Remarks on the Formation of Different Types of Scales on 'Pure' Metals

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ABSTRACT

Different types of scales on metals were discussed in terms of thermodynamics, crystallographic structure as well as ionic and electronic imperfections in the metal-oxide system. Equilibrium pressure of the oxidant was related to the bond energy of phases coexisting in equilibrium by means of standard free enthalpies of cohesion. This approach made it possible to explain why magnetite (Fe_3O_4) is formed on iron at temperatures lower than 855 K and wustite ($Fe_{0.947}$) at higher temperatures. The reasons for phase transformations in oxides occurring as a result of increasing oxidant activity or temperature were discussed with reference to the structure of electronic and ionic defects and related changes in the crystallographic structure.

1. INTRODUCTION

The composition and morphology of scales on metals are generally well described in the literature /1-5/. When 'pure' metals oxidize and no impurities are present at interphases (local equilibrium is maintained), the composition of each scale layer should be consistent with the metal-oxidant phase diagram /1,6/. Most of the corrosion handbooks do not discuss unusual cases when different oxide phases coexist with metal, e.g. iron and different iron oxides. Stability ranges of oxide phases (oxidant pressures) are also surprisingly diversified. The explanations are not always satisfactory. Some detailed problems are dealt with in the literature but in the available handbooks on solid state chemistry or corrosion they are not given much attention /1-6/.

In this work the authors attempt to explain the formation of compounds with different metal/oxidant ratio (M/X) on metal surface and phase transformations of compounds as a result of oxidant activity changes, with reference to the thermodynamics of metal-oxidant systems and to the structure of point defects.

2. TYPE OF COMPOUND IN EQUILIBRIUM WITH METAL

On analyzing different phase diagrams, e.g. metal-oxygen systems, we can notice that metal coexists with one of the following oxide phases: M_2O, MO, M_3O_4 or MO_2. These compounds have different metal/oxidant ratios and their composition is generally related to the lowest stable oxidation number of metal. There are some exceptions though; e.g. sulfidation of nickel leads to the formation of Ni_3S_2, sulfidation of cobalt – to Co_9S_8, where metal ions occur with different oxidation numbers. Another exception is observed in the case of oxidation of iron when up to 855 K the only oxidation product is Fe_3O_4 and at higher temperatures – $Fe_{0.947}O$. How to explain this behavior?

Let us first consider iron oxidation. The formation of two different oxide phases can be described in the following way:

$$3/2\ \mathrm{Fe} + \mathrm{O_2} = ½\ \mathrm{Fe_3O_4} \qquad \Delta G_1^o = ½\ \Delta_f G^o_{Fe_3O_4} \qquad (1)$$

$$1{,}894\ \mathrm{Fe} + \mathrm{O_2} = 2\ \mathrm{Fe_{0.947}O} \qquad \Delta G_2^o = 2\,\Delta_f G^o_{FeO} \qquad (2)$$

Reactions written in this way allow comparison of the quantities of oxides in which iron combines with one mole of oxygen. From the point of view of thermodynamics the reason for the formation of Fe_3O_4 (at temperatures lower than 855 K) is that the value of ΔG_1^o for reaction (1) is more negative than ΔG_2^o for $Fe_{0.947}O$ ($2\Delta_f G^o_{FeO}$). A question arises however: what components decide about the value of $\Delta_f G^o$ of the considered oxides?

Let us imagine the following chemical equilibria: iron in equilibrium with iron vapor, oxygen dissociation and reaction that defines cohesion energy of a given oxide phase. For Fe_3O_4 these reactions are:

$$3/2\ \mathrm{Fe_{(cry)}} = 3/2\ \mathrm{Fe_{(g)}} \qquad \Delta G_3^o = 3/2\,\Delta G^o_{sub\ Fe} \qquad (3)$$

$$\mathrm{O_2} = 2\ \mathrm{O_{(g)}} \qquad \Delta G_4^o = \Delta G^o_{dis\ O_2} \qquad (4)$$

$$3/2\ \mathrm{Fe_{(g)}} + 2\ \mathrm{O_{(g)}} = 1/2\ \mathrm{Fe_3O_{4(cry)}}$$
$$\Delta G_5^o = -1/2\,\Delta G^o_{coh\ Fe_3O_4} \qquad (5)$$

whereas for wustite, $Fe_{0.947}O$

$$1.894\ \mathrm{Fe_{(cry)}} = 1{,}894\ \mathrm{Fe_{(g)}} \qquad \Delta G_3^o = 1.894\,\Delta G^o_{sub.Fe} \qquad (3')$$

$$1.894\ \mathrm{Fe_{(g)}} + 2\ \mathrm{O_{(g)}} = 2\ \mathrm{Fe_{0.947}O_{(cry)}}$$
$$\Delta G_6^o = -2\ \Delta G^o_{coh.\ FeO} \qquad (6)$$

Standard free enthalpy of formation for the discussed oxides will therefore depend on standard free enthalpies of reactions (3)-(6) in the following way:

- for Fe_3O_4

$$\Delta G_1^o = ½\ \Delta_f G^o_{Fe_3O_4} =$$
$$-(1/2\,\Delta G^o_{coh.\ Fe_3O_4} - 3/2\ \Delta G^o_{sub\ Fe} - \Delta G^o_{dis.O_2}) \qquad (7)$$

- and for wustite

$$\Delta G_2^o = 2\ \Delta_f G^o_{FeO} =$$
$$-(2\ \Delta G^o_{coh.FeO} - 1{,}894\ \Delta G^o_{sub.Fe} - \Delta G^o_{dis.O_2}) \qquad (8)$$

As mentioned above, the type of oxide phase in equilibrium with iron depends on standard free enthalpies of formation of these phases and their dependence on temperature. Equations (7) and (8) show that the formation enthalpy of the oxides is a difference between the free enthalpy of cohesion and free enthalpy of metal sublimation and of oxidant molecule dissociation, i.e. atomization of phases in equilibrium. Fig. 1 presents temperature dependence of standard free enthalpy of iron sublimation and oxygen dissociation, standard free enthalpies of formation for $Fe_{0.947}O$ ($2\,\Delta_f G^o_{FeO}$) and Fe_3O_4 ($½\ \Delta_f G^o_{Fe_3O_4}$) and free enthalpies of cohesion of these oxides calculated from equation (7) and (8), on the basis of available thermodynamic data /7-9/. As can be seen, the standard free enthalpy of iron sublimation and oxygen dissociation remarkably changes with temperature. Different amount of iron necessary for the formation of these oxides brings about quite big differences in ΔG^o_{sub}. Due to a larger amount of iron in $Fe_{0.947}O$, there are also differences in free enthalpies of cohesion

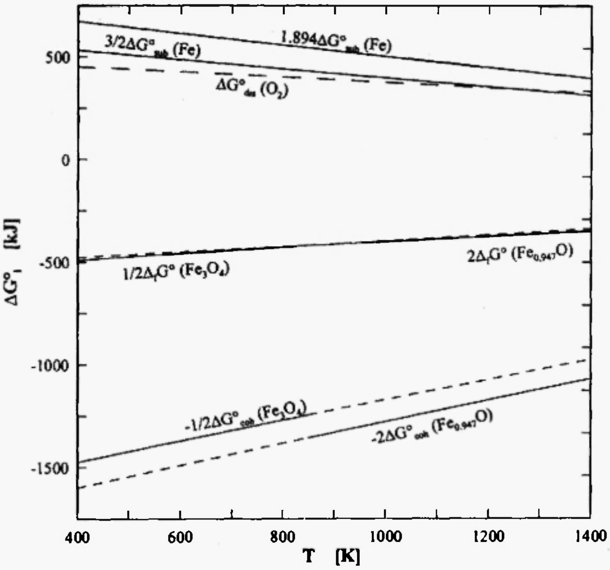

Fig. 1: Temperature dependence of standard free energy of iron sublimation ($\Delta G^o_{sub\ Fe}$) and oxygen dissociation ($\Delta G^o_{dis\ O_2}$), standard free enthalpy of cohesion (ΔG^o_{coh}) and standard free enthalpy of formation ($\Delta_f G^o$) for Fe_3O_4 and $Fe_{0.947}O$

(ΔG^{o}_{coh}) related to bond energy in oxide crystal lattices. The differences in the values of the above functions cause functions describing temperature-dependences of standard free enthalpy of formation of the oxides ($\Delta_f G^{o}$) to have different slopes and to intercept at 855 K. From thermodynamic calculations it follows therefore that up to 855 K the energy gain related to the formation of magnetite, Fe_3O_4, minus free enthalpy of iron sublimation and oxygen dissociation, is bigger than in the case of $Fe_{0.947}O$ formation. The opposite is true when temperature exceeds 855 K. If, at lower temperatures, the free enthalpy of cohesion were more negative for wustite, this phase would form instead of Fe_3O_4.

The formation of Fe_3O_4 on iron can be explained on the grounds of crystallographic structures. Wustite ($Fe_{1-y}O$) has a cubic structure, while Fe_3O_4 has a spinel structure. In both oxides, in spite of different composition ($Fe_{0.947}O$, $Fe_{0.75}O$), the oxygen sublattice is identical; i.e. face centered cubic A1 /11/. Iron ions in wustite take mainly the octahedral positions, but a small number of interstitial iron ions forms complexes with cation vacancies ($4V_{Fe}Fe_i$) /12-14/. In magnetite the octahedral and tetrahedral sites of the A1 structure are occupied in the way typical of spinels. Because of the lower amount of iron in magnetite compared to wustite a significant number of these sites remains vacant. Up to 855 K iron coexists with Fe_3O_4, which has a more loosely packed structure, compared to wustite. At higher temperature the vibrations of atoms increase which must lead to weakening of the interatomic bonds. A slight rearrangement of the crystal lattice brings about formation of an oxide phase with closer distances of iron atoms, which raises the cohesion energy. At temperatures lower than 855 K, the repulsive interactions between the iron ions in wustite become so strong that rearrangement of crystal lattice must take place toward the magnetite structure, which contains less iron ions.

The example given above can answer the question why, in many systems, oxide phases with a higher chemical potential of metal (e.g. M_2O) are not formed at all or why gaseous products coexist with metal. When the interactions between the metal ions in their oxides are too strong, e.g. Cr, Mo, Zr, W, the MO-type solid phase is not formed at all. Instead oxides with a loosely packed structure are formed, such as M_2O_3 or MO_2. Formation of MO-type oxides might be possible at very high temperatures. Weakening of the repulsive interactions between metal ions by anions with a bigger radius, such as sulfur, makes possible formation of solid phases of MS-type on the majority of these metals (Pt, Ru, Rh, Os) or formation of sulfides richer in metals, such as Ni_3S_3 or Co_4S_3 in the case of nickel and cobalt.

3. MULTIPHASE SCALES – STABILITY RANGE OF PHASES

Another problem worth consideration concerns point defects in oxidation products of metals, and dependence of their concentration on oxidant pressure or the formation of multiphase and multilayer oxide scales. Which parameters affect the activity of oxidant at interphases and the stability range of each phase? Let us first consider the thermodynamics of the system. When local equilibria are maintained at interphases the scale layers have composition consistent with the phase diagram. For simplification let us assume that the only point defects in the oxide phases are cation vacancies and that there is a concentration gradient of ionic defects across the scale layer. Let us assume further that the oxide phase in equilibrium with metal is practically stoichiometric (defect free) and that the same is true for consecutive oxide phases in equilibrium with the oxide having a higher chemical potential of metal. The equilibria in such a multilayer oxide system can be expressed by the following reactions, in which one oxygen molecule takes part:

$$4M + O_2 = 2M_2O \quad \Delta G^{o}_{0} \tag{9}$$

$$2/(1-\delta)M_{2-\delta}O + O_2 = (4-2\delta)/(1-\delta)MO \quad \Delta G^{o}_{0} \tag{10}$$

$$6/(1-4x)M_{1-x}O + O_2 = (2-2x)/(1-4x)M_3O_4 \quad \Delta G^{o}_{1} \tag{11}$$

$$4/(1-3y)M_{3-y}O_4 + O_2 = (6-2y)/(1-3y)Me_2O_3 \quad \Delta G^{o}_{2} \tag{12}$$

where δ, *x*, *y* denote deviations from stoichiometry of the respective oxides at interphases. It should be noted that in calculating ΔG^{o} for each reaction, we should use thermodynamic data for the phases in equilibrium, neither those for stoichiometric compounds nor for undefined compositions. Otherwise, especially when highly nonstoichiometric compounds are involved, significant errors might be expected.

The equilibrium constant for each of the reactions (9)-(12) is related to the equilibrium pressure of the oxidant:

$$-\Delta G^o = RT\ln K_i = -RT\ln a_{O_2} = -RT\ln(p_{O_2}/p'(1\ \mathrm{atm})) \qquad (13)$$

Fig. 2 presents temperature dependence of ΔG^o_i for a number of oxide systems. On analyzing these data along with other metal-oxidant systems (oxides, sulfides) one can see that some metals form one oxide phase only, e.g. Ni/NiO, whereas others form multiphase and multilayer scales, e.g. Fe, Ti, V. It can be noticed (eq.(13)) that the equilibrium pressure of the oxidant ($\ln p_{O_2}$) at any interphase is dependent on standard free enthalpies of the above-written reactions. When we consider an equilibrium given by eq.(10) similarly as in the case of iron oxidation, i.e. as a cycle of atomization reactions for the phases in equilibrium:

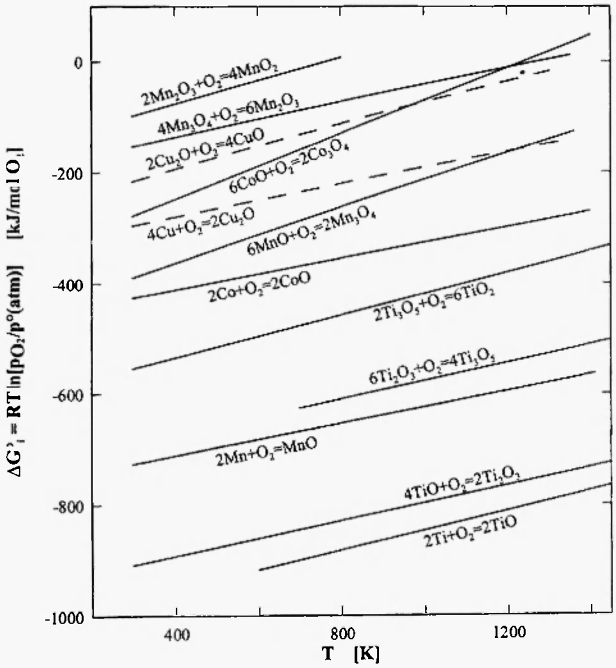

Fig. 2: Temperature dependence of standard free enthalpy of formation and transformation of oxides (equations (9)-(12)) for a number of M-O systems /7,8/.

$$2/(1-\delta)M_{2-\delta}O = (4-2\delta)/(1-\delta)M_{(g)} + 2/(1-\delta)O_{(g)}$$
$$\Delta G^o_{14} = 2/(1-\delta)\Delta G^o_{coh.\,M_2O} \qquad (14)$$

$$O_2 = 2\,O_{(g)} \qquad \Delta G^o_{15} = \Delta G^o_{dis.\,O_2} \qquad (15)$$

$$(4-2\delta)/(1-\delta)M_{(g)} + (4-2\delta)/(1-\delta)\,O_{(g)} = (4-2\delta)/(1-\delta)\,MO$$
$$\Delta G^o_6 = -(4-2\delta)/(1-\delta)\,\Delta G^o_{coh.\,MO} \qquad (16)$$

then the standard free enthalpy of reaction (10) can be expressed as:

$$\Delta G^o_{10} = RT\ln p_{O_2} = -[(4-2\delta)/(1-\delta)\Delta G^o_{coh.\,MO} - 2/(1-\delta)\Delta G^o_{coh.\,M_{2-\delta}O} - \Delta G^o_{dis.O_2}] \qquad (17)$$

which is a difference between the free enthalpy of cohesion in coexisting oxides and free enthalpy of oxygen dissociation. As can be seen from eq. (17), when the oxidant pressure exceeds the equilibrium pressure, the MO oxide is formed. Since the equilibrium pressures are lower than 1 atm, the values of ΔG^o_{10} for reaction (10) will be negative. This fact implies that the following inequality must be satisfied:

$$(4-2\delta)/(1-\delta)\Delta G^o_{coh\,MO} > 2/(1-\delta)\Delta G^o_{coh.M_2O} + \Delta G^o_{dis.O_2} \qquad (18)$$

which indicates that with the increasing oxidant pressure a consecutive oxide phase is formed (MO) with a lower chemical potential of metal. The sum of bond energies in this new phase will be higher in comparison with M_2O. Thus the pressure of oxidant at the interphase depends on the difference between the interaction energy of atoms, referred to the same amount of metal, and the energy necessary for the dissociation of oxidant in order to transform the oxide richer in metal into the oxide with lower chemical potential of metal. The magnitude of this difference between the interaction energies in coexisting phases can be calculated from eq. (17) by subtracting the free enthalpy of oxidant dissociation from the free enthalpy of reaction (1) (ΔG^o_{10}). The obtained functions will be parallel to the lines presented in Fig.2.

In agreement with eq. (13) the curves presented in Fig. 2 illustrate the temperature dependence of the equilibrium pressure of oxidant. It can be noticed that the equilibrium pressures for different metal oxides are strongly diversified. What decides about the stability range of each phase? When we consider the stability range of MO the equilibrium pressures can be calculated from eqs. (11) and (10). Expression (17) applied to reaction (10) and (11) assumes the following form:

$$\Delta G^o_{11} - \Delta G^o_{10} =$$

$$\frac{6}{1-4x}\Delta^{''}G^o_{coh.\ M_{1-x}O} - \frac{2-2x}{1-4x}\Delta^{''}G^o_{coh.\ M_3O_4} - \left(\frac{2}{1-\delta}\Delta^{'}G^o_{coh.\ M_{2-\delta}O} - \frac{4-2\delta}{1-\delta}\Delta^{'}G^o_{coh.\ MO}\right) \qquad (19a)$$

$$\Delta G^o_{11} - \Delta G^o_{10} = RT(\ln p^{''}_{O_2} - \ln p^{'}_{O_2}) = \mu^{''}_{O_2} - \mu^{'}_{O_2} = \Delta\mu_{O_2} \qquad (19b)$$

Thus it can be seen that the differences between the standard free enthalpies of reactions describing the states of equilibrium and thereby oxidant pressures at both interphases depend on the difference between the free enthalpies of cohesion in the coexisting oxides. From eq. (19b) another conclusion can be drawn: the stability range of any oxide phase is mainly related to the range of chemical potential changes of the oxidant in this phase. Fig. 3 shows temperature dependence of the stability range for a number of oxide phases, calculated from eq. (19) on the basis of standard free enthalpies ΔG^o_i for the corresponding equilibrium states /7-10/. The obtained stability ranges are strongly diversified.

4. EFFECT OF IONIC AND ELECTRONIC DEFECTS ON THE PARAMETERS OF PHASE TRANSFORMATION

As stated above, the stability range of any phase depends on the chemical potential of the oxidant, which also influences the type and concentration of point defects (ionic and electronic defects) in the considered phase. On analyzing phase diagrams (log p_{O_2} -1/T), e.g. Fig. 2, we can notice a general rule: when oxidant pressure exceeds the equilibrium value an oxide phase with the highest concentration of metal in the M-O system is formed, i.e. metal is in equilibrium with the oxide having the highest chemical potential of metal. The predominant defects should be interstitial cations if it is possible from the point of view of structure and interactions between the constituent elements. Such imperfections occur in $Zn_{1+y}O$ within the whole stability range /16/. Zinc oxide has a wurtzite type structure (hexagonal B4-type), relatively loosely packed, which can be classified as a covalent structure (possible to derive from the diamond structure /11/). It is not typical of transition metal oxides and results from high polarizability of zinc ions and significant polarization susceptibility of oxygen. In the relatively loose structure of $Zn_{1+y}O$ the zinc interstitials (Zn_i) strengthen the cohesion forces. In other oxides of 3d metals with a NaCl structure, because of close packing of ions, very small (if any) concentration of interstitials can be

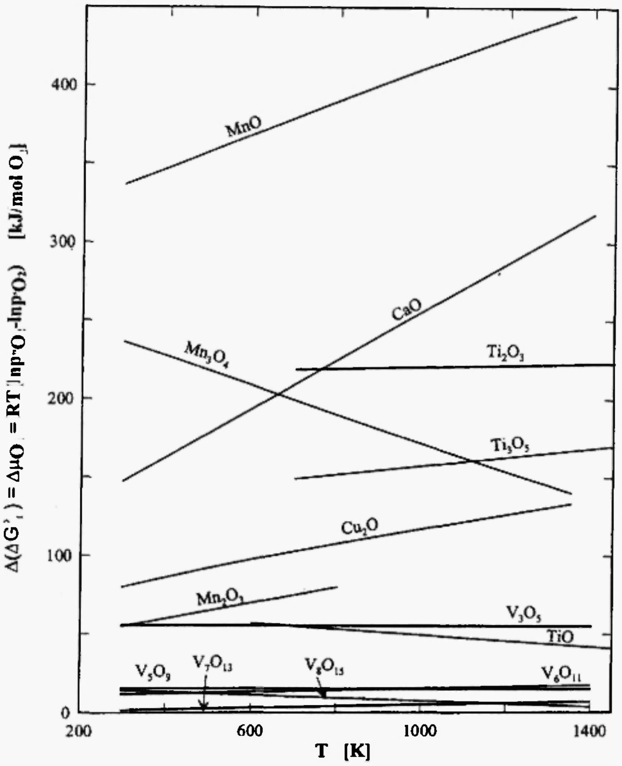

Fig. 3: Temperature dependence of maximum difference of chemical potential of oxygen in the stability range of different oxides calculated from thermodynamic data /7,8,10/.

expected. For instance in MnO at low oxygen pressure the character of electrical conductivity and the sign of thermoelectric power change (n-p transition), which indicates the appearance of interstitial ions near the Mn/MnO interphase /6,16/. In the majority of oxides in equilibrium with metal the dominating defects are cation vacancies at the highest possible ionization degree; their concentration being dependent on oxygen pressure in the following way (when the oxide formula is MO):

$$[V_M''] = A\, p_{O_2}^{1/6} \tag{20}$$

As follows from this equation the concentration of cation vacancies increases with oxygen pressure (activity). The higher the vacancy concentration the weaker the ionic interactions. We can expect that for a given structure there is some critical concentration of defects that can be tolerated. When this concentration is exceeded another oxide (e.g. M_3O_4) with a different crystallographic structure must be formed, which is accompanied by at least partial change of the oxidation number of metal. As a result of such transformation an abrupt change of O/M ratio is observed. The oxide thus formed has a lower density but higher free energy of cohesion (referred to the same amount of metal) as follows from eq. (18).

Chemical compounds in addition to ionic defects have also electronic defects, with concentrations dependent on the oxidant pressure. For the MO-type oxide, where cation vacancies are doubly ionized $[V_M'']$, the dependence of electron hole concentration on oxygen pressure can be expressed as /16/:

$$[h^\cdot] = K_h p_{O_2}^{1/6} \tag{21}$$

The interactions of electronic and ionic defects lead to the formation of vacancies with a lower ionization degree, e.g. singly ionized ones:

$$V_M'' + h^\cdot = (V_M'' h^\cdot)' = V_M' \tag{22}$$

as in the case of cobaltous oxide $Co_{1-y}O$ /17-19/ or neutral ones as in the case of cuprous oxide $Cu_{2-y}O$, $(V_{Cu}' h^\cdot) = V_{Cu}^{x}$ /20/. In the electronic structure of such compounds, in the energy gap, there must appear additional energy levels related to the ionic defects – acceptor or donor levels, which are available for electrons. As the concentration of ionic defects increases due to the increasing activity (pressure) of the oxidant, so does the concentration of electronic defects, which gives rise to cation vacancies with a lower oxidation number (shift of equilibrium). When all the available energy levels are filled, the concentrations of electronic and ionic defects cannot increase anymore. Rigid electronic structure, typical of compounds with quite a wide energy gap, can be a barrier for the formation of ionic defects. Such compounds show small concentrations of electronic and ionic defects and are stable in a wide range of oxidant pressure, e.g. MnO, CoO, or systems with one oxide phase only, such as Al/Al_2O_3, Ni/NiO, Mn/MnS etc.

At higher concentrations of ionic defects, ionic interactions may bring about modification of the electronic structure and formation of an additional energy band or even its overlapping with the valence band, like in the case of ferrous oxide $Fe_{1-y}O$ /21/ or with the conduction band, as in the case of $Ti_{1+y}S_2$ /22,23/. In the electronic structure of a compound there appear numerous states available for electrons. As the concentration of the oxidant increases semiconducting properties transform into metallic ones or the metallic properties improve. The compounds have a significant concentration of ionic defects because the electronic structure does not hinder their formation.

Phases with metallic properties may show remarkable variations of defect concentration (both ionic and electronic defects) and their stability range is quite narrow, e.g. TiO, FeO, homologous oxides of vanadium or titanium (M_nO_{2n-1}), (compare Fig. 3) or most of transition metal sulfides /15/. The above observation refers to all phases with metallic properties, which have a narrow band with high density of states and can accommodate significant numbers of the electronic and ionic defects. At sufficiently high concentrations ordering of the ionic defects may take place. Slight displacements of ions may cause substantial modifications of the crystallographic structure, like in the case of chromium or vanadium sulfides /11,24,25/. Such a change does not influence the electronic structure to any remarkable degree and the new phase remains metallic, like in the case of vanadium or titanium oxides with the formulas M_nO_{2n-1}. Thus the range of oxidant pressure determining the stability field of any oxide phase will depend on the possibility of its modification under the influence of increasing activity of the oxidant. This problem is rather complex and has been extensively discussed in the previous paper /15/. When in a given phase diagram the number of oxides is small (up to 3), these compounds are insulators or semiconductors with low concentration of ionic defects and their electronic structure is rigid (with an energy gap). On the other hand, in the metal-oxidant phase diagrams with numerous oxide phases, the majority of them exhibit high electrical conductivity and charge transport occurs within one energy band. The electronic structure generally does not restrict the formation of ionic defects and such phases are known to have significant concentrations of ionic defects.

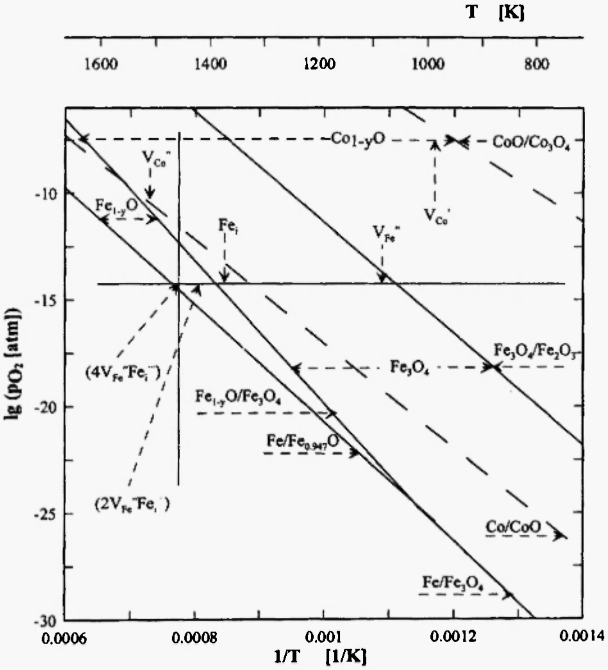

Fig. 4: Part of phase diagram representing equilibrium curves for the Co-O system (broken lines), Fe-O system (thick solid lines) /7-9/. Symbols denote: V_{Fe}'', V_{Co}' – cation vacancies in iron oxide and cobalt oxide respectively, $Fe_i^{\cdot\cdot\cdot}$ – iron ions in the interstitial positions, $(4\,V_{Fe}''\,Fe_i^{\cdot\cdot\cdot})$, $(2\,V_{Fe}''\,Fe_i^{\cdot\cdot\cdot})$– defect complexes (Kröger-Vink notation of defects).

5. CHANGES IN CRYSTALLOGRAPHIC STRUCTURE AND DEFECT STRUCTURE DURING PHASE TRANSFORMATIONS OF OXIDES AND SULFIDES

Let us consider changes in the crystallographic structure and in the defect structure, taking place when oxidant activity increases at constant temperature in a relatively simple Co-O system, a part of which is shown in Fig. 4. Near the metal/scale interphase the concentration of doubly ionized cation vacancies in cobaltous oxide is low. According to some researchers the predominant defects are cobalt interstitials /17/. As the oxygen pressure increases at constant temperature the concentration of cation vacancies increases and in the vicinity of CoO/Co_3O_4 interphase the dominating defects are singly ionized cation vacancies V_{Co}' /16,18,19/. Further increase in oxygen pressure brings about phase transformation to Co_3O_4 with a spinel structure. In the same plot (Fig. 4) we have presented a part of Fe-O phase diagram which should be similar because both metals take the neighboring positions in the periodic table. There are however considerable differences. Firstly, ferrous oxide $Fe_{1-y}O$ (wustite) forms at temperatures exceeding 855 K. Its stability range in terms of oxygen pressure is much wider than that of cobaltous oxide. Moreover, the type and concentration of ionic defects are different. In addition to cation vacancies $Fe_{1-y}O$ contains cation interstitials in tetrahedral sites, which together with vacancies form defect clusters, such as $(4V_{Fe},Fe_i)$ or more complex /12-14,26/. Their concentration increases with oxygen activity. The occurrence of such defect complexes can be treated as local formation of a spinel type phase within the wustite lattice /27/.

Transformation of a cubic NaCl-type structure, MO, into a spinel-type M_3O_4, is particularly interesting and characteristic of many compounds. The oxygen lattice remains unchanged and preserves the A1-type cubic symmetry. In the elementary cell with a doubled parameter *a* (A1-type) cations occupy half of the available octahedral sites (16 out of 32) and eight tetrahedral sites (1/8 of 64). The discussed ferrous oxide Fe_3O_4 is a reversed spinel in which Fe^{3+} ions take the tetrahedral positions and the remaining Fe^{2+} and Fe^{3+} take the octahedral positions. Thus we can write its formula in the following way $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$, where ions in brackets are in octahedral coordination. In this structure the unoccupied octahedral and tetrahedral positions are not treated as cation vacancies. Compared to wustite the discussed oxide has totally different type and concentration of ionic defects and a different structure of electronic defects, the M-M distances being bigger and the overlap of orbitals being smaller. As a result Fe_3O_4 has a rigid electronic structure of a semiconductor with the energy gap much wider than $Fe_{1-y}O$, with the acceptor and donor levels. The FeO → Fe_3O_4 transformation is associated with an enhancement of semiconducting properties. The spinel-type phases show low concentration and low mobility of defects although a significant number of octahedral and tetrahedral sites remains unoccupied, as mentioned above. In magnetite, Fe_3O_4, at the lowest oxygen pressures (near the interphase with $Fe_{1-y}O$) the concentration of iron interstitials (Fe_i) is very low and it decreases with the increasing pressure of oxygen. On the other hand the concentration of doubly ionized cation vacancies and further singly ionized cation vacancies increases. The latter are predominant defects near the Fe_3O_4/ Fe_2O_3 interphase (Fig. 4) /16,18/.

At still higher oxygen pressure M_3O_4 transforms into M_2O_3, generally with the corundum-type structure (α-Al_2O_3). This structure can be obtained by joining of the MO_6 octahedra with common edges and walls /11/. Such compounds even at high temperatures exhibit very small deviations from stoichiometry (low concentration of ionic and electronic defects).

Thus it can be seen that lowering of the M/O ratio in an oxide causes some changes in the crystallographic structure, due to which the M-M interactions become weaker and an oxide with a wider energy is formed (with enhanced semiconducting properties).

In many M-O systems further increase of oxidant pressure leads to the formation of MO_2 and MO_3 type oxides. The structure of the latter can be derived from MO_6 octahedra, which are joined by corners and edges /11/. In such structures there are unoccupied positions which have dimensions of cation vacancies but quite different properties. The predominant defects are oxygen vacancies (lack of oxygen that joins two structural octahedra). In the Ti-O or V-O systems, between the M_2O_3 and MO_2 oxides there is a series of M_nO_{2n-1} phases, which can be derived from MO_2 structure by eliminating oxygen vacancies /11,28/. In such oxides the octahedra join along the edges to eliminate oxygen vacancies, forming shear structures, referred to as the Magneli phases. It should be noted that with the increasing O/M ratio the octahedra undergo distortions, due to which some of the M-O bonds become longer and weaker than others. In a limiting case, e.g. in V_2O_5 the structural elements are trigonal pyramids with V-$O_1(1)$ distance of 1.585 Å and V-$O_1(2)$ of 1.878 Å /29/. As a consequence the V-$O_1(2)$ interaction is much weaker than the V-$O_1(1)$ one and two layers of trigonal pyramids are formed, joined together by weak van der Waals forces.

Thus we can see that transformation of one oxide into another implies quite important changes in the spatial distribution of ions. Not only the change in crystal symmetry takes place but also such a rearrangement of the structure that cohesion is preserved in spite of the smaller number of M-O bonds. In the case of oxides it is possible owing to proper joining of the MO_6 octahedra. A classical example is that of a silicate structures in which the SiO_4 tetrahedra constitute basic structural elements.

Let us now consider the formation of oxide phases under the influence of increasing temperature at constant oxygen pressure (in a selected phase diagram). As can be seen in Figs. 2 and 4 the standard free energy of formation or transformation of one oxide phase into another decreases together with temperature which means that the equilibrium pressure of oxygen also decreases (Fig. 2). So, the stability range of each oxide phase shifts toward lower oxygen pressure. The oxides with a higher concentration of oxygen (higher chemical potential of oxygen) become thermodynamically stable at much lower oxygen pressures than at higher temperatures. In the Fe-O system when temperature is lower than 855 K the $Fe_{1-y}O$ phase decomposes and Fe_3O_4 becomes stable in contact with metal (Fig.1). In many systems metal rich oxides, like M_2O, MO or

M_3O_4, are not formed at all.

We shall now cut the Co-O phase diagram with a line parallel to the 1/T axis (Fig. 4). At the given pressure and the lowest temperature the stable phase is Co_3O_4. When the temperature becomes higher it transforms into $Co_{1-y}O$, an oxide with more closely packed metal ions. Such rearrangement strengthens the bonds, which tend to be weaker as a result of increasing vibrations of atoms in the crystal lattice. In the stability range of a given oxide phase such changes of defect types and concentrations should occur, which would increase the cohesion of the crystal lattice. As mentioned above in the Fe_3O_4 oxide, near the Fe_3O_4/ Fe_3O_4/Fe_2O_3 interphase the dominating defects are cation vacancies, while near the Fe_3O_4/FeO interphase in the spinel phase these are iron interstitials (Fig. 2). A rise in temperature will lead to the increased concentration of iron interstitials and decreased concentration of cation vacancies. When the critical defect concentration is exceeded a transformation of the oxide takes place toward a phase richer in metal, with a bigger number of M-O bonds. The resultant oxide, MO, has a cubic structure with the highest chemical potential of the oxidant and cation vacancies at low ionization degree, like in the case of $Cu_{2-y}O$, or $Co_{1-y}O$. The equilibrium constant for the formation of defects increases with temperature (endothermic reaction) and therefore the concentration of cation vacancies should increase (at constant oxidant pressure). When, on an increase in temperature, the MO/M interphase is reached the concentration of cation vacancies should be higher compared to M_3O_4/MO interphase at a lower temperature. If one type of defects were present in the MO-type crystal, e.g. cation vacancies, the discussed process would reduce stability of the crystal. Therefore there must be another process in which cohesive forces increase, e.g. formation of interstitial cations and simultaneous disappearance of cation vacancies. A more complex rearrangement is observed in $Fe_{1-y}O$ where iron ions shift to tetrahedral positions, becoming interstitials. At the same time they form defect complexes with cation vacancies. Roth's clusters $[2\,V_{Fe}^{''}\,Fe_i^{\bullet\bullet\bullet}]$ /29/ in $Fe_{1-y}O$ near the $Fe_{1-y}O/Fe_3O_4$ interphase transform into $[4\,V_{Fe}^{''}\,Fe_i^{\bullet\bullet\bullet}]$ /12-14/. Increasing concentration of the latter at higher temperature causes cohesive forces in the crystal to become stronger. In general at higher temperatures the cohesive forces in the crystal lattice become weaker and such defects must be formed which would counteract this tendency. For instance concentration of cation vacancies should decrease, that of interstitial ions should dominate, defect complexes should form, etc. Changes of defect concentrations are certainly associated with respective defect equilibria (dependent on temperature and oxidant activity). The result of defect concentration changes with the increasing temperature is that the number of metal atoms per oxidant atom in the oxide phase increases (M/O ratio becomes higher).

To sum up, the following can be stated: phase transformation taking place on decreasing the oxidant pressure at constant temperature, or on increasing the temperature at constant oxidant pressure, leads to a new oxide phase in which metal-oxidant interactions are stronger and the M/O ratio is bigger. When critical parameters are exceeded the oxide phase decomposes to metal and oxygen.

Somewhat different changes in the crystallographic structure and defect structure are observed in sulfides. As the atomic radius of sulfur is bigger than that of oxygen and 'covalent' type interactions appear between the sulfur atoms, most sulfides form close-packed structures of sulfur ions, such as cubic or hexagonal (generally deformed to some extent). Metal ions are distributed over the available octahedral or tetrahedral sites. Such a situation is encountered in nickel or cobalt sulfides at $S/M \leq 1$ /11/. When $S/M = 1$ the sulfides have close packed hexagonal structure of NiAs or similar, with metal ions located in octahedral positions /11/. At higher chemical potential of sulfur, $1 < S/M < 2$ the structures are intermediate between NiAs and CdI_2. The NiAs structure can be described as composed of a sequence of alternative layers of metal and sulfur /11/. Removal of some metal ions from each layer and ordering of thus formed vacancies allows deriving the structures of a variety of sulfide phases such as titanium sulfides. The structures of vanadium sulfides or chromium sulfides can be obtained by ordering of cation vacancies in NiAs /24/. Strong interactions between the sulfur atoms occur in the pyrite type sulfides, MS_2, where S^{2-} ions appear in the cubic lattice. Such an arrangement can be accounted for by the following facts: the S-S distance in homopolar crystals of sulfur is about 2.06 Å while in FeS_2 it is 2.171 Å and similarly in NiS_2 it is 2.065 Å. The M-S distances are bigger, i.e. 2.259 and 2.396 Å, respectively /11/.

The above examples indicate that in sulfides, owing to the stability of the anion sublattice, the formation of cation vacancies is easier than in oxides and ordering of vacancies can lead to a variety of structures. It should be noted that most of the sulfide phases have metallic properties so in spite of lattice rearrangements the electronic structure is only slightly modified because the distances between atoms, responsible for the formation of a narrow-band structure with high density of states, remain almost unchanged.

6. CONCLUSIONS

The discussion presented in this paper can be summarized as follows:

- The formation of a compound on a metal surface is dependent on the values of standard free energies of cohesion of the oxidation product, of metal sublimation and of oxidant dissociation according to equation (7). It has been explained why at temperatures lower than 855 K iron coexists with magnetite, Fe_3O_4, and at higher temperatures with wustite, $Fe_{1-y}O$. The reasons were related to the values of thermodynamic functions describing these systems, to the differences in crystallographic structures and in the interactions between atoms in these oxides as a function of temperature.
- The range of oxidant pressures necessary for thermodynamic stability of a given compound depends on its cohesion energy changes, which in turn are strongly dependent on possible changes of defect type and concentration (modification of electronic structure) as a function of oxidant activity.
    - Stability in a wide range of oxidant pressure is characteristic of compounds with a rigid electronic structure (with an energy gap) in which the number of states available for electrons is relatively small. They have low concentrations of electronic and of ionic defects (e.g. CaO, Al_2O3, NiO, MnS etc)
    - Stability in a narrow range of oxidant pressure is typical of compounds with a narrow-band electronic structure and high density of states. In these compounds the concentration of electronic defects and of ionic defects may change to a significant degree (e.g. vanadium or titanium oxides or $Fe_{1-y}O$).
- Transformation of one compound into another when the oxidant pressure exceeds the equilibrium one occurs due to weaker interactions between the ions caused by increasing concentration of the ionic defects (e.g. cation vacancies) or by filling-up of the available electronic states. This implies the necessity of lattice rearrangement toward a crystallographic structure with a higher free enthalpy of cohesion (referred to the same amount of metal).
- The change of interactions between atoms as a result of phase transformation (in a new structure) causes changes in the electronic structure, generally worsening of metallic properties or enhancement of semiconducting properties.
- The transformation of one compound into another may also consist in the ordering of ionic defects or in their elimination. The new phase acquires a different symmetry (e.g. Magneli phases) but the positions of ions remain almost unchanged which means that the electronic structure is only slightly modified (metallic properties are preserved).
- If in the metal-oxidant system the number of compounds is small (up to 3) these compounds are insulators or semiconductors with low concentration of ionic defects and rigid electronic structure (with an energy gap).
- If in the metal-oxidant system the number of compounds is big the majority of phases show high electrical conductivity and charge transport takes place within the energy band. The electronic structure generally does not restrict the formation of ionic defects and the concentrations of ionic defects are high.

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