Journal of Nuclear Materials 296 (2001) 295–300

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Experimental setup for steel corrosion characterization in lead bath

V. Ghetta [a,*], F. Gamaoun [a], J. Fouletier [b], M. Hénault [b], A. Lemoulec [c]

[a] *LTPCM/ENSEEG, BP 75, 38402 Saint Martin d'Hères cedex, France*
[b] *LEPMI/ENSEEG, BP 75, 38402 Saint Martin d'Hères cedex, France*
[c] *ENSEEG BP 75, 38402 Saint Martin d'Hères cedex, France*

Abstract

Steel samples in a lead bath under controlled oxygen activity were studied for corrosion in a new experimental device (COXCIMEL). The static lead bath has a volume of ∼0.5 and was kept under helium or hydrogenated helium atmosphere. The oxygen content in the bath and in the flowing gas was controlled and monitored using yttria-stabilized zirconia (YSZ)-based sensors and an oxygen zirconia pump. The steel sample treatments were carried out in the temperature range of 450–500°C for ca 30 days. Special attempts were carried out to find steel embrittlement conditions. Samples were characterized after extraction from the bath. The description of the experimental setup functioning is given. The preliminary characterization of the samples and other results obtained are presented in this paper. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In the course of the research program for the development of a hybrid nuclear reactor, liquid lead and liquid lead–bismuth eutectics have been chosen as potential candidates for spallation target material and cooling agent. The long time contact effects have to be studied between these liquid metals and the structural materials, taking into account that the important parameter for the liquid–solid interaction is the oxygen content in the whole system. Although the experimental conditions employed in a stagnant laboratory setup seem to be very different from those of the reactor project, they allow one to point out potential risks which are not easily provable in a forced circulation loop. In such a device, the oxygen concentration is not truly controlled up till now. In Pb17Li loops used to test the compatibility between the Pb–Li eutectic and structural materials [1–3], no oxygen content measurement apparatus was included in the loop circuit. The maximal oxygen concentration was however imposed by the solubility limit of the Pb–Li eutectic which is somewhat low. On the contrary for lead and even more for bismuth–lead mixture [4–7], the oxygen solubility limit is quite high (above 0.01 at.% at 530°C). The whole system is free to vary between this maximum limit and very low oxygen concentration. These low oxygen concentrations could be induced, for example, by formation of reducing elements in the course of a working nuclear reactor. The effect of prolonged contacts between lead (or bismuth–lead eutectic) and structural materials have to be studied, taking into account the whole range of oxygen concentration under the solubility limit in the chosen cooling agent. With this aim in mind, we have designed a new experimental device with a metallic bath under controlled oxygen activity. The working tests and the first steel treatments have been carried out with lead.

2. Experimental setup description

2.1. Oxygen in liquid lead

The atomic fraction of oxygen dissolved in lead x_O is linked to the oxygen partial pressure by the following relations:

---

[*] Corresponding author. Tel.: +33-4 76 82 66 49; fax: +33-4 76 82 67 45.

E-mail address: ghetta@ltpcm.inpg.fr (V. Ghetta).

0022-3115/01/$ - see front matter
PII: S0022-3115(01)00532-3

$$\frac{1}{2}O_2\ (g) = (O)_{Pb} \quad \text{and} \quad pO_2^{1/2} = a_O = \gamma_O^0 x_O. \tag{1}$$

Using the 1 at.% standard state, the free enthalpy of mixing oxygen in lead between 510°C and 1100°C is given in the compilation of Chang et al. [8]:

$$RT\ln\left(\frac{\gamma_O^0}{100}\right) = -119100 + 14.6\ T\ \text{J/g atom O}. \tag{2}$$

The atomic oxygen mole fraction in lead between 510°C and 1100°C can be deduced from activity measurements by

$$x_O = 0.01a_O\exp\left(\frac{119100 - 14.6\ T}{RT}\right). \tag{3}$$

When x_O reaches the solubility limit, the formation of lead oxide PbO limits the atomic oxygen mole fraction in lead.

2.2. Operating principles

The traditional 'pump–gauge system' used for gas analysis [9] was adapted to the metal bath oxygen regulation. The original pump–gauge system was already used for wetting experiments in sessile drop configuration [10]. However, long duration annealings require the use of liquid metal amounts larger than a drop or than the amounts of liquid metal in a traditional galvanic cells used for oxygen solubility measurements [11–13].

The pump and the gauge of our setup are based on yttria-stabilized zirconia (YSZ) (ZrO_2–Y_2O_3, 9 mol%) tubes. Earlier oxygen diffusivity studies were carried out by using calcia-stabilized zirconia (CSZ) [11–13]. The use of CSZ is not recommended due to its generally noticeable electronic conductivity induced by impurities in the electrolyte.

For the pump and the gauge, a close-ended zirconia tube separates the liquid lead from air. The electromotive force, E, of the gauge with reference to oxygen pressure in air is expressed as a function of the oxygen activity in liquid lead as

$$E = \frac{RT}{2F}\ln\left(\frac{a_O}{(pO_2^{air})^{1/2}}\right). \tag{4}$$

The oxygen activity is then

$$a_O = (pO_2^{air})^{1/2}\exp\left(\frac{2FE}{RT}\right), \tag{5}$$

where E is the emf (V), R the gas constant (8.314 J/K mole), T, the bath temperature (K), F the Faraday constant (96484 C) and pO_2^{air}, the oxygen partial pressure of the ambient air.

When an external voltage V_p is applied to the zirconia wall, an oxygen flux appears through the pump that changes the oxygen concentration in the liquid bath. The resultant variation of the oxygen moles in the bath is

$$\Delta\eta_O = \frac{Q}{2F}, \tag{6}$$

where Q is the electricity quantity which has gone through the pump (C). The calculation of the oxygen concentration variation requires the accurate determination of the lead weight.

The association of such a pump and a gauge in the same bath, may lead to the oxygen regulation. It also allows activity coefficient measurements, as long as the bath weight is known with extreme accuracy.

2.3. Setup description

Fig. 1 shows the schematic drawing of the whole COXCIMEL setup (in French: Corrosion sous OXygène Contrôlé et Interaction avec les MEtaux Liquides). The lead bath was in a cylindrical steel vessel, which was secondary vacuum proofed and placed inside a cylindrical furnace. The lead bath was not in contact with the steel chamber, but in an alumina crucible 110 mm in diameter providing electric insulation. The top of the steel-made vessel was water-cooled in order to protect the various in-out systems:

1. gas intake and outflow,
2. sample introduction systems,
3. electrochemical gauge and pump supports.

The flowing gas above the bath (mixture of He and H_2 in 0–100%) was controlled upstream with mass flowmeters and flew through an oxygen gas sensor down the lead vessel. The temperature of the lead bath was taken with a thermocouple inside the gauge tube. The electrical contacts required for both the pump and the gauge were rhenium wires plunged in the lead.

Lead pieces are mechanically cleaned before their introduction in the alumina crucible and molten under hydrogen. Afterwards, the lead was always kept liquid, independent of an experiment was running or not.

The oxygen activity in the lead bath was continuously measured by the zirconia gauge using a high impedance voltmeter. The gauge was used over a period of more than six months without change of its characteristics, i.e., impedance, response time, etc. When a change in the oxygen concentration occurred, the response time of the gauge was about 30 s for oxygen activity between 10^{-10} and 10^{-6} at a working temperature close to 530°C. A typical emf variation is schematically drawn as a function of time in Fig. 2(a). If a local perturbation occurred in either the bath (oxygen flux through the pump for example) or above the bath (gas composition change) the homogenization time, which depends on the size of the bath, is defined as the time necessary for gauge signal to restore the same slope as before the perturbation. The schematic

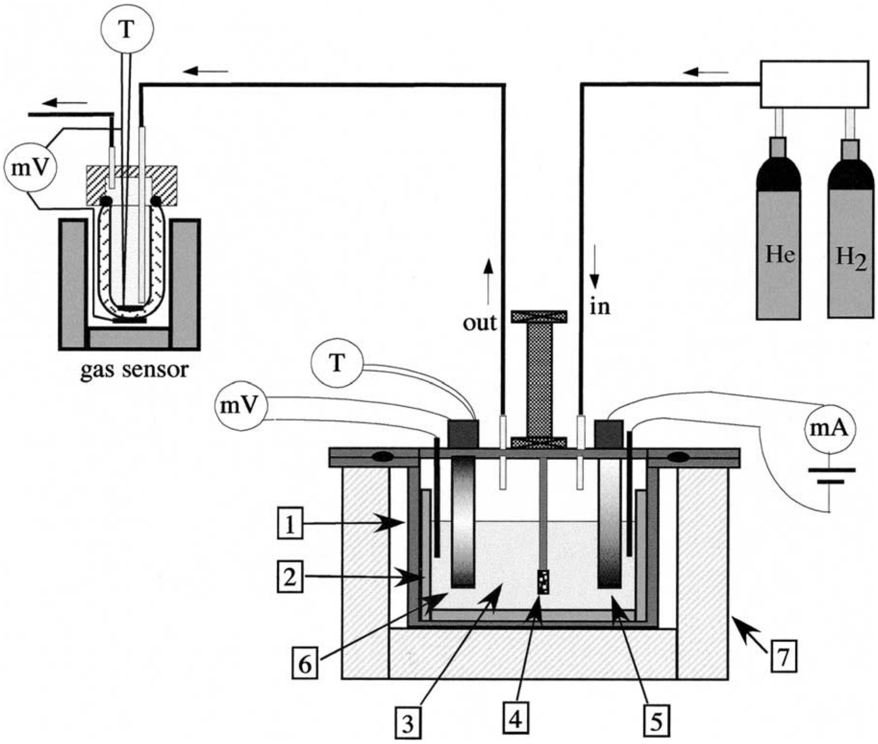

Fig. 1. Schematic drawing of the COXCIMEL setup: (1) steel vessel; (2) alumina crucible; (3) lead bath; (4) T91 sample; (5) oxygen pump; (6) oxygen sensor; (7) furnace.

drawing of Fig. 2(a) is only valid for strictly neutral gas. If, for example, hydrogen and helium gas mixtures are used, the variation with time for the gauge signal is schematized in Fig. 2(b). The effect of the non-neutrality of the flowing gas on the slope of the gauge signal depends on the oxygen activity range within lead.

Two cases of working mode may be considered for the oxygen pump: the oxidation mode corresponding to oxygen injection into the liquid bath, and the reducing mode in which the oxygen is extracted from the molten lead through the zirconia wall.

In our setup the lead bath volume was nearly 0.5 l. The contact area of pump tube (9.5 mm in diameter) with the molten lead was of the order of 12 cm^2. It is admitted that the maximum current density with zirconia cells is ca 0.2 A cm^{-2}. Under these conditions, it may easily be demonstrated that the solubility limit is never involuntarily reached even locally, near the pump surface.

For the reduction mode, oxygen dissolved in lead has to diffuse in the bath towards the cathode of the pump. Under these conditions, oxygen reduction in the bath can take place, provided the applied current is lower than a limiting one. This limiting current depends on the oxygen concentration, bath temperature, etc. From a practical point of view, we have shown that, for oxygen concentration lower than 1 ppm, a partial electrochemical reduction of the zirconia tube cannot be avoided. During the further oxidation stages, a reduction of zirconia in a previous reducing cycle induces local formation of lead zirconate $PbZrO_3$ [14]. The precipitation of this non-conducting phase on the pump surface in contact with the lead bath leads to an increase of the effective local current density that becomes noticeably higher than its limiting value even for small applied cathodic current. Avoiding zirconia tube reduction conditions, the pump was continuously used over more than six months without degradation.

The lowest oxygen concentration reached was about 10^{-4} ppm (at 527°C). Such a low concentration was achieved by hydrogen treatment.

2.4. Testing procedure

To check the functioning of the pump–gauge coupling in lead, we applied a method close to that used for the gas system [15] which is a verification of the Faraday law. For a flowing gas system, the method consists in the verification of the relationship between oxygen partial pressure and current intensity. In the case of a static bath (which is a closed system), the method involves the

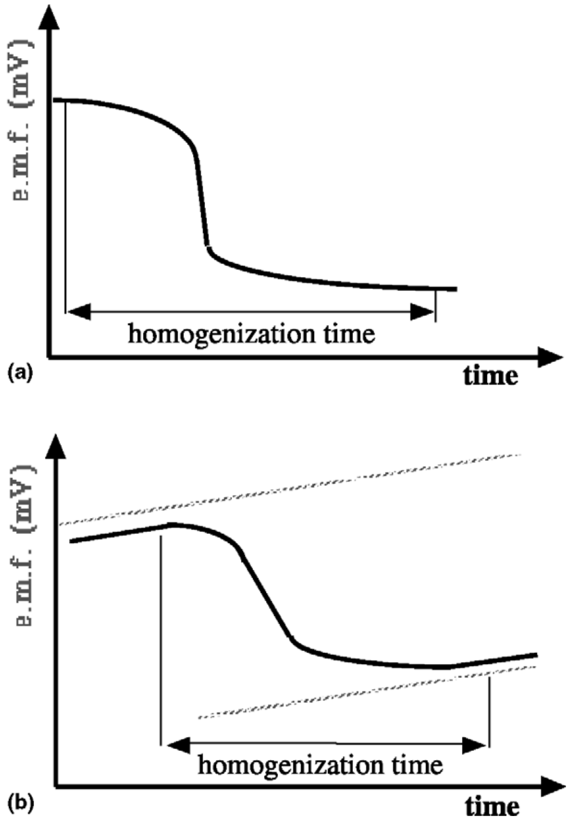

Fig. 2. Definition of the homogenization time for neutral gas flow (a) and for hydrogenated gas flow (b), respectively.

verification of the relationship between the oxygen mole number in the liquid deduced from the gauge emf and the quantity of electricity passed through the pump.

We have checked that the variation of the oxygen mole numbers in the bath, deduced from gauge measurements, is a linear function of the quantity of Coulomb passed through the pump circuit. From gauge measurements the variation of the bath oxygen mole numbers, may be calculated from the following equation:

$$\eta_{\mathrm{O}}^{\mathrm{f}} - \eta_{\mathrm{O}}^{\mathrm{i}} = \frac{1}{\gamma_{\mathrm{O}}^{0}} \frac{m_{\mathrm{Pb}}}{M_{\mathrm{Pb}}} (p\mathrm{O}_2^{\mathrm{air}})^{1/2} \left(\mathrm{e}^{2FE_{\mathrm{f}}/RT} - \mathrm{e}^{2FE_{\mathrm{i}}/RT}\right), \tag{7}$$

where E_{i} and E_{f} are the initial and final gauge emf, respectively, while the Faraday law applied to the pump leads to

$$\eta_{\mathrm{O}}^{\mathrm{f}} - \eta_{\mathrm{O}}^{\mathrm{i}} = \frac{Q}{2F}. \tag{8}$$

The plot of the $(\eta_{\mathrm{O}}^{\mathrm{f}} - \eta_{\mathrm{O}}^{\mathrm{i}})$ values deduced from Eq. (7) as a function of Q is given in Fig. 3. The experiments were carried out at 527°C in the oxidation mode. The straight line obtained demonstrates the good functioning of both independent electrochemical units at 527°C. From this figure and knowing the bath weight (5150 g for this experiment) we can deduce the capacity of the oxygen bath regulation which is of the order of 0.2 ppm of oxygen per Coulomb.

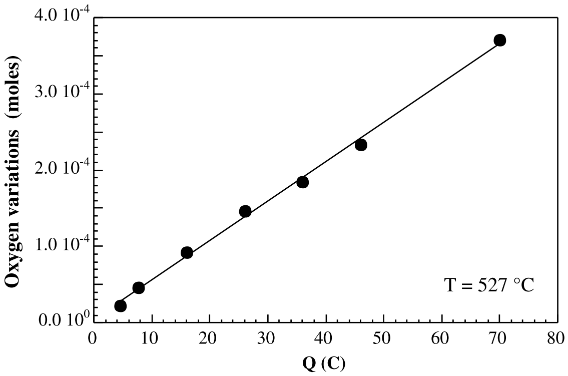

Fig. 3. Plot of the $(\eta_{\mathrm{O}}^{\mathrm{f}} - \eta_{\mathrm{O}}^{\mathrm{i}})$ values deduced from the Eq. (7) as a function of the quantity Q of coulomb gone through the pump at 527°C.

Other tests were carried out to specify the range of good functioning of the setup. A test at a lower temperature (450°C) in oxidation mode between 0.1 ppm and 10 ppm which proved that the whole system worked correctly at 450°C. A second test in reducing mode was carried out in the range 70–7 ppm, at 527°C.

2.5. Testing results of the commercial Setnag sensor

After verifying that our laboratory-made pump–gauge system in liquid lead was working correctly, we tested a commercial oxygen sensor. [1] This potentiometric zirconia sensor has an internal oxygen reference fixed by a palladium/palladium oxide mixture, instead of air. The Setnag sensor offers the advantage of being very small (3 mm in diameter and 10 mm long) and having a good thermal shock resistance.

The Setnag sensor was immersed in the lead bath, simultaneously with the pump–gauge system previously described. The evolution of the emf given by the Setnag sensor was continuously compared to that of our air reference gauge.

The emf of the Setnag sensor follows the Nernst law:

$$E = \frac{RT}{2F} \ln \left(\frac{a_{\mathrm{O}}}{\left(p\mathrm{O}_2^{\mathrm{Pd/PdO}}\right)^{1/2}} \right). \tag{9}$$

---

[1] SETNAG, 31 bd de Magallon-13015 Marseille, France. Setnag@aix.pacwan.net

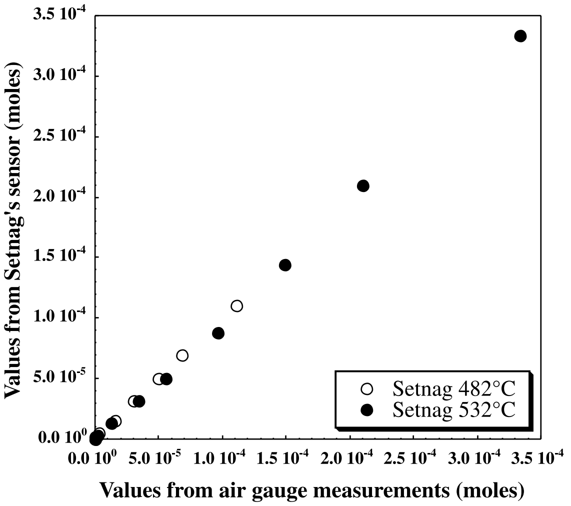

Fig. 4. Comparison of atomic oxygen mole number deduced from the gauge and the Setnag sensor measurements during a bath oxidation cycle at 532°C and 482°C.

The measurements were made at 532°C and 482°C, respectively. The values used for the Pd/PdO reference correspond to the following Gibbs free energy of formation of PdO, $\Delta G^0(T)$:

$$\Delta G^0(482°\mathrm{C}) = -37723\ \mathrm{J/mol} \quad \text{and} \quad \Delta G^0(532°\mathrm{C}) = -32831\ \mathrm{J/mol}. \tag{10}$$

These values are very close to those given by the COACH Thermodynamical Data Base [16] or those previously published by Fouletier [9], with a maximum difference of 372 J.

The atomic oxygen mole numbers in the bath deduced from the gauge and the Setnag sensor measurements during oxidation cycle at 532°C and 482°C are plotted in abscissa and ordinate of Fig. 4. Both sensors agree with a correlation coefficient of 0.99.

We did not test the lifetime of the Setnag sensor over more than one month, but the conclusion of this test was that for short time the use of the Setnag sensor can substitute our air gauge system, but care must be taken for the sensor calibration, and the Pd/PdO mixture regeneration.

2.6. Conclusion of the experimental setup part

We built and tested a new setup, which allows measuring and accurate control of the oxygen concentration in a lead bath from very low concentration (10^{-4} ppm) to the solubility limit. This was achieved by simultaneous use of two methods: the use of He and H_2 gas mixtures and the electrochemical pump–gauge system. We have shown that the pump–gauge electrochemical system worked correctly between 450°C and 550°C.

The behavior of the commercial Setnag sensor in lead bath is encouraging.

3. Steel treatments

Owing to the lead volume used and the accuracy of our electrochemical system, the setup described in the previous section of this paper allows long time annealing. In order to obtain preliminary results we have limited the length of sample treatment of the first samples tested to about 1000 h.

3.1. Materials and procedure

Sogemet supplied lead, 99.97 % pure. [2] T91 steel was provided by CLI. [3] Samples of size 10 × 10 × 40 mm^3 were cut of from a larger bar of steel which was submitted to the standard heat treatment for steel 91 plus a heat treatment at 770°C for 7 h to release residual stresses. After drilling a hole into the sample and polished all faces with SiC grinding papers of graduation up to 4000, the sample was attached to the end of an alumina rod (45 cm in length). The sample was then introduced in the lead cell through a lock chamber in order to limit the bath pollution with oxygen.

3.2. Preliminary results

Four samples were treated in the lead bath with very low fixed oxygen concentration or with oxygen concentration cycles between low (i.e. 10^{-3} ppm) and high (i.e. 10 ppm) contents, at about 530°C. After exposition, the sample is taken out of the liquid lead and slowly brought up again in a cold area of the chamber before the final extraction. The existence of a thin and smooth oxidized layer on the surface leads to a bad wettability by the liquid metal and under the present extraction conditions, there is no remaining lead on the sample if its surface has not become rough. As shown by SEM micrography (Fig. 5), no liquid lead penetration within the steel sample was observed; but in all the samples cavities appeared, more numerous near the sample surface. Investigations of the samples before and after treatment show that cavities appear during the exposure and are spread near the surface all along the periphery of the sample.

The size distribution of the cavities varies from 0.2 up to 5 μm. The formation of an oxide layer (Chromite

---

[2] 2 Société Générale des Métaux, Neuilly sur Seine, France.

[3] Creusot-Loire Industries, Le Creusot, France.

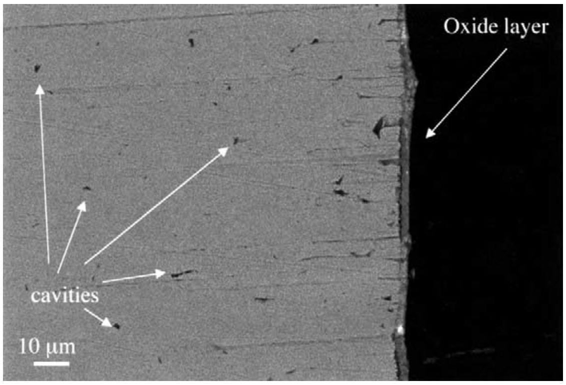

Fig. 5. SEM micrography of treated T91 sample cross-section (30 days, 540°C, bath under flowing hydrogen, oxygen in lead: about 0.001 ppm).

$FeCr_2O_4$) on the steel surface did not protect the sample from this cavitation phenomenon.

4. Discussion and conclusion

The first four samples were submitted all for sometime under very low oxygen concentration stage and present different levels of cavity formation. It should be pointed out that cavities did not appear in previously published studies carried out for higher oxygen concentration (see for example, Benamati studies up to 3700 h on F82H steel [17]). Therefore we think that it is absolutely essential, that all the possible ranges of oxygen concentration should be taken into account in the course of steel/lead or bismuth–lead contact studies. As the rate of the bath reduction to very low oxygen concentration using reducing gas is slow, a direct measurement of the oxygen content of the liquid bath is indispensable. The indirect bath regulation method used by Müller [18] needs an accurate control of the oxygen concentration.

It is not recommended to limit the investigation field to the high oxygen range only, and the COXCIMEL setup is the right tool for the whole field study.

Acknowledgements

This work was carried out within the framework of the GDR GEDEON on D. Gorse's instigation. We thank her for her encouragement. The authors also wish to thank S. Goldstein (CEA-Saclay) for his initial contribution to this project.

References

[1] O. Chopra, D. Smith, J. Nucl. Mater. 122&123 (1984) 1219.
[2] A. Terlain, T. Flament, T. Dufrenoy, J. Sannier, J. Nucl. Mater. 191–194 (1992) 984.
[3] T. Sample, V. Coen, H. Kolbe, L. Orecchia, J. Nucl. Mater. 191–194 (1992) 979.
[4] C.B. Alcock, T.N. Belford, Trans. Faraday Soc. 60 (1964) 822.
[5] W.B. White, R. Roy, J. Am. Ceram. 47 (1964) 242.
[6] H.A. Wriedt, Bull. Alloy Phase Diagrams 9 (1988) 106.
[7] D. Risold, B. Hallstedt, L.J. Gauckler, H.L. Lukas, S.G. Fries, J. Phases Equilibria 16 (3) (1995) 223.
[8] Y.A. Chang, K. Fitzner, M-X. Zhang, Prog. Mater. Sci. 32 (1988) 97.
[9] J. Fouletier, G. Vitter, M. Kleitz, J. Appl. Electrochem. 5 (1975) 111.
[10] D. Chatain, F. Chabert, V. Ghetta, J. Fouletier, J. Am. Ceram. Soc. 76 (1993) 1568.
[11] R. Szwarc, K.E. Oberg, R. Rapp, High Temp. Sci. 4 (1972) 347.
[12] A. Taskinen, Scand. J. Metall. 8 (1979) 185.
[13] S. Otsuka, Z. Kozuka, Metall. Trans. B 10B (1979) 565.
[14] K.T. Jacob, W.W. Shim, J. Am. Ceram. 64 (1981) 573.
[15] J. Fouletier, E. Mantel, M. Kleitz, Solid State Ionics 6 (1982) 1.
[16] COACH, Computer Aided Chemistry, Version 3.1.0, Thermodata 1992/1996.
[17] G. Benamati, P. Buttol, V. Imbeni, C. Martini, G. Palombarini, J. Nucl. Mater. 279 (2000) 308.
[18] G. Müller, G. Schumacher, F. Zimmermann, J. Nucl. Mater. 278 (2000) 85.