Material Properties of Ni-P-B Electrodeposits for Steam Generator Tube Repair

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This work investigated the material properties of Ni-P-B alloy electrodeposits obtained from a Ni sulfamate bath as a function of the contents of the P and B sources(H_3PO_3 and dimethyl amine borane complex(DMAB), respectively) with/without additives. Chemical composition, residual stress, microstructure and micro hardness were investigated using ICP(inductively coupled plasma) mass spectrometer, flexible strip, XRD, TEM and micro Vickers hardness tester, respectively. From the results of the compositional analysis, it was observed that P and B are incorporated competitively during the electrodeposition and the sulfur from the additive is codeposited into the electrodeposit. The measured residual stress value increased in the order of Ni, Ni-P, Ni-B and Ni-P-B electrodeposits indicating that boron affects the residual tensile stress greater than phosphorus. As the contents of the alloying element sources of P and B increased, crystallinity and the grain size of the electrodeposit decreased. The effect of boron on crystallinity and grain size was also relatively larger than the phosphorus. It can be explained that the boron with a smaller atomic radius contributes to the increase of residual stress in the tensile direction and the larger restraining force against the grain growth more significantly than the phosphorus with a larger atomic radius. Introduction of an additive into the bath retarded crystallization and grain growth, which may be attributed to the change of the grain growth kinetics induced by the additive adsorbed on the substrate and electrodeposit surfaces during electrodeposition.

Keywords : Ni-P-B alloy electrodeposits, sulfamate bath, additive, residual stress, crystallinity, grain size

1. Introduction

Degradation of nuclear steam generator tubing due to localized corrosion such as stress corrosion cracking, pitting etc., often leads to costly forced outages and system derating.[1] A commonly applied approach to rehabilitation has been to repair the damaged areas of the tubes via the insertion of tubular sleeves which are either welded or mechanically bonded at their extremities to the host tube. Such intrusive sleeves have weak points, such as the crevices, the tube deformation and an introduction of stress onto the host tube which then usually requires stress relief to improve the in-service life. Therefore, the focus on sleeve design shifted to a repair method to eliminate the weak points.

An electrodeposited sleeve was developed as a repair method free from these weak points.[2,3] The electrodeposited sleeve provides a continuous bond of high-strength micro-alloyed nickel to the host tube, spanning the defective region. Since no deformation of the host tube occurs, post heat treatment for stress relief is not required, thus avoiding the associated heat affected zone. However, there is a limitation to the electrodeposited sleeve method which is that the sleeve made through electrodeposition is quite low in the sleeving rate compared with the intrusive sleeve method. Therefore, a great attention should be paid to nickel electrodeposition in view of a high electrodeposition rate and low residual stress.

There are extensive works about Ni alloy electrodeposition to improve corrosion, mechanical and magnetic properties mainly in chloride and sulfate baths.[4-7] It is also reported[7,8] that the Ni electrodeposits of a relatively higher deposition rate and lower internal stress are obtained in the Ni sulfamate bath rather than the Ni chloride and sulfate baths.

Under these circumstances, a study on material evaluation of the Ni alloy electrodeposits obtained from the Ni sulfamate bath as a function of various alloying elements is needed. This work is concerned with the evaluation of the material properties of Ni-P-B alloy

electrodeposits obtained from a Ni sulfamate bath as a function of the contents of the P and B sources(H_3PO_3 and the dimethyl amine borane complex(DMAB), respectively) with/without additives by analyzing the chemical composition, residual stress, microstructure and micro hardness results.

2. Experimental

Ni sulfamate, phosphorus acid and DMAB(dimethyl amine borane complex) are used as a Ni source, a P source and a B source, respectively. The bath is composed of Ni sulfamate of 1.39mol, phosphorus acid ranging from 0.001 to 0.007mol and DMAB ranging from 0.001 to 0.03mol. Boric acid of 0.65mol and the additives(saccharin as a stress reducer, coumarin as a leveler and sodium lauryl sulfate as a surfactant) are added to the bath. Measured pH of the prepared bath was about 3.5.

Pt wire and alloy 600 plate with a surface area of 2 x 2 cm^2 were used as an anode and a cathode, respectively. The cathode was prepared by polishing to #1000 emery paper, followed by activation treatment in a 5wt.% H_2SO_4 solution for 10 sec. During electrodeposition, the applied current density was 100 mA/cm^2 and the temperature was controlled at 50°C.

Alloy composition analysis of the deposit was performed using an ICP analyzer(Model JY80C(Jobin Yvon)). Stress in the deposit was measured using the flexible strip bend method.

In order to determine the crystallinity and preferred orientation of the deposits, the X-ray diffraction pattern was obtained by the Rigaku X-ray diffractometer(Cu-Kα). TEM microstructure of the specimen was investigated using a Jeol 2000FX equipped with an Oxford Link(Model ISIS-5947) EDX. Thin foil was prepared by jet polishing using a 90% acetic acid + 10% perchloric acid solution at 10°C and DC 20V.

The electrodeposit from the sulfamate bath was heat treated at a temperature in the range of 250 to 600°C for 2hrs under a vacuum of 10^{-3} torr and was cooled in air. Hardnesses for the as-deposited specimens and heat treated specimens were measured with a load of 100gf using a Vickers hardness tester(MXT-CX(Matssuzawa)).

3. Results and discussion

Table 1 shows the chemical composition results for the electrodeposits obtained from various experimental splits. As the H_3PO_3 concentration as a P source increased, the P concentration in the electrodeposit increased but the B concentration decreased, while the B concentration in the electrodeposit increased as the DMAB concentration as a B source increased but the P concentration decreased. This indicates that P and B are incorporated competitively during the electrodeposition.

When additives are added to the electrodeposition bath, the sulfur content greatly increased. It could be attributed to the codeposition of sulfur consisting of an additive during electrodeposition. It was reported[7),9)-11)] that sulfur induces compressive stress and a ductility reduction, accompanied with a hardness increase.

It is worthwhile to note that the sulfur content greatly increased when nickel chloride was added to the bath. Greene[11)] has reported that nickel chloride played an important role in the reduction of the sulfur content in the pure Ni electrodeposit obtained from the sulfamate bath. Greene's work was restricted to pure Ni rather than a Ni alloy electrodeposition system and the electrodeposition conditions were very different from the conditions of this work i.e. nickel ion concentration, current density, pH, etc, which is related to this discrepant result. In this study, therefore it can be expected that the ductility of the

Table 1. Chemical composition results for the electrodeposits obtained from various experimental splits.

| Split | P (mol) | B (mol) | Additives | Chemical Composition (wt.%) | | | Remark | Atomic % | |
				P	B	S		P	B
PB1	0.001	0.001	×	0.13	0.14	0.007	P Increase	0.24	0.74
PB1-1	0.007	0.001	×	0.65	0.05	No Result		1.22	0.26
PB1-2	0.007	0.01	×	0.54	0.29	No Result	B Increase	1.01	1.53
PB1-3	0.007	0.03	×	0.28	0.53	No Result		0.52	2.79
PB2	0.001	0.001	○	0.2	0.03	0.056	Additive	0.37	0.16
PB3	0.001	0	×	0.28	-	0.005	NiCl₂	0.52	-
PB3-1	0.001	0	NiCl₂	0.25	-	0.05		0.47	-
PB4	0.001	0.003	○	0.09	0.08	0.068	B Increase	0.17	0.42
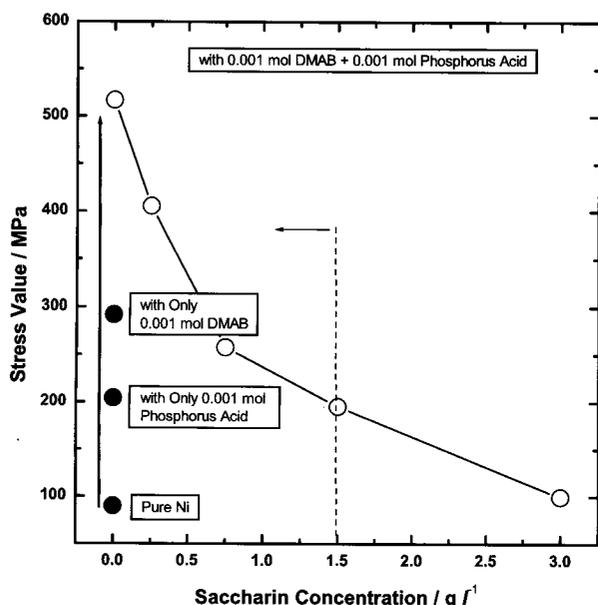
Fig. 1. Stress values measured for the Ni alloy electrodeposits prepared from electrodeposition solutions having various saccharin concentrations.

electrodeposit is degraded relatively as the electrodeposit is formed in the bath which the additive or nickel chloride is added to.

Fig. 1 presents the stress values measured for the Ni-P-B electrodeposits obtained from the electrodeposition solutions having various saccharin concentrations as a stress reducer at room temp. By increasing the stress reducer concentration, the residual stress decreased monotonously. The current efficiency was nearly constant as the stress reducer concentration in the solution varied in the range from 0 to 1.5 g/l while the current efficiency decreased in the solution having a stress reducer above a critical amount of 1.5 g/l.

Fig. 1 also shows the stress values measured for pure Ni, Ni-P, Ni-B and Ni-P-B electrodeposits obtained from the solutions without the additives. The measured stress value increased in the order of Ni, Ni-P, Ni-B and Ni-P-B electrodeposits indicating that the boron in the alloy affects the residual tensile stress greater than the phosphorus. In general, the tensile stress is generated as the lattice is contracted whereas the compressive stress is induced as the lattice is expanded. In the case that an alloying element smaller than nickel in atomic radius is substituted for nickel, it is expected that the tensile stress could be newly generated in the alloy. Therefore it is reasonable to think that the boron with a smaller atomic radius contributes to the increase of residual stress in the tensile direction more significantly than the phosphorus with a relatively

larger atomic radius.

As the electrodeposition temperature increased from room temperature to 50°C, the residual stresses without an additive and with an additive decreased, from about 520 to 110 MPa and 200 to 40 MPa, respectively.

Fig. 2(a) and (b) represent the X-ray diffraction patterns and TEM micrographs obtained from Ni-P-B electrodeposits containing various P and B contents. As the contents of the P and B sources increased, crystallinity decreased. Grain size of the electrodeposit decreased from about 30 to 20 nm as the P source concentration increased from 0.001 to 0.007 mol and about 30 to 10 nm as the B source concentration increased from 0.001 to 0.003 mol indicating that an increase of the B source rather than the P source made the grain size more refined.

P is segregated along the grain boundary during Ni-P electrodeposition and NiP$_x$ is formed above a heat treatment temperature of about 300°C.[12],[13] Considering the material properties of the electroless Ni-B-P deposit,[14] it is expected that the behavior of boron during electrodeposition and heat treatment is probably similar to the phosphorus.

Restraining force against grain growth by particle per unit area of the boundary can be described as in Eq. (1).[15]

$$\tau = \frac{3f\gamma}{2r} \tag{1}$$

where, τ, f, γ and r are the restraining force against the grain growth, volume fraction of the particle, grain boundary energy and radius of the particle, respectively. Eq. (1) can be obtained from the facts that the maximum force exerted by a single particle is given by $\pi r \gamma$ and the mean number of particles intersecting the unit area of a random plane is $3f/2\pi r^2$. It is obvious from Eq. (1) that B with a smaller atomic radius than P affects more the restraining force against grain growth.

Fig. 3 illustrates the TEM micrographs obtained from the Ni, Ni-P and Ni-B alloy electrodeposits without additives. Grain sizes for the Ni alloy electrodeposit for Ni-P and Ni-B, respectively, are about 500 nm and 30 nm smaller than that for the pure Ni electrodeposit of about 2 μm. Moreover, grain size and crystallinity of the Ni-B electrodeposit are smaller and lower than those of the Ni-P electrodeposit. From the results of the XRD and TEM shown in Figs. 2 and 3, it seems that the P and B segregated at the grain boundary effectively impede grain growth and the B with a smaller atomic radius induces a larger restraining force against grain growth rather than the P.

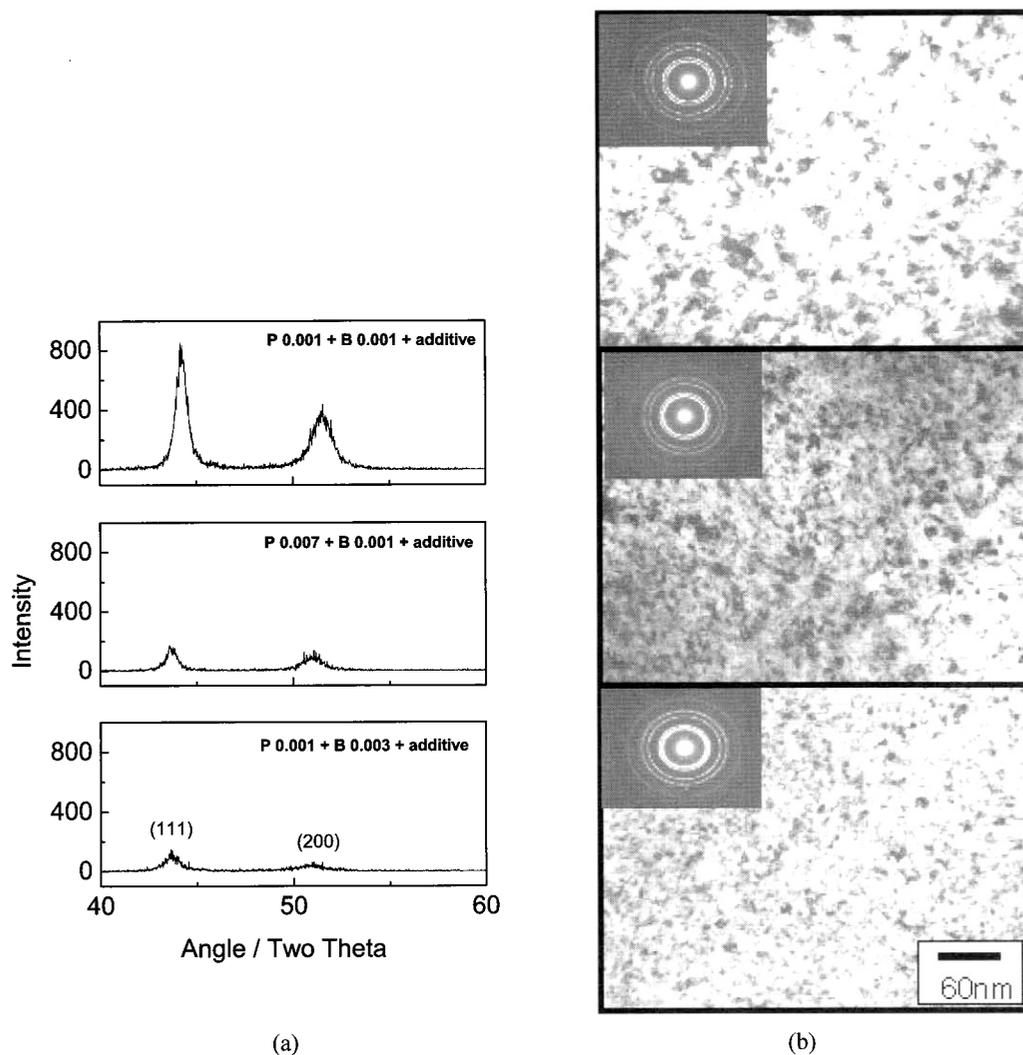Fig. 4 (a) and (b) show the X-ray diffraction patterns

(a)   (b)

Fig. 2. (a) X-ray diffraction patterns and (b) TEM micrographs obtained from Ni-P-B electrodeposits containing various P and B contents.
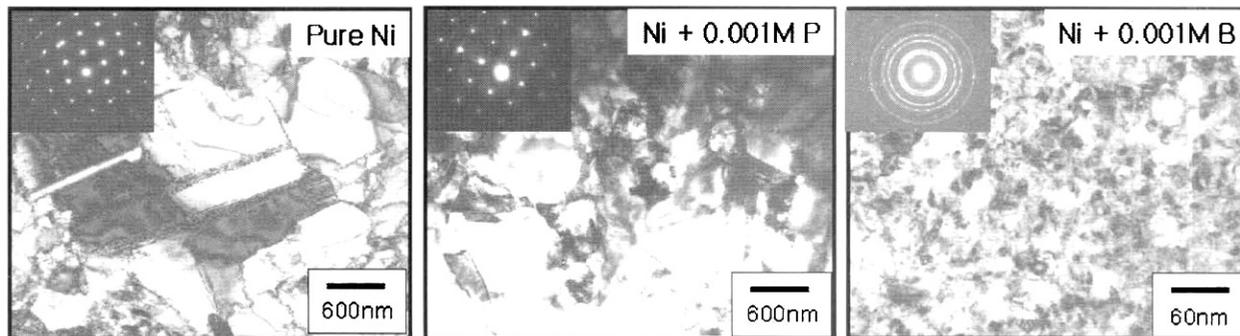

Fig. 3. TEM micrographs obtained from the Ni, Ni-P and Ni-B alloy electrodeposits without additives.

for the pure Ni electrodeposit with/without an additive and for the Ni-P alloy electrodeposit with/without an additive, respectively. By adding additives to the electrodeposition solution, the X-ray diffraction plane showing the highest
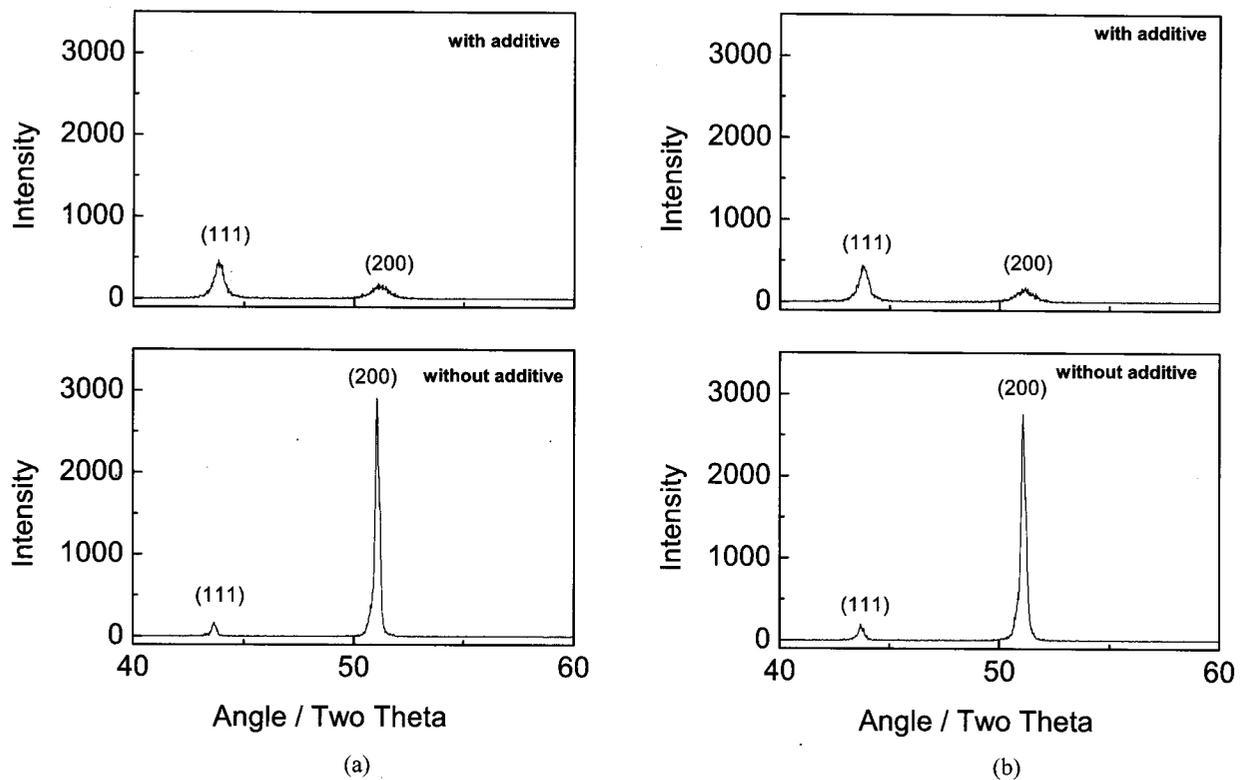
Fig. 4. X-ray diffraction patterns for (a) pure Ni electrodeposit with/without additive and (b) Ni-P alloy electrodeposit with/ without additive, respectively.
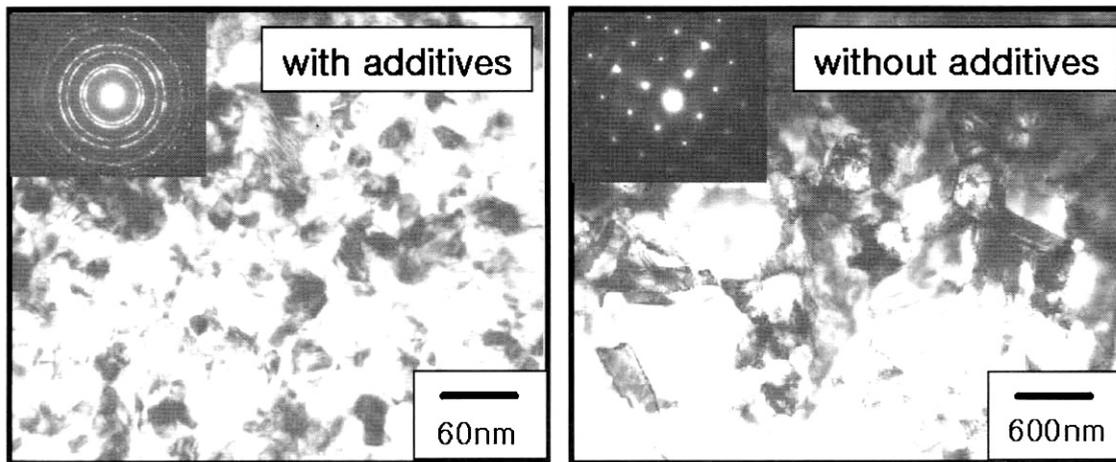

Fig. 5. TEM micrographs obtained from the Ni-P alloy electrodeposits with and without additive.

intensity was changed from (200) to (111) and the crystallinity decreased. It seems that the surface energy state at the substrate and electrodepositing plane during electrodeposition is changed due to the adsorbed additive, which affects the electrodeposition growth kinetics leading to the change of the preferred orientation.

Fig. 5 is the TEM micrographs obtained from the Ni-P alloy electrodeposits with and without an additive. It was found that the crystallinity decreased and grain size also decreased from about 1(m to 50 nm by adding an additive to the bath. It can be explained that the mean free path for the grain growth was decreased due to the additives adsorbed at the substrate and electrodeposit during the electrodeposition.
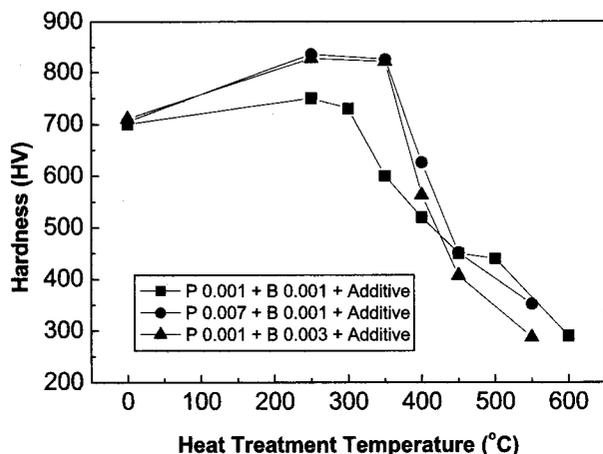
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Fig. 6. Vickers hardness of Ni-P-B electrodeposit containing various P and B contents as a function of heat treatment temperature.

Fig. 6 presents the Vickers hardness of the Ni-P-B electrodeposits containing various P and B contents as a function of the heat treatment temperature. Hardness reached a maximum value in the temperature range of 250 to 350°C, followed by an abrupt decrease above the temperature range. The P and B segregated and the Ni alloys(NiP$_x$ and NiB$_y$) precipitated at the grain boundary effectively impede grain growth leading to a hardness of a high value. However, as the heat treatment temperature increased, a rapid decrease of hardness caused by precipitate coarsening, grain growth and recrystallization took place. It should be noted that the hardness value increased more or less as the P and B contents increased. It seems that the restraining force against the grain growth caused by an increase of the particle fraction increased as the P and B contents increased.

4. Conclusions

The result of this work is concerned with the material properties of Ni-P-B alloy electrodeposits obtained from a Ni sulfamate bath as a function of the contents of the P and B sources(H$_3$PO$_3$ and DMAB, respectively) with/without additives and can be summarized as follows.

From the results of the compositional analysis, it was found that P and B are incorporated competitively during the electrodeposition and the sulfur consisting of an additive is codeposited into the electrodeposit.

The measured stress value increased in the order of Ni, Ni-P, Ni-B and Ni-P-B electrodeposits indicating that boron affects the residual tensile stress greater than the phosphorus. Crystallinity and grain size of the electrodeposit decreased as the contents of the phosphorus and boron sources increased. The effect of boron on crystallization and grain growth retardation was also relatively larger than that of the phosphorus. It can be expected that the boron with a smaller atomic radius contributes to the increase of residual stress in the tensile direction and the larger restraining force against the grain growth more significantly than the phosphorus with a larger atomic radius.

Crystallization and grain growth was retarded by the introduction of an additive into the bath, which seems to be concerned with the grain growth kinetics changed by the additive adsorbed on the substrate and electrodeposit surfaces during electrodeposition.

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