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Does hydrogen affect oxygen permeability in alloys?

V. Shemet*, M. Hänsel

Forschungszentrum Juelich GmbH, Institute of Energy and Climate Research (IEK-2), 52425 Juelich, Germany

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ABSTRACT

Water vapour and/or steam are well known to accelerate breakaway oxidation of chromia-forming alloys. Some authors have proposed that hydrogen promotes internal oxidation of chromium, resulting in breakaway oxidation. We tested this hypothesis by directly measuring oxygen permeability after oxidation in high p_{O_2} atmospheres containing water vapour. Palladium with 1 wt% chromium alloy was oxidized in dry and wet Ar-1%O_2 at 850 °C. The internal oxidation in all cases obeyed parabolic kinetics. The oxygen permeability deduced from Wagner's diffusion model showed small differences in the internal oxidation of the Pd-1Cr alloy in these gases. We conclude that hydrogen has no influence on oxygen permeability in chromium-containing alloys.

1. Introduction

It is well known that the presence of water vapour in high and low p_{O_2} atmospheres at medium and/or high temperatures alters the oxide scaling of chromia forming alloys [1–5]. Under specific circumstances, an accelerated degradation of high temperature alloys is therefore likely to occur [6]. A comprehensive description of the problem of scale deterioration by water vapour can be found in [7].

The change in the chromia scale growth rate in water-containing atmospheres is linked with many factors: e.g. modification of the Cr_2O_3 lattice point defect structure [8–10], which may accelerate the diffusion of chromium through chromia scale [9,10]. The presence of water vapour is also thought to promote oxygen transport within pores inside the oxide scale [2,11]. Other authors have additionally proposed that hydrogen stemming from the water vapour contained in the gas alter the solubility and diffusivity of oxygen in the alloy's substrate, thereby promoting the consumption of a chromium reservoir by internal oxidation, which consequently leads to an earlier onset of breakaway [12,13]. If the later assumption is correct, then the oxygen permeability of the alloy should increase with increasing hydrogen in the alloy substrate.

To determine the oxygen permeability in alloys, i.e. the product of the solubility and diffusivity, we oxidized specimens of the metal in question which were slightly diluted with chromium and measured the depth of the internal oxidation zone (IOZ) [14]. To avoid the formation of external oxide scale on the base metal, the p_{O_2} must be kept lower than the dissociation pressure of the oxide. For this reason, such experiments are usually performed at low p_{O_2} [14]. To be able to measure the effect of H_2O under high p_{O_2} gases, a base metal is required that does not form an external oxide scale under high p_{O_2} conditions. Selecting a model alloy from the palladium–chromium system, we proceeded from the fact that palladium does not form an external oxide scale under experimental conditions and that it exhibits high hydrogen solubility.

When the process is controlled by inward oxygen diffusion, in accordance with Wagner's theory [14], the depth of internal oxidation is:

$$X_i^2 = \frac{2t\varepsilon N_o^{(s)} D_o}{\nu N_{Cr}} \qquad (1)$$

where X_i is the depth of the internal oxidation zone (IOZ) reached in time, t, ε is a tortuosity factor (time-independent) reflecting the diffusional blocking effect of the oxide precipitates, $N_o^{(s)}$ is the equilibrium concentration of dissolved oxygen at the alloy surface, D_o is the oxygen self-diffusion coefficient in the alloy, ν is the stoichiometric ratio O/Cr in the precipitated chromium oxide and N_{Cr} is the molar fraction of chromium in the alloy.

Therefore, if water vapour additions increase the internal oxidation of chromium in the alloy substrate, an increase in oxygen permeability, $N_o^{(s)} D_o$ is implied. Under conditions where the internal oxidation is diffusion controlled, the depth X_i of the internally oxidized zone (IOZ) should increase with oxidation time, t, at constant temperature.

Wagner showed [14] that ε can be evaluated for such limiting cases. During the internal oxidation of dilute solutions of chromium in alloy, the outward diffusion of chromium towards the oxidation front is very slow [15] in comparison to the inward

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* Corresponding author.
E-mail address: v.shemet@fz-juelich.de (V. Shemet).

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diffusion of oxygen. In addition, the equilibrium concentration of dissolved oxygen at the alloy surface $N_o^{(s)}$is much smaller than the chromium concentration N_{Cr} in the bulk alloy. Strictly speaking, $N_o^{(s)}$ and D_o are the solubility and diffusivity, respectively, of oxygen in the internally oxidized edge zone. However, as the added chromium contents of only 1 wt% are precipitated as an oxide, the difference compared to the corresponding data on pure metal is negligible [16]. Since for 800–900 °C, the ratio $N_o^{(s)}/N_{Cr}$ amounts on average to 10^{-2} [17], the conditions $D_{Cr}\ /D_o \ll N_o^{(s)}/\ N_{Cr} \ll 1$ are fulfilled, which indicates that during the internal oxidation of dilute alloys, the movement of the precipitation front is essentially determined by the diffusion of oxygen in the alloys [18]. Thus, Eq. (1) may be expressed as:

$$N_o^{(s)}D_o = X_i^2\frac{\nu N_{Cr}}{2t\varepsilon} \tag{2}$$

Thus, oxygen permeation constant $N_o^{(s)}D_o$ for the alloy can be calculated from the experimental data at different water vapour contents.

Such measurements were used in the past to determine oxygen permeabilities using Rhines packs [19–22] and direct measurement of oxygen permeability in the gas mixtures [23–25]. For Fe–Cr alloys, it was found that increased oxygen permeabilities were associated with the change in precipitate morphology from fine grained in dry packs to relatively large and acicular in wet packs. Diffusion along precipitate/matrix interfaces in the latter case was thought to accelerate oxygen diffusion [20].

In the present paper, oxygen permeability was measured using Pd-1 wt% Cr alloy in dry and wet Ar-1%O_2 at 850 °C. Very few studies can be found in the literature reporting about data on the solubility and diffusivity of oxygen in palladium [17,26–28]. Early results stem from gravimetric investigations of the interaction of oxygen with palladium including the oxidation of the pure metal [26–28]. However, like the solubility values, the values for the diffusion coefficients are very low, and, therefore, do not fit the well-known kinetics of the internal oxidation of iron during annealing in oxygen [29].

2. Experimental procedures

The Pd-1 wt% Cr alloy was prepared by argon arc melting of high purity metals (Pd- 99.99% and Cr- 99.99%), using levitation induction melting. As shown in Fig. 1, the added chromium content of 1 wt% was within the range of the Pd-rich α solid solution:

The alloy ingot was cut into discs with diameters of 10 mm and thicknesses of 2 mm, surface ground with 1200-grit SiC paper and degreased with acetone immediately before use. The oxidation experiments were carried out at 850 °C for up to 96 h in three different gas mixtures: Ar-1%O_2, Ar-1%O_2-1%H_2O and Ar-1%O_2-10% H_2O. The water vapour was fixed by passing Ar-1%O_2 through distilled water in a vial at the required temperature. After a certain time of exposure, specimens were withdrawn from the hot zone and cooled to room temperature.

To avoid the formation of the surface oxide PdO during oxygen exposure, the pressure p_{O_2} at temperature T was set below the dissociation pressure $p_{O_2}^d$ of PdO. The relationship between $p_{O_2}^d$ (PdO) and the reciprocal temperature $1/T$ obeys the following relation according to literature data [31]:

$$p_{O_2}^d(\text{PdO})=1.\ 91\times10^{15}\exp\left(-\frac{27055}{T}\right) \tag{3}$$

Thus the dissociation pressure $p_{O_2}^d$ of PdO at 850 °C is calculated according to Eq. (3) was 6.6×10^4 Pa that is substantially higher than the oxygen partial pressure p_{O_2} in the experiments (1.06×10^3 Pa). It should be noted that the behaviour of palladium in an oxygen atmosphere can principally be influenced by the process of formation and evaporation of the volatile oxide PdO. Since this reaction only occurs at much higher temperatures (1000 °C) than those in the present work, it was not considered here.

The depth of the internal oxidation zone (IOZ) was measured on metallographic cross-sections by optical and/or scanning electron microscopy (SEM) coupled with energy dispersive X-ray microanalysis.

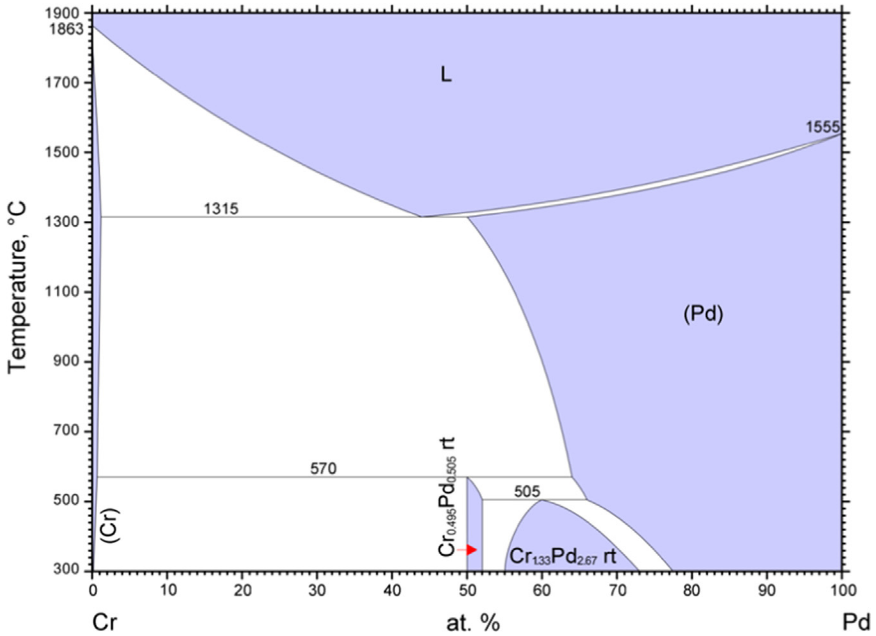

Fig. 1. Pd–Cr phase diagram [30].