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Effect of Heat Treatment on Properties of Various Electroless NiCoFe-B Coatings

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ABSTRACT

The influence of coating bath composition and heat treatment on morphology and microstructure of electroless NiCoFe-B magnetic coatings were investigated. Energy dispersive X-ray analysis (EDX) and scanning electron microscope (SEM) were used to study the coatings composition and their morphology respectively. Phase structure of coatings was investigated by X-ray diffraction. According to the results, Addition of the Ni²⁺ to electroless coating bath, not only changes the coating composition, but it also influences the morphology and microstructure of the coatings. Increase in molar ratio of NiSO₄ / (NiSO₄+CoSO₄) in the coating bath from 0.25 to 0.75 increased the particulate size and lead to higher tendency to amorphous structure. Heat treatment at 400°C for one hour also affected the morphology of coatings by smoothing of their surfaces and lead to crystallization of as deposited amorphous coatings and formation of some new phases as Ni₃B, Co₂B, Ni-Fe and Co-Fe phases.

KEYWORDS

Electroless Coating; NiCoFe alloy; Bath Composition; Heat Treatment.

1- INTRODUCTION

Electroless deposition process has undergone numerous modifications to meet the challenging needs of a variety of industrial applications since Brenner and Riddell invented the process in 1946. Among the variety of metals that can be plated using this method, electroless nickel has proved its supremacy for producing coatings with excellent corrosion and wear resistance [1]. Electroless nickel processes are grouped as Ni-P, Ni-B and pure Ni, based, respectively, on the reducing agents used (i.e., hypophosphite, borohydride or dialkylamino borane and hydrazine) in the plating bath. Hypophosphite-reduced electroless nickel plating process has received commercial success because of its low cost, ease of control and ability to offer good corrosion resistance. However, borohydride- or dimethylamine borane (DMAB)-reduced electroless nickel deposits have also received considerable attention in recent years [2]-[5].

Electroless Ni-B coatings are more wear resistant than tool steel and hard chromium coatings and it can replace gold in electronic industries. Borohydride-reduced electroless Ni-B deposits offer high hardness and superior wear resistance in the as-deposited condition [6].

Electroless plating of components used in electronic applications require a plating bath that operates at a relatively lower temperature. Hence, DMAB-reduced electroless plating baths are commonly used for these applications [6].

Development of electroless nickel poly-alloy deposits is considered as the most effective method to alter the chemical and physical properties of binary Ni-B alloy deposits. The choice of the additional element bases on the basis of the chemical and physical property to be imparted to the deposit. Cobalt and iron are considered to be the most useful additional elements for imparting magnetic properties to the coatings. Therefore, electroless NiCoFe-B ternary deposits were found in widespread use in the thin magnetic recording media and catalysis material [7].

NiCoFe films, especially the Co-rich alloys, possess unique magnetic properties and the

Ferich alloys, good thermophysical properties, thus making them suitable for varied applications [8]. The use of $\text{Co}_{73}\text{Ni}_{15}\text{Fe}_{12}$ alloy for thin film magnetic head fabrication for ultrahigh density recording has been reported [8]. The $\text{Fe}_{64}\text{Ni}_{31}\text{Co}_5$ alloy, which exhibits low thermal expansion characteristics, is used in microwave guides, space craft optics and laser housings [9].

The applied heat treatment in the final stage of EN coating changes its properties significantly. Mechanical properties of EN coatings such as hardness and wear resistance are enhanced by heat treatment at different temperatures. In the papers, there are reports of obtaining maximum hardness after heat treatment of the coated specimen at 400°C for one hour [10], [11].

In this work, a brass plate is used as the template and the deposition of electroless NiCoFe-B films from plating baths with a mole ratio of $\text{NiSO}_4/\text{NiSO}_4 + \text{CoSO}_4$ ranging from 0 to 1 was studied and the effect of the mole ratio of $\text{NiSO}_4/\text{NiSO}_4 + \text{CoSO}_4$ in plating bath on the chemical composition, surface morphology and microstructure of the electroless NiCoFe-B films was extensively investigated. The effects of heat treatment on the structure and the morphology of the electroless NiCoFe-B coatings were also studied.

2- EXPERIMENTAL DETAILS

Brass plates were used as the substrate materials for the deposition of electroless CoNiFe-B coatings.

Prior to the electroless deposition, the brass substrates were degreased with acetone, cleaned using HNO_3 solution and washed thoroughly with DI water. After this process, the brass substrates were sensitized by immersing in an aqueous mixture of 19g l^{-1} SnCl_2 and 50g l^{-1} HCl for 10 min and washing with DI water solution, followed by immersion in an aqueous mixture of 1g l^{-1} PdCl_2 and 12g l^{-1} HCl for 2 min. Subsequently, the substrates were rinsed with DI water several times.

An alkaline bath having nickel sulphate, cobalt

sulphate and iron sulphate as the sources of metallic elements of coatings and dimethylamine borane (DMAB) as the reducing agent was used to prepare the electroless CoNiFe–B deposits. The detail of chemical composition of the electroless plating baths of coatings and their operating conditions are given in Table 1. The temperature of the coating bath was maintained at 70 °C. During plating, the bath solution was agitated using a magnetic stirrer at 250 rpm.

The electroless CoNiFe coatings obtained from different bath composition with various NiSO₄ /NiSO₄+CoSO₄ molar ratios of 0, 0.25, 0.5, 0.75 and 1 in order to study the effect of bath

composition on coating properties. Heat treatment of electroless NiCoFe-B coatings was performed at 400°C for 60 minutes and in argon atmosphere to prevent the oxidation and the sample during heating and cooling. The surface morphology of the films was imaged using the scanning electron microscope (SEM) and the energy dispersive X-ray analysis (EDX) was carried out to obtain the composition of the films. The effect of coating bath composition and also heat treatment on phase structure of NiCoFe-B coatings were investigated by X-ray diffraction (Philips PW 3710, Netherlands).

TABLE 1

CHEMICAL COMPOSITION OF THE ELECTROLESS PLATING BATHS OF COATINGS AND THEIR OPERATING CONDITIONS

Component	NiSO4.6H2O	CoSO4.7H2O	FeSO4.7H2O	Lactic Acid	DMAB
Concentration (Molar)	0-0.034	0-0.034	0.01	0.24	0.07

3- RESULT AND DISCUSSION

3-1- Bath Composition

The contents of Ni, Co, and Fe in various NiCoFe–B films were determined by EDX analysis and shown in Fig. 1. Except the boron content in the deposit which can not be detected by EDX analysis, the content of cobalt falls from 79.75% to 0%, the content of nickel increases from 0% to 71.44% and that of iron changes from 20.25% to 28.56 % as the molar ratio of NiSO₄ /NiSO₄+CoSO₄ varies from 0 to 1.

Table 2 shows the mol ratio of Ni/Ni+Co in the coatings and in related plating bath. The mol ratio of Ni/Ni+Co in film is smaller than that in plating bath (with the exception of the film deposited in the bath with 0 and 1 mol ratio of NiSO₄ /(NiSO₄+CoSO₄). This means that the Co²⁺ ion is easier to be reduced into atom and attach to film surface than Ni²⁺ ion. It is interesting to note that the cobalt content of the deposits is higher than that of nickel compared with that of molar ratio of NiSO₄ /NiSO₄+CoSO₄ in the electroless plating bath, suggesting an anomalous behavior that involves a preferential deposition of electrochemically less noble cobalt in the deposit [7], [12]. Wang [7] have also observed this anomalous phenomenon and suggested that the low over-potential for cobalt deposition was the reason for preferential deposition of cobalt in the NiCo–B coatings fabricated by electroless deposition.

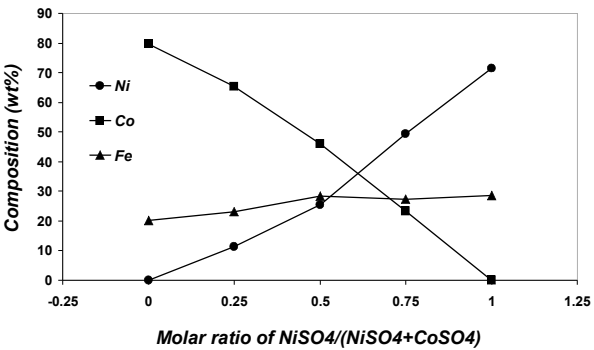


Figure 1: composition of CoNiFe coatings

Fig.2 shows the morphological images (SEM) of the CoNiFe-B films deposited on brass substrate from various molar ratios of NiSO₄ /NiSO₄+CoSO₄ in the coating bath.

As mentioned before, the activation of brass carried out in two steps. In first one, the stannous ion (Sn²⁺) was adsorbed onto the brass surface. In the second step, when substrate with the stannous ion was immersed in PdCl₂ solution, Pd²⁺ ions are reduced to atomic Pd according to the following reaction:

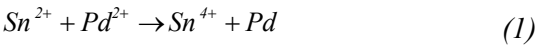


Fig.2 indicates that CoFe-B coatings obtained from bath with the molar ratio of 0 has the

globular morphologies. Addition of the nickel to this coating bath ($\text{NiSO}_4 / \text{NiSO}_4 + \text{CoSO}_4$ molar ratio of 0.25) leads to less particulate size of coating and change the morphology of coating. This coating has pyramidal-shape morphology. More increase in nickel content of coating changes the coating morphology to a mixture of pyramidal-shape and cauliflower-shape for deposition obtained from the equal content of the nickel and cobalt in the coating bath. $\text{NiSO}_4 / \text{NiSO}_4 + \text{CoSO}_4$ molar ratio of 0.75 and 1 show

depositions with larger morphology than the other investigated coating. These coatings indicate the smooth surface with globular morphology.

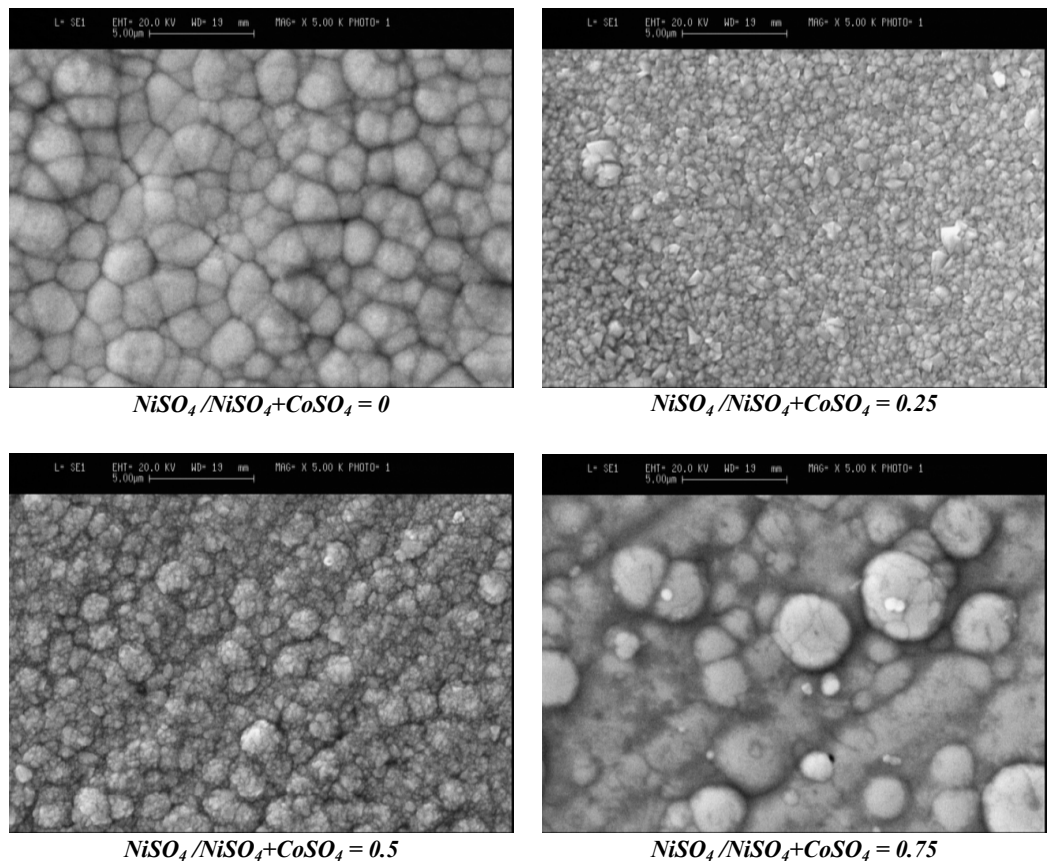
Fig. 3 displays the XRD patterns of the coatings obtained from the baths with various molar ratios of $\text{NiSO}_4 / \text{NiSO}_4 + \text{CoSO}_4$. Careful analysis of these diffraction data shows that the crystalline nature of the films depends obviously on the coating bath composition.

TABLE 2
MOL RATIO OF Ni/Ni+Co IN THE COATINGS AND IN RELATED PLATING BATH

<i>mol ratio of Ni/Ni+Co in plating bath</i>	0	0.25	0.5	0.75	1
<i>mol ratio of Ni/Ni+Co in the coating</i>	0	11.6	25.95	51.52	-

As indicated in Fig. 3, the main peak of CoFe alloy ($2\theta = 44^\circ$) in XRD pattern of coating obtained from bath with mentioned molar ratio of 0 is sharp and shows the crystallite structure of CoFe-B coating. The half-widths of the main peak increases with the increasing metallic salt

ratio, indicating the microstructure change of the films while the coatings prepared with metallic salt ratio $\text{NiSO}_4 / \text{NiSO}_4 + \text{CoSO}_4$ equal to 0.5 and 0.75, indicating mixture of microcrystalline and amorphous and typical amorphous structure of the NiCoFe-B film, respectively [13].



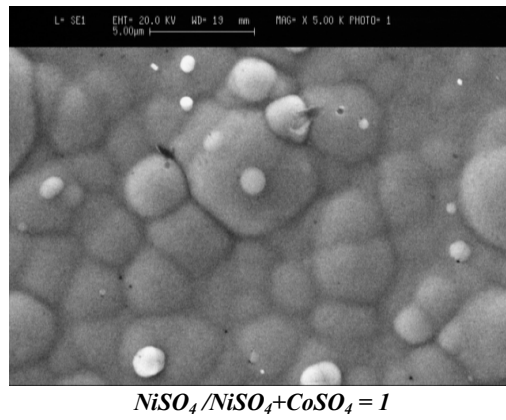


Figure 2: SEM morphology of as deposited electroless NiCoFe-B coatings obtained from baths with different composition

Besides, the half-width of this peak decrease with omission of cobalt salt from coating bath and the coating obtained from molar ratio of 1 in the bath indicates less amorphous behaviour than those obtained from molar ratio of 0.5 and 0.75 in the bath. Comparing between CoFe-B and NiFe-B coatings (obtained from molar ratio of 0 and 1 in the bath, respectively) it can be concluded that deposition of B in the deposition from DMAB reductant agent, leads to amorphous structure of nickel but it does not have this ability for cobalt coating.

3-2- Heat Treatment

The coatings obtained from the bath with different molar ratio of nickel and cobalt salt were heat treated at 400°C for one hour using the nitrogen atmosphere to prevent the oxidation and

the sample was cooled to room temperature in the furnace itself.

The surface morphology for the heat treated coatings are presented in Fig. 4. Comparing between Fig. 2 and Fig. 4 indicates that the heat treatment cause the smoother surface of coating. This phenomenon is due to diffusion of atoms at high temperature of 400°C which takes place because of difference in element content. The results are related also to crystallization of the alloy in an amorphous state and change in phase structure of coatings [7].

The effect of heat treatment on the microstructure of the electroless NiCoFe-B coatings obtained from the baths with various molar ratios of $\text{NiSO}_4/\text{NiSO}_4+\text{CoSO}_4$ were analyzed.

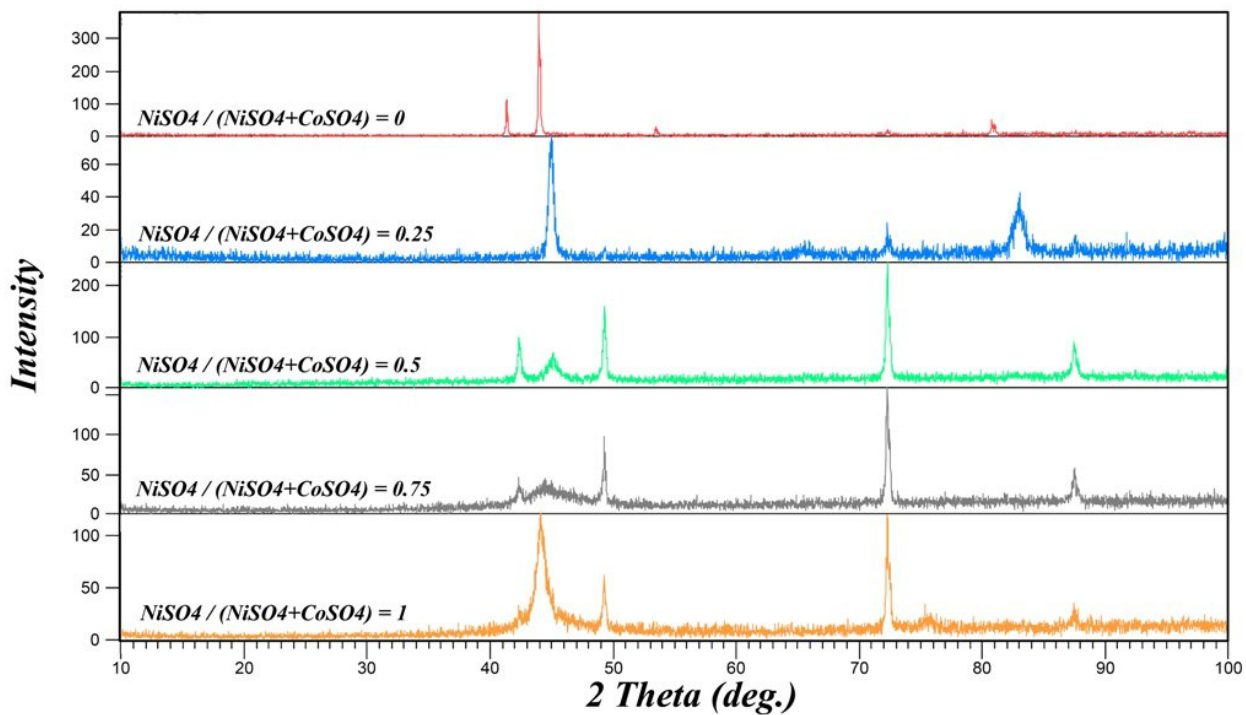
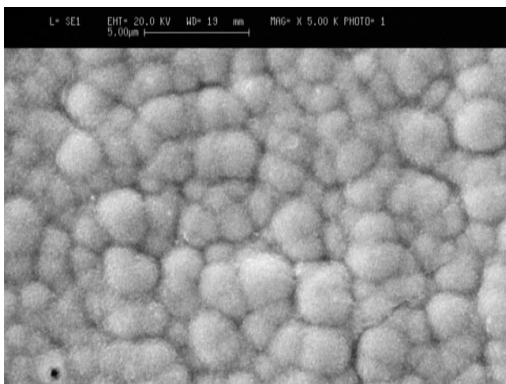


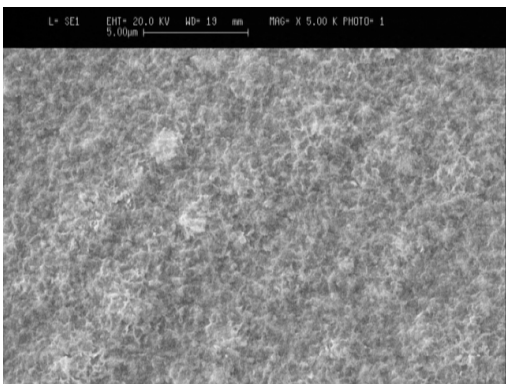
Figure 3: XRD patterns of as deposited electroless NiCoFe-B coatings obtained from baths with different composition

XRD patterns of the heat treated coatings reported in Fig. 5. Crystallization of amorphous coating and formation of new phase are clear by comparison the XRD patterns of as deposited and heat treated coatings. Heat treatment at 400 °C for 1 h causes the formation of Ni₃B, Ni₂B and

Ni-Fe phases in the coatings except the coating obtained from the bath with molar ratio equal to 0 which is CoFe-B [6], [7]. The XRD pattern of the later coating after heat treatment indicates the formation of Co₂B and Co-Fe phases.



NiSO₄ / NiSO₄+CoSO₄ = 0



NiSO₄ / NiSO₄+CoSO₄ = 0.25

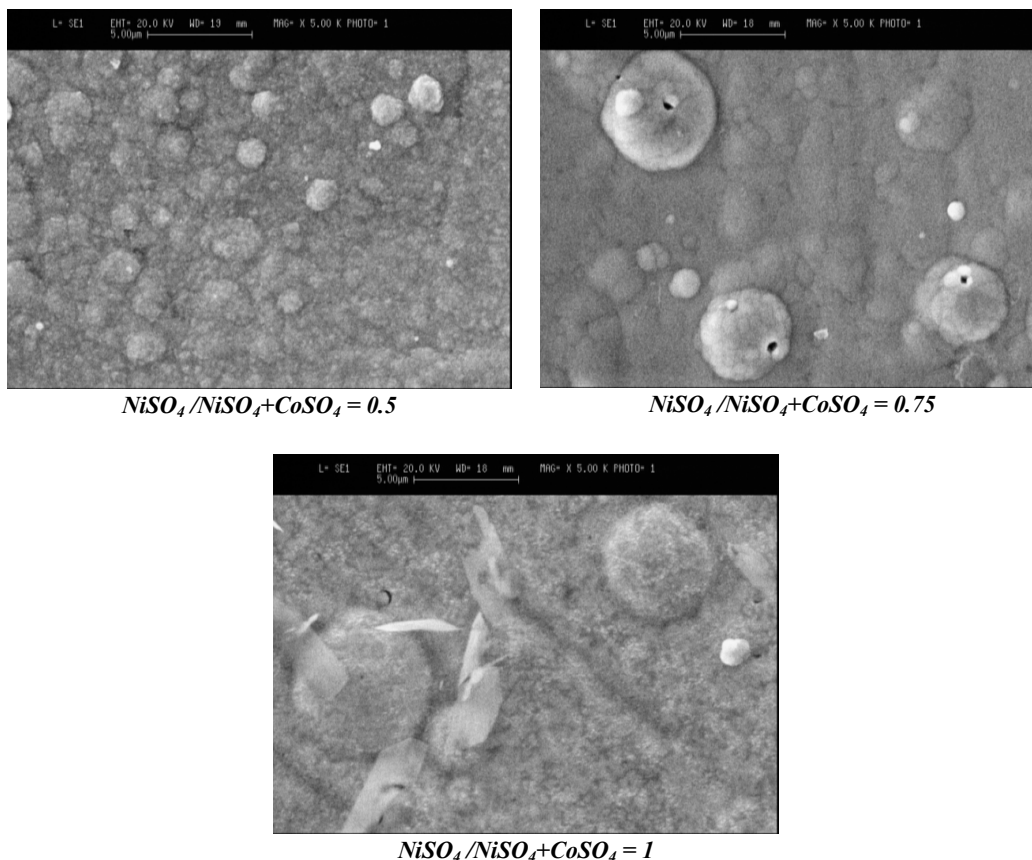


Figure 4: SEM morphology of Heat treated electroless NiCoFe-B coatings obtained from baths with different composition

All coatings except which obtained from the bath with molar ratio of 0 and 1 may contain Ni-Co and Ni-Co-Fe phase after heat treatment. The detailed analysis of the X-ray diffraction patterns of the heat treated Ni-B electroless coatings and its other alloys are well reported in the literature [6], [7].

4- CONCLUSION

The effect of coating bath composition and heat treatment on properties of electroless NiCoFe-B coatings were investigated. Different composition of these coatings successfully deposited on activated brass substrates. Adding of the Ni^{2+} to electroless coating bath leads to

change in composition, morphology and microstructure of coatings. CoFe-B coating show crystalline structure while NiCoFe-B coatings with different composition show some amorphous structure. The particulate size of NiCoFe-B coatings (except %Ni=0) increase with increasing nickel salt concentration in the coating bath. Heat treatment affects the morphology of coatings by making them smoother. Furthermore, microstructure of coatings was changed with heat treatment that caused crystallization of coating and formation some new phases in the coatings such as Ni_3B , Co_2B , Ni-Fe and also Co-Fe phases.

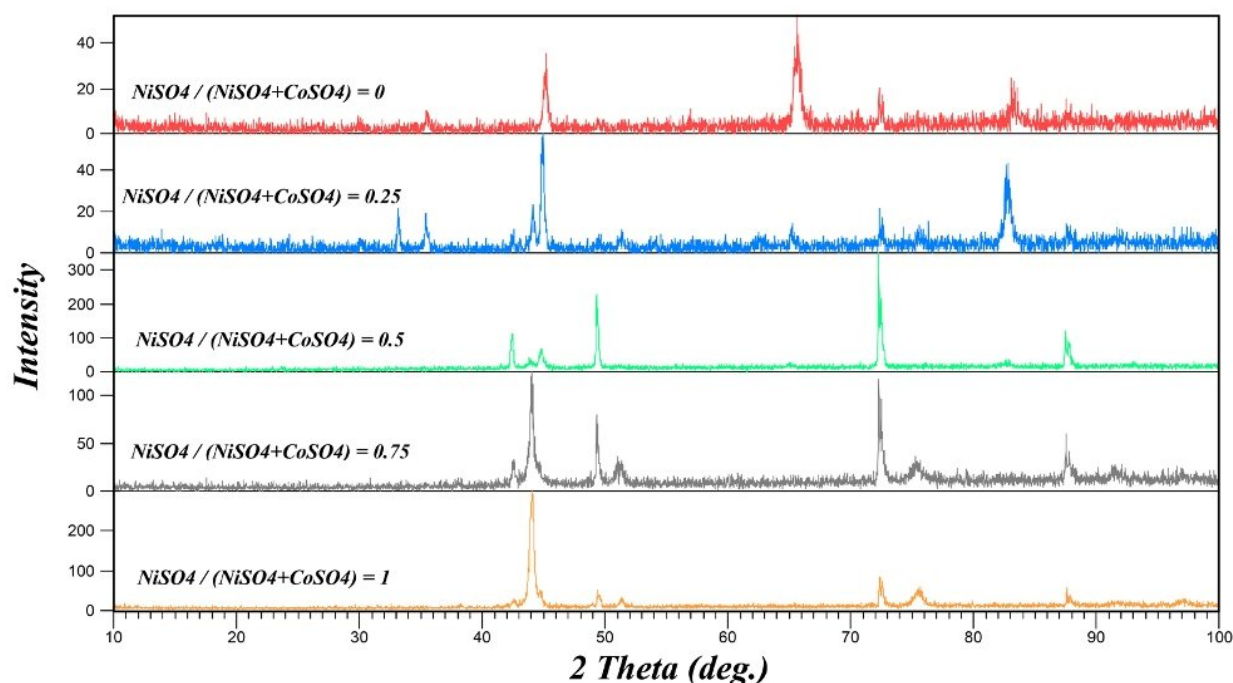


Figure 5: XRD patterns of heat treated electroless NiCoFe-B coatings obtained from baths with different composition

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