CHEMISTRY LETTERS, pp. 337-340, 1987.

Chemical Deposition in Liquid Phase (CDL). A Convenient Method for Cobalt- or Nickel-coating of Carbon Fibers Using Zerovalent Organometallic Compounds[1)]

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$Co_2(CO)_8$ and $Ni(COD)_2$ (COD=1,5-cyclooctadiene) can be used for Co- and Ni-coating of carbon fibers, respectively, by the chemical deposition in liquid phase (CDL) method in sharp contrast to the chemical vapor deposition (CVD) method which requires vaporization of organometallic compounds.

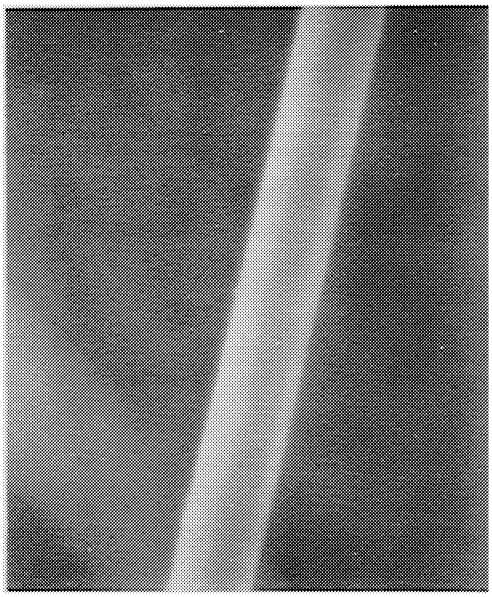
Coating of carbon fibers with metals, especially Fe, Co, or Ni which is unreactive with carbon at ambient temperature,[2)] is very attractive not only for the protection of carbon fibers from the reaction with aluminum in CF/Al composites (carbon fibers reinforced aluminum composites)[3)] but for the development of novel functionalized fibers. We have recently reported the chemical deposition in liquid phase (CDL) method using organometallic compounds such as triisobutylaluminum and iron pentacarbonyl is very useful for improving the wettability and for uniformly coating carbon fibers with corresponding metal.[1,4)]

The CVD method using organometallic compounds has been one of the methods for metal-coating at low temperature.[5)] However, a very limited number of organometallic compounds have been used to produce pure metals, because the CVD method requires vaporization of organometallic compounds. It is, therefore, difficult to use organometallic compounds which do not have low boiling points such as commercially available $Co_2(CO)_8$ as the starting materials for coating by the CVD method. In fact, there have been no reports on successful cobalt-coating by the CVD method using $Co_2(CO)_8$.[6)] This presents a major limitation of the CVD method using organometallic compounds. On the other hand, no organonickel compounds except extremely toxic $Ni(CO)_4$[7)] have been used for nickel-coating by the CVD method.

These situations prompted us to investigate Co- or Ni-coating of carbon fibers by our CDL method using zerovalent organometallic compounds such as $Co_2(CO)_8$ and $Ni(COD)_2$ which are not vaporizable at low temperature. Zerovalent metal compounds ML_n (L = ligand) can afford pure metals without reducing agents by the thermal decomposition along with quantitative recovery of ligands, as exemplified in the following equation. Although several papers, thus far, suggested the metal deposition from zerovalent transition metal complexes used as catalysts for organic syntheses, its applications to materials were rarely reported.[8)]

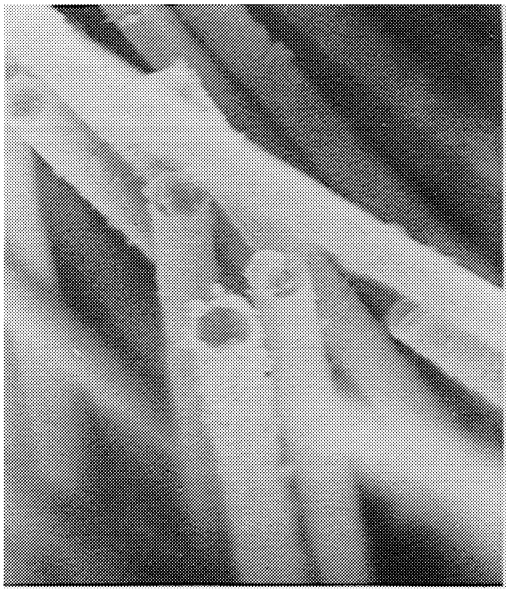
$$ML_n \longrightarrow M + n\,L$$

A representative CDL procedure for cobalt coating of carbon fibers using $Co_2(CO)_8$ is as follows. To a solution of 2.1 g of $Co_2(CO)_8$ in 80 ml of diphenylmethane were immersed 0.22 g of carbon fibers under a nitrogen atmosphere and the mixture was heated up to 150 °C. After stirring it at the same temperature for 6 h, the solvent was removed. The coated carbon fibers and cobalt metal deposited were washed with hexane and dried in vacuo. Cobalt metal was deposited from $Co_2(CO)_8$ in 86% yield. The carbon fibers were coated with 62% of cobalt metal based on $Co_2(CO)_8$.[9] Nickel coating was carried out in a similar manner using $Ni(COD)_2$. Nickel metal was produced in 80% in total at 180 °C for 1 h. On the fibers 54% of nickel metal was deposited. Carbon fibers coated with nickel or cobalt metal by the CDL method were observed by Scanning Electron Microscope (SEM) and Electron Probe Microanalyzer (EPMA) as shown in Photos. Nickel and cobalt metals on carbon fibers were investigated by X-ray diffractometer(Figs. 1 and 2). Nickel metal obtained from $Ni(COD)_2$ was a mixture of the cubic and hexagonal types, according to its X-ray diffraction spectrum as shown in Fig. 1. In the case of cobalt coating, it is noteworthy that only cubic crystals were obtained.



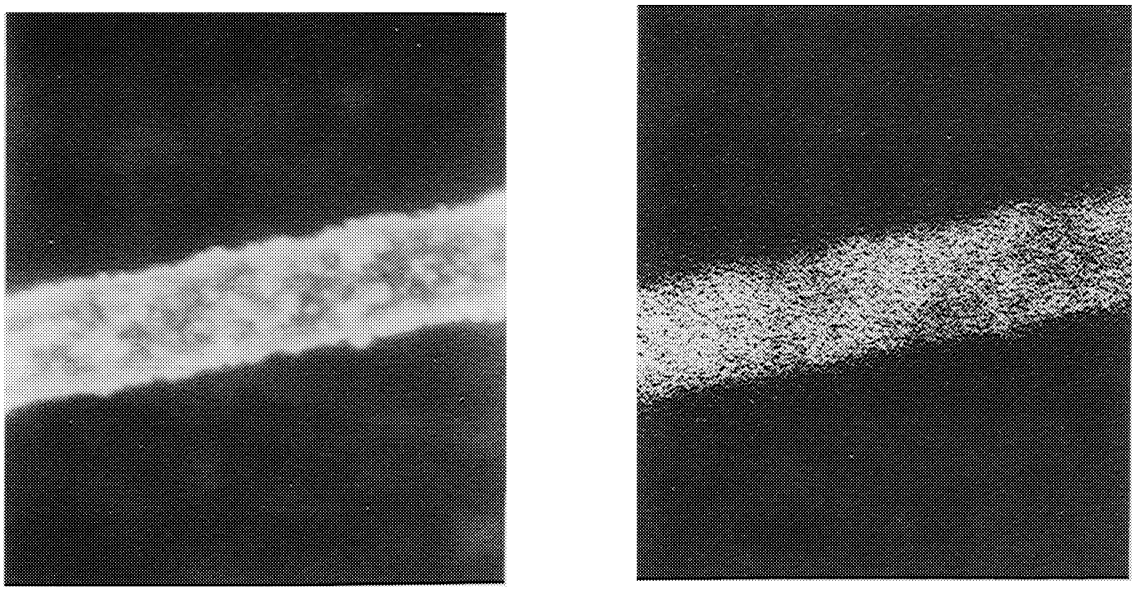
6 μm

Photo 1. The SEM picture of carbon fibers without coating.



9 μm

Photo 3. The SEM picture of Carbon fibers with cobalt metal.



(a) The SEM picture (b) The characteristic X-ray picture

Photo 2. The pictures of carbon fibers coated with nickel metal by CDL.

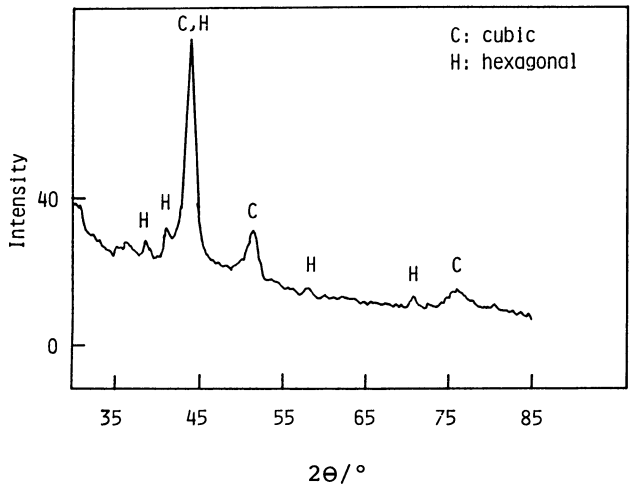


Fig 1. X-Ray diffraction spectrum of Ni metal deposited by CDL.

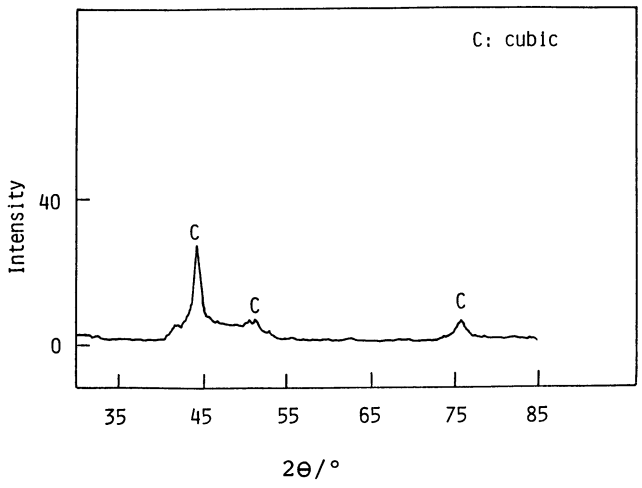


Fig. 2. X-Ray diffraction spectrum of Co metal deposited by CDL.

The effect of ligands on complexes is remarkable. Nickel zerovalent compound with olefin such as $Ni(COD)_2$ gave pure nickel metal in high yields, whereas $Ni(PPh_3)_4$, which is a common catalyst for cross coupling reactions,[10] afforded only trace amount of nickel metal even at 250 ℃ as shown in Table. $Ni(bpy)_2$ gave nickel

Table 1 Yields of nickel or cobalt from nickel or cobalt compounds by CDL method[a)]

Organometallic Compounds	T / ℃	Time /h	Yields of metal/%
$Ni(COD)_2$	180	1	80
$Ni(PPh_3)_4$	180	1	tr
	250	1	tr
$Ni(bpy)_2$	180	1	25[b]
$Co_2(CO)_8$	150	6	86

a)The decomposition reaction was carried out in diphenylmethane. b)X-Ray diffraction spectrum showed several unknown peaks in addition to peaks assigned to nickel cubic and hexagonal crystals.

metal in 25% yield. Labile ligands such as olefin compared with phosphine or 2,2'-bipyridine[11)] are effective for producing pure metal. The deposition of nickel metal under CDL condition has no relations to the decomposition points of nickel compounds in the solid state (135-140 ℃ for $Ni(COD)_2$;[12)] 122-124 ℃ for $Ni(PPh_3)_4$[13)] and 155 ℃ for $Ni(bpy)_2$[13)]).

Further investigations of advantage of CDL method are now in progress.

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(Received November 25, 1986)