Corrosion and Finishing of Magnesium Alloys

Preface

The corrosion properties of the most common magnesium alloys, along with galvanic corrosion prevention and surface finishing methods for magnesium, are described herein.

Further technical inquiries may be directed to Hydro Magnesium at the addresses given on the back cover.

Magnesium alloys

The most common magnesium alloys are shown in Table 1. The alloys may be divided into three groups: AZ91D is an alloy with excellent castability and high strength, AM50A and AM60B are alloys with higher ductility and greater fracture toughness suitable for components such as instrument panels and steering wheels, while AS21 and AE42 are alloys with good creep resistance suitable for elevated temperature applications.

Table I. Chemical composition (weight %).

Alloy	Al	Mn	Zn max	Si max	Cu max	Ni max	Fe max	RE	other each max
AZ91D [1])	8.3-9.7	0.15-0.50	0.35-1.0	0.10	0.030	0.002	0.005		0.02
AM60B [1])	5.5-6.5	0.24-0.6	0.22	0.10	0.010	0.002	0.005		0.02
AM50A [1])	4.4-5.4	0.26-0.6	0.22	0.10	0.010	0.002	0.004		0.02
AM20 [2])	1.6-2.6	min. 0.1	0.2	0.10	0.010	0.0012	0.005		0.02
AS21 [2])	1.8-2.6	min. 0.1	0.2	0.7-1.2	0.010	0.002	0.005		0.02
AE42 [2])	3.5-4.5	min. 0.1	0.2	0.10	0.02	0.002	0.005	2.0-3.0	0.02

1) ASTM B94-94a, 2) Recommended values.

General Corrosion

Environment, temperature, surface condition, alloy composition, metal impurities, microstructure, contact with other materials and stresses are factors which affect the corrosion behaviour of magnesium alloys.

With the introduction of the high purity alloys, corrosion resistance of magnesium alloys to saline environments was significantly improved. All alloys shown in Table 1 satisfy the requirements of high purity, i.e., the content of critical impurities like nickel, iron and copper is strictly limited. Figure 1 schematically illustrates the general effect of these elements on the corrosion resistance of magnesium alloys. The nickel and copper contents are kept to a minimum by careful selection of raw materials, while iron is limited by controlled addition of manganese. The die caster must have proper procedures for melt handling in order to keep the high purity quality of die cast products (reference 1).

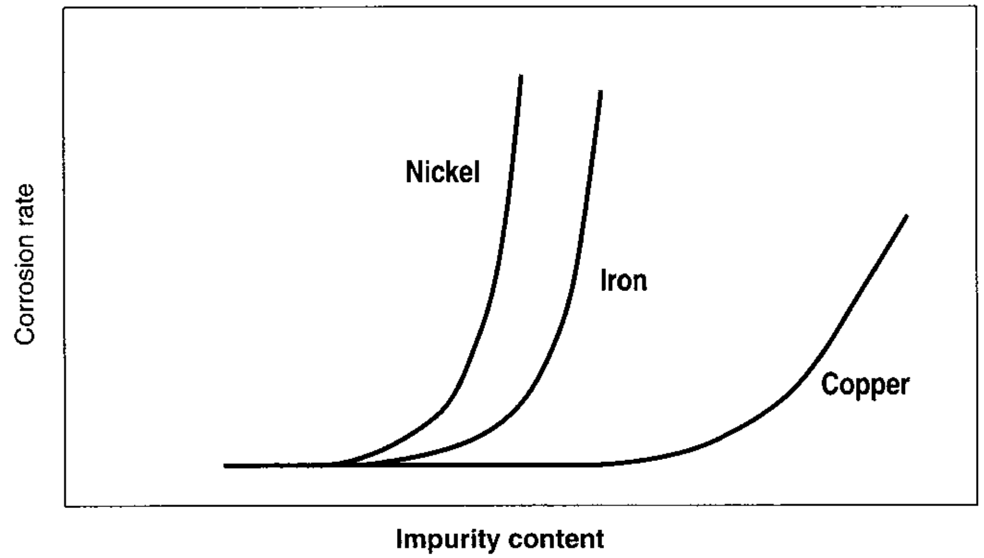

Figure 1. Effect of impurities on the corrosion resistance of die cast magnesium alloys.

In general, the corrosion resistance of magnesium alloys increases with increased aluminium content. Figure 2 shows typical corrosion rates of the most common alloys in salt spray. Salt spray data are only meant to give a general indication of the relative corrosion resistance of the various alloys. The corrosion resistance of AZ91D, AM60B and AM50A is better than the aluminium alloy A380 in salt spray.

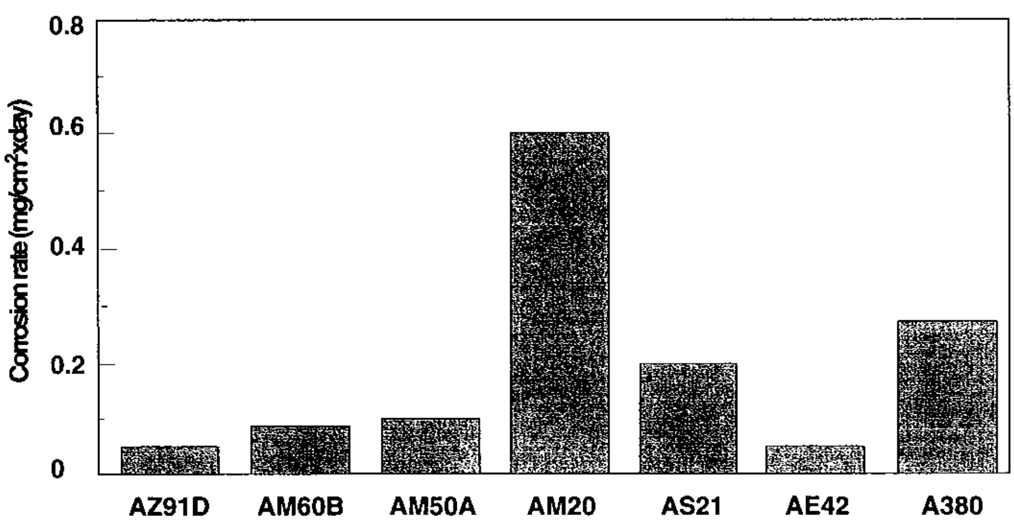

Figure 2. Corrosion rates of die cast specimens of magnesium alloys and aluminium A380 alloy (Al4250) in ASTM B117 salt spray.

Figure 3 shows a comparison of relative corrosion rates in salt spray and cyclic humidity conditions. The corrosion rates are significantly lower in the latter environment.

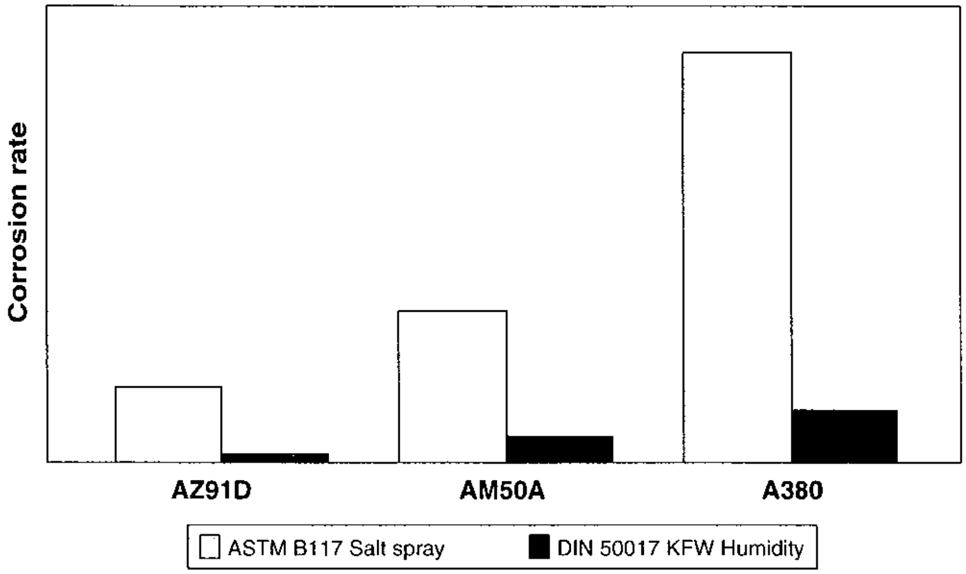

Figure 3. Relative difference in corrosion rates of die cast test specimens in salt spray and cyclic humidity environment.

The corrosion resistance of high purity magnesium alloys is sufficient for many applications, and no extra corrosion protection is needed.

Galvanic corrosion

Galvanic corrosion is an important type of corrosion for magnesium alloys. Practically all other structural metals are more noble than magnesium. Figure 4 shows the principle of galvanic corrosion.

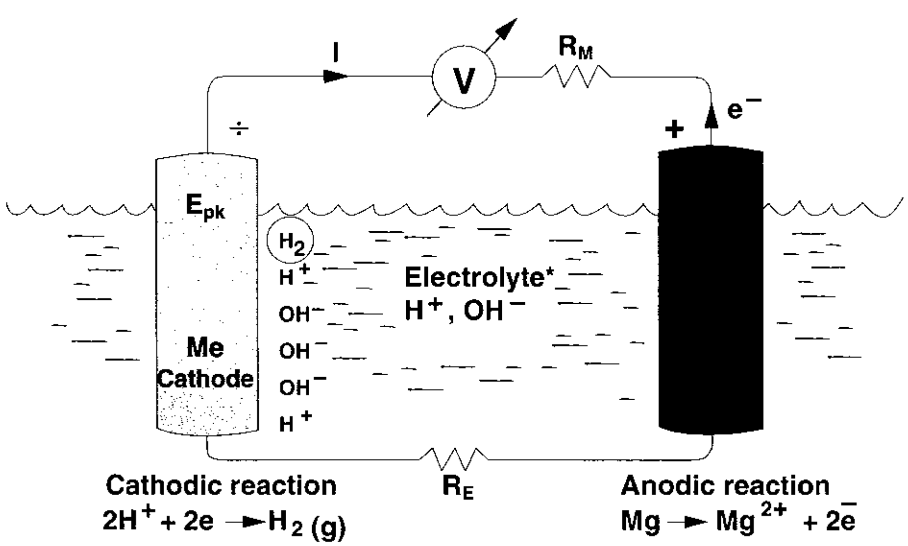

Figure 4. Principle of galvanic corrosion. E_{pk} and E_{pa} is the polarised potential of the cathode and anode, respectively. R_m is the metal circuit resistivity and R_e is the electrolyte resistivity.

For simplification, one can say that the anodic reaction occurs on magnesium, while the cathodic reaction occurs on the second material. These two reactions must balance with each other; when decreasing the rate of the cathodic reaction, the anodic reaction is decreased correspondingly (galvanic attack on magnesium). The galvanic current, I, can be expressed as follows:

$$I = \frac{E_{pk} - E_{pa}}{R_e + R_m} \qquad (1)$$

If there is no electrolyte present or the electrolyte has very high resistivity, the galvanic current, I, is zero or very low (equation 1). Similar conditions occur when there is no electrical contact between magnesium and the other metal. Then R_m is infinity and the electrical circuit in Figure 4 is broken. In such cases, galvanic attack is either insignificant or absent.

Effective methods for preventing galvanic corrosion are:

1. Proper design of the assembly.
2. Selection of materials compatible with magnesium.
3. Selective use of coatings and insulation materials.

Proper design allows for water, condensation etc. to be effectively drained away from the assembly, thus eliminating the electrolyte. Some examples of poor and improved design are shown in Figure 5.

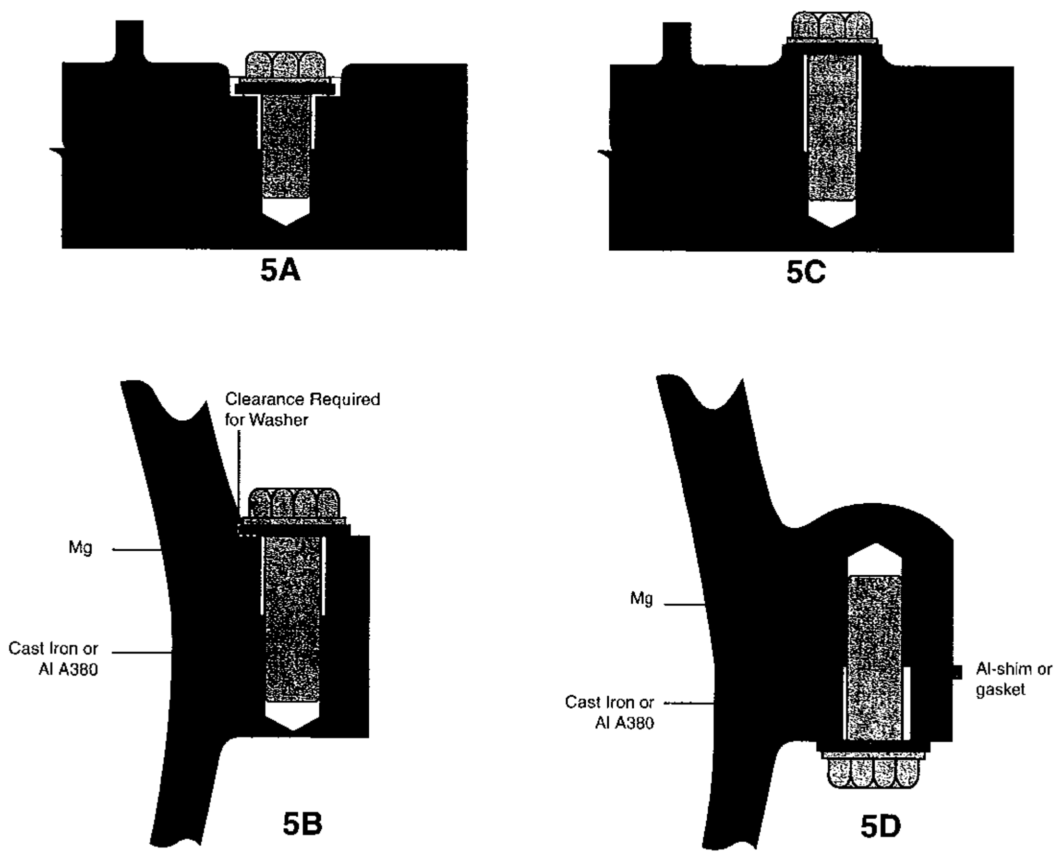

Figure 5. Examples of poor (5A and B) and improved design (5C and D) for the prevention of galvanic corrosion.

Proper design, combined with the use of either non-conductive or compatible aluminium shims or washers, is a very simple and efficient way to prevent galvanic corrosion at fastener connections. The size of the washer should be such that the total distance between the bolt head and the magnesium is minimum 5 mm (excess diameter plus washer thickness). (Reference 2). Proper clearance between the bolt head and the die casting walls is important in order to avoid water entrapment. The clearance should be at least 5 mm.

The degree of galvanic corrosion attack on magnesium is strongly influenced by the second metal. Some metals are quite compatible with magnesium. Compatibility is determined by both the relative nobility, and the efficiency of the cathodic reaction on the second metal. For some metals the cathodic reaction is very slow.

Figure 6 shows a compatibility series for various metals with magnesium. The most compatible metal is Al 5052, while the least compatible metals are stainless and mild steels.

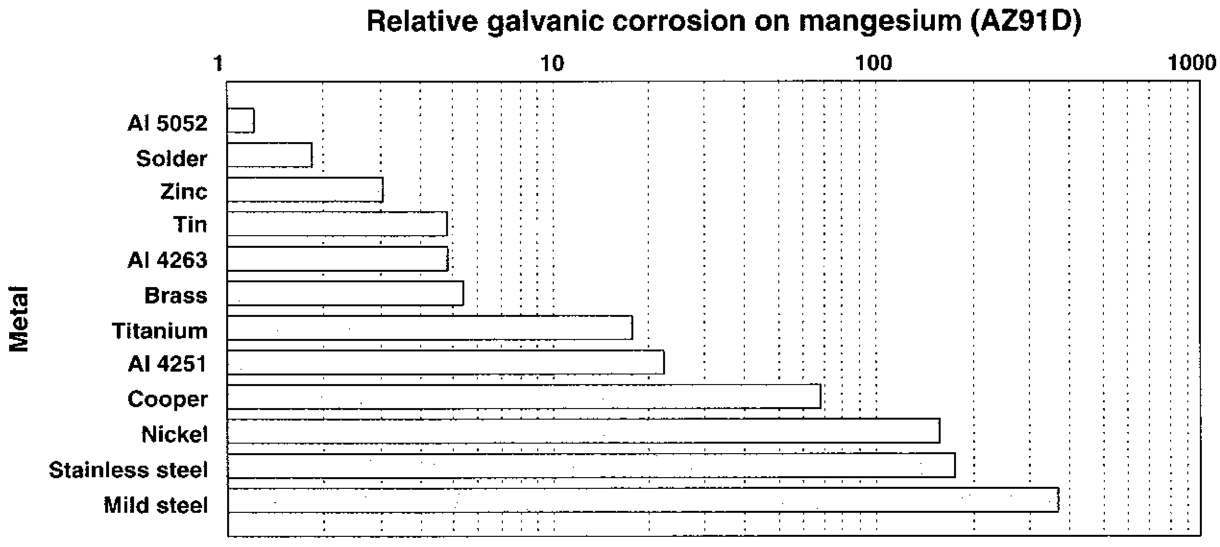

Figure 6. *Relative compatibility series of various metals coupled to magnesium. The galvanic assembly was immersed in 5% NaCl-solution. The anode/cathode area ratio was approximately 1.8.*

In galvanic couples with aluminium, the composition of the aluminium alloy is important for compatibility with magnesium. The most compatible aluminium alloys are those with both a magnesium addition and with low iron and copper content (such as Al 5052, Al 5056 and Al 6061).

Zinc is also quite compatible with magnesium and can be used as a plating on steel to improve the compatibility of mild steel with magnesium alloys. However, there are various other platings, organic coatings and insulation materials which are more effective in limiting the galvanic corrosion of magnesium in contact with steel. Figure 7 shows test results of some coatings, platings and protective caps on mild steel fasteners connected to magnesium (reference 3).

Four fastener systems are efficient in reducing the risk for galvanic corrosion:

- Nylon coated fasteners.
- JS 500 plated fasteners.
- Tin/zinc alloy plated fasteners.
- Fasteners with plastic caps.

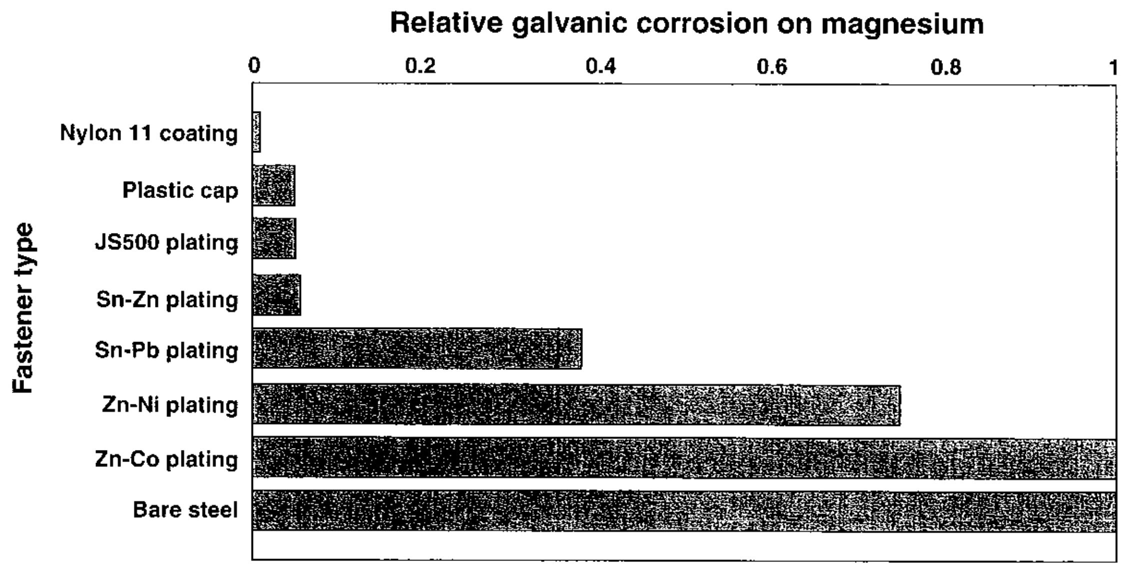

Figure 7. Galvanic corrosion of magnesium caused by various types of plated/coated fasteners relative to uncoated mild steel fasteners. The galvanic assemblies were tested in ASTM B117 salt spray for 240 hours (reference 3).

The nylon coating covers the fastener head of the socket head bolt. The coating thickness should not be less than 200 μm. The plastic caps, made of polypropylene, are designed to cover the fastener head as shown in Figure 8. They are available both as pre-fitted caps on socket head bolts or as caps to be assembled after installation of hex head fasteners.

The nylon coating and the plastic cap utilise the same principle for galvanic corrosion reduction; they prevent electrolyte from coming into contact with most of the bolt head and thus limit the cathodic reaction. The anodic reaction is reduced correspondingly.

JS 500 is a commercial plating process consisting of a yellow chromate zinc plate sealed with a silicate sealer. The tin/zinc alloy plating is comprised of 80 % tin and balance zinc. These platings are approximately 10 μm thick and cover the whole fastener.

Other types of plating/coating than the four best alternatives listed in Figure 7 should not be selected without advanced testing in the service environment.

The optimum type of coated/plated fasteners are normally of socket head design (internal drive fasteners). For these types, the chance for plating/coating damage during installation is far less than for external drive fasteners. In the latter case, plating/coating damage on side walls of the bolt head can expose bare steel and consequently cause increased risk for galvanic corrosion attack on magnesium.

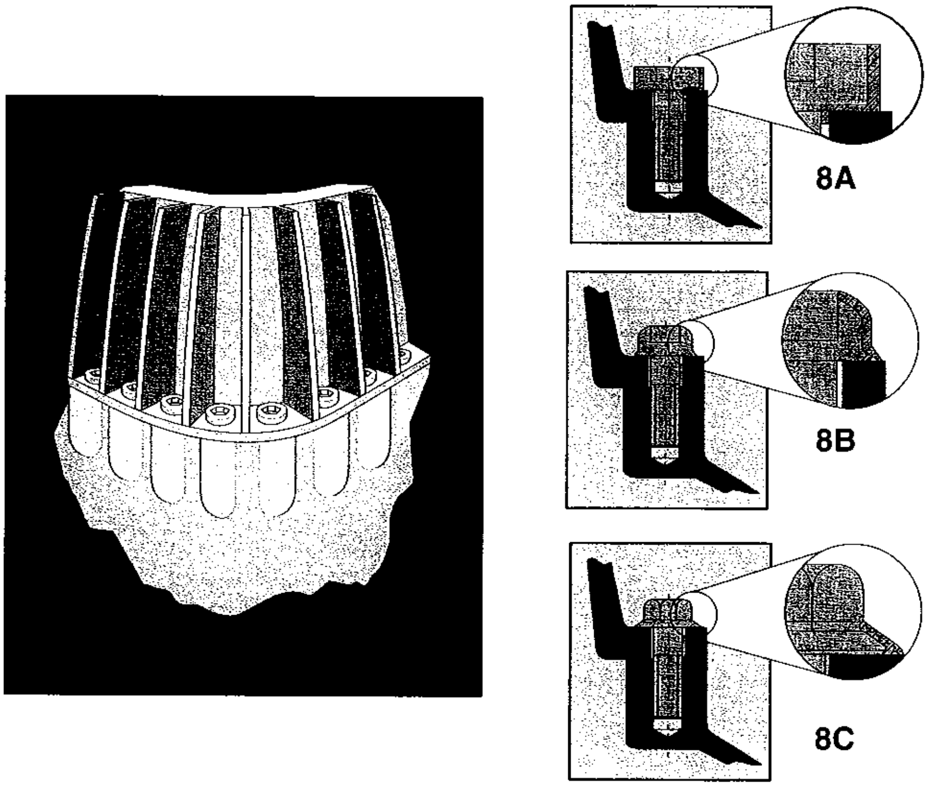

Figure 8. Nylon coated fasteners and plastic caps. 8A shows a nylon coated fastener; 8B and 8C show plastic caps.

Using organic coatings on the magnesium component in a galvanic assembly may lead to severe corrosion attack due to small defects in the coating. These defects become the sites of concentrated galvanic corrosion. When an application requires that magnesium is coated, and there is also a risk for galvanic corrosion, a very thick coating should be used (200 μm or more). The coating underneath the bolt heads must be protected by washers. Plastic or rubber washers are preferred, but compatible aluminium washers can also be used. Generally, coating the magnesium to prevent galvanic corrosion is not recommended.

For automotive interior magnesium applications such as steering wheel, steering column components and instrument panel, special attention for prevention of galvanic corrosion is not needed. For other applications such as transmission and transfer cases, inner door panels etc., special preventive measures like those given above are necessary.

Surface treatment and painting

Magnesium components are painted either for decorative purposes or occasionally for additional atmospheric corrosion protection. Prior to painting, the surface is commonly treated with a conversion coating. Figure 9 shows various treatment schemes for magnesium die castings.

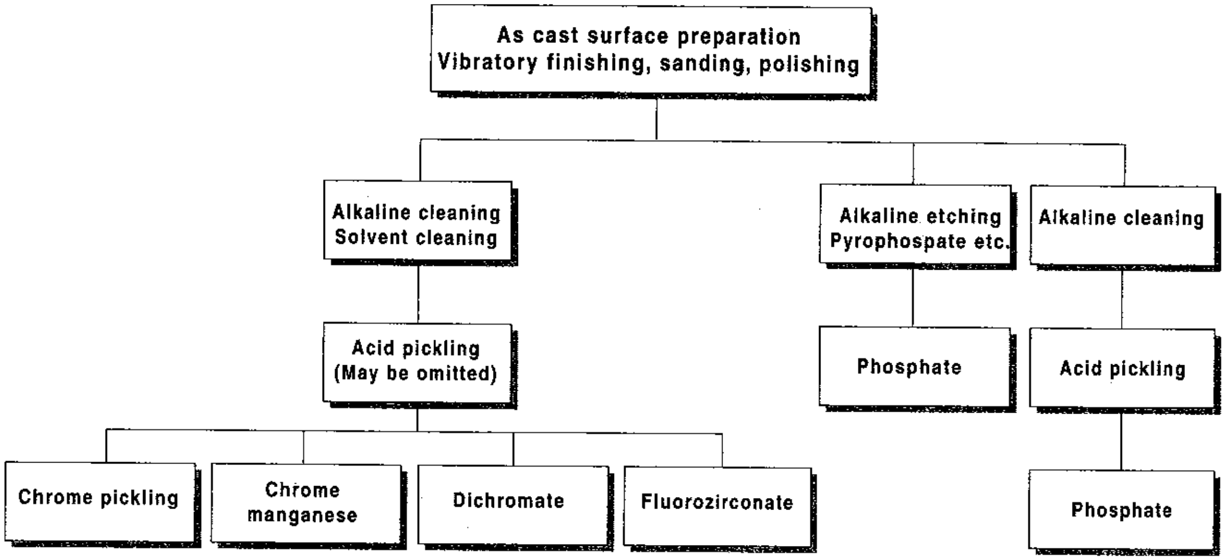

Figure 9. Conversion coating treatment schemes for magnesium die castings. A water rinse is needed between each step.

Cleaning

Surface treatment starts with a mechanical cleaning process. Vibratory finishing in plastic or ceramic media is very often used, but grinding, buffing or other processes may be practiced. Magnesium can also be blast cleaned. Recommended blasting media are aluminium shot, glass spheres and aluminium oxide provided they are free from iron, nickel and copper contamination. Acid pickling is strongly recommended after blasting in order to remove residues of the blasting medium on the magnesium surface.

Wet blasting either by ultra high pressure pure water (water jetting) or water with abrasive particles (slurry methods) can also be used on magnesium die castings. Regarding the slurry methods, the selection of particles is critical in a similar manner to the selection of blasting media.

Mechanical cleaning is followed by either alkaline cleaning or solvent cleaning. Alkaline cleaning is preferred due to environmental concerns related to the solvent cleaning baths. Since magnesium is resistant to alkaline attack, strong alkaline solutions can be used to remove severe surface contamination. Alkaline cleaners containing pyrophosphates deoxidise the surface slightly. Examples of alkaline cleaning procedures are given in references 4 and 5.

To further improve corrosion resistance and paint adhesion, the magnesium surface may be acid pickled. During pickling, surface segregates are removed and the surface becomes more homogenous. Acid pickling is often a necessary step to activate the surface for the subsequent treatment. For die castings, baths based on chromic acid, hydrofluoric acid or a mixture of these two with nitric acid are often used. Other suitable acid pickling solutions are phosphoric acid or sulphuric acid. Compositions and acid pickling procedures suitable for magnesium are described in references 4 and 5.

Chemical conversion coatings

The most common conversion coatings are based on dichromate solutions (180 g/l sodium dichromate, $Na_2Cr_2O_7$).Many chromate conversion coatings are proprietary; however, a number of bath compositions and procedures are given in references 4 and 5.

Norsk Hydro has developed a dilute chrome pickle solution denoted NH35, which gives excellent corrosion resistance and paint adhesion. NH35 has only one-fifth of the dichromate content (35 g/l) of traditional chrome pickle solutions used for magnesium. Due to the low dichromate content, NH35 treatment is less expensive and less harmful to the environment than other chrome pickle baths. Tests in salt spray and cyclic climate test such as VDA 612-415 have proved that NH35 gives excellent paint adhesion. Data sheets are available from the addresses on the back cover.

Selected phosphate treatments are alternatives to chromium treatments. Some of these have shown very good performance (references 6 and 7). The key to successful phosphate treatment is to etch the surface prior to the phosphate treatment (remove 2 - 10 µm of the surface). The etching can be achieved either by an alkaline etch (pyrophosphate alkaline cleaner) or by acid pickling. The two alternatives are outlined in Figure 9. Due to their extremely low impact on the environment compared to hexavalent chromium treatments, phosphate treatments should be used for magnesium applications in mild corrosive atmospheres.

A new phosphate process, based on a mixture of phosphate and permanganate, has shown results similar to chrome pickle as a base for subsequent paint films in laboratory tests. The bath is a mixture of sodium dihydrogen phosphate and potassium permanganate, and the conversion coating is applied at ambient temperature during 3 - 10 minutes (references 8 and 9). Literature is available from the addresses on the back cover.

Another chromium free treatment showing very good performance as a paint base is fluorozirconate. Figure 10 shows corrosion creep from an x-scribe in the coating on samples of two alloys treated with fluorozirconate and chrome pickle (reference 9).

Fluorozirconate treatment is a straightforward method, and it can replace chrome pickle directly.

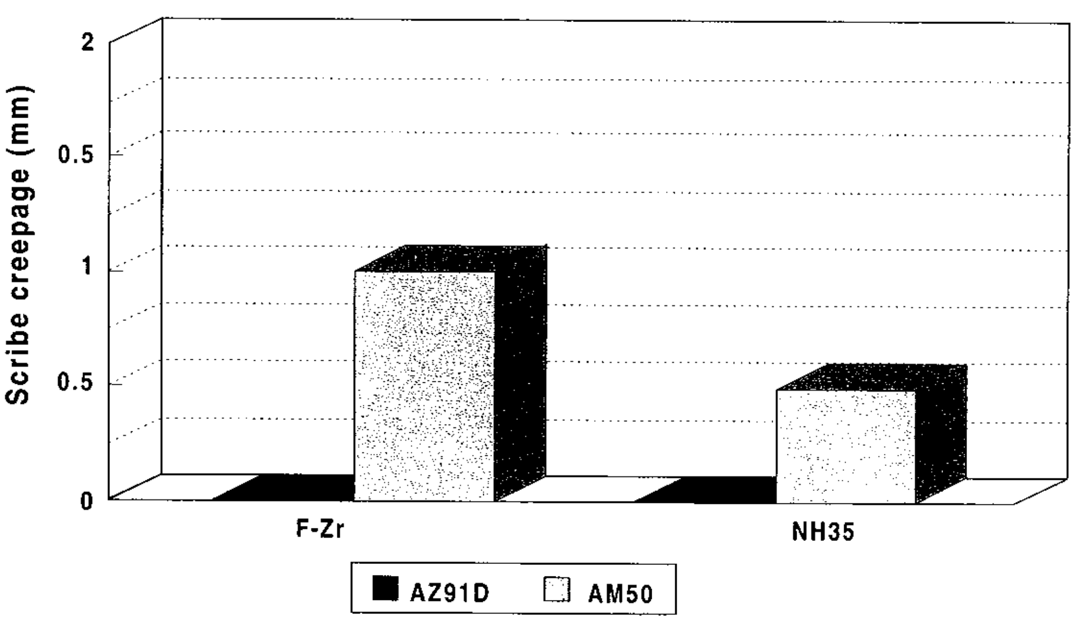

Figure 10. Corrosion creep from a scribe in the coating on fluorozirconate (F-Zr) and chrome pickled (NH35) samples in cyclic climate test (VDA 621-415). The test duration was 12 weeks (12 cycles). The fluorozirconate tested was NP Bonder C4740 from Chemetall GmbH, and the paint was an epoxy-polyester powder (80 -100 µm).

The cost of chemicals used in the fluorozirconate treatment is typically lower than those for the chromate and phosphate treatments. Other important factors which influence treatment cost are bath life, replenishment, waste treatment and operator protection. Waste treatment and operator protection costs are markedly lower for fluorozirconate and phosphate treatments than for chromate treatments.

Anodising

Like aluminium, magnesium can also be anodised. Older traditional anodising processes are HAE and Treatment #17. In recent years, new anodising processes such as Magoxide®, Tagnite® and others have been developed. These conversion coatings exhibit similar or better properties than HAE anodising (references 10 and 11). Anodising is used to improve wear resistance as well as corrosion resistance and paint base properties. Traditionally, it has not been possible to dye anodic coatings on magnesium similar to what is done on aluminium. A recently developed anodic process (Anomag), however, makes it possible to get a range of coloured anodic films on magnesium alloys.

Painting

Painting magnesium is similar to that of other metals. Normally, the paint is applied over a conversion coating (as discussed in the previous section). For some components, however, the conversion coating may not be necessary, i.e. when a long lasting paint is not needed, or in a very mild corrosive environment.

Powder or wet paint may be used for magnesium alloys. In both cases, alkaline resistant primers are strongly recommended. Generic types of coating which have been successfully used on magnesium are epoxy, epoxy-polyester, vinyl, acrylic, polyurethane, etc. Cathodic electropainting (E-coating) is also used on magnesium, both as a primer and as a final finish. Paint systems vary from simple one-coat systems to systems using an E-coat primer, filler coat, base coat and clear top coat.

Interconnected porosity in some die castings may cause pinholes in the paint due to gas escaping from pores during curing of the paint at elevated temperatures. Special anti-bubble grade coatings can prevent formation of pinholes. Other preventive methods are:

- Preheat die castings at higher temperature than the paint curing temperature.
- Lower the curing temperature and increase curing time.
- Start curing at lower temperature and finish at higher temperature.

The paint curing temperature for magnesium die castings should not be raised above 200°C.

Plating

In principle, the basic plating process of magnesium is very similar to plating of aluminium. The process includes proper cleaning, activation and zincate plating. A patented Norsk Hydro process consists of a two-step activation; first an acid treatment, followed by rinsing and secondary alkaline activation. On top of the zincate coating which is only 0.1 - 0.2 µm, a copper strike is applied from a cyanide copper bath. Any plating procedure can be applied after proper copper plating. Plating through the procedure above is difficult on alloys which have more than 6 - 7 % aluminium, e.g., AZ91D.

Electroless nickel plating has become more important due to increased use of magnesium in electronic equipment (mobile phones and computer components). Electroless nickel can be applied on a copper strike, but there are also processes where the electroless nickel is applied more directly on an activated surface. One of these is the Sakata process which uses the same principle for activation as the zincate plating. This process is suitable for alloys containing higher levels of aluminium such as AZ91D alloy (reference 12).

Storage protection

For some very critical applications, corrosion protection of magnesium components during transport and storage may be needed. Several methods and products are available:

- Storage in sealed containers with desiccant.
- Apply an oil or wax coating.
- Conversion coatings.

Proprietary oil and wax coatings suitable for magnesium include:

- CRC 3-36 (CRC Chemicals).
- Tectyl 511 or 2100 (Valvoline Industrial Coatings).
- Mercasol 73C (Geveko Industrier AB).

Most conversion coatings will give adequate corrosion protection under normal storage conditions, but the conversion coating may become ineffective as a paint base during storage in humid conditions over long times.

List of references

1. Melting & Handling Magnesium for Die Casting, Hydro Magnesium Brochure, 1996.

2. D. Hawke, J. E. Ellis, W. Unsworth, «Preventive Practice for Controlling the Galvanic Corrosion of Magnesium Alloys», Tech. Commitee Report, IMA, 1988.

3. D. Hawke, T. Ruden, «Galvanic Compatibility of Coated Steel Fasteners with Magnesium», SAE Tech. Paper 950429, 1995

4. IMA Brochure «Surface Finishes for Magnesium», IMA 1989.

5. Metals Handbook, 9th Ed. Vol. 5, ASM 1982.

6. D. Hawke, K. Gaw, «Effects of Chemical Surface Treatments on the Performance of an Automotive Paint System on Die Cast Magnesium», SAE Tech. Paper 920074, 1992

7. J. E. Hillis, R. W. Murray, «Finishing Alternatives for High Purity Magnesium Alloys», Paper no. G-T87-003, SDCE 14th. Int. Die Cast. Cong. & Ex., 1987.

8. D. Hawke, D. Albright, «A Phosphate-Permangnate Conversion Coating for Magnesium», Metal Finishing, ***93,*** No. 4, 1995, p. 36-38.

9. J. I. Skar, M. Walter, D. Albright, «Non-Chromate Conversion Coatings for Magnesium Die Castings», SAE Tech. Paper 970324, SAE 1997.

10. B. Olbertz, A. T. Haug, «Oberflächenschutz für Magnesiumwerkstoffe», Metalloberfläche, ***43,*** no. 4, 1989, p. 174-178.

11. J. H. Hawkins, «Assesment of Protective Finishing Systems for Magnesium», 50th. Ann. World Mag. Conf., May 11-13, 1993, Washington D.C.

12. Y. Sakata, «Electroless Nickel Plating Directly on Magnesium Alloy Die Castings», Proceedings Sur/Fin '87, Chicago, Ill., July 13 -16, 1987.