

THE CORROSION BEHAVIOUR OF SHEET ALUMINIUM UNDER DIFFERENT SURFACE TREATMENT CONDITIONS

by
Dr. M. B. Kahawatte

Abstract

Aluminium is one of the metals, which is resistant to corrosion, due to the formation of an oxide layer on its surface within a very short time period. In this research work, the rate of corrosion of Aluminium of purity 99.99% was measured in different media and under different conditions of heat treatment and surface treatments. The results show an increase in the rate of corrosion with the increase in temperature and concentration of the corrosive media. The heat treatments too, have some effect on the rate of corrosion of the material. The surface treatments have a clear influence on the rate of corrosion, but at high temperatures this influence is over shadowed by the presence of impurities on the surface of the material.

1.0 Introduction

Aluminium is supposed to be one of the metals which to a certain extent is resistant to corrosion. The reason for this behaviour is due to the formation of a thin oxide layer on the surface of the material within a very short period of exposure (1,2,3,4). According to Hunter and Fowler (5) the oxide film consists of two layers. The first layer which is directly on the surface of the metal is an amorphous layer and the second layer depends on the conditions and temperature of the surrounding atmosphere. Within a very short period these layers are formed and the thickness of these layers grows upto about 20 to 30 Å⁰. But the thickness of the oxide film varies with the purity of the material and the nature of the surface of the material. In the corrosion studies of Aluminium it is very important to study the behaviour of this oxide layer under varying conditions. Kaesche (6) studied the behaviour of Aluminium in Chloride media. The character of the oxide film, the film thickness, the structure of the film and its chemical resistance differs very much from media to media and the surrounding temperature (4,5,6). In this research work, the corrosion rate of Aluminium of 99.99% purity was measured in different media and at different temperatures after various surface treatments.

2.0 Experimental Procedure and Results

5mm thick sheet Aluminium from the Firm VEB MetalHalbzeugwerke, Merseburg/Germany with a chemical composition of 99.99% Al; 0.0031% Fe; 0.0005% Si; 0.0007% Cu was used. The supplied material had the following degree of cold-work (10%, 30%, 50%, 80%, 90%, 95%). The degree of cold-work is measured by the percent of reduction of thickness of the material during cold rolling from the original state.

To conduct the experiments, rectangular pieces were cut to the size of 30mm x 20mm x 5mm. All the specimens were cleaned with acetone and alcohol to remove oil and dust on the surface of the material. They were then washed with distilled water, dried and kept in a desiccator. To measure the rate of corrosion two methods were adopted. In the first method the loss in weight due to corrosion was calculated. For this purpose the samples were weighed before the experiments were conducted. After finishing the experiments the samples were washed with distilled water, dried and weighed again to determine the loss in weight due to corrosion. The accuracy of the balance was upto 0.21 mg. In the second method a volumetric titration was conducted with the corrosive media after the end of each experiment. Using the volumetric titration method described by Pribil (7), the amount of Aluminium dissolved in the corrosive media was estimated. A formula given by Pribil (7) was used for this purpose.

In the first set of experiments samples were taken only from the 10% cold-worked material. Before they were placed in different concentrations of HCl, the samples

Dr. M.B. Kahawatte, B.Sc, Dr.-Ing. is presently attached to the Faculty of Engineering in Peradeniya. He graduated from the University of Ceylon in 1963 and proceeded to Germany on a scholarship given by the Government of East Germany. He did his Post-graduate studies on corrosion of Metals at Bergakademie/Freiberg in Germany. From 1970 to 1990 he was involved in teaching, research and consultancy activities in Germany.

underwent a 4 minute polarization in 10% H_2SO_4 at 50°C by using a current density of 100 mA/cm^2 . Polarization was done to remove the oxide layer. After the polarization, the samples were washed with distilled water, dried and weighed. These samples were then kept in different concentrations of HCl and the experimental time was varied. The results are given in figure 1.

In the second set of experiments samples were taken from different degrees of cold-worked material and placed in 20% HF at 25°C . The experimental time was varied. The results are shown in figure 2.

In the third set of experiments, samples were taken from different degrees of cold-worked material and divided into four groups. Three groups were given a heat treatment. They were kept in a furnace at 550°C for one hour. They underwent the following cooling methods. One part was quenched in water at room temperature, the second part cooled in air (normalized) and the third portion cooled in the turned off furnace (annealed). All the specimens were cleaned with alcohol and then washed with distilled water and dried. Some of these specimens were placed in 5% HCl at 25°C for three hours and the others in 20% HCl at 25°C for 15 minutes. The results are given in figures 3 and 4.

In the final set of experiments samples were taken from different degrees of cold-worked material and divided into four groups for further treatment. Each group underwent a different surface treatment as described below.

Surface Treatment I - cleaned with alcohol and then washed with distilled water

Surface Treatment II - etched one minute in 15% NaOH at 65°C and then washed with distilled water

Surface Treatment III - etched one minute in 37% HCl at 20°C and then washed with distilled water

Surface Treatment IV - three minutes electropolished in 80% by Volume $\text{C}_2\text{H}_5\text{OH}$ + 20% by Volume HClO_4 at 20°C and then washed with distilled water

They were then placed in different concentrations of HCl at different temperatures. The results are given in figures 5,6,7,8 and 9. The amount of Fe present on the surface of the material was analysed and the results are given in figure 9.

3.0 Discussion of Results

As expected of many metals, the rate of corrosion of Aluminium too increases with the increase in concentration of the corrosive media and the experimental time as

discussed previously (see figure 1). In the study of the rate of corrosion with the degree of cold-work, the results vary according to the corrosive media, temperature of the media and the experimental time. In 20% HF the rate of corrosion increases with time, but the rate of corrosion decreases with the increase in the degree of cold-work (see figure 2). In HF, the oxide layer will be completely dissolved causing a uniform attack on the Aluminium surface. As explained by Engelhard (8), the decrease in the rate of corrosion could be due to the crystallographic orientation of the grains on the surface of the material. According to Engelhard (8) and Kunze (9) crystals with a certain orientation will be preferably attacked than the others. The second reason could be attributed to the fact that during cold-working a certain amount of heat is produced causing the impurities to move into the grains of the material by means of increased diffusion and thereby a decrease in the rate of corrosion.

Figures 3 and 4 show the rate of corrosion of heat treated Aluminium in 5% and 20% HCl. The rate of corrosion increases with the increase in concentration of HCl, but decreases with the increase in the degree of cold-work. The reasons are the same as in the case of HF. The untreated and water quenched specimens show a higher corrosion rate than the normalised and annealed specimens. In the case of untreated specimens, the impurities like Fe, Si and Cu are present in Aluminium. Some percentage of these impurities is on the surface of the material and therefore influences the rate of corrosion of Aluminium. When the specimens are quenched in water after heat treatment the impurities have less time to diffuse into the grains of the material. At the same time a complete phase transformation cannot take place. Due to the fast cooling process a complete recovery of crystal defects cannot take place (10,11,12,13). Due to these reasons there is an increase in the rate of corrosion. When the material is normalized or annealed, there is enough time for diffusion of the impurities to the grains of the material and also enough time for complete phase transformation. The number of crystal defects would be minimized due to proper diffusion taking place (13). Therefore the rate of corrosion is reduced.

Figure (5,6,7,8 and 9) show the rate of corrosion of Aluminium after different surface treatments. In the case of 5% HCl at 25°C the surface treatments I and III show a reduction in the rate of corrosion, except for 90% cold-worked material and the surface treatments II and IV an increase in the rate of corrosion with the increase in the degree of cold-work. In 20% HCl at 20°C and 45°C , the rate of corrosion decreases with the increase in the degree of cold-work for the surface treatments I, II and III except for the electropolished samples. Figures 5,6 and 7 show that the surface treatment has some influence on the rate of corrosion of Aluminium. When a comparison is made

regarding the rate of corrosion and the art of the surface treatment, the electropolished samples had the lowest rate of corrosion and with the surface treatments, I, II and III had a higher corrosion rate. When the material is electropolished the whole surface layer is removed to a certain depth and thereby the impurities on the surface are removed. In the case of surface treatments, I II and III, the whole surface layer is not removed leaving behind most of the impurities. The higher rate of corrosion could be explained as due to the presence of impurities on the surface of the material (see figures 8 & 9). With the increase in temperature of 20% HCl, the rate of corrosion is rapidly increased. The surface treatment methods have very little effect on the rate of corrosion. All four surface treatment methods show similar corrosion characteristics with regard to the degree of cold-work. There is an increase as well as a decrease in the rate of corrosion for all four surface treatment methods. To find out the reason for this behaviour, the corrosive media was analysed after the end of each experiment. Presence of Fe was detected from the analysis. These results are shown in the figure 9. This shows very clearly how even traces of Fe could influence the rate of corrosion of Aluminium.

4.0 Conclusion

The rate of corrosion of Aluminium increases with the increase in concentration and the temperature of the corrosive media. When material is normalised or annealed, the rate of corrosion is lower than in the case of water quenched and untreated material. The reasons for this behaviour were given in the discussions of the results. The art of surface treatment has some influence on the rate of corrosion of Aluminium. But when the temperature of the corrosive media is increased the influence of surface treatment on corrosion is decreased. The rate of corrosion is generally increased due to three factors. The aggressiveness of the media, the increase in temperature of the media and the presence of Fe in Aluminium as an impurity.

References

1. E. Maass, Korrosion und Korrosionsschutz Vol. 1, P. 3-4, (1926)
2. H. Thiel, Zeitschrift fUr Elektrochemie, P.370, (1927)
3. F. Eisenkolb, Einführung in die Werkstoffkunde, Verlag Gruyer & Co. Berlin 1965.
4. H. Kaesche, Werkstoffe und Korrosion, P.557-559, (1963)
5. S. Hunter & P. Fowler, Journal of Electrochemical Society, P.103 & P.482, (1956)
6. H. Kaesche, Technische Universität Berlin, Habilitationsschrift, Berlin (1962)
7. R. Pribil, Komplexometrie Band 1 & 2, Leipziger Verlag (1963)
8. R. Engelhard, Dissertation, Bergakademie Freiberg, (1968)
9. E. J. Kunze, Dissertation, Technische Universität Dresden, (1965)
10. R. Bakisch, Journal of Electrochemical Society, P.791, (1962)
11. P. Moritze, Metaux et Corrosion, P. 139-140, (1947)
12. F. Todt, Korrosion und Korrosionsschutz, Verlag Gruyer & Co., Berlin, (1961)
13. G. Masing, Zeitschrift fur Metallkunde, P. 311-312, (1949)

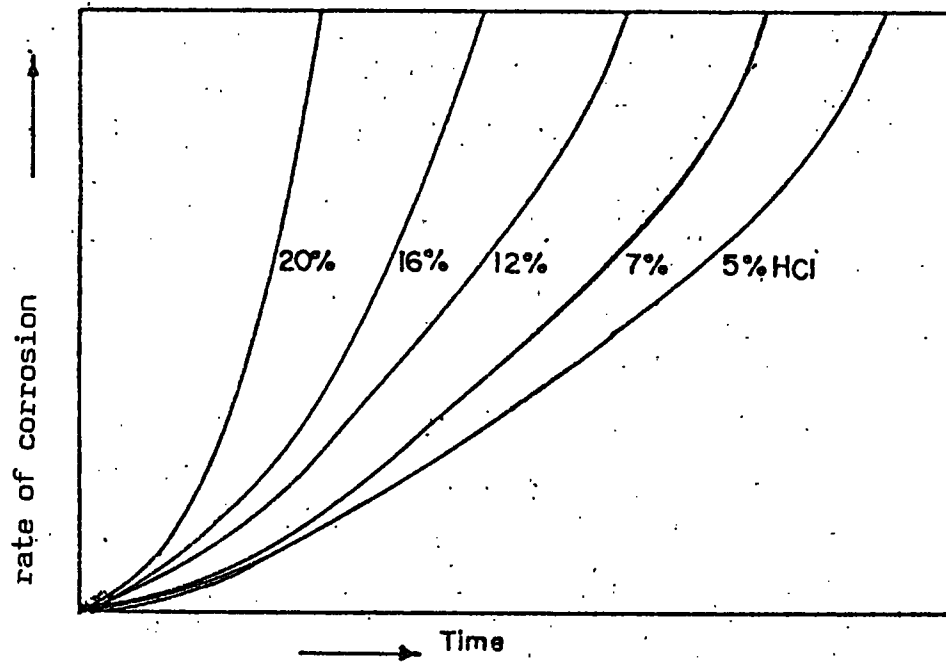


Fig. 1 Typical variation of the rate of corrosion

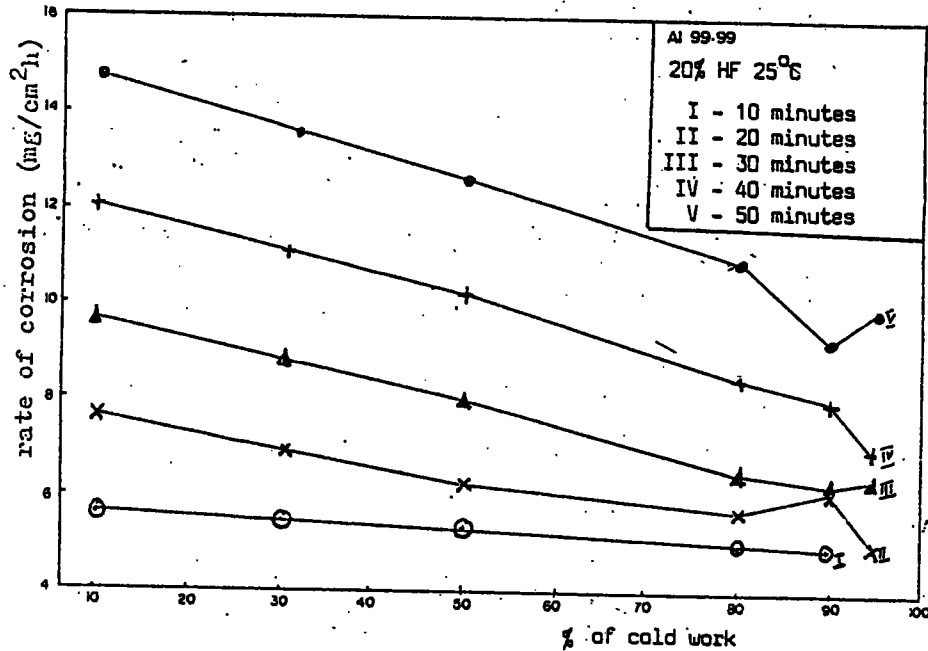


Fig. 2 Variation of the rate of corrosion with % cold work for different experimental time

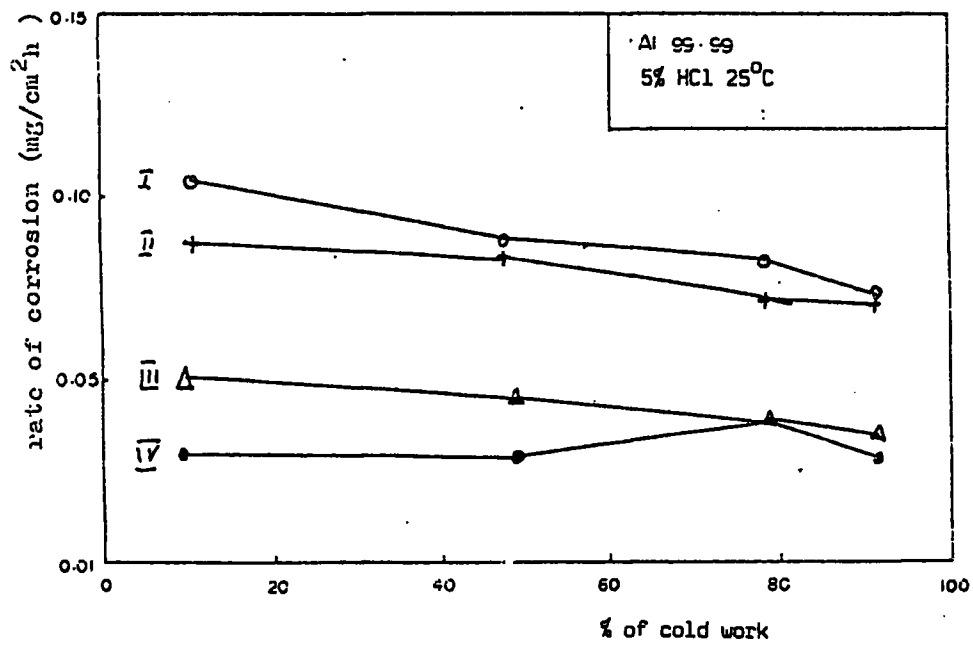


Fig. 3 Aluminium samples with different treatments in 5% HCl
 I - washed with alcohol and then with distilled water ;
 II - water quenched ; III - normalized ; IV - annealed

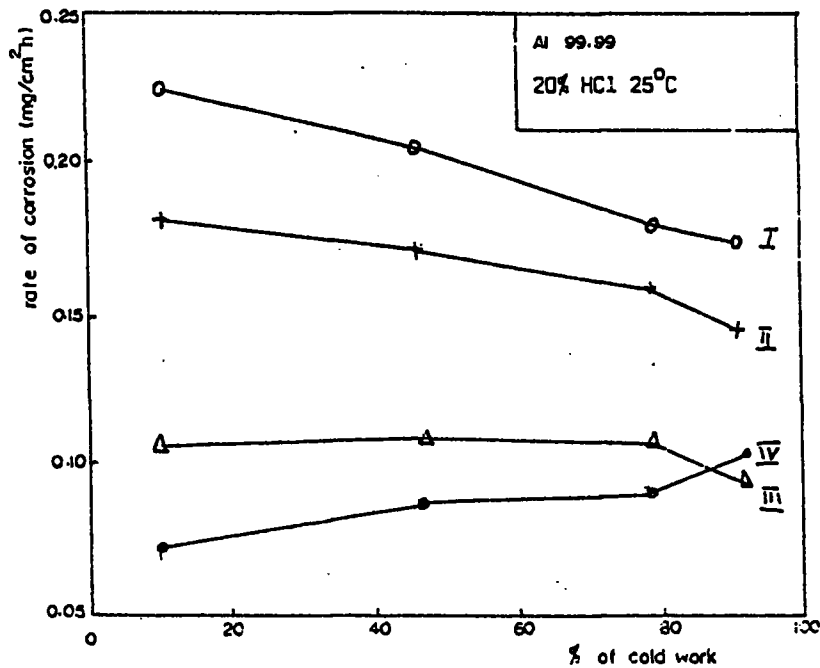


Fig. 4 Aluminium samples with different treatments in 20% HCl
 I - washed with alcohol and then with distilled water;
 II - water quenched ; III - normalized ; IV - annealed

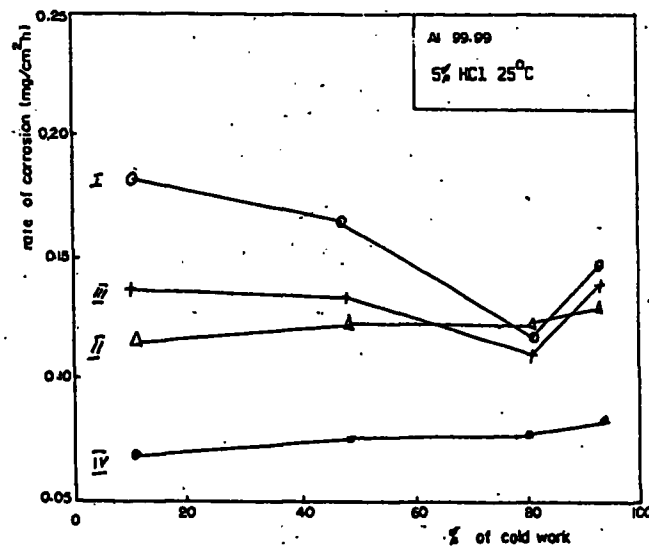


Fig. 5 Variation of rate of corrosion with % cold work for aluminium samples after different surface treatments (experimental time 4 hours).

I - cleaned with alcohol and then washed with distilled water; II - etched 1 minute in 15% NaOH at 65°C and then washed with distilled water; III - etched 1 minute in 37% HCl at 25°C and then washed with distilled water; IV - 3 minutes electropolished in 80 Vol. % C₂H₅OH + 20 Vol. % HClO₄ at 20°C and then washed with distilled water.

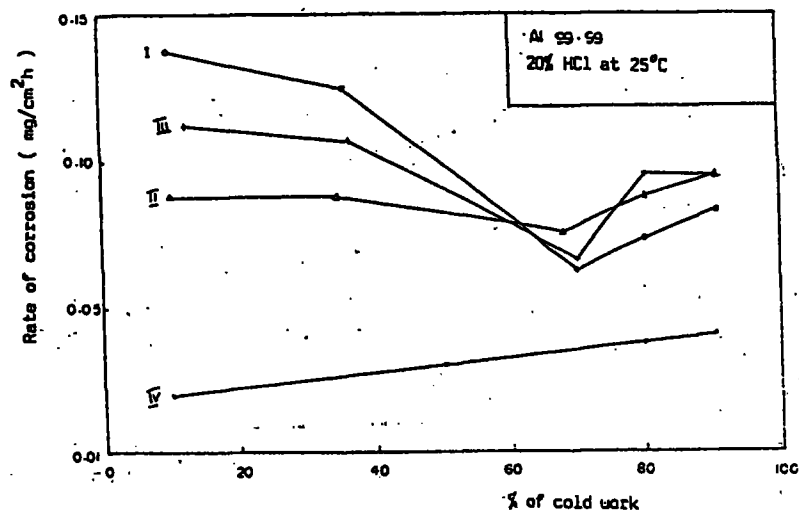


Fig. 6 Variation of rate of corrosion with % cold work for aluminium samples after different surface treatments (experimental time 20 minutes)

I - cleaned with alcohol and then washed with distilled water; II - etched 1 minute in 15% NaOH at 65°C and then washed with distilled water; III - etched 1 minute in 37% HCl at 25°C and then washed with distilled water; IV - 3 minutes electropolished in 80 Vol. % C₂H₅OH + 20 Vol. % HClO₄ at 20°C and then washed with distilled water.

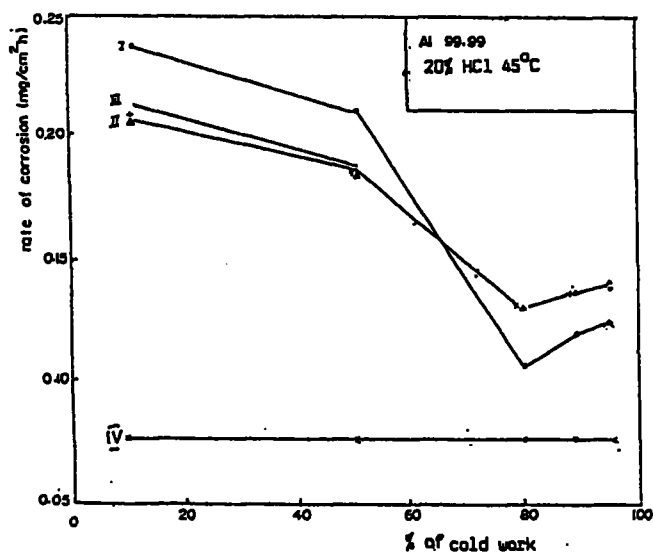


Fig. 7 Variation of rate of corrosion with % cold work for aluminium samples after different surface treatments (experimental time 10 minutes)

I - cleaned with alcohol and then washed with distilled water; II - etched 1 minute in 15% NaOH at 65°C and then washed with distilled water; III - etched 1 minute in 37% HCl at 25°C and then washed with distilled water ; IV - 3 minutes electropolished in 80 Vol. % C_2H_5OH + 20 Vol. % $HClO_4$ at 20°C and then washed with distilled water.

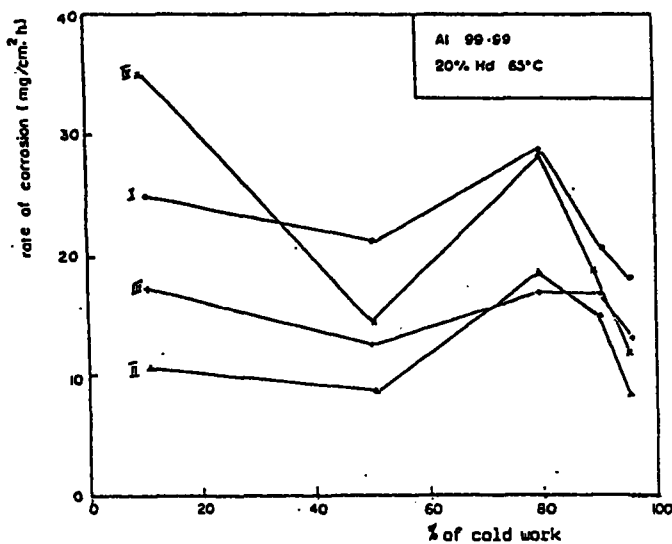


Fig. 8 Variation of rate of corrosion with % cold work for aluminium samples after different surface treatments (experimental time 10 minutes)

I - cleaned with alcohol and then washed with distilled water; II - etched 1 minute in 15% NaOH at 65°C and then washed with distilled water; III - etched 1 minute in 37% HCl at 25°C and then washed with distilled water ; IV - 3 minutes electropolished in 80 Vol. % C_2H_5OH + 20 Vol. % $HClO_4$ at 20°C and then washed with distilled water.

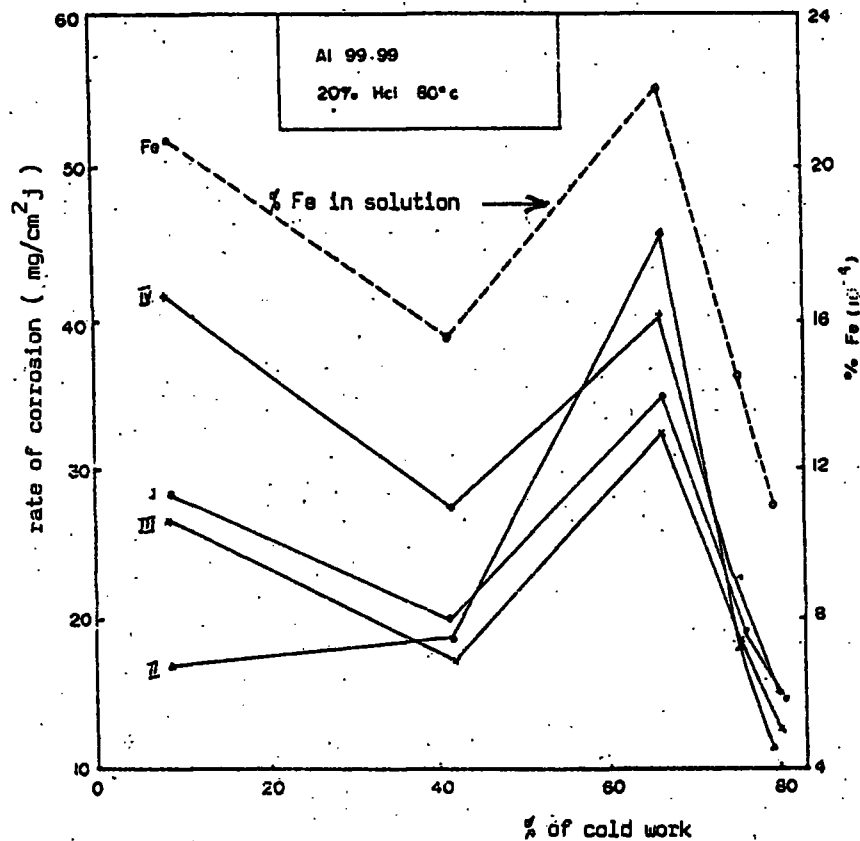


Fig.9 Variation of rate of corrosion with % cold work for aluminium samples after different surface treatments (experimental time 10 minutes)

I - cleaned with alcohol and then washed with distilled water; II - etched 1 minute in 15% NaOH at 85°C and then washed with distilled water; III - etched 1 minute in 37% HCl at 25°C and then washed with distilled water ; IV - 3 minutes electropolished in 80 Vol. % C_2H_5OH + 20 Vol. % $HClO_4$ at 20°C and then washed with distilled water.