C in equation (3) would be $4{\cdot}07 \times 10^{-5}$ SI units[3]. Vacuum deposited polycrystalline anthracene films produced in this laboratory give results consistent with Schottky emission across grain boundaries, with $\Delta E = 1{\cdot}9$ eV.

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Effect of Reactor Irradiation on the Internal Surface Area of Corrosion Films on Zirconium Alloys

THE corrosion of zirconium alloys can, in certain circumstances, be enhanced by reactor radiation. The parameters controlling the enhancement are incompletely understood and work is in progress in several laboratories to elucidate possible mechanisms. At Harwell one approach has been to study the effect of reactor radiation on the surface area of corroding specimens. The preliminary results show interesting trends.

The surface areas studied were quite small (down to ~ 1 cm^2) and they were determined by the BET procedure[1] from the adsorption of Xe^{133} at 77° K using a technique based on that of Chenébault and Schürenkämper[2].

Two zirconium alloys have been studied, Zircaloy-2 and Zr 2·5 per cent Nb alloy. The specimens were tubes 0·61 cm diameter, 0·635 cm long and 0·05 cm thick, corroded at temperatures in the range 300°–480° C in corrodents which were basically steam or moist CO_2 10 per cent air mixture by volume[3]. In some instances long corrosion times were simulated by giving the specimens a pre-oxidation treatment for a short period at a higher temperature (450° C) followed by a long period at the lower temperature of interest (for example, 300° C) to eliminate any "memory" of the higher temperature treatment. The corrosion of specimens under radiation was carried out in the reactor DIDO ($\sim 3 \times 10^{13}$ neutrons cm^{-2} s^{-1} >1 MeV; 10^8–10^9 R h^{-1} γ) in equipment already described[3].

The results are summarized in Table 1, where the degree of corrosion of each specimen is expressed as the increase in weight for unit geometric area (1 dm^2) of the specimen. The surface area figures are given on the basis of specimens of the same geometric area. The experiments have incorporated a range of different corrodents, pre-treatments, corrosion temperatures and alloys, but despite this variation an important general conclusion is immediately apparent—that irradiation consistently increases the surface area. Thus the surface areas of specimens corroded in the absence of radiation are all below 4 dm^2 whereas after irradiation values range from 4·2 to 82.

In the absence of radiation the surface area increases rapidly from ~ 1 dm^2 for the unoxidized metal and remains approximately constant (that is, between 1·8 and 3·6 dm^2) for oxidized samples having weight increases ranging from 9 mg dm^{-2} up to 141 mg dm^{-2}. There seems to be no change in surface area associated with the major transition in the corrosion kinetics which typically occurs at ~ 30 mg dm^{-2} in this system. This is surprising, for the transition is commonly thought to represent a breakdown of the outer layers of the oxide, giving a layer of porous oxide which increases in thickness as corrosion proceeds further. The present results seem to imply that this interpretation is incorrect, at least for these corrodents.

The irradiated specimens show quite different behaviour. In general terms the surface area increases steadily as the corrosion progresses and in several cases the ratio of surface area to weight gain is approximately unity. It is interesting that high values of surface area were found even for specimens which had been pre-oxidized. Most of their corrosion had taken place in the absence of radiation and it appears that only a relatively short irradiation period is sufficient to increase the surface area dramatically (though in these cases the ratio of surface area to weight gain was rather less than unity).

Further work is in progress to clarify in detail the profound effects of radiation on the structure of the oxide film. Our preliminary observations are consistent with the suggestion[4] that the enhancement of corrosion observed in these systems results, at least in part, from irradiation embrittlement of the film, which leads to extensive breakdown and so to an increase in internal surface area.

Table 1

In absence of radiation					Under radiation				
Weight gain mg dm^{-2}	Surface area* dm^2	Pre-oxidation at 450° C	Corrosion conditions	Alloy	Weight gain mg dm^{-2}	Surface area* dm^2	Pre-oxidation at 450°	Corrosion conditions	Alloy
0	1·1	None	None	Zirc-2					
9	3·6	None	CO_2/H_2O/air 300° C; 66 days	Zirc-2	15	9·1	None	D_2O steam 340° C; 22 days	Zr2·5%Nb
16	2·7	None	D_2O steam 340° C; 22 days	Zirc-2	16	4·2	None	D_2O steam 340° C; 22 days	Zirc-2
60	3·1	None	H_2O steam 480° C; 6 days	Zirc-2	18	16	None	CO_2/H_2O/air 300° C; 66 days	Zr2·5%Nb
66	3·3	None	H_2O steam 350° C; 28 days	Zirc-2	28	21	None	CO_2/H_2O/air 300° C; 66 days	Zirc-2
90	2·3	For 6 days	H_2O steam 300° C; 62 days	Zirc-2	40	31	None	D_2O steam + O_2 340° C; 105 days	Zirc-2
92	3·3	For 6 days	H_2O steam 300° C; 62 days	Zirc-2	43	42	None	D_2O steam + O_2 340° C; 105 days	Zr2·5%Nb
141	1·8	For 6 days	H_2O steam 340° C; 35 days	Zirc-2	85	23	For 6 days	H_2O steam + O_2 300° C; 74 days	Zirc-2
					152	82	For 6 days	H_2O steam + O_2 300° C; 74 days	Zr2·5%Nb
					180	77	For 6 days	H_2O steam + O_2 300° C; 74 days	Zirc-2

* For specimens of 1 dm^2 geometric area.

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