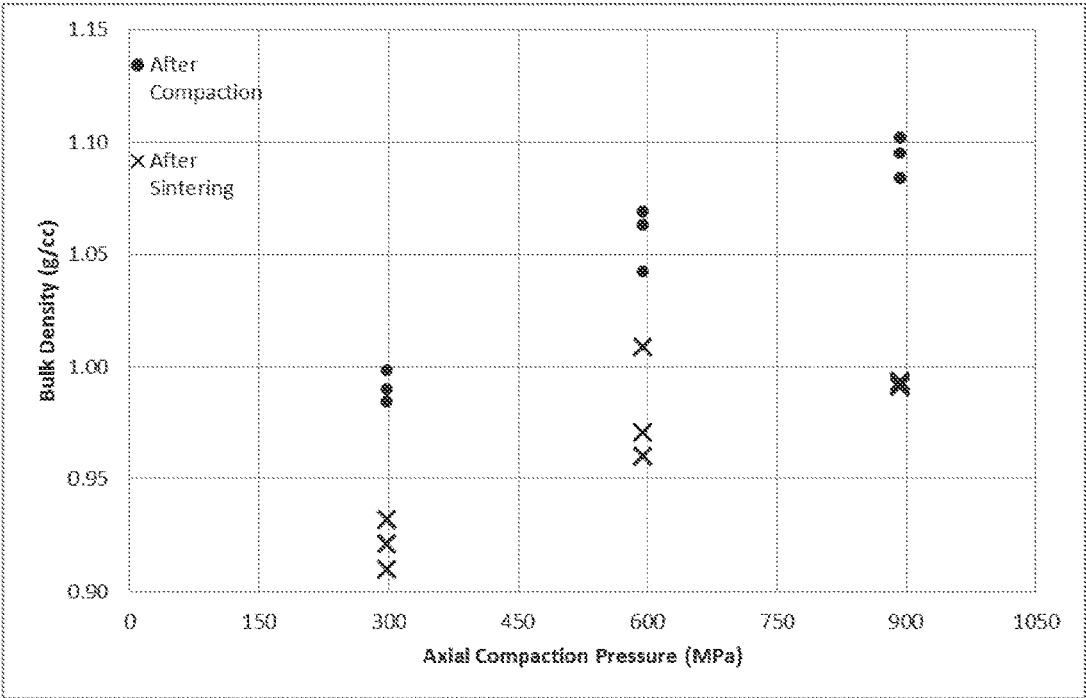


FIG. 12



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**SOLID CARBON PRODUCTS COMPRISING  
CARBON NANOTUBES AND METHODS OF  
FORMING SAME**

PRIORITY CLAIM

This application claims the benefit of the filing date of U.S. Provisional Patent Application Ser. No. 61/671,022, filed Jul. 12, 2012, for "Solid Carbon Products Comprising Carbon Nanotubes and Methods of Forming Same," the disclosure of which is hereby incorporated herein in its entirety by this reference.

FIELD

Embodiments of the present disclosure relate to methods and systems for forming solid carbon products from carbon nanotubes including mixtures of various types of carbon nanotubes and mixtures of carbon nanotubes with other substances.

BACKGROUND

The following documents, each published in the name of Dallas B. Noyes, disclose background information hereto, and each is hereby incorporated herein in its entirety by this reference:

1. U.S. Patent Publication No. 2012/0034150 A1, published Feb. 9, 2012;
2. International Application No. PCT/US2013/000071, filed Mar. 15, 2013;
3. International Application No. PCT/US2013/000072, filed Mar. 15, 2013;
4. International Application No. PCT/US2013/000073, filed Mar. 15, 2013;
5. International Application No. PCT/US2013/000075, filed Mar. 15, 2013;
6. International Application No. PCT/US2013/000076, filed Mar. 15, 2013;
7. International Application No. PCT/US2013/000077, filed Mar. 15, 2013;
8. International Application No. PCT/US2013/000078, filed Mar. 15, 2013;
9. International Application No. PCT/US2013/000079, filed Mar. 15, 2013; and
10. International Application No. PCT/US2013/000081, filed Mar. 15, 2013.

Conventional methods of using CNTs ("carbon nanotubes") in engineering materials generally rely on embedding the CNTs in a matrix material. CNTs are currently processed in a wide variety of composite structures using metals, plastics, thermoset resins, epoxies, and other substances as the matrix to hold the CNTs together, thus creating solid objects. The CNTs act as reinforcing material to improve properties of the materials. Typical objectives of using carbon nanotubes in a matrix are to increase the strength, decrease weight, or to increase electrical and thermal conductivity of the composite.

Methods to make materials composed primarily of carbon nanotubes include spinning the carbon nanotubes into fibers and making "buckyrock." U.S. Pat. No. 6,899,945, issued May 31, 2005, and entitled "Entangled single-wall carbon nanotube solid material and methods for making same" discloses a method for making buckyrock. Buckyrock is a three-dimensional, solid block material including an entangled network of single-wall CNTs. Buckyrock is mechanically strong, tough, and impact resistant with a bulk

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density of about 0.72 g/cm<sup>3</sup> (see Example 3 of U.S. Pat. No. 6,899,945). The single-wall CNTs in a buckyrock form are present in a random network. The random network of the CNTs appears to be held in place by Van der Waals forces between the CNTs and by physical entanglement or interference of the CNTs. One type of buckyrock is made by forming a slurry of CNTs in water, slowly removing water from the slurry to create a paste, and allowing the paste to dry very slowly, such that the CNT network of the paste is preserved during solvent evaporation. Buckyrock can be used in various applications requiring lightweight material with mechanical strength, toughness, and impact resistance, such as ballistic protection systems.

Though conventional materials including CNTs have interesting and useful properties, the individual CNTs comprising these materials have significantly different properties. It would therefore be beneficial to produce materials having properties more comparable to the properties of individual CNTs.

Disclosure

Methods of forming solid carbon products include pressure compaction methods such as extruding, die pressing, roller pressing, injection molding etc. to form solid shapes comprising a plurality of carbon nanotubes. The carbon nanotubes may optionally be mixed with other substances. Such solid shapes may be further processed by heating in an inert atmosphere to temperatures sufficient to sinter at least some of the CNTs so that covalent bonds form between adjacent CNTs. The methods may include forming a plurality of nanotubes, disposing the plurality of nanotubes in a press, and applying heat and pressure to the plurality of carbon nanotubes to form the solid carbon product. When sintered, the resulting material is a novel composition of matter having two or more CNTs with covalent bonding between them.

The solid carbon products, whether sintered or not, include interlocked CNTs that define a plurality of voids throughout the material. The dimension of the interstitial voids may be controlled by a variety of methods including controlling the characteristic diameter of the CNTs comprising the solid carbon products, the inclusion of other materials that may create voids when removed from the solid carbon products, and the pressure and temperatures at which the solid carbon products are formed.

Sintered solid carbon products include a plurality of covalently bonded carbon nanotubes. Some methods include compressing a material comprising carbon nanotubes, heating the compressed material in a non-reactive environment to form chemical bonds between adjacent carbon nanotubes and form a bonded carbon nanotube structure, and cooling the bonded carbon nanotube structure to a temperature at which carbon of the carbon nanotubes does not react with oxygen.

Other methods include first forming a solid carbon product by compressing a material comprising carbon nanotubes and subsequently placing the resulting solid carbon product into sintering conditions. The sintering conditions may include an inert environment, such as a vacuum or inert atmosphere (e.g., argon or helium). The solid carbon product is heated to a desired temperature for a period of time to induce covalent bonding between adjacent CNTs, after which the object is cooled below the oxidation temperature of carbon in air. The product may then be removed from the sintering conditions.

Such methods may include any of a variety of standard industrial processing methods such as extrusion, die pressing, injection molding, isostatic pressing, and roll pressing. The sintering of the solid carbon products can be performed in a variety of apparatus such as are commonly used in sintered powder metallurgy and sintered ceramic processing. The sintering of the solid carbon products may include any of a variety of means including induction heating, plasma arc discharge, high temperature autoclaves and annealing furnaces, and other related devices and methods as are known in the art.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 through 4 are simplified illustrations of carbon nanotubes;

FIGS. 5 through 9 are simplified cross-sectional views of presses for forming solid carbon products;

FIGS. 10 and 11 are simplified illustrations depicting the structures of linked carbon nanotubes; and

FIG. 12 is a graph showing bulk densities of solid carbon products formed by compaction and sintering.

#### MODE(S) FOR CARRYING OUT THE INVENTION

This disclosure includes methods of forming solid carbon products by applying pressure to carbon nanotubes, and to methods for applying heat to the solid products formed by such processes. Solid carbon products may be useful in various applications, such as filters, reactors, electrical components (e.g., electrodes, wires, batteries), structures (e.g., beams, frames, pipes), fasteners, molded parts (e.g., gears, bushings, pistons, turbines, turbine blades, engine blocks), etc. Such solid carbon products may exhibit enhanced properties (e.g., strength, electrical or thermal conductivity, specific surface area, porosity, etc.) with respect to conventional materials. This disclosure includes a new class of materials that contain a plurality of CNTs formed into solid shapes under pressure. When such solid shapes are sintered, covalent bonds form between at least some of the CNTs, forming solid shapes. This material has numerous useful properties.

As used herein, the term “sintering” means and includes annealing or pyrolyzing CNTs at temperatures and pressures sufficient to induce carbon-carbon covalent bonding between at least some of the adjacent CNTs between at least some of their contact points.

As used herein, the term “catalyst residual” means and includes any non-carbon elements associated with the CNTs. Such non-carbon elements may include a nanoparticle of a metal catalyst in the growth tip of the CNTs, and metal atoms or groups of atoms randomly or otherwise distributed throughout and on the surfaces of the CNTs.

As used herein, the term “green” means and includes any solid carbon product that has not been sintered.

CNTs may be created through any method known to the art, including arc discharge, laser ablation, hydrocarbon pyrolysis, the Boudouard reaction, the Bosch reaction and related carbon oxide reduction reactions, or wet chemistry methods (e.g., the Diels-Alder reaction). The methods described herein are applicable to carbon nanotubes regardless of the method of manufacture or synthesis.

CNTs may occur as single-wall and multi-wall carbon nanotubes of various diameters ranging from a few nanometers to 100 nanometers in diameter or more. CNTs may have a wide variety of lengths and morphologies, and may occur as substantially parallel “forests”, randomly tangled

masses, or “pillows” of structured agglomerations. CNTs may also form or be compounded to form many different mixtures of CNTs with various combinations and distribution of the above characteristics (number of walls, diameters, lengths, morphology, orientation, etc.). Various mixtures, when compounded and used to form the solid carbon products described herein, may result in products with specifically engineered properties. For example, the median void size of interstitial spaces between CNTs comprising solid carbon products typically is approximately proportional to the characteristic diameters of the CNTs used in forming the solid carbon products. The median void size influences the overall porosity and density of the solid carbon products.

Various CNT features and configurations are illustrated in FIGS. 1 through 4. FIG. 1 shows a single-wall CNT 100, in which carbon atoms 102 are linked together in the shape of a single cylinder. The carbon atoms 102 are covalently bonded into a hexagonal lattice, and thus form a CNT 100 that appears as a single graphitic layer rolled into the form of a tube. The CNT 100 may be conceptualized as a “rolled graphene sheet” lattice pattern oriented so that the carbon atoms 102 spiral at various angles with regard to the axis of the CNT 100. The angle is called the “chirality” and common named forms include armchair and zigzag, as described in Mildred S. Dresselhaus & Phaedon Avouris, Introduction to Carbon Materials Research, in Carbon Nanotubes: Synthesis, Structure, Properties, and Applications, 1, 6 (Mildred S. Dresselhaus, Gene Dresselhaus, & Phaedon Avouris, eds., 2001), the entire contents of which are incorporated herein by this reference. Many chiralities are possible; CNTs 100 with different chiralities may exhibit different properties (e.g., CNTs 100 may have either semiconductor or metallic electrical properties).

The CNT 100 has an inside diameter related to the number of carbon atoms 102 in a circumferential cross section. The CNT 100 depicted in FIG. 1 has a zigzag pattern, as shown at the end of the CNT 100. The diameter may also affect properties of the CNT 100. Single-walled CNTs 100 can have many different diameters, such as from approximately 1.0 nm (nanometer) to 10 nm or more. A CNT 100 may have a length from about 10 nm to about 1 μm (micron), such as from about 20 nm to about 500 nm or from about 50 nm to about 100 nm. CNTs 100 typically have an aspect ratio (i.e., a ratio of the length of the CNT to the diameter of the CNT) of about 100:1 to 1000:1 or greater.

CNTs having more than one wall are called multi-wall CNTs. FIG. 2 schematically depicts a multi-wall CNT 120 having multiple graphitic layers 122, 124, 126, 128 arranged generally concentrically about a common axis. Double-walled and triple-walled carbon nanotubes are occasionally described as distinct classes; however, they may be considered as the smallest categories of multi-walled CNTs 120. Diameters of multi-wall CNTs 120 can range from approximately 3 nm to well over 100 nm. Multi-wall CNTs 120 having outside diameters of about 40 nm or more are sometimes referred to as carbon nanofibers in the art.

FIG. 3 depicts two forms of multi-wall CNTs 140, 150. In the CNT 140, one single-wall CNT 142 is disposed within a larger diameter single-wall CNT 144, which may in turn be disposed within another even larger diameter single-wall CNT 146. This CNT 140 is similar to the CNT 120 shown in FIG. 2, but includes three single-wall CNTs 142, 144, 146 instead of four. Another form of multi-wall CNTs shown in FIG. 3 is CNT 150, which may be conceptualized as a single graphene sheet 152 rolled into tubes.

FIG. 4 schematically depicts a single-wall CNT **180** with an attached nanobud **182**. The nanobud **182** has a structure similar to a spherical buckminsterfullerene (“buckyball”), and is bonded to the single-wall CNT **180** by carbon-carbon bonds. As suggested by the structure shown in FIG. 4, modifications may be made to the wall of a single-wall CNT **180** or to the outer wall of a multi-wall CNT. At the point of bonding between the nanobud **182** and the CNT **180**, carbon double-bonds can break and result in “holes” in the wall of the CNT **180**. These holes may affect the mechanical and electrical properties of the CNT **180**. In single-wall CNTs, these holes may introduce a relative weakness when compared unmodified cylindrical CNTs. In multi-wall CNTs, the outer wall may be affected, but any inner walls likely remain intact.

Carbon nanotubes are typically formed in such a way that a nanoparticle of catalyst is embedded in the growth tip of the carbon nanotube. This catalyst may optionally be removed by mild washing (e.g., by an acid wash). Without being bound to a particular theory, it is believed that if the catalyst is left in place, catalyst atoms become mobilized during the sintering process, and may migrate to the surface or within the pores of the carbon nanotubes. This process may disperse the catalyst atoms randomly, uniformly, or otherwise throughout the solid carbon product mass and may have a significant influence on the properties of the solid carbon product. For example, catalyst material may affect electrical conductivity or the ability to catalyze other chemical reactions.

The catalyst particles may be selected to catalyze other reactions in addition to the formation of solid carbon. Catalyst particles may be any material, such as a transition metal or any compound or alloy thereof. For example, catalyst particles may include nickel, vanadium oxide, palladium, platinum, gold, ruthenium, rhodium, iridium, etc. Because the catalyst particles are attached to or otherwise associated with CNTs, each catalyst particle may be physically separated from other catalyst particles. Thus, the catalyst particles may collectively have a much higher surface area than a bulk material having the same mass of catalyst. Catalyst particles attached to CNTs may therefore be particularly beneficial for decreasing the amount of catalyst material needed to catalyze a reaction and reducing the cost of catalysts. Compressed solid carbon products used as catalysts may, in many applications, benefit from the catalytic activity of both the CNT and the metal catalyst particles embedded in the growth tip of the CNTs.

The CNTs used in the processes herein may be single-wall CNTs, multi-wall CNTs, or combinations thereof, including bi-modally sized combinations of CNTs, mixtures of single-wall and multi-wall CNTs, mixtures of various sizes of single-wall CNTs, mixtures of various sizes of multi-wall CNTs, etc. The CNTs may be in forms such as a sheet-molded compound, a pressure-molded compound, or as a pourable liquid. The CNTs may be disposed within a press any other device structured and configured to provide pressure to the material. The press may include an extrusion die, a mold, a cavity, etc.

For example, in the press **200** shown in FIG. 5, CNTs **202** may be placed in a hopper **204** configured to feed material through an extrusion die **206**. The press **200** includes an extrusion barrel **208** with a screw mechanism **210** connected to a drive motor **212** to carry the CNTs **202** through the extrusion barrel **208** to the extrusion die **206**. The extrusion barrel **208** may optionally include means for heating the CNTs **202** as the CNTs **202** pass through the extrusion barrel **208**. The extrusion die **206** has an opening with a shape

corresponding to the cross-sectional shape of a part to be formed in the press **200**. Extrusion dies **206** may be interchangeable, depending on the shape of objects desired. Some possible shapes of extrusion dies **206a**, **206b**, **206c** are shown. For example, the extrusion die **206** may have an opening shaped like a circle, a regular polygon, an irregular polygon, an I-beam, etc. Extrusion dies **206** can be structured to create objects of extruded CNTs of a variety of shapes and sizes: symmetrical or asymmetrical, small to large. The CNTs **202** may optionally be mixed with another material before or within the press **200**.

In some embodiments and as shown in the press **220** of FIG. 6, the CNTs **202** are placed into a hopper **224** configured to feed material to a mold **226**. The press **220** includes a barrel **228** with a screw mechanism **230** connected to a drive motor **232** to carry the CNTs **202** through the barrel **228** to the mold **226**. The barrel **228** may optionally include means for heating the CNTs **202** as the CNTs **202** pass through the barrel **228**. The mold **226** has an opening with an interior shape corresponding to the exterior shape of a part to be formed in the press **220**. Molds **226** may be interchangeable, depending on the shape of objects desired. Some possible shapes of molds **226a** and **226b** are shown. For example, the mold **226** may have a shape of a screw or a propeller. The CNTs **202** may optionally be mixed with another material before or within the press **200** to improve flowability, mold release, or other process properties. Such materials may be subsequently removed by suitable means such as etching, pyrolysis, evaporation, etc. The resulting solid carbon product may substantially free of the additional material, and may include essentially carbon and, in some embodiments, residual catalyst material.

In other embodiments and as shown in the press **240** of FIG. 7, the CNTs **202** are placed into a body **244** having an interior shape defining an exterior of a product to be formed. The CNTs **202** may be placed between two pistons **246**, **248** surrounded by the body **244**. The body **244** may have walls **250** defining an interior cavity and configured to allow the pistons **246**, **248** to slide freely. In other embodiments, a single piston may be configured to press CNTs against a body.

In an embodiment as shown in the press **260** of FIG. 8, CNTs **202** are placed within a mold portion **262** having one or more surfaces corresponding to a shape of a product to be formed. One or more additional mold portions **264** are configured to press the CNTs **202** against the mold portion **262**, when pressed by pistons **266**, **268**, as shown in FIG. 9. Together, the mold portions **262**, **264** define the shape of the product to be formed.

Pressure is applied to form the CNTs into a cohesive “green” body. For example, the screw mechanisms **210**, **230** shown in FIGS. 5 and 6 apply pressure to the CNTs **202** as the CNTs **202** pass through the presses **200**, **220**. Extrusion through a die **206** as shown in FIG. 5 may be continuous (theoretically producing an infinitely long product) or semi-continuous (producing many pieces). Examples of extruded material include wire, tubing, structural shapes, etc. Molding, as in the press **220** shown in FIG. 6, is the process of manufacturing by shaping pliable raw material (e.g., CNTs **202**) using a rigid pattern (the mold **226**). The CNTs **202** adopt the shape of the mold.

The pistons **266**, **268** shown in FIGS. 8 and 9 are pressed toward the CNTs **202**, forming the CNTs **202** into a green body **270**. The resulting green body **270** formed may be held together by relatively weak forces, such that the green body **270** may easily be further shaped (e.g., machined, drilled,

etc.), but still holds its shape when handled. The CNTs of the green body **270** may each be in physical contact with one or more other CNTs.

Heat is applied to green bodies to link the CNTs together into a more cohesive body in which at least some of the adjacent CNTs form covalent bonds between one another. For example, the CNTs may be heated at a heating rate from about 1° C./min to about 50° C./min to a temperature of at least 1500° C., 1800° C., 2100° C., 2400° C., 2500° C., 2700° C. or even to just below the sublimation temperature of carbon (approximately 3600° C.). Pressure may also be applied concurrently with, before, or after heat is applied. For example, the CNTs may be pressed at 10 to 1000 MPa, such as 30 MPa, 60 MPa, 250 MPa, 500 MPa, or 750 MPa. The green bodies may be subjected to a heated inert environment, such as helium or argon, in an annealing furnace. Sintering CNTs (i.e., subjecting them to heat in an oxygen-free environment) apparently creates covalent bonds between the CNTs at points of contact. The sintering of the CNTs typically occurs in a non-oxidizing environment, such as a vacuum or inert atmosphere so that the carbon nanotubes are not oxidized during the sintering. Sintering CNTs to induce chemical bonding at the contact surfaces may improve desirable material properties such as strength, toughness, impact resistance, electrical conductivity, or thermal conductivity in the solid structure product when compared to the green material. The CNTs may also be sintered in the presence of additional constituents such as metals or ceramics to form composite structures, lubricants to aid processing, or binders (e.g., water, ethanol, polyvinyl alcohol, coal, tar pitch etc.). Materials may be introduced as powders, shavings, liquids, etc. Suitable metals may include, for example, iron, aluminum, titanium, antimony, Babbitt metals, etc. Suitable ceramics may include materials such as oxides (e.g., alumina, beryllia, ceria, zirconia, etc.), carbides, boride, nitrides, silicides, etc. In embodiments in which materials other than CNTs are present, covalent bonding occurs between at least some of the CNTs, and the additional materials may become locked into a matrix of CNTs.

The CNTs in the sintered body have chemical bonds connecting one another. Chemical bonds, which are generally stronger than physical bonds, impart different properties on the collection of CNTs than physical bonds. That is, the sintered body may have higher strength, thermal conductivity, electrical conductivity, or other properties than the green body from which it was formed.

When single-wall CNTs are covalently bonded to adjacent single-wall CNTs, holes can form on the surface of the CNTs as some of the carbon-carbon bonds break, thus modifying the mechanical and electrical properties of each single-wall CNT. The sintered single-wall CNTs, however, may still typically exceed non-sintered single-wall CNTs in such properties as strength, toughness, impact resistance, electrical conductivity, and thermal conductivity. With multi-wall CNTs, typically only the wall of the outer tube is modified; the internal walls remain intact. Thus, using multi-walled and bi-modally sized CNTs in, for example, extrusion and molding processes, may yield solid structures with properties that, in many respects, exceed practical limitations of single-walled CNTs.

Sintering appears to cause covalent bonds to form between the walls of CNTs at their contact points. That is, any given CNT may “cross-link” with an adjacent CNT at the physical point of contact of the two CNTs. Any given CNT having undergone sintering may be covalently bound to numerous other CNTs (both single-wall CNTs and multi-

wall CNTs). This increases the strength of the resulting structure because the CNTs do not slide or slip at the bonding points. Unsintered, CNTs (e.g., in buckyrock) may slide with respect to each other. Because the covalent bonding caused by sintering may occur at numerous sites in the mass of CNTs, the sintered body has significantly increased strength, toughness, impact resistance, and conductivity over convention agglomerations of CNTs.

FIG. **10** schematically depicts the cross-linked structure of two covalently bound CNTs **280**, **282** produced by sintering. When sintered, CNTs **280**, **282** covalently bond at their contact points **284**. Each CNT may form covalent bonds with some or all of the other CNTs with which it is in contact during sintering. Due to the internal layering in a multi-wall CNT, covalent bonding between the individual walls of the multi-wall CNT is likely to occur under sintering conditions. However, this covalent bonding has not yet been confirmed in testing. The heating and optional pressurization of the CNTs in a sintering process are maintained until the desired level of cross-linking has occurred. The sintered CNTs are then cooled to a temperature at which the CNTs will not spontaneously react with oxygen. Thereafter, the mixture may be exposed to air for further processing, storage, packaging, shipment, sale, etc.

In another embodiment, a CNT mixture is heated in a reactive environment (e.g., in the presence of oxygen, hydrogen, a hydrocarbon, and/or another material). In this embodiment, heat and pressure are maintained as needed until the reactants in the reactive environment have reacted with one another or with the CNTs. The product is then cooled. In such a process, the reactants may form additional holes or pores in the CNTs, increasing the specific surface area of the sintered body. Alternatively, the reactants may deposit materials on the surface of the CNTs without affecting the underlying CNT structure.

In another embodiment, the CNT mixture is initially heated and sintered in a nonreactive environment (e.g., in a vacuum, in the presence of helium, or in the presence of argon). Subsequent to sintering, the heat and pressure are changed to suitable reaction conditions and reactants are added to the environment. Such reactants may include a variety of metals (as liquid or vapor), metal carbonyls, silanes, or hydrocarbons. The reaction of the reactants with one another or with the carbon of the CNT may fill some or all of the interstices of the CNT lattice with products of the reactions. Such processing with additional reactants may in some cases be conducted during sintering, but may also be performed separately. The heat and pressure are maintained until the desired level of reaction (both cross-linking within the CNTs, and the reaction between the CNTs and the reactant) has occurred. The reacted mixture is then cooled and removed from the reaction environment for further processing, storage, packaging, shipment, sale, etc.

FIG. **11** schematically depicts a mass **300** of covalently bound CNTs **302**. The CNTs **302** bind through sintering with other CNTs **302** (multi-wall or single-wall CNTs) through mutual contact points **304**, binding the aggregate together into a highly cross-linked structure. The resultant binding may create a material of significant strength, toughness, impact resistance, and electrical and thermal conductivity.

During the sintering process, the green body may shrink, corresponding with a decrease in the size of voids among the CNTs. However, the sintered body may remain porous due to the porosity of each CNT (i.e., the center of the CNT) and due to voids between and among CNTs. The sintered body may have pores or voids having a median minimum dimension of less than about 1 μm, less than about 500 nm, less

than about 100 nm, less than about 50 nm, or even less than about 10 nm. That is, each void may have two or more dimensions (e.g., a length, a width, and a height, each perpendicular to the others, or a diameter and a length), measured in different directions. The voids need not be regularly shaped. The “minimum dimension” is defined as the minimum of the two or more dimensions of a single void. The “median minimum dimension” is defined as the median of these minimum dimensions for a group of voids.

A sintered body as described herein may have a high specific surface area, due to voids between CNTs and within CNTs (i.e., because the CNTs are hollow). For example, a sintered body may have a specific surface area of at least about 100 m<sup>2</sup>/g, at least about 500 m<sup>2</sup>/g, at least about 750 m<sup>2</sup>/g, at least about 900 m<sup>2</sup>/g, or even at least about 1000 m<sup>2</sup>/g. The specific surface area can be controlled by the characteristic diameters or mixture of diameters of the CNTs used in forming the solid carbon product. For example, small-diameter single-wall CNTs have specific surface areas up to approximately 3000 m<sup>2</sup>/g, while large-diameter multi-wall CNTs have specific surface areas of approximately 100 m<sup>2</sup>/g.

A sintered body may have a high electrical conductivity. For example, a sintered body may have an electrical conductivity of at least about 1×10<sup>5</sup> S/m (Siemens per meter), at least about 1×10<sup>6</sup> S/m, at least about 1×10<sup>7</sup> S/m, or even at least about 1×10<sup>8</sup> S/m. The electrical conductivity can be controlled by the types of CNTs used, the chirality of the CNTs used, the sintering conditions, and the quantity of resulting covalent bonds in the solid carbon product. For example, single-wall CNTs with a metallic chirality have a much higher electrical conductivity than multi-wall CNTs. As a further example, an increase in the number of covalent bonds appears to correlate with an increase in conductivity.

A sintered body may also have a high thermal conductivity. For example, a sintered body may have a thermal conductivity of at least about 400 W/m·K (watts per meter per Kelvin), at least about 1000 W/m·K, at least about 2000 W/m·K, or even at least about 4000 W/m·K. The thermal conductivity of the resulting solid carbon product may be controlled by the types of CNTs used and the chirality of CNTs used. For example, single-wall CNTs with a metallic chirality have much high thermal conductivity than large multi-wall CNTs.

CNTs may alternatively be pressed after the sintering process by, for example, extrusion or molding, as described above with respect to FIGS. 5 through 9. In some embodiments, the sintering process may be part of the formation of the desired object. For example, a section of the extrusion barrel may heat the CNTs to the sintering temperature in an inert atmosphere for an appropriate amount of time to cause sintering. Such heating may be, for example, induction heating or plasma arc heating. Thus, sintered CNTs may be extruded. The sintered CNTs may optionally be mixed with another material such as a metal, a ceramic, or glass. The material may be pressed or pulled through a die under either extreme heat or cold. The material, forced into a given shape, is held in place for a period of time and at sintering temperatures and pressures, and then returned to normal atmospheric conditions. The products may be continuous, such as wires, or may be discrete pieces, such as bolts, propellers, gears, etc. Molding of sintered or sintering CNTs typically involves either using the CNT material in concentrated form (i.e., with minimal impurities) or in forming a moldable composite with another material, such as a metal.

The moldable material is placed or poured into a rigid mold, held at a particular temperature and pressure, and then cooled back to normal atmospheric conditions.

In some embodiments, an incremental manufacturing method may be employed wherein CNTs (either compressed or not) are placed in a nonreactive environment, such as in an inert gas autoclave. The CNTs are sintered to form covalent bonds between the CNTs in the surface layer and the underlying layer. For example, a laser may irradiate a portion of the CNTs in a pattern. Additional CNTs are deposited over the sintered CNTs, and in turn sintered. The sintering process is repeated as many times as necessary to achieve a selected thickness of sintered CNTs. The sintered CNTs are then cooled to a temperature below which the CNTs do not react with oxygen or other atmospheric gases. The sintered CNTs may then be removed from the nonreactive environment without contaminating the sintered CNTs. In some embodiments, the sintered CNTs are cooled and removed from the nonreactive environment before deposition of each additional portion of CNTs.

In certain embodiments, sintered solid carbon products are formed in a belt-casting operation. A layer of CNTs is placed on a moveable belt. The belt moves the CNTs into a chamber containing a nonreactive environment. The CNTs are sintered in the chamber, then cooled (e.g., in a portion of the chamber), and removed from the chamber. The process may be operated continuously, such as to form a sheet of sintered CNTs.

In some embodiments, solid carbon products are further treated by electrodeposition to fill interstices in the solid carbon products with another material. A solution having materials to be deposited is prepared. The solvent of the solution may be water, an organic solvent, or an inorganic solvent. The solute may include a material such as a metal salt, an organic salt, a metalorganic salt, etc. Electroplating solutions are known in the art and not described in detail herein. The solid carbon product to be treated is contacted with the solution, such as by immersing the body in the solution. An electric potential (a direct-current voltage or an alternating-current voltage) is applied to the body to induce electrodeposition of one or more components of the solution. The composition, potential, temperature, and/or pressure are maintained until a selected amount of the material is deposited onto the solid carbon product. The solid carbon product is then removed from the solution and rinsed to remove excess solution.

Solid carbon products formed as described herein each include a plurality of cross-linked CNTs. The CNTs define a plurality of voids, which may have a median minimum dimension of less than about 1 μm, less than about 500 nm, less than about 100 nm, less than about 50 nm, or even less than about 10 nm. Some or all of the CNTs may include a metal, such as a metal particle from which the CNTs were formed, or a metal coating on the CNTs. The solid carbon products may be structural members (e.g., beams), fasteners (e.g., screws), moving parts (e.g., propellers, crankshafts, etc.), electrically conductive members (e.g., electrodes, wires, etc.), or any other form. The solid carbon product may include another material dispersed in a continuous matrix surrounding and in contact with the CNTs. The solid carbon products may have improved strength, toughness, impact resistance, and electrical and thermal conductivity in comparison to conventional materials.

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In some embodiments, the solid carbon products also include other morphologies of carbon, interspersed with or otherwise secured to the CNTs. For example, buckyballs may be connected to some of the CNTs. As another example, one or more graphene sheets may be formed over all or a portion of a solid carbon product.

Both the compressed solid carbon products and the sintered solid carbon products described herein have a wide variety of potentially useful applications. For example, the compressed solid carbon products may be used as filters, molecular sieves, catalysts, and electrodes in applications where the additional mechanical integrity achieved through sintering is not necessary. The sintered solid carbon products can be used in the applications in which compressed solid carbon products can be used and in a wide variety of additional applications requiring additional mechanical integrity, electrical properties, and other material-property enhancements achieved through sintering.

Sintered solid carbon products may be useful components of armor because of their mechanical integrity, ability to absorb compressive loads with a high spring constant, and ability to dissipate heat. That is, sintered solid carbon products may be used to form projectile-resistant materials, such as armor plates, bullet-proof vests, etc. The light weight of the solid carbon products could improve mission payloads, increase vehicle range, and alter the center of gravity. For example, armor materials including sintered solid carbon products may be beneficial in preventing injury and death of occupants of vehicles such as Mine Resistant Ambush Protected vehicles ("MRAPs"), which are prone to tipping. Sintered solid carbon products as described herein may be effective in light-weight armament systems such as mortar tubes, gun barrels, cannon barrels, and other components. Sintered solid carbon products may also be beneficial in aerial vehicles, such as aircraft, spacecraft, missiles, etc.

## EXAMPLES

## Example 1

## Sintering of Compacted CNTs

CNTs were formed as described in U.S. Patent Publication No. 2012/0034150 A1. Samples of approximately 1.0 grams to 1.25 grams of CNTs each were pressed in 15-mm diameter dies using a 100-ton (890-kN) press. The pressed samples were placed in an inert gas furnace (Model 1000-3060-FP20, available from Thermal Technology, LLC, of Santa Rosa, Calif.) and heated under vacuum at a rate of 25° C. until the samples reached 400° C. This temperature was maintained for 30 minutes to allow the samples to outgas any oxygen, water, or other materials present. The furnace was then filled with inert gas (argon or helium) at 3-5 psi (21 to 34 kPa) above atmospheric pressure. The furnace was heated at a rate of 20° C./min until the sample reached 1500° C. This temperature was maintained for 30 minutes. Heating continued at 5° C./min to a sintering temperature, which was maintained for a dwell time of 60 minutes. The samples were then cooled at 50° C./min to 1000° C., after which the furnace was shut down until the samples reached ambient temperature. The sample masses, compaction pressures, and sintering temperatures for the samples are shown in Table 1 below. The inert gas was helium for the samples sintered at 2400° C. and was argon for the other samples.

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TABLE 1

Samples prepared in Example 1			
Sample	Mass (g)	Compaction Pressure (MPa)	Sintering Temperature (° C.)
1	1.076	500	1800
2	1.225	750	1800
3	1.176	250	1800
4	1.113	500	2100
5	1.107	750	2100
6	1.147	250	2100
7	1.103	500	2400
8	1.198	750	2400
9	1.121	250	2400
10	1.128	250	1900
11	1.209	500	1900
12	1.212	750	1900
13	1.101	250	2000
14	1.091	500	2000
15	1.225	750	2000
16	1.078	250	1700
17	1.179	500	1700
18	1.157	750	1700

Samples 1 through 18 were harder and more robust than were the samples before the heating process. At the highest sintering temperature of 2400° C. (samples 7 through 9), the sintered pellets are flakier than the other sintered samples. All the samples prepared in Example 1 were qualitatively observed to be hard.

Pycnometry tests show that the skeletal density decreases from 2.2 g/cm<sup>3</sup> for raw powders and raw compactions to 2.1 g/cm<sup>3</sup>, 2.08 g/cm<sup>3</sup>, and 2.05 g/cm<sup>3</sup> for the samples sintered at 1800° C., 2100° C., and 2400° C., respectively. Bulk density also decreased after sintering, in almost every case to less than 1.0 g/cm<sup>3</sup>. Pellet thickness increased 5% to 9% during sintering, with the higher pressure compactions expanding more than the lower pressure compactions. The bulk densities of Samples 1 through 9 are shown in Table 2 and in FIG. 12.

TABLE 2

Properties of samples prepared in Example 1:						
Sample	After Compaction			After Sintering		
	Compaction Pressure (MPa)	Skeletal Density (g/cc)	Bulk Density (g/cc)	Sintering Temperature (° C.)	Skeletal Density (g/cc)	Bulk Density (g/cc)
1	600	2.1992	1.043	1800	2.1095	0.960
2	900	2.2090	1.095	1800	2.0993	0.994
3	300		0.990	1800	2.1131	0.921
4	600		1.063	2100	2.0680	0.971
5	900		1.084	2100	2.0817	0.992
6	300		0.999	2100	2.0829	0.910
7	300		0.985	2400	2.0553	0.932
8	600		1.069	2400	2.0479	1.009
9	900		1.102	2400	2.0666	0.991

## Example 2

## Spark Plasma Sintering of CNTs

CNTs were formed as described in U.S. Patent Publication No. 2012/0034150 A1. Graphite foil (available from Mineral Seal Corp., of Tucson, Ariz.) was lined into 20-mm diameter dies, and 2.0 g to 4.0 g of CNTs were placed over the foil. The samples were placed in a spark plasma sintering

(SPS) system (model SPS 25-10, available from Thermal Technology, LLC, of Santa Rosa, Calif.). An axial pressure of approximately 5 MPa was applied to the CNT samples, and the SPS system was then evacuated to less than 3 mTorr (0.4 Pa). The sample was heated at 150° C./min to 650° C., and this temperature was maintained for one minute to allow the vacuum pump to re-evacuate any materials out-gassed. The pressure was increased to the compaction pressure of 30 MPa or 57 MPa, while simultaneously increasing the temperature at a rate of 50° C./min to 1500° C. The temperature and pressure were maintained for one minute. The temperature was then increased at 50° C./min to the sintering temperature, and maintained for 10 min or 20 min. After the dwell, the pressure was reduced to 5 MPa, and the sample allowed to cool at 150° C./min to 1000° C., after which the furnace was shut off until the samples reached ambient temperature.

The sample masses, compaction pressures, compaction rates, sintering temperatures, and dwell times for the samples are shown in Table 2 below.

TABLE 3

Samples prepared in Example 2:					
Sample	Mass (g)	Compaction Pressure (MPa)	Compaction rate (MPa/min)	Sintering Temperature (° C.)	Dwell time (min)
19	2.449	57	13.0	1800	10
20	3.027	57	13.0	2100	10
21	4.180	57	13.0	1800	20
22	4.210	30	6.0	1800	10
23	4.417	30	6.0	1800	20

The SPS-sintered pellets formed in Example 2 were about 10 mm thick and had bulk densities between 1.3 g/cm<sup>3</sup> and 1.5 g/cm<sup>3</sup>. To illustrate the strength of these samples, sample #20 was planned to be sintered 2100° C., but at about 1900° C., the die broke. The ram traveled significantly, crushing the graphite die. After the test was completed, the die was broken away from the sample. The sample remained visibly intact, though slightly thinner than expected. This would indicate that the sintering occurs at temperatures less than 1900° C., that the strength of SPS-sintered pellets is high, even at extreme temperatures, and that the sintered samples are strong enough to resist an applied force without fracturing.

The bulk densities of the samples with the graphite foil still attached were determined. For the samples weighing about 4 g (i.e., samples #21, #22, and #23), bulk densities were between 1.35 g/cm<sup>3</sup> and 1.50 g/cm<sup>3</sup>. The volume resistivity and electrical conductivity of the samples were also measured. These data are shown in Table 4. The samples are more conductive than amorphous carbon, and nearly as conductive as graphite.

TABLE 4

Properties of samples prepared in Example 2:				
Sample	Density (g/cm <sup>3</sup> )	Resistance (Ω)	Resistivity (Ω · m)	Electrical Conductivity (S/m)
19	1.588	2.42 × 10 <sup>-3</sup>	4.98 × 10 <sup>-5</sup>	2.01 × 10 <sup>-4</sup>
20	1.715	2.02 × 10 <sup>-3</sup>	4.77 × 10 <sup>-5</sup>	2.10 × 10 <sup>-4</sup>
21	1.494	3.24 × 10 <sup>-3</sup>	1.23 × 10 <sup>-4</sup>	8.14 × 10 <sup>-3</sup>
22	1.350	3.80 × 10 <sup>-3</sup>	1.62 × 10 <sup>-4</sup>	6.19 × 10 <sup>-3</sup>
23	1.429	3.7 × 10 <sup>-3</sup>	1.57 × 10 <sup>-4</sup>	6.37 × 10 <sup>-3</sup>

Although the foregoing description contains many specifics, these are not to be construed as limiting the scope of the present invention, but merely as providing certain embodiments. Similarly, other embodiments of the invention may be devised which do not depart from the scope of the present invention. For example, features described herein with reference to one embodiment also may be provided in others of the embodiments described herein. The scope of the invention is, therefore, indicated and limited only by the appended claims and their legal equivalents, rather than by the foregoing description. All additions, deletions, and modifications to the invention, as disclosed herein, which fall within the meaning and scope of the claims, are encompassed by the present invention.

What is claimed is:

1. A method of forming a solid carbon product, the method comprising:

disposing a plurality of carbon nanotubes comprising a residual metal catalyst in a press;

applying pressure to the plurality of carbon nanotubes; and

sintering the plurality of carbon nanotubes at a temperature of at least about 2,100° C. to form covalent bonds between adjacent carbon nanotubes and produce a sintered solid carbon product comprising the residual metal catalyst and covalently bonded carbon nanotubes.

2. The method of claim 1, further comprising after sintering the plurality of carbon nanotubes, exposing the sintered solid carbon product to at least one reactant selected from the group consisting of metals, metal carbonyls, silanes, and hydrocarbons.

3. The method of claim 1, wherein sintering the plurality of carbon nanotubes comprises sintering the plurality of carbon nanotubes in an inert atmosphere or in a vacuum.

4. The method of claim 1, wherein disposing a plurality of carbon nanotubes comprising a residual metal catalyst in a press comprises disposing a plurality of carbon nanotubes comprising a metal selected from the group consisting of the elements of Groups 5 through 10 of the periodic table in the press.

5. The method of claim 1, wherein applying pressure to the plurality of carbon nanotubes and sintering the plurality of carbon nanotubes to form the sintered solid carbon product comprises forming a porous sintered solid carbon product.

6. The method of claim 1, wherein applying pressure to the plurality of carbon nanotubes and sintering the plurality of carbon nanotubes to form the sintered solid carbon product comprises forming an electrically conductive sintered solid carbon product.

7. The method of claim 6, wherein forming an electrically conductive sintered solid carbon product comprises forming an electrode.

8. The method of claim 1, wherein applying pressure to the plurality of carbon nanotubes and sintering the plurality of carbon nanotubes to form the sintered solid carbon product comprises extruding the sintered solid carbon product through a die.

9. The method of claim 1, wherein applying pressure to the plurality of carbon nanotubes and sintering the plurality of carbon nanotubes to form the sintered solid carbon product comprises pressing the plurality of carbon nanotubes into a mold.

10. The method of claim 1, wherein disposing the plurality of carbon nanotubes in a press comprises disposing the plurality of carbon nanotubes in a mold within the press.

**11.** The method of claim 1, further comprising:  
preparing a liquid solution comprising a salt;  
contacting the sintered solid carbon product with the  
liquid solution;  
applying an electric potential to the sintered solid carbon 5  
product to induce electrodeposition of at least one  
component of the liquid solution onto surfaces of the  
sintered solid carbon product and to form a plated  
sintered solid carbon product; and  
rinsing the plated sintered solid carbon product to remove 10  
the liquid solution therefrom.

**12.** The method of claim 1, wherein the residual metal  
catalyst comprises at least one material selected from the  
group consisting of vanadium oxide, palladium, platinum,  
gold, ruthenium, rhodium, and iridium. 15

**13.** The method of claim 1, wherein sintering the plurality  
of carbon nanotubes comprises sintering the plurality of  
carbon nanotubes in the presence of a ceramic material  
selected from the group consisting of boride(s), silicide(s),  
and combinations thereof. 20

**14.** The method of claim 1, further comprising mixing the  
sintered solid carbon product with at least one material  
selected from the group consisting of a metal, a ceramic, and  
a glass to form a material and pressing or pulling the  
material through a die. 25

**15.** The method of claim 1, wherein forming a sintered  
solid carbon product comprising the residual metal catalyst  
comprises forming the sintered solid carbon product to have  
an electrical conductivity of at least about  $1 \times 10^5$  Siemens  
per meter. 30

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