Studies on Chromating of Magnesium Alloys

C. G. KRISHNADAS NAIR, T. L. RAMASWAMY AND A. NARAYANA
Central Laboratory, Hindustan Aeronautics Ltd., Bangalore-560 017

Presented at E.C.S.I. A.T.M. (1980) Bangalore

Mg Alloy castings are protected from corrosion by surface chromating. Three types of chromating baths have been studied and optimum conditions established for obtaining uniform coating of chromate film. The adhesion of chromate films and their resistance to corrosion, and abrasion, have been evaluated and results interpreted in terms of chemistry, soundness and structure of the films. Both optical and scanning electron microscope have been used to study the structure of chromate films

MAGNESIUM alloy castings combine high strength with light weight and therefore are extensively used in aerospace vehicles, automobiles and other transport vehicles and also are preferred by designers for moving part of the machines.[1,2] However, a major drawback is their poor resistance to corrosion. Hence they require extensive protection during manufacture and service. Surface chromating, a chemical conversion process has been recognised as a reliable protective treatment for Magnesium alloy castings.[3] Castings are chromated to avoid corrosion during their transit, waiting/storage period before taking them up for machining and they are further chromated immediately after machining. Corrosion resistance is further enhanced by complimenting the chromated film with suitable epoxy coating. Hindustan Aeronautics Limited has been developing indigenous competence in magnesium alloy castings over the past years and as part of this programme extensive experimentation followed by industrial trials have been conducted to evaluate various types of chromating.

Magnesium alloy components are chromated by immersion in a suitable solution containing chromate anions, and sulphate or nitrate anions. It is found from literature survey that three categories of acidic chromating solutions are employed in the west.[4] One is highly acidic and the other two are moderateiy acidic. Highly acidic bath was developed in Germany and it operated only in cold condition and contains potassinm dichromate and nitric acid as the constituents. Moderately acidic baths were developed in U.K. One is termed "RAE hot half hour bath" and the other is known as Chrome-manganese bath. RAE bath operates only in boiling condition and contains ammonium sulphate, ammonium dichromate, potassium dichromate and ammonia as the constituents. Chrome-manganese bath operates both in cold and in hot condition and contains sodium dichromate, manganese sulphate and magnesium sulphate as the constituents.

Detailed comparative performance of three types of chromating is not published in literature. This paper discusses the results of investigations carried out to establish the relative performance of these three types of chromating and to select the best bath for regular production.

EXPERIMENTAL

Magnesium alloy castings contain Zn, Zr, Al and Rare earths as the principal alloying elements. Zinc is common in all the alloys. An alloy containing 4.5% Zn and 0.7% Zr was selected for chromating studies initially and later, the investigations were extended to other alloys.

Initially experiments were carried out to study the kinetics of the reaction qualitatively and to standardise the composition of respective chromating baths and select optimum pH and temperature. Taking into account results of these trials the test samples were chromated under standard conditions as shown in Table I.

Specimens measuring 40×50 mm^2 and 5 mm thick were prepared from the sand cast magnesium alloy. These were degreased in trichloroetylene, etched for 10 minutes in boiling 5% w/v caustic soda and 3 minutes in 40% v/v hydroclouric acid at room temperature. After etching, separate batches of the specimens were chromated by immersing in the respective chromating solutions. Chromated specimens were swilled in hot water at 50°C to 60°C and dried.

TABLE I

Composition, Operating Conditions of the 3 Types of Chromating Baths Experimented

Name of the bath	Composition of the bath	Operating conditions		pH maintained
		Temperature in °C	Minimum time req. for uniform casting	
Acid Chromating bath	Potassium dichromate 130 – 150 g/l Nitric acid (Sp. gr. 1.42) 200 – 250 ml/l	Room Temperature	2	0.6-1.0
RAE half on hour hot bath	Ammonium sulphate 20 – 30 g/l Ammonium dichromate 10 – 15 g/l Potassium dichromate 10 – 15 g/l Ammonia (088 sp.gr 2.7 to 4.3 ml/l	Boiling	30	5-6
Chrome-manganese	Sodium dichromate 80 – 100 g/l Manganese sulphate 40 – 50 g/l Magnesium sulphate 40 – 50 g/l	(i) 55±5°C (ii) Room temperature	30 60	4-6

Quality evaluation of chromate films was carried out by subjecting the specimens to various tests, keeping in view the environmental conditions to which the components are subjected in general.

Colour and conditions : Each type of chromate bath produces film of distinct colour, acid chromate film is golden yellow, RAE bath chromate film is chacolate brown and chrome-manganese film is black. Visual examination can thus assess qualitatively the coverage and uniformity of films. Condition of the chromate film was studied by placing a piece of filter paper on the chromate surface and rubbing the film with mild hand pressure and examining pick up of powdery deposit if any on the filter paper. The colour and surface texture were examined visually and with the aid of low power optical stereoscan microscope. Further, examination of the chromate film upto 400 magnification was done using an optical microscope, at higher magnifications using a Scanning Electron Microscope.

Adhesion : Adhesion of chromate film was determined by chequer method. A number of of vertical and horizontal parallel lines were scribed using a sharp tool of needle type on chromate film to give 3 to 4mm cheques. Cotton fabric backed adhesive tape of 10 mm width × 100 mm length was placed on cheques, to cover an area of 10 × 25 mm leaving the remaining tape free. The adhesive tape in contact with the cheques was well pressed by thumb finger so that tape adheres firmly. Adhesive tape was pulled out with a sharp outward movement in a fraction of a second. The tape as well as chromate film was examined to see whether the film remained intact or was detached.

Hardness : Hardness of the film was determained by scratch test. A suitable apparatus as specified in clause 15.1.1 of IS 101-1964, was used to carry out this test. The end of the hard steel needle is hemispherical and one mm diameter. The chromate film was drawn under the needle at a rate of 30 to 40 mm per second and simultaneously applying different loads of the order of

50, 100, 150..... 2000 grams and the maximum load that the chromate film could withstand without the scratch penetrating to the substrate was noted.

Corrosion test : Corrosion test by salt spray as per IS 1572-1960 ; B-2 on chromate film was carried out. Test panels were waxed at their edges and placed in the salt spray cabinet at an angle of approximately 15° from the vertical. The salt spray was on for 8 hours during day time and off for remaining 16 hours each day. The exposed surface was examined for signs of corrosion at intervals of every 2 hours during continuous salt spray and once after 16 hours off *i.e.* just before starting continuous salt spray. (The salt solution used for the corrosion test consisted ofsodium chloride 21.4 g/1, Magnesium chloride – 2.6 g/1, Magnesium sulphate – 1.7 g/1 and Calcium sulphate–1.3 g/1).

RESULTS AND DISCUSSION

Magnesium develops passivity in chromating solutions. Sulphate or nitrate anions present break the passivity and activate the surface by attacking the metal. During attack some metal is dissolved liberating hydrogen which reduces some of the chromate ions and a slightly soluble hydrated chromium chromate ($Cr_2O_3.CrO_3.XH_2O$) is is formed. ([4])

Magnesium oxide is present on the magnesium surface. Hence the chromating film is a complex basic double chromate with magnesium oxide. The chemical reactions of each chromating bath is given below : In Acid bath Magnesium alloy surface is cleaned by etching during immersion period. Most of the film formation occurs during the draining period, as per the following reactions :

$$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2\uparrow \quad ...(i)$$

$$2K_2Cr_2O_7 + 6H^+ \rightarrow 2K_2CrO_4 + Cr_2O_3 + 3H_2O \quad ... (ii)$$

$$Mg + K_2CrO_4 + Cr_2O_3 + nH_2O \rightarrow MgK_2CrO_4.Cr_2O_3.xH_2O + (nH_2O - xH_2O) ... (iii)$$

In RAE hot half hour bath, the solution is well buffered against rise of pH due to magnesium dissolution and partly by loss of ammonia during boiling. Chemical reactions are as below :

$$Mg + (NH_4)_2SO_4 \rightarrow MgSO_4 + 2NH_3\uparrow + H_2\uparrow \quad ...(i)$$

$$2K_2Cr_2O_7 + 6H^+ \rightarrow 2K_2CrO_4 + Cr_2O_3 + 3H_2O \quad ... (ii)$$

$$Mg + K_2CrO_4 + Cr_2O_3 + nH_2O \rightarrow Mg.K_2CrO_4.Cr_2O_3.xH_2O + (nH_2O - xH_2O) ... (iii)$$

In Chrome-manganese bath Magnesium sulphate functions as a source of sulphate, while manganese sulphate functions both as a source of sulphate and as a buffering agent and also takes part in film formation. Chemical reactions are as below :

$$Mg + 2H.OH \xrightarrow[Mg\,SO_4]{\text{Activator}} Mg(OH)_2 + H_2\uparrow \quad ... (i)$$

$$Mg + MnSO_4 + 2H.OH \rightarrow Mg.SO_4 + MnO_2 + H_2\uparrow ...(ii)$$

$$2Na_2Cr_2O_7 + 6H^+ \rightarrow 2Na_2CrO_4 + Cr_2O_3 + MnO_2 + H_2\uparrow \quad ... (iii)$$

$$Mg + Na_2CrO_4 + Cr_2O_3 + MnO_2 + n.H_2O \rightarrow Mg.Na_2CrO_4.Cr_2O_3.MnO_2xH_2O + (nH_2O - xH_2O) ... (iv)$$

The above chemical reactions clearly indicate that the composition of chromate film is the same for acid chromating and RAE "hot half hour bath" whereas in the case of chrome-manganese bath the film contains manganese dioxide in addition to the basic double chromate. MnO_2 formed in the reaction is taking part in the film formation and has been confirmed by the analysis of film. Among three types of chromating discussed in this paper, only chrome-manganese film is resistant to rubbing by filter paper whereas in the case of RAE half hr. hot bath and acid chromating bath, the film is not resistant and this is confirmed by the transfer of more brown stain to the filter paper. Thus the chrome manganese film has better abrasion resistance and this avoids damage of chromate film due to rubbing of components in transit.

Table II shows change in weight and coverage of chromate film on specimens subjected to chromating for different periods. Decrease in weight is considerably more in acid chromating and comparatively less in RAE bath though composition of the chromating film is the same for both. More decrease in weight for acid chromating is due to more dissolution of magnesium from the surface. This confirms the fact that etching takes place in solution and most or all of the film forms during the short period of draining *i.e.* five

TABLE II

Weight Change and coverage of Chromate Films in the three Types of baths

Name of the bath	Treatment time in minutes	Temperature	Change in weight of the specimen after chromating in grams	Coverage
Acid Chromating	(i) ½	Room Temperature	—0.0715	Poor
	(ii) 1		—0.0899	At some places film colour not observed
	(iii) 1½		—0.1443	,, ,,
	(iv) 2		—0.2418	,, ,,
REA half an hour hot bath	(i) 15	Boiling	—0.0268	Uniform
	(ii) 30		—0.0413	Uniform
	(iii) 45		—0.0599	Uniform
Chromo-manganese	(i) 15	55±5 C	+0.0006	Uniform
	(ii) 30		+0.0028	Uniform
	(iii) 45		+0.0053	Uniform
	(i) 30	Room Temperature	—0.0003	Uniform but not formed at the edges.
	(ii) 60		+0.0005	Uniform all ever
	(iii) 75		+0.0026	,, ,,
	(iv) 90		+0.0066	,, ,,
	(v) 105		+0.0029	,, ,,
	(vi) 120		+0.0030	,, ,,

seconds. In the case of RAE bath, dissolution of magnesium is less and film formation takes place in the solution. This explains the reason for less decrease in weight in the case of RAE bath. Chromating from chrome-manganese solution shows marginal increase in weight because of less magnesium dissolution than in RAE bath and presence of manganese dioxide in the film in addition to complex basic double chromate.

Surface topography studies of chromate film using an optical microscope showed that all the three types of chromate films have cracked structure. Fig. 1, 2 and 3 show typical film structure at X400 These had no bearing to the microstructure of the base matel (see Fig 4) and was characteristic of the type of chromoting bath. Film is severely cracked and the cell size is large in the case of chromate film formed from RAE bath. The cells and cell boundary width was very large compared to the chrome-manganese chromate film. The chromate film from the acid bath showed large and small cells of elongated shape and again had wider (cracks) cell boundries as comparad to chrome-manganese chromate film. These are



Fig. 1



Fig. 2

Fig. 1 Surface Topograph of Acid Chromate Film by Optical Microscope ×400

Fig. 2 Surface Topograph of RAE Chromate Film by Optical Microscope ×400



Fig. 3



Fig 4

Fig. 3 Surface Topograph of Cr-Mn Chromate Film by Optical Microscope ×400

Fig. 4 Microstructure of Mg Alloy Surface by Optical Microscope ×100

more evident is SEM pictures, shown in Fig. 5, 6 and 7.



Fig. 5

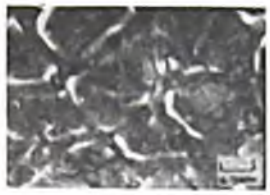


Fig. 6

Fig. 5 Surface Topograph of Acid Chromate film by SEM ×1500

Fig. 6 Surface Topograph of RAE Chromate Film by SEM ×1500



Fig. 7 Surface Topograph of Cr.-Mn Chromate Film by SEM ×1500

Adhesion studies have shown that all the three types of chromate films do not detach or damage when tested by chequer method. Table III Indicates scratch hardness values for different times of immersion for various chromating baths. Scratch hardness indicates the resistance of the film to scratching under load indicating the degree of hardness as well the quality of film adhesion. In the case of chromating film obtained from RAE bath, the scratch does not penetrate to substrate up to 100 grams load but penetrates partly at 150 grams and completely at 200 grams. Scratch is free from jagged edges in all the cases. A load of 50 grams is sufficient for the scratch to penetrate to the substrate in the case of chromate film from acid chromating bath. However scratch is free from jagged edges. Scratch hardness of chrome manganese chromate film was superior. The scratch in this case did not penetrate to the substrate even under a load of 2000 grams. The denser film with finer net work compared to the other types of chromate films may be contributing factors to this superior hardness.

TABLE III

Scratch Hardness of Chromate Films

Name of the bath	Treatment time in minutes	Temperature	Scratch hardness characteristics Penetration of substrate			Nature of scratch
			Does not penetrete at a of (grams)	Partially penetrates at a load of (grams)	Completely penetrates at a load of (grams)	
Acid chromating bath	(i) ½	Room	—	—	50	Scratch is free from jagged edges in all the cases
	(ii) 1		—	—	60	
	(iii) 1½		—	—	50	,,
	(iv) 2		—	—	50	,,
RAE half an hour hot both	(i) 15	Boiling	100	150	200	,,
	(ii) 30		100	150	200	,,
	(iii) 45		100	150	200	,,
Chrome-manganese bath	(i) 30	55±5°C	2000	—	—	,,
	(ii) 45		2000	—	—	,,
	(i) 30	Room	—	2000	—	,,
	(ii) 60		—	2000	—	,,
	(iii) 75		—	2000	—	,,
	(iv) 90		—	2000	—	,,
	(v) 105		—	2000	—	,,
	(vi) 120		—	2000	—	,,

Results of corrosion test carried out on chromate film obtained from acid chromating bath, RAE ½ hour hot both and chrome-manganese bath (hot & cold) are as below. Acid chromate film yielded to corrosion by showing black spots at corners after 30 hours exposure to salt spray and at the middle of the specimen after 48 hours exposure. Chromate films from RAE and chrome-manganesese baths did not show any corrosion upto 66 hours but showed corrosion after 72 hours. In this case corrosion was less severe for the chrome-mangenese chromate film compared to RAE film. Further the corrosion resistance of chrome-manganese chromate films from cold and hot baths were identical. Fig. 8 and 9 show the

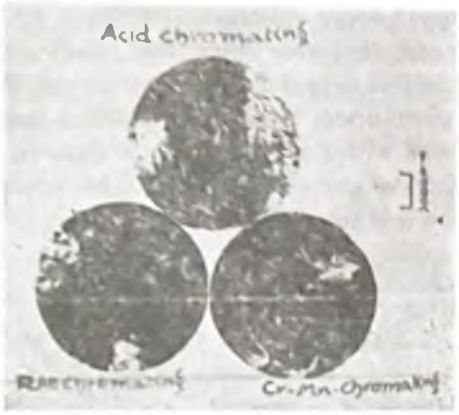


Fig. 8 Optical Stereoscanned Corrosion photographs of different chromate films × 10

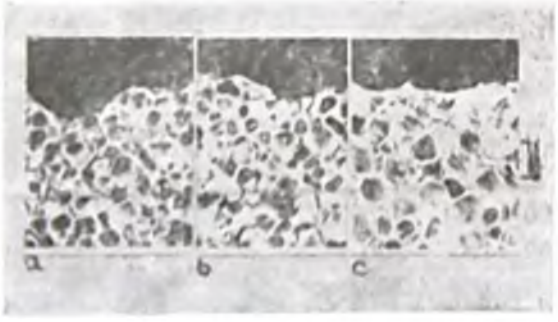


Fig. 9 Micro sections across corrosion pits of specimens with different Chromate films indicating relative depth of corrosion a) Acid Chromatin b) RAE Chromating and c) Cr-Mn Chromating - 100

extent of surface corrosion and depth of corrosion respectively for Acid, RAE and Chrome-Manganese chromate films after 96 hours exposure to salt spray. Depth of corrosion observed in these specimens were about 70 microns, 60 microns and 30 microns respectively for chromate films obtained from acid, RAE and Chrome-manganese bath. Thus the depth and extent (area) of corrosion was more for acid chromate film and RAE chromate film compared to chrome manganese film. This is in direct correlation to the superior soundness, scratch hardness and surface structure of the chrome manganese film, as already discussed earlier.

Results of industrial trials on castings : Above studies have confirmed that Chrome-manganese chromate film has superior scratch hardness, resistance to abrasion and better resistance to corrosion than RAE and acid chromate films, since there is a further advantage of energy saving by the use of cold chrome-manganese chromating, this process was selected for extensive industrial trials for various types of magnesium alloy castings.

Castings made from four types of magnesium alloys (for composition refer Table IV) were

TABLE IV

Magnesium Alloy Composition

[*RE—for Rare Earths*]

	Nominal composition (weight per cent)				
	Zn	Zr	Mn	Al	RE
Alloy—1	3.0	0.68	0.08	—	2.7
Alloy—2	5.0	0.88	0.06	—	—
Alloy—3	5.0	0.90	0.06	—	1.5
Alloy—4	0.8	—	0.27	8.0	—

subjected to chromating in cold chrome-manganese bath. It was noted that the chromate films were satisfactory and had a good surface texture. Some components chromated using this method are shown in Figure 10.

Industrial trials on castings were also carried out using RAE bath which required heating and hence electrical energy. RAE bath operates only in boiling condition, whereas chrome-manganese bath operates in cold condition and hence considerable energy saving can be realised by adopting the cold chrome manganese bath in the industry. Trials have shown that adoption of cold chrome-manganese bath results in energy saving of 230 KW hr. per shift of 8 hours, per batch. Capacity of the bath being 1000 litres.



Fig. 10 Chromated Castings Size × 3.0)

Conclusion : Chromo-manganese chromating is superior to acid and RAE chromating with respect to scratch hardness, resistance to abrasion and resistance to corrosion.

Adoption of chrome-manganese bath, capable of operating at room temperature, can save considerable amount of electrical energy.

Acid Chromating can be used economically for temporary protection of castings, but not when dimensional tolerance are very small.

REFERENCES

1) "Materials for Airframe" by Krishnadas Naik, Eastern Metals Review-Annual Number (1972).
2) "Magnesium Alloys for engineering applications" Devaraj, *Proc. Seminar on Newer Materials*, Institute of Prod. Engineers, Bangalore (1971).
3) Principles of Magnesium Technology by E. F. Emley Pergamon Press, London.
4) Corrosion, Volume 2, by L. L. Shreir, George Newnes Limited London.
5) Metal Process Engineering under the editorship of Prof. P. Rafukhin, Mir Publisher, Moscow, 1973.
6) Electroplating engineering hand book by A. Kenneth Graham, 1962, Rheinhold Publishing Corporation, New York.