

## Studies on the influence of metal oxides on the galvanic characteristics of hot-dip zinc coating

S.M.A. Shibli<sup>a,\*</sup>, R. Manu<sup>b</sup>, Semina Beegum<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum, 695 581, India

<sup>b</sup> Central Electrochemical Research institute, Karaikudi, Tamil Nadu, 630 006 India

Received 16 February 2007; accepted in revised form 19 July 2007

Available online 31 July 2007

### Abstract

In the present work, hot dip zinc coating incorporated with various composite was developed. The effect of ZnO and V<sub>2</sub>O<sub>5</sub> in the galvanizing characteristics of zinc coating was studied with a view to apply the coating for functional application. The pretreatment conditions and bath compositions were fixed based on the available literatures and on the preliminary test results. Different electrochemical techniques were followed to study the corrosion tolerance of the coating. The presence of ZnO had a beneficial influence on the protection span of the coating compared to that of V<sub>2</sub>O<sub>5</sub>. The presence of composite reinforced inner layer influenced the alloying reaction between Fe and Zn. The surface topography of the coating was also improved due to the metal oxide incorporation.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Zinc coating; Galvanic coating; Corrosion; Composites; Alloying

### 1. Introduction

Galvanization has long been extensively employed for corrosion protection of steel structures exposed to various environments. From the literature survey it is clear that the galvanization process has undergone tremendous modification since its origin. The process has gone through various modifications in bath alloying, steel chemistry and in the post treatment techniques. Alloying elements such as Al, Bi, Ni, Mg etc. are commonly added as bath additives in the molten bath to increase the fluidity and to control the zinc diffusion during galvanization [1–3]. The formation of inter-metallic phases or alloys during galvanization depends on the diffusion rate of zinc into the substrate and the subsequent alloying reaction between iron and zinc [4–6]. The bond strength between the substrate and the coating mainly depends on the surface feature of the metal substrate and on the galvanizing conditions.

Various metal oxides such as ZnO, ZrO<sub>2</sub> and TiO<sub>2</sub> have been used as bath additives to form oxide barrier galvanic coating on steel substrates [7–9]. The presence of metallic composites could influence the microstructure and layer-wise morphology of the metallic coating [10,11]. Incorporation of ZnO improves the wear and corrosion resistance characteristics of the Ni–P alloy plate [12]. ZnO could act as an efficient additive during metallic coating. V<sub>2</sub>O<sub>5</sub> is an efficient bath additive in the plating process as its composite nature could significantly influence the plating process and the electrochemical behavior of the plate [13,14]. Though V<sub>2</sub>O<sub>5</sub> is known for inducing hot corrosion of metals such as nickel, zinc and iron it can be an efficient additive for metallic coatings in ambient temperatures [15,16].

In the present work, composite incorporated hot dip coatings were developed through ZnO and V<sub>2</sub>O<sub>5</sub> addition in the galvanizing bath. The coatings were compared based on their physico-chemical, surface morphological and electrochemical characteristics. The influence of such composite addition in the zinc coatings and its influence on its subsequent performance were studied and reported briefly here.

\* Corresponding author. Tel.: +91 471 2418782 (Off), +91 471 2167230 (Res).

E-mail address: [smashibli@yahoo.com](mailto:smashibli@yahoo.com) (S.M.A. Shibli).

## 2. Experimental methods

### 2.1. Optimization of the coating composition

Different concentrations of ZnO (99% pure, Product No. 40617, supplied by Sd. Fine Chemicals Ltd; India) and V<sub>2</sub>O<sub>5</sub> (99% pure, Product No. 40565, supplied by Sd. Fine Chemicals Ltd; India) were added into the molten zinc bath. High concentration of ZnO and V<sub>2</sub>O<sub>5</sub> caused segregation in the molten bath, resulting in irregular coating structure. But very low concentration of ZnO/V<sub>2</sub>O<sub>5</sub> had not much effect on the coating character. Based on available literature and preliminary test results, 0.1 and 0.01% by weight of ZnO and V<sub>2</sub>O<sub>5</sub> were chosen to incorporate into the molten zinc bath for further studies [11,12].

### 2.2. Galvanization process

Steel coupons of 5 cm × 5 cm × 0.1 cm cut size bearing the composition — Carbon: 0.90%, Manganese: 0.340%, Phosphorous: 0.36%, Silicon: 0.0487% and Aluminium: 0.029%, were abraded with different grades of emery paper to obtain a fine and smooth surface. The steel substrate after degreasing in 15% NaOH solution was washed with water and then pickled with 8% HCl solution. The steel coupons were thoroughly washed with water and then fluxed with 30% NH<sub>4</sub>Cl solution [17–19]. The galvanization bath consisted of molten pure zinc incorporated with different concentrations of ZnO and V<sub>2</sub>O<sub>5</sub> and kept at 450 ± 10 °C [20,21]. The bath was continuously stirred to maintain the homogeneity of the melt. The dipping time was fixed to be 10–12 s [17]. The excess zinc on the surface was removed by hot air blowing. The galvanization process parameters were fixed based on available literature and the results of preliminary studies.

### 2.3. Characterization techniques

The galvanised coupons were subjected to Vicker's hardness test as per ASTM E 384-899 using a shimadzu HMV-2000 instrument. The test load was 50 gf for an indentation time of 12 s at 22.9 °C. To determine the adhesion of the coating, the coupons were bent until the two ends became parallel and then returned to their initial condition. The surface of the coupons was examined visually using a magnifying lens to check cracks and other defects. Thickness measurement of the zinc coating was carried out as per ASTM standard A 525-93 [22,23]. The galvanized coupons were subjected to weldability test as per ASTM B 571-79. The zinc coating was etched with 5% HCl solution for five minutes, washed thoroughly with water and dried prior to characterization of the surface topographical feature of the coating by SEM (Hitachi S-2400). Long-term immersion studies were carried out to assess the potential decay characteristics of the galvanized coupons under saline conditions. Cleaned coupons having definite exposed area were individually dipped into 5% NaCl solution kept in different beakers. The change in electrode potential with respect to saturated calomel electrode (SCE) was measured at regular

intervals continuously for 30 days. Self-corrosion rate was determined based on the data of difference in weight of the coupons and the time of each exposure. Salt spray test was carried out as per ASTM B.117 standard for a period of 30 days at 35 °C. The edges of the pre-weighed coupons were covered with adhesive tapes before placing the coupons in the salt spray chamber. The corroded coupons were washed with 10% ammonium per sulphate ([NH<sub>4</sub>]<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) solution at room temperature, dried and weighed.

## 3. Results and discussion

### 3.1. Physico-chemical properties

The performance of the galvanic coating can be improved by using metallic composites as bath additives. In the present work ZnO and V<sub>2</sub>O<sub>5</sub> were incorporated as bath additives. As already mentioned, two different concentrations of ZnO and V<sub>2</sub>O<sub>5</sub> were added. The oxides got distributed easily in the molten zinc bath as it had fine particle size and the zinc bath was thoroughly agitated after each addition. In the presence of inert metallic composites on the surface of the substrate, the diffusion of zinc during galvanization is lowered. The physico-chemical properties of the zinc coatings incorporated with ZnO and V<sub>2</sub>O<sub>5</sub> were compared with those of the pure zinc coating (Table 1). The hardness value, i.e., Vickers Hardness Number (VHN) of the V<sub>2</sub>O<sub>5</sub>-incorporated coating was greater than pure zinc coating. This could be due to the reinforcement of the metal oxides and the composite nature of the coating. The adherence and thickness of the ZnO-incorporated coating were found improved compared to the pure zinc and V<sub>2</sub>O<sub>5</sub>-incorporated zinc coating. To compare the adherence of the coating the steel coupon were bent and was observed for any surface irregularities. After bending, the surface did not have any blemishes or peeling layers. This was in accordance with the already reported evidences on ZnO-incorporated coating [12]. This envisaged the good alloying nature and the compact structural character of the coatings. The observation of thinner coating revealed more compact alloy layers as observed in the case of zinc coating incorporated with ZnO. But in the case of V<sub>2</sub>O<sub>5</sub> incorporated zinc coating there was surface cracks with peeling of outer layers after bend test. As the thickness of the coating increases, it is likely to develop surface cracks during bend tests. The peeling of outer layers after bend test in the case of the V<sub>2</sub>O<sub>5</sub>-incorporated zinc coating might be due to the segregation of the composite and the irregular Fe–Zn alloy

Table 1  
The comparison of physical properties of the galvanic coatings with and without incorporation of ZnO or V<sub>2</sub>O<sub>5</sub>

Coating composition	Adherence	Hardness (VHN)	Thickness (μm)	Mean coating weight (g/cm <sup>2</sup> )
Pure zinc coating	Good	50	40	1.308
0.01% ZnO	Fair	52	37	0.9716
0.1% ZnO	Good	56	33	0.8306
0.01% V <sub>2</sub> O <sub>5</sub>	Fair	57	48	1.654
0.1% V <sub>2</sub> O <sub>5</sub>	Good	57	44	1.410

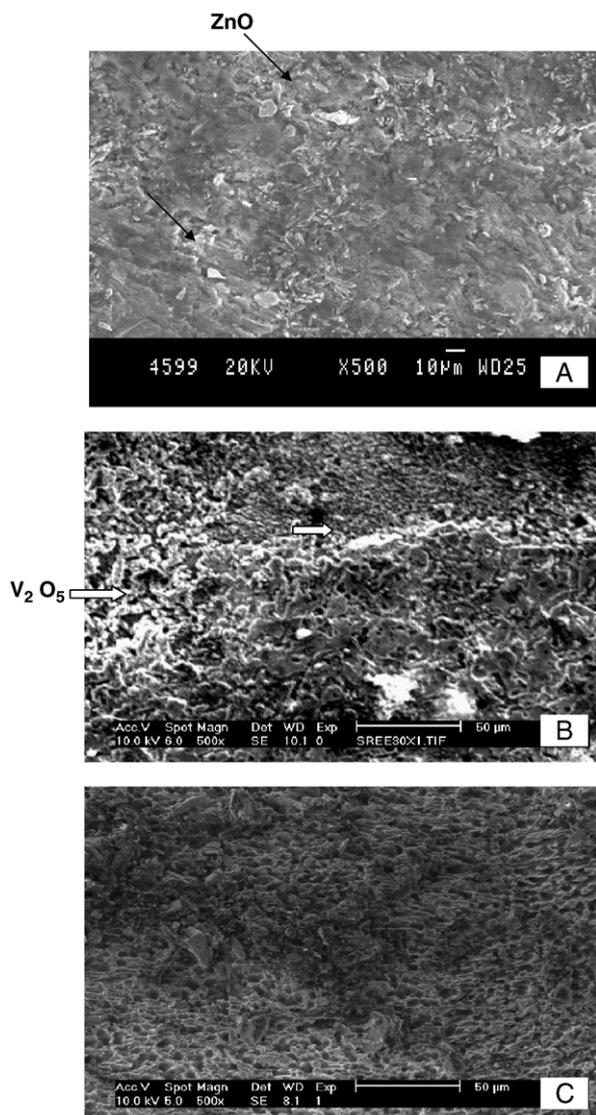


Fig. 1. The SEM micrographs of the coatings (A) incorporated with ZnO (B) incorporated with  $V_2O_5$  (C) pure zinc coating.

structure of the coating. In the presence of inert metallic composites on the surface of the substrate, the diffusion of zinc during galvanization is lowered. The diffusion of zinc during galvanization was gradual for the ZnO-incorporated coating compared to the pure zinc and  $V_2O_5$ -incorporated zinc coating. This could influence the Zn–Fe alloying reaction in the presence of ZnO during the galvanization process. Generally thicker zinc coatings are prone to have surface cracks leading to peeling off layers during bent test as in the case of  $V_2O_5$  incorporated zinc coating.

### 3.2. Surface morphology

The surface morphology of the ZnO-incorporated galvanic coating is shown in Fig. 1A. The surface consisted of well-defined grains and had smooth surface feature compared to conventional zinc coating. The incorporation of ZnO had improved reinforcement nature causing formation of more

compact alloy layers. There was no segregation. The surface of the  $V_2O_5$ -incorporated zinc coating (Fig. 1 B) consisted of micro voids and there was segregation of the composite at certain regions. Generally the ridged spangle surfaces are populated with precipitates present in relatively large size [24,25]. In the case of  $V_2O_5$ -incorporated coating, the grain size differed where the luster of each spangle was also differed, yielding the surface a non-uniform appearance. There were small pits on the pure zinc coating (Fig. 1 C). This could be attributed to the preferential dissolution of zinc from the outer layer during the etching process. On consolidating the surface morphological analysis, we could conclude that the incorporation of ZnO would result in more uniform coating structure with compact inner alloy layers.

### 3.3. Electrochemical characterization

#### 3.3.1. Testing in stagnant sodium chloride solution

After physico-chemical and morphological analyses, the coated coupons were evaluated by various electrochemical tests. All the coatings exhibited a stable and high negative Open Circuit Potential (OCP) values (the equilibrium electrode potential without any external electrochemical contact) during the initial hours of exposure in 5% NaCl medium. This could be ascribed that the top layer which consisted of pure zinc ( $\eta$  phase) sacrificed itself protecting the inner alloy layers from corrosion during the exposure. During the course of exposure, the ZnO incorporated coating had an instantaneous protective barrier layer minimizing the dissolution of zinc. As the dissolution progressed the OCP of the coupons shifted to more anodic regions (Fig. 2). The extent of potential shift was lesser in the case of zinc coating containing 0.1% ZnO compared to the pure zinc coating or the other containing lesser concentration of ZnO. This could be attributed to the formation of more compact and adherent protective layer of ZnO along with the corrosion products. It was revealed that the fine texture of the coating improved the corrosion resistance of the coating. As reported elsewhere, the corrosion resistance as well as the mechanical properties of composite incorporated

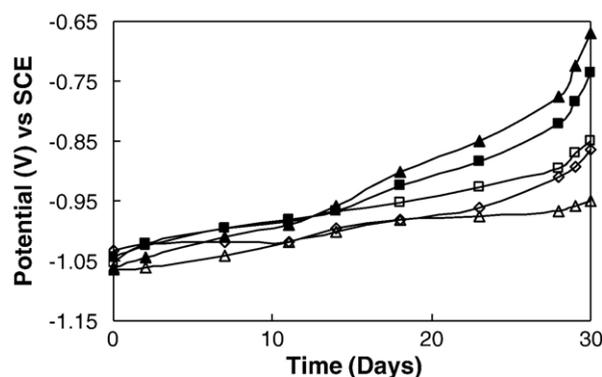


Fig. 2. The variation in OCP decay curves of the galvanized coupons during long-term immersion test.  $\Delta$  — 0.1% ZnO,  $\diamond$  — 0.01% ZnO,  $\square$  — pure zinc coating,  $\blacksquare$  — 0.01%  $V_2O_5$ ,  $\blacktriangle$  — 0.1%  $V_2O_5$ . Medium: stagnant 5% NaCl solution, temperature:  $35 \pm 2$  °C.

coatings could be substantially improved by incorporation of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$  and  $\text{FeO}$  [12,25].

Although the oxides are inert, the surface of the coatings form double layer of varying structure depending on the coating structure. Thus the resultant potential also varies depending on the coating structure. The potential also varies depending on the structural changes in the double layer with time (e.g., OCP data).

In the present work, the galvanic coating incorporated with  $\text{ZnO}$  was found to have brighter surface than conventional zinc coating. The surface characteristics of the coating also played an important role during the course of exposure. In the case of the pure zinc and the  $\text{V}_2\text{O}_5$ -incorporated coatings, there were lack of compact alloying nature and the formation of soluble corrosion products aggravated the condition that resulted in anodic potential shift. Although the zinc coating incorporated with various amounts of  $\text{V}_2\text{O}_5$  exhibited a high negative potential during initial days of the exposure, there was more anodic shift during its long term exposure. The zinc coating having  $\text{V}_2\text{O}_5$  had rougher surface and the alloy layers were less adherent. The presence of  $\text{V}_2\text{O}_5$  did not influence the alloying reaction and the coating growth during galvanization to the extent of that  $\text{ZnO}$  had. The presence of  $\text{V}_2\text{O}_5$  induced corrosion and was largely unsuccessful owing to the transition semi conductance of  $\text{V}_2\text{O}_5$  [15,16]. Comparing the two oxide incorporated coatings with that of the pure zinc coating the one with  $\text{ZnO}$  incorporation was found to have more stable potential during the stipulated exposure time. The nature of the  $\text{ZnO}$  composite and its uniform distribution influenced the coating structure. The influence of  $\text{V}_2\text{O}_5$  on the coating structure might be the probable reason for the change in the double-layer structure that resulted in comparatively higher polarization. The weight loss of the coupons (Table 1) recorded at the end of each exposure also revealed the earlier inference that  $\text{ZnO}$ -incorporated coating had better performance.

### 3.3.2. Testing in salt fog

Salt spray test was carried out as a simulated accelerated test to examine the influence of humidity and aggressive ion ( $\text{Cl}^-$ ) concentration on the galvanized coating. The test was carried out in a salt spray fog chamber in 5%  $\text{NaCl}$  medium for 720 h. During the salt spray fog test the signs of onset of corrosion were observed with the white rust formation, (Table 2). White

Table 2  
The visual observation of the galvanized coupons noted during salt spray test

Coating system	Number of days of exposure			*Self corrosion rate (g/cm <sup>2</sup> /h)
	5	20	30	
Pure zinc coating	*20%	42%	65%	18.9
0.01% $\text{ZnO}$	15%	25%	43%	17.9
0.1% $\text{ZnO}$	5%	15%	20%	10.8
0.01% $\text{V}_2\text{O}_5$	45%	68%	80%	26.3
0.1% $\text{V}_2\text{O}_5$	50%	79%	100%	31.6

\*% white rust formation, weight loss during salt spray analysis.

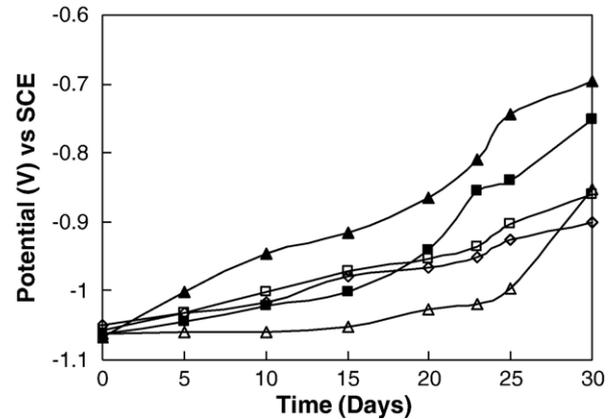


Fig. 3. The OCP decay curves of the galvanized coupons during salt spray test.  $\Delta$  — 0.1%  $\text{ZnO}$ ,  $\diamond$  — 0.01%  $\text{ZnO}$ ,  $\square$  — pure zinc coating,  $\blacksquare$  — 0.01%  $\text{V}_2\text{O}_5$ ,  $\blacktriangle$  — 0.1%  $\text{V}_2\text{O}_5$ . Medium: 5%  $\text{NaCl}$  solution, temperature:  $35 \pm 2$  °C.

rust was formed on the surface within 48 h of exposure in all types of the coatings, but the area covered with white rust was less on the  $\text{ZnO}$ -incorporated coating. The percentage of white rust covered over the surface is referred in the table. The incorporation of  $\text{ZnO}$  would have caused formation of a quasi-stable passive layer that could minimize dissolution of zinc. In the case of the pure zinc coating the corrosion product formed were unstable and got easily washed off during the spray process. After 20 days of exposure, appearance of red tinges revealed the corrosion of underneath steel substrate. But in the case of the  $\text{ZnO}$ -incorporated coating red rust was observed after 26 days of exposure. This could be ascribed to the better coating morphology and the bright surface feature of the coating [12,26]. The bright surface performed well due to its low surface energy and minimum segregation under aggressive condition. The area covered with brown rust was lesser on the  $\text{ZnO}$ -incorporated zinc coating compared to the  $\text{V}_2\text{O}_5$ -incorporated and pure zinc coating. The presence of  $\text{ZnO}$  in the under layer could prevent the penetration of aggressive ions during exposure of the coating in the salt fog. In the case of  $\text{V}_2\text{O}_5$ -incorporated zinc coating the catalytic nature of  $\text{V}_2\text{O}_5$  adversely affected the dissolution of zinc during saline exposure.

In the case of the  $\text{V}_2\text{O}_5$ -incorporated zinc coating the corrosion product did not get much ageing time to grow as barrier and to protect the under layer from corrosion. During a parallel set of salt spray analysis a provision was made to check the potential decay of the coupons. Fig. 3 shows the potential decay of the coating during the exposure. The  $\text{ZnO}$ -incorporated coating exhibited better performance in accordance with the earlier observations of polarization analysis. In short the corrosion resistance of the galvanic coating containing  $\text{ZnO}$  exhibited better performance compared to the  $\text{V}_2\text{O}_5$ -containing and the pure zinc coating during the salt fog test.

## 4. Conclusions

The physico-chemical properties of the composite-reinforced zinc coating were found to be superior to that of conventional zinc coating. The surface morphology and microstructure of the

zinc coating were improved due to the incorporation of ZnO that resulted in the formation of more compact inner alloy layers with reduced thickness. Of the two types of the metal oxides studied, viz ZnO and V<sub>2</sub>O<sub>5</sub>, the incorporation of ZnO had a beneficial influence on the galvanic performance of the coating. Although both the types of metal oxides had the role in modifying the zinc coating structure, the presence of ZnO had significant role in improving the inner alloy structure yielding higher protection span.

### Acknowledgement

The authors thank the head of the Department of Chemistry, University of Kerala for extending support to carry out the research work.

### References

- [1] R. Fratesi, N. Ruffini, M. Malavolta, T. Belleze, Surf. Coat. Technol. 157 (2002) 34.
- [2] H.J. Lee, J.S. Kim, J. Mater. Sci. Lett. 20 (2001) 955.
- [3] N. Pistofidis, G. Vourlias, S. Konidaris, El. Pavlidou, G. Stergioudis, Mat. Lett. 61 (2007) 2007.
- [4] C.E. Jordan, A.R. Marder, J. Mater. Sci. 32 (1997) 5603.
- [5] G.D.S. Price, J.A. Charles, J. Iron Steel Inst. (1973) Dec.
- [6] E.J. Daniels, J. Inst. Met. 46 (1931) 81.
- [7] R.L. Ibanez, J.R.R. Barrado, F. Martin, F. Brucker, D. Leinen, Surf. Coat. Technol. 188–189 (2004) 675.
- [8] F. Martin, M.C. Lopez, P. Carrera, J.R.R. Barrado, D. Leinen, Surf. Interface Anal. 36 (2004) 8.
- [9] R. Ayouchi, F. Martin, D. Leinen, J.R.R. Barrado, J. Cryst. Growth 247 (2003) 497.
- [10] S.M.A. Shibli, R. Manu, Appl. Surf. Sci. 252 (2006) 3058.
- [11] S.M.A. Shibli, V.S. Dilimon, S.P. Antony, R. Manu, Surf. Coat. Technol. 200 (2006) 4791.
- [12] S.M.A. Shibli, B. Jabeera, R.I. Anupama, Surf. Coat. Technol. 200 (2006) 3903.
- [13] N. Ozer, C.M. Lampert, Thin Solid Films 349 (1999) 205.
- [14] G.N.K.R. Babu, M.M. Yusuf, Mater. Chem. Phys. 36 (1993) 134.
- [15] M. Amaya, M.A. Espinosa-Medina, J. Porcayo-Calderon, L. Martinez, J.G. Rodriguez, Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process. 349 (2003) 12.
- [16] E. Chassagneux, G. Thomas, Mater. Chem. Phys. 17 (1987) 273.
- [17] S.M.A. Shibli, R. Manu, Surf. Coat. Technol. 252 (2006) 3058.
- [18] M. Jun, Y. Shinichi, I. Teruaki, Japan Patent, 81 538 (2001).
- [19] T. Uchida, S. Murotani, K. Hagimori, Japan Patent, 64 009 (2000). Flux.
- [20] J. Mackowiak, N.R. Short, Corros. Sci. 16 (1976) 519.
- [21] G.M. Stefanick, US Patent 6 277 443 (2001).
- [22] A.K. Singh, G. Jha, S. Chakrabarti, Corrosion 59 (2003) 190.
- [23] H.B. Chen, Alloy Layer Formation and Spangle Growth on Hot-Dip galvanizing Steel, China Steel Technical Report, No: 5 (Kashsiung, Taiwan, Republic of China: China Steel Corpn.), 1991, p. 52.
- [24] H.E. Biber, Metall. Trans., A, Phys. Metall. Mater. Sci. 19 (1988) 1603.
- [25] J. Strutzenberger, J. Faderl, Metall. Mater. Trans., A Phys. Metall. Mater. Sci. 29 (1998) 631.
- [26] P.R. Sere, J.D. Culcasi, C.I. Elsner, A.R.D. Sarli, Surf. Coat. Technol. 122 (1999) 143.