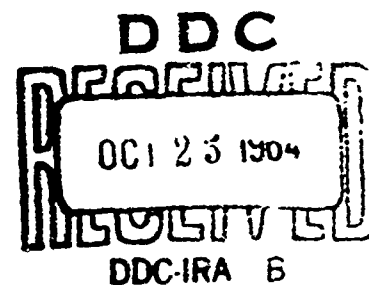


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NON-EQUILIBRIUM COMBUSTION

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SUMMARY

A combination manometric and volumetric system has been constructed for determining the oxidation rates of both solid and molten aluminum. Preliminary experiments indicate that the sensitivity and accuracy of the system are adequate for the present study. A number of runs have been made using aluminum foil at 600°C. Although the actual oxidation rates were not reproducible, the total amount of oxygen consumed was approximately the same in all cases. The inconsistency in the results confirm the findings of Cochran and Sleppy (1), i.e. oxidation rates depend greatly on the way the surface is originally treated. This is apparently true even in the case of molten aluminum. The total oxygen consumed per square centimeter at a given temperature agrees reasonably well with the findings of both Cochran and Sleppy (1) and Blackburn and Gulbransen (2). Aluminum foil, at 600°C, gained approximately 5.2 $\mu\text{gm}/\text{cm}^2$ as compared with approximately 5.7 $\mu\text{gm}/\text{cm}^2$ reported by Cochran and Sleppy or 5.0 $\mu\text{gm}/\text{cm}^2$ reported by Blackburn and Gulbransen. Initial experiments with molten aluminum indicate much higher weight gains than those obtained with aluminum foil. Sleppy (3) observed a similar increase in weight gain in the molten state, but his values were considerably lower than the ones observed in the present investigation. The reason for the discrepancy has not been determined, although it may well be due to differences in the purity of the samples.

I. INTRODUCTION

The oxidation of aluminum at temperatures below its melting point has been studied by a number of investigators in recent years and, although there is considerable discrepancy in the numerical data, there is general agreement on the overall mechanism involved. Both Cochran and Sleppy (1) and Blackburn and Gulbransen (2), working with "as rolled" aluminum foil of 99.99% purity and dry oxygen, observed that the oxidation rates were temperature dependent and near linear to a weight gain of about 3 micrograms/cm², followed by a rate that decreased rapidly with further weight gain. It was further found that the ultimate weight gain could be increased by as much as 20 fold by increasing the surface roughness through chemical etching. In addition, water vapor was found to react with aluminum faster than oxygen, although the difference was not great. The increased rate is thought to be due to blister formations on the surface of the aluminum that disrupt the oxide film and expose fresh metal surface to the oxidizing atmosphere. The oxidation of a commercially available aluminum-magnesium alloy - 5052 - in both dry oxygen and moist air, was found to be much faster than for high-purity aluminum and proceeded to much higher weight gains.

Very little work has been done on the oxidation of molten aluminum. Sleppy (3), working with molten aluminum in an atmosphere of dry oxygen, found the oxidation rate was strongly influenced by initial surface conditions of the solid sample. He further found the oxidation is characterized by a logarithmic scale oxide growth at temperatures of up to about 700°C, while at temperatures near 750°C, a modified parabolic oxidation law is obeyed. Under these conditions, oxidation is still occurring at a rapid rate even after a lapse of one hour. No information is available on oxidation of molten aluminum in atmospheres other than dry oxygen.

The present program is aimed at obtaining a better understanding of the oxidation of molten aluminum. By so doing, it is hoped that methods of influencing this rate may be found.

II. EXPERIMENTAL.

A. Apparatus

A schematic diagram of the oxidation apparatus is shown in Figure 1. It is similar to the apparatus used by Sleppy (1,3) in his oxidation studies except that a gas burette was added to one side of the system to permit volumetric measurements of the amount of oxygen used. This technique was believed to have some advantages over the manometric system in that it permitted oxidation measurements to be carried out at constant pressure, and did not require an accurate knowledge of the volume of the system. The more direct gravimetric method (4), in which the weight gain is measured directly on a sensitive balance, was not suitable for the present studies because of the necessity of using a crucible to contain the molten sample. It was felt that suitable crucibles were too heavy to permit accurate measurements.

B. Procedure

Before making a run, the aluminum sample was cleaned and weighed before being placed in the sample cell. The system was then evacuated to a pressure of 10^{-5} mm Hg, after which the preheated furnace was raised into position around the reference and test cells. The reference cell, equal in volume to the test cell, is used to prevent, as much as possible, fluctuations in pressure in the two cells which is caused by variations in temperature and possible outgassing. Precautions were necessary to prevent draughts around the cells because even small draughts cause rather large fluctuations in the oil manometer. Evacuation of the system was continued for approximately one hour to permit degassing of the sample. The three-way valve (Fig. 1) was then closed, and the upper manifold of the system was pressurized with dry oxygen. The three-way valve was then opened, which allowed the oxygen to enter the remainder of the system, including the two cells. Pressures of 200- to 250-mm Hg were used in the present studies. Approximately 15 seconds was allowed for the pressure to equilibrate. The three-way valve was then closed, which isolated the reference and test cells from each other and from the rest of the system. Under these conditions, the two cells are connected only through the oil manometer: any difference in pressure in the two cells is indicated on this instrument. By changing the level of mercury in the gas burette, pressures in the two cells can again be equalized. The amount of oxygen that was consumed in the oxidation process is then obtained from the difference in readings of the gas burette. Volume changes of 0.01 ml can be determined with the present system. The gas burette was submerged in a water bath for accurate temperature determination. Volume changes are recorded every 60 seconds during a normal oxidation run which usually varies in duration between 60

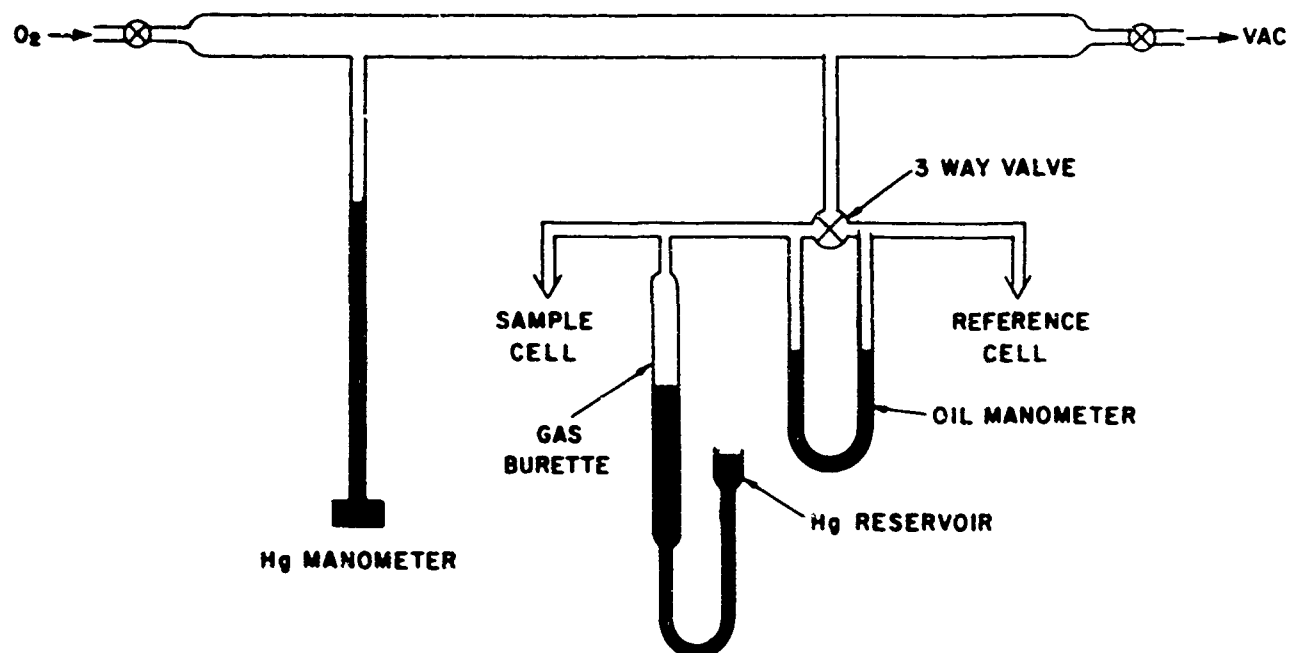


Fig. 1 Oxidation Apparatus

and 90 minutes. All temperatures were held to within $\pm 1.0^{\circ}\text{C}$ during a run. At the end of each run, the oxygen was replaced with helium, the cells isolated as before, and the system checked for leaks. (Leaks were indicated by a displacement on the oil manometer.)

C. Sample Preparation

In earlier studies, at temperatures below the melting point of aluminum, samples of aluminum foil that had a total surface area of 100 cm^2 were used. In later experiments involving molten aluminum, test samples were cut to size ($1/4$ in. by $1/4$ in. by $2-1/8$ in.) from a larger block of high-purity metal and then smoothed with a file. Unless otherwise stated, both types of samples were etched with a solution of hydrochloric acid and copper nitrate at 80°C as outlined by Sleppy (1). During the investigation, several of the sample blocks were etched with a solution of 6 percent nitric acid and 94 percent phosphoric acid at 95°C . These samples showed a much lower weight gain during oxidation, indicating the importance of surface preparation on oxidation rates. Similar effects have been observed by other investigations (1, 3, 5) and is attributed to the varying degrees of surface roughness of the samples that were used.

D. Sample Cells

Because of the reactivity of molten aluminum, suitable container materials have proven to be a problem. Quartz reacts with molten aluminum so that upon cooling, the quartz cell shatters: the nature of the reaction is not certain. Al_2O_3 is practically nonreactive with aluminum, but the cells are not uniform enough to permit the samples to be extracted once they have solidified. In some cases it is desirable to examine the oxidized samples. Boron nitride has proven quite good as a container material and will be used in future studies. Boron-nitride crucibles, sealed inside a quartz cell, will be used to contain the molten aluminum.

III. RESULTS AND DISCUSSION

Before attempting studies with molten aluminum, a number of tests were conducted with aluminum foil in the temperature range of 400 to 600°C. The purpose of these experiments was primarily to determine the reliability of the volumetric technique for measuring oxidant consumption as a function of time, and to determine the limitations of the system. By working below the melting point of the metal, it was possible to use rather large surface areas in these tests so that the total amount of oxygen uptake was appreciable. Commercial aluminum foil (.001-in. thick), having an assay of 98.5 percent aluminum alloyed with 0.7-1.0 percent Si and Fe, 0.1-0.2 percent Cu, 0.05 percent Mn, 0.1 percent Zn, plus traces of other metals, was used in all these tests. Apparent surface area of the samples was held at 100 cm². The surface was cleaned and etched with a solution of hydrochloric acid and copper nitrate as outlined above. After etching, the foil was much thinner than before, and, in some cases, actually had what appeared to be a multitude of tiny holes in it. This caused considerable uncertainty as to the actual area of the active surface.

Although oxidation rates varied slightly from one sample to another, the total amount of oxygen uptake was quite consistent. Oxygen uptake was rapid at first and decreased with time. Usually after about 90 minutes, the rate of oxygen uptake was practically zero. At 600°C, this amounted to approximately 5.2 μgm/cm² which was in good agreement with the work of Cochran and Sleppy (1) and Blackburn and Gulbransen (2). Figure 2 shows a plot of weight gain as a function of time for aluminum foil at a temperature of 600°C. Shown on the same plot is the curve of the work Blackburn and Gulbransen obtained under similar conditions. The agreement between the two is remarkably good. Reliability of the volumetric measurements was further verified by several determinations of the actual weight gained during a run. This was done by weighing the sample before and after a run and assuming the difference in weight was due to the oxide formation. At the higher temperatures (above 600°C), evaporation of metal from the surface caused an appreciable discrepancy in the two methods. However, at the lower temperatures (400°C), agreement between the two methods was quite good, offering further evidence that the volumetric technique should be quite adequate for the present investigation. Once this was proven, emphasis was shifted to oxidation of molten aluminum. These studies have just gotten underway. Preliminary results indicate rather large oxygen uptake at temperatures in the neighborhood of 750°C, although further investigations will be necessary before any actual data are obtained. There was some concern at first as to whether or not the present system would be sensitive enough to measure oxidation rates of molten aluminum at temperatures near the melting point due to the decrease in surface area of the molten sample. In the earlier studies, where temperatures

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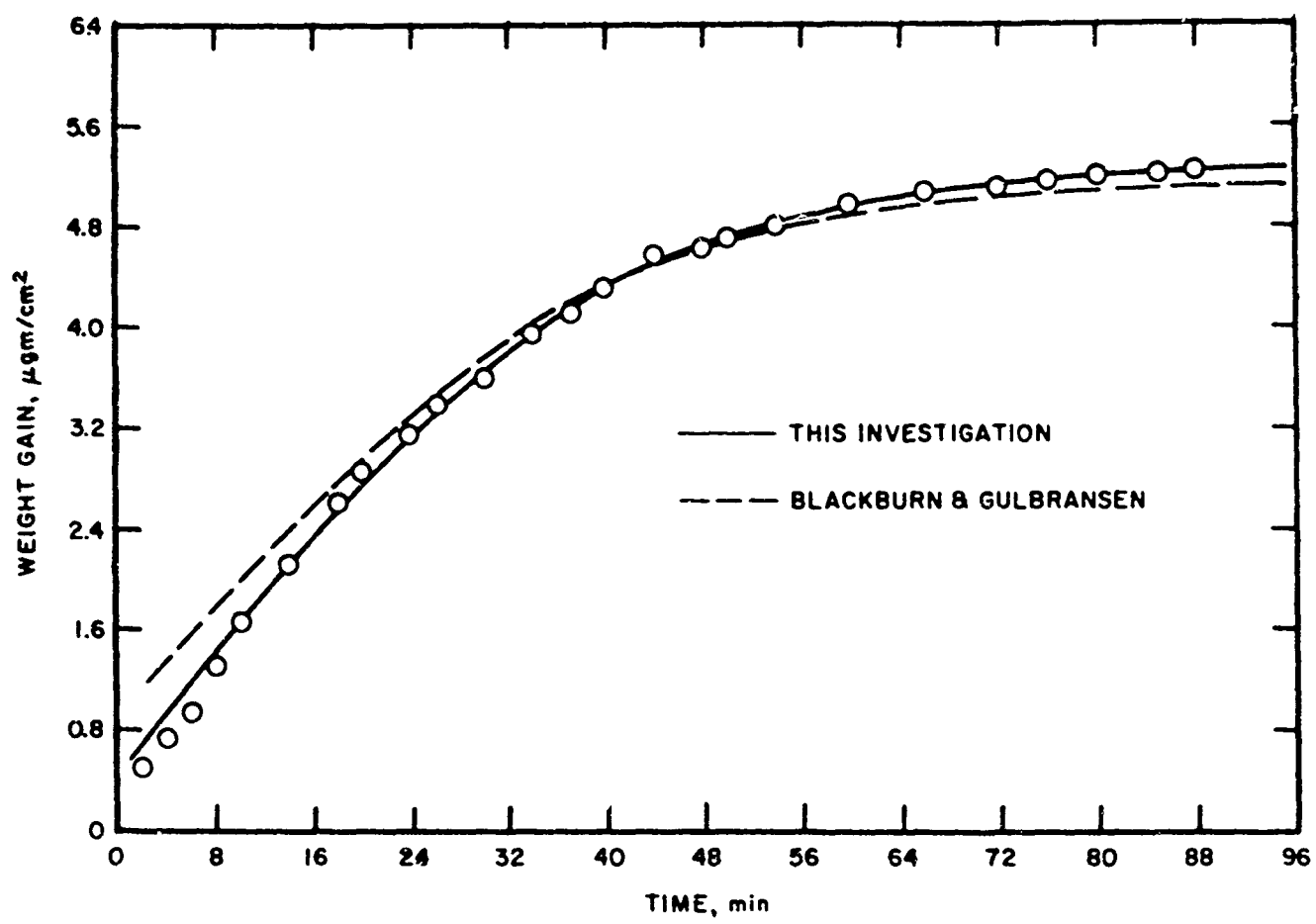


Fig. 2 Oxidation of Chemically Polished Aluminum Foil in 232 mm Dry Oxygen at 600°C

were below the melting point, corrugated aluminum foil having a surface area of 100 cm^2 was used. In the molten sample, the active surface is reduced to the cross-sectional area of the sample tube. This amounts to a 200-fold reduction in surface area. Accordingly, it was anticipated that (using the current apparatus with dry oxygen) there would be a zone of temperature above the aluminum's melting point where (because of the limited surface area of the molten aluminum) the amount of oxidation would be imperceptible, but which at higher temperatures, should be measurable. This appears to be the case. However, this zone is quite narrow, and therefore should not cause difficulty in interpreting the data.

IV. FUTURE PLANS

Plans for the immediate future are for obtaining more detailed information on the oxidation rates of molten aluminum in atmospheres of air, oxygen, and water vapor. Some information on the effect of temperature and pressure on oxidation rates will also be obtained. The oxidation of aluminum alloys will also be investigated since there is fairly strong evidence that, in certain aluminum alloys, oxidation is considerably faster and more complete than in pure aluminum (4). In addition, the construction of an apparatus for bubbling oxygen through molten aluminum (?) and measuring the rate of oxygen uptake is under consideration.

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