das Oberflächenelement einer Kugel vom Radius $[\overline{\overline{V^2}}\cdot\overline{\overline{(\Delta R)^2}}]^{1/2}\cdot t/\Delta R$, das vom Kugelmittelpunkt aus unter dem Raumwinkel $\Delta\Omega$ erscheint, und sei ΔW das Volumen $=\Delta F\cdot$Einheitslänge. Dann ändert sich erwartungsgemäß die Gasteilchenzahl

$$Z\equiv(n-n^{(0)})\cdot\Delta W$$

nach (19) für $\Delta\mathbf{R}\perp\mathbf{c}$ entsprechend der Diffusionsgleichung des Brownschen Teilchens:

$$[\partial_t-\delta\cdot(\partial_r)^2]\,Z=0\,.$$

Herrn Prof. Dr. G. LUDWIG danke ich für fördernde, kritische Diskussionen; ebenso danke ich den Herren Dr. S. FÖRSTER und Dr. O. SEEBERG für ihre ständige Diskussionsbereitschaft.

High Temperature Electrochemical Determination of the Thermodynamic Stability of the Iron-Rich, Iron-Niobium Intermetallic Phase

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A non-stationary technique of e.m.f. measurements after polarization of solid galvanic cells, previously applied to the determination of the standard free energy of formation of metal oxides, has been extended to intermetallic phases.

The chief condition of applicability of this technique to intermetallic compounds is that the rates of recombination of the cathodic reduction products to yield the stable intermetallic phase be high as compared with that of chemical oxidation at the interface with the solid intermediate electrolyte, due to oxygen impurities in the gas phase.

In particular, the solid electrolytic cell:

$$\mathrm{Pt}\;\Big|\;\mathrm{Fe}+\text{“FeO”}\;\Big|\;\begin{matrix}\mathrm{ThO_2}\\(+\mathrm{LaO_{1,5}})\end{matrix}\;\Big|\;\mathrm{Fe}+\mathrm{Fe}_{7-y}\mathrm{Nb_2}+\mathrm{NbO_2}\;\Big|\;\mathrm{Pt}$$

(y values expressing the ε-phase iron-rich boundary compositions according to different authors investigations) was examined.

Values of the standard free energy of formation of $\mathrm{Fe}_{7-y}\mathrm{Nb}_2$ from the elements, ranging between $-3.77+0.72\cdot10^{-3}\,T$ and $-5.66+1.09\cdot10^{-3}\,T$ kcal/atom were found.

According to GOLDSCHMIDT[1], the hexagonal, $\mathrm{MgZn_2}$-type ε-phase of the system iron – niobium shows a wide range of stability, extending from 58 to 78 at.% of iron up to 1590 °K. REZUKHINA and PROSHINA[2], however, found a narrower homogeneity field embracing the stoichiometric composition $\mathrm{Fe_2Nb}$, while KLYACHKO and YAKOVLEVA[3] reported a substoichiometric phase with $\mathrm{Fe_{1,93}Nb}$ and $\mathrm{Fe_{1,99}Nb}$ as boundary compositions. Because of these discrepancies, the composition at the iron-rich boundary will henceforth be written in the general form $\mathrm{Fe}_{7-y}\mathrm{Nb}_2$.

The standard molar free energy of formation of the intermetallic phase in equilibrium with the iron phase

$$(7-y)\;\mathrm{Fe}+2\;\mathrm{Nb}\rightleftarrows\mathrm{Fe}_{7-y}\mathrm{Nb}_2$$

is directly related to the thermodynamic activity of the niobium component by the fundamental equation:

$$\Delta G^0_{\mathrm{f},\,\mathrm{Fe}_{7-y}\mathrm{Nb}_2}=2\,R\,T\,\ln a_{\mathrm{Nb}}\tag{1}$$

provided that the deviation from unity of the activity of iron, due to the slight solubility of niobium in iron is neglected in a first approximation, i. e. the metallic iron in equilibrium is regarded as a pure phase. With this assumption, in the ternary system iron + niobium + oxygen, the oxygen versus metal ratio of the oxide phase in equilibrium is conditioned by the thermodynamic activity of niobium.

The oxygen exchange reactions may be confined to the simple disproportionation reaction:

$$2\;\mathrm{NbO}\rightleftarrows\mathrm{NbO_2}+\mathrm{Nb}\,.\tag{2}$$

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[1] H. J. GOLDSCHMIDT, J. Iron Steel Inst. London **194**, 169 [1960].

[2] T. N. REZUKHINA and Z. V. PROSHINA, Zh. Fiz. Kim. **36**, 637 [1962].

[3] YU. A. KLYACHKO and E. F. YAKOVLEVA, Sb. Tr. Nauchn. Issled Inst. Chernoi Met. **24**, 30 [1962].

Denoting by a^{*}_{Nb} the activity of niobium in equilibrium with the biphasic system $\mathrm{NbO} + \mathrm{NbO_2}$, the condition for the existence, in thermodynamic equilibrium, of the system $\mathrm{Fe} + \varepsilon$-phase $+ \mathrm{NbO_2}$ is:

$$a_{\mathrm{Nb}} \leqq a^{*}_{\mathrm{Nb}} \tag{2 a}$$

whereas that for the existence of the system $\mathrm{Fe} + \varepsilon$-phase $+ \mathrm{NbO}$ is

$$a_{\mathrm{Nb}} \geqq a^{*}_{\mathrm{Nb}} \,. \tag{2 b}$$

In fact, the conditions (2 a) and (2 b) mean respectively that reaction (2) is shifted to the right or to the left hand side. So, by equilibration experiments on $\mathrm{Fe} + \mathrm{Nb} + \mathrm{O}$ system containing an excess of iron it is possible to state the upper limit for the standard free energy of formation of $\mathrm{Fe_{7-\mathit{y}}Nb_2}$ in the case that the resulting system would be

$$\mathrm{Fe} + \mathrm{Fe_{7-\mathit{y}}Nb_2} + \mathrm{NbO}$$

or the lower limit in the case that

$$\mathrm{Fe} + \mathrm{Fe_{7-\mathit{y}}Nb_2} + \mathrm{NbO_2}$$

would be found to be the most stable system.

This limit is obviously determined by the values of the standard molar free energy of formation of NbO and $\mathrm{NbO_2}$. On the ground of the values given by WORRELL[4]:

$$\Delta G^{0}_{\mathrm{f,Nbo_2}} = -185.6 + 39.0 \cdot 10^{-3}\, T \text{ kcal/mole} \tag{3}$$

and by BARBI[5]:

$$\Delta G^{0}_{\mathrm{f,Nbo}} = -100.2 + 22.1 \cdot 10^{-3}\, T \text{ kcal/mole}$$

the value of a^{*}_{Nb} could be readily calculated if NbO and $\mathrm{NbO_2}$ would be considered, in a rough approximation, as stoichiometric phases. For instance, at 1200 °K, it is found that $\ln a^{*}_{\mathrm{Nb}} \approx -3.6$ which means that NbO is capable of existence in equilibrium with both iron and $\mathrm{Fe_{7-\mathit{y}}Nb_2}$ at 1200 °K only if the standard free energy of formation of the latter is more positive than ≈ -17.2 kcal/mole.

It is worthy to note that only the oxygen exchange reaction between NbO and $\mathrm{NbO_2}$ has been taken into consideration, since the presence of the iron oxides would require an unreliable, extremely negative free energy of formation of the intermetallic phase, because of the strong difference of stability between niobium oxides and iron oxides.

Fundamentals

In the present work the electromotive force of the all-solid chain

$$\mathrm{Pt} \left| \mathrm{Fe} + \mathrm{Fe_{0,95}O} \right| \begin{matrix} \mathrm{ThO_2} \\ (+\mathrm{LaO_{1,5}}) \end{matrix} \left| \mathrm{Fe} + \mathrm{Fe_{7-\mathit{y}}Nb_2} + \mathrm{NbO_\mathit{x}} \right| \mathrm{Pt}$$

was measured.

As has been demonstrated[6, 7], the solid solution of $\mathrm{LaO_{1,5}}$ in $\mathrm{ThO_2}$ shows a pure oxygen ion conductivity, while the two systems in contact with thoria interfaces are pure electronic conductors. Since the e.m.f. values are directly related to the oxygen chemical potential difference at the two interfaces with the intermediate electrolyte[8, 9], it is possible to calculate the oxygen activity at the right hand side interface provided that the same function at the left hand one is known. Besides, since the activity of iron has been assumed to be unity, it is possible to evaluate a_{Nb} and then $\Delta G^{0}_{\mathrm{f,Fe_{7-\mathit{y}}Nb_2}}$.

On the other hand, we consider the elementary electrochemical reactions at the two interfaces

$$2\,x\,\mathrm{Fe_{0,95}O} + 4\,x\,\Theta \rightleftarrows 1.90\,x\,\mathrm{Fe} + 2\,x\,\mathrm{O^{=}},$$

$$\mathrm{Fe_{7-\mathit{y}}Nb_2} + 2\,x\,\mathrm{O^{=}} \rightleftarrows (7-y)\,\mathrm{Fe} + 2\,\mathrm{NbO_\mathit{x}} + 4\,x\,\Theta$$

the resulting overall process being

$$2\,x\,\mathrm{Fe_{0,95}O} + \mathrm{Fe_{7-\mathit{y}}Nb_2} \rightleftarrows (7-y+1.90\,x)\,\mathrm{Fe} + 2\,\mathrm{NbO_\mathit{x}}\,. \tag{4}$$

The Nernst relationship allows the calculation of the free energy change associated with reaction (4) and then the free energy of formation of the ε-phase at the iron-rich boundary composition, since the corresponding functions of the iron and niobium oxides are known.

Preliminary equilibration experiments were carried out with the aim of determining the niobium valence, x, in the niobium oxide thermodynamically equilibrated with the other two metallic phases and, at the same time, of assuring the presence of true equilibrium conditions for the materials further employed as electrodes in the electrochemical cells. This composition was then controlled by X-ray diffraction analysis.

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Equilibration Experiments

At first, some NbO_2-free NbO was prepared. To this purpose, very fine powders (previously passed through a 25 000 mesh/cm^2 sieve) of niobium (purity better than 99.8%) and niobium pentoxide (purity better than 99.7%) were thoroughly blended in such ratio to get a final composition of about 10 at.% of niobium metal in excess of the stoichiometric composition NbO. The mixture was cold-compacted at 10 tons/cm^2, treated at 1470 °K for two hours and then at 1870 °K for four hours under a vacuum better than 10^{-5} mm Hg. The X-ray diffraction patterns showed the compact to consist only of NbO with a slight excess of metallic niobium, NbO_2 being completely undetectable.

Two series of specimens were prepared for the equilibration experiments:

Series a) by blending 18.652 g of iron powder, 7.432 g of niobium powder and 2.128 g of Fe_2O_3 powder;

Series b) by blending 10.052 g of iron, 1.858 g of niobium and 3.268 g of the previously prepared NbO.

The mixtures were then pressed in the shape of cylindrical tablets of 12 mm diameter and 2 – 3 mm thickness. The two series of samples were thermally treated for 20 hours at 1590 °K under vacuum better than 10^{-5} mm Hg and the structural analysis of both after the treatment, showed only the X-ray peaks of iron, niobium dioxide and intermetallic phase (Fig. 1).

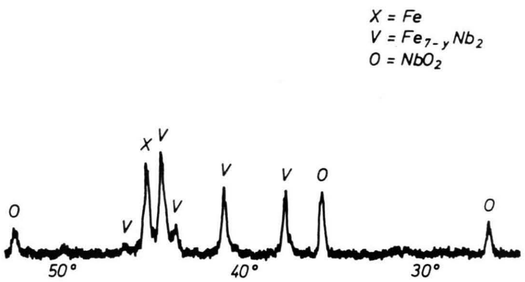

Fig. 1. X-ray diffraction patterns (Cu Kα) of the system Fe+Nb+O containing an iron excess, after equilibration at 1590 °K.

Sample a) was subsequently heated under vacuum at 1880 °K (above the melting point) for three hours and then quenched (after one minute the temperature fell down to about 1250 °K). The X-ray diagram changed, owing to the curvature of the ε-phase boundary but, after a further annealing at 1590 °K the situation depicted by Fig. 1 was restored, i. e. the X-ray diagram was found to be practically indistinguishable from that obtained before the highest temperature treatment.

All the operations were carried out in alumina crucibles discarding the pellets which were in contact with the walls during the heatings.

These experiments show that, starting from an initial system containing either an oxide (Fe_2O_3) with a relatively high chemical potential of oxygen in equilibrium, or an oxide (NbO) with a relatively low chemical potential, after equilibration, only NbO_2 is capable of existence with both iron and the ε-phase and thus $Fe + Fe_{7-y}Nb_2 + NbO_2$ can be considered as the true equilibrium system.

EMF Measurements

The previous equilibration experiments determined the electrochemical chain as

$$\mathrm{Pt}\,\Big|\,\mathrm{Fe}+\mathrm{Fe}_{0,95}\mathrm{O}\,\Big|\,\begin{matrix}\mathrm{ThO_2}\\(+\mathrm{LaO}_{1,5})\end{matrix}\,\Big|\,\mathrm{Fe}+\mathrm{Fe}_{7-y}\mathrm{Nb}_2+\mathrm{NbO}_2\,\Big|\,\mathrm{Pt}$$

which means that the corresponding electrochemical processes may be represented by the overall reaction

$$4\,\mathrm{Fe}_{0,95}\mathrm{O}+\mathrm{Fe}_{7-y}\mathrm{Nb}_2 \rightleftarrows (10.80-y)\ \mathrm{Fe}+2\,\mathrm{NbO}_2\,. \tag{5}$$

This involves the transport of four oxygen ions throughout the intermediate electrolyte, i. e. eight electrons in the external circuit; so, the e.m.f. of the cell, E, measured from left to right, is related to the standard molar free energy of formation, ΔG_f^0, of the various phases by the equation

$$4\,\Delta G^0_{\mathrm{f,\,FeO_{0,95}O}}+\Delta G^0_{\mathrm{f,\,Fe_{7-y}Nb_2}}-2\,\Delta G^0_{\mathrm{f,\,NbO_2}}=8\,F\,E. \tag{6}$$

Apparatus and Materials

The elements of the galvanic chain consist of cylindrical pellets of about 12 mm diameter and 3 – 4 mm thickness.

The Fe+"FeO" pellets were made up by thoroughly blending Fe and Fe_2O_3 powders, the mixture having a global oxygen content of about 15 at. %. After pressing at about 10 tons/cm^2, they were vacuum-treated at 1250 °K for 24 hours.

The tablets of the 15 mole % of $LaO_{1.5}$ in ThO_2 solid solution were obtained as follows. From the nitric solution of thorium and lanthanum ions, the hydroxides were precipitated with concentrated ammonia. They were then washed, dried and calcined at 1300 °K. The powder was then pressed at 10 tons/cm^2 and the pellets fired under vacuum at ≈ 2000 °K for eight hours. They were then annealed overnight at 1470 °K in air and, after this treatment, their grey colour turned to orange. A further prolonged heating at 1270 °K under vacuum changed again the colour to white. They are hard, brittle and compact, showing a waxy appearance.

The $Fe + \varepsilon$-phase $+ NbO_2$ pellets were those employed in the equilibrating experiments. Furthermore there were prepared some other ones by mixing pure iron and niobium (atomic ratio 10 : 1) without adding any oxide. After a 10 hours vacuum treatment at 1400 °K, X-ray analysis showed the presence of only iron and ε-phase.

Before assembling in the cell, the pellets were polished with very fine diamond paste, after embedding in plastics to assure a good flatness of the surfaces.

The cell is shown in Fig. 2. A description of the e.m.f. measuring and recording device was given previously [5].

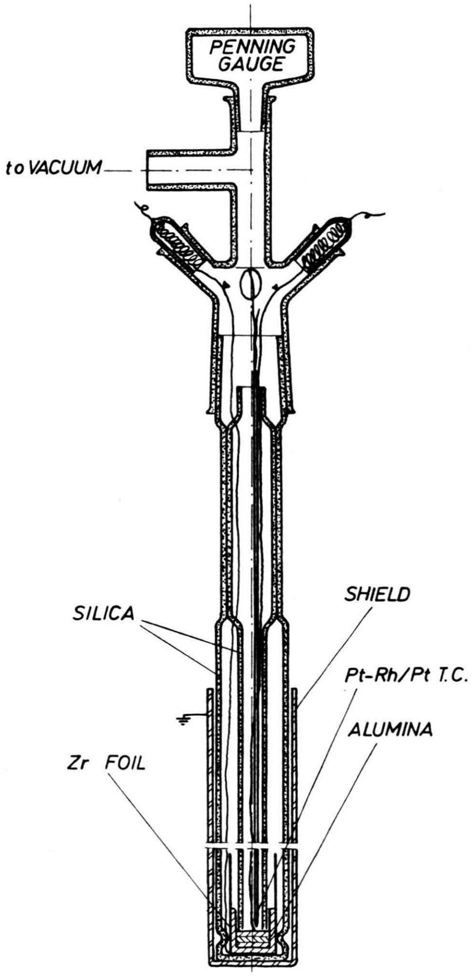

Fig. 2. The cell assembly.

Results and Discussion

The stationary open circuit voltage supplied by this cell is poorly reproducible and remarkable depending on the residual gas pressure in the cell. These spurious potentials arise from the concurrence of surface chemical oxidation due to oxygen impurities in the gas phase and diffusion of the oxidation products into the bulk materials and viceversa. If the oxidation rate is sufficiently fast, the presence of the three phase system cannot be maintained at the interface with thoria.

A wrapping of a zirconium foil around the alumina crucible containing the pellets improves the situation, resulting in an increase of the long-time stationary electrical potential, since this oxygen getter lowers the rate of oxidation; nevertheless, this artifice, in this case, did not assure the oxygen residual pressure to be so low as to exclude the possibility of establishment of mixed potentials.

Therefore a non-stationary technique was adopted. The conditions of applicability of this technique were stated and its reliability confirmed previously (l. c. [5, 10]). It consists of a cathodic polarization of the $Fe + Fe_{7-y}Nb_2 + NbO_2$ electrode obtained by forcing a constant current to flow through the cell, thus yielding the reduction of the niobium oxide at the thoria interface. After the current is interrupted ($t = t_0$) the e.m.f. decay curve is recorded.

At $t > t_0$, the processes occurring at the interface with thoria are mainly 1st) the recombination of the thin niobium metal layer resulting from the cathodic reduction with both the iron excess present at the interface and the iron coming by diffusion from the bulk and 2nd) the oxidation of the intermetallic phase to niobium dioxide by oxygen impurities of the gas. If the temperature is sufficiently high and the oxygen residual pressure sufficiently low, the formation of the intermetallic phase is practically completed and niobium metal combined with the iron excess before the contact with thoria is completely covered by a new niobium oxide oxidation layer. In order to attempt this condition, it is necessary that the contact between the thoria and the electrode pellets be as good as possible and the residual oxygen pressure as low as possible; this was achieved by making up pellets having perfectly flat surfaces and by using also an oxygen getter.

[10] G. B. Barbi, Trans. Faraday Soc. **62**, 1589 [1966].

In fact, a good "true" contact, together with high vacuum conditions hamper the influence of the oxidizing gas phase.

NbO eventually formed from NbO_2 and niobium, coming from the cathodic reduction, before its complete combination with iron, should finally transform into the most stable oxide NbO_2.

Under these conditions, it is possible to maintain, even for a long time, the simultaneous presence of Fe, ε-phase and NbO_2 at the interface with the solid electrolyte and thus a constant, well-defined electrical potential difference, since, at a given temperature, the presence of a three phase, three component system fixes the values of the oxygen thermodynamic activity.

This situation lasts as long as some intermetallic compound is present at the thoria interface, i. e. as long as oxygen impurities have not completely consumed the intermetallic phase by oxidation of its niobium to niobium dioxide at the interface with thoria; afterwards, a further decay in the E vs. t curve takes place, E reaching, after a long time, the stationary, above-mentioned, ill-defined potentials.

In Figs. 3 – 7 some e.m.f. decay curves, obtained at different temperatures after different cathodic polarization intensities (currents × times) are reported. These plots show that the rest potential portions of the decay curves last for a time well sufficient to perform a precise measurement of the rest-potential.

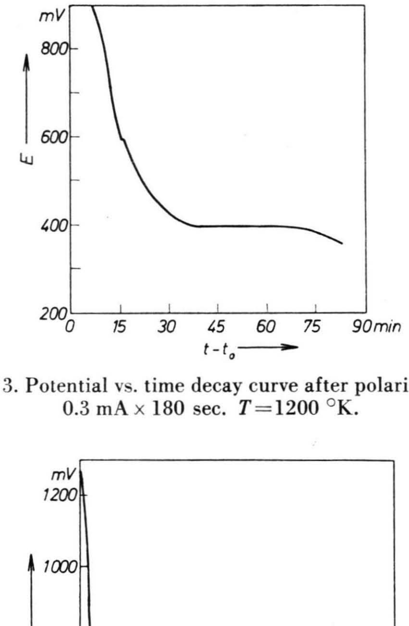

Fig. 3. Potential vs. time decay curve after polarization 0.3 mA × 180 sec. $T = 1200$ °K.

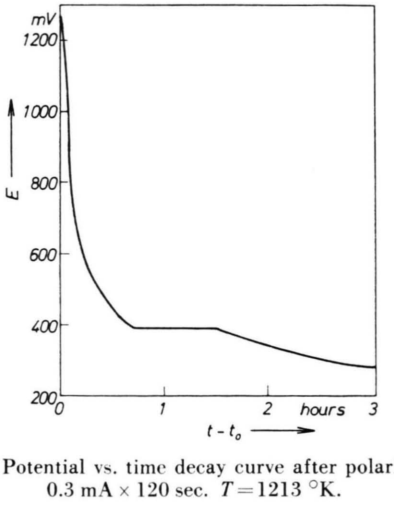

Fig. 4. Potential vs. time decay curve after polarization 0.3 mA × 120 sec. $T = 1213$ °K.

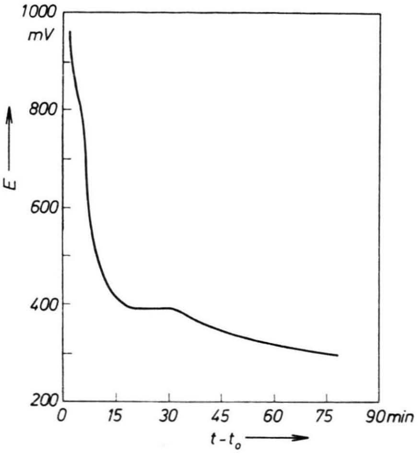

Fig. 5. Potential vs. time decay curve after polarization 1 mA × 60 sec. $T = 1241$ °K.

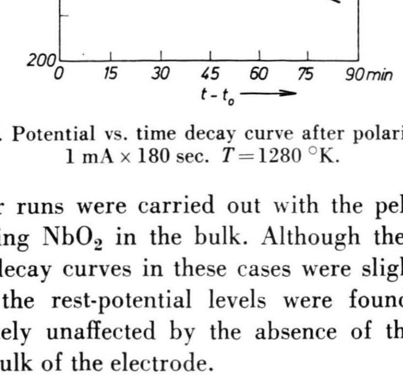

Fig. 6. Potential vs. time decay curve after polarization 1 mA × 180 sec. $T = 1280$ °K.

Other runs were carried out with the pellets not containing NbO_2 in the bulk. Although the shapes of the decay curves in these cases were slightly different, the rest-potential levels were found to be completely unaffected by the absence of the oxide in the bulk of the electrode.

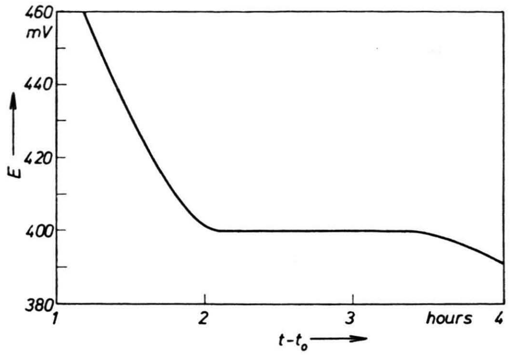

Fig. 7. Potential vs. time decay curve after polarization 0,1 mA × 120 sec. $T=1126$ °K.

The length of the rest-potential portion of the decay curve, but not the corresponding E value, increases as the total polarization intensity increases and the residual oxygen pressure decreases. Figure 8 shows a cumulative plot of the rest potential values versus temperature for different runs containing and not containing NbO_2 in the bulk electrode.

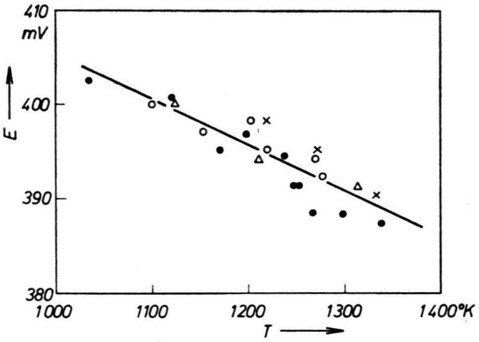

Fig. 8. Rest potential values vs. temperature (different symbols refer to different runs).

A least squares, best-fit program yields the equation:

$$E(\mathrm{mV}) = 455.9 - 50.2 \cdot 10^{-3}\, T\ (^\circ\mathrm{K}). \qquad (7)$$

Taking the thermodynamic data for the standard (Gibbs) free energy of formation of $Fe_{0,95}O$ in the interval 1000 – 1400 °K [11]

$$\Delta G^0_{\mathrm{f,\,FeO_{0,95}O}} = -63.23 + 15.54 \cdot 10^{-3}\, T \text{ cal/mole} \qquad (8)$$

and introducing Eqs. (3), (7) and (8) in Eq. (6), gives:

$$\Delta G^0_{\mathrm{f,\,Fe_{7-y}Nb_2}} = -34.0 + 6.5 \cdot 10^{-3}\, T \text{ kcal/mole.}$$

This corresponds to a standard free energy of formation from the elements of $-3.77 + 0.72 \cdot 10^{-3}\, T$ and $-5.66 + 1.09 \cdot 10^{-3}\, T$ kcal/atom for the extreme values $y=0$ and $y=3$ respectively.

Remark

Obviously, the applicability of the non-stationary, two-electrodes technique is conditioned by a rapid interdiffusion overall process at the anodic interface.

Polarization experiments, carried out in a symmetrical Fe + "FeO" cell having calcia-stabilized zirconia as intermediate electrolyte, proved that the interdiffusion depolarization processes are considerably faster than those involved at the $Fe + Fe_{7-y}Nb_2 + NbO_2$ interface in cell (4), thus assuming, under our polarization intensity conditions and temperatures, that the Fe + "FeO" electrode behaves, after a reasonably short time, as a potential determining, oxygen reference electrode [12].

Acknowledgement

The author thanks Dr. H. W. SCHLEICHER for a discussion and E. CAZZANIGA for X-ray analyses.

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[11] JANAF, Thermochemical Tables Addendum PB-168/370-1, Clearinghouse 1966.

[12] G. B. BARBI, unpublished results.