Ni–P Alloy–Carbon Black Composite Films Fabricated by Electrodeposition

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Abstract

Ni–P alloy–carbon black (CB) composite films were fabricated by electroplating and their microstructures and properties were examined. The CB and phosphorus contents of the composite films were also investigated. The CB particles were found to be embedded in the Ni–P alloy matrix. The CB content in the deposits increased, reached a maximum value of 0.77 mass % with increasing CB concentration in the bath up to 10 g dm^{-3}, and then decreased with a further increase in the CB concentration in the bath. Both before and after heat treatment, the composite films had higher hardnesses and lower friction coefficients than the Ni–P alloy films. Both before and after heat treatment, the friction coefficient of 0.77 mass % CB composite films was about half that of Ni–P alloy films without CB.

Keywords: Carbon black; Ni-P alloy; Composite film; Electrodeposition

1. Introduction

Grease and lubricant oils cannot be used under certain conditions, such as high temperatures and in a vacuum. Instead, solid lubricants are used to reduce friction and wear. In addition, self-lubricating composites can be prepared from solid lubricants.

Graphite is moderate in price and is an effective solid lubricant. Consequently, methods for fabricating graphite composites (including resin–graphite [1–3], ceramic–graphite [4] and metal–graphite composites [5–8]) have been actively researched. Metal–graphite composites have been fabricated by electrodeposition; for example, chromium–graphite composite coatings [9], graphite–bronze composite coatings [10] and Ni–graphite composites have been prepared by electroforming [11]. However, most research has focused on using micron-sized graphite to form metal–graphite composites.

Coating mechanical components requires a dimensional accuracy of the order of microns, but it is difficult to fabricate composite films that are less than 1 μm thick using micron-sized graphite. However, we believe that this problem can be overcome if composite films are fabricated using nanosized graphite. Since it is difficult to produce nanosized graphite of uniform size, we considered using carbon black (CB) instead.

CB consists of artificially produced nanosized carbon particles with diameters of about

3–500 nm. CB particles are moderate in price and have been used to fabricate various composites, including polymer–CB [12] and rubber–CB [13]. However, there are few reports of metal–CB composites being fabricated.

In the present study, we fabricated composite films from CB by electrodeposition using an Ni–P alloy with a moderate phosphorus content (about 11~18 atom%) as the matrix composite film. In general, Ni–P alloy plating has good corrosion resistance and it can achieve a high hardness by being heat treated. We characterized Ni–P alloy–CB composite films and investigated their microstructures.

2. Experimental

We used a commercially available CB in the present study (Vulcan® XC72, Caboto Co.). The CB particles were about 40 nm in diameter. A Ni–P alloy plating bath (1 M $NiSO_4 \cdot 6H_2O$ + 0.2 M $NiCl_2 \cdot 6H_2O$ + 0.5 M H_3BO_3 + 1 M H_3PO_3 + 0.5 M $C_6H_5Na_3O_7$) was used as the base bath. The CB particles did not disperse uniformly in the base bath, but a homogeneous dispersion of CB particles could be obtained by adding a dispersing agent, polyacrylic acid [14–17] (PA5000; mean molecular weight: 5000), to the base bath and stirring. The composition of the plating baths used in the present study was 1 M $NiSO_4 \cdot 6H_2O$ + 0.2 M $NiCl_2 \cdot 6H_2O$ + 0.5 M H_3BO_3 + 1 M H_3PO_3 + 0.5 M $C_6H_5Na_3O_7$ + 2×10^{-4} M PA5000 + 2–20 g dm^{-3} CB. The plating baths had a pH of about 2.5. The baths were agitated with a magnetic stirrer for 12 h prior to plating. Plating was performed at 50 °C with aeration under galvanostatic conditions (current density: 5 A dm^{-2}, electric charge: 3600 C). A commercially available electrolytic cell (model I, Yamamoto-Ms. Co., Ltd.) with internal dimensions of 65×65×95 mm was employed for electrodeposition. The volume of the plating bath was 250 cm^3. A pure copper plate (C1020P) and a stainless plate (SUS304) with exposed surface areas of 10 cm^2 (3×3.3 cm^2) were used as substrates. A pure nickel plate was used as the anode. The phosphorus content was measured by a calibration method by wavelength-dispersive X-ray fluorescence spectroscopy (ZSX Primus II, Rigaku Co.). The phosphorus content of the standard samples used for calibration was determined quantitatively by an inductively coupled plasma (ICPS-7500, Shimadzu Seisakusho Co.). The CB content in the composite films was determined directly by weighing. For this weight measurement, thick Ni−P alloy−CB composite films (over 2 g in weight) were electrodeposited. In this process, the plating bath was replaced with a new one every 1 h to ensure a uniform phosphorus content in the Ni−P alloy matrix. Subsequently, the Ni−P alloy matrix of the composite films was dissolved in hot nitric acid. The CB in the nitric acid solution was then filtrated, dried and weighed. The deposited films were heated at 400 °C for 1 h in an infrared heating furnace (mini lamp annealer; MILA-3000, ULVAC-RIKO Inc.) in vacuum. Phase structure analysis of the films and the CB particles was performed using by X-ray diffraction (XRD; XRD-6000, Shimadzu Seisakusho Co.). The morphology of the CB particles was observed using an ultrahigh-resolution field-emission scanning electron microscope (S-5500, Hitachi). The surface morphology and cross-sectional texture were observed using a field-emission scanning electron microscope (JSM-7000F, JEOL). A cross-section polisher (SM-09010, JEOL) was used to prepare cross-sectional samples for observation. Hardness testing of the films was performed in the cross-sectional direction using a micro Vickers hardness tester (DUH-201, Shimadzu Seisakusho Co.). The tribological properties of the films were measured using a ball-on-plate reciprocating friction tester (MMS-2419, Nissho Denki Co.). A 6.1-mm-diameter alumina ball (Hv = 1500) was used as the counter surface. The reciprocating friction stroke was 10 mm, and the tests were conducted under a normal load of 2 N. The sliding speed was 0.5 mm s^{-1} and the number of cycles was 50. All measurements were performed under ambient conditions without any lubricants.

3. Results and Discussion

Figure 1 shows SEM image of the CB particles used in this study. The particles were about 20−100 nm in size and their shape was irregular. The CB particles were highly agglomerated. This result demonstrates the necessity of dispersing the CB particles by adding a dispersing agent and agitating the prepared bath in the plating bath to fabricate composite films with uniformly embedded particles.

Figure 2 shows the relationship between the CB concentration in the bath and the CB content in the deposited films. It also shows the phosphorus content in the deposited films. The CB content in the composite films increased with increasing CB concentration for CB concentrations in the range 0 to 10 g dm^{-3}. It is reasonable to assume that the CB concentration on the depositing cathode surface increased with increasing CB concentration in the composite plating bath, resulting in increased incorporation of CB particles in the deposited films. In contrast, with a CB concentration of 20 g dm^{-3} in the composite plating bath, the CB content in the deposited film decreased to less than half that at 10 g dm^{-3}. It is conjectured that the dispersion state of the CB particles in the composite plating bath changed at a CB concentration of 20 g dm^{-3} in the composite plating bath and that the particles condensed. Therefore, it was concluded that at a CB concentration of 20 g dm^{-3} in the composite plating bath, the CB particles condense and form large clusters, which reduces the incorporation of CB particles into the deposited film. The phosphorus content was approximately constant (11.2–13.2 atom%) as a function of the CB concentration in the plating bath. Thus, the CB content in the films has little effect on the phosphorus content in the films.

Figures 3(a) and (b) show surface and cross-sectional SEM images of a Ni–P alloy–0.77 mass % CB composite film, respectively. CB particles were incorporated in the Ni–P alloy matrix, but they agglomerated, producing secondary particles that are homogeneously distributed throughout the matrix. The surface of the composite film was relatively smooth and no voids were observed.

Figures 4(a) and (b) show XRD patterns of the Ni–P alloy–0.77 mass % CB composite film before and after heat treatment, respectively. Before heat treatment, a broad peak assigned to nickel was observed at around 44°. After heat treatment, weak, sharp peaks assigned to nickel and strong, sharp peaks assigned to Ni_3P were observed. These results indicate that heat treatment converts the films into the stable crystalline phase, in agreement with the Ni–P binary alloy phase diagram. No graphite peaks were observed in XRD patterns of the Ni–P alloy–0.77 mass % CB either before or after heat treatment. This is attributed to the amorphous structure of the CB. According to the Ni–C binary alloy phase diagram, Ni–C compounds and solid solutions of nickel and carbon are not formed. Consequently, heat treatment only converted the Ni–P matrix from the amorphous phase into the crystalline phase.

Figure 5 shows the effect of the CB content in the Ni–P alloy–CB composite films on the hardnesses of these films before and after heat treatment. The phosphorus content is almost the same (about 25 atm %) in every film, as shown in Fig. 1. The hardnesses of both the Ni–P alloy film and the Ni–P alloy–CB composite films increased on heat treatment. This is attributed to precipitation of the Ni_3P phase in these films [18–19]. Both before and after heat treatment, the hardness of the Ni–P alloy–CB composite films was higher than that of the CB-free Ni–P alloy film. This increase in the hardness is conjectured to be caused by dispersion hardening of the CB. The hardnesses of the Ni–P alloy–CB composite films remained approximately constant with increasing CB content.

Figure 6 shows the variation in the friction coefficient as a function of the number of cycles for the Ni–P alloy film and the Ni–P alloy–CB composite films prior to heat treatment. The friction coefficient of the Ni–P alloy film increased rapidly in the early stages and then reached a steady value of 0.37. On the other hand, at very low cycle numbers, all the Ni–P alloy–CB composite films had higher friction coefficients than the Ni–P alloy film. However, the friction coefficient of each Ni–P alloy–CB composite film decreased rapidly and then reached a steady value, which is clearly lower than that of the Ni–P alloy film. The friction coefficient of the Ni–P alloy–0.77 mass % CB composite film was 0.17. The friction coefficient of the Ni–P alloy–CB composite films decreased with increasing CB content in these films, which agrees with the trend reported for graphite composite coating [11].

Figure 7 shows the variation in the friction coefficient as a function of the number of cycles for the Ni–P alloy film and the Ni–P alloy–CB composite films after heat treatment. As was the case before heat treatment, the friction coefficient decreased with increasing CB content. The friction coefficient of the Ni–P alloy film increased rapidly in the early stages and then reached a steady value of 0.40. On the other hand, at very low cycle numbers, the Ni–P alloy–CB composite film had higher friction coefficients than the Ni–P alloy film. However, the friction coefficient of each Ni–P alloy–CB composite film decreased rapidly and then reached a steady value, which is clearly lower than that of the Ni–P alloy film. The Ni–P alloy–0.77 mass % CB composite film had a friction coefficient of 0.24. Thus, Ni–P alloy–CB composite films clearly exhibited solid lubrication.

Figure 8 shows SEM images of worn surfaces of the Ni–P alloy film and the Ni–P alloy–0.77 mass % CB composite film before and after heat treatment. CB particles were observed on the worn surface of the Ni–P alloy–0.77 mass % CB composite film both before and after heat treatment. This result also indicates that the CB particles appear to function as a solid lubricant.

4. Conclusions

Ni–P alloy–CB composite films were electrodeposited and their properties were investigated. The main conclusions are as follows:

(1) The CB content in the deposits increased, reached a maximum value of 0.77 mass % with increasing CB concentration in the bath up to 10 g dm^{-3}, and then decreased with a further increase in the CB concentration in the bath due to increasing aggregation of the CB particles. But the phosphorus content remained approximately constant regardless of the CB concentration in the plating bath.

(2) The Ni–P alloy–CB composite films were relatively flat and smooth.

(3) Both before and after heat treatment, the Ni–P alloy–CB composite films had higher hardnesses than the Ni–P alloy film.

(4) The Ni–P alloy–CB composite film had a lower friction coefficient than the Ni–P alloy film under dry conditions before and after heat treatment.

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Figure captions

Fig. 1. SEM image of the CB particles.

Fig. 2. Variation of CB and phosphorus contents in the deposited films with CB concentration in the plating bath.

Fig. 3. (a) Surface and (b) cross-sectional images of a Ni–P alloy–0.77 mass % CB composite film.

Fig. 4. XRD patterns of the Ni–P alloy–0.77 mass % CB composite film (a) before and (b) after heat treatment.

Fig. 5. Relationship between CB content in the films and film hardness before and after heat treatment.

Fig. 6. Variation of the friction coefficient with CB content in a film before heat treatment.

Fig. 7. Variation of the friction coefficient with CB content in a film after heat treatment.

Fig. 8. SEM images of worn surfaces: Ni–P alloy film (a) before and (c) after heat treatment, Ni–P alloy–0.77 mass % CB composite film (b) before and (d) after heat treatment.

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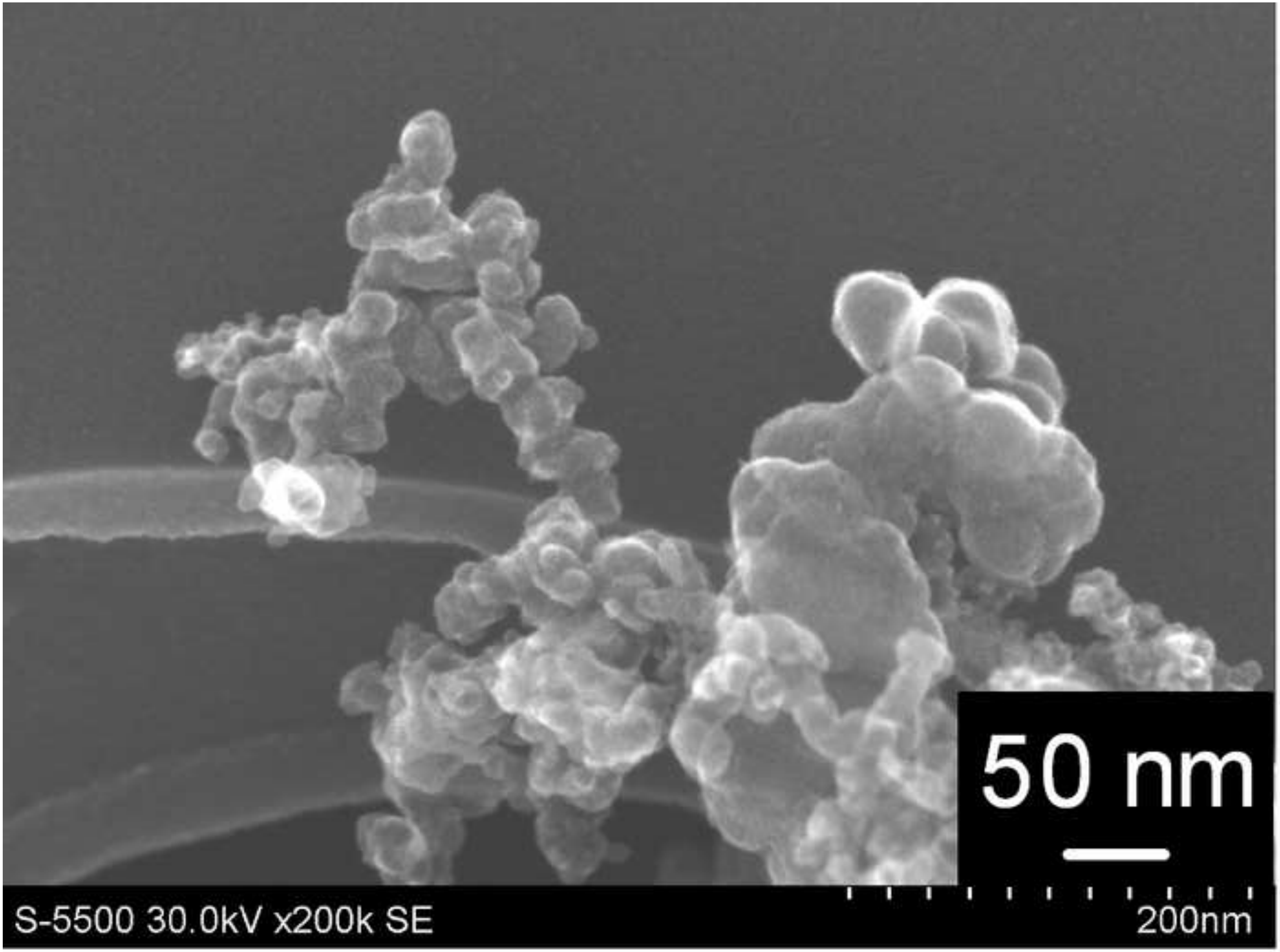
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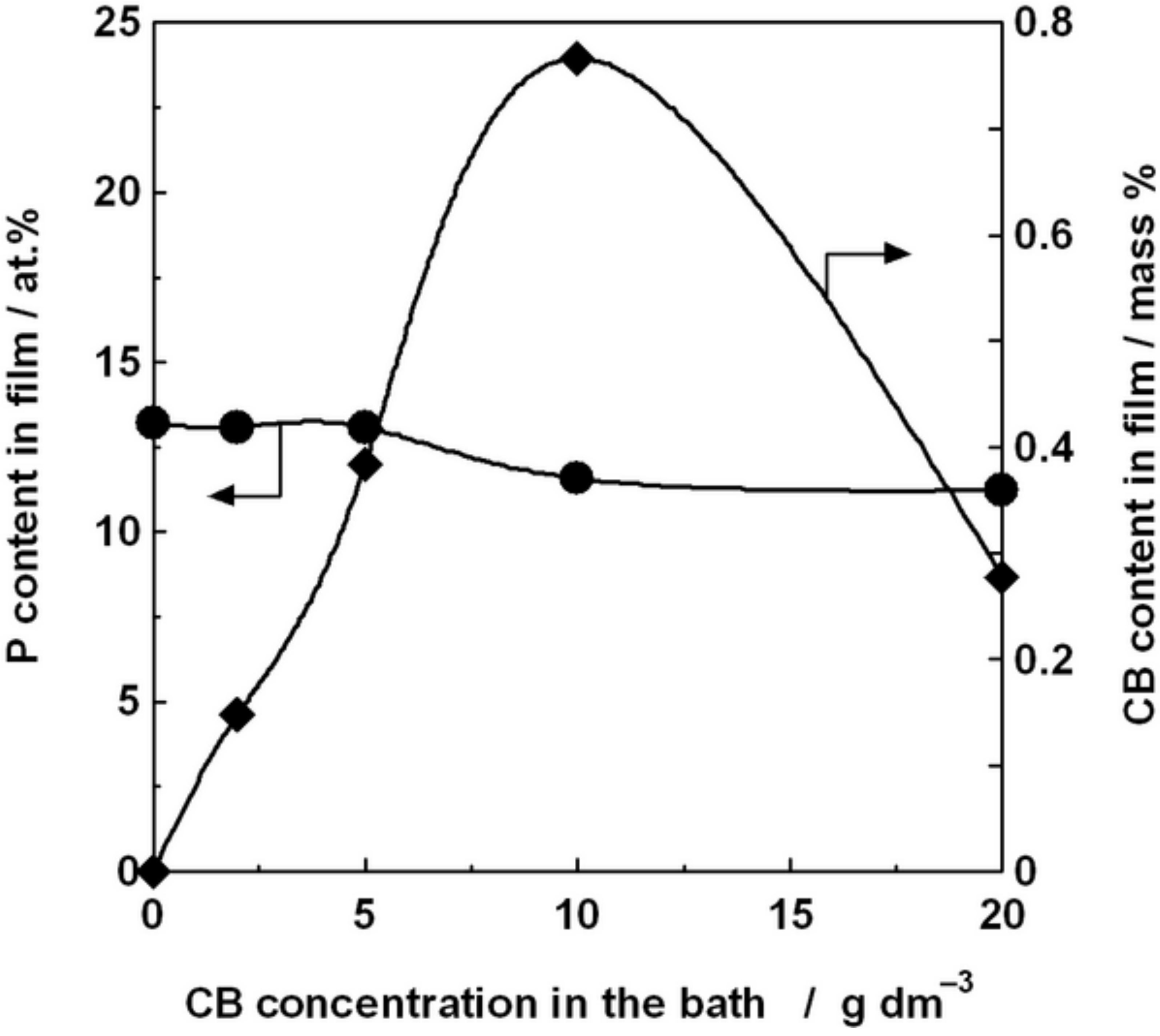

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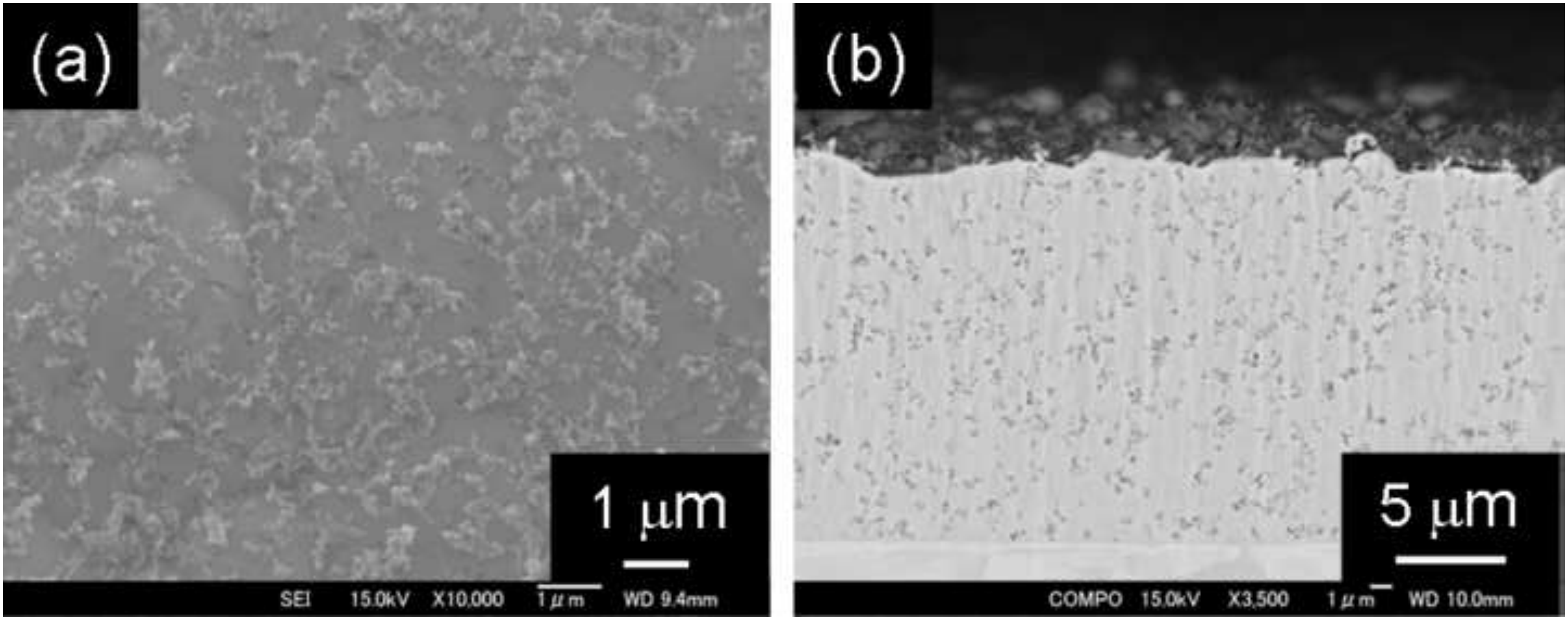

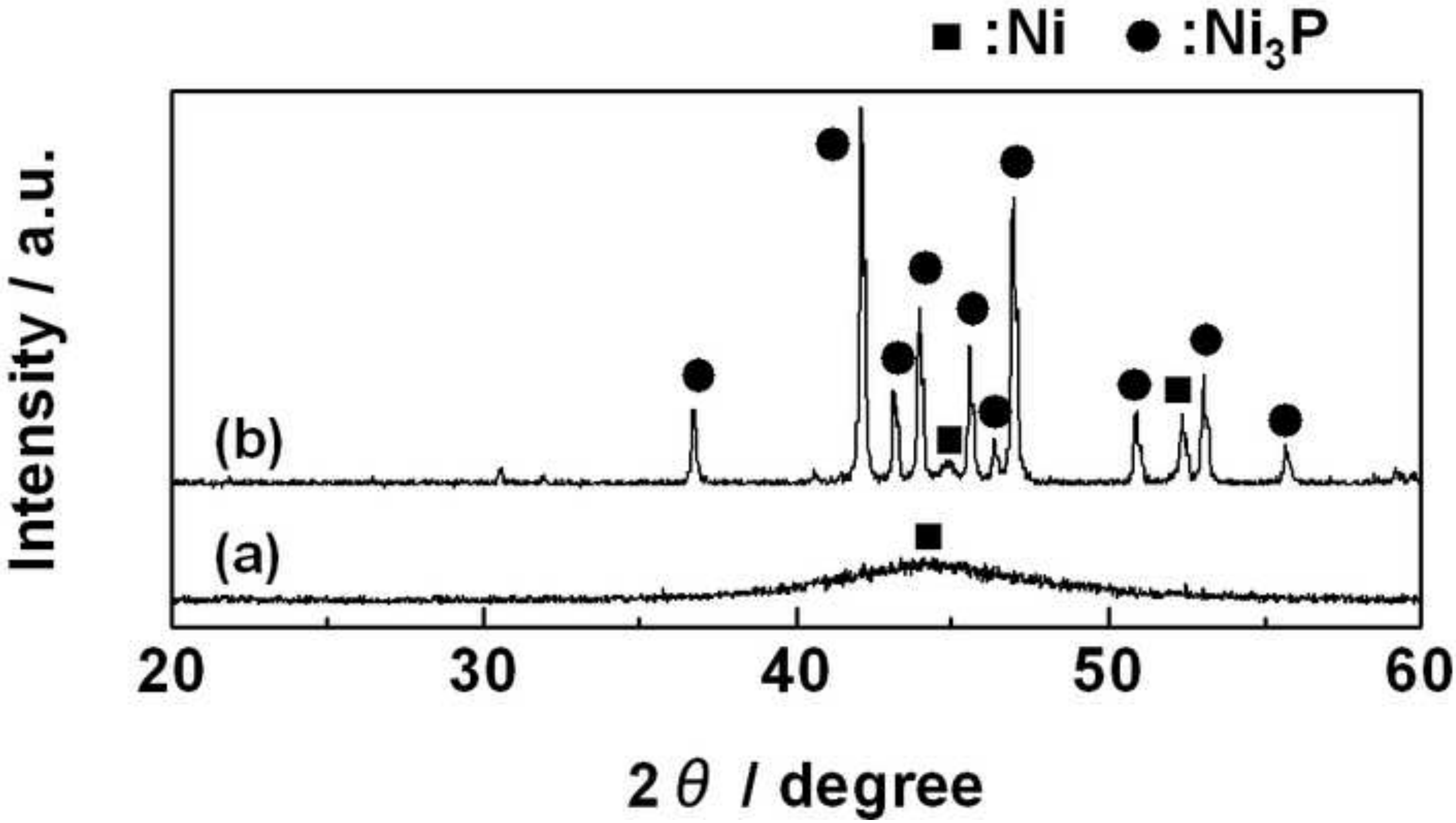
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● :Ni_3P
(b)
(a)
Intensity / a.u.
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30
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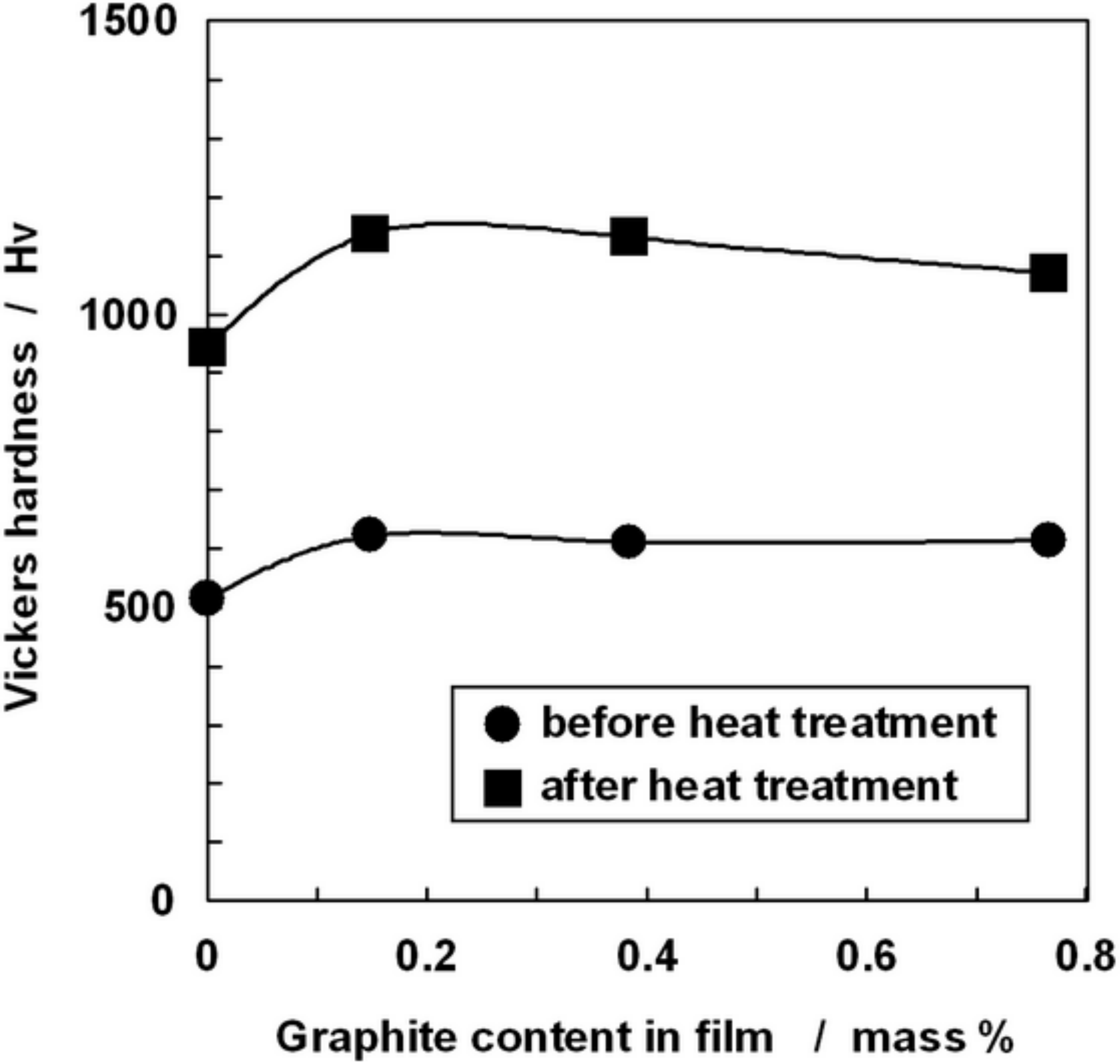
2θ / degree


1500
1000
500
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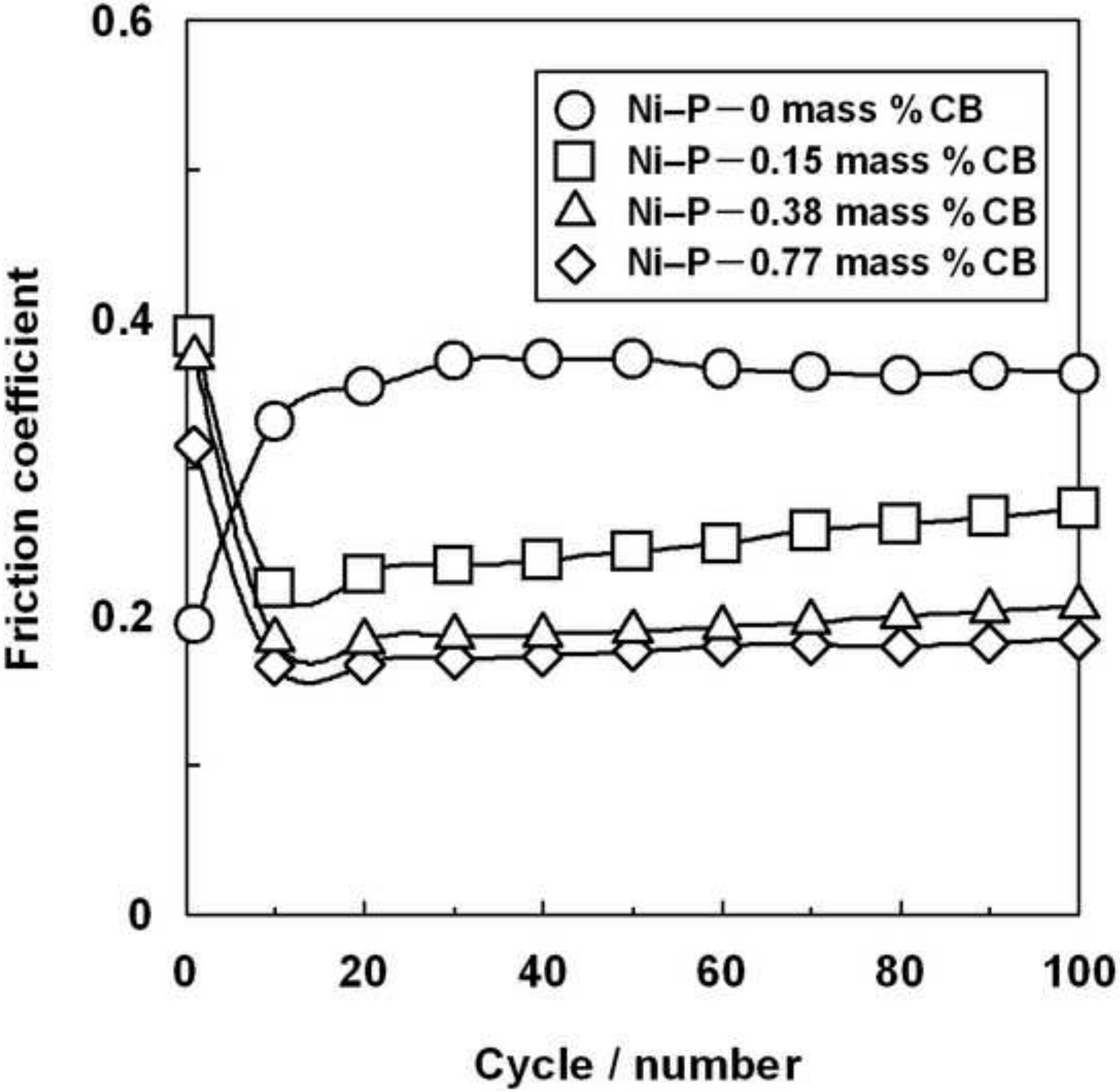
Vickers hardness / Hv
0
0.2
0.4
0.6
0.8
Graphite content in film / mass %
● before heat treatment
■ after heat treatment


0.6
0.4
0.2
0
Friction coefficient
0
20
40
60
80
100
Cycle / number
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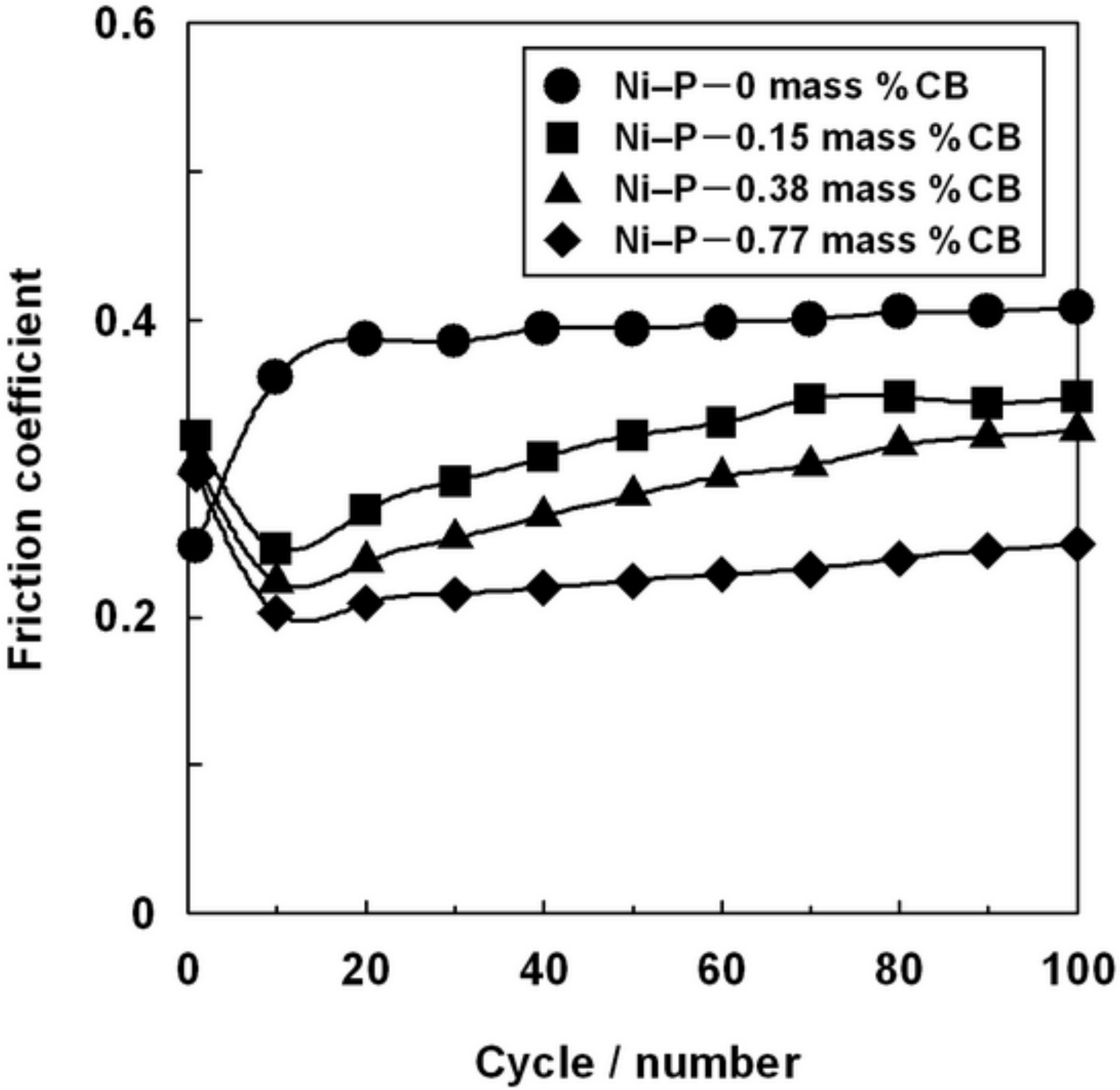
△ Ni–P−0.38 mass % CB
◇ Ni–P−0.77 mass % CB


● Ni–P−0 mass % CB
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Friction coefficient
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Cycle / number

Figure(s)

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