

Oxidation of dissolved iron in platinum

Oksidacija železa, raztopljenega v platini

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Abstract: Platinum is used as material for high temperature applications as sensors and heating elements. For example, the most vital parts of the simultaneous thermal analysis device (STA) are commonly made of platinum: thermocouples and platinum sample holder. STA is a combination of two thermal analysis techniques: thermogravimetry (TG) and differential scanning calorimetry (DSC). An uncontaminated holder is needed in TG analysis by which mass change of examined sample is determined as function of temperature and time. When holder is exposed to various steels (especially low alloyed steels) at higher temperatures there exists some risk of contamination of measuring parts (made of platinum) with elements, especially if measurements take place without a proper protection of the sample holder (cover on crucible, protective atmosphere etc.). When a pure melt of elements like iron is in contact with platinum sample holder, local contamination occurs. Dissolved iron can oxidize in the platinum holder. Heat transfer from heating elements to platinum and further to examined sample is changed. Contamination also affects obtained thermogravimetric curves.

Izveček: Platina se večinoma uporablja v visokotemperaturnih aplikacijah, v senzorjih ali grelnih elementih. Večina vitalnih delov simultane termične analize (STA) je narejena iz platine: termoelementi in nosilec. STA je kombinacija dveh termičnih analiz: termogravimetrije (TG) in diferenčne vrstične kalorimetrije (DSC). Za ugotavljanje sprememb mase preiskovanega vzorca uporabljamo TG-analizo v odvisnosti od časa in temperature. Meritve se morajo izvajati s

čistim nosilcem. Izpostavljanje nosilca različnim jeklom (predvsem malolegiranim) pri višjih temperaturah lahko povzroči kontaminacijo merilnih (platinastih) delov, kadar zaščita platinastega nosilca ni ustrezna (pokrivanje lončkov, zaščitna atmosfera itd.). Taljenje železa v platinastem nosilcu povzroči lokalno kontaminacijo. Raztopljeno železo se lahko v platinskem nosilcu oksidira ter spremeni prenos toplote iz grelnih elementov na platino, obenem pa ima kontaminacija tudi vpliv na meritve termogravimetričnih krivulj.

Key words: thermodynamics, oxidation, platinum

Ključne besede: termodinamika, oksidacija, platina

INTRODUCTION

Knowing the activity of iron in the Pt-Fe binary system the calculation of equilibrium partial pressure of oxygen for metal oxides can be done. Calculation was done with the known data of iron activity a_{Fe} in the Fe-Pt binary phase system. Some data can be found in references (Gudmondsson and Holloway).^[1] In this paper thermodynamic calculations were performed using a_{Fe} , at different temperatures, with the TCW4 software. Many authors were studying oxidation (of iron) and the importance of mass gain for protection of material itself by adding modifiers.^[2, 3] This paper deals with analysis of mass reduction of oxides due to oxide reduction process.

Phase diagram in Figure 1 represents the Fe-Pt binary phase diagram. If contamination of platinum holder with iron is rather high, some intermediate phases can be formed (Pt_3Fe , PtFe and

Fe_3Pt). When mole fraction of iron is higher than $x_{\text{Fe}} = 0.2$, the liquidus temperatures are below 1550 °C which usually represents the maximum temperature for examination of steels with the STA device. Result is possible presence of iron in platinum sample holder.

THERMODYNAMIC CALCULATIONS

Thermodynamics of iron oxidation

Pourbaix diagrams are known as the high temperature oxidation temperature diagrams or the predominance diagrams with multivariate equilibria between elements and their oxides or between two oxides as a function of equilibrium partial pressure of oxygen and the temperature of system.^[4] This diagram enables to study behavior of multivariate oxide system, in our case system of iron oxides (wüstite, hematite, magnetite) that are formed on contaminated platinum. Equilibrium of each reaction (oxidation) is determined by:

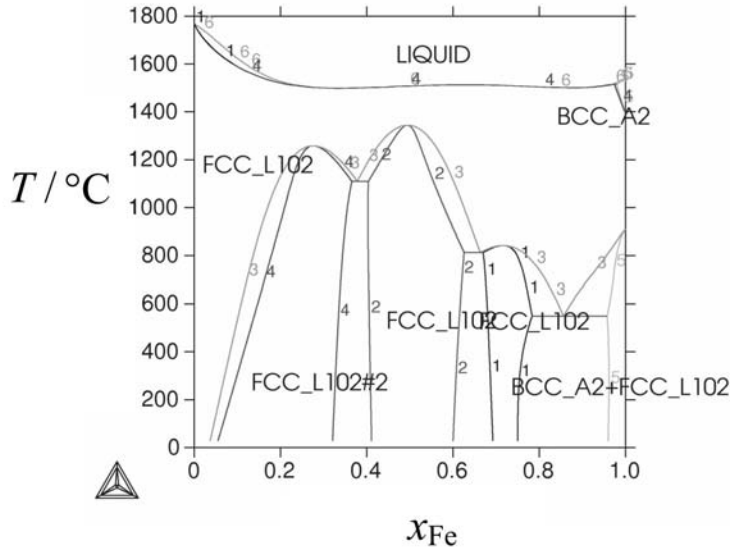


Figure 1. Binary phase diagram Fe-Pt

$$\Delta G^0 = -RT \ln K$$

$$(1) \quad \Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 = -RT \ln f + RT \ln p_{O_2} \quad (4)$$

where is:

R – gas constant (8.3144 J/mol K),

T – temperature (K),

K – equilibrium constant.

For the reaction of oxidation:



$$(2) \quad \ln p_{O_2} = \frac{\Delta H^0}{RT} + \ln f - \frac{\Delta S^0}{R} \quad (5)$$

where:

R – reactant and

P – product,

equation 1 can be rewritten as:

$$\Delta G^0 = -RT \ln \frac{a_P^y}{a_R^x p_{O_2}} \quad (3)$$

where are:

a_P^y, a_R^x – activity of product and reactant. Further:

where $f = a_P^y/a_R^x$ is the predominance ratio. When the ratio is $f \gg 1$ product component in the reaction predominates over equilibrium, if $f \ll 1$, reactant predominates. According to this information, eq. 4 can be rewritten:

In our case the predominance ratio is 1 and the value of $\ln f$ is therefore 0. In this case the Pourbaix diagram is constructed with equal activity coefficients of product and reactant. This means that Pourbaix diagram is constructed only for oxidation of pure and un-dissolved iron. The construction of oxidation predominance diagram is done when all the possible reactions are col-

lected with known values of enthalpies and entropies of formation, ΔH^0 and ΔS^0 (BARIN & KNACKEL^[5]). In this case it can be assumed that ΔH^0 and ΔS^0 are temperature independent. Calculations of these two values are based on the following oxidation reaction:

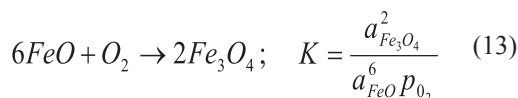
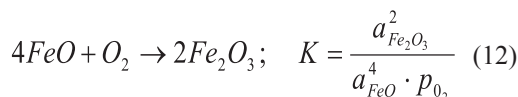
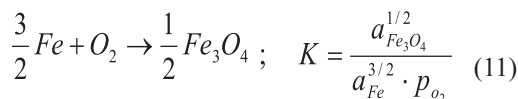
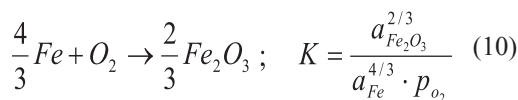
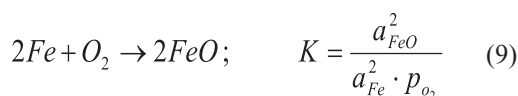


The enthalpy of formation ΔH^0 is calculated by applying the following equations:

$$\Delta H_j^0 = y \cdot \Delta H_{f, M_u O_v}^0 - x \cdot \Delta H_{f, M_a O_b}^0 \quad (7)$$

$$\Delta S_j^0 = y \cdot \Delta S_{f, M_u O_v}^0 - x \cdot \Delta S_{f, M_a O_b}^0 \quad (8)$$

Knowing data of enthalpies and entropies of formation based on the reaction of oxidation, calculation of p_{O_2} can be performed for the possible reactions of oxidation:



where:

a_{Fe} – activity of iron,

$a_{MuOv} = 1$ – activity of oxide,

p_{O_2} – partial pressure of oxygen.

The oxidation affinity in the platinum – iron system

Platinum may be treated as an inert component. Active component in this case is only the dissolved iron in platinum. For calculation of partial pressure of oxygen for formation of oxides from dissolved iron, the activity coefficients are needed (lower values than 1). In this case the predominance ratio f is no longer 1 and it depends on real values of activities of dissolved iron. With the known value of ΔG_T^0 for separate reaction of oxidation, the equilibrium constant of corresponding oxidation condition can be calculated from the eq.1:

$$K = e^{-(\Delta G^0 / RT)} = \frac{a_{M_u O_v}^Y}{a_{Fe}^X \cdot p_{O_2}} \quad (14)$$

Knowing activities the calculation of the partial pressure needed for formation of an oxide can be performed for different temperatures and concentrations of iron dissolved in platinum. The affinity (further A) for oxidation of dissolved iron is calculated from the chemical potential of oxygen which depends on partial pressure of the system (furnace):

$$\mu_{O_2} = \mu_{O_2}^0 + RT \ln a_{O_2} \quad (15)$$

where:

μ_{O_2} – chemical potential of oxygen (depends on partial pressure in the system),

$\mu_{O_2}^0$ – standard chemical potential of oxygen.

If the reference state is 1 bar the activity coefficient of oxygen is equal to the partial pressure $a_{O_2} = p_{O_2}$. The affinity is calculated from the difference of Gibbs free energies between equilibrium partial pressure of oxygen and the pressure in furnace (eq. 16). Negative affinity (A) indicates possible existence of an oxide. Positive affinity represents decomposition of oxide at existent partial pressure of oxygen in the system.

$$A = RT \ln(p_{O_2})_{eq} - RT \ln(p_{O_2}) = RT \ln \frac{(p_{O_2})_{eq}}{(p_{O_2})} \quad (16)$$

EXPERIMENTAL

Measurements of characteristic temperatures were performed with iron 99.8 % pure. The STA 449-C device of Netzsch Company was applied. The maximal temperature reached was 1550 °C at heating rate of 10 K/min, followed by 15 min of holding at 1480 °C. An empty crucible was used as reference. Crucible was made of highly pure Al_2O_3 . After experiment, both crucibles (for sample and reference) were removed from the

platinum sample holder, where contamination was detected. Another TG measurement was done without sample or crucibles. Heating rate was also 10 K/min under inert argon protective atmosphere was applied.

In the case when highly pure argon atmosphere was applied and content of oxygen was known, partial pressure of oxygen was determined to be $p_{O_2} = 10^{-6}$ bar at the total pressure of $p = 1$ bar inside the furnace.^[6]

The effect of contamination of platinum with iron / iron oxide visible on TG curve can be calculated if thermodynamic properties (activities) of the platinum – iron binary system are known. In order to determine the activity of iron in the platinum-iron system a Thermo Calc for Windows (TCW4) with the TC binary solutions database V1 was applied.

Thermodynamic calculation to construct Pourbaix high temperature diagram for un-dissolved iron and its oxides was performed by using equations 9–13. The oxygen affinities for dissolved iron in platinum were calculated by eq. 16 using equations 9–11.

RESULTS AND DISCUSSION

DSC heating curve, Figure 2, of iron revealed that characteristic tempera-

tures slightly differ from the values listed in reference¹. Additional peaks that appeared represented impurities in iron wire. TG heating curve shows drastic drop at the holding temperature 1480 °C which takes place also by further heating to temperature 1550 °C. Contamination of the platinum surface with iron is presented in Figure 3. Because of drastic mass decrease determined by TG curve it was expected that vapors could have contaminated the sample platinum holder. By analyzing TG curve and by removing the crucibles a local contamination was revealed (Figure 3).

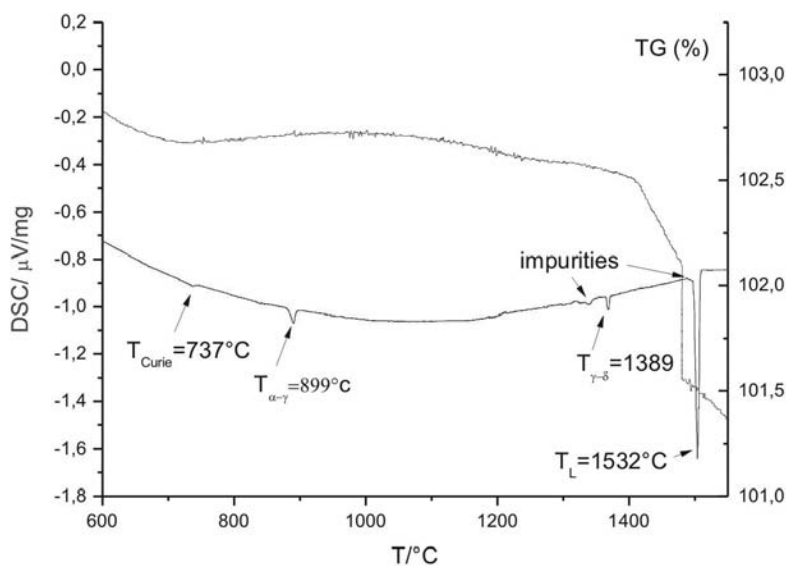


Figure 2. DSC and TG heating curves for iron sample

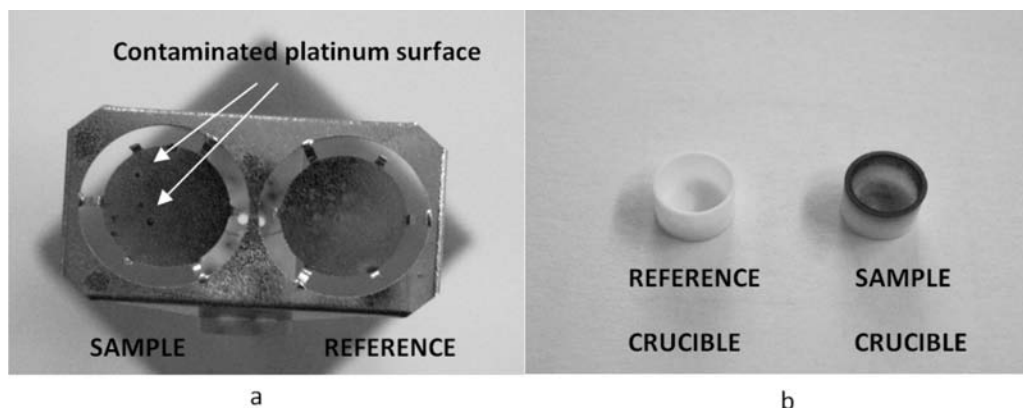


Figure 3. Contaminated platinum sample holder (a), Al_2O_3 crucible (b)

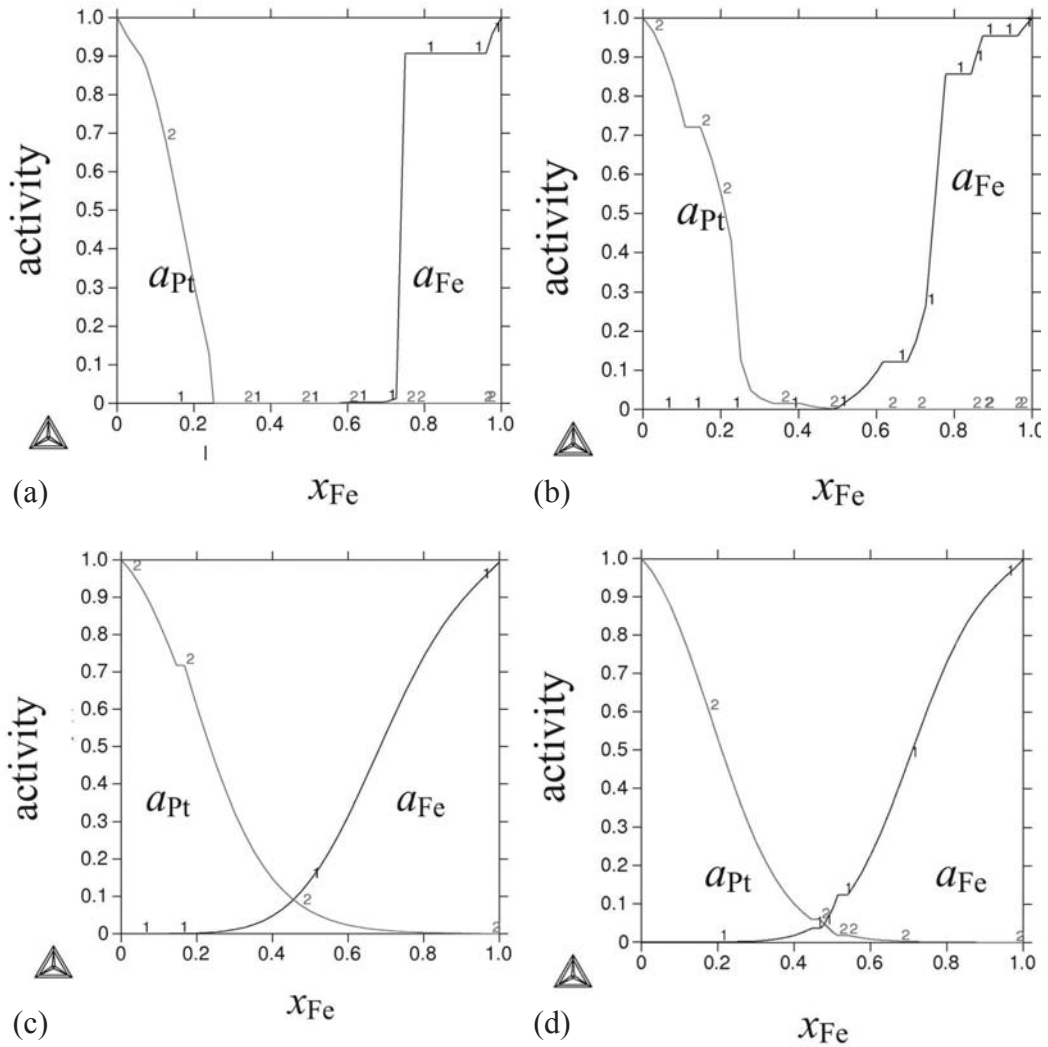


Figure 4. Activity of iron in the Pt-Fe binary system: at 50 °C (a), 600 °C (b), 1300 °C (c) and 1550 °C (d)

Values of iron activity coefficients vary with composition and temperature (Figure 4). The activity of iron in the temperature range from 50 °C to 1550 °C is mostly lower than that of ideal solution where ($a_{\text{Fe}} = x_{\text{Fe}}$), and typical for systems with intermediate phases.

Thermodynamic calculations indicate formation of oxides in the temperature range between 700 °C and 4000 °C, based on possible reactions of oxidation, Figure 5. Figure 5 shows that most probable reaction in oxidative atmosphere will take place by oxidation

of iron to hematite at lower temperatures (≈ 800 °C) and further oxidation of wüstite to hematite at higher temperatures ($> \approx 800$ °C). Decomposition of the formed oxide to elementary iron is not possible at the system's partial pressure of oxygen ($p_{O_2} = 10^{-6}$ bar) and the maximum temperature 1550 °C. At least 1700 °C is needed for decomposition of the high temperature oxide FeO. At the temperature around 1700 °C, FeO decomposes to elementary iron and oxygen that is swept off with argon purge gas. At higher temperatures (> 1700 °C), the less stable reaction in this system is further oxidation of FeO to the higher oxide of Fe_2O_3 . Temperature of decomposition will be different if iron is dissolved in platinum.

Partial pressure of oxygen that is needed for oxidation (colored regions) of dissolved iron in platinum is presented in Figure 6. The diagrams show that much lower partial (dissociation) pressures of oxygen in the system are needed for decomposition of formed oxides in pure iron and in the region of higher iron contamination. From Figure 6, the partial pressure of oxygen in the furnace, $p_{O_2} = 10^{-6}$ bar, is already low enough to achieve decomposition of formed iron oxide in the regions with small iron molar content. For complete decomposition of formed oxides in all concentration regions, at rather low temperatures, proper vacuum system should be used. The use of vacuum during heating has

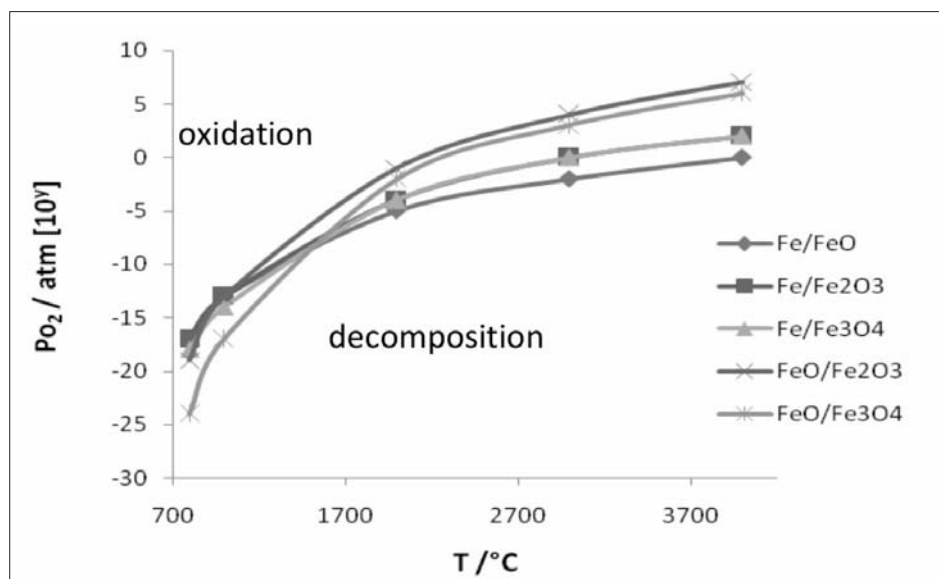


Figure 5. Pourbaix high temperature diagram for un-dissolved iron and its oxide

also effect on evaporation of other elements in the investigated samples and as consequence possible contamination with new elements and formation of new and more complex oxides with the existing one. Nevertheless, when system's temperature is increased high enough thermodynamically calculated partial pressure of oxygen in the Pt-Fe system shows that all the oxides are less stable in some point and eventually they decompose.

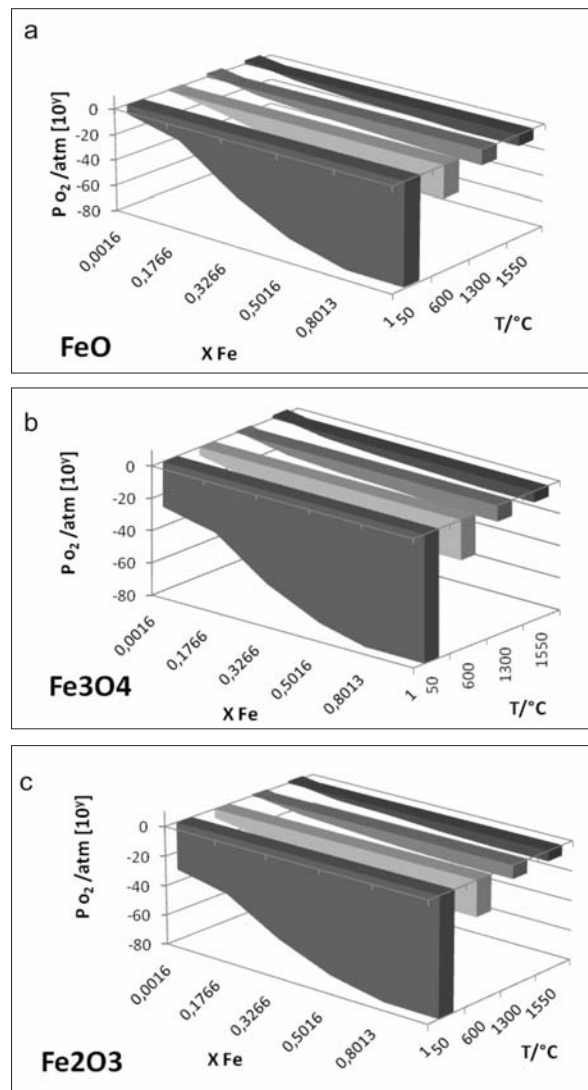


Figure 6. Pourbaix high temperature diagram for the Pt-Fe binary system at different temperatures: FeO (a), Fe₃O₄ (b) and Fe₂O₃ (c)

Oxygen affinities for dissolved iron were calculated with the eq. 16 and the results are presented in Figure 7 for four different temperatures of the system. At 50 °C, the calculated oxygen affinities are negative for all the three oxides formed according to eqs. 9, 10 and 11 and as that all thermodynamically possible. Both formed oxides, Fe_2O_3 and Fe_3O_4 are thermodynamically more possible as FeO . With increased system's temperature to 600 °C, Figure 7 b, the first dissociation can appear if FeO is present. From Figure 7 b, affinities of Fe_2O_3 is more negative than the affinity of Fe_3O_4 and FeO in regions of small iron

content ($x_{\text{Fe}} < 0.05$). That means that the Fe_2O_3 oxide is most probable and will began to decompose at 600 °C. Nevertheless, first mass decrease is expected at 600 °C regardless on the type of existed iron oxide. From Figure 7 c, d, the decomposition of iron oxides will take place in regions with higher iron contaminations if temperatures are higher than 600 °C. When riching the maximum temperature in furnace, 1550 °C, the absolute dissociation of formed iron oxide FeO in regions of higher iron content is impossible as a consequence of rather low temperature reached inside furnace and low partial pressure, seen also in Figure 5, 6.

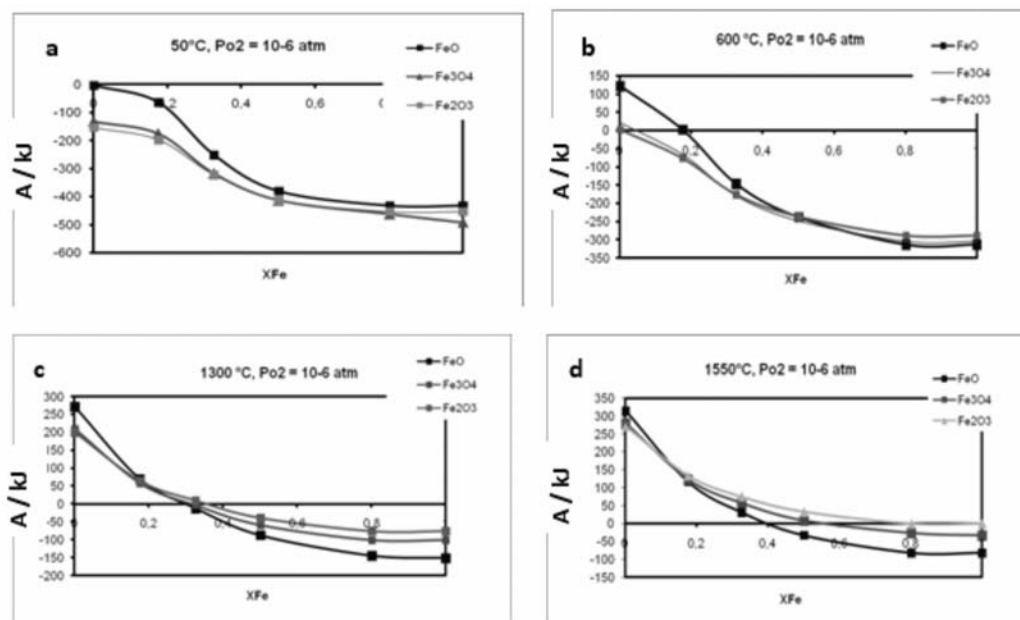


Figure 7. Diagram of oxygen affinities at various temperatures : 50 °C (a), 600 °C (b), 1300 °C (c) and 1550 °C (d)

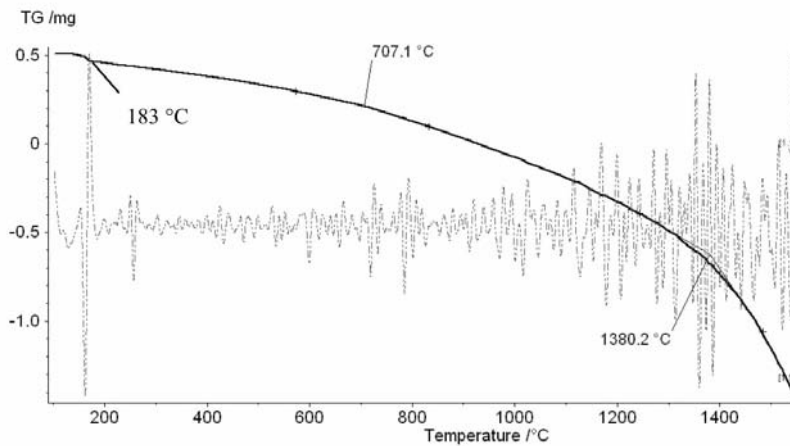


Figure 8. TG heating curve of an empty and of contaminated platinum sample holder

TG heating curve of an empty and of contaminated platinum sample holder after exposure to iron containing samples is presented in Figure 8. First peak appears at 183 °C as result of loss of humidity inside the furnace. At temperature 707 °C, the first reduction of mass was determined as a consequence of reduction of formed iron oxides. Figure 7b shows that most probable decomposition takes place with the hematite in concentrations under $x_{\text{Fe}} = 0.1$. The second reduction of mass, at 1380 °C, indicated a higher local contamination or longer reduction time of formed oxides. Figure 7 c shows that all three oxides can contribute to the mass decrease in TG curve. At higher temperatures, 1550 °C the most probable decomposition of wüstite takes place in the regions up to $x_{\text{Fe}} = 0.4$.

CONCLUSIONS

Process of oxide decomposition is complex and not sudden. The partial pressure of oxygen in the system is high enough, that oxides will not decompose to elementary iron in all concentration regions. The first change in the TG curve was expected to be at temperatures above 600 °C which is in good agreement with our experimental results. Plotted TG curve shows first visible mass decrease as a result of decomposition of hematite to elementary iron, at 707 °C, followed by continuous drop of the TG curve with decomposition of magnetite and wüstite. When contamination with other elements is present, the characteristic TG curve is changed again. And to eliminate phenomena that are not in relation to the

measured sample, basic curve should be recorded without a sample.

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