METAL COATING CARBON SUBSTRATES
James S. Hill, Cranford, N.J., assignor to Engelhard Minerals & Chemicals Corporation, Newark, N.J., a corporation of Delaware
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ABSTRACT OF THE DISCLOSURE

Carbonaceous materials are provided with an adherent solderable metal coating by initially depositing a nickel coating on the carbon surface by immersion plating, treating the coated substrate at elevated temperature until substantially non-metallic in appearance, replating the treated substrate with a second metal and heating to diffusion bond the second metal to the initially deposited coating.

This invention relates to coatings on carbon and, particularly, to a process for coating a carbonaceous surface with an adherent metal coating having good solderability. Carbon, particularly the graphite form of carbon, has utility in the fabrication of electrical contacts, e.g., for use as contact points in motors and generators and as semiconductor contact points. In order to effectively employ graphite in electrical contact applications, it is necessary to provide a firm, adherent and solderable metallic film to the contact element. Graphite is relatively porous and readily penetrated by many liquids and gases. The high porosity and poor surface hardness of graphite render it difficult to provide an adherent metallic coating to the graphite surface and to which electrical leads can be soldered without causing spalling and flaking of the metallic coating.

In accordance with the present invention, an improved adherent metal coating is applied to a carbon substrate by electron beam depositing a thin layer of nickel on the carbon substrate; heating the coated substrate at a temperature above about 800° C. until substantially non-metallic in appearance; depositing a second metal coating on the treated substrate and heating the coated substrate at a temperature of from about 500° C. to about 700° C., for a time sufficient to bond the second metal to the treated substrate.

In practicing the process of the present invention, carbonaceous material, for example graphite contact points which are preferably fabricated of pyrolytic graphite, are first brushed free of loose surface material and then coated with a thin deposit of nickel by the chemical reduction method. This chemical reduction method, more commonly known as electroless plating, employs a series of specific steps which include "sensitizing" the substrate surface with a reducing agent in the form of a stannous salt bath, rinsing off the stannous solution, "activating" the surface in a noble metal salt solution, and then electroless plating. Such techniques of electroless plating are by now well known in the art, and need not be further described in detail. For the purpose of depositing nickel on the "activated" and "sensitized" surface, well-known electroless nickel plating baths, e.g., baths of the type disclosed in Buell and Reddell, U.S. Pat. No. 2,532,281, or in Gutzeit et al., U.S. Pat. Nos. 2,658,841 and 2,658,842, may be employed in the practice of the present invention.

I have found that graphite pellets, nickel coated by the electroless process, cannot be fitted with contact wires by soldering. Attempts to lead solder a copper wire to the nicked coated pellets results in severe spalling and complete lack of adherence of the copper wire to the substrate.

In order to obtain readily solderable surfaces on graphite, the nickel-coated graphite substrate is first heated to a temperature of at least 800° C. and to 1100° C., preferably 900° C. to 950° C. in a non-oxidizing atmosphere until the metallic appearance of the coated graphite substantially disappears and the surface becomes black in color, followed by cooling in a non-oxidizing atmosphere to ambient temperature. Generally the heat treatment is effected for a period of from 0.5 to about 2 hours and the loss of metallic appearance probably indicates the formation at least in part of nickel carbide in the surface layer.

As a second step in the process of the present invention, the heated graphite substrate is reactivated and sensitized, and a second metallic layer deposited electrolessly thereon employing well-known electroless plating solutions. As the second metallic layer, any metal which will diffusion bond with the nickel and/or nickel carbide layer already present on the substrate surface can be used, e.g., cooper, nickel, chromium, iron, cobalt and the like. Preferably, the second metal is cooper or nickel. After depositing the second metal on the substrate, the coated substrate is heated to a temperature of about 500° C. to about 700° C., sufficient to cause diffusion bonding of the second metal coating with the first coating, but below the temperature at which substantial formation of any metallic carbide will occur.

Graphite substrates metallized as described herein could be readily fitted with soldered wire leads without spalling of the surface coating.

EXAMPLE 1
Graphite pellets of 0.5" diameter and .05" thickness were sensitized by immersion in a stannous chloride activator solution consisting of:
Stannous chloride—10 gm.
Concentrated hydrochloric acid—40 ml.
Distilled water—1 liter.
for a period of two minutes.

The pellets were then washed with water and immersed for about two minutes in a sensitizing solution consisting of:
\[ \text{PdCl}_2 \]—1 gm.
Concentrated hydrochloric acid—1 ml.
Distilled water—1 liter

The sensitized pellets were washed thoroughly with distilled water and then nickel-plated by the electroless method at 70°-75° C. for one hour in a proprietary nickel plating solution prepared by mixing 250 ml. Enplate 410A and 125 ml. Enplate 410B (products of the Ethnene Corp., West Haven, Conn.) diluting with 400 ml. water and adjusted to a pH of 4.5 by addition of 2 M NaOH, then filtering and adding 1100 ml. water.

At the end of one hour, at which time approximately 50 mg. Ni/cm² had been deposited, the pellets were removed from the plating solution, washed with distilled water and dried.

Attempts to lead-solder a copper wire to the nickel-coated pellets resulted in spalling.

EXAMPLE 2
The procedure of Example 1 was repeated, except that the plated pellets after drying were placed in an alundum boat containing alundum sand to prevent the pellets from sticking together. The pellets were then heated in a hydrogen atmosphere at 930° C. for 3½ hour, followed by cooling in H₂ to ambient temperature. The heated pellets...
no longer had a metallic appearance and were black in color.

The treated pellets were then reactivated and sensitized by the procedure of Example 1, and subsequently immersion-plated in the nickel solution of Example 1 for one hour. After remetallizing, the pellets were heated as before to a temperature of 600° C. in H₂ followed by cooling in H₂ to ambient temperature. The pellets retained their metallic appearance and a copper wire was readily lead soldered to the coated pellets of this Example.

EXAMPLE 3

Pyrolytic graphite pellets were activated and sensitized by treatment with stannous chloride and palladium chloride solutions as described in Example 1.

The treated pellets were washed thoroughly with distilled water and then nickel plated by the electroless method at 85° C. by immersion for one hour in a solution consisting of

\[ \text{NiCl}_2 \cdot 6\text{H}_2\text{O} - 30 \text{ gm.} \]
\[ \text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O} - 10 \text{ gm.} \]
\[ \text{Sodium acetate} - 3 \text{ gm.} \]
\[ \text{Distilled water} - 1 \text{ liter} \]

The pellets were then removed from the plating solution, washed with distilled water, dried, and then heated in a hydrogen atmosphere at 930° C. for ½ hour followed by cooling to ambient temperature in a hydrogen atmosphere.

The pellets, now black in appearance, were again activated and sensitized as before and subsequently immersed for one hour in a plating solution at 95° C. consisting of

\[ \text{NiSCN} \cdot 6\text{H}_2\text{O} - 17 \text{ gm.} \]
\[ \text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O} - 24 \text{ gm.} \]
\[ \text{Sodium acetate} - 41 \text{ gm.} \]
\[ \text{Acetic acid} - 30 \text{ gm.} \]
\[ \text{Distilled water} - 1 \text{ liter} \]

After remetallizing the pellets were heated to 600° C. followed by cooling in hydrogen.

A copper wire was readily lead soldered to the coated pellets of this example without spalling.

EXAMPLE 4

Pyrolytic graphite pellets were activated and sensitized in accordance with the procedures outlined above. Then the treated pellets were washed with distilled water and metallized by immersion for one hour at 85° C. in the nickel chloride plating solution of Example 3. Next the metallized pellets were washed with distilled water, dried and heated for ½ hour in hydrogen at 930° C. followed by cooling to room temperature in a hydrogen atmosphere.

The pellets were reactivated and sensitized by the procedure previously described and subsequently immersed for ½ hour in an electroless copper plating bath consisting of

Potassium sodium tartrate—79 gm.
Copper sulfate—28 gm.
Sodium hydroxide—20 gm.
Sodium carbonate—32 gm.
Distilled water—1.5 liters
Formaldehyde—10 cc.

After metallizing with copper, the pellets were heated to 600° C. in a hydrogen atmosphere followed by cooling. The pellets retained their bright copper metallic appearance.

The copper coated pellets were found to be readily solderable.

What is claimed is:

1. A method for providing a solderable metal coating on a carbonaceous substrate which method comprises depositing a nickel film on the substrate by plating from an electroless nickel plating solution, treating the coated substrate in a non-oxidizing atmosphere at a temperature between about 800° C. and about 1100° C. for a period of from 0.5 to about 2 hours until substantially non-metallic in appearance, cooling the coated substrate in a non-oxidizing atmosphere to ambient temperature, depositing a second metallic film on said treated substrate by electroless plating and heating the thus coated substrate at a temperature of about 500° C. to about 700° C. to cause diffusion bonding of said second metal coating with the first formed coating.

2. The method of claim 1 wherein said second metallic film is composed of nickel.

3. The method of claim 1 wherein said second metallic film is composed of copper.

4. The method of claim 1 wherein the carbonaceous substrate is pyrolytic carbon.

References Cited

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ALFRED L. LEAVITT, Primary Examiner
C. K. WEIFFENBACH, Assistant Examiner

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