Zinc Anodizing & Coloring by Chemical Conversion & Spark Discharges

By H.C. Shih, F.Y. Shyr, J.W. Hsu, S.C. Chung & S.L. Sung

Zinc is an active element and is often employed as a sacrificial coating on steel articles for cathodic protection. Conventional hot dip galvanized steel objects, however, exhibit a monotonous silver gray that lacks aesthetics and limits the field of usage. For this reason, various colored surface layers on zinc were developed in aqueous environments basically containing sodium silicate, sodium tetraborate and sodium hydroxide as an electrolyte. The anodic treatment in this study involves a two-step process, the steps are: (1) A chemical conversion layer on zinc in the form of a bright film produced in 0.25 M $Na_2Cr_2O_7$ solution at 50-70 °C for 1.5 min, and (2) an alternating current of 2O A/dm^2 applied to zinc at 0 °C for 10 min. The result of the first step provides an oxide film that is able to retard the anodic dissolution of zinc and therefore to act as a barrier layer for the subsequent spark discharge (second step). In the second step, an adequate amount of transition metal salts is mixed into the bath to obtain various colors on the finished anodic coating. Salt fog tests prove that the treated pure zinc sheets possess much better corrosion resistance than the untreated ones. According to ASTM B 117, white rust spots appear on zinc after 120 hr of the salt fog test, while the treated zinc can last at least 500 hr before rust spots are observed. The resultant coating provides excellent adherence to the substrate and a hardness of 20 percent more than for untreated zinc. Moreover, the colored appearance is steady and uniform, independent of viewing angles.

Zinc is active electrochemically and is often employed as a sacrificial anode to protect steel articles from premature corrosion failures. Zinc exposed to the atmosphere is susceptible to a reaction with moisture and corrosive elements by forming a typical white corrosion rust. To inhibit the formation of such corrosion products and simultaneously to provide a better wear resistance on zinc, much attention has been drawn to the relevant studies for years.[1]

A method of forming colorful anodic coatings on pure zinc is also developed in this study. The experimental results show that the anodic coating, mainly comprising glassy silicates, provides not only better corrosion resistance to the formation of white corrosion products, but also provides a harder surface to prevent zinc from abrasion during use.

Experimental Procedure

Pure zinc (99.95%) machined in the form of 50 x 30 x 3 mm was used in this study. Specimens were polished with 600-grit emery paper, then washed in distilled water prior to each experiment. The anodizing process was divided into two consecutive stages. Zinc specimens were first immersed in a 0.25 M sodium dichromate solution at 70 °C for 1.5 min as the first stage. A uniform bright film on the zinc surface was thus produced mainly because of oxidation. In the second stage of the process, an aqueous bath containing 180 g/L sodium silicate, 90 g/L sodium tetraborate and 30 g/L sodium hydroxide was mixed as an electrolyte at 0 °C by circulating the electrolyte through a stainless steel coil immersed in an ice water bath. An alternating current (60 Hz) of 20 A/dm^2 was applied to the anodizing cell. Initially, the potential increased linearly with time to keep the current constant. When the voltage reached 90, electric sparks suddenly appeared on the surface of both chromated electrodes. The spark sizes were generally small and disappeared rather quickly, but were subsequently replaced by larger and less mobile sparks as the voltage increased to higher values (*e.g.*, 160 V over a period of about 10 min). The result of this spark discharge was a smooth and opaque anodic coating which covered the entire surface of the zinc specimen. Various colors were obtained through addition of an adequate amount of transition metal salts into the basic bath (*e.g.*, Cu for dark red, Ni for green, Co for blue, etc. The potential-with-time measurements were carried out to monitor the formation of chromate conversion films. Potential measurements were made against a saturated calomel electrode (SCE). XPS was used to identify the compositions and the chemical states of the chromate conversion film. EPMA was employed to analyze the element distributions of the anodic coating. Surface hardness was measured with an applied load of 20 grams. Exposure tests were conducted in a salt spray cabinet according to ASTM B 117 procedure, using 3.5 percent NaCl solution with a pH value adjusted to 7. After a period of exposure, the degree of rusting was evaluated according to ASTM D 1654. In this method, ratings from 0 to 10 are assigned; 10 means no failure and 0 means failure over at least 75 percent of the exposed area (see table).

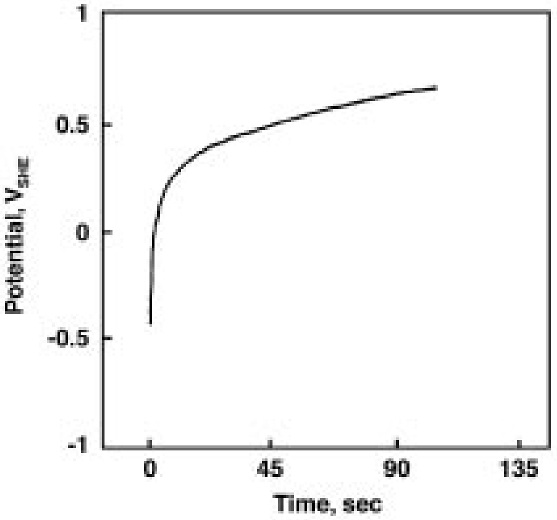

Fig. 1—Potential-time curve of zinc when immersed in 0.25 M sodium dichromate solution at 70 °C.

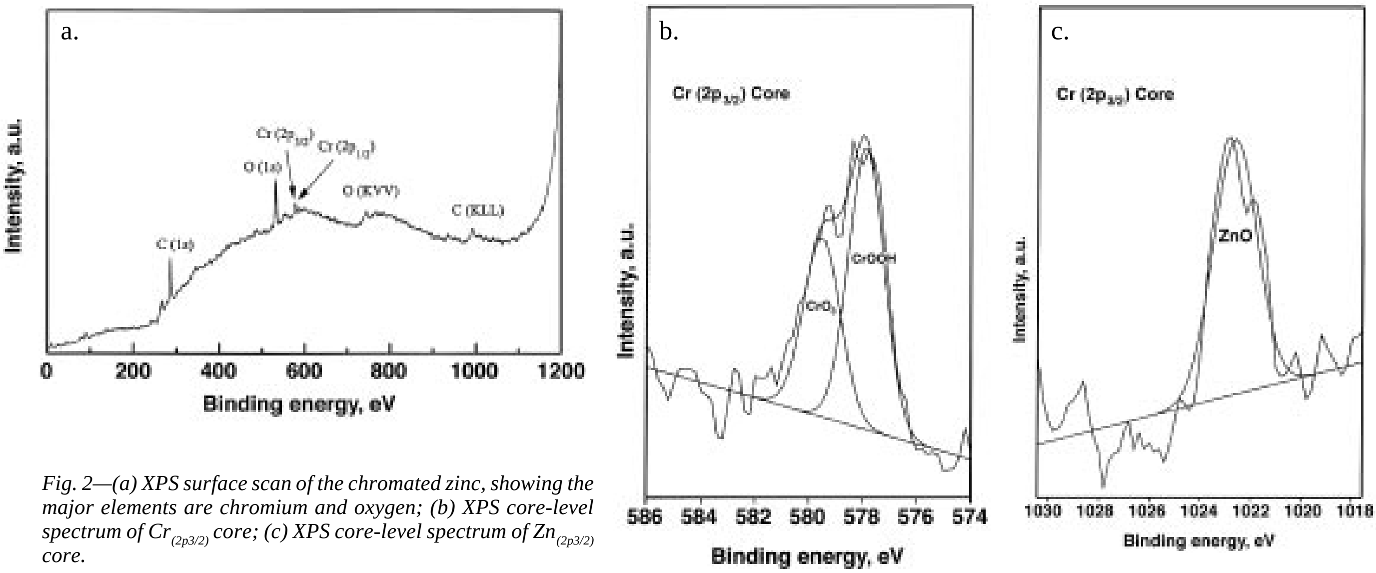

Fig. 2—(a) XPS surface scan of the chromated zinc, showing the major elements are chromium and oxygen; (b) XPS core-level spectrum of $Cr_{(2p3/2)}$ core; (c) XPS core-level spectrum of $Zn_{(2p3/2)}$ core.

Results & Discussion

Potential-Time Profile

The properties of zinc as a result of chromate conversion are characterized by the electrochemical potential changes during the film formation. Figure 1 shows the potential-time curve of zinc in a 0.25 M sodium dichromate bath at 70 °C for chemical conversion. The potential increases sharply at the beginning but slows after about 30 sec, indicating an oxide insulating layer being formed on the zinc surface resulting from the chromate conversion. Chromate treatment applied to galvanized steel articles is a normal practice widely used in all galvanizing plants to minimize the formation of white corrosion products.

Chemical Analysis

Four elements, oxygen, chromium, zinc and sodium were expected to exist in the chromate conversion layer. The XPS result, however, indicated that only oxygen and chromium appeared on the survey scan with a resolution of 1.6 eV, as shown in Fig. 2a. The $Cr_{2p3/2}$-line spectrum was analyzed by means of a best Gaussian fit to reconcile with the two chromium species. The species with a lower $Cr_{2p3/2}$ binding energy of 577.5 eV is assigned to the chromium oxyhydroxide, while the one with a higher binding energy of 579.3 eV is attributed to the chromic oxide, as shown in Fig. 2b.

It is apparent that zinc could also exist in the chromate conversion layer, but in much less quantity, which can therefore be resolved in the core-level spectrum with a resolution of 0.2 eV. In a similar manner, the $Zn_{2p3/2}$-line spectrum was analyzed and it was found that the $Zn_{2p3/2}$ binding energy of 1022.5 eV results simply from the formation of zinc oxide in the chromate conversion layer, as shown in Fig. 2c.

Results of Salt Spray Tests For Various Anodic Coatings

		Time (hr)			
		120	500	2160	3000
Pure Zinc		6	4	0	0
Anodized Zinc*	Cr (green)	10	10	8	6
	Co (blue)	10	10	10	9
	Mn (brown)	10	10	9	8
	Sn (gray)	10	10	10	9
	Fe (white)	10	10	7	6
	Cu (red)	10	9	6	5

* Various transition metal salts, including Cr, Co, Mn, Sn, Fe and Cu (0.03-0.1 M) were added to the basic electrolyte of $Na_2O \cdot 2SiO_2$ 180 g/L, $Na_2B_4O_7 \cdot 10H_2O$ 90 g/L, and NaOH 30 g/L.

Effect of Bath Temperature on the Spark Reaction

Figure 3a shows the potential-time curve for anodizing the chromated zinc specimens by applying a constant alternating current of 20 A/dm^2 to the anodized cell. Apparently, the bath temperature maintained at as low as 0 °C, is beneficial for triggering the spark discharge for the reaction. This phenomenon is related to reduction of the mean field strength (E) within the film as the bath temperature rises. An experimental relation between the mean field strength (E) and the bath temperature (T) under galvanostatic control can be described as $E = b - cT$, where b and c are constants.[2] This E(T) was also observed in this study, in which the potential reaches a steady state at about 10 sec after the application of 20 A/dm^2, irrespective of the bath temperature (*e.g.*, 0, 5 or 15 °C). Bath temperature apparently determines the potential where the steady state begins, for instance, 140 V at 0 °C, 100 V at 5 °C and 40 V at 15 °C. The rate change of the potential (dV/dt) within 10 sec depends on the bath temperature too (*i.e.*, the lower the bath temperature, the greater the potential rate). Consequently, it is interesting to note that both the potential (V) and its derivative, dV/dt, vary linearly with the bath temperature, as shown in Fig. 3b.

Microstructure & Chemical Composition of the Anodic Coating

The anodic coating on zinc apparently forms an integral bond with the zinc, the thickness of the coating being about 30 µin. Fig. 4a shows the EPMA photomicrograph and the surface of a blue anodic coating. Two types of surface morphology were observed: island-like and fritted glass-like structures that were also observed on galvanized steels previously.[3,4] The X-ray mapping of elements Si, Na and O reveals the island-like

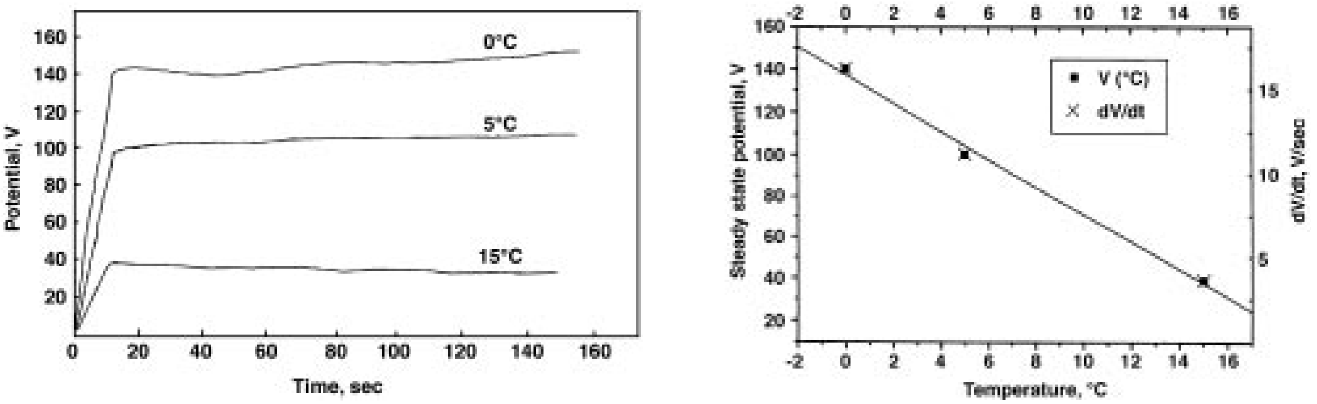

Fig. 3—(a) Potential-time curve of the chromated zinc at a constant alternating current of 20 A/dm^2 in an electrolyte bath of 180 g/L sodium silicate, 90 g/L sodium tetraborate, and 30 g/L sodium hydroxide; (b) effect of bath temperature on the steady state potential V at $t \geq 10$ sec and on the rate change of the potential dV/dt at $t \leq 10$ sec.

structure, whereas Zn and Co are homogeneously distributed on the surface of the anodic coating, as shown in Figs. 4b-f. As a result, the uniform distribution of Co exhibits a unique blue. Moreover, no cracks were observed on the anodic coating surface when tested by cyclic heating and cooling. This may be related to the micropores intrinsic to the fritted-glass structure, that can properly accommodate the thermal expansion and contraction. Such glass-like structure[5,6] with micropores resulting from the anodizing gives a long-lasting and uniform color that is independent of the viewing angle.

Accelerated Corrosion Tests & Hardness Measurements

The corrosion resistance of both untreated and anodized zinc specimens was tested in a salt spray cabinet for 3,000 hr. The results showed that white corrosion products formed on the untreated zinc specimens after 120 hr, while the anodized zinc specimens lasted at least 500 hr before white rust appeared. A comparison of the corrosion resistance capacity between various anodic coatings on zinc is shown in the table.[7] The hardness of the anodic coating is greater than 100 VHN, which is 20 percent more than that of the pure zinc surface.

Findings

1. The anodizing of zinc in this study was divided into two stages. In the first stage, a bright chromate conversion film is formed on the zinc and in the second stage, a macroscopically uniform and colored anodic coating can be obtained.
2. The resulting chromate conversion film, as in the first stage of the process, is composed of chromium oxyhydroxide and chromic oxide, together with a trace amount of zinc oxide, which provides an electric insulation layer for the subsequent anodic coating formation.
3. Two kinds of structure were observed on the anodic coating surface (*i.e.*, island-like and fritted glass-like structures). Elements, including silicon, oxygen and sodium are concentrated on the island-like structures, whereas zinc and transition metals are homogeneously distributed in both these structures.
4. Adding a particular transition metal salt into the basic electrolyte bath can yield a specific color on the anodic coating. The hardness of the anodic coating is about 20 percent greater than that of pure metallic zinc.
5. The anodizing of pure metallic zinc offers excellent corrosion- and abrasion-resistant coatings.

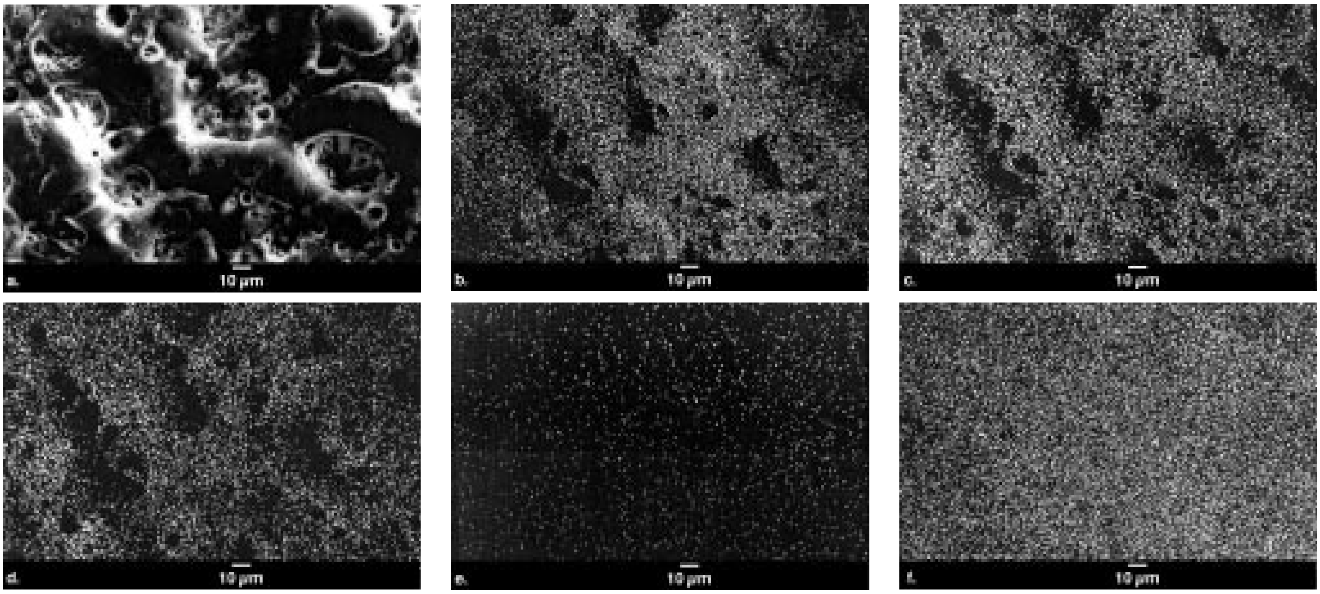

Fig. 4—(a) Surface morphology of the anodic coating of zinc by spark discharge; X-ray mapping of elements on the anodic coating of zinc: (b) silicon; (c) oxygen; (d) sodium; (e) cobalt; (f) zinc.

***Editor's note:** Manuscript received, March 1998.*

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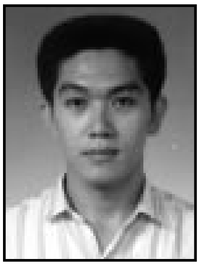
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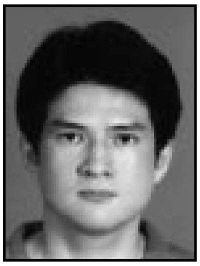
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