The Role of Dissolved Oxygen in the Corrosion of Titanium and Zirconium by Liquid Sodium

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The corrosion of titanium and zirconium by liquid sodium containing dissolved oxygen has been shown to take place by the formation of non-adherent ternary oxides, in addition to the well known binary oxides, and oxygen solid solution in the metals. The compounds Na_4TiO_4 and Na_2ZrO_3 have been identified on the surface of titanium and zirconium after immersion in liquid sodium containing dissolved oxygen at temperatures close to 600 °C. The oxides were identified by their *X*-ray powder diffraction patterns which were recorded through a matrix of sodium. The lattice parameters of the underlying transition metal were measured enabling the approximate amount of oxygen in solid solution in the metal to be calculated. The characterisation of ternary oxide corrosion products, in addition to binary oxides and solid solutions of oxygen in the metal, enables a comprehensive mechanism of corrosion for titanium and zirconium in the presence of liquid sodium to be postulated.

THE behaviour of titanium and zirconium in high-purity flowing-liquid sodium circuits has been investigated when they have been used both as constituent parts of alloys, and as oxygen getters in hot traps. They have been included in alloys so as to react with oxygen absorbed from the sodium, producing protective oxide layers at the metal surface which effectively prevent further extensive corrosion of the alloys. When used in hot traps at temperatures near 600 °C titanium and zirconium reduce the amount of dissolved oxygen in flowing liquid sodium, thereby reducing the corrosion of constructional materials. Davis and Draycott,[1] examining the effectiveness of titanium and zirconium as oxygen getters, found that they differed in one important respect. Zirconium formed an adherent oxide layer of ZrO_2, whereas the oxide which formed on titanium was non-adherent, and a fresh surface was continually exposed in flowing liquid sodium. Bowman and Cubicciotti[2] claimed that zirconium absorbs oxygen forming a solid solution, being embrittled as a result. Miller[3] reported that in an oxidising atmosphere at temperatures in the region of 450 °C the protective film on zirconium dissolved in the metal and the factor inhibiting oxygen absorption was thus removed. Thorley and Bardsley,[4] however, have shown that a black adherent film of zirconium dioxide, ZrO_2, does form on zirconium and is unaffected by flowing sodium. They indicate that the weight gains measured in experiments on the corrosion of zirconium in sodium are essentially due to the formation and growth of this oxide. Zirconium has been investigated[5] in the temperature range 400—635 °C in a static liquid sodium system with an oxygen content of 10 p.p.m., and the process controlling corrosion was determined as the transfer of oxygen through the ZrO_2 layer and into the metal. The reactions of the titanium oxides in liquid sodium have shown[6] that the only oxide stable up to 600 °C is titanium monoxide, TiO; both titanium dioxide, TiO_2, and titanium sesquioxide, Ti_2O_3, react with liquid sodium at this temperature to produce ternary oxide products, amongst which the compound Na_4TiO_4 is prominent. In previous investigations no ternary oxide corrosion product has been observed on titanium and zirconium, but this is not surprising since samples were always washed with water or alcohol before further examination. The formation of the ternary oxides Na_2ZrO_3 and Na_2TiO_3 in liquid sodium, by reactions (1) and (2) at the metal surfaces, has been postulated[7] but not experimentally verified.

$$Na_2O + TiO_2 \longrightarrow Na_2TiO_3 \qquad (1)$$

$$Na_2O + ZrO_2 \longrightarrow Na_2ZrO_3 \qquad (2)$$

Methods of identification which involve treatment of the metal with alcoholic or aqueous solutions may decompose or remove any alkali-rich sodium titanate or zirconate corrosion products. Removal of sodium by vacuum distillation may also initiate reactions[8] between sodium oxide and the metal of the type (3) and (4). We

$$3Na_2O + M \longrightarrow Na_2MO_3 + 4Na \qquad (3)$$

$$4Na_2O + M \longrightarrow Na_4MO_4 + 4Na \qquad (4)$$

have therefore examined by *X*-ray diffraction the surfaces of titanium and zirconium metal plates which have been exposed to static sodium at different oxygen levels, and temperatures near 600 °C. The ternary oxides Na_4TiO_4 and Na_2ZrO_3 have been observed on the metal plates in the presence of adherent sodium, together with the binary oxides TiO and ZrO_2, and solid solutions of oxygen in the metals.

EXPERIMENTAL

The metal samples were in the form of metal plates (3 cm × 2 cm). The experimental procedure was similar to that described[9] for the metals niobium and tantalum, except that reaction times varied from two to seven days. The important aspect of this experimental procedure was that the *X*-ray diffraction analysis was carried out with sodium still present on the metal surface.

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Lattice Constant of Metal.—The positions of several diffraction peaks on each plate were measured accurately by use of a scan rate of $\frac{1}{8}$° 2θ per minute. The structures of titanium and zirconium being known to be hexagonal, and the *hkl* values of the diffraction peaks being measured, the lattice constants of the metal were measured for each plate which had been corroded in liquid sodium. The metal lattice constant values are quoted to a lower degree of accuracy than those of niobium and tantalum previously reported.[9] This was necessary since only low-angle *X*-ray diffraction peaks could be used for the measurement of lattice constant values owing both to preferred orientation effects, and to the diffuse character of the metal peaks caused by extensive oxygen solid solubility.

Oxygen Content of the Metal.—Oxygen forms a solid solution in titanium and zirconium causing an increase in the size of the metal lattice and a shift of the diffraction peaks to lower angles. The solid solubility of oxygen in α-titanium, and α-zirconium, shows only small changes with temperature, below 900 °C being *ca.* 30 atom % (12 weight %) and 28·5 atom % (6·5 weight %), respectively.[10] The change in lattice constants for titanium and zirconium has been related to oxygen solubility in the metal, and thus measurements of the positions of diffraction peaks, which give values for the lattice constants, indicate the concentration of oxygen in the metal lattice at the surface of the plate.

TABLE 1

Corrosion of titanium and zirconium in liquid sodium

Experiment no.	Metal	t/°C	Time days	Oxygen content of sodium p.p.m.	Corrosion product [a]	Metal lattice constants a/Å	c/Å	Oxygen content of metal/ %(w/w)
1	Ti	600	3	3400	A	2·96	4·75	6·0
2	Ti	600	8	12,000	A	2·96	4·75	6·0
3	Ti	600	14	100	A + B	2·96	4·72	3·2
4	Ti	600	14	1600	A + B	2·96	4·72	3·2
5	Ti	700	14	7000	A + B	2·96	4·72	3·2
Standard Ti plate						2·95	4·680	0
6	Zr	600	2	3000	C	3·24	5·15	0·5
7	Zr	600	14	2300	C + D	3·25	5·17	2·2
8	Zr	550	24	3000	C + E	3·25	5·16	1·1
Standard Zr plate						3·24	5·144	0

[a] A = Na_4TiO_4, B = TiO, C = ZrO_2, D = β-Na_2ZrO_3, E = α-Na_2ZrO_3.

The lattice spacings of the hexagonal Ti–O solid solution have been measured as a function of oxygen content by a number of investigators.[11–15] Clark [11] covers only a small range of oxygen content, and Bumps *et al.*,[12] Schofield and Bacon,[13] and Rostoker [14] report an almost linear relationship for increase in the '*c*' lattice constant, whilst the '*a*' lattice constant remains constant after a small initial increase. However, Andersson *et al.*[15] have shown that the *a* lattice constant goes through a maximum at $TiO_{0.35}$ and at this composition the *c* lattice constant begins to increase more rapidly with oxygen content. The results of Andersson *et al.* have been used to derive oxygen contents of the titanium–oxygen solid solution from experimental lattice constant measurements.

Domagala and McPherson [16] and Treco [17] have reported increases in the lattice constants of zirconium with oxygen content, but Treco's results are for very low oxygen contents only, and Domagala and McPherson give results which show abnormally high values for the lattice constants of pure zirconium metal. The results of a more comprehensive study by Holmberg and Dagerhamm,[18] which shows a maximum in the *a* lattice constant at the composition $ZrO_{0·25}$ and a marked change in the rate of increase of the *c* lattice constant at $ZrO_{0·33}$, have been used as the standard data to derive oxygen contents of the zirconium from experimental lattice constant measurements.

RESULTS AND DISCUSSION

The experimental data (Table 1) on the corrosion of titanium and zirconium in liquid sodium show that in all experiments with titanium metal the corrosion product Na_4TiO_4 was formed, and Na_2ZrO_3 was found on the surface of zirconium in two of the experiments. The ternary oxide corrosion products were non-adherent and could easily be scraped from the plates.

As with the corrosion experiments previously described [9] the figures quoted as oxygen content of the sodium refer to the actual oxygen level at the beginning of the experiment, and will reduce to a very low level as corrosion of the metal proceeds. The metal plates used in experiments 3, 4, and 7 were weighed before immersion in sodium, and after completion of the experiments when all ternary oxide corrosion products had been washed from their surfaces. The titanium plates used in experiments 3 and 4 exhibited small weight losses whilst the zirconium plate used in experiment 7 exhibited a small weight gain. This difference in weight-change behaviour indicates a basic difference in the corrosion mechanisms of titanium and zirconium in liquid sodium. The formation of ternary oxide corrosion products leads to weight losses whereas the absorption of oxygen into the metal lattice and the formation of binary oxides leads to weight

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gains. Although ternary oxide corrosion products were observed on the surfaces of both metals, the weight changes indicate that the formation of such a product is likely to be the primary corrosion mechanism only with titanium. With zirconium the formation of zirconium dioxide must predominate, and because of this difference in behaviour the two metals will be discussed separately.

Titanium.—Only one ternary oxide corrosion product, Na_4TiO_4, was formed at oxygen concentrations varying from 100 p.p.m. to 12,000 p.p.m., indicating its high stability in a liquid sodium environment. On water washing, the compound Na_4TiO_4 was removed from the surface of the metal. In experiments 1 and 2, only the diffuse *X*-ray diffraction pattern of titanium metal was observed, but in experiments 3, 4, and 5 extra peaks were visible which could be assigned to titanium monoxide. Table 1 shows that titanium monoxide was only formed in experiments having the longest reaction times. This suggests that the formation of Na_4TiO_4 was the initial reaction, followed by the absorption of oxygen into the metal lattice until the composition TiO was reached at the surface. The formation of titanium monoxide in experiments 3, 4, and 5 lowered the oxygen contents of the titanium–oxygen solid solutions significantly when compared with the values calculated for experiments 1 and 2.

In a supplementary experiment, the stability of Na_4TiO_4 in an environment of liquid sodium was investigated. A sample of Na_4TiO_4, prepared by reaction of sodium oxide and titanium dioxide,[8] was heated in liquid sodium, containing *ca.* 20 p.p.m. oxygen for 6 days at 600 °C; the excess of sodium was then distilled off at 300 °C under vacuum. The *X*-ray diffraction pattern of the product was identical to that of the original sample, indicating that Na_4TiO_4 can be considered stable to liquid sodium containing very low levels of oxygen at 600 °C.

Zirconium.—Two different phases of the ternary oxide corrosion product Na_2ZrO_3 were formed in experiments 7 and 8, owing to the temperatures of the reactions being above (experiment 7) and below (experiment 8) the phase transition temperature (α-Na_2ZrO_3 transforms into the β-form at 570 °C).[19]

It is evident with the three experiments performed with zirconium that the initial rapid formation of a zirconium dioxide layer is followed by a much slower reaction forming the ternary oxide Na_2ZrO_3. Experiment 6, with a reaction time of only 2 days, showed no formation of Na_2ZrO_3, although an adherent black layer of zirconium dioxide was present.

Washing the samples with water removed any trace of the compound Na_2ZrO_3, leaving a surface layer of zirconium dioxide above a zirconium–oxygen solid solution. The difference in the oxygen contents of the metal samples in experiments 7 and 8 may be attributed to the difference in reaction temperatures.

Although the maximum solubility values for oxygen are approximately the same, the oxygen contents of the zirconium–oxygen solid solutions are significantly less than those of the titanium–oxygen solid solutions in the experiments performed. This is probably due to the rapid formation of zirconium dioxide, forming a barrier to further oxygen solid solution. The controlling corrosion process for zirconium in sodium has been described[5] as the transfer of oxygen through the zirconium dioxide layer. Although this mechanism was postulated on the assumption that no other product was present on the zirconium surface, it certainly indicates that the process is slow.

Mechanisms of Corrosion.—Titanium. The first stage in the corrosion mechanism of titanium in liquid sodium is the solution of oxygen in the metal. Although it is thermodynamically possible for the oxides TiO, Ti_2O_3, and Ti_3O_5 to exist as films on the metal surface, studies[20-22] of the surface indicate that titanium dioxide is the only oxide present. Thus, at a temperature above 136 °C any surface oxide will react[23] with the liquid sodium so that the metal will not be protected by an oxide layer, and a titanium–oxygen solid solution will be formed. This process will continue, but the solid-state reaction of sodium oxide and titanium[8] indicates that above a temperature in the region of 340 °C the compound Na_4TiO_4 will be formed on the surface of the metal. The free energies of formation of the titanium oxides at 600 °C (Table 2)[24] show that titanium monoxide is, thermodynamically, the most stable. Thus the gradual absorption of oxygen into the titanium metal lattice should lead to the eventual formation of the monoxide, and this was observed in experiments 3, 4, and 5 where a surface layer of TiO was formed beneath the Na_4TiO_4 layer. Experiment 3 indicates that Na_4TiO_4 can readily be formed at low oxygen levels, and it is likely to be present on titanium metal exposed to flowing liquid sodium containing low concentrations of oxygen. It will be eroded by the flowing liquid metal leading to continual fresh attack of sodium oxide on the exposed titanium surface. Titanium exposed to low oxygen-content flowing liquid sodium will thus be corroded both by the formation of Na_4TiO_4 and its erosion, and embrittled by oxygen absorption up to the composition of the monoxide.

TABLE 2

Free energies of formation of the titanium oxides at 600 °C

Oxide	TiO	Ti_2O_3	Ti_3O_5	TiO_2
$-\Delta G_f°$(600 °C)/kcal g-atom O	103·9	101·4	98·7	93·9

Zirconium. The first stage in the corrosion mechanism of zirconium in liquid sodium appears to be the solution of oxygen in the metal and the formation of

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zirconium dioxide. The corrosion rate would then depend on the diffusion rate of oxygen through the zirconium dioxide layer. Experiment 6 confirms the fact that this is the initial corrosion mechanism since no ternary oxide was observed, although a zirconium dioxide surface layer was present. This behaviour differs from that of titanium owing to the increased free energy of formation of zirconium dioxide at 600 °C [$-G_f^\circ$ (600 °C) = 110·8 kcal/g-atom O)[24] relative to the titanium oxides. Zirconium dioxide is stable to pure liquid sodium at 600 °C. Once a zirconium dioxide layer has been formed a much slower reaction then proceeds in the presence of sodium containing sodium oxide to give the ternary oxide corrosion product Na_2ZrO_3. For the reaction (5)

$$Na_2O + ZrO_2 \longrightarrow Na_2ZrO_3 \qquad (5)$$

to be favourable at 600 °C, the free energy of formation of Na_2ZrO_3 must be at least 292 kcal mol^{-1}. In flowing liquid sodium circuits containing low concentrations of oxygen any Na_2ZrO_3 layer would be eroded, but its formation is a slow process and the dominating reaction would still be the formation of zirconium dioxide and further diffusion of oxygen into the zirconium metal lattice leading to weight gains.

Klueh[25] has studied the feasibility of determining oxygen in liquid alkali metals by zirconium gettering. He exposed zirconium samples to liquid sodium containing between 500 and 2100 p.p.m. oxygen at 815 °C, and the oxygen content of the zirconium after the tests was determined by vacuum fusion analysis. The initial oxygen content of the sodium, and the amount absorbed by the zirconium, being known, the percentage of oxygen recovered could be calculated. He found that the oxygen recovered for initial concentrations of less than 1000 p.p.m. was greater than 90%, but at higher concentrations the amount recovered decreased significantly. These decreases, leading to apparent losses in gettering efficiency of zirconium for oxygen, were attributed to possible losses of zirconium dioxide surface scale when the specimens were prepared for vacuum-fusion analysis. However, zirconium dioxide is generally thought to form as an adherent surface layer,[1,4] and a possible alternative explanation for the loss of oxygen recovered at high initial oxygen concentrations in the liquid sodium could be that an Na_2ZrO_3 layer is formed on the zirconium dioxide. The Na_2ZrO_3 layer would be less adherent and may be lost in the liquid-metal environment, or on washing the zirconium samples, leading to losses in the percentage of oxygen recovered.

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