A Study on the Effects of Inorganic Additives on the Properties of Zinc Electrodeposits

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This study was performed to investigate the variation of crystal orientation of zinc electrodeposits with various additives, and the microstructure, surface appearance and formability was also estimated. The addition of Fe additive shows mediate (002) crystal index, low friction coefficient and good formability. It was observed that (002) crystal index and whiteness was raised by tungsten additive. The addition of cobalt decreased (002) crystal index and whiteness. Simultaneous addition of antimony remarkably decreased (002) crystal index and slightly decreased friction constant. It is determined that good formability can be obtained with fine crystallite size and randomized crystal orientation. But Formability got worse if crystallite is aggregated excessively.

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1. Introduction

Zinc electrogalvanized steel sheet is widely used for automobile and home appliance owing to its good corrosion resistance and appearance[1-7]. For these applications, zinc electrodeposits are demanded imposing and uniform appearance. And it is also needed good formability that has low exfoliation and blackening of the electrodeposits during pressing or shearing. Good phophatability and paintability must be considered, too.

It is generally known that the characteristics that mentioned above are dominated by the surface morphology and structure of the electrodeposits, and the crystallographic structure and microstructure have dominant effects on these properties. The crystallographic structure and microstructure of electrodeposits are varied with the electroplating conditions, such as current density, concentration of the metal ions, agitation, temperature, pH, cation/anion ratio, inhibition, substrate, etc. Among various methods to control electroplating condition, the addition of organic/inorganic additives in electrolyte is significant because they make remarkable effect on the properties of the electrodeposits although they are existed in electrolyte with very small quantity.

Organic additive reacts as an inhibitors, it suppresses the crystal growth of the electrodeposits during electroplating[8, 9], preventing the electrodeposits from dendritic growth of the electrodeposits (burnt electrodeposits) due to non-uniform electroplating overvoltage. And it improves gloss of the electrodeposit due to reduced crystallite size. Inorganic additives such as cation, metal ion and anion also have effect on the properties for the electrodeposits. A cation works as an inhibitor according to pH of the electrolyte, and an anion has little effect because there are few anions in electrolyte except SO_4^{2-} or Cl^- for a sulfate or a chloride bath[8].

In Zinc electrodeposition, if other metal ion besides zinc exists, several works found that the concentration of the other metal in electrodeposits is less than the concentration in electrolyte due to anomalous codeposition[10-13]. According to these works, the microstructure and crystallographic structure of the electrodeposits can be controlled by adding small quantity of metal ion with little change of the chemical composition of the electrodeposit. In this point of view, it can be understood that the metal ion acts as an additive for electroplating.

In this paper, the effect of the inorganic additives on the crystallographic structure and microstructure of the zinc electrodeposits was studied. The effects on surface appearance and formability are also investigated.

2. Experiment

Sample preparation and electroplating

A cold-rolled steel sheet from same coil was used for a substrate for electroplating. The sheet was cut with 200mm in length and 150mm in width and degreased by dipping method using NaOH based commercial degreaser. 5% HCl was used for pickling followed by water rinsing. Electroplating was performed in laboratory flow cell with horizontal type and its exposure area is 90mm X 200mm. Electroplating condition is summarized in Table 1. The conditions except the concentration of the inorganic additives were similar to that of our EG production line and fixed through whole experiment.

Table 1 Electroplating condition

Current density	$40A/dm^2$
Coating weight	20g/㎡
PH	1.7
Temperature	55
Flow rate	2.0m/s
Conc. of zinc	80g/L
Additives	Na_2SO_4(25g/L)

Electrolyte Preparation

Fe, Co and W were added to electrolyte to investigate their effects and also Sb was added simultaneously to estimate the effect of the Sb on the zinc anomalous codeposition and the properties of the electrodeposit. Composition of the electrolyte is shown at Table 2.

Table 2 the composition of the electrolyte

Additive	Chemical	Concentration in the electrolyte (mol/L)			Presence of Sb (5mg/L)
Fe	Iron Sulfate Heptahydrate ($FeSO_4$ $7H_2O$)	0.001	0.01	0.1	X
		0.001	0.01	0.1	O
Co	Cobalt Sulfate Heptahydrate ($CoSO_4$ $7H_2O$)	0.001	0.01	0.1	X
		0.001	0.01	0.1	O
W	Sodium Tungstate Dihydrate ($NaWSO_4 2H_2O$)	0.001	0.01	0.1	X
		0.001	0.01	0.1	O

Analysis and estimation of electrodeposit

Coating weight was measured to calculate current efficiency by GDS (Glow Discharge Spectrometer). Chemical composition of the electrodeposit was analyzed by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometer) and GDS. Surface appearance was estimated by measuring lightness and gloss with colorimeter and gloss meter. Surface roughness was determined by using roughness meter. XRD analysis was carried out to study crystallographic structure. Microstructure and surface morphology could be obtained by using SEM and AFM. Drawbead test is performed to estimate formability. The degree of the exfoliation and blackening of the electrodeposits was evaluated by the difference of the surface appearance before and after the test, and the friction coefficient can be obtained from this test. The condition of drawbead test is shown at Fig. 1.

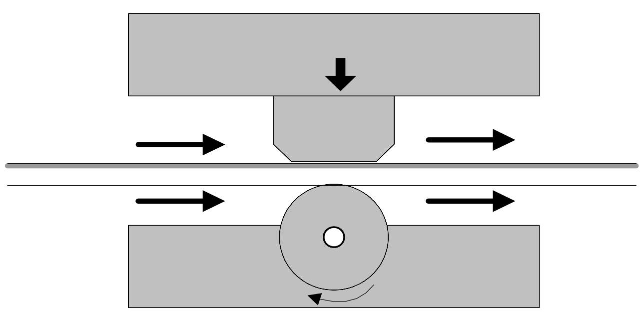


Fig. 1 Schematic diagram for drawbead test

3. Results and Discussion

Current efficiency, surface appearance and composition of the electrodeposit

In Fig. 2, it was shown that current efficiency was lowest for adding tungsten and highest for adding iron. And a rapid decrease of the current efficiency was observed in proportion to the increase of the concentration of the tungsten. No obvious tendency was shown, however, according to the concentration of the iron and cobalt. Adding antimony to each condition, an increase of the current efficiency could be found for adding cobalt and tungsten but there is little change of the current efficiency for adding iron.

The concentration of the additive metal in electrodeposit was comparatively high and had little tendency with iron additive, it is inferred that it is due to the presence of the iron ions from steel substrate in electrolyte due to low pH of the electroplating condition. (Fig. 3) Adding cobalt, the concentration in electrodeposit increased proportionately with that in the electrolyte, but the concentration of the cobalt in the electrodeposit was very low. It was found that the concentration of tungsten in electrodeposit increase dramatically in proportion to that in electrolyte. No antimony could be detected in electrodeposit.

Lightness increased in proportion to tungsten concentration in electrolyte, diminished proportionately with cobalt concentration. Adding iron made little difference in lightness. (Fig. 4) There is no obvious change in gloss with iron and cobalt addition, but gloss increased dramatically with tungsten addition. In general, it is known that lightness and gloss increase according to decreasing coating weight, therefore, high lightness owing to low coating weight was observed come from strong inhibition of the tungsten. With antimony addition, a decrease in lightness was found with cobalt additives, but no significant relation was observed with other additives.

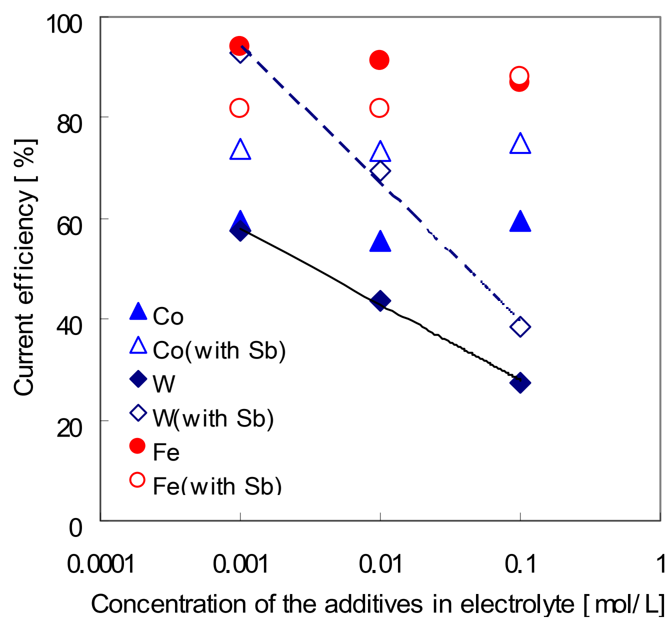


Fig. 2 The effect of additives on the current density

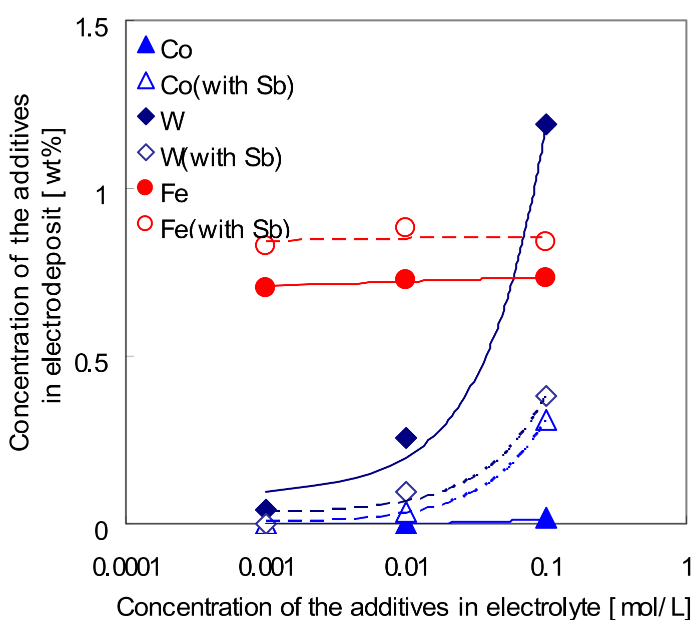
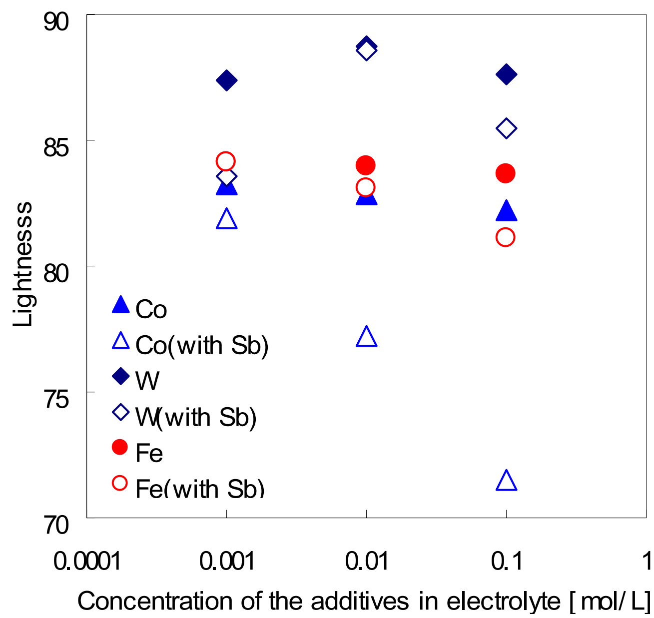


Fig. 3 The effect of additives on the additive metal content of electrodeposit

(a)



(b)

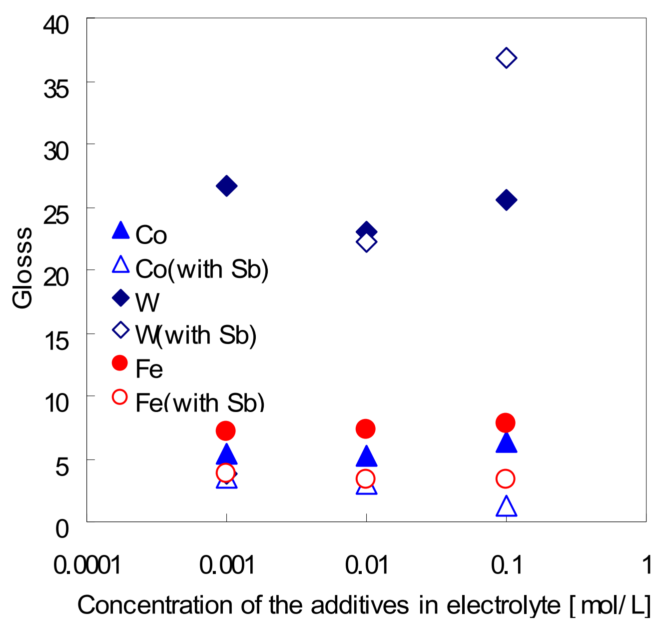


Fig. 4 The Effects of additives on the surface appearance: (a) Lightness, (b) Whiteness

Crystallographic Structure and Microstructure

Crystallographic analysis was carried out by the equation[14] shown below,

$$P_{(hkl)} = \frac{\left(\dfrac{I_{(hkl)}}{\Sigma I_{(hkl)}}\right)}{\left(\dfrac{I_{st(hkl)}}{\Sigma I_{st(hkl)}}\right)} \times 100 \qquad (1)$$

in which $I_{(hkl)}$ stands for the intensity of (hkl) plane, $I_{st(hkl)}$ stands for the intensity of (hkl) plane for standard zinc sample (zinc powder), and $P_{(hkl)}$ stands for the crystal orientation index of the (hkl) plane. In earlier works, it is said that zinc crystal grows epitaxy to the substrate initially[14-17], the (002) orientation is most preferred, and other plane appeared as secondary nucleation occurred. Inhibition of crystal growth or stimulation of the nucleation, accordingly, make (002) orientation index decreased, having a significant effect on the morphology and structure of the electrodeposit.

In Fig. 5, the crystal orientation index was shown. With iron additives, no obvious change in crystal orientation was found, on the other hand, (002) crystal orientation index decrease in proportion to the concentration of cobalt additives. It was examined that $P_{(002)}$ increased for 0.01mol/L of tungsten additive, and then decreased for 0.1mol/L. Adding antimony made large decrease in $P_{(002)}$ over whole electroplating condition. No alloy phase was observed.

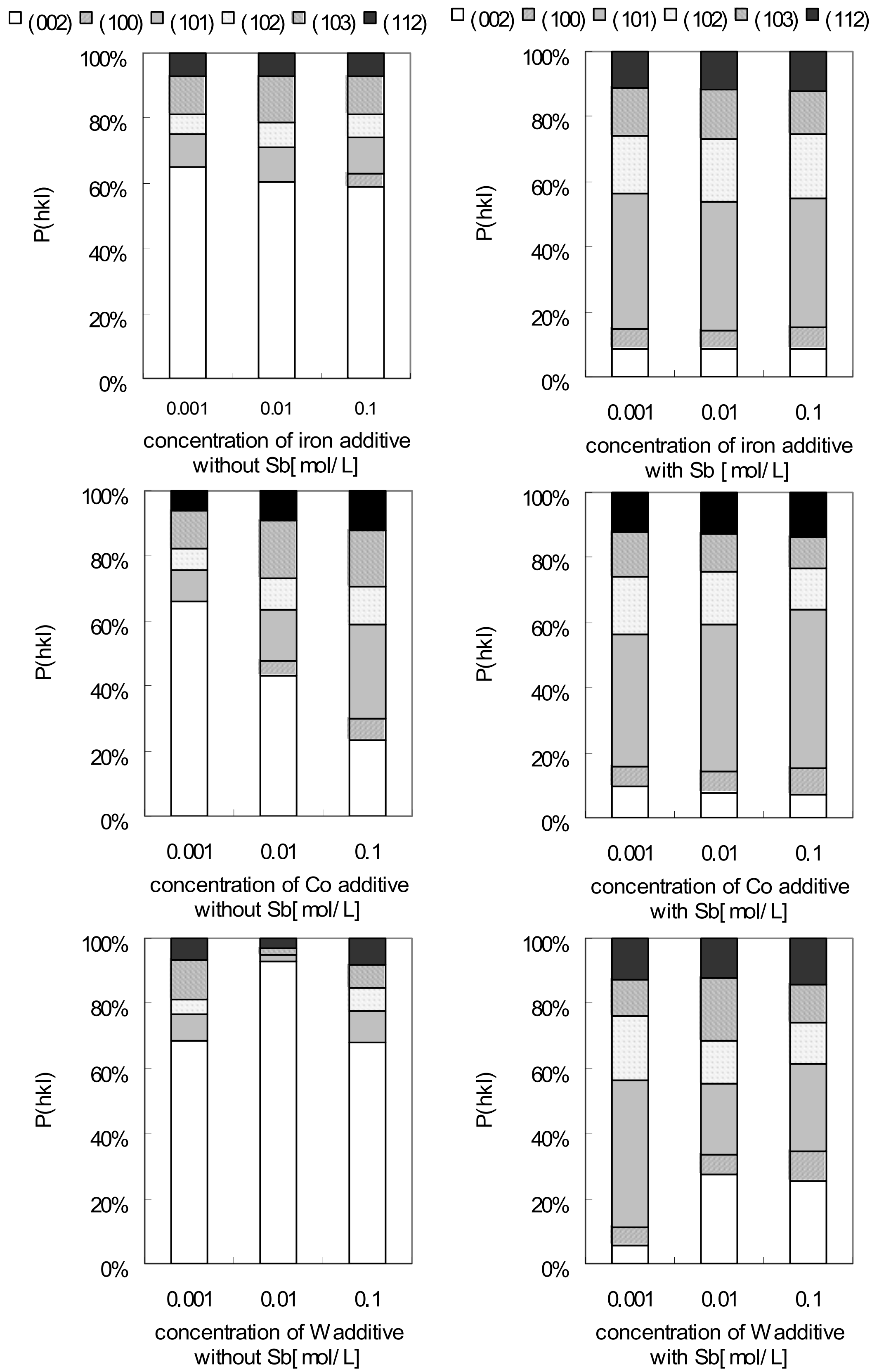
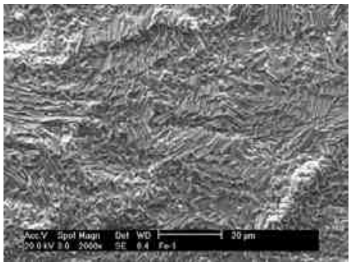


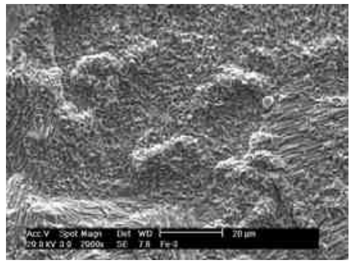
Fig. 5 The effect of additives on the crystal orientation of electrodeposit

Decrease in (002) crystal orientation index means nucleation occurred more frequent than growth of the crystal, making the size of the crystallite of electrodeposit reduced. Actually, it was observed that the crystallites size was not change apparently with iron addition. And crystallite became smaller as the increase of the cobalt additive. (Fig. 6) It is evident, hence, that cobalt ion give more inhibition to crystal growth than iron ion. With tungsten addition, the crystallite size was very small though $P_{(002)}$ increased. It thought to be come from the insufficient crystal growth and coating weight owing to very strong inhibition of tungsten, considering low current efficiency and high concentration in the electrodeposit exhibited above. In AFM study, there was a similar relationship between the crystallite size and additive concentration. (Fig. 7) The crystallite size became smaller and the micro roughness was reduced as the concentration of additives, and the morphology of the crystallite became angular type rather than hexagonal planar type. But AFM images could not be obtained with cobalt additive because of the great fluctuation of micro roughness resulted from partial aggregation of the crystallites. For tungsten addition, crystallite was very fine and micro roughness was relatively low owing to low coating weight and insufficient crystal growth.

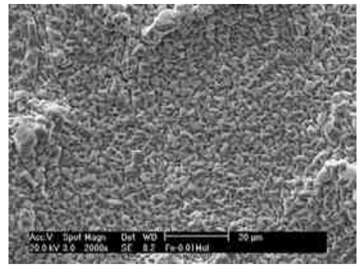
Antimony addition made $P_{(002)}$ decreased considerably and it was determined that the crystallite was very fine from AFM analysis showed that round shaped morphology which was observed in SEM image was an aggregate of the small crystallites. As known, anomalous codeposition of zinc was inhibited due to antimony[12, 13], therefore, the additive has more effect on the zinc crystal growth evidently. It could be determined that less concentration of inorganic additive would be enough to modify microstructure with the presence of antimony than without it.



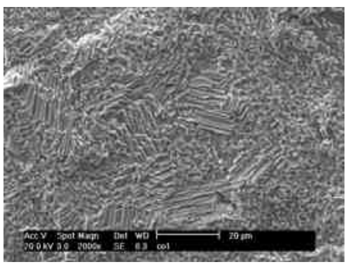
a) Fe 0.001 mol/L



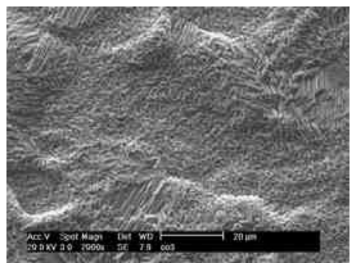
b) Fe 0.1 mol/L



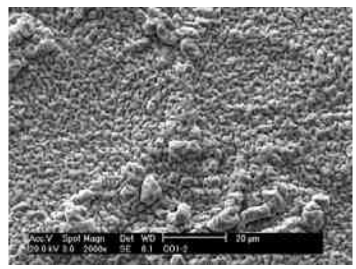
c) Fe 0.01 mol/L with Sb



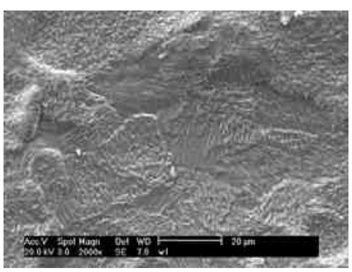
d) Co 0.001 mol/L



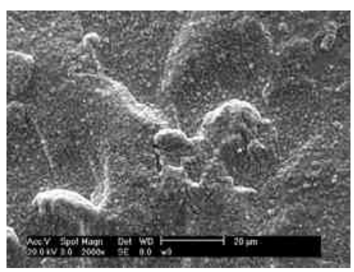
e) Co 0.1 mol/L



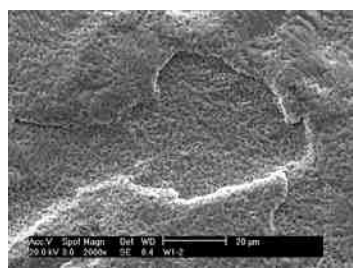
f) Co 0.01 mol/L with Sb



g) W 0.001 mol/L



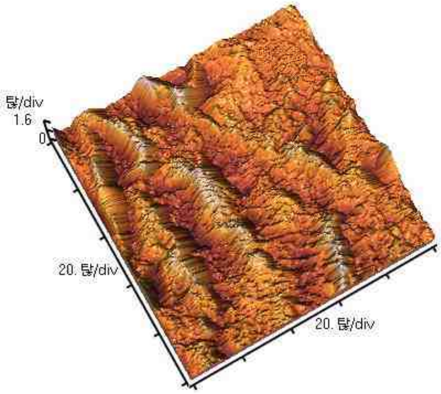
h) W 0.1 mol/L



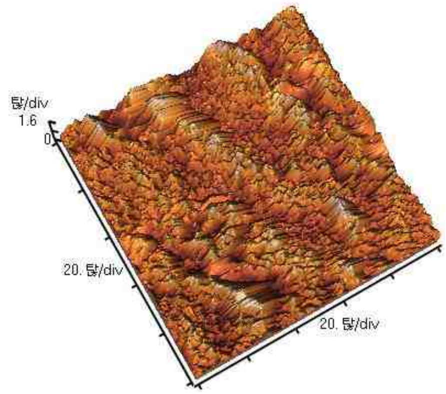
i) W 0.01 mol/L with Sb

Fig. 6 The effect of the additives on microstructure of electrodeposit

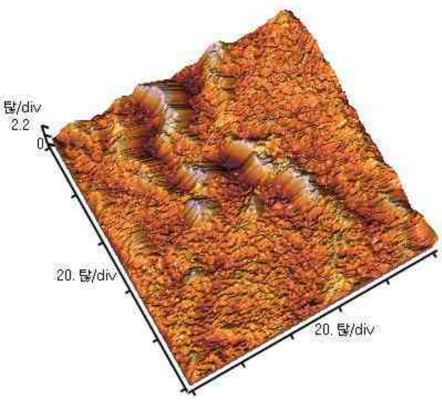
(SEM image, x2000)



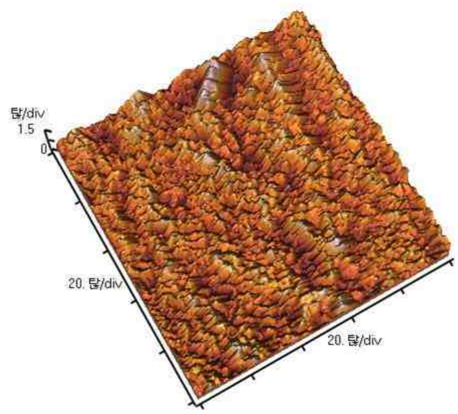
a) Fe 0.01 mol/L



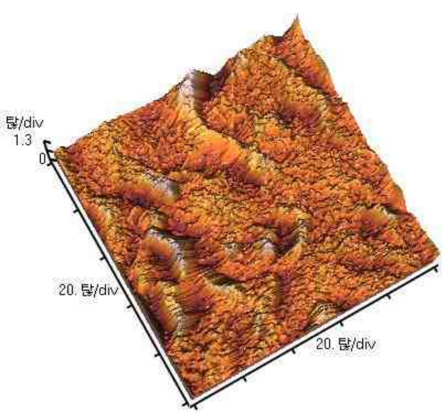
b) Fe 0.01 mol/L with Sb



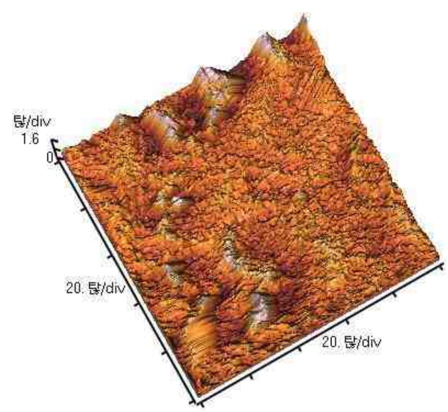
c) Co 0.001 mol/L



d) Co 0.001 mol/L with Sb



f) W 0.01 mol/L



d) W 0.001 mol/L with Sb

Fig. 7 The effect of additives on surface morphology of the electrodeposit

(AFM image, 10㎛ x 10㎛ size)

Formability

Formability is important characteristic of the zinc electrodeposited steel sheet for industrial application. Formability of electrodeposited steel sheet is much affected by mechanical properties of the substrate, the structure and properties of the electrodeposit are also significant, however, to minimize exfoliation and blackening of the electrodeposit during the forming process such as pressing or shearing etc. Friction coefficient and surface roughness also must be considered because it determines surface lubrication characteristics.

In Fig. 8, surface roughness and friction coefficient was shown, and it is found that friction coefficient was in proportional to surface roughness roughly. Friction coefficient is lower with iron addition than with other additives relatively. Adding antimony has little effect on surface roughness, but made friction coefficient decreased. So it found that crystallite aggregation due to antimony addition made friction coefficient decreased without affecting surface roughness despite increase in micro roughness.

The exfoliation was estimated by measuring gloss, the blackening by measuring lightness before and after drawbead test. The best result was found in whole concentration range with the lowest difference in lightness and gloss when iron was added. (Fig. 9) With antimony addition, no obvious tendency could be observed.

The relationship between the properties of the electrodeposit and the formability were summarized in Fig. 10. As $P_{(002)}$ increased, without antimony, surface roughness decreased and blackening (difference in lightness) increased. Both cobalt and iron addition made blackening lowered, but iron addition had less exfoliation (difference in gloss) and lower friction coefficient comparing with cobalt addition. It was found to be no distinct correlation between $P_{(002)}$ and formability for antimony addition, however, the electrodeposit with iron additive was superior due to its lower exfoliation, blackening, and friction coefficient.

From these results, it can be concluded that the crystallite must be fine for good formability. It is thought, however, that the excess aggregation of crystallite, which makes formability worse, occurs if the size of crystallite is too much fine. It is also required that $P_{(002)}$ should not be too much low by similar meaning.

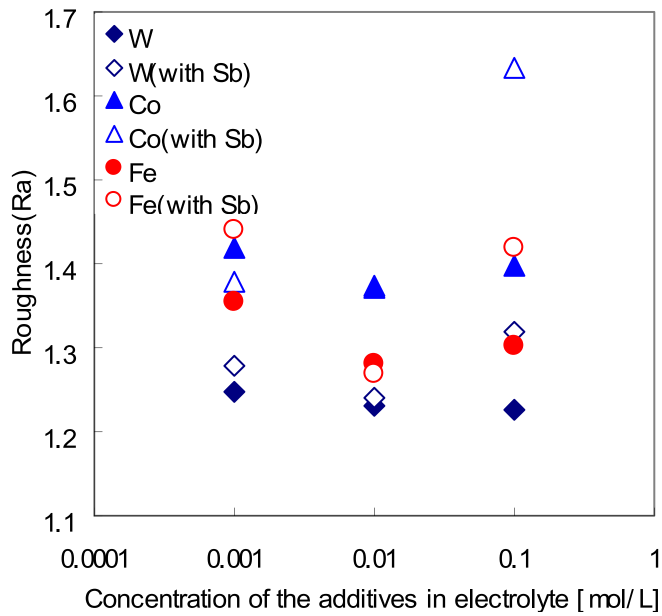


Fig. 8 The effect of additive on roughness of the electrodeposit

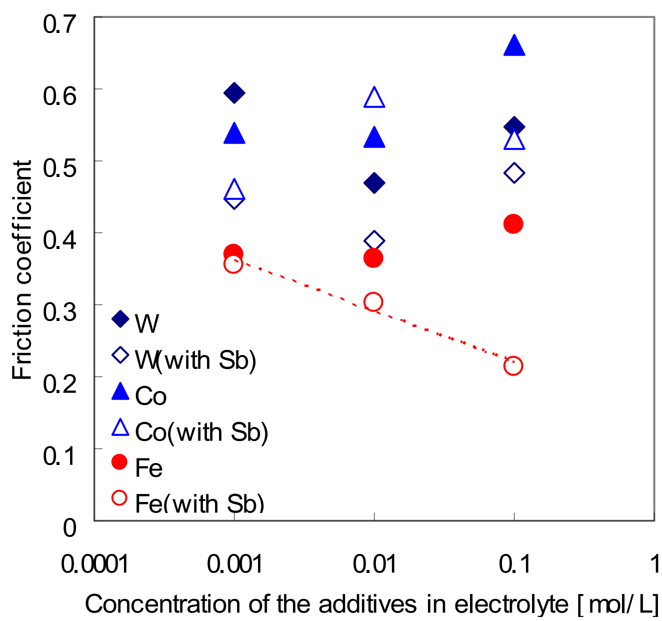


Fig. 9 The effect of additives on friction coefficient of the electrodeposit

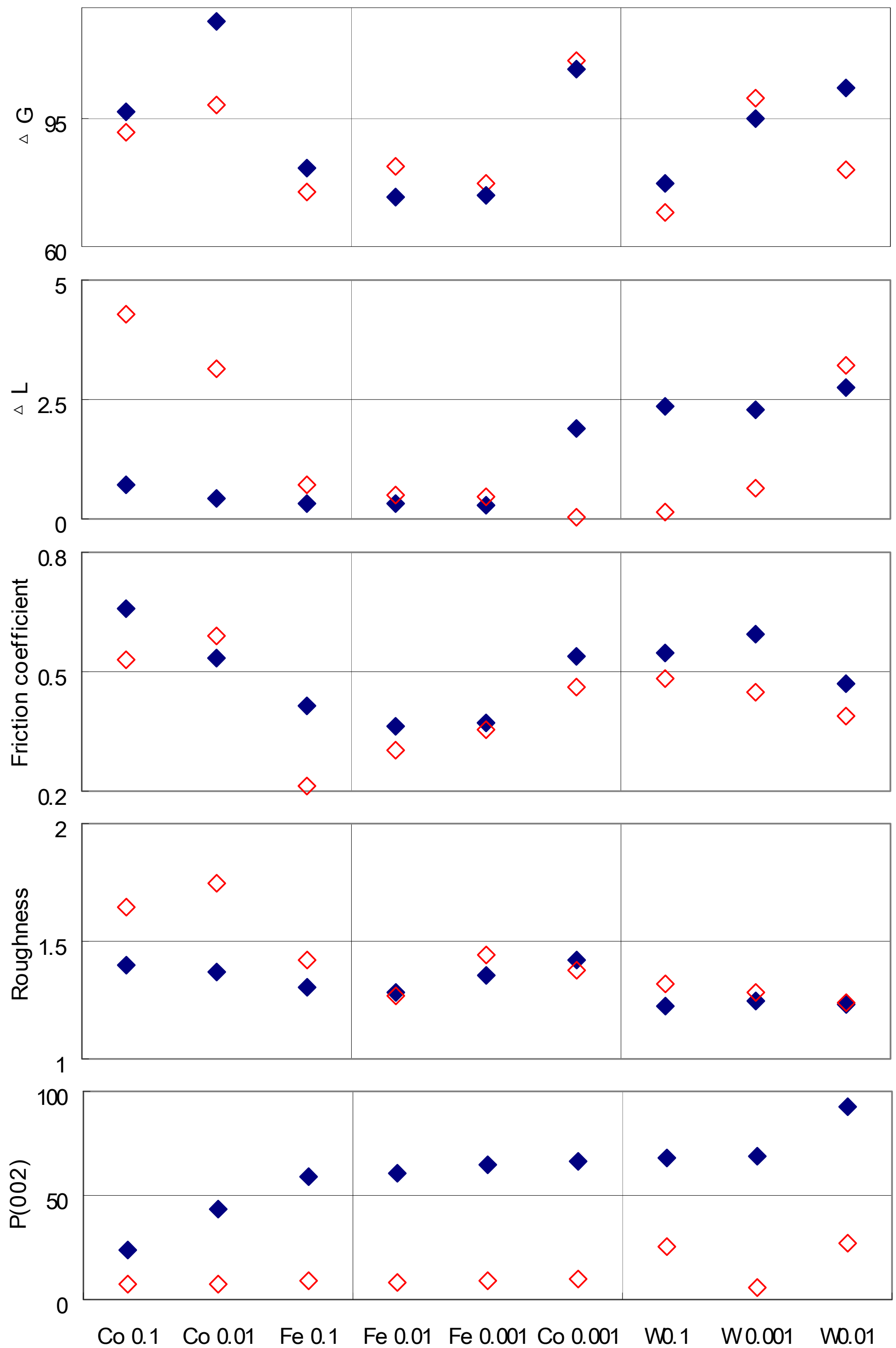


Fig. 10 The effect of additives on formability of the electrodeposited steel sheet, ΔL is the difference of lightness(deformation blackening) and ΔG is the difference of gloss(exfoliation of deposits)

4. Conclusions

The effect of inorganic additives on the properties of zinc deposit was investigated, and the formability was estimated. The result shows as follows.

(1) Current efficiency, chemical composition and by surface appearance of the electrodeposit were not markedly changed for iron additives. Crystallite size was slightly diminished with little change of crystal orientation.

(2) With cobalt addition, little change in current efficiency and chemical composition was occurred. Lightness was not reduced without simultaneous antimony addition. Crystallite size decreased with obvious change of crystal orientation as concentration of cobalt additive increased. Aggregation of crystallite observed at high concentration of cobalt additives.

(3) Tungsten addition made current efficiency worse, and large amount of codeposition was examined relatively. High lightness and gloss were observed due to low coating weight of electrodeposit. (002) crystal orientation increased but crystallite size was reduced because crystal growth was insufficient.

(4) Antimony which was added simultaneously, have (002) crystal orientation and crystallite size reduced remarkably. It is also found that crystallite is aggregated, so that friction coefficient was lowered.

(5) It is determined that good formability (low exfoliation, blackening and friction coefficient) can be obtained with fine crystallites which are randomly oriented. Formability got worse, however, if crystallite size was so fine that it is aggregated excessively.

5. References

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