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SUBJECT: Determination of Oxygen in Oxide Films by Neutron Activation Analysis

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Abstract

Preliminary experiments have been conducted to evaluate the use of the nuclear reactions $Li^6(n,\alpha)H^3$ and $O^{16}(H^3,n)F^{18}$ to determine the thickness of oxide films on metals. Sheets of thin paper and of aluminum, imbedded in powdered LiF, were irradiated with pile neutrons at a flux of 6×10^{11} n/cm^2/sec and counted with an end-window proportional counter. A saturation activity of 1.87 hr F^{18} of 150 dis/min per microgram of oxygen was observed in the paper, but radioactivity due to impurities masked F^{18} in the aluminum. It is concluded that a 1 A (0.01 μgm/cm^2) oxide film thickness may be measured by a neutron irradiation at a flux of 10^{14} n/cm^2/sec but chemical separation of induced radioactivity from the bulk metal is essential.

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DISCLAIMER

Introduction

The possibility of determining the thickness of oxide films on metals by neutron activation analysis has been studied. It is of some interest in corrosion research to know the thickness of thin oxide films formed on electrodes during electrolytic oxidation. Existing methods of measurement, based on interference colors and on weight determined by a microbalance, are not sensitive to films much thinner than 100 A (~ 1 microgram/cm^2). On the basis of the experiment described below, sensitivity by neutron activation analysis may be great enough to measure oxide film thicknesses as small as 1 A (~ 0.01 microgram/cm^2).

Experimental

Osmond and Smales[1] and Leddicotte and Bate[2] have demonstrated that small amounts of oxygen may be determined by neutron activation by means of the nuclear reactions $Li^6(n,\alpha)H^3$ and $O^{16}(H^3,n)F^{18}$. Neutron capture by Li^6 produces energetic tritons which induce 1.87 hr F^{18} radioactivity proportional to the oxygen content of the sample.*

The following experiments were carried out to test the feasibility of inducing 1.87 hr F^{18} radioactivity by a triton reaction with oxide films on metals. The sample is imbedded in dry powdered lithium fluoride, and after neutron irradiation, the induced radioactivity is measured. The

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*The possibility has also been considered to determine oxygen by triton activation directly using the nuclear reaction $O^{16}(H^3,n)F^{18}$ and a van de Graaf generator. Although experimentally feasible, this activation analysis method was considered impractical because the machine could be contaminated by tritium and thus make it virtually impossible to carry out any other existing experimental projects at the same time. However, irradiations with other particles, e.g. deuterons or protons, are possible with an accelerator. In addition to measuring induced F^{18} radioactivity, the possibility of γ-ray counting during irradiation should be considered.

amount of induced radioactivity should vary directly with the oxide film thickness.

Four pieces of lens paper (1.4 mg/cm^2) and three pieces of aluminum sheet (61 mg/cm^2), each piece about 1 cm^2 in area, were imbedded in powdered anhydrous lithium fluoride and irradiated for two hours in the ORNL Graphite Reactor at a neutron flux of 6 x 10^{11} n/cm^2/sec. Decay curves of the β radioactivity were obtained with an end-window preportional flow counter during the period 2 to 9 hours after irradiation and γ spectra were obtained about 3.5 hours after irradiation by means of a γ scintillation spectrometer. Both the irradiated paper and the aluminum displayed prominent γ-ray peaks at 0.51 Mev and 1.38 Mev suggesting the presence of 15 hr Na^{24} in addition to 1.87 hr F^{18}. The 0.51 Mev peak was more prominent in the paper than the aluminum. Decay curves were resolved into an assumed 15 hr half-life component (Na^{24}) and a shorter lived component of half-life 1.7 to 1.9 hours for the paper and 2.0 to 2.5 hours for the aluminum. The shorter lived component in the paper is attributed to 1.87 hr F^{18} but in the aluminum it is attributed to impurities.* Figure 1 is the decay curve obtained for one of the irradiated paper samples.

From the observed counting rates of four paper samples, the radioactivities for a neutron irradiation to saturation (i.e. an irradiation for at least 10 half-lives of 1.87 hr F^{18}) are 35, 31, 31 and 32 counts

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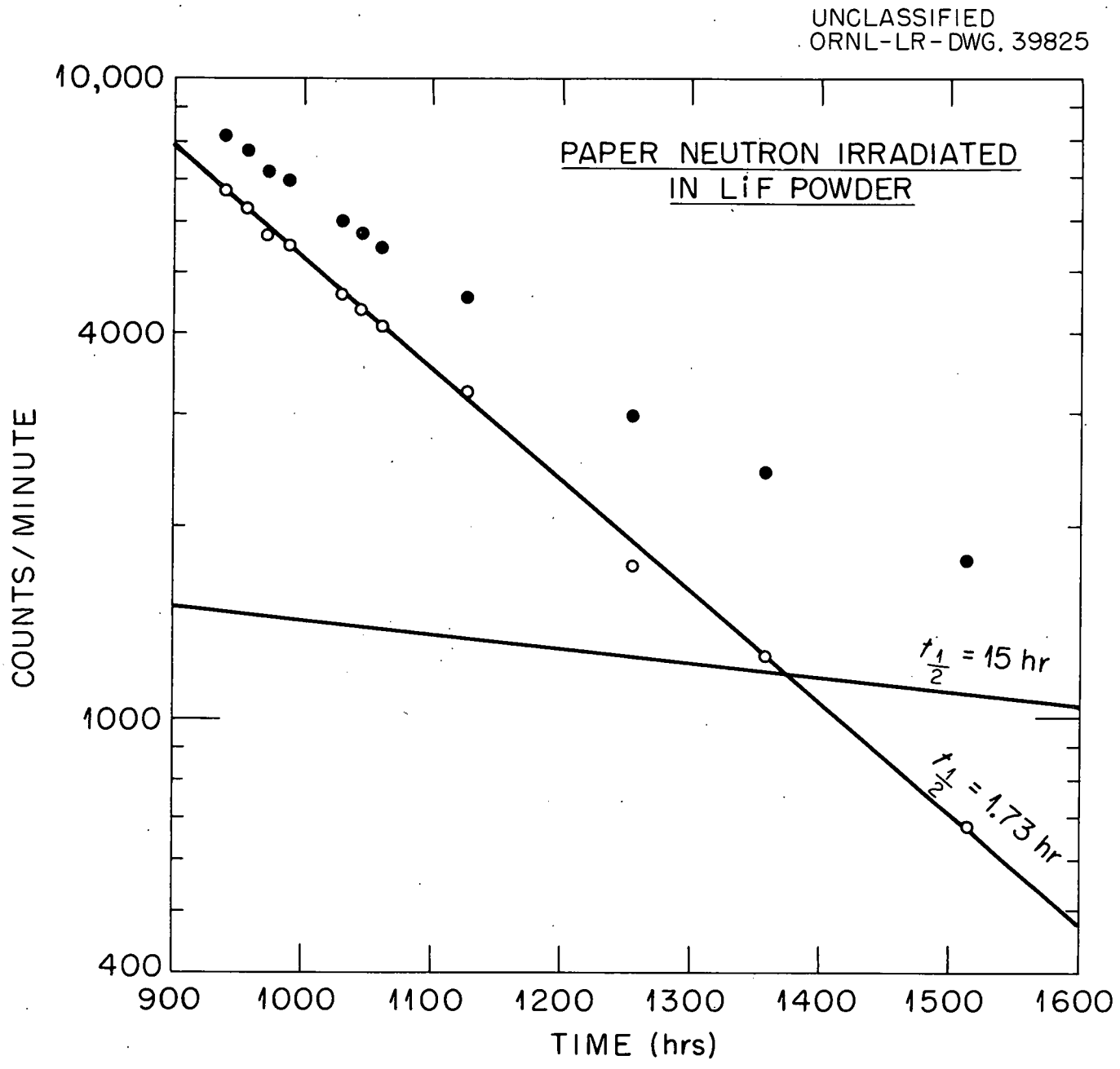
*10 ppm Mn in the aluminum would be sufficient to give rise to all the observed shorter lived radioactivity (as 2.58 h Mn^{56}).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PAPER NEUTRON IRRADIATED
IN LiF POWDER
10,000
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COUNTS/MINUTE
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1000
1100
1200
1300
1400
1500
1600
TIME (hrs)
$t_{\frac{1}{2}}$ = 15 hr
$t_{\frac{1}{2}}$ = 1.73 hr

FIGURE 1

per minute per microgram of oxygen in the paper* or approximately 150 disintegrations per minute per microgram of oxygen. The amount of radioactivity may be increased 2000-fold by irradiation in the intense neutron flux of the new Oak Ridge reactor (ORR), 1×10^{14} n/cm^2/sec, and by using LiF of enriched in Li^6. Radioactivity induced under these conditions, 3×10^5 dis/min per microgram of oxygen, permits detection of 0.001 microgram, i.e. the oxygen contained in a 1 cm^2 area 0.1 A thick. Measurements of oxide films of the order of 1 A to a precision of 10% should be feasible.**

Conclusions

If the neutron activation analysis method for oxide film thickness measurement is pursued further, we may say that, on the basis of these preliminary measurements, the theoretical sensitivity is great enough to measure oxygen in films as thin as 1 A, i.e. films of the order of one monolayer of oxide. However, experimental problems which must be considered in the application of the method to high sensitivity determinations include the following:

(1) Chemical separation of the radioactivity induced in the film must be made to separate it from large amounts of radioactivity induced in the bulk metal. It is most advisable to remove the oxide coating after

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*Assuming paper is cellulose, $(C_6H_{10}O_5)_x$, 49.8% oxygen by weight.

**These calculations are made assuming that neutron self-shielding by the LiF was negligible in these experiments and that all oxygen in the paper, interior as well as that on the surface, was equally subject to nuclear reaction with the tritons produced in the LiF. Since neither assumption is strictly valid, the ultimate sensitivity of the method will be somewhat better than that calculated.

irradiation without dissolving any of the bulk metal, although this is not mandatory. Fusion pyrolysis[3,4] may be used to remove fluoride from oxide. Also, liquid sodium may be a suitable solvent for some metal oxide films[5].

(2) Interference by impurities of oxygen either in the bulk metal or in the LiF may be considerable in determining the smallest amounts of oxygen and must be eliminated.

References

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