The Role of Dissolved Oxygen in the Corrosion of Niobium and Tantalum by Liquid Sodium

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The corrosion of niobium and tantalum in liquid sodium is strongly influenced by the quantity of dissolved oxygen in the liquid metal. The oxides Na_3TaO_4 and Na_3NbO_4 have been identified on the surface of tantalum and niobium after immersion in liquid sodium containing dissolved oxygen at temperatures in excess of 300°. The oxides were identified by their *X*-ray powder diffraction patterns which were recorded through a matrix of sodium. Measurement of the lattice constant of the underlying transition element enabled the extent of oxygen solid solution to be calculated. The formation of an oxide, together with oxygen in solid solution, enables a mechanism of corrosion for niobium and tantalum in the presence of liquid sodium to be established.

THE use of liquid sodium as a reactor-coolant has led to a need for more detailed information on factors which are responsible for the corrosion of the structural components. Compatibility tests [1-5] have shown that the corrosion of metals in liquid sodium is dependent upon the temperature, the oxygen content, and the flow-rate of the liquid metal. The effect of some of these variables on the rate of corrosion of niobium in liquid sodium is shown in Table 1. The rate of corrosion is expressed in terms of a weight loss, but this does not necessarily imply that the corrosion product is removed from the surface by the liquid metal. Niobium is wetted by liquid sodium above 150°, and the adherent sodium is removed by washing with alcohol or water. The corrosion product may also be removed during the cleaning process, giving rise to apparent weight losses.

The rate of corrosion is clearly increased by a rise in the oxygen level of the sodium; the solubility of oxygen in liquid sodium [6,7] rises rapidly between 400 and 600 °C. Increases in temperature and velocity of the liquid metal also enhance the corrosion rate. These effects suggest that the corrosion of niobium by liquid sodium involves the formation of either a surface oxide of niobium, or a ternary oxide of sodium and niobium.

The corrosion of tantalum resembles that of niobium. A preliminary study [5] on the nature of the corrosion product of tantalum in sodium has indicated the formation of a mixed oxide Na_3TaO_4. Compounds of the type A_3MO_4 are known to be stable in liquid sodium [8,9] and liquid potassium,[10] and the compound K_3TaO_4 has

TABLE 1

Weight loss data for the corrosion of niobium and tantalum in liquid sodium

Niobium[1] Velocity of sodium = 760 cm. sec^{-1}

Temperature (°C)	Oxygen level (p.p.m.)	Wt loss (mg/cm^2/month)
500	5	15
	10	30
	15	50
550	5	25
	10	55
	15	85
600	5	190
	10	385
	15	575

Tantalum[4] Velocity of sodium = 6 cm. sec^{-1}

Temperature (°C)	Oxygen level (p.p.m.)	Wt loss (mg/cm^2/month)
500	10	0·7
	40	1·8
550	10	0·9
	40	3·8
600	10	1·4
	40	9·3

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[10] C. C. Addison, M. G. Barker, and R. M. Lintonbon, *J. Chem. Soc.* (*A*), 1970, 1465.

been identified[11] as the corrosion product formed when tantalum metal containing interstitial oxygen is placed in liquid potassium.

Until now, there has been no absolute identification of the corrosion product as it is formed on the surface of the metal and in the presence of sodium. Methods of identification which involve treatment of the metal with alcoholic or aqueous solutions will undoubtedly decompose or remove any alkali-rich niobate or tantalate corrosion products. Removal of the liquid metal by vacuum distillation may also initiate reactions between sodium oxide and the metal of the type

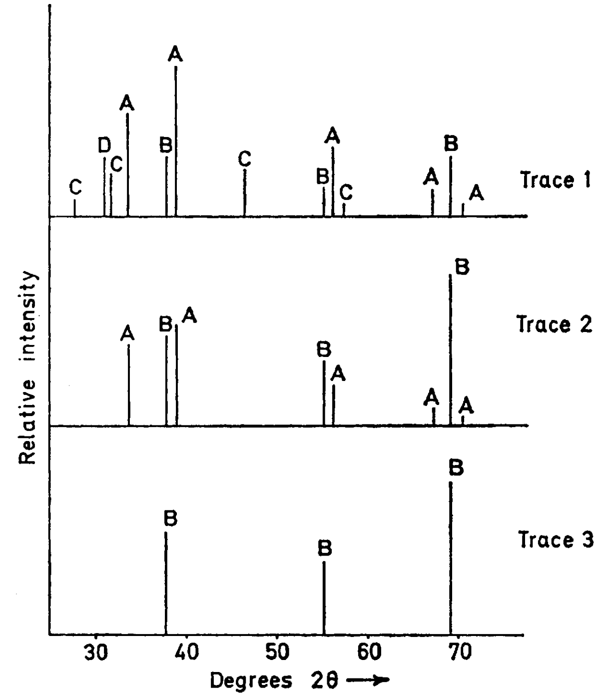
$$4Na_2O + M \longrightarrow Na_3MO_4 + 5Na$$

We have, therefore, examined by X-ray diffraction the surfaces of niobium and tantalum metal plates which have been exposed to static sodium at different temperatures and oxygen levels. The existence of ternary oxides in the presence of adherent sodium has been confirmed, and the corrosion products identified as Na_3NbO_4 and Na_3TaO_4.

EXPERIMENTAL

The metal samples, in the form of thin wires (1 mm diameter) or plates (3 cm × 2 cm) were placed in liquid sodium contained in nickel crucibles. The liquid sodium, obtained directly from a circulating loop,[8] contains only about 20 p.p.m. oxygen and it was therefore necessary to add solid sodium oxide to raise the oxygen content of the sodium to the desired level. The nickel crucibles were sealed in a stainless steel vessel and heated at the required temperature for periods of between one and seven days. The crucibles were then removed from the steel vessel in an argon-filled dry-box, and the metal samples withdrawn from the molten sodium. At the temperature used, all the samples were wetted by liquid sodium, so that on removal of the samples from the liquid metal an adherent layer of sodium covered the immersed portion. It was an important aspect of the experimental procedure that the X-ray diffraction analysis be carried out with this sodium still present on the surface, and protection of the sodium from atmospheric attack was therefore essential. Wire samples were covered with a polystyrene film while still in the dry-box; this gave sufficient protection during the time taken to mount the sample in an X-ray powder camera and to take an X-ray diffraction photograph. Only one photograph of the corrosion product could be taken on any one specimen, as removal of the polymer film disrupted the sample.

The surface of metal plates could, however, be examined in a powder X-ray diffractometer without the need for a protective coating. The sample chamber of the diffractometer (Philips vertical goniometer PW 1050/25 using Cu-K_α radiation) was modified so that a thin Mylar window replaced the open area through which the incident and diffracted X-ray beam travelled. An air-tight cover allowed access to the sample and enabled dry nitrogen gas (purified by passing through molecular sieve immersed in liquid nitrogen) to be flushed over the sample whilst the diffraction pattern was recorded. Successive X-ray diffraction patterns of the surface were obtained by scraping sodium from the metal plate between recordings. When no further sodium could be removed by scraping, the sample was washed with water and the lattice parameter of the metal determined. The results of the X-ray analysis were a series of X-ray diffractometer traces showing how the surface layers varied on moving closer to the metal surface (Figure).



Line representations of the X-ray diffraction patterns from a tantalum metal plate after exposure to liquid sodium containing dissolved oxygen: Trace 1, as removed from the liquid sodium; Trace 2, after removal of the adherent sodium; Trace 3, after washing with water. The diffraction lines are designated A, the cubic form of the compound Na_3TaO_4; B, tantalum metal; C, sodium oxide; D, sodium metal

Lattice Constant of Metal.—The position of one high angle diffraction peak on each plate was measured accurately using a fixed time counting technique to give an estimated accuracy of $\pm 0{\cdot}005^\circ(2\theta)$. Knowing the structure of niobium and tantalum to be body centred cubic, and the *hkl* values of the particular diffraction peak being measured, the lattice constant of the metal was measured for each plate which had been corroded by liquid sodium. The use of these high angle diffraction peaks leads to high precision in lattice parameter determination, and the application of extrapolation methods is not necessary.[13]

Oxygen Content of the Metal.—Oxygen forms a solid solution in niobium and tantalum, which causes an increase in the size of the metal lattice and a shift of the diffraction peaks to lower angles. The change in lattice constants of niobium and tantalum has been related to oxygen solubility in the metal, and thus a measurement of the position of a high angle diffraction peak, which gives a value for the lattice constant, indicates the concentration of oxygen in the metal lattice at the surface of the plate.

The lattice spacings of the niobium–oxygen solid solution

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have been examined by Taylor and Doyle,[14] and these results have been used to calculate oxygen contents in preference to the results of Gebhardt and Rothenbacher,[15] and Seybolt.[16]

The lattice spacings of the tantalum–oxygen solid solution have been examined by Vaughan *et al.*,[17] Kofstad,[18] Anuchkin *et al.*,[19] and Gebhardt and Seghezzi.[20] The results of these workers are in close agreement with one another, but differ appreciably from those of Wasilewski.[21] In the present investigation the results of Vaughan *et al.* have been used to calculate oxygen contents of the tantalum–oxygen solid solutions.

RESULTS AND DISCUSSION

The data collected in Table 2 show that, at temperatures above 300 °C, niobium forms the corrosion product Na_3NbO_4, and that tantalum forms the corresponding tantalate Na_3TaO_4.

TABLE 2

The corrosion of niobium and tantalum in liquid sodium

Experiment number	Metal	Temperature (°C)	Time (days)	Oxygen content of sodium (p.p.m.)	Corrosion Product	Metal lattice constant (Å)	Oxygen content of metal (wt %)
1	Nb	600	2	3100	C	3·3058	0·32
2	Nb	600	2	10,600	C + D	3·3079	0·40
3	Nb	450	7	900	C	3·3112	0·57
4	Nb	300	7	400	—	3·3051	0·29
Standard Nb plate						3·3001	0·01
5	Ta	600	2	2600	A	3·3137	0·21
6	Ta	600	2	20	A	3·3120	0·18
7	Ta	600	2	10,400	A + B	3·3069	0·08
8	Ta	500	3	800	A	3·3087	0·12
9	Ta	450	7	800	A	3·3119	0·18
10	Ta	300	7	200	—	3·3122	0·18
Standard Ta plate						3·3037	0·02

A = cubic Na_3TaO_4
B = orthorhombic Na_3TaO_4
C = cubic Na_3NbO_4
D = orthorhombic Na_3NbO_4

The figures quoted as the oxygen content of the sodium refer to the actual oxygen level at the start of the experiment. As the experiment continues oxygen is removed from the sodium in the formation of the corrosion product. In most instances the oxygen content of the sodium at the end of the experiment was less than saturation at 100°, *i.e.* less than 10 p.p.m.

Effect of Temperature.—No corrosion product was found on the metal surface at temperatures less than 300°. This confirms a previous observation [22] that corrosion rates of niobium were negligible at 200° and 300°. However, a significant increase was observed at 350°. The corrosion rate of tantalum in oxygen saturated sodium was also found [5] to be negligible at 300° but showed a large increase in rate at 390°. The partial wetting temperatures of niobium and tantalum with liquid sodium are 150° and 160° respectively,[23] so that the increase in corrosion rate cannot be attributed to the onset of surface wetting. The temperatures of reaction of Nb_2O_5 and Ta_2O_5 with liquid sodium are 230° and 330° respectively,[8] thus the reduction of any protective film of oxide should also have taken place before corrosion is seen to commence. Corrosion might therefore be considered to be a process which involves the clean metal surface and liquid sodium containing oxygen.

Oxygen Level of the Sodium.—In all but one experiment the initial oxygen levels were at a very high value so that extensive formation of the corrosion product took place. This was, in part, necessary for the detection of the *X*-ray powder diffraction pattern of the corrosion product. Samples exposed to liquid sodium having an oxygen content approximately equal to the saturation value at that temperature all developed films of the same ternary oxide A_3MO_4 (M = Nb or Ta) at all temperatures above 300 °C. The corrosion rate undoubtedly increased with temperature and oxygen content as can be seen from the exposure time necessary to obtain a diffraction pattern.

In experiments 2 and 7, where the oxygen content was some four times greater than the saturation level, a second phase [24] of the ternary oxide A_3MO_4 (M = Nb or Ta) was formed. The significance of this change in phase type will be discussed later in the paper.

Experiment 6 was carried out using liquid sodium containing 20 p.p.m. oxygen initially. The tantalum specimen used was the sample from experiment 5 from which the corrosion product had been removed by water washing. The layer of Na_3TaO_4 which would be formed on a fresh tantalum sample in sodium containing as little as 20 p.p.m. of oxygen would normally be so thin that detection would be difficult. However, by the use of a specimen already containing oxygen in solid solution, the limited quantity of oxygen in the sodium is not depleted by the formation of a solid solution, but is available to give the corrosion product Na_3TaO_4. This

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[24] M. G. Barker and D. J. Wood, preceding paper.

product is thus formed in greater quantity than would have been the case with a fresh metal specimen, and is readily identified.

The Nature of the Corrosion Product.—The corrosion products of niobium and tantalum in liquid sodium have been identified as the tetraoxoniobate(v) Na_3NbO_4 and tetraoxotantalate(v) Na_3TaO_4. Cubic, orthorhombic, and monoclinic forms of the compound A_3MO_4 (M = Nb, Ta) have been identified.[24] The phase formed in all the corrosion experiments was the cubic phase with cell constants $a = 4{\cdot}606$ Å and $a = 4{\cdot}616$ Å for Na_3NbO_4 and Na_3TaO_4 respectively.

The two samples exposed to sodium containing a large excess of oxygen (experiments 2 and 7) developed films of the cubic and orthorhombic forms, with the latter as the minor constituent. The pentoxides of niobium and tantalum react with liquid sodium to give a mixture of the transition metal and the oxides Na_3NbO_4 and Na_3TaO_4 in the cubic modification.[25] The obvious conclusion to be drawn is that the tetraoxoniobate and tetraoxotantalate must be the most energetically stable compounds in the Na–Nb–O and Na–Ta–O systems, and that of the three forms of this compound the cubic phase is the most stable.

Samples of niobium exposed for long periods to flowing liquid sodium containing between 10 and 40 p.p.m. oxygen at temperatures between 450 °C and 600 °C were found [2,3] to form a corrosion product which had the sodium chloride structure with a cell constant of approximately 4·6 Å. When this work was published the identity of the compound was unknown, but it is now clear that the corrosion product of niobium in liquid sodium containing very low oxygen levels is the same cubic phase of Na_3NbO_4 as is formed at much higher oxygen levels.

Severe embrittlement of the transition metal was apparent with all the samples exposed to sodium, presumably due to the formation of a metal–oxygen solid solution beneath the mixed oxide phase. In order to quantify this effect each sample was washed with water; during washing the corrosion product could be seen to float away from the surface before dissolving in the solution, and subsequent *X*-ray examination of the plate showed only the diffraction peaks of the metal. The oxygen content of the metal was determined by accurate measurement of the position of a high angle diffraction peak. All the samples showed an appreciable gain in oxygen content after exposure to sodium, of particular significance being the values for the samples exposed to sodium at 300° for which no ternary oxide corrosion product was observed (Table 2).

Mechanism of Corrosion.—The first stage in the corrosion mechanism must be the solution of oxygen in the metal. At temperatures above 300° the transition metal cannot be protected by an oxide layer since the oxides react with liquid sodium below this temperature, and the solid metal surface will therefore take up oxygen from the sodium with the formation of a metal–oxygen solid solution. Oxygen will continue to transfer from the sodium to the solid metal until saturation is reached and should then proceed by formation of the binary oxides. The extent to which this process may proceed can be derived from a consideration of the standard free energies of formation of the niobium oxides and of oxygen dissolved in sodium as a function of temperature. The relevant isopleths indicate that niobium pentoxide may be formed in sodium containing more than 100 p.p.m. oxygen, niobium dioxide in sodium containing more than 30 or 40 p.p.m. oxygen, and niobium monoxide in sodium containing 5 p.p.m. oxygen. No thermodynamic data exist for the compounds Na_3NbO_4 and Na_3TaO_4, but the absence of the monoxide as a corrosion product indicates that these compounds are more stable than the respective monoxide. Oxygen solution will not therefore proceed up to the composition of a binary oxide (or indeed a sub-oxide, since none of the known sub-oxides of niobium or tantalum were observed) but at some value above 0·57 wt% of oxygen in the metal, formation of Na_3NbO_4 will take place instead. Formation of Na_3TaO_4 must likewise commence when the oxygen content of the metal is above 0·21 wt% oxygen at 600°. Although the heats of formation of Na_3TaO_4 and Na_3NbO_4 are not known, the heats of formation of compounds containing the $MO_4{}^{n-}$ formula are all of a high value. The reaction

$$15Na + 4Nb_2O_5 \longrightarrow 3Nb + 5Na_3NbO_4$$

indicates that the free energy of formation at 600° of Na_3NbO_4 and Na_3TaO_4 must be at least 300 and 320 kcal mol^{-1}, respectively. It has already been reported [24] that the reactions of sodium oxide with tantalum metal, and Ta_2O_5, are exothermic when the compound Na_3TaO_4 is formed.

The corrosion of niobium in liquid sodium has been explained [26] on the basis of a solution mechanism in which a ternary liquid solution is proposed to exist at equilibrium, the oxygen level increasing the solubility of niobium in liquid sodium. The mechanism relied upon an interpretation of the Phase Rule based upon the absence of oxygen in solid solution in the niobium after exposure to sodium. A surface product which was observed could not be characterised by *X*-ray techniques, and it was concluded that the surface product formed during the rapid cooling of the test sample. Since the majority of workers report an increase in oxygen content for niobium and tantalum on exposure to liquid sodium, the solution theory seems less satisfactory than the ternary oxide theory outlined above.

The authors thank the S.R.C. for a Maintenance Grant (to D. J. W.).

[1/1248 *Received, July 22nd,* 1971]

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