Fabrication of Metal/Carbon Nanotube Composites by Electrochemical Deposition

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Metal/carbon nanotube (CNT) composites are promising functional materials due to the various superior properties of CNTs in addition to the characteristics of metals. Electrochemical deposition can be classified into three types: (1) composite plating by electrodeposition or electroless deposition, (2) metal coating on CNT by electroless deposition, and (3) electrodeposition using CNT templates, such as CNT sheets and CNT yarns.

Keywords: metal/carbon nanotube composite ; electrochemical deposition ; electrodeposition ; electroless deposition ; composite plating ; carbon nanotube sheet ; carbon nanotube yarn

1. Introduction

Carbon nanotubes (CNTs) [1][2] have excellent mechanical characteristics such as high tensile strength and high elastic modulus, and also possess high thermal and electrical conductivity. Therefore, research into the practical applications of carbon nanotubes has been expanding into wide field, and composite materials of such nano-sized filler materials, such as polymer/CNT composites, have been studied expecting their innovative functions. Metal/CNT composites also have been investigated to enhance properties of metals and/or to give new innovative functions to metals. However, in general, the wettability of molten metals against CNTs is poor, resulting in difficulties of controlling the interface between the filler and matrix. In addition, since CNTs are nanosized fibrous materials and easily form aggregates, it is very difficult to form a metal/CNT composite with well-distributed CNTs in the metal matrix.

Electrochemical deposition is roughly classified into electrodeposition and electroless deposition, and the fabrication processes of metal/CNT composites by the electrochemical deposition can be categorized into three types: (1) composite plating by electrodeposition or electroless deposition, (2) CNT coating by electroless deposition, and (3) electrodeposition using CNT templates (**Figure 1**). “Composite plating” is one of the electrochemical deposition techniques. CNTs are incorporated in deposited metal matrix during plating. In the case of “metal coating on CNTs by electroless deposition”, the prepared metal-coated CNTs are mainly used as filler of composites, such as resin composites. In the case of “electrodeposition on CNT templates”, CNT yarns or CNT sheets are used as CNT templates. The electrochemical deposition is a nano-scale or atomic scale process to fabricate metal materials and hence is effective to form atomic scall boundary between metals and CNTs. Moreover, this method is a wet process and consequently is likely advantageous to form metal/CNT composites with well-distributed CNTs in the metal matrix, especially in the case of the composite plating.

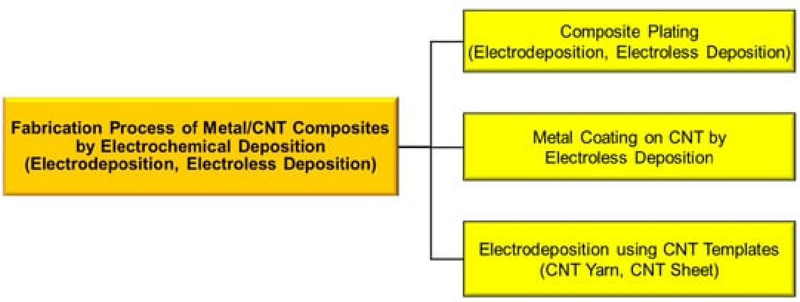

Figure 1. Classification of fabrication process for metal/CNT composites by electrochemical deposition.

2. Fabrication of Metal/CNT Composites Using Composite Plating by

Electrodeposition or Electro Less Deposition

2.1. Composite Plating

Rough schematics of composite plating by electrodeposition and electroless deposition are displayed in **Figure 2** and **Figure 3**, respectively. In the case of electrodeposition, inert particles are dispersed homogeneously in a plating bath. When a voltage is applied, metal is electrodeposited on a cathode and the particles adsorb on the surface of the deposited metal. Then, the particles are embedded in depositing metal, resulting in a metal composite (**Figure 2**). In the case of CNT composite plating by electrodeposition, inert particles are dispersed homogeneously in a plating bath containing a reducing agent. When a substrate is soaked in the bath, metal is reductively deposited on the substrate accepting electrons from the reducing agent and, at the same time, the particles adsorb on the surface of the deposited metal. The particles are then embedded in depositing metal, resulting in a metal composite (**Figure 3**). In general, the substrate is pre-treated and catalyst particles, such as Pd particles, are fixed on the surface of the substrate before soaking into the plating bath. As far as was searched, the first article of the composite plating is on Cu/graphite composites by electrodeposition and was reported in 1928 [3]. Regarding the mechanism of the composite plating, several models have been proposed [4][5][6][7][8].

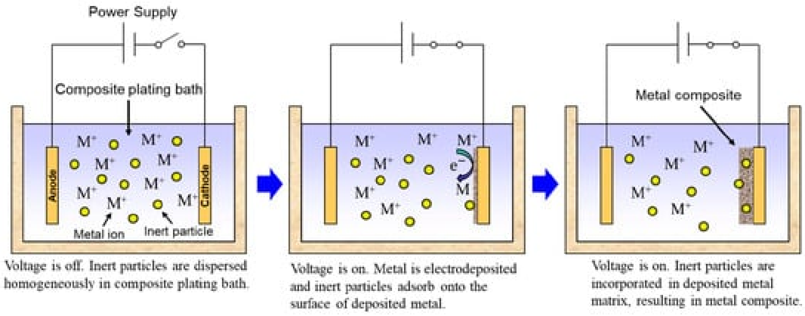

Figure 2. Schematic of composite plating by electrodeposition.

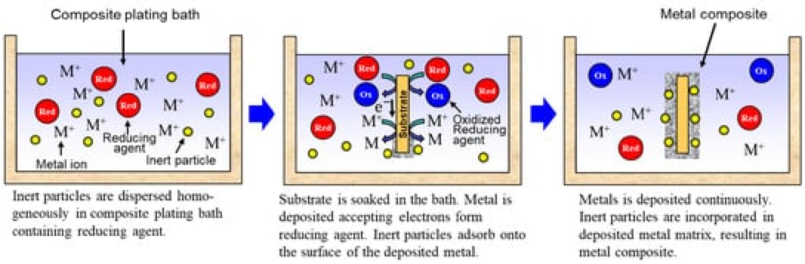

Figure 3. Schematic of composite plating by electroless deposition.

2.2. Preparation of Plating Bath for Metal/CNT Composite Plating

To fabricate metal/CNT composites with uniform distribution of CNTs, the preparation of plating baths with homogeneous dispersion of CNTs is important. In general, plating baths are aqueous solutions, while CNTs are hydrophobic. Therefore, hydrophilization of CNTs have been examined by the addition of surfactants or the direct introduction of hydrophilic groups on the surfaces of CNTs (**Figure 4**). The addition of surfactants in plating baths is a common method. Various kinds of surfactants [9][10][11][12][13][14][15][16][17][18][19][20][21][22][23][24][25][26], such as sodium dodecylbenzene sulfonate and sodium deoxycholate, have been examined for the homogeneous dispersion of CNTs in a pure water. However, effective surfactants for the dispersion in a pure water are not always effective in plating baths which contain great amounts of ions. Moreover, even if the surfactant is effective for the dispersion of CNTs in a plating bath, CNTs are not always co-deposited by electrochemical deposition. Therefore, the selection of appropriate surfactants is essential. Since the surfactants are likely incorporated in deposited metal matrix during electrochemical deposition, the concentration of surfactants should be examined. On the contrary, the direct introduction of hydrophilic groups, such as -COOH, onto the surfaces of CNTs has been examined using a chemical treatment [27], a plasma treatment [28], a heat treatment [29], and so on. These methods destroy the sp^2 carbon bonding of the surfaces of CNTs. Therefore, the conditions of the treatments should be examined.

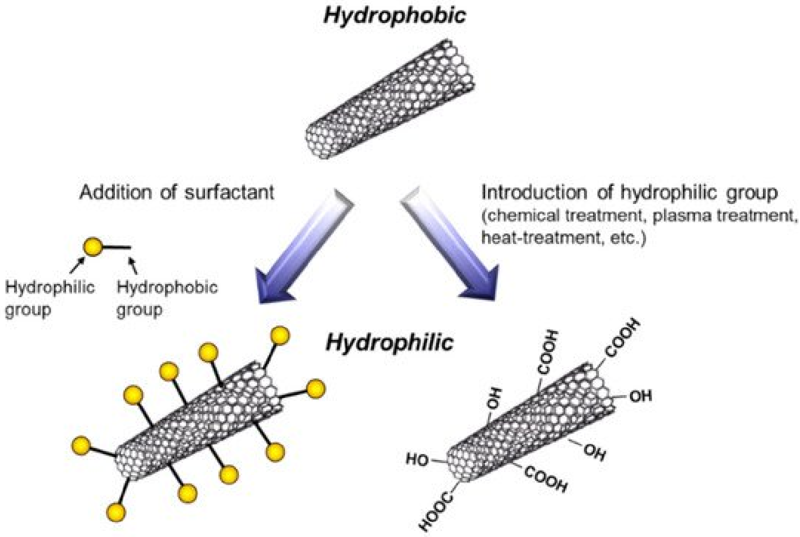

Figure 4. Schematic of hydrophilization of CNTs.

On the contrary, CNTs are nanosized fibrous material and consequently tend to aggregate. In particular, SWCNTs have the thinnest (ca. 1–4 nm in diameter) among the various types of CNTs and can thus easily form aggregates referred to as bundles (**Figure 5**).

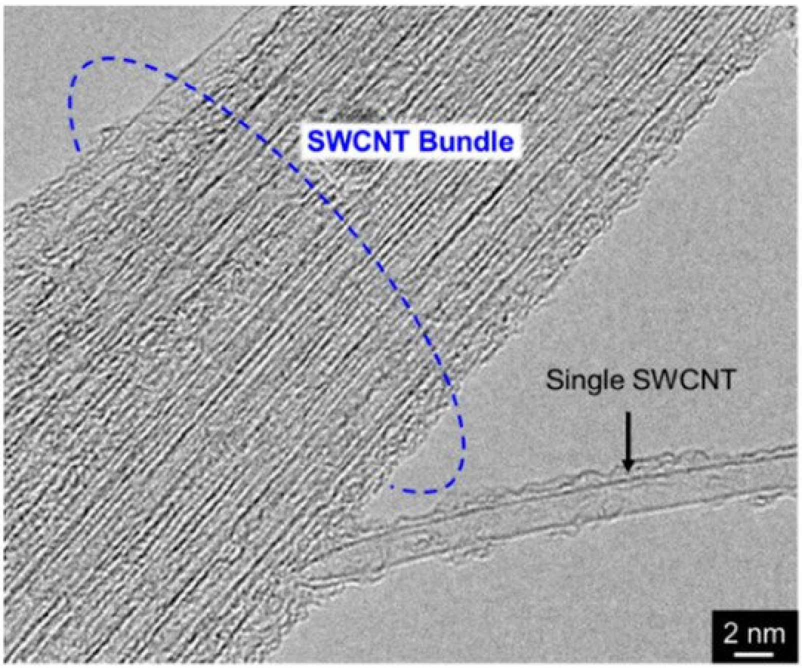

Figure 5. TEM image of SWCNT bundle.

2.3. Unique Feature of Composite Plating Using CNTs as Inert Particles

Since a single CNT, especially multi-walled CNT (MWCNT) has a fibrous shape with large aspect ratio in addition to a high electrical conductivity in the axis direction. Therefore, composite plating using CNTs as inert particles often shows a unique feature unlike other composite plating using insulation particles such as Al_2O_3 particles. The schematic of the unique feature is showed in **Figure 6** [30]. When a part of a MWCNT is incorporated in the deposited metal matrix during electrodeposition, the metal can be electrodeposited not only on the deposited metal but also on the protruding edge (a defect site) of the MWCNT. If the defect sites exist on the sidewall of the MWCNT, the metal can also be electrodeposited on the defect sites.

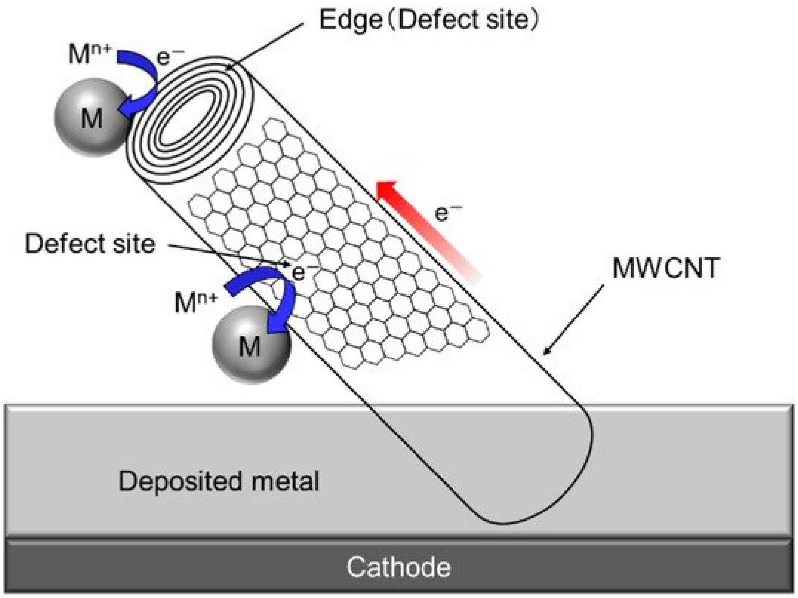

Figure 6. Schematic of unique phenomenon of composite plating using MWCNTs as inert particles. (**Figure 6** is adapted from reference [30]).

Using this unique phenomena, powder Cu/MWCNT composites could be obtained [31]. **Figure 7**a displays the surface morphology of Cu/MWCNT composites just after the electrodeposition. Many Cu/MWCNT composites particles are seen. These particles are fixed loosely on the cathode substrate and can be separated easily by ultrasonification. **Figure 7**b displays the morphology of the Cu/MWCNT composite powder after the separation from the substrate by ultrasonification. A large number of MWCNTs stick out from the Cu particles, resulting in a sea urchin shape. The size of the Cu spheres is 2–15 µm.

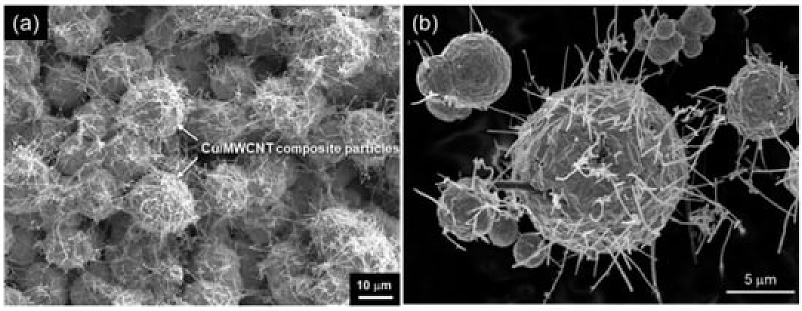

Figure 7. SEM images of (**a**) Cu/MWCNT composite immediately after electrodeposition and (**b**) Cu/MWCNT composite powder separated by ultrasonification. (**Figure 8** is adapted from reference [31]).

2.4. Fabrication of Metal/CNT Composites Using Composite Plating by Electrodeposition

Fabrication conditions in these articles are listed in **Table 1**.

Table 1. Fabrication conditions of metal/CNT composites using composite plating by electrodeposition.

Metal	CNT	Treatment of CNT	Base Plating Bath	Surfactant	Remarks	Year	Ref.
Ni	MWCNT	Chemical treatment	Dull Watts bath	Sodium lauryl sulfate	Corrosion behavior	2020	[32]
Ni	MWCNT	Chemical treatment	Dull Watts bath	Sodium lauryl sulfate	Corrosion protection	2020	[33]
Ni	MWCNT	Wrapped by polydopamine	Dull Watts bath	Non	Wear and corrosion resistance	2019	[34]
Ni	MWCNT	Non	Ionic liquid (choline chloride/carbamide)	Non	Non-aqueous solvent	2017	[35]
Ni	MWCNT	Non	Sulfamate bath	Cationic surfactant, compound name is unknown	Improvement in tool life	2014	[36]

Metal	CNT	Treatment of CNT	Base Plating Bath	Surfactant	Remarks	Year	Ref.
Ni	MWCNT	Non	$NiSO_4$+NaCl	Polyvinylpyrrolidone	Cyclic voltametric route	2011	[37]
Ni	MWCNT	Ball milling	Bright Watts bath	Sodium lauryl sulfate and Hydroxypropylcellulose	Corrosion behavior	2011	[38]
Ni	MWCNT	Chemical treatment	Choline chloride/urea	Non	Non-aqueous solvent	2010	[39]
Ni	MWCNT	Non	Bright Watts bath	Polyacrylic acid	Solid lubrication	2008	[40]
Ni	MWCNT	Ball milling	Watts type bath	Sodium lauryl sulfate, Cetyltrimethylammonium bromide	Effects of surfactants	2008	[41]
Ni	MWCNT	Chemical treatment	Dull Watts bath	Non	Effects of current density	2008	[42]
Ni	MWCNT	Ball milling	Bright Watts bath	Sodium lauryl sulfate and Hydroxypropylcellulose	Mechanical properties	2008	[43]
Ni	MWCNT	Non	Bright Watts bath	Non	Mechanical properties	2008	[44]
Ni	MWCNT	Non	Bright Sulfamate bath	Polyacrylic acid	Low internal stress	2007	[45]
Ni	MWCNT	Non	Dull Watts bath	Non	Pulse-reverse parameter	2007	[46]
Ni	MWCNT	Non	Bright Watts bath	Polyacrylic acid	Thermal conductivity	2006	[47]
Ni	MWCNT	Non	Dull Watts bath	Poly(diallyldimethylammonium chrolide)	Pulse-reverse electrodeposition	2005	[48]
Ni	MWCNT	Chemical treatment	Dull Watts bath	Cetyltrimethylammonium bromide	Corrosion behavior	2005	[49]
Ni	MWCNT	Non	Dull Watts bath	Polyacrylic acid	Ni deposition on incorporated CNT	2004	[30]
Ni	MWCNT	Ball milling	Dull Watts bath	Non	CNT content	2002	[50]
Ni	MWCNT	Ball milling	Dull Watts bath	Non	Tribological property	2001	[51]
Ni-Co	MWCNT	Chemical treatment	Dull Watts bath + Co salt	Non	Corrosion behavior	2019	[52]
Ni-P	MWCNT	Non	Dull Watts bath + citric acid + P compound	Polyacrylic acid	Tribological properties	2010	[53]
Ni-Co	MWCNT	Non	Dull Watts bath + Co salt	Compound name is unknown	Mechanical and tribological properties	2006	[54]
Ni-P	MWCNT	Non	Ni salts + citric acid + P compounds	Compound name is unknown	Corrosion properties	2004	[55]
Cu	MWCNT	Chemical treatment	Citric bath	Non	Corrosion behavior	2021	[56]
Cu	MWCNT	Chemical treatment	Sulfate bath	Non	Pulse reverse, electrical conductivity	2020	[57]
Cu	MWCNT	Chemical treatment?	Sulfate bath	Non-ionic surfactants, Compound name is unknown	Mechanical properties, Microlaminated structure	2020	[58]
Cu	SWCNT	Non	Sulfate bath	Stearyltrimethylammonium chloride	Mechanical properties	2020	[59]

Metal	CNT	Treatment of CNT	Base Plating Bath	Surfactant	Remarks	Year	Ref.
Cu	**SWCNT**	**Non**	**Sulfate bath**	**Non**	**Microstructure**	**2019**	[60]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Sodium lauryl sulfate**	**Jet electrodeposition, Tribological properties**	**2019**	[61]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Current collector for LIB anode**	**2019**	[62]
Cu	**MWCNT**	**Chemical treatment**	**Sulfate bath**	**Stearyltrimethylammonium bromide**	**Electrical conductivity, Corrosion resistance**	**2018**	[63]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Non-ionic surfactants, Compound name is unknown**	**Mechanical properties, Laminated structure**	**2018**	[64]
Cu	**MWCNT**	**Chemical treatment**	**Sulfate bath**	**Non**	**Cu/CNT powder + powder metallurgy**	**2018**	[65]
Cu	**MWCNT**	**Chemical treatment**	**Sulfate bath**	**Non**	**Cu/CNT powder + powder metallurgy**	**2018**	[66]
Cu	**MWCNT**	**Chemical treatment**	**Sulfate bath**	**Non**	**Cu/CNT powder + powder metallurgy**	**2017**	[67]
Cu	**MWCNT**	**Chemical treatment**	**Commercially available**	**Nano diamond**	**Periodic pulse reverse electrodeposition**	**2016**	[68]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Current collector for LIB anode**	**2016**	[69]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Co-deposition mechanism of CNT**	**2013**	[70]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Non**	**Electrochemical reduction behavior**	**2011**	[71]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Pulse-reverse**	**2011**	[72]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Surface morphology, Hardness, Internal stress**	**2010**	[73]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Patterned field emitter**	**2008**	[74]
Cu	**SWCNT**	**Non**	**Sulfate bath**	**Commercial products**	**Mechanical properties**	**2008**	[75]
Cu	**SWCNT**	**Chemical treatment**	**Sulfate bath**	**Cetyltrimethylammonium chloride**	**Mechanical properties**	**2008**	[76]
Cu	**Cup-stacked CNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Various CNTs**	**2005**	[77]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Microstructure**	**2004**	[78]
Cu	**MWCNT**	**Non**	**Sulfate bath**	**Polyacrylic acid**	**Cu/MWCNT composite powder**	**2003**	[31]
Zn	**MWCNT**	**Chemical treatment**	**Sulfate bath**	**Cetyltrimethylammonium bromide**	**Corrosion resistance**	**2021**	[79]

Metal	CNT	Treatment of CNT	Base Plating Bath	Surfactant	Remarks	Year	Ref.
Zn	MWCNT	Non	Zincate bath	Unknown	Pulse electrodeposition, Corrosion resistance	2020	[80]
Zn	MWCNT	Chemical treatment	Sulfate bath	Cetyltrimethylammonium bromide	Corrosion resistance	2007	[81]
Zn-Ni	MWCNT	Non	Chloride bath	Non	Pulse reverse, Tribological and Corrosion properties	2016	[82]
Cr	MWCNT	Non	Trivalent Cr bath	Sodium lauryl sulfate	Tribological properties, Corrosion resistance	2020	[83]
Cr	MWCNT	Non	Trivalent Cr bath	Sodium lauryl sulfate	Tribological properties	2018	[84]
Cr	MWCNT	Non	Trivalent Cr bath	Non	Mechanical properties	2009	[85]
Co	MWCNT	Non	Choline chloride/urea	Non	Non-aqueous solvent	2017	[86]
Co	MWCNT	Non	Sulfate bath	Polyacrylic acid	Field emission properties	2013	[87]
Co	MWCNT	Non	Sulfate bath	Polyacrylic acid	Tribological properties	2013	[88]
Co	MWCNT	Acid-treatment	Sulfate bath + citrate	Sodium lauryl sulfate	Tribological properties, Corrosion properties	2013	[89]
Co-W	MWCNT	Non	Co salt + Tungstate + Citrate	Polyacrylic acid	Tribological properties Corrosion properties	2015	[90]
Co-W	MWCNT	Non	Co salt + Tungstate + Citrate	Polyacrylic acid	Tribological properties	2013	[91]
Au	MWCNT	Non	Sulfite bath	Stearyltrimethylammonium chloride	Electrical conductivity, Tribological properties	2009	[92]
Ag	MWCNT	Non	Choline chloride + glycerol	Poly (N-vinyl pyrrolidone)	Pulse reverse electrodeposition	2021	[93]
Ag	MWCNT	Non	Iodide bath	Non	Electrical contact resistance against H_2S gas	2021	[94]
Ag	MWCNT	Non	Iodide bath	Non	Hardness, Electrical and Tribological properties	2020	[95]
Ag	MWCNT	Non	Cyanide bath	Unknown	Electrical contact resistance against H_2S gas	2010	[96]
Al	MWCNT	Acid treatment	Diethylene glycol dimethyl ether	Non	Hardness	2020	[97]
Al	MWCNT	Non	1-ethyl-3-methylimidazolium chloride	Non	Hardness	2006	[98]
Sn	MWCNT	Non	Choline chloride + ethylene glycole	Non	Nucleation study	2019	[99]

Metal	CNT	Treatment of CNT	Base Plating Bath	Surfactant	Remarks	Year	Ref.
Pb-Sn	MWCNT	Acid treatment	Fluoroborate bath	Polyacrylic acid	Corrosion resistance	2010	[100]

2.5. Fabrication of Metal/CNT Composites Using Composite Plating by Electroless Deposition

Regarding the number of published articles on metal/CNT composite plating using electroless deposition, those on the Ni-P alloy/CNT is large. In the case of electroless deposition of Ni, phosphorous compounds such as sodium hypophosphite (NaH_2PO_2) are usually used as the reducing agent and the P derived from the NaH_2PO_2 is co-deposited with Ni, resulting in Ni-P alloy deposit. Most of the purpose of the fabrication of Ni-P alloy/CNT composites is the improvement of tribological properties. Fabrication conditions in these articles are listed in **Table 2**.

Table 2. Fabrication conditions of metal/CNT composites by electroless deposition.

Metal	CNT	Pre-Treatment of CNT	Reducing Agent	Surfactant	Remarks	Year	Ref.
Ni-P	MWCNT	Non	NaH_2PO_2	Sodium lauryl sulfate	Tribological properties, Corrosion resistance	2021	[101]
Ni-P	MWCNT	Ball milling	NaH_2PO_2	Cetyltrimethylammonium bromide	Tribological properties	2012	[102]
Ni-P	MWCNT	Ball milling, Chemical treatment	NaH_2PO_2	Commercial product	Tribological properties, Corrosion resistance	2012	[103]
Ni-P	MWCNT	Chemical treatment Ball milling	NaH_2PO_2	Sodium lauryl sulfate	Mechanical attrition, Tribological properties	2012	[104]
Ni-P	MWCNT	HNO_3	Commercial product	Commercial product	Substrate: Mg powder	2011	[105]
Ni-P	MWCNT	Non	NaH_2PO_2	Stearyltrimethylammonium chloride	Substrate: ABS resin Tribological properties	2011	[106]
Ni-P	MWCNT	Non	NaH_2PO_2	Stearyltrimethylammonium chloride	Various P content, Tribological properties	2010	[107]
Ni-P	MWCNT	Chemical treatment	NaH_2PO_2	Unknown	Effects on solder joint	2009	[108]
Ni-P	MWCNT	Chemical treatment	NaH_2PO_2	Cetyltrimethylammonium bromide	Tribological properties	2009	[109]
Ni-P	MWCNT	Chemical treatment	NaH_2PO_2	unknown	Tribological properties	2006	[110]
Ni-P	MWCNT	Ball milling	NaH_2PO_2	Compound name is unknown	Hardness, Corrosion resistance	2005	[111]
Ni-P	SWCNT	Heat treatment	NaH_2PO_2	Compound name is unknown	Tribological properties	2004	[112]
Ni-P	MWCNT	Ball milling	NaH_2PO_2	Cetyltrimethylammonium bromide	Tribological properties	2003	[113]
Ni-P	MWCNT	Ball milling	NaH_2PO_2	Cetyltrimethylammonium bromide	Tribological properties	2003	[114]
Ni-P	MWCNT	Ball milling	NaH_2PO_2	Cetyltrimethylammonium bromide	Tribological properties	2002	[115]
Cu	SWCNT	Non	CHOCOOH	Sodium lauryl sulfate Hydroxypropylcellulose	Mechanical disintegration,	2016	[116]
Cu	MWCNT	Non	CHOCOOH	Sodium lauryl sulfate Hydroxypropylcellulose	Various CNTs Tribological properties	2014	[117]
Co-P	MWCNT	Non	NaH_2PO_2	Non	Magnetic properties	2016	[118]

3. Metal-Coated CNTs by Electroless Deposition

3.1. Fabrication Process

A fabrication process of metal-coated CNTs by an autocatalytic electroless deposition is schematically showed in **Figure 13**. Even in the case of electroless deposition, homogeneous dispersion of CNTs in the plating bath is important. The introduction of functional groups on the surface of CNTs likely effective to increase deposition sites, resulting in CNTs coated by metal films and not metal particles.

3.2. Metal-Coated CNTs

Fabrication conditions in these articles are listed in **Table 3**.

Table 3. Fabrication conditions of metal-coated CNTs by electroless deposition.

Metal	CNT	Pre-Treatment of CNT	Reducing Agent	Surfactant	Remarks	Year	Ref.
Ni-P	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Non	Microstructure, Co-coated CNTs	2020	[119]
Ni-P	MWCNT	Introduction of -COOH on CNT + Pd^{2+}	NaH_2PO_2	Non	EMI properties, Cotton fabric substrate	2020	[120]
Ni-P	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Non	Arc discharge synthesized CNTs	2015	[121]
Ni-P	MWCNT	Sn^{2+}/Pd^{2+} commercial product	NaH_2PO_2	Non	Fe-50Co composites, magnetic properties	2014	[122]
Au/Ni-P	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Polyacrylic acid (Pre-treatment)	Improved wettability with molten Al	2012	[123]
Fe-B/Ni-P	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2, KBH_4	Non	Microwave absorbing properties	2011	[124]
Ni-P	SWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Non	Microstructure of Ni-layer	2011	[125]
Ni-B	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	$(CH_3)_2NH \cdot BH_3$	Polyacrylic acid (Pre-treatment)	Graphitized MWCNTs Heat treatment	2011	[126]
Ni	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	N_2H_4	Polyacrylic acid (Pre-treatment)	Graphitized MWCNTs Magnetic properties	2010	[127]
Ni-P	MWCNT	$K_2Cr_2O_7$+H_2SO_4 Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Non	Microwave absorbing properties, Ni-N alloy	2008	[128]
Ni-P	MWCNT	HNO_3 Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Diallyl-dimethylammonium chloride	Graphitized MWCNTs	2005	[129]
Ni-P	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Polyacrylic acid (Pre-treatment)	Graphitized MWCNTs	2004	[130]
Ni-P	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Non	Continuous Ni-layer	2002	[131]
Ni-P	MWCNT	Mixed Pd^{2+}/Sn^{2+}	NaH_2PO_2	Non	Pd-coated CNTs	1999	[132]
Ni-P	MWCNT	Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Non	Magnetic property	1997	[133]
Al	MWCNT	Sn^{2+}/Pd^{2+} commercial product	$LiAlH_4$	Non	Non-aqueous bath: $AlCl_3$-urea	2020	[134]
Ag	MWCNT	H_2SO_4 + HNO_3 Sn^{2+}sensitization + Pd^{2+}activation	HCHO	Non	Interfacial adhesion of composites	2004	[135]

Metal	CNT	Pre-Treatment of CNT	Reducing Agent	Surfactant	Remarks	Year	Ref.
Cu	MWCNT	Sulphoric acid + HNO_3 Sn^{2+}sensitization + Cu^{2+}activation	HCHO	Non	Electrical and mechanical properties	2009	[136]
Cu	MWCNT	HNO_3 Sn^{2+}sensitization + Pd^{2+}activation HNO_3	CHOCOOH	Diallyl-dimethylammonium chloride	Graphitized MWCNTs	2004	[137]
Co-P	MWCNT	$K_2Cr_2O_7$+H_2SO_4 Sn^{2+}sensitization + Pd^{2+}activation	NaH_2PO_2	Non	Heat-treatment	2000	[138]

4. Metal/CNT Composites by Electrodeposition Using CNT Templates (Sheet, Yarn)

CNT templates, such as CNT sheets [139][140][141][142] and CNT yarns or fibers [143][144][145][146], have been developed and their various practical applications have been researched. Although a single CNT has a high electrical conductivity, electrical conductivities of those templates are far less than metals such as Cu, due to the contact resistance between each CNT of which they consist. Therefore, metallization of the CNT templates is a promising process to give them enough electrical conductivity. On the contrary, CNTs have strong anisotropy in electrical and thermal properties [147]. Therefore, the orientation of CNTs which make up the templates is also important in order to achieve the expected properties of metal/CNT composites. Fabrication conditions in these articles are listed in **Table 4**.

Table 4. Fabrication conditions of Metal/CNT Composites by Electrodeposition using CNT Template.

CNT Template	Feature of CNT Template	Metal	Plating Bath	Remarks	Year	Ref.
MWCNT film	Super-aligned	Cu, Ni	Acid sulfuric bath + glucose Dull Watts Bath	Improved mechanical and electrical properties	2019	[148]
MWCNT film	Super-aligned	Ni	Dull Watts Bath	Improved mechanical properties	2019	[149]
SWCNT paper (Bucky paper)	Orientation: in-plane direction	Cu	Acid sulfate bath + polyethylene glycol + Cl^- + bis(3-sulfopropyl) disulfide + Janus green B	One-step electrodeposition by a combination of additives	2017	[150]
MWCNT paper	Super-aligned	Cu	Acid sulfuric bath + glucose + polyethylene glycol + Cl^- Alkaline bath (EDTA, Citrate)	Electrical conductivity	2017	[151]
MWCNT film	Super-aligned	Cu	Acid sulfuric bath + glucose	Improved mechanical properties	2016	[152]
MWCNT film	Super-aligned	Cu	Acid sulfuric bath + glucose	Improved mechanical properties	2015	[153]
SWCNT yarn	Straight	Cu	Acid sulfate bath	Graphen growth on the surface of electrodeposited Cu	2021	[154]
MWCNT yarn	Twisted	Cu	Acid sulfate bath + polyethylene glycol + Cl^- + bis(3-sulfopropyl) disulfide + Janus green B	One-step electrodeposition by a combination of additives	2020	[155]
CNT yarn	Straight	Cu	Acid sulfate bath	Superior current carrying capacity	2018	[156]
MWCNT yarn	Twisted	Cu	$(CH_3COO)_2$ + CH_3CN Acid sulfuric bath	Effect of CNT yarn density	2018	[157]
MWCNT yarn	Twisted	Cu	Cu $(CH_3COO)_2$ + CH_3CN Acid sulfuric bath	Two-step electrodeposition Uniform composite wire	2017	[158]
MWCNT yarn	Twisted	Cu	$(CH_3COO)_2$ + CH_3CN Acid sulfuric bath	Two-step electrodeposition Electrical properties, Solderability,	2017	[159]

CNT Template	Feature of CNT Template	Metal	Plating Bath	Remarks	Year	Ref.
MWCNT yarn	Straight	Cu	Acid sulfuric bath	Electrodeposition of Cu interior of CNT yarn	2016	[160]
MWCNT yarn	Twisted	Ag, Pt	KNO_3+$AgNO_3$ H_2SO_4 + $H_2Pt_6Cl_6$	Improved tensile strength and electrical conductivity	2013	[161]
MWCNT yarn	Twisted	Cu	Acid sulfuric bath + octyl phenyl poly (ethylene gylcol) ether	Continuous process: fiber spinning, anodization, electrodeposition	2011	[162]
MWCNT yarn	Twisted	Au, Pd, Pt, Cu, Ag, Ni	Metal salt solution	Self-fueled electrodeposition Improved electrical conductivity	2010	[163]

5. Conclusions

The fabrication process can be classified into three types: (1) composite plating by electrodeposition and electroless deposition, (2) metal coating on CNTs by electroless deposition, and (3) electrodeposition using CNT templates. In the composite plating, homogeneous dispersion of CNTs in plating baths is essential and, consequently, various processes, such as the addition of dispersants and introduction of hydrophilic groups on CNTs, have been studied. Numerous articles on Ni/CNT or Ni-P alloy/CNT composites by composite plating have been published and their excellent tribological properties and improved corrosion resistances have been reported. Many papers on Cu/CNT composites have also been published and their properties, such as electrical conductivity, have been investigated. The further elucidation of the mechanism of CNT composite plating process is expected. In the metal coating on CNTs by electroless deposition, the pre-treatments, such as sensitization and activation, are important. Oxidization of CNTs is useful for coating CNTs perfectly. A lot of articles on Ni-P alloy-coated CNTs have been published. In the electrodeposition using CNT templates, many papers on Cu/CNT composites using CNT sheets and CNT yarns have been published and their electrical properties have been reported. The preparation process to deposit Cu not only on the surfaces but also on the interior of CNT templates is likely the key technical point.

The practical applications of these technologies are expected in future work.

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