CORROSION OF AIRCRAFT ALUMINIUM ALLOYS IN ACID SOLUTIONS AND ITS PREVENTION BY INHIBITORS

K. G. Sheth
J. Sundararajan
T. L. Rama Char

THE corrosion of metals is a serious problem confronting the industrially advanced countries of the world. Modern developments and war-time experiences have made it possible to manufacture metals at lower costs than before. Secondly, new sources of minerals have been discovered, thereby enabling each nation to increase its capacity for the production of metals. Iron and steel, aluminium, copper and zinc are amongst the metals in common use. In practice all of them are liable to corrode in various environments: atmosphere, soil and liquid medium. The loss of metal due to corrosion necessitating repair or removal of metal parts is one of fundamental importance affecting the economy of a country. The cost of corrosion control is rather high, the estimated figures per annum for some of the countries being U.S.A.[1] close to 10 billion dollars, U.K.[2] 600 million pounds, Canada[3] 500 million dollars, Australia[4] 100 million pounds, and India[5] 154 crore rupees. It becomes increasingly important to preserve available metals in use since a time may come when some of them approach exhaustion. From the available figures it has been indicated that immediate attention should be given to the non-ferrous metals, and greater attention to ferrous resources. In the case of iron the losses due to corrosion are estimated to be about 7·6 per cent a year. Corrosion control methods, therefore, assume great importance[6].

Aluminium is today a versatile metal with many desirable properties: light weight, low cost and fair corrosion resistance. The consumption of this metal for various purposes has increased tremendously in the leading countries of the world, replacing steel in some cases. It is used for utensils, building, the aircraft and navy, the electrical, automobile, food and packing industries, and for many articles of common use. In India there are abundant resources of aluminium. In view of the fact that there is a shortage of the common non-ferrous metals and also in view of the steel position not being quite satisfactory, it is necessary that in this country aluminium should be used wherever possible.

The resistance of aluminium to corrosion is due to the very thin oxide film that is present on its surface. But in many cases encountered in practice, indoor as well as outdoor, the metal is subject to corrosion due to the breakdown of the oxide film. In order to obtain the desirable properties aluminium is alloyed with other elements such as manganese, copper, iron, silicon, zinc, magnesium and nickel in amounts up to 10 per cent by weight. The corrosion of the metal is altered by the alloying elements. Methods of preventing the corrosion of aluminium under various corrosive media are therefore important. The general methods of preventing or minimising the corrosion of a metal are: by the use of protective coatings, surface conversion coatings which include anodising in the case of aluminium, use of inhibitors in the corrosive medium, and cathodic as well as anodic protection. The choice of the method depends upon the metal, the environment, the degree of protection offered and the cost.

The corrosion of aluminium in acid solutions and its inhibition has been studied by several workers, and these investigations have been covered in several reviews[7-10]. The present work formed part of the general programme on the corrosion of aluminium alloys of different compositions and its inhibition in acid and alkaline solutions. The investigations on 92 per cent aluminium alloy and pure aluminium in hydrochloric acid solutions have been reported in earlier papers[10-17]. The possibilities of cathodic protection have also been discussed[18, 19]. This paper presents the results of corrosion studies with aircraft aluminium-zinc and aluminium-copper alloys.

Messrs K. G. Sheth, J. Sundararajan and Dr. T. L. Rama Char, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore.

Experimental

The composition of the aluminium alloys were : (a) DTD 687 aircraft zinc alloy, aluminium 86, zinc 4·5–6·5, copper 1·5 (max), magnesium 2–3·5, iron 0·5, silicon 0·5 (max) per cent, and (b) DTD 603B aircraft copper alloy, aluminium 91, copper 3·5–4·8, iron 1·0 (max), manganese 1·2 (max), silicon 1·5 (max) per cent. The metal coupon was punched in one piece with a steel die. It was of a circular design to minimise the edge effects, diameter 2 cm., with a handle 3 cm. long and 0·3 cm wide, the total weight being approximately 800 mgm. The handle was coated with perspex from a chloroform solution leaving only the circular portion of apparent surface area 6·3 sq cm exposed to the corrosive medium. The corrosion rates and inhibitor efficiencies were determined by the weight loss method. The following inhibitors were used : acridine, nicotinic acid and thiourea for both the alloys, and in addition strychnine and quinine hydrochloride for the copper alloy.

Experimental results and discussion

Tables I and II present the results on corrosion rates, and Tables III and IV on inhibitor efficiencies.

Corrosion rates

The weight loss increases with an increase in the immersion period or electrolyte concentration. The weight loss-time curves are practically linear. This is to be expected since there is no deposit on the surface due to corrosion products in alkaline medium[20]. In the absence of contamination, high-purity aluminium will show much higher resistance towards acids than the less pure varieties. The corrosion rate of the zinc alloy is greater than that of the copper alloy, and both these have a higher corrosion rate than 92 per cent alloy containing 3 per cent iron and 4 per cent manganese, and pure aluminium[12].

TABLE I
Corrosion rates for aluminium-zinc alloy.
Temperature 32°C throughout.

Time, hrs.	Weight loss, mgm, for acid conc.		
	0·5 N	0·75 N	1·0 N
1·0	13	36	55
1·5	—	82	—
2·0	45	161	327
2·5	—	330	—
3·0	86	—	532
4·0	191	—	—
5·0	300	—	—
6·0	414	—	—

TABLE II
Corrosion rates for aluminium alloys.

Time, hrs.	Weight loss, mgm, for acid conc.	
	0·75 N	1·0 N
1·0	3	4·5
1·5	—	40
2·0	10	99
2·5	—	191
3·0	72	368
4·0	139	—
5·0	232	—
6·0	335	—

TABLE III
Inhibitor efficiencies for aluminium-zinc alloy.
Acid conc. IN, inhibitor conc. optimum.

Inhibitor	conc.g/l	Inhibitor efficiency %, for time, hrs.					
		1	2	3	4	5	6
Acridine	2	97	99	95	good protection		
Nicotinic acid	2	94	98	88	,,		
Thiourea	5	89	96	94	,,		
Dextrin	10	40			less protection		

TABLE IV
Inhibitor efficiencies for aluminium-copper alloy.
Acid conc. IN, inhibitor conc. optimum.

Inhibitor	conc.g/l	Inhibitor efficiency %, for time, hrs.			
		1·5	2·0	2·5	3·0
Acridine	2·0	98	97	98	98
Nicotinic acid	2·0	95	98	98	99
Thiourea	2·5		>99		
Strychnine	1·0	95	97	98	99
Quinine hydrochloride	1·0	94	96	97	97

Where copper is the alloying element the segregation of the $CuAl_2$-phase may accelerate the corrosion since it is cathodic[21]. On the other hand $NiAl_3$ and $MnAl_3$ are only feebly cathodic. It has been stated that the addition of 0·5 per cent manganese prevents the formation of undesirable $AlSi_2Fe$ crystals[22]. Mikami and Hashiura[21] have found that the corrosion of aluminium is accelerated remarkably by an electrochemical reaction between copper and aluminium-copper solid solution. The lower corrosion rate for the 92 per cent alloy can perhaps be attributed to the observation that the acceleration of the corrosion rate by iron is much less than that of an equal amount of copper[23]. The high corrosion for the zinc alloy is due to the fact that zinc as well as magnesium are anodic to aluminium in acids[24]. The overall corrosion is increased, and aluminium may not be completely protected. The differences

in the corrosion rates for different compositions can be attributed to the alloying elements, galvanic action, and possibly also on account of hydrogen overvoltage effects.

Inhibitor efficiencies

All the substances used are efficient inhibitors except dextrin. The literature values for the inhibitor efficiencies are : 99 per cent for 0·5 g/l acridine[25] in 3N acid, and 75 per cent for 0·4 g/l thiourea[26] in 1·4N acid. The weight loss of the aluminium-zinc alloy is too high beyond 3 hours, and therefore the determinations have been made with an inhibitor. Acridine gives pale yellow and brown deposits respectively on the surfaces of zinc and copper alloys. Its role as an inhibitor appears to be due to the formation of a mechanical barrier layer which is adequate enough to prevent access of the corrosive medium to the metal surface. The efficiency is practically independent of time as is to be expected for highly efficient inhibitors. A comparison of the efficiency of these inhibitors for the corrosion of 92 per cent alloy and pure aluminium shows that acridine is a good inhibitor for all the compositions. In view of the adherent brown deposit on the metal surface it will not be suitable for the protection of the copper alloy, although efficiency values are quite high. For this composition all the other inhibitors mentioned in Table IV have to be preferred.

Thiourea and nicotinic acid are fairly efficient for the 92 per cent alloy, but less so for pure aluminium possibly because of the lower corrosion rate. Dextrin is not satisfactory for all the compositions even though it has been found to be an inhibitor for steel in acid medium[27]. This suggests that a substance may not be equally efficient as an inhibitor for two different metals in the same medium. Acridine[1] and thiourea[28] have also been mentioned as inhibitors for steel in acid solutions. Nicotine sulphate has been stated to be an effective inhibitor for aluminium in hydrochloric acid. Alkaloids have also been reported in this connection, the efficiency of 0·0025 M strychnine in 1 N acid being 75 per cent[8]. The inhibitor efficiency for the same concentration of strychnine is much higher, vide Table IV. Alkaloids like strychnine have been mentioned as very powerful inhibitors for steel in sulphuric acid[29].

Mechanism of inhibition

In general the efficiency of inhibitors is greater in acid than in alkaline medium. Secondly the minimum concentration of an inhibitor required for maximum protection is also less in acid medium. Acridine is a very efficient inhibitor even at 0·02 g/l for the corrosion of 92 per cent alloy and pure aluminium in 1 N acid, and protects the metal at higher concentrations of the acid. The high efficiency for thiourea in the case of the copper and zinc alloys can be attributed to complex formation in situ[30]. Many of these inhibitors are effective for the corrosion of other aluminium alloys as well as steel in acid solutions. The adsorption

mechanism has been proposed to explain inhibitor action in the case of steel. Investigations carried out in this laboratory on corrosion rates, inhibitor efficiencies, corrosion potentials and polarisation have also indicated the adsorption theory for inhibition by thiourea during the corrosion of 92 per cent alloy and pure aluminium in hydrochloric acid solutions. The corrosion process with an inhibitor has been found to be essentially under cathodic control. A similar mechanism has been found to be valid for the inhibition of the corrosion of aluminium-copper alloy by quinine hydrochloride[17]. It appears that the mechanism of corrosion inhibition for the zinc and copper alloys is similar to that for the other aluminium compositions. Detailed investigations are being continued in order to throw further light on the mechanism of the corrosion process as well as the prevention of metallic corrosion by inhibitors.

Acknowledgement

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DISCUSSIONS

Dr. B. R. Nijhawan, NML: Corrosion is highly important from many angles. One might get, after precipitation or hardening suitable properties that may be wholly nullified by corrosion, the extent and scope of which is unlimited. As very little is known about what exactly is happening in the case of corrosion under different media, we might like to know something more of the mechanism and the havoc it thereby causes. We are making some efforts to counteract the corrosion of aircraft aluminium alloys used for the fuselage by cladding it with pure aluminium, etc. But the subject, I think, has not fully received the attention it really deserves in India. As it does not appear to be so attractive at first sight, it is often relegated to the background whilst it is agreed by all that it can nullify all the beneficial properties of precipitation hardening, dispersion hardening and ultimately what is left is a broken and damaged piece. I think it is a very highly important subject and in which we are putting up an active school of workers in the National Metallurgical Laboratory. We wish to considerably expand this activity of ours in which co-operation and collaboration of industrial establishments like the Hindustan Aircraft Ltd. will be sought. Perhaps on some future day, we might have a Symposium on "Corrosion" itself to really focus attention on the collosal damage that can be brought about by corrosion under India's tropical hot and humid weather conditions.

Mr. J. Sundararajan (Author): We agree with Dr. Nijhawan that the subject of corrosion really deserves more serious attention in India. The art of anti-corrosion methods has advanced much more than the science, and therefore, there is an urgent need for fundamental investigations on the mechanism of inhibition and other aspects of corrosion. We are glad to know that the NML is putting an active school in this field. At the Indian Institute of Science, we have been engaged with research work on different branches of corrosion, particularly inhibition. Contributions have also been made to International Conferences organised in recent years. It is proposed to continue these investigations, with special reference to aluminium, which is a very important material in the present context in this country.

Dr. T. Banerjee, NML: I must thank Dr. Rama Char and his colleagues for taking up this very important work. The lecturer has said that they have taken up the work mostly from electrochemical point of view; the results have, however, been obtained more from the practical side. The authors have taken different types of inhibitors and have actually found under what condition corrosion is more or less. But from the electrochemical point of view, he has not given anything about the pH. I have already forgotten the formula of acridine, might remember a little of nicotinic acid and thiourea. These inhibitors in different acid solutions will not behave similarly. The amount of adsorption that has taken place is not of thiourea or nicotinic acid but of the complex that will be formed before there is adsorption. Specially for thiourea, I agree with what has been stated by the authors; it will give very complicated result at different pH or as he said in acid solution. I lay stress to different pH and there is a limiting concentration which he has not given us in his results probably due to shortage of time. Another point that comes to our mind is that the mechanism has been rushed through on the basis of tables, of data projected. Because if there is anodic and cathodic surfaces and at the same time there is the general adsorption or in other words if we think of van der Waals Force as the prominent factor in adsorption and we have also got surfaces—anodic or cathodic, the results will not be the same. The curve that you will get when the van der Waals Force alone will work and the curve that you will get with the van der Walls Force and the portion of the surface as anodic, will not be the same. Because adsorption on the anodic or cathodic surface will be rapid while that due to the other force will not be rapid. It will require some time for equilibrium. If you plot the curve, it will be an ideal logarithmic curve in one case and in the other case the logarithmic curve will fail in the initial state.

Mr. J. Sundararajan (Author): We are grateful to Dr. Banerjee for his kind comments on our work, and also his suggestions. This paper confines itself to experimental data on the efficiencies of some inhibitors. A large amount of work has been carried out in this Laboratory on the electrochemical aspects of inhibition. With the help of cathodic and anodic polarisation and other data, we have been able to comment on the mechanism of corrosion inhibition with reference to factors like cathodic and anodic areas, adsorption, etc. The results have been incorporated in many publications, and similar investigations have been extended

to corrosion in the alkaline medium. On the completion of the studies that are currently in progress, we feel that it will be possible to present a fair picture of the mechanism of inhibition for aluminium and its alloys.

Mr. P. C. Sen, NML : I want to know whether the alloy taken by the authors is quite a homogeneous one or not. Suppose if there is some precipitation hardening in the alloy, then preferential corrosion will take place. I think the authors have not taken this into consideration. Since the rate of corrosion is not uniform all over in the specimen it may be due to preferential corrosion.

Mr. J. Sundararajan (Author) : The formation of the $CuAl_2$-phase will occur in the copper alloy and it will act as the cathodic region of the corrosion cell. We were mainly interested in the corrosion behaviour and the possibilities of inhibition of pure aluminium and different types of alloys. It would, of course, be interesting to consider the metallurgical aspects of the problem.

Dr. Y. N. Trehan, NML : I think the authors should also take into consideration the history of the specimen. As they are using the specimens received from the trade only, they may not know in what condition the metal has been treated and worked. The chemical composition of the alloy might be the same in all cases, but will behave differently due to the pretreatment given to them.

Mr. J. Sundararajan (Author) : It is desirable to take into consideration such factors also.