An estimate of the diffusion parameters of oxygen and silicon in β-cobalt from studies of internal oxidation

A study of the internal oxidation of dilute alloys can provide diffusion data on oxygen that can be applied to pure metals because the oxidation process is interpreted as being diffusion controlled [1]. The precipitated oxide serves as a marker and, at sufficiently small concentrations of the solute, the effect of the oxide dispersion on the diffusion of oxygen is assumed to be negligible. Determinations of oxygen diffusion constants have been made from internal oxidation experiments on silver [2], nickel [3-5] and iron [3, 6, 7] alloys and other alloys containing a relatively inert solvent. The purpose here is to present values of the diffusion constants of oxygen in fcc β-cobalt for the temperature range 1000 to 1300°C.

Under certain conditions of internal oxidation, more concentrated silicon-bearing alloys can exhibit a filamentary form of the oxide dispersion [8]. Approximate values of the diffusion constants of silicon in cobalt have been calculated using a theory relating the depth at which filamentary growth commences with the diffusion coefficient of the solute.

The phenomenon of internal oxidation is fairly well understood [1, 10]. Rhines *et al* [11] and others, e.g. [10], have obtained equations describing the rate of internal oxidation in terms of material parameters. If the concentrations of free oxygen and solute in the alloy are assumed zero at the oxidation front, i.e. at a plane reaction front at a depth X from the free surface of the alloy, Rhines *et al* obtain:

$$D_g \simeq \frac{X^2}{t}\left[\frac{C_s G}{2C_g S} + 0.16\right] - 0.84\,\frac{C_s D_s G}{C_g S} \qquad (1)$$

D_g and D_s are the diffusion coefficients of oxygen and solute, C_g is the oxygen concentration at the free surface at the solubility limit, C_s is the original concentration of solute and G/S is the weight ratio of oxygen to solute in the oxide precipitated. Theoretical treatments leading to equations of the form of Equation 1 relating the rate of oxidation X^2/t to D_g are usually effected under the assumption that $D_g \gg D_s$; this is generally the case in "normal" internal oxidation.

The rate of internal oxidation X^2/t can be considered as the "diffusion coefficient" of the oxidation front, D_f, such that an Arrhenius-type equation

$$\frac{X^2}{t} = D_f = D_{fo} \exp\left(\frac{-Q_f}{RT}\right) \qquad (2)$$

governs the oxidation. Measurement of X^2/t at various temperatures T enables D_f to be calculated over a range of temperatures, and substitution into equations such as Equation 1 gives D_g at various temperatures and hence the pre-exponental term D_{go} and the activation energy Q_g for an equation of the form of Equation 2.

Nolan and Grundy [9] have shown that if filamentary growths of silica commence at a depth X_F and if the growth direction is normal to the oxidation front then X_F is related to D_s as

$$X_F = \frac{X^2}{t}\left[\frac{S\rho}{2VC_s D_s M}\right]. \qquad (3)$$

X^2/t relates to the oxidation front, which can be expressed as Equation 2, ρ is the radius of curvature of the filament tip and S/M is the ratio of silicon to matrix atomic weights. Measurement of X_F and ρ and a knowledge of D_{fo} and Q_f enables D_s to be estimated.

Two alloys of composition Co-0.08 and Co-0.55 wt% Si were prepared from Johnson Matthey Ltd, spectroscopically pure materials by melting and homogenizing under argon. The specimens were prepared for oxidation and measurement as in [3] except here the Rhines pack [11] consisted of a mixture of Co_3O_4-Co_2O_3 and Co powders and X and X_F were measured by scanning electron microscopy to an accuracy better than 5 μm. The oxidation temperatures were accurate to 5°C. Values of X and, where appropriate, X_F were obtained for oxidation at several temperatures between 1050 and 1300°C for periods between 0.5 and 50 h. Graphs of $\ln(X^2/t)$ against $1/T$ were drawn and values of D_{fo} and Q_f obtained from an equation of the best fitting line obtained by the method of least squares. Values of X^2/t calculated for the temperatures shown in Table I were substituted into Equation 1 and values of D_g obtained. The temperature dependent values of C_g used were those obtained by Seybolt and Mathewson [12]. A plot of $\ln D_g$ against the $1/T$ values gave D_{go} and Q_g. The results for D_g, and D_{go} and Q_g are given in Table I.

In the calculation of D_g from Equation 1 the negative term in D_s was neglected because of a

TABLE I Diffusion constants for oxygen in cobalt calculated from measurements on (a) Co-0.08 wt % Si alloy and (b) Co-0.55 wt % Si alloys.

	Temp. (°C)	$D_g$cm²/sec	D_{go}cm²/sec	$Q_g$kcal/g atom
(a) Co-0.08				
wt % Si	1050	2.42×10^{-8}		
	1100	5.20×10^{-8}		
	1150	1.10×10^{-7}		
	1200	2.08×10^{-7}		
	1250	4.21×10^{-7}		
	1300	7.73×10^{-7}	67.8 ± 1.3	57.6 ± 0.1
(b) Co-0.55				
wt % Si	1050	2.09×10^{-8}		
	1100	4.20×10^{-8}		
	1150	9.83×10^{-8}		
	1200	1.58×10^{-7}		
	1250	2.88×10^{-7}		
	1300	5.05×10^{-7}	10.0 ± 1.5	52.8 ± 0.2

TABLE II Diffusion constants for silicon in cobalt calculated from measurements on a Co-0.55 wt % Si alloy

Temp. (°C)	$D_s$cm²/sec	D_{so}cm²/sec	$Q_s$kcal/g atom
1050	5.5×10^{-11}		
1100	1.1×10^{-11}		
1150	2.4×10^{-10}		
1200	3.8×10^{-10}		
1250	6.8×10^{-10}		
1300	1.2×10^{-9}	3.4×10^{-2}	53.2

lack of knowledge of the diffusion coefficient of silicon in cobalt. This approximation introduces little error in D_g as, by comparison with the case of Ni-Si alloys [3] and by substitution of typical values, we should expect $X^2/tD_S \sim 10^2$ and an error of the order of 1 % in D_g. This assumption is corroborated by calculation of D_S from Equation 3 using D_{fo} and Q_f as 9.2 cm²/sec and Q_f as 31 kcals/g-atom. The values of D_S given in Table II, along with values of D_{go} and Q_S, show that X^2/tD_S is of the order of 5×10^2 at any given temperature. There is, to the authors' knowledge, scant information on D_S for silicon in cobalt in the literature. The values calculated here are reasonable in that they compare with those for silicon in nickel as determined by Swalin *et al* [13]. However, they are at the best approximate and have a minimum error of the order 10%, but in the absence of other data they are of value.

The results for D_g suggest that the presence of a coarse internal oxide product in the more concentrated alloy, i.e. long and fairly close packed filaments, provides a barrier to the diffusion of oxygen. It is suggested, therefore, that the results for the more dilute alloy should be given more weight and it can be expected that an alloy as dilute as 0.08 wt % Si in Co should apply fairly well to the pure metal. A similar conclusion was made in [3] and [5] for the diffusion of oxygen in Ni-Si and Ni-Be alloys where results for alloys with solute concentrations $\gtrsim$ 0.1 at.% are typical of the pure metal. The fact that the values of D_g are smaller for cobalt than for nickel is consistent with the slower rates of internal oxidation in cobalt.

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