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Development of an electroless CoNiZnP solution for high coercivity films

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This paper describes the development of an electrolessly deposited CoNiZnP film for use in magnetic storage devices. A low temperature type solution, which can be operated at 310 K, has been developed. High coercivity films, which have a coercivity of 135 kA m^{-1} (1700 Oe) at a film thickness of 80 nm, are deposited from the solution

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1. Introduction

Electrolessly deposited cobalt phosphorus films are the most reliable and advantageous means for mass production of a material for use in magnetic storage devices, as this method produces highly uniform film, with characteristic high coercivities [1, 2].

To improve the recording density of a magnetic storage device, demagnetization effects must be minimized and therefore the coercivities increased further. With these two aims in mind, many investigations have been carried out, studying electroless plating of CoP-based alloy containing a variety of elements, including Ni [3], Sn [4], Zn [5], or Mn [6]. Such studies have shown excellent recording characteristics obtainable for the plated alloy with Zn [7, 8].

Most of these conventional CoP-based alloy solutions are of the Brenner type where it is necessary to perform the deposition within a temperature range of 340–360 K [9–11]. If good recording characteristics are to be maintained in devices such as recording tapes and floppy disks, where the recording materials used are often of poor heat-resistant substrate type, the prerequisite is for a lower temperature deposition of the cobalt alloy film, whilst still observing a high coercivity.

In this study deposition from an electroless CoNiZnP solution for high coercivity films at low temperature is described.

2. Experimental details

As substrate material, polyethylene terephthalate sheet (thickness 25 μm) was used. Because catalytic activity is essential for the initiation of the deposition, sputtered palladium nuclei were previously deposited on one side of the sheet. Solutions were prepared using pure grade reagents and distilled water. The deposition rate (nm s^{-1}) was evaluated from the weight gain of the film per unit area per unit time (5000 mm^2, 3600 s) assuming a deposit density of 8000 kg m^{-3}. Magnetic properties were measured with a vibrating sample magnetometer (Toei Kogyo, VSM-5). The maximum applied external magnetic field was 8×10^5 A m^{-1} (10 kOe). The plotted values both in deposition rate and magnetic properties are the average of ten measurements. The degree of scatter in each plot is within 10%.

3. Results and discussion

3.1. *Screening of complexing agents*

The selection of complexing agents is crucial in ultimately determining the characteristics of the electroless plating solutions. It has been discovered that low temperature (< 320 K) type solutions need two or more complexing agents, and that malic acid is the optimum first complexing agent for the CoNiZnP plating solution [12].

The choice of the second complexing agent is made from a preliminary screening of seven possible viable organic compounds; namely, sodium succinate, sodium tartrate, sodium citrate, sodium acetate, sodium malonate, lactic acid and gluconic acid. Assessed against a performance criteria of: (a) minimum deposition rate of 0·10 nm s^{-1} (at 310 K); and (b) minimum coercivity of 80 kA m^{-1} (at a film thickness of 80 nm).

It was found that both sodium malonate and sodium succinate were acceptable. The surface appearance of films produced using sodium succinate, rather than sodium malonate, favoured the use of sodium succinate as the second agent for CoNiZnP solution.

3.2. *Basic condition*

This choice of complexing agents defines the basic plating conditions and limits the concentration regions suitable for various components, namely metallic salt (cobalt sulphate + nickel sulphate), sodium hypophosphite (reducing agent), malic acid and ammonium sulphate, which induce spontaneous decomposition, inhibition of deposition or surface irregularity of the deposited film. However such disadvantageous effects are minimized by fixing the following concentration regimes for these chemicals;

(i) cobalt sulphate + nickel sulphate 100 mol m^{-3} (Co^{2+}/Ni^{2+} ratio is variable)
(ii) sodium hypophosphite 300 mol m^{-3}
(iii) malic acid 50 mol m^{-3}
(iv) ammonium sulphate 500 mol m^{-3}

The concentrations of the following components were variable, namely sodium succinate concentration, cobalt sulphate/nickel sulphate ratio and zinc sulphate concentration. Under the above basic condition, the individual effect of sodium succinate concentration, cobalt sulphate/nickel sulphate ratio and zinc sulphate concentration on the deposition rate or magnetic properties was investigated.

3.3. *Deposition rate*

The deposition rate in electroless plating is generally influenced by the pH and composition of the solution. The composition of complexing agent and pH is particularly important.

First, the influence of the pH and sodium succinate concentration on the deposition rate was investigated under the basic condition. Figure 1 shows that the deposition proceeds within the pH range 8.0 to 10.0, and each curve has a peak deposition rate between pH of 8.5 to 9.5. The solution decomposes spontaneously at a sodium succinate concentration under 100 mol m^{-3}. The deposition is barely initiated at concentrations above 600 mol m^{-3}. The deposition proceeds successfully within the concentration range from 100 to 500 mol m^{-3}. Within this range, as the concentration increases, the deposition rate decreases, and the position of the peak gradually shifts from pH 9.25 to pH 8.75. The decrease in deposition rate below the peak at pH 8.75–9.25 probably originates from the decrease in driving force of the reducing agent [13]. It is inferred that the decrease of deposition rate at higher pH originates from the increased stability of the metallic complex.

In Fig. 2, the effect of pH and metallic ion ratio $Co^{2+}/(Co^{2+} + Ni^{2+})$ on the deposition rate is shown. The deposition proceeds for the whole range of metallic ion ratios; however, the solution readily decomposes at a ratio under 0.2. The deposition rate increases as the metallic ion ratio decreases, because the catalytic activity of nickel is higher than that of cobalt.

The effect of pH and zinc sulphate concentration is shown in Fig. 3. The deposition rate decreases linearly as the concentration increases. The uniformity of film thickness falls in the concentration region above 30 mol m^{-3}. It may be inferred that zinc acts as a catalytic poison for the electroless process.

At conditions of; (i) pH 8.75–9.25, (ii) sodium succinate concentration 100–400 mol m^{-3}, (iii) $Co^{2+}/(Co^{2+} + Ni^{2+})$ ratio 0.4–0.8 and (iv) $ZnSO_4 \leq$ 20 mol m^{-3}, deposition rates > 0.2 nm s^{-1} are measured.

3.4. *Coercivity of the films*

Figure 4 shows the influence of pH and sodium succinate concentration on coercivity (at a thickness of 80 nm); each pH–coercivity curve has a peak. In conventional ammonia alkaline cobalt solutions, the decrease of coercivity in the higher pH region has not previously been observed [14, 15]. The stability of the

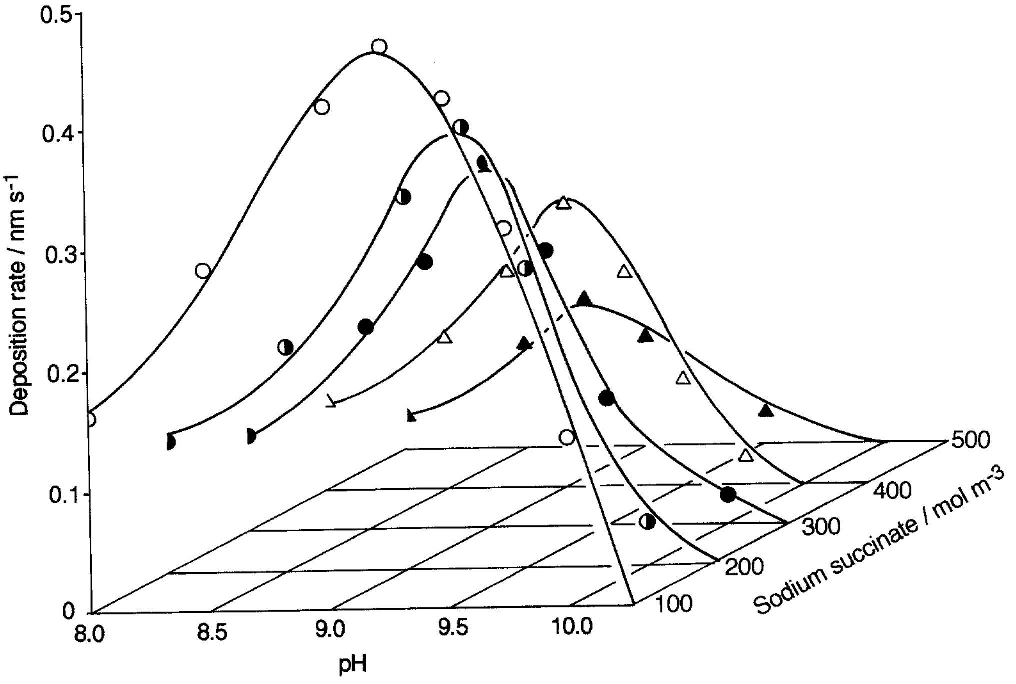

Fig. 1. Effect of pH and sodium succinate concentration on the deposition rate of electroless CoNiZnP deposition. Legend: ○, 100; ◑, 200; ●, 300; △, 400; ▲, 500 mol m^{-3} sodium succinate.

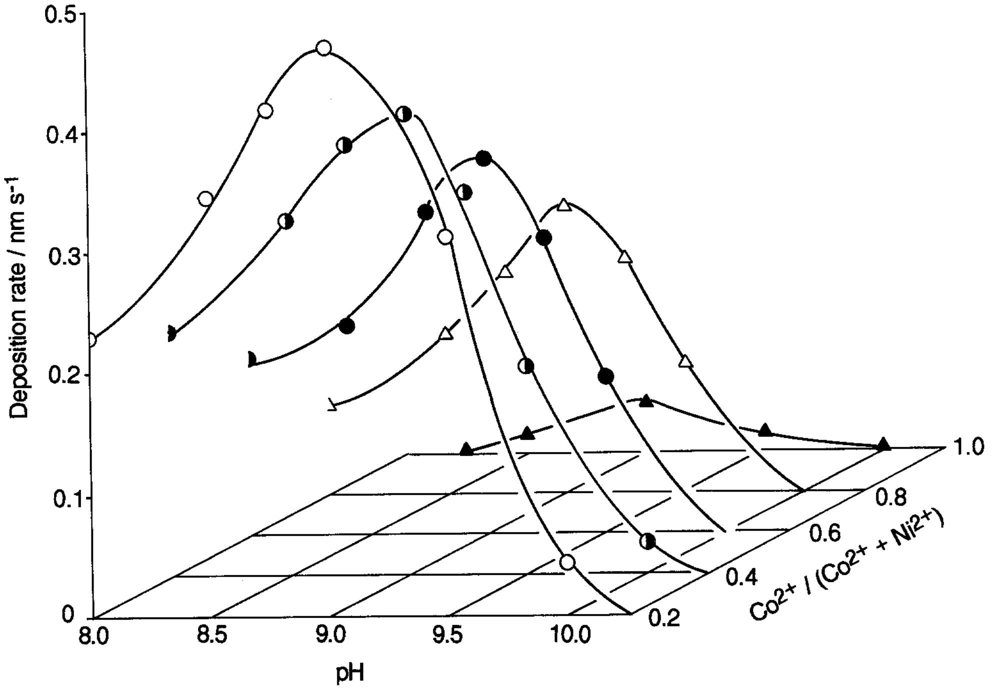

Fig. 2. Effect of pH and $Co^{2+}/(Co^{2+} + Ni^{2+})$ ratio on the deposition rate of electroless CoNiZnP deposition. Legend: ○, 0.2; ◑, 0.4; ●, 0.6; △, 0.8; ▲, 1.0 $Co^{2+}/(Co^{2+} + Ni^{2+})$.

complexes in this solution increases at the higher pH region, and accordingly, the free metallic ion concentration decreases at the deposition interface and fine grains, which are deposited from the dilute metallic ion solution, act as superparamagnetic particles, thus reducing the coercivity. This further explains the decrease in deposition rate at higher pH.

As the sodium succinate concentration increases, the peak of coercivity varies between 80 and 135 kA m^{-1}, and the position of the peak gradually shifts from pH 9.5 to 8.5. The maximum coercivity is obtained at a pH of 9.0 and sodium succinate concentration of 400 mol m^{-3}.

The pH and the ion ratio $Co^{2+}/(Co^{2+} + Ni^{2+})$ of the solutions influence the coercivity of the deposited films. The dependence of the coercivity on pH is similar to that shown in Fig. 5. The coercivity exceeds 80 kA m^{-1} at an ion ratio above 0.6. The optimum ion ratio for obtaining the highest coercivity is 0.8. It has been reported that co-deposited nickel mainly influences the grain size in electrolessly deposited CoNiP films and that the optimum grain size for

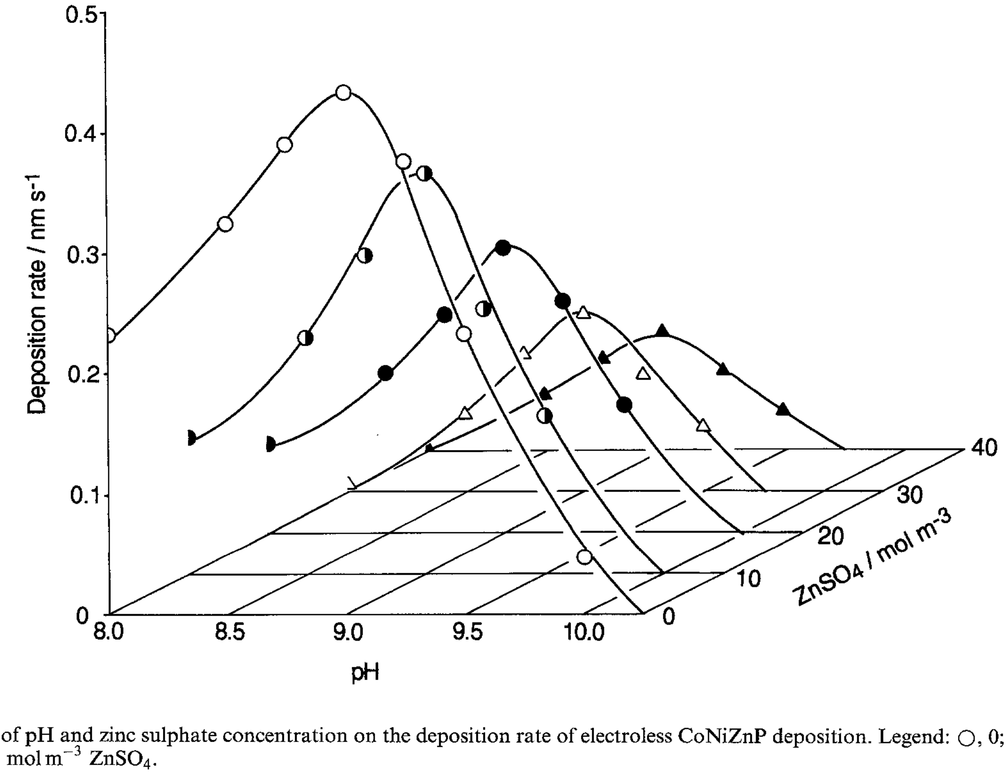

Fig. 3. Effect of pH and zinc sulphate concentration on the deposition rate of electroless CoNiZnP deposition. Legend: ○, 0; ◑, 10; ●, 20; △, 30; ▲, 40 mol m^{-3} $ZnSO_4$.

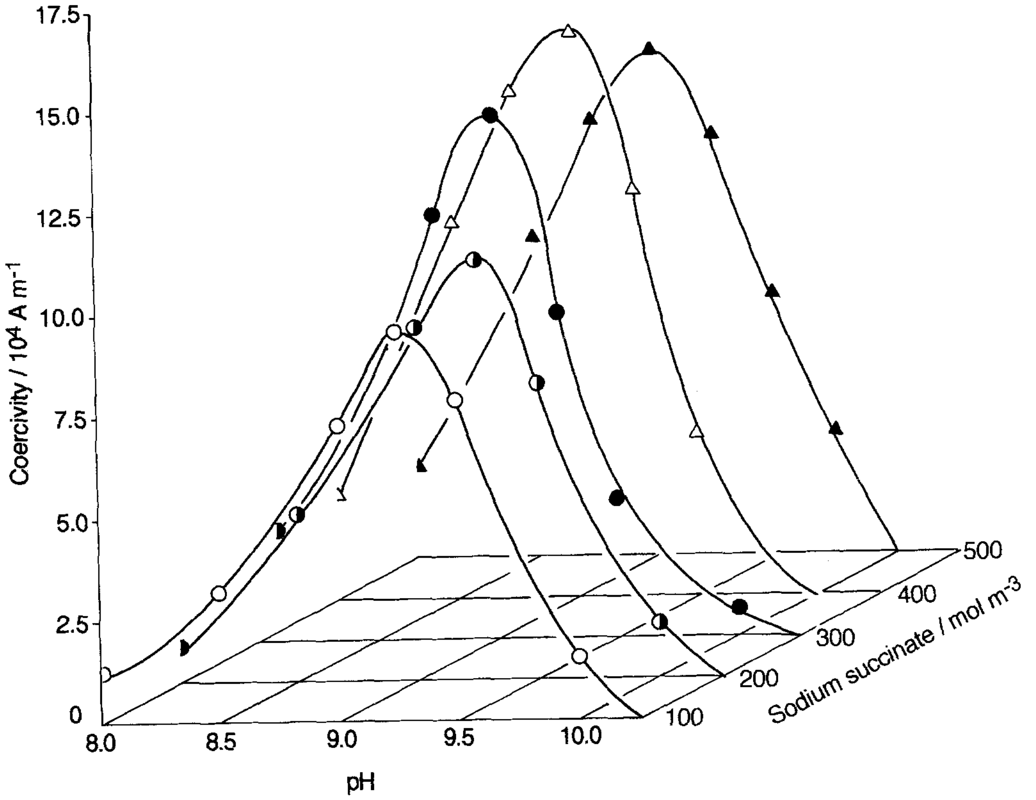

Fig.4. Effect of pH and sodium succinate concentration on the coercivity of electroless CoNiZnP deposited films. Legend: ○, 100; ◑, 200; ●, 300; △, 400; ▲, 500 mol m^{-3} sodium succinate.

high coercivity, which corresponds to the single domain particle, is obtained in the nickel content region of 10–20% [3, 15]. The significant decrease of coercivity in the lower $Co^{2+}/(Co^{2+}+Ni^{2+})$ ratio (nickel content > 30%) region originates from a change in crystalline structure to an amorphous structure [3]. A similar structural change probably occurs in this film.

Figure 6 shows the effect of zinc sulphate concentration on the coercivity of deposited films. Each

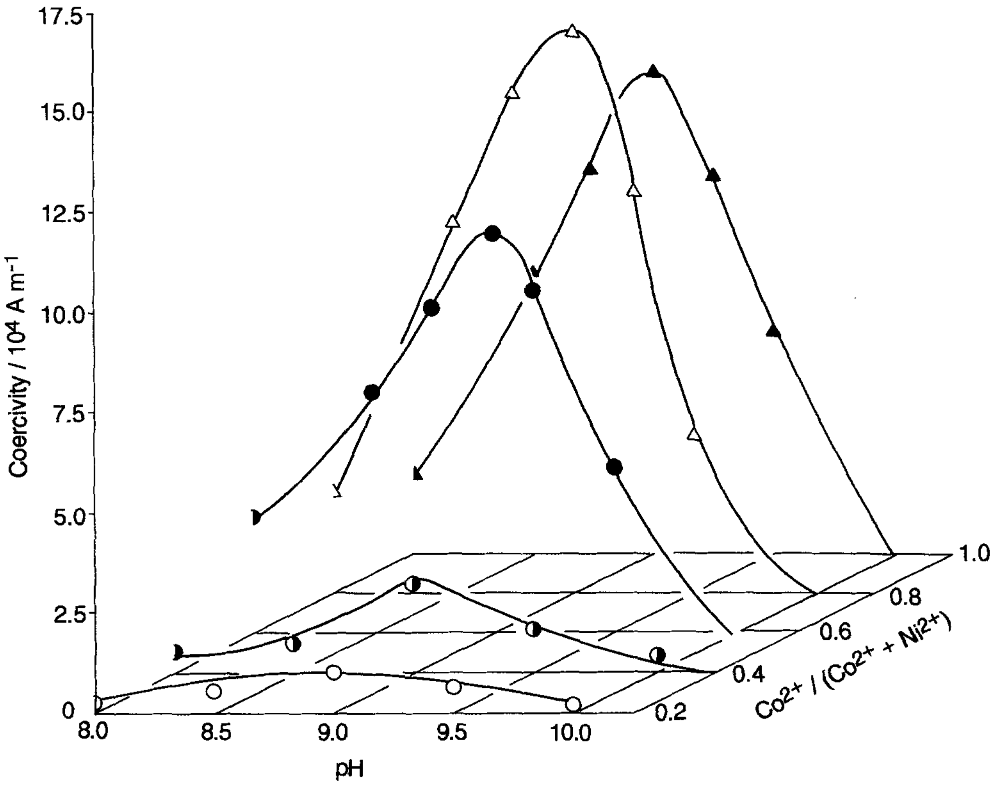

Fig. 5. Effect of pH and $Co^{2+}/(Co^{2+}+Ni^{2+})$ ratio on the coercivity of electroless CoNiZnP deposited films. Legend: ○, 0.2; ◑, 0.4; ●, 0.6; △, 0.8; ▲, 1.0 $Co^{2+}/(Co^{2+}+Ni^{2+})$.

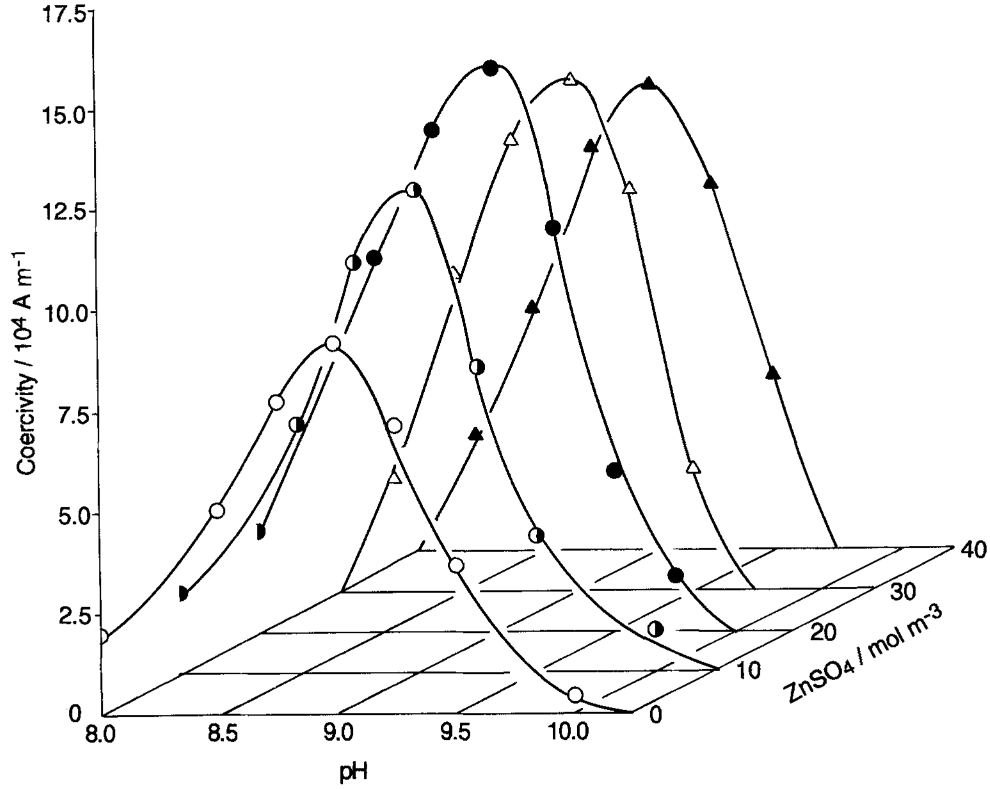

Fig. 6. Effect of pH and zinc sulphate concentration on the coercivity of electroless CoNiZnP deposited films. Legend: ○, 0; ◑, 10; ●, 20; △; 30; ▲, 40 mol m^{-3} $ZnSO_4$.

zinc sulphate concentration–coercivity curve has a peak coercivity. In another study, it has been confirmed that zinc segregates in the grain boundary regions in the form of $Zn(OH)_2$, which accelerates the magnetic isolation between grains, resulting in high coercivity [5]. The fall in coercivity past the peak originates from the non-uniformity of the film thickness at concentration over 30 mol m^{-3}.

Coercivities 100 kA m^{-1} are measured under conditions of; (i) pH 9.0, (ii) sodium succinate concentration 200–500 mol m^{-3}, (iii) $Co^{2+}/(Co^{2+} + Ni^{2+})$ ratio 0.6–1.0, and (iv) zinc sulphate concentration 20–40 mol m^{-3}.

3.5. *Characteristics of new solution*

From the above results, an optimum operating condition for high coercivity films can be deduced. The condition is as follows; pH 9.0, 80 mol m^{-3} cobalt sulphate, 20 mol m^{-3} nickel sulphate, 20 mol m^{-3}

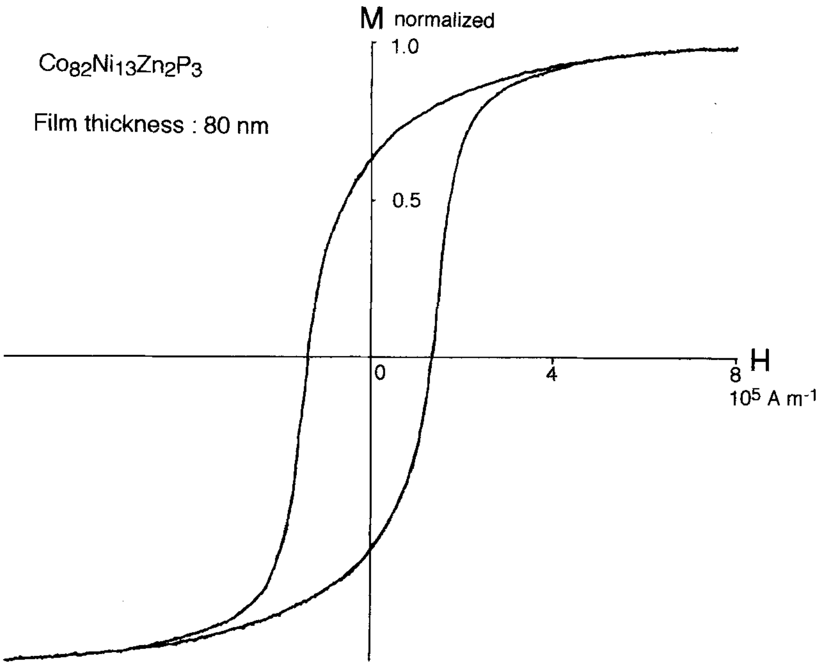

Fig. 7. Magnetic hysteresis loop of electrolessly deposited CoNiZnP films.

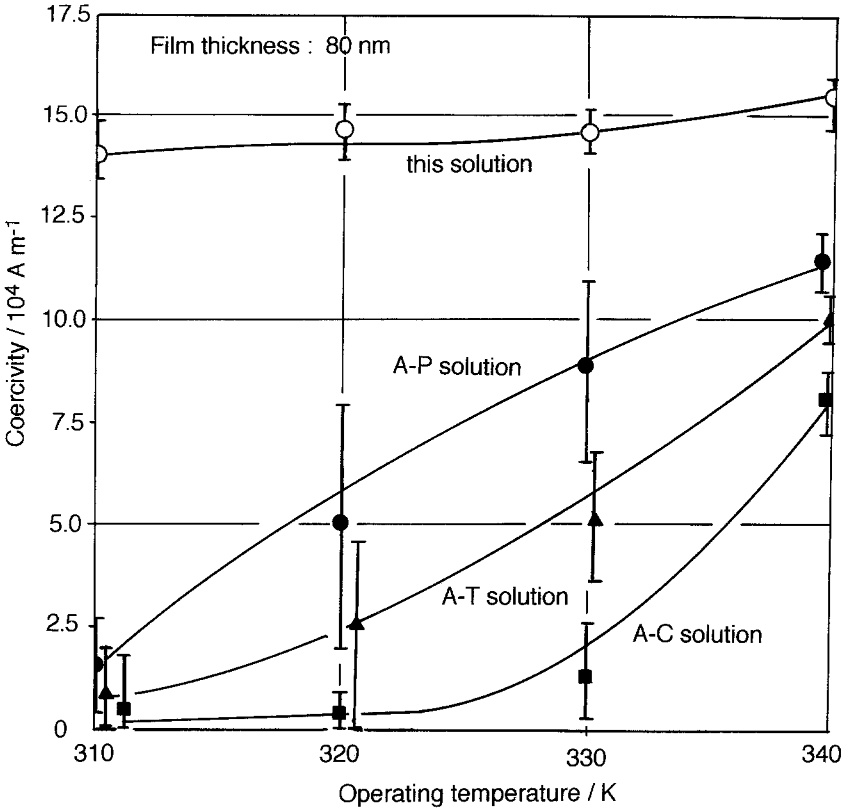

Fig. 8. Relation between deposition temperature and the coercivity of electrolessly deposited Co alloy films. Legend: ○, present solutions; ●, A–P solution; ▲, A–T solution; ■, A–C solution.

zinc sulphate, 300 mol m^{-3} sodium hypophosphite, 50 mol m^{-3} malic acid, 400 mol m^{-3} sodium succinate and 500 mol m^{-3} ammonium sulphate. Under this condition, a deposition rate of 0.23 nm s^{-1} and a film of composition $Co_{82}Ni_{13}Zn_2P_3$ is deposited. The magnetic hysteresis loop of the film (at a thickness of 80 nm) is shown in Fig. 7. A film coercivity of 135 kA m^{-1} is obtained in this film.

The relation between deposition temperature and coercivity (at a film thickness of 80 nm) is shown in Fig. 8. The new solution is compared with three conventional CoP solution types, namely ammonia alkaline tartaric solution [15], ammonia alkaline citric solution [15] and ammonia alkaline pyrophosphoric solution [16]. In Fig. 8, acronyms A–T, A–C and A–P are used for abbreviation. The new solution shows unique behaviour for coercivity in the plating range below 330 K. In conventional solutions, the coercivity decreases with temperature, falling to < 5 kA m^{-1} at 310 K. In the new solution, the coercivity is almost independent of temperature, and is approximately constant at 135 kA m^{-1}, even at a temperature as low as 310 K.

4. Conclusion

An electroless CoNiZnP plating solution which can be used to deposit films at a temperature of 310 K has been developed. The optimum deposition conditions are as follows, 80 mol m^{-3} cobalt sulphate, 20 mol m^{-3} nickel sulphate, 20 mol m^{-3} zinc sulphate, 300 mol m^{-3} sodium hypophosphite, 50 mol m^{-3} malic acid, 400 mol m^{-3} sodium succinate and 500 mol m^{-3} ammonium sulphate. Under the optimum condition, the deposition rate is 0.23 nm s^{-1} and the coercivity of deposited film is 135 kA m^{-1} at a film thickness of 80 nm.

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