Synthesis of Cobalt Coated Nickel Powders for Improving the Stability of the Resistivity of PPTC Materials

Bin Fang, Sheng Gao, Xueping Ge, Cunzhong Yang

Institute of Nuclear Technology and Application, School of Science, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, People's Republic of China

Correspondence to: B. Fang (E-mail: binfang@ecust.edu.cn)

ABSTRACT: Nickel powders coated by cobalt (Co@Ni powders) on the surface have been obtained by reduction in the ethylene glycol. The morphology and composition were characterized by scanning electron microscope and energy dispersive X-ray spectroscopy. The valence states of cobalt in the sample were determined by X-ray photoelectron spectroscopy. The Co@Ni powders were used as the electrically conductive fillers in the polymeric positive temperature coefficient (PPTC) materials in which polyethylene was used as the matrix. The stability of the resistivity of PPTC materials has been improved due to the protection and electrical conductivity of the cobalt layers on the surface of Ni powders. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polymer-based positive temperature coefficient (PPTC) materials are composites of electrically conductive fillers incorporated into a polymer matrix. In recent years, this kind of composites is of special interest because of its great potential application in temperature-sensitive devices.[1–6] To obtain the ideal properties, different electrically conductive fillers have been applied. Carbon black[7] (CB) is the most universal conductive filler among them. However, CB-filled PPTC composites suffer from some drawbacks, especially the relatively high ambient temperature resistivity. To lower the resistivity, the metal powders are introduced as the conductive fillers into the polymer matrix alternatively. From the economical and practical point of view, Ni powders are more attractive because the lower price and better electrical conductivity. Unfortunately, Ni powders have lower weathering resistance due to the oxidation, which will reduce the stability of PPTC materials by increasing its ambient resistivity.[8] To overcome this drawback, the surface modification of Ni powders has been conducted. For example, Ni powders were coated by silver and used as electrically conductive fillers for PPTC materials,[9] but the stability was still not improved. Besides, the high price of noble metal also limits the general application of this method. In a recent work by Kato et al., Ni/Co alloy powders through reducing the nickel chloride and cobalt chloride had been prepared,[8]

and used as electrically conductive fillers in PPTC materials. The stability of the resistivity of this kind of PPTC material was improved to some extent; however, the ambient temperature resistivity was relatively high compared with Ni-filled PPTC materials, in addition the preparation procedure was very complex.

In this article, a novel preparation route was introduced to improve the weathering resistance of Ni powders. The surface of Ni powders was modified by coating a layer of cobalt (Co@Ni powders) and investigated by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). The Co@Ni powders were introduced into PPTC materials as the electrically conductive fillers, and the stability of the resistivity of PPTC materials was found to be improved obviously.

EXPERIMENTAL

Materials

Ni powders (Shenzhen Dongdalai Chemical Co, Guangdong, China) were washed in dilute hydrochloric acid to remove the oxidized layer before use. Cobalt (II) chloride hexahydrate (analytical grade, Sinopharm Chemical Reagent Co, Shanghai, China), ethylene glycol, and hydrazine hydrate (analytical grade, Lingfeng Chemical Reagent Co., Shanghai, China) were all used as received.
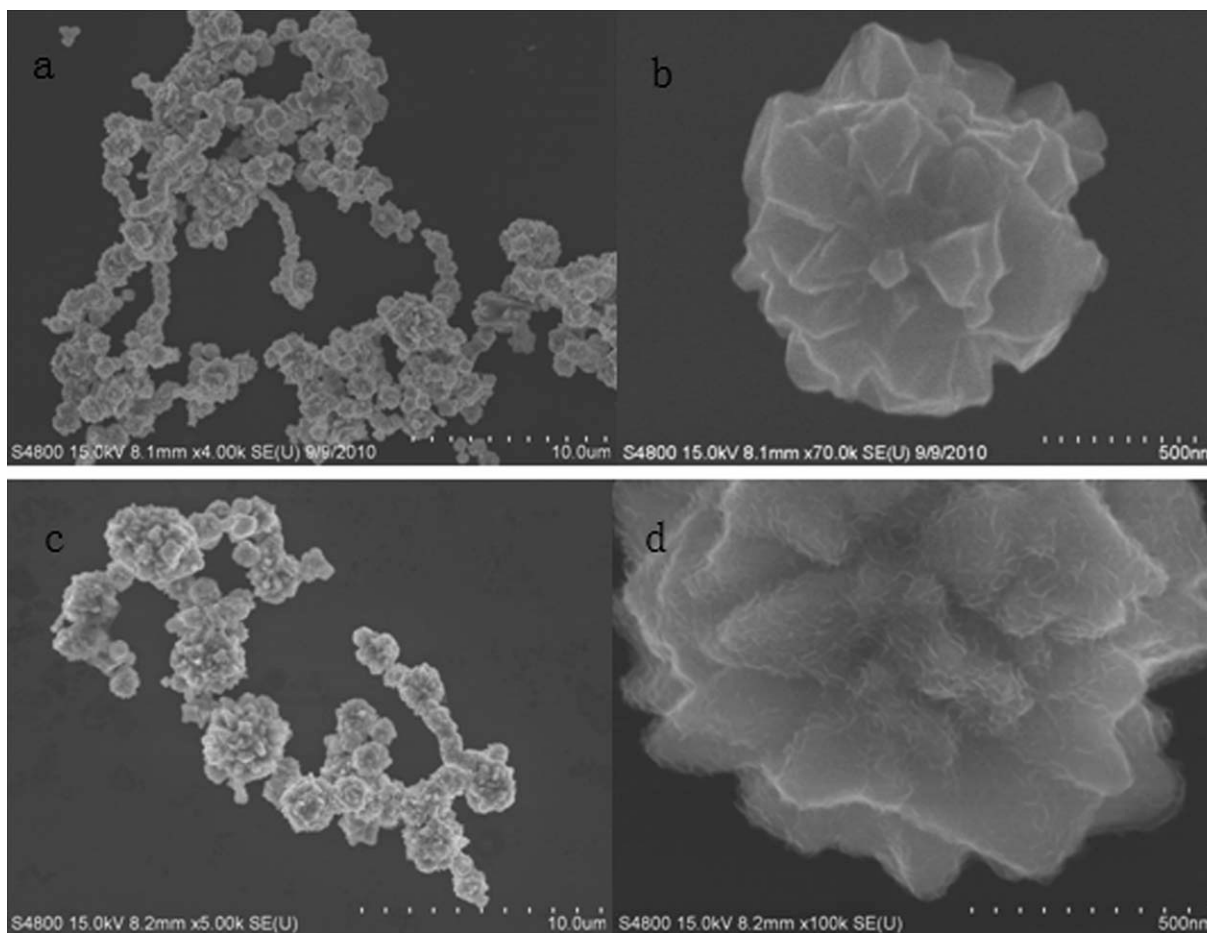
Figure 1. SEM images of the commercially obtained Ni powders (a and b) and the Co@Ni powders (c and d).

Preparation of the Co@Ni Powders

The cobalt (II) chloride hexahydrate (2 g) was first dissolved in ethylene glycol (50 mL) to form the solution, then the solution was mixed with ethylene glycol (750 mL) and Ni powders (160 g) in a flask. The mixture was stirred and heated to 81°C while hydrazine (40 mL) mixed with an appropriate amount of NaOH was dropwise added. After 1 h, the reaction products were collected by filtration and then washed with ethanol several times. The resulting powders were dried in vacuum at 80°C for 12 h.

Preparation of PPTC Materials Sample

The Co@Ni powders (140 g) prepared above or commercially obtained Ni powders were mixed with polyethylene (20 g) in the roll mill at 160°C for 10 min. The resulting conductive composites and two layers of nickel foils were hot pressed under 10 Mpa at 160°C for 5 min to obtain the sandwich-structure devices with nickel foils covered on both sides. The devices were then irradiated in a ^{60}Co γ-ray source with 0.72 MGy dose. The devices were further punched into pieces of $3 \times 4 \times 0.4$ mm^3.

The Characterization of the Co@Ni Powders

The morphology of the Co@Ni powders was investigated with a Hitachi S-4800 SEM. The composition was determined by EDS. XPS was carried out on a RBD instruments upgraded PHI-5000C
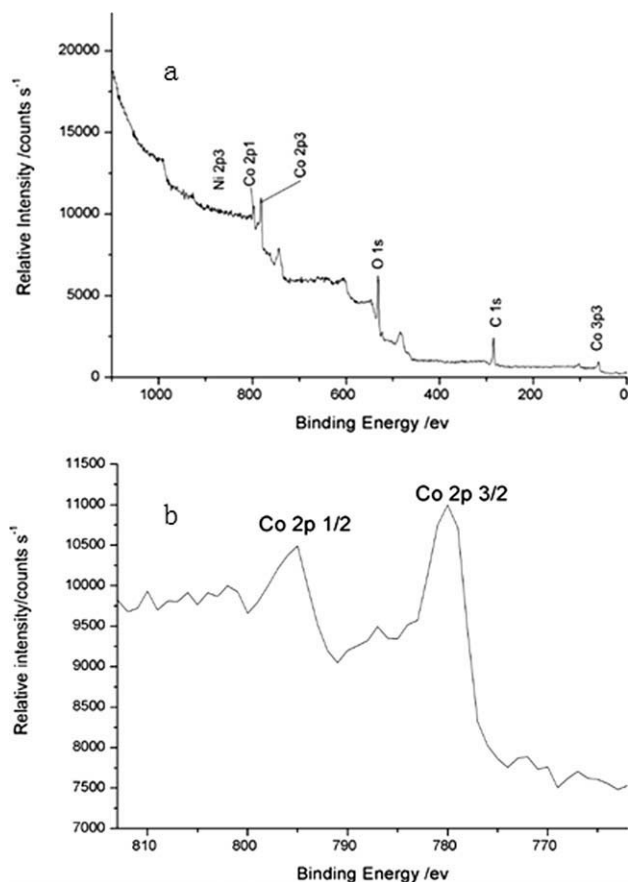
ESCA system (Perkin Elmer) with Mg Kα radiation ($hv = 1253.6$ eV) to investigate the valence states of the coated cobalt.

The Measurements of the Resistances of PPTC Materials

The resistance of PPTC materials was measured on an AT510 resistance test instrument (range: 1 $\mu\Omega$–3 MΩ) through the
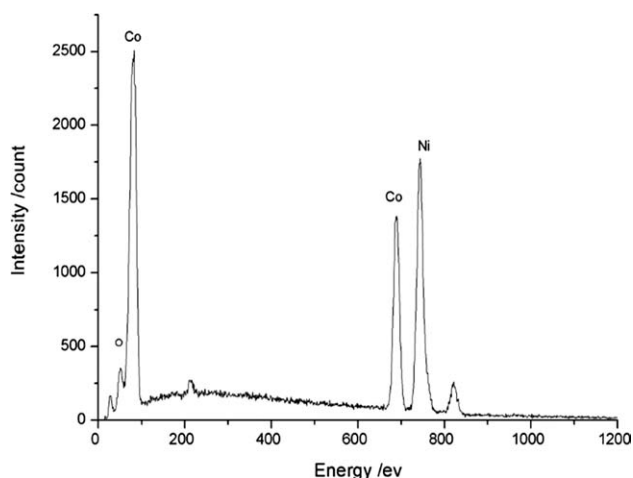
Figure 2. EDS spectrum of the Co@Ni powders.

Figure 3. XPS spectra (a) survey spectrum of the Co@Ni powders (b) close-up spectrum of Co 2p.

four-point method. After the initial resistance test, PPTC materials were thermally aged at 150°C for half an hour then slowly cooled down to room temperature. The thermal aging treatment was performed every 24 h and lasted for 11 days. After each thermal aging treatment, the resistivity of the samples was measured.

RESULTS AND DISCUSSION

Morphology and Composition Analysis
Figure 1 shows the SEM images of the commercially obtained Ni powders and the Co@Ni powders obtained through reduction. For commercially obtained Ni powders, no obvious deposition was observed on the surface [Figure 1(b)]. While for the Co@Ni powders, threadlike deposition was observed evidently [Figure 1(d)]. It could be concluded that the coating on the surface of Ni powders was successful.

The Co@Ni powders were further characterized by energy dispersive X-ray Spectroscopy (EDS) to determine the composition. The results from Figure 2 indicate that the dominating elements in the powders are Co and Ni. As the oxygen peak which is much smaller than the peaks of Co and Ni was also observed, it could be believed that the Co layers were successfully coated onto the surface of the Ni powders and parts of the Co layers were oxidized.

XPS Analysis
The results of XPS analysis are shown in Figure 3. As seen from the Figure 3(a), the peak for oxygen further indicates that the cobalt layers were partially oxidized. Meanwhile, the peak for Ni was very weak, because the XPS signal might not penetrate the layer of cobalt. The results further confirm that the Ni powders were well coated by cobalt on the surface.

The close-up spectrum of Co 2p is shown in Figure 3(b). It was found that part of coated cobalt was in metallic state with $2P_{1/2}$ and $2P_{3/2}$ peaks at 793.1 and 778.2 ev, while part of the cobalt was oxidized with $2P_{1/2}$ and $2P_{3/2}$ peaks at 797.1 and 780.0 ev. That is, the Co layers on the surface of the Ni powders are miscellanies that consist of metallic and oxidized cobalt.

Mechanism of the Reductive Reaction
Hydrazine hydrate as reducing agent behaves powerfully to reduce the Co^{2+} ion into metallic Cobalt under the alkaline condition. Hydrazine hydrate is oxidized into nitrogen without contamination to the product.
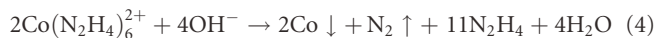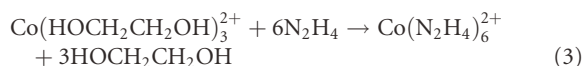
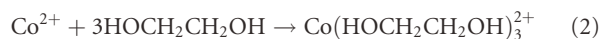$$2Co^{2+} + N_2H_4 + 4OH^- \rightarrow 2Co \downarrow + N_2 \uparrow + 4H_2O \qquad (1)$$
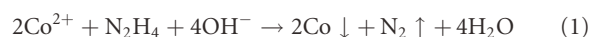
Hydrazine hydrate not only serves as the reducing agent but also can form complex with Co^{2+} in ethanol.[10,11] The reactions
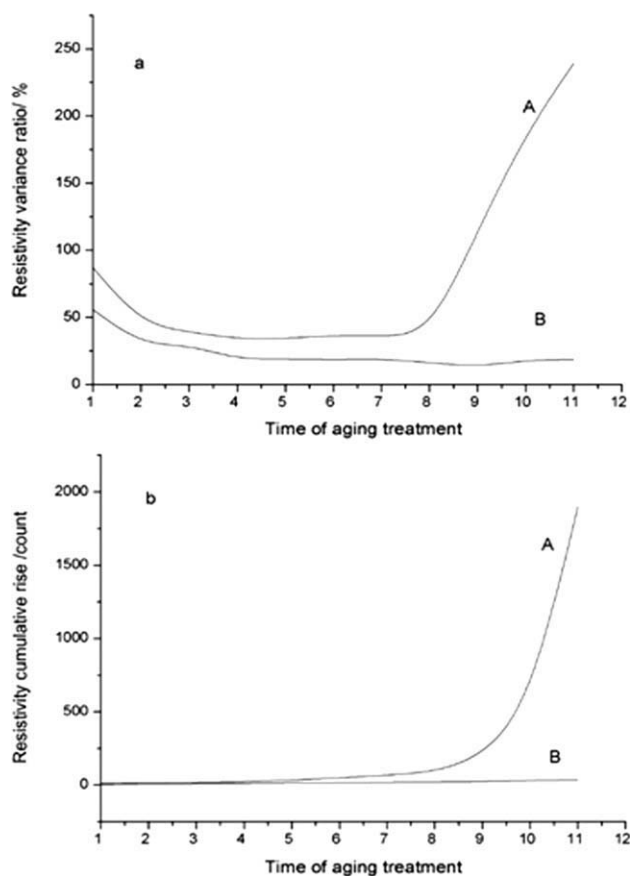
Figure 4. (a) Resistivity variance ratio (k) (b) resistivity cumulative rise (V) (A: PPTC materials with commercially obtained Ni powders; B: PPTC materials with the Co@Ni powders).

of hydrazine hydrate reducing Co^{2+} under the ethylene glycol condition might be as follows:

$$Co^{2+} + 3HOCH_2CH_2OH \rightarrow Co(HOCH_2CH_2OH)_3^{2+} \quad (2)$$

$$Co(HOCH_2CH_2OH)_3^{2+} + 6N_2H_4 \rightarrow Co(N_2H_4)_6^{2+} + 3HOCH_2CH_2OH \quad (3)$$

$$2Co(N_2H_4)_6^{2+} + 4OH^- \rightarrow 2Co \downarrow + N_2 \uparrow + 11N_2H_4 + 4H_2O \quad (4)$$

Study of the Stability of the Resistivity of PPTC Materials

The stability of the resistivity of PPTC materials can be characterized by two parameters:

$$k = (a_{n+1} - a_n)/a_n \quad (5)$$

$$V = a_n/a_0 \quad (6)$$

Where k is the resistivity variance ratio and V is the resistivity cumulative rise of PPTC materials. a_0, a_n, and a_{n+1} stand for the resistivity value of PPTC samples after the 0, n, and $n+1$ time of aging treatment, respectively.

The resistivity variance ratio and resistivity cumulative rise dependence of thermal aging treatment times is shown in Figure 4(a) and (b), respectively. For Ni-filled PPTC materials, the resistivity variance ratio is 90% after the first time of treatment and decreases to about 50% between the second and the seventh treatment. From the eighth treatment, the value of resistivity variance ratio goes up and reaches about 250% after the eleventh treatment. The sharp increase is generally believed to be caused by the oxidation of Ni powders. Whereas, for PPTC materials with the Co@Ni powders, the resistivity variance ratio continuously decreases from 50% after the first time of thermal aging treatment to 18% after the eleventh treatment. The resistivity cumulative rise of PPTC materials is shown in Figure 4(b), it is clearly evident that the resistivity of Ni-filled PPTC materials is almost 2000 times of its initial value after 11 times of thermal aging treatments. In contrast, the resistivity of PPTC materials with the Co@Ni powders only increases 36 times of its initial value.

The results indicate that the stability of the resistivity of PPTC materials with the Co@Ni powders has been improved. The cobalt and oxidized cobalt layer coated on the surface of Ni powders might reduce further corrosion of Ni powders, due to that the addition of cobalt to the nickel plaque as a nickel–cobalt alloy was suggested as a way to reduce corrosion of nickel plaque.[12] Moreover, the good electrical conductivity[13,14] of the cobalt layer on the surface of Ni powders might also enhance that of Ni powders.

CONCLUSION

In summary, the Co@Ni powders were prepared through reduction in the ethylene glycol. Subsequently, the surface-modified Ni powders were used as the electrically conductive fillers in PPTC materials. The resistivity variance ratio was observed as 250% for Ni-filled PPTC materials after 11 times of thermal aging treatments, whereas the value for PPTC materials with the Co@Ni powders decreased from 50% of the first-time treatment to 18% of the eleventh treatment. Furthermore, the resistivity cumulative rise decreased from 2000 of the Ni-filled PPTC materials to 36 of PPTC materials with the Co@Ni powders. The stability of the resistivity of PPTC materials with Co@Ni powders has been improved apparently due to the protection and electrical conductivity of the cobalt layer on the surface of Ni powders.

REFERENCES

1. Naofumi, M. US, Pat 7,652,860 (**2010**).
2. Shi, C. L. US, Pat 0,290,785 (**2007**).
3. David, A. H.; Bernard, J. L.; Robert, S. J. US, Pat 4,654,511 (**1987**).
4. Lee, M. M.; Joseph, H. E.; Pettengill, D. F. US, Pat 4,238,812 (**1980**).
5. Niets, P. T.; Bjarke, H. US, Pat 5,033,713 (**1991**).
6. Cédric, C.; Vladan, K.; Maryline, L.; Claude, D. *J. sensors* **2007**, *7*, 473.
7. Yu, G.; Zhang, M. Q.; Zeng, H. M. *J. Appl. Polym. Sci.* **1998**, *70*, 559.
8. Kato, T.; Itou, K.; Okada, S.; Tanaka A.; Nomura, K. Eur. Pat 1,974,840 (**2008**).
9. Kato, T.; Okada, S.; Futaki, S. US, Pat 7,186,289 (**2007**).
10. Zheng, H.-G.; Zeng J.-H.; Liang, J.-H. *J. Acta Metall. Sin.* **1999**, *35*, 837.
11. Zheng, H. G.; Liang, J.-H.; Zeng, J.-H. *J. Mater. Res. Bull.* **2001**, *36*, 47.
12. Kuklinski, J.; Russell, P.G. *J. Power Sources* **1998**, *76*, 11.
13. Lichtenberg, F.; Kleinsorgen, K. *J. Power Sources* **1996**, *62*, 207.
14. Pralong, V.; Chabre; Y.; Delahaye V. A.; Tarascon J. M. *J. Solid State Ionics* **2002**, *147*, 73.