

# Electroless plating and magnetic properties of Co–Zn–P coating on short carbon fibres

XINGHUA SU<sup>†</sup> and CHENGWEN QIANG\*

Institute of Modern Physics, Chinese Academy of Science, Lanzhou 730000, China

<sup>†</sup>School of Materials Science and Engineering, Chang'an University, Xi'an 710061, China

MS received 28 February 2011; revised 26 March 2012

**Abstract.** A layer of Co–Zn–P alloys was coated on short carbon fibre (CFs) surfaces using electroless plating method. The influence of the concentration of Co<sup>2+</sup> and Zn<sup>2+</sup> and reaction time on the plating rate were measured by comparing the relative mass gain rate of Co–Zn–P-coated fibres with uncoated carbon fibres prepared under different conditions. The materials characterizations were analysed by field emission scanning electron microscopy, X-ray diffraction and energy dispersive spectroscopy. The magnetic properties of Co–Zn–P/CFs composites prepared in different Zn<sup>2+</sup> concentration baths were measured by the vibrating sample magnetometer. The best processing parameters of electroless plating of Co–Zn–P coating on short carbon fibres were obtained.

**Keywords.** Electroless plating; magnetic properties; Co–Zn–P coating; short carbon fibres.

## 1. Introduction

Since carbon fibres and carbon fibre composites have many advantages such as high specific strength, high modulus, high temperature resistance, corrosion resistance, fatigue and creep resistance, electrical and thermal conductivity, light weight, low thermal expansion coefficient (Peebles 1995), they have always been new compelling industrial materials used in aviation, aerospace, machinery, chemical and medical industries, as well as sports and other fields (Donnet *et al* 1990; Chand 2000). Since a major breakthrough was achieved in the production process of carbon fibres prepared from organic precursor in the 60s, carbon fibre composites preparation process, protecting and improving the compatibility between carbon fibres and matrix by modification of carbon fibre surface become important. During the past few years, researchers coated inorganic non-metallic or metallic substances on carbon fibres for the surface modification by processes such as sol–gel method, chemical vapour deposition, physical sputtering, precursor impregnation paralysis method, electro and electroless plating, plasma spray, etc (Georgolios *et al* 1989; Abraham *et al* 1990; Matsumoto *et al* 1993; Severini *et al* 2002; Park and Kim 2005; Hackl *et al* 2006; Tang *et al* 2008; Tang and Kardos 2010), and achieved many important results. Among them, electroless plating is widely used in the surface modification of carbon fibres and carbon fibres composites preparation, with uniform thickness and low pinhole rate of coatings, simple equipment and convenient operation features (Li and Tu 2003). On the other hand, carbon fibres surface metallization can expand its further use. Carbon fibres with metal coating can be used as

shielding materials with good shielding effect (Huang and Wu 2000); improve infiltration between metal matrix and carbon fibres effectively and has a wide range of use in making a high-capacity but small capacitors, thin magnetic films and a variety of functional applications (Fitzer *et al* 1984; Abraham *et al* 1990; Yang *et al* 2003). Due to the excellent electromagnetic properties of Co–Zn–P alloy (Matsuda and Akano 1988; Saito 2006; Yuan *et al* 2007), we tried to make Co–Zn–P alloy on short carbon fibres by electroless plating to modify the carbon fibre surfaces and prepared a new kind of magnetic carbon composites in this work.

## 2. Experimental

### 2.1 Electroless Co–Zn–P deposition

The carbon fibres with 3000 filaments were used. The diameter of the single flakes was from 7 to 9  $\mu\text{m}$ . Before deposition, carbon fibre bundles were cut into short fibres with length of 2 ~ 3 mm, the sizing materials on carbon fibre surfaces were removed by immersing them into acetone solution for 2 h. A two-step pre-treatment, sensitization and activation were used for catalyzing the carbon fibres. The sensitizer and activator were stannous chloride/hydrochloric acid (30 g/l SnCl<sub>2</sub>·2H<sub>2</sub>O and 50 ml/l HCl) and silver nitrate/ammonia (5 g/l AgNO<sub>3</sub> and 15 ml/l NH<sub>3</sub>·H<sub>2</sub>O). Ultrasonic vibration was applied during catalyzing treatment to facilitate uniform activation throughout entire surfaces of the carbon fibres. The Co–Zn–P coatings were deposited on carbon fibres using an alkaline bath containing cobalt sulfate and zinc sulfate as the source of cobalt and zinc. Sodium hypophosphite was used as the reduction agent and sodium citrate as a complex. Table 1 lists bath composition, deposition temperature and

\*Author for correspondence (qiangchw04@gmail.com)

pH value. Different electroless plating solutions were prepared in stoichiometric proportion, in which  $[\text{CoSO}_4 \cdot 6\text{H}_2\text{O}] + [\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}] : [\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}] : [\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}] = 1:1:3$ , and NaOH solution were used to adjust its pH value to 9. Argon gas was used to stirring in the bath throughout the whole electroless plating process. Co–Zn–P/CFs composites were washed with distilled water and dried in a vacuum drying oven at 60 °C for 6 h. The purity of chemicals used in this work was of AR level.

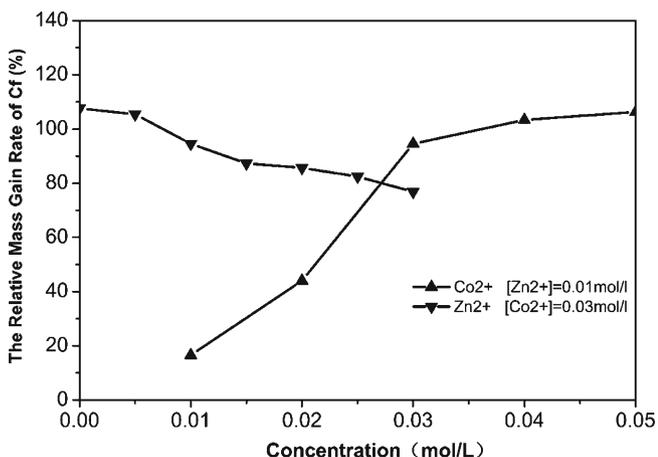
## 2.2 Characterizations

In order to investigate effect of concentration of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  and reaction time on the rate of electroless plating, an electronic weighing scale with an accuracy of 0.00001 g was used to weigh the quality of carbon fibres before and after electroless plating under different conditions. The composition, structure and morphology of Co–Zn–P/CF composites were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM, S4800 and JSM-6701F) and energy dispersive spectrometer (EDS). The magnetic properties of Co–Zn–P/CFs composites were measured with a vibrating sample magnetometer (VSM, Lake Shore 7304) at room temperature.

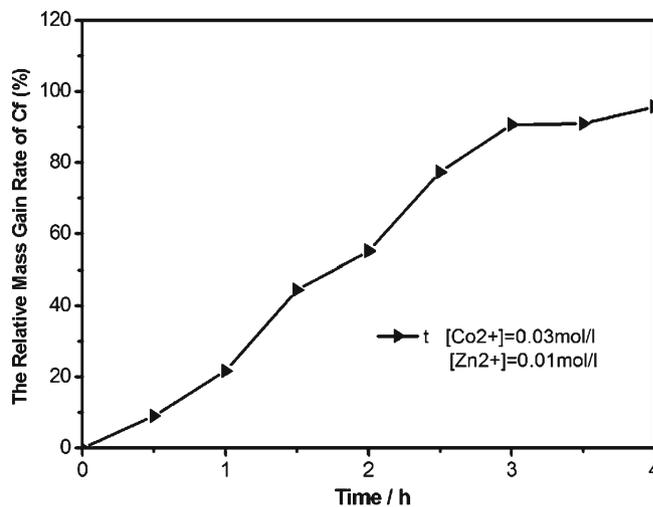
**Table 1.** Formulations and operation conditions of electroless cobalt–zinc plating baths.

Chemical	Formula	Content (mol/l)
Cobalt sulfate	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	0.01~0.05
Zinc sulfate	$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$	0~0.03
Sodium hypophosphite	$\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$	0.01~0.08
Sodium citrate	$\text{Na}_3\text{C}_6\text{H}_7 \cdot 2\text{H}_2\text{O}$	0.03~0.24
Boric acid	$\text{H}_3\text{BO}_3$	0.05
Sodium hydroxide	NaOH	0.01 (pH adjustment)

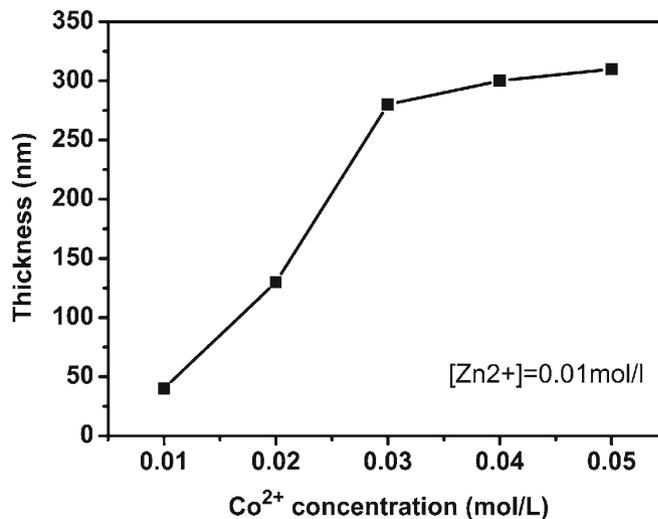
\*Bath temperature, 90 °C; pH value, 9.



**Figure 1.** Relative mass gain rate of Co–Zn–P/CFs prepared in different  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  concentration baths.



**Figure 2.** Relative mass gain rate of Co–Zn–P/CFs with electroless plating time increasing.

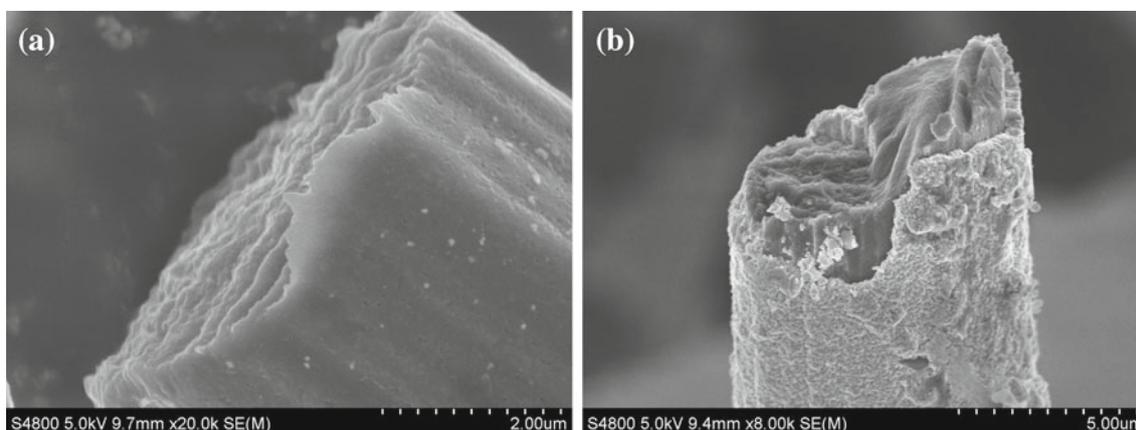


**Figure 3.** Correlation between  $\text{Co}^{2+}$  concentration and thickness of Co–Zn–P coatings.

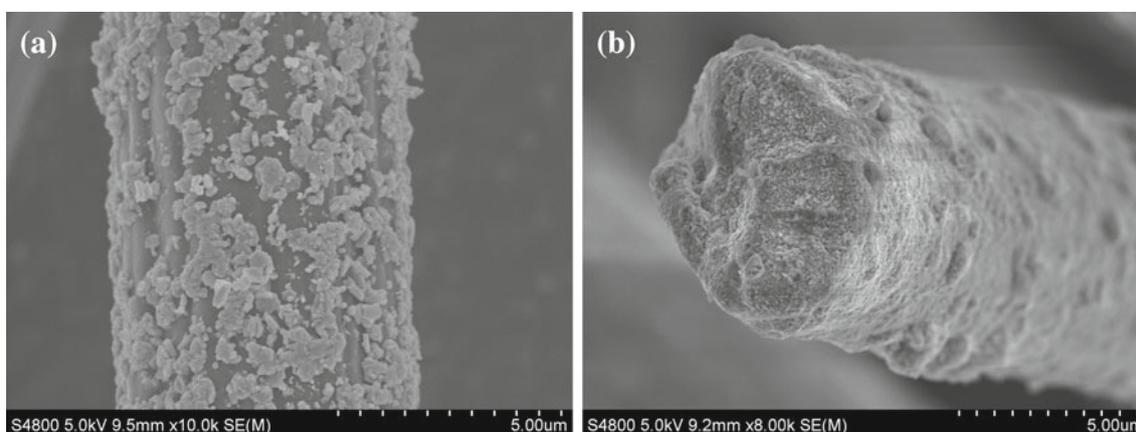
## 3. Results and discussion

### 3.1 Factors affected on plating rate

The effects of concentrations of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  on the plating rate in different cobalt–zinc baths are shown in figure 1. The bath temperature is 90 °C, pH = 9 and reaction time is 4 h. It is clear that when the concentration of  $\text{Zn}^{2+}$  is 0.01 mol/l, the relative mass gain rate of carbon fibres before and after plating initially increases significantly as the concentration of  $\text{Co}^{2+}$  increased, but the increasing trend becomes slow when the concentration of  $\text{Co}^{2+}$  is more than 0.03 mol/l. When the concentration of  $\text{Co}^{2+}$  is 0.03 mol/l, the relative mass gain rate of Co–Zn–P/CFs can reach 94.6%. On the other hand, relative mass gain rate of Co–Zn–P/CFs composites before and after plating decreases from 107.6% to 76.9% as the



**Figure 4.** SEM images of Co–Zn–P/CFs electroless plating for 3 h in different  $\text{Co}^{2+}$  concentration baths. (a)  $[\text{Co}^{2+}] = 0.01 \text{ mol/l}$ ,  $[\text{Zn}^{2+}] = 0.01 \text{ mol/l}$  and (b)  $[\text{Co}^{2+}] = 0.03 \text{ mol/l}$ ,  $[\text{Zn}^{2+}] = 0.01 \text{ mol/l}$ .



**Figure 5.** SEM images of Co–Zn–P/CFs prepared in a plating bath containing  $\text{Co}^{2+}$  concentration of  $0.03 \text{ mol/l}$  and  $\text{Zn}^{2+}$  concentration of  $0.02 \text{ mol/l}$  with different times for (a)  $0.5 \text{ h}$  and (b)  $3 \text{ h}$ .

concentration of  $\text{Zn}^{2+}$  increased due to the inhibitory effect of zinc on alloy deposition in electroless plating process (Bouanani *et al* 1999), when the concentration of  $\text{Co}^{2+}$  is  $0.03 \text{ mol/l}$  in the plating baths. Figure 2 shows that with the reaction time increasing, relative mass gain rate of Co–Zn–P/CFs composites increases under a certain condition. The relative mass gain rate can reach 90.6% when the electroless plating process lasts for 3 h and then the increasing rate becomes slow. The correlation between  $\text{Co}^{2+}$  concentrations and thickness of Co–Zn–P films is shown in figure 3.

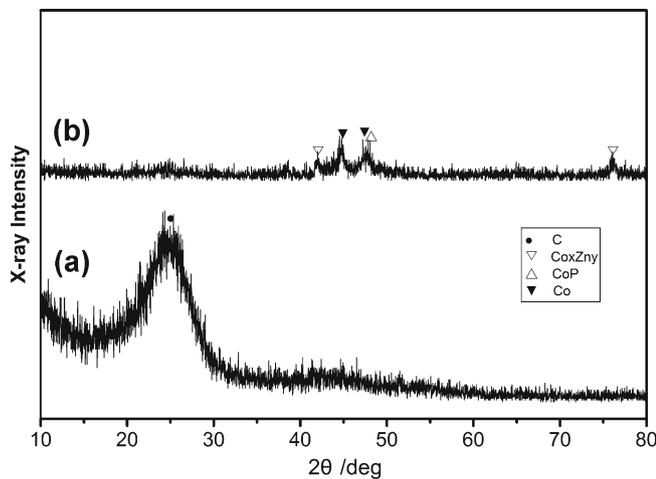
Figure 4 shows SEM images of Co–Zn–P/CFs composites prepared in different  $\text{Co}^{2+}$  content plating baths. The surface morphology shows Co–Zn–P coating on carbon fibres is thin (about 40 nm) but very smooth in a low  $\text{Co}^{2+}$  concentration bath. As the concentration of cobalt increases gradually, thickness and surface roughness of Co–Zn–P coating increase, the coating thickness is about 300 nm when the concentration of  $\text{Co}^{2+}$  is  $0.04 \text{ mol/l}$ . It indirectly indicates that the deposition rate of alloys increase with increasing of  $\text{Co}^{2+}$  content in plating baths.

Figure 5 shows coating at the early growth period when the plating time is  $0.5 \text{ h}$ , chemical deposition reaction starts around the discontinuous catalytic active centres on short carbon fibres and Co–Zn–P alloys deposited and formed a number of isolated nucleuses. Alloys deposited continuously as the reaction time increased, nucleus grew up into a uniformly continuous coating when plated for 3 h.

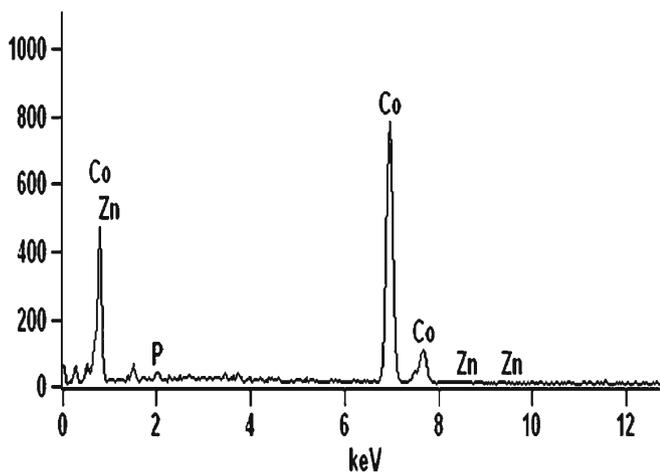
### 3.2 Composition and structure analysis

XRD is used to analyse phases of the products. In this work, XRD measurement is carried out using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ nm}$ ) from a sealed tube operated at 45 kV and 40 mA. Figure 6 shows XRD pattern of uncoated and coated carbon fibres. It is found that Co–Zn–P coatings have an amorphous structure but contain a small amount of dispersed  $\text{Co}_x\text{Zn}_y$ , CoP and Co microcrystalline with some weak and broadening diffraction peaks emerging at  $2\theta = 45^\circ$ ,  $48^\circ$  and  $77^\circ$ .

Figure 7 shows energy dispersive spectroscopy (EDS) image of Co–Zn–P/CFs composites prepared in a plating



**Figure 6.** XRD pattern of (a) uncoated and (b) coated carbon fibres.

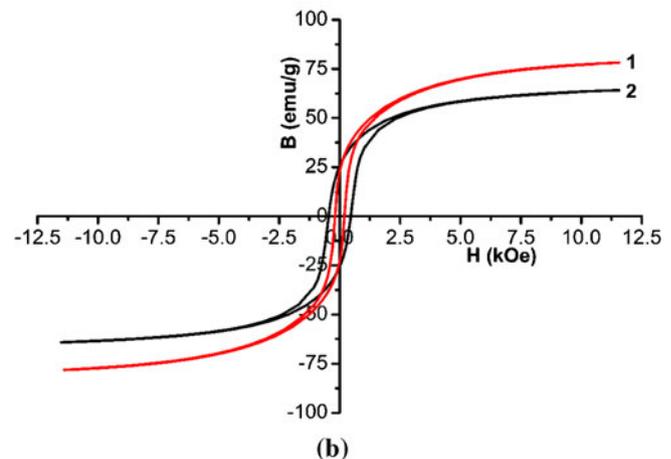
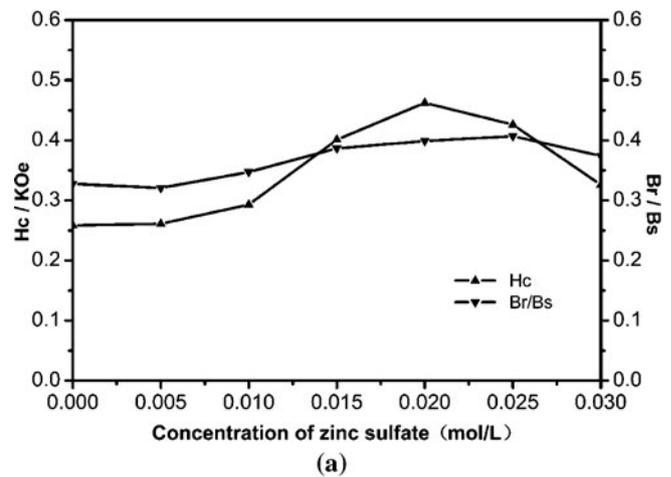


**Figure 7.** Energy dispersive spectroscopy image of Co-Zn-P/CFs.

bath with  $\text{Co}^{2+}$  concentration of 0.03 mol/l and  $\text{Zn}^{2+}$  concentration of 0.02 mol/l. The atomic ratio of Co:Zn:P is 95:62:2.93:1.45 and it confirms that the coatings are composed of Co, Zn and P.

### 3.3 Effect of zinc concentration on Co-Zn-P/CFs composites magnetic properties

As shown in figure 8a, when other conditions remain unchanged, the coercivity ( $H_c$ ) and remanence square ratio ( $B_r/B_s$ ) of Co-Zn-P/CFs composites increase at first and then decrease as the concentration of  $\text{Zn}^{2+}$  in the baths increased further, the coercivity reaches its maximum of 462.4 Oe when  $[\text{Zn}^{2+}] = 0.02$  mol/l and the remanence square ratio reaches its maximum of 0.407. On comparing the static magnetic hysteresis loop line of Co-P/CFs composites with that of Co-Zn-P/CFs composites (figure 8b), it is found that coercivity and remanence square ratio of the materials are much large, but saturation magnetization is



**Figure 8.** (a) Effect of  $\text{Zn}^{2+}$  concentration on Co-Zn-P/CFs composites magnetic properties and (b) magnetic hysteresis loop line of Co-P/CFs (1) and Co-Zn-P/CFs (2) electroless plating for 3 h in bath containing  $\text{Co}^{2+}$  concentration of 0.03 mol/l and  $\text{Zn}^{2+}$  concentration of 0.025 mol/l.

**Table 2.** Best processing parameters of electroless plating of Co-Zn-P on short carbon fibres.

Chemicals	Formula	Content (mol/l)
Cobalt sulfate	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	0.03
Zinc sulfate	$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$	0.02~0.025
Sodium hypophosphite	$\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$	0.05~0.055
Sodium citrate	$\text{Na}_3\text{C}_6\text{H}_7 \cdot 2\text{H}_2\text{O}$	0.15
Boric acid	$\text{H}_3\text{BO}_3$	0.05
Sodium hydroxide	NaOH	0.01 (pH adjustment)
Temperature		90 °C
Time		3 h
pH value		9

small when the coatings contain zinc. This is related to the small amounts of  $\text{Co}_x\text{Zn}_y$  phase existing in coatings. Zeng *et al* reported that the carbon fibres exhibited paramagnetism (Zeng and Xu 2009; Zeng *et al* 2009). These results indicate that the change of zinc concentration in Co-Zn-P coatings

has a great effect on materials magnetic properties (Matsuda and Akano 1988; Saito 2006).

The best processing parameters of electroless plating of Co–Zn–P on short carbon fibres obtained from the above experimental results are shown in table 2.

#### 4. Conclusions

The relative mass gain rate of Co–Zn–P/CFs significantly increased as the concentration of  $\text{Co}^{2+}$  increased, and then it increased slowly when  $[\text{Co}^{2+}]$  was over 0.03 mol/l. But it gradually decreased as the concentration of  $\text{Zn}^{2+}$  increased and then it continuously increased with the reaction time prolonging when the Co–Zn–P/CFs composites were prepared under certain conditions. The coercivity and remanence square ratio of Co–Zn–P/CFs composites increased at first and then decreased with the concentration of  $\text{Zn}^{2+}$  in plating baths increased.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China under grant No. 51102022, the China Postdoctoral Science Foundation under grant No. 2011M501426, the Specialized Research Fund for the Doctoral Program of Higher Education under grant No. 20110205120001, the Special Fund for Basic Scientific Research of Central Colleges, Chang'an University under grant No. CHD2012ZD015 and CHD2011JC134 and the Special Fund for Basic Research support programs of Chang'an University.

#### References

- Abraham S, Pal B C, Satyanarayana K G and Vaidyan V K 1990 *J. Mater. Sci.* **28** 39 25
- Bouanani M, Cherkaoui F, Belcadi S, Fratest P and Roventi G 1999 *J. Appl. Electrochem.* **11** 71 29
- Chand S 2000 *J. Mater. Sci.* **13** 03 35
- Donnet J B, Bansal R C and Wang M J 1990 (New York: Bulletin of Materials Science)
- Fitzer E, Gkogkidis A and Heine M 1984 *High Temp. High Press.* **3** 63 16
- Georgolios N, Jannakoudakis D and Karabinas P 1989 *J. Electroanal. Chem.* **234** 264
- Hackl G, Gerhard H and Popovska N 2006 *Thin Solid Films* **217** 513
- Huang C Y and Wu C C 2000 *Eur. Polym. J.* **27** 29 36
- Li N and Tu Z 2003 *Electroless plating and magnetic properties of Co–Zn–P coating on short carbon fibres* (Beijing: Chemical Industry Press)
- Matsuda H and Akano O 1988 *J. Jap. Inst. Metals* **41** 4 52
- Matsumoto A, Ruike M, Suzuki T and Kaneko K 1993 *Colloid. Surf.* **A15** 74
- Park S J and Kim B J 2005 *J. Colloid. Interf. Sci.* **124** 282
- Peebles L H Jr 1995 *Carbon fibres* (USA: CRC Press)
- Saito T 2006 *J. Appl. Phys.* **90** 6 99
- Severini F, Formaro L, Pegoraro M and Posca L 2002 *Carbon* **73** 5 40
- Tang L G and Kardos John L 2010 *Polym. Compos.* **100** 18
- Tang Y P, Deng Y D, Zhang K, Liu L, Wu Y T and Hu W B 2008 *Ceram. Int.* **17** 87 34
- Yang Y *et al* 2003 *J. Magn. Magn. Mater.* **129** 256
- Yuan X Y, Du C S, Sun G and Pan N 2007 *Appl. Surf. Sci.* **45** 46 25
- Zeng J and Xu J C 2009 *Mater. Charact.* **10** 68 60
- Zeng J, Xu J C, Tao P and Hua W 2009 *J. Alloy Compd.* **48** 7 304