Selection & Applications of Inorganic Finishes: Anodic Coatings for 'Other' Metals*

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Many readers will be surprised to know about the numerous applications of anodized metals other than aluminum. This article describes processes for anodizing zinc, titanium, beryllium and magnesium, and discusses the properties and common uses of each finished metal.

Zinc

Anodizing of zinc appears to be a relatively neglected process since its development in the early 1960s. This is somewhat surprising when one considers the ability of the coating to provide a number of outstanding applications and a high order of resistance to corrosion and abrasion.

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The anodic coating on zinc has a fritted structure of fused particles from anodic spark discharges and thus more closely resembles anodic coatings on magnesium (to be discussed later) than on aluminum. Anodic coatings can be formed on zinc die castings, wrought zinc or on steel coated with zinc by electrodeposition, peen plating, metal spraying or galvanizing. The thickness of zinc on steel should not be less than about 15 μ m (0.6 mil) at any area, and 25 μ m (1.0 mil) is preferred.

There are four types of anodic coatings for zinc differentiated by color and classified by MIL-A- 81801: Class I - APCF (Green); Class 2 - SSC (Light Gray); Class 3 -SSCV (Dark Gray); Class 4 - SSCMn (Brown). Some characteristics of the coating and of the process are summarized in Table 1.

It is evident that the deposit properties of anodized zinc

Typical Characteristics	Anodic Coating Color			
	Green	Light gray	Dark gray	Brown
Terminal voltage	200	105	90	105
Current density, A/dm ² (A/ft ²), direct	15 (139)	15 (139)	15 (139)	15 (139)
Current density, A/dm ² (A/ft ²), ac*	4.4 (41)	4.4 (41)	4.4 (41)	4.4 (41)
Bath composition	NH ₄ ⁺ ;	SiO ₃ -2;	SiO ₃ -2;	SiO ₃ - ² ;
	CrO ₃ ;	CrO_4^{-2}	$CrO_{4}^{-2};$	$CrO_{4}^{-2};$
	PO ₄ -3; F-		VO ₃ ⁻	MnO ₄ ⁻²
Bath temperature, °C (°F)	70 (158)	70 (158)	80 (176)	70 (158)
Bath pH	7.0	12.8	12.8	12.6
Anodizing time, min	7	9	10	8
Nominal coating thickness, µm (mil)	32 (1.25)	41 (1.6)	41 (1.6)	38 (1.5)
Acetic acid salt spray**, days to failure	10	16	32	22
Neutral salt spray, days to failure	> 8,000	> 2,000		
Abrasion resistance***, cycles to failure	1,000	> 1,200	> 2,000	> 2,000
Dielectric strength, V	300	500	550	500

* Three-phase ac power is recommended.

** ASTM B-287

*** Taber abraser, 500-g load, CS-10 wheels (Method 6192 of Federal Test Method Std. No. 141

are far superior to those of chromate coatings on zinc (see Shop Talk article in P&SF December 2002 issue) and that the corrosion resistance is not adversely affected by exposure to heat, as is the chromate coating. Anodized zinc has proven capable of withstanding up to three years of marine exposure at Kure Beach, NC, and outperformed both 5537 aluminum with an 8-µm (0.3-mil) thick sulfuric acid anodic coating and microcracked chromium-plated zinc with a 30-µm (1.2 mil) thick double layer of nickel.1 Anodic coatings on zinc also provide an excellent base for organic finishes such as polyurethanes and lacquers.

Racks of copper splines and contact tips, with conventional plastisol coating, are satisfactory for anodizing zinc parts and provide rigid contact to prevent movement. Zinc die castings can be anodized with limited areas of exposed aluminum, brass, copper, nickel or steel inserts. About 8 µm (0.3 mil) of the coating represents a loss of original zinc; the remainder represents an increase in the dimension of the coating. Thus, a $32-\mu m$ (1.3-mil) thick anodic coating will result in about a $24-\mu m$ (0.9-mil) increase in dimension for each surface.

Anodic coatings on zinc are ordinarily sealed to improve corrosion/abrasion resistance even above that indicated in Table 1. Most commonly, sealing is accomplished by immersing parts in a hot, 10 vol% solution of 41.5° Baume sodium silicate (SiO₂:Na₂O = 3.22), and then by air-drying.

Limitations

Anodized zinc is not recommended for food handling applications because toxic hexavalent chromium in the electrolyte may be retained in the coating. The anodic coating is also quite brittle and cannot withstand substantial deformation of the basis metal without cracking or spalling.²

Applications

Anodic coatings for washing-machine parts (housings and impellers) made of zinc die castings are capable of providing serviceability in contact with detergents for many years. Anodized zinc auto-generator pulleys have provided far better wear resistance than chromium-plated parts.³ Nuts and washers made of galvanized steel have been used to join sonar systems to the exterior hulls of submarines/ships, but required replacement after about two months; anodizing the parts extended the maintenance period to two years.⁴ Anodized galvanized-steel brackets have been used for outdoor service.

Additional commercial applications of anodized zinc die castings include: auto window-crank assemblies, mufflers, transformer boxes, plumbing fixtures, marine hardware, door locks and firehose screens.

Titanium

Titanium is a metal with certain outstanding properties, including high strength-to-weight ratio (even at elevated temperatures) and excellent corrosion resistance. Therefore, titanium finds important applications in the aircraft, aerospace and chemical-processing industries, in underwater oceanography vessels and for surgical implants.

However, the metal has a tendency to gall and seize when subjected to sliding and bearing action. Also, titanium alloys are susceptible to marked reduction of fatigue life under conditions of fretting (slight relative motion between metal surfaces intended to be stationary).

Moreover, there are special precautions (MIL-S-5002/MIL-STD-1568) that should be taken when handling and using titanium. For example, any application entailing contact with chlorides should not be permitted to reach temperatures above 380°C (600°F) as brittle fracture may occur from a "hot salt cracking" phenomenon that appears similar in behavior to hydrogen embrittlement of high-strength steels. Also, even minor or chance contact of titanium with cadmium or silver should be avoided as intergranular corrosion and reduced tensile strength may result.

Normally, such deficiencies might be corrected by depositing another metal on the titanium. However, it is virtually impossible to achieve a high order of adhesion for metal deposits because of the pervasive and tenacious oxide film on titanium. Hence, anodic coatings have been given increasing attention for preventing some of the adverse effects to which titanium is subject.

The best prevention against the seizing, galling and fretting of titanium is an anodic coating followed by application of a resinbonded dry-film lubricant. The adhesion and performance of the dry



Applications of anodized zinc: (a) pump parts for washing machine, (b) gears and motor rotor.

film is a function of the quality of the anodic coating. Titanium can be anodized to form a very thin barrier layer in any number of electrolytes. Aluminum anodizers who use titanium racks are probably familar with the fact that a violet barrier layer is formed on titanium at 18V in 15 wt% H_2SO_4 . Dry-film lubricants may be applied to this thin anodic coating, but such treatment provides only minimal protection and is unacceptable for critical applications.

Various Processes

Pochily⁵ investigated numerous solutions for anodizing titanium and found a combination that best satisfied the requirements for a heavy coating (> 50 μ m; 2 mil) to effectively prevent galling, seizing and fretting without introducing any adverse effects on the basis metal. His results call for treatment in a highly alkaline solution containing silicate, activated carbon and titanium dioxide at 18°C (65°F) with about 4.5 A/dm² (42 A/ft²) direct current. There is, in fact, evidence that the fatigue life of titanium is substantially increased when the coating is applied. This anodic coating is unusual in that it is electrically conductive, presumably owing to a network of carbon particles trapped in the coating. The coating consists of a hard, compact inner layer and a soft, white outer layer that is easily removed by brushing. Further, the coating is highly receptive to resin-bonded dry-film lubricants, which provide exceptional resistance to wear and prevent metal-to-metal contact. The military frowns on the use of dry-film lubricants containing graphite for most applications on titanium because the treated metal, in service, is so often in contact with aluminum; the adverse effects of graphite in accelerating corrosion of aluminum are well known.

A proprietary process* is similar to the Pochily process in that direct current is applied in an alkaline solution and a dual coating is formed.⁶ However, the coating is relatively thin [2.5 μ m (0.1 mil) hard layer and 2.5 to 7.5 μ m (0.1 to 0.3 mil) soft outer layer] and is considered a semiconductor (~10⁸ -cm). The as-formed coating is said to be ideal for application of dry-film lubricants and particularly the vacuum-compatible MIL-L-81329. Some successful applications include fasteners, cams, bearings, gears, ratchets and hinges. The anodic coating is also an excellent base for adhesive bonding. The soft outer layer is removed by burnishing or ultrasonic cleaning prior to lubrication with oils, greases or hydraulic fluids for applications on servo-mechanisms, hydraulic systems, pumps, actuator bodies, sliding bearings or other components requiring wet lubrication.

Electrically insulating, monolithic anodic coatings are produced commercially** at a significant thickness (> 43 mg/dm²; 400 mg/ft²) from a neutral solution of phosphates using half-wave, rectified direct current. The coating has found numerous applications on components of supersonic aircraft and precision underwater devices. The coating is nonreflective and has been applied to optical equipment; it is also an excellent base for paint and resinbonded dry-film lubricants, when necessary for decorative or functional applications. The nonconductive anodic coating effectively prevents adverse galvanic effects on any aluminum or magnesium that it may contact.

The ever-increasing commercial and military applications for titanium should spur interest in the anodic coatings so that advantage can be taken of the important properties of the metal while overcoming the deficiencies that otherwise would limit its use.

Consideration should be given the use of chemically produced phosphate coatings on titanium for noncritical applications when optimum properties are not required. Deposits can be formed on unalloyed titanium by activating in 35 wt% $\text{HNO}_3 + 2.5$ wt% HF, rinsing and then immersing for 2 min in a solution comprised of 50 g/L (6.7 oz/gal) Na₃PO₄12 H₂O + 20 g/L (2.7 oz/gal) KF:2H₂O + 26 mL/L (3.3 fl. oz/gal) HF (50%) at 25°C (77°F).*** Immersion time and bath formulation will vary depending on alloy composition. The phosphate coatings can prevent seizing (with dry-film lubricant), facilitate metal deformation (with soap or oil), and enhance paint/adhesive bonding.

Beryllium

Beryllium, with a density only slightly above that of magnesium, has many important functional characteristics. Its high strength-toweight ratio, outstanding stiffness, specific heat, high melting point and low neutron-capture characteristics make it uniquely suitable for application in missile inertial-guidance systems, jet engines, braking systems, space vehicles, and nuclear-engineering projects.

The metal is, however, subject to corrosion in aqueous salt environments and undergoes oxidation at high temperatures. Such

Specifications

Specifications for coating processes discussed in this article include:

- •Anodic coatings on zinc: MIL-A-81801, "Anodic Coatings for Zinc and Zinc Alloys;"
- Limitations on use of titanium: MIL-S-5002 and MIL-STD-1568;
- Dry-film Lubricants: MIL-L-8937, MIL-L-46010, and MIL-L-81329;
- Anodic coatings on magnesium: MIL-M-45202, "Magnesium Alloy, Anodic Treatment of"; and MIL-HDBK-132, "Protective Finishes;"
- Anodic coatings on magnesium for aerospace applications: MIL-STD-1568, "Materials and Processes for Corrosion Prevention and Control in Aerospace Weapons Systems."

oxidation can be catastrophic at temperatures greater than 700°C (1292°F), particularly in the presence of small amounts of moisture. In fact, water vapor is the most aggressive agent in oxidation and beryllium oxidizes as rapidly in moist nitrogen as in moist air. But for many applications of beryllium, exposure to atmospheric environments and/or high temperature is expected and protective measures must be taken. Laboratory studies indicate that anodic coatings should be extremely effective in this regard and are superior to the chromate films discussed earlier.

Jet-black coatings

A suitable electrolyte for anodizing beryllium^{7,8} is 50 g/L (6.7 oz/gal) CrO₃; a jet-black anodic coating about 5- μ m (0.2-mil) thick is formed at 18°C (64°F) with 11 A/dm² (100 A/ft²) direct current applied for 30 min. The current efficiency of coating formation is quite low compared to most commercial electrochemical coating processes. Satisfactory coatings are also produced from a 200 g/L (27 oz/ gal) CrO₃ solution at 25°C (77°F) and 30A/dm² (280 A/ft²); a 4- μ m (0.15-mil) thick coating is produced in about 10 min.

The anodizing process is unusual in that the coating appears to offer little or no resistance to current flow during formation, since the applied voltage remains constant and relatively low during anodizing at constant current density. Normally, the potential increases with coating formation during anodizing processes. The throwing power is poor compared to other anodizing processes and is more typical of that obtained with electroplating processes. Yet the anodic coating is a nonconductor and comprised mainly of BeO with minor chromium content. The reason anodic coatings on beryllium are black instead of white (the normal color of BeO) has not been convincingly explained. In any case, these coatings provide excellent corrosion resistance during salt-spray exposure and exceptional protection against high-temperature oxidation without any sealing post-treatments. There is some evidence that adding about 40 mL/L (5 fl. oz/gal) of HNO, to the CrO, anodizing electrolyte improves Faradaic efficiency of coating formation.

A jet-black anodic coating, similar in appearance to that formed in CrO_3 electrolyte, is produced in 100 g/L (13 oz/gal) NaOH at 40°C (104°F) with 11 A/dm² (100 A/ft²)(~4V direct current) applied for 60 min. These coatings may be particularly suitable as heat-absorbing surfaces of solar radiation.⁹ It would be interesting

^{*}Tiodize®, Tiodize Co., Inc., Huntington Beach, CA.

^{**}Titanium Finishing Co., Lansdale, PA.

^{***}Metal and Ceramics Information Center, Columbus, OH.

to ascertain whether these coatings provide protection equivalent to those formed in CrO_3 solutions.

Beryllium can also be anodized using alternating current in HAE-type solution used for anodizing magnesium. In this process, a spark-discharge reaction occurs at high voltage and the result is completely different in appearance from the coatings described above. This coating, which may warrant further study, is light in color and apparently contains fusion products.

Magnesium

The most popular anodizing processes for magnesium are those covered by MIL-M-45202 that produce relatively thick (25 to 37 μ m; 1.0 to 1.4 mil) coatings with good resistance to corrosion and abrasion. MIL-M-45202 thoroughly describes the equipment, materials and procedures for anodizing magnesium. Anodic coatings on magnesium are also an excellent base for paint; for aerospace applications, two coats of epoxy polyamide primer (MIL-P-23377) and two coats of aliphatic polyurethane (MIL-C-81773/83286) should be applied.

The coatings referred to above are a proprietary dark green coating* and the HAE hard brown coating. These coatings are opaque with a finely granular surface quite different in appearance from anodic coatings on aluminum. The coatings are formed by a sparkreaction process that produces a complex ceramic-like structure; glassy fusion products are visible under magnification. These coatings are in demand for aircraft, missile and aerospace applications where optimum protective properties are required and advantage can be taken of the low density and high strength of magnesium alloys. Aircraft engine casings and rocket motor cases are examples of such applications.

The painted anodic coatings are considerably more protective than similarly painted chemical- conversion coatings. Magnesium anodizing is not commonly done at plating shops but at least several commercial firms have large-scale capabilities and provide service on a contractual basis.

Parameters

The proprietary dark green process may be applied using either ac or dc current in an aqueous solution containing NH₄HF₂, Na₂Cr₂O₇ and H₃PO₄ at about 80°C (176°F).¹⁰ Parts are normally racked with firm contacts using either magnesium or aluminum rack-tip materials. An advantage of this process is its ability to treat magnesium that contains aluminum inserts or rivets. If the part coated by the proprietary dark green process is not to be painted, corrosion resistance may be increased by sealing 15 min in 55 g/L (7.3 oz/ gal) Na₂Si₄O₉ (waterglass) at 95°C (203°F). A thinner version of the anodic coating, about 7-µm (0.3-mil) thick, is sometimes used but usually offers little advantage over the chromate conversion coatings.

The HAE process was developed at Frankford Arsenal by Harry A. Evangelides. The coating is formed by applying alternating current to parts firmly secured on magnesium racks. At least two racks of approximately equal areas of magnesium, each used as a separate electrode, are processed simultaneously. The electrolyte is a highly alkaline solution containing KOH, Al(OH)₃, KF, Na₃PO₄ and K₂MnO₄ (or KMnO₄) at about 22°C (72°F). The coating is normally "sealed" by a 1-min immersion in 80 g/L (10.7 oz/gal) NH₄HF₂ + 20g/L Na₂Cr₂O₇.2H₂O at 25°C (77°F); it may be allowed to dry without rinsing but is sometimes rinsed prior to drying.

The HAE coating is extremely hard and resistant to wear from sliding; coated panels have been used as a whetstone for sharpening knives. When HAE-coated parts are properly painted, synergistic performance in corrosion resistance during environmental exposure is achieved. The unpainted HAE coating may be impregnated with certain proprietary inhibited oils, greases or lard oil to provide a high degree of corrosion resistance. Variations of the HAE process produce thinner and less-protective anodic coatings.

The heavy proprietary dark green and HAE coatings are typically 30 μ m (1.2 mil) in thickness and produce an increase in dimension of about 20 μ m (0.8 mil) per surface; this factor must be taken into account when close dimensional tolerances must be met. The coatings are also brittle and can crack or spall when subjected to severe compressive stress such as that which occurs when bending thin sections or during high-impact riveting operations. *Pass*

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Eidtor s note: The preceding article is based on material contributed by Fred Pearlstein for the "AES Update" series that ran in this journal. Since this article was written much has changed, but these processes remain revelant to a large portion of the finishing community. The reader may benefit both from that information and the historical perspective of the technology. The "Update" series was begun and coordinated by the late Dr. Donald Swalheim to provide practical information to the metal finisher. In some cases here, words were altered for context.

^{*}Dow 17, Dow Chemical Co., Midland, MI