Journal of Nuclear Materials 383 (2009) 267–269

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Letter to the Editor

Determination of dissolution rates of f/m steels in LBE from measured evolutions of oxide scale thickness

H. Steiner

Forschungszentrum Karlsruhe GmbH, Institut für Materialforschung III, Postfach 3640, 76021 Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 11 March 2008
Accepted 18 September 2008

ABSTRACT

The knowledge of oxide scale growth under forced flow conditions in LBE systems is of great importance for long-term design calculations, as they have a big influence on the thermal behavior of heat transfer components. In the high temperature part of a reactor system there may be dissolution effects on the oxide scale increasing with temperature and flow velocity. Experimental values of oxide scale dissolution rates are rather scarce; amongst them are those of [M. Machut, K. Sridharan, N. Li, S. Ukai, T. Allen, J. Nucl. Mater. 371 (2007) 134]. A critical assessment of the adopted method seems necessary. An alternative method based on measurements of metal recession may help to clarify the situation.

1. Introduction

During the long-term operation of stainless steel components in LBE systems the formation of oxides scales is a viable means to guarantee against catastrophic liquid metal corrosion. On the other hand, grown oxide scales have a considerable influence on the thermal behavior of such components. One has also to consider the possibility of mechanical effects like cracking and spalling of the scales due to the build-up of thermal and growth stresses. The propensity for spalling should increase with the thickness of the scale, as the flaw size increases with time.

Thus, it is indispensable for design calculations of components to have a good knowledge of the long-term evolution of oxide scales.

2. Methods for the determination of dissolution rates

In flowing LBE there are in principle two effects contributing to oxide scale growth, namely diffusion transport of species through the scale like oxygen and iron followed by formation of magnetite and Fe/Cr spinels and some action of the flowing liquid metal leading either to some dissolution/erosion of the oxide scale or to precipitation of oxide onto the scale depending on the axial position of the component in the system. The main concern is with the high temperature part of the system as there the corrosion effects are maximal. Hence, we are mainly interested in dissolution effects of oxide scales by the flowing LBE. The dissolution effects should increase with temperature and flow velocity as the main test parameters and they are viewed to be much higher for magnetite than for Fe/Cr spinels.

There are theoretical models for the dissolution effect on magnetite in flowing LBE available in the literature (see e.g. Refs. [2] and [3]), but experimental values of the dissolution rate are rather rare. Recently, values for the oxide scale dissolution rate have been given by Machut et al. [1].

We should note that we have to distinguish between the oxide scale removal rate K_r and the metal recession rate R_r. They are linked in the following way:

$$R_r = K_r/\Phi, \tag{1}$$

Φ is the Pilling–Bedworth ratio.

The values for the metal recession rate R_r given in [1] range between 22 and 65 μm/yr.

For our new calculations of K_r and R_r (both in μm/yr) we have used a Pilling–Bedworth ratio of 2.1, which is appropriate for magnetite and Fe–Cr spinels as well, and that a dissolution rate of $1{\cdot}10^{-12}$ m/s is equivalent to 31.6 μm/yr.

Some of the values in Table 1 seem to be unrealistically high. A value of 211 μm/yr for the oxide scale dissolution rate does not seem to be realistic. This is an order of magnitude typical for liquid metal steel dissolution under turbulent flow conditions without the presence of protective oxide scales [6,7]. Although there are no experimental data in this respect available for LBE we can obtain rough estimates of unprotected steel dissolution rates by using data from other liquid metal coolants like Pb [6] and Pb–17Li [7] by applying relation (2) and using values for the iron solubility in the liquid metals known from the literature.

The values of the dissolution rate in Ref. [1] were obtained from measured values of oxide scale thickness by using an analytical solution for the Tedmon model of oxide scale growth [4]. The use of this model in liquid metal corrosion was originally proposed in Ref. [5]. Dissolution rates of about $1{\cdot}10^{-12}$ m/s are given in this

---

E-mail address: helmut.steiner@imf.fzk.de

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.09.022

Table 1
Oxide scale removal and metal recession rates for different steels

	K_r (10^{-12} m/s)	R_r (μm/yr)	K_r (μm/yr)	R_r (μm/yr) Eq. (1)
NF616	2.31[a]	22.4[a]	72.9	34.7
ODS	6.7[a]	65.1[a]	211.4	100.6
HCM12A	4.45[a]	43.2[a]	140.4	66.9
HT9	1.005[b]	14[a]	31.7	15.1
D9	0.704[b]	9.8[a]	22.2	10.6

[a] From [1].
[b] From [5].

reference corresponding to metal recession rates between about 11 and 15 μm/yr.

Oxide scale dissolution rates are mainly determined by the mass transfer coefficient h_{fl} and the iron solubility c^s_{Fe} over the oxide exposed to the liquid metal [3]:

$$K_r \propto h_{fl} \cdot c^s_{Fe}. \tag{2}$$

The iron solubility increases with increasing temperature and with decreasing oxygen content in the liquid metal. The solubility product of iron and oxygen depends on the nature of the oxide leading to considerably higher dissolution rates for magnetite than for Fe–Cr spinels [8]. The mass transfer coefficient depends on the flow type (laminar or turbulent), on the flow velocity u_{fl}, the iron diffusivity D_{Fe}, and the hydraulic diameter of the flow channel d_{hyd}. For turbulent flow we have roughly the following dependence on these parameters:

$$h_{fl} \propto u_{fl}^{0.9} \cdot D_{Fe}^{0.7} / d_{hyd}^{0.125}. \tag{3}$$

The test conditions in [1] were rather moderate ($T = 530\,°C$, $u_{fl} = 1.2$ m/s, $c_o = 1 \cdot 10^{-6}$ wt%) and do not guarantee very high oxide scale dissolution rates. The test conditions in Ref. [5] were somewhat different from that in Ref. [1] with the test temperature and the flow velocity and the oxygen content in the liquid metal being somewhat higher ($T = 550\,°C$, $u_{fl} = 1.9$ m/s, $c_o = 3$–$5 \cdot 10^{-6}$ wt%). The first two test parameters would suggest some increase of the dissolution rate and the last one some decrease by a factor of about 0.2. The differences in test conditions of Machut et al. [1] and Zhang and Li [5] do not support the big differences in the K_r values in Table 1.

Generally, the curves for oxide scale growth gained from loop tests are obtained from different test specimens unloaded after different exposure times. It may be that the different specimens have experienced somewhat different test conditions especially with regard to oxygen activity. This could lead to some variation in the oxidation rate constant. It has been found in Ref. [9] for tests under gas atmospheres that the oxidation rate constant of AISI316 depends on the oxygen partial pressure. We think that in liquid metals we have a dependence on the oxygen activity [8].

A significant tendency for lower oxidation rate constants towards the end of the test campaign can then lead to too high dissolution rates if a constant oxidation rate is used for the evaluation. Early removal of the outer magnetite layer was observed on the specimens in Ref. [1]. This should have led to a change in the oxidation rate constant, an effect which is not taken into account in the model.

A critical appraisal of the method used in Refs. [1] and [5] has to take into account the scatter of experimental data on oxide scale thickness. It is well known from tests under static conditions [10] that the scatter of oxide thickness values can be considerable. But it is also evident from [5] that the data points deviate considerably from the fitted curves suggesting an underlying scatter of the data. Thus, the Tedmon equation should be written as follows:

$$\frac{d}{dt}\delta_{ox}(t) = \frac{K_p^{mean} + / - \Delta K_p}{2 \cdot \delta_{ox}(t)} - (K_r^{mean} + / - \Delta K_r), \tag{4}$$

where δ_{ox} is the oxide scale thickness, K_p is the oxidation rate constant and t is the time.

It is not feasible to determine, to small uncertainty, the mean values and the variances of the oxidation and dissolution rate with only a few data points. We have error margins largely determined by the uncertainty on the oxidation rate constant. This has also a decisive influence on the value of the dissolution rate constant determined from the experimental data. If ΔK_p is rather high it may be that all the data points are located within this uncertainty range and in this case it would not be possible to determine meaningful K_r values by applying Eq. (4).

The consequences which scattering of the experimental data may have for the applied method should be obvious from Fig. 1, which is meant to serve as a heuristic argument. In an ideal situation all the data points lie on the oxide scale growth curve typical for the steel under the assumed test conditions. There is no scatter of data at all. But the probability that we encounter such an ideal situation is practically zero. If the scattering of data is rather low and if we have many data points we have a favorable situation and the proposed method should deliver realistic values for the oxide scale dissolution rate. If the scatter of data is large and if there are only a few data points available the results cannot be trusted under any circumstances.

Thus, in case of long-term tests with many data points the method for the determination of the oxide scale dissolution rate proposed in Ref. [5] can be expected to yield trustworthy results. But for short-term tests with only a few data points the application of this method seems problematic.

It should also be mentioned that the oxide scales in static tests in LBE seem in certain cases grow according to a cubic growth law. Thus, in such cases the Tedmon model has to be modified replacing the parabolic growth term by a cubic one. This would of course lead to somewhat different values for the dissolution rates. Also, the parabolic rate constant may change with exposure time if, for example, the magnetite subscale disappears after a certain exposure time or if the oxygen activity decreases in the course of time. There could also occur partial spalling of the magnetite subscale pretending in this way much higher dissolution rates than were physically reasonable.

But the main objection is against the simplistic application of the proposed method. Namely it can reasonably only be applied to evolutions of oxide scale thickness based on well-established mean values. This would mean that one has to repeat the tests n-times ($n > 6$). But as tests in LBE loops are expensive and time consuming this procedure may not be applicable on practical reasons. As static tests are much cheaper and easier to perform than dynamic tests and not limited in number by the test positions in a loop, a promising procedure would be to gain well-established values for K_p^{mean} and may be also for ΔK_p and to insert these values into the Tedmon equation and to look whether reasonable values of K_r can be obtained in this way from dynamic tests. These 'experimental' K_r values could then be compared to values gained from models. We could also check whether oxide scale growth under static test conditions really follows a parabolic growth law.

But one could also try to devise a different method for the evaluation of dissolution rates independent of the application of the Tedmon equation. One possibility consists in using measured values of metal recession and oxide scale thickness. But for this procedure to be successful one needs long-term tests in LBE loops.

The loss term on the oxide scale Δ_{loss} can be calculated with the help of the following equation:

$$\Delta_{loss}(t) = (\Delta_{recess}(t) - \delta_{i.o.z.}(t)) \cdot \Phi - \delta_{ox}(t), \tag{5}$$

where Δ_{recess} is the metal recession, $\delta_{i.o.z.}$ is the thickness of the internal oxidation zone, δ_{ox} is the oxide scale thickness and t is the time.

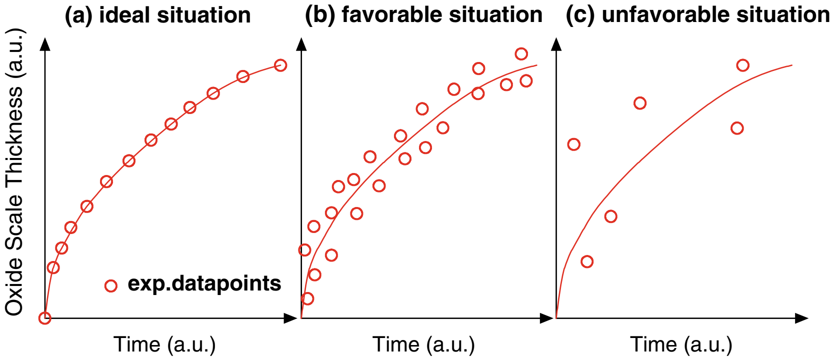

Fig. 1. Schematic view of different experimental situations in establishing as for oxide scale growth in LBE.

With the data given in Ref. [11] for tests with the f/m steel T91 done in the CORRIDA loop we have estimated the oxide scale loss rates to be in the range of 0–5 μm/yr for a test temperature of 550 °C, a flow velocity of 2 m/s and a nominal value of 10^{-6} wt% for the oxygen concentration in the LBE. The oxide scales consisted mainly of Fe/Cr spinel with some traces of thin magnetite scales. It is an unresolved question why these traces are still present after exposure times of more than 10,000 h, as we expect magnetite subscales to dissolve much faster than Fe/Cr spinels. It is clear that this method may, in general, be inappropriate for short-term tests as the metal recession should be rather small in such cases.

This newly proposed method is entirely based on values measured in post test examinations and therefore independent of assumptions on rate laws. But it also has its problems. Whereas the oxide scale thickness can be measured with high accuracy this may not be the case for the metal recession and a great effort must be made to reach an accuracy of better than +/−10 μm. Also, we have obtained for some intermediate exposure times small negative values for the loss term with the data of Schroer [11].

If we would have many experimental data on metal recession we could, of course, apply a statistical analysis to the loss terms gained from Eq. (5) and also study the influence of test parameters like oxygen content and flow velocity. For the time being, we dispose only of a few values for different test durations.

3. Conclusion

Dissolution rates on oxide scales are of great importance for the long-term operation of structural components in LBE systems as they determine the amount of wall thinning in the hot leg and the amount of material transported from the hot leg of the system to the cold leg. The latter effect may lead to plugging of flow channels with small cross sections as we may also expect particulate formation and deposition. Dissolution rates are also influencing the long-term evolution of oxide scales and are therefore important for the thermal behavior of structural components as the thermal conductivity of oxide scales is rather low.

There seem to be two methods to gain information on the dissolution/erosion rates from experimental values of oxide scale thickness. One method consists in fitting solutions of Tedmon's equation on experimental data using a least square technique. The second method uses measured values of metal recession and oxide scale thickness. We think that the first method should only be applied to well-established mean values otherwise the method is prone to the stochastic scattering of experimental values. The second method may help to improve the situation, but it seems only of use for long-term tests.

References

[1] M. Machut, K. Sridharan, N. Li, S. Ukai, T. Allen, J. Nucl. Mater. 371 (2007) 134.
[2] X. He, N. Li, M. Mineev, J. Nucl. Mater. 289 (2001) 227.
[3] H. Steiner, J. Konys, J. Nucl. Mater. 338 (2006) 16.
[4] C.S. Tedmon, J. Eletrochem. Soc. 113 (1967) 766.
[5] J. Zhang, N. Li, Oxid. Met. 63 (5/6) (2005) 353.
[6] V. Markov, Seminar on the Concept of Lead-Cooled Fast Reactor, Cadarache, 1997.
[7] J. Sannier, M. Broc, T. Flament, S. Terlain, Fus. Eng. Des. 14 (1991) 299.
[8] H. Steiner, C. Schroer, Z. Voss, O. Wedemeyer, J. Konys, J. Nucl. Mater. 374 (2008) 211.
[9] M. Saito, H. Furuya, M. Sugisaki, J. Nucl. Mater. 135 (1985) 11.
[10] T. Furukawa, G. Müller, G. Schumacher, A. Weisenburger, A. Heinzel, K. Aoto, J. Nucl. Mater. 335 (2004) 189.
[11] C. Schroer, Private Communication (2007).