The Influence of Atmosphere on High Temperature Crystal Growth

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Abstract

The growth of crystals with high melting points $t_{fus} \geq 1600\,°C$ faces the researcher with experimental problems, as the choice of materials that withstand such high t is rather limited. Many metallic construction materials are in this high t range already molten or exhibit at least a drastically reduced mechanical strength. The very few materials with $t_{fus} \gg 1600\,°C$ as e.g. W, Mo, and partially even Ir are more or less sensitive against oxygen upon heating. Whenever possible, high t crystal growth is performed under inert atmosphere (noble gases). Unfortunately, many oxides are not thermodynamically stable under such conditions, as reduction takes place within such atmosphere. A thoroughly search for suitable growth conditions has to be performed, that are on the one side "oxidative enough" to keep the oxides stable and on the other side "reductive enough" to avoid destruction of constructive parts of the crystal growth assembly. The relevant parameters are t and the oxygen partial pressure p_{O_2}. The paper discusses quantitatively relevant properties of interesting oxides and construction materials and ways to forecast their behavior under growth conditions.

1   Introduction

Many metal oxides that are used as starting materials for oxide crystal growth from the melt exhibit high melting points t_{fus}. Only for $t_{fus} \lesssim 1600\,°C$ an extended choice of construction materials is available for the use as crucibles, seed holders in CZOCHRALSKI setups, and as other parts that are in contact with the molten substance. Very often platinum or alloys of platinum with other noble metals as iridium, gold, or rhodium are used for this purpose. Unfortunately, Pt with $t_{fus}^{Pt} = 1770\,°C$ and its alloys do not withstand considerably higher temperatures, as these materials will melt or do at least show a drastically reduced mechanical strength. To avoid these problems, one has either to apply crucible free crystal growth techniques (e.g. float zone or pedestal heated growth), "cold crucibles" (skull melting [1]) or one has to look for alternative construction materials with more extended temperature range.

Unfortunately, the application of ceramics based on alumina and other oxides is usually only possible for parts that are not in direct contact to the melt, as otherwise chemical reactions between the oxide melt and the construction parts could occur. Alternative materials are some very high melting metals as iridium ($t_{\text{fus}}^{\text{Ir}} = 2450\,°C$), tungsten ($t_{\text{fus}}^{\text{W}} = 3400\,°C$), molybdenum ($t_{\text{fus}}^{\text{Mo}} = 2600\,°C$) or the non-metal carbon as graphite or vitreous carbon. In contrast to Pt and its alloys, these materials are more or less sensitive against oxidation – accordingly they have to be kept under vacuum or within inert gases upon heating. Such "inert" atmosphere is uncritical or even favorable, if semiconductors as Si, $A^{\text{III}}B^{\text{V}}$- or $A^{\text{II}}B^{\text{VI}}$-compounds are grown; but for the growth of oxides it must be taken into account, that some finite oxygen partial pressure p_{O_2} is always necessary to remain within the stability limit of the oxide.

The adjustment of p_{O_2} can either be done by application of vacuum or, with higher accuracy, by application of defined gas mixtures. The paper discusses quantitatively the following questions:

(1) Which $p_{O_2}^{\text{min}}(t)$ is at least necessary to remain within the stability limit of a certain oxide at the growth temperature t?
(2) Which $p_{O_2}^{\text{max}}(t)$ is allowed to avoid destruction of constructive parts?
(3) How can a predefined $p_{O_2}(t)$ be achieved?

In the course of this paper the symbol t will be used for the temperature on the CELSIUS scale, whereas T will be used for the absolute temperature: $t = T - 273.15$ K.

2   Thermodynamic background

A system at constant T and pressure p will approach an equilibrium state by minimizing the GIBBS energy

$$G = H - TS \tag{1}$$

that is defined in terms of its enthalpy $H = U - pV$ (U – internal energy, V – volume), and entropy S. The differential of the GIBBS energy at $T, p = \text{const}$

$$\mathrm{d}G = \sum_{i=1}^{c} \mu_i \, \mathrm{d}n_i \tag{2}$$

vanishes upon thermodynamic equilibration [2]. (c is the number of components within the system.) In equilibrium all μ_i within any phase must be identical for every i.

The partial molar GIBBS energy ("chemical potential") of an ideal gas is given by

$$\mu_i = \mu_i^0 + RT \ln p_i \qquad (3)$$

where μ_i^0 is the standard molar GIBBS energy at 1 atm, p_i is the partial pressure of the gas within a mixture and R is the gas constant.

The redox equilibrium reaction
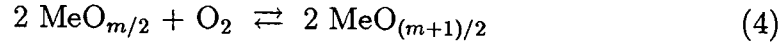
$$2\,MeO_{m/2} + O_2 \rightleftarrows 2\,MeO_{(m+1)/2} \qquad (4)$$

for the oxidation of $2\,dn$ mole metal oxide from the m valent state to the $m + 1$ valent state proceeds under the consumption of dn mole oxygen. The GIBBS energy of the system varies as

$$
\begin{aligned}
dG/dn &= 2\mu_{MeO_{(m+1)/2}} - 2\mu_{MeO_{m/2}} - \mu_{O_2} \\
&= \left(2\mu^0_{MeO_{(m+1)/2}} - 2\mu^0_{MeO_{m/2}} - \mu^0_{O_2}\right) + RT \ln \left(\frac{p^2_{MeO_{(m+1)/2}}}{p^2_{MeO_{m/2}} p_{O_2}}\right) \\
&= \Delta G^0 + RT \ln \left(\frac{p^2_{MeO_{(m+1)/2}}}{p^2_{MeO_{m/2}} p_{O_2}}\right) \\
&= \Delta G
\end{aligned}
\qquad (5)
$$

until equilibration is obtained with $\Delta G = 0$. (5) simplifies, if the vapor pressures of the oxides can be neglected.

For the equilibrium state

$$\Delta G^0 = -RT \ln K = -RT \ln \left(\frac{p^2_{MeO_{(m+1)/2}}}{p^2_{MeO_{m/2}} p_{O_2}}\right) \qquad (6)$$

can be written with the equilibrium constant K. The left hand side of (6) can be calculated from pure substance data only; for negligible vapor pressures of the metal oxides one obtains the simple expression

$$-RT \ln K = RT \ln p_{O_2} = \Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (7)$$

for the equilibrium state. In this case one can expect nearly linear plots $RT \ln p_{O_2}(T)$ with a slope close to one for redox equilibria similar to equation (4).

Predominance diagrams (or "ELLINGHAM diagrams") [3] of redox equilibria obtained for one metal with different oxidation states illustrate regions of stability for the different oxidation states of this metal in dependence on T and p_{O_2}. The diagrams given in the following chapter were computed using

the PC program "ChemSage" and the "SPS96T02 – SGTE Pure Substance Database" [4]. Regions of existence are plotted within the $t-p_{O_2}$ plane for some metals with oxides that are common components of oxide crystals (Pb, Ga, Pr; for comparison Cu) and for common high t construction materials (Ir, C). It should be noted, that all computations were performed for pure substances. The GIBBS energy change (2) of mixtures contains additional mixture terms that depend on stoichiometry. But at least upon the first heating of mixtures used for oxide crystal growth the single grains of the different substances can be regarded as pure; the practical behavior of the different metals and of oxides as observed during actual growth experiments proved to be well described by the diagrams.

3   Results

3.1   Oxides

Predominance diagrams are presented here for copper, lead, gallium, and praseodymium. The upper abscissa of all diagrams corresponds to pure oxygen with a pressure of 1 bar.
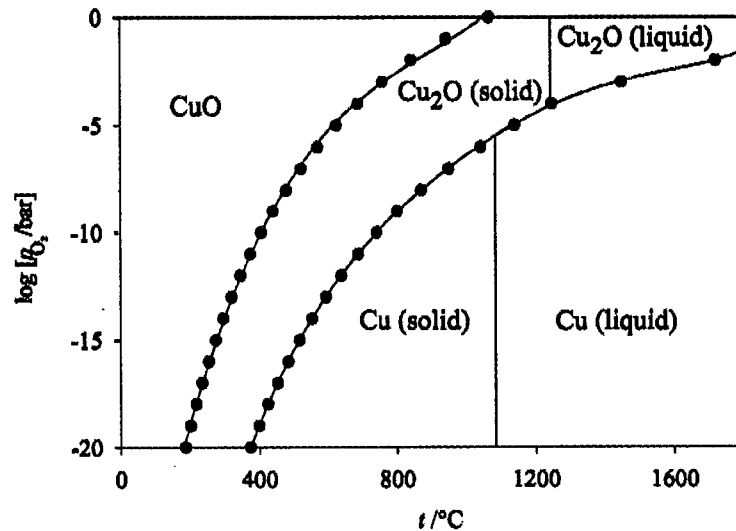

Fig. 1. Predominance diagram for Cu and its oxides Cu_2O and CuO in the $t - p_{O_2}$ plane

The diagram $\log p_{O_2}(T)$ for copper (Fig. 1) is given here for comparison with literature data by PELTON [3]. These literature data do not consider CuO. Moreover, PELTON simplified the temperature dependence of K according to (7) and neglected the (indeed small) partial vapor pressures of the solid and liquid phases. These simplifications allowed an analytical treatment

of the problem and resulted in straight phase boundaries between all pre-dominance regions $RT \ln p_{O_2}(T)$. Nevertheless, the coincidence between the diagram given by PELTON and Fig. 1 is satisfactory: For the triple point Cu(solid)–Cu(liquid)–Cu_2O(solid) one reads from the PELTON diagram $\log p_{O_2}$ $= -5.75$ which corresponds to the value than can be read from Fig. 1. From the diagram it becomes obvious, why Cu oxides are scarce used as compo-nents for high t oxide crystal growth: At growth temperatures $t > 1100\,°C$ and at ambient air ($\log p_{O_2} = -0.68$) Cu^I is the stable ion, but already at cooling below the $1100\,°C$ limit Cu^{II} becomes stable. As the valency change can be expected to proceed quickly at such high t, the transformation will occur and will often destroy the crystal. Working at considerably lower p_{O_2} is not possible, as Cu metal would be formed upon heating.
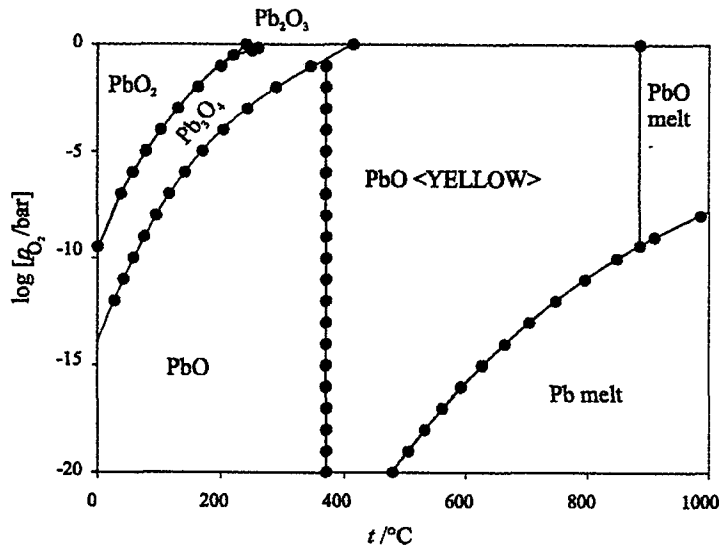

Fig. 2. Predominance diagram for Pb and its oxides PbO, Pb_3O_4, Pb_2O_3 and PbO_2 in the $t - p_{O_2}$ plane

The most frequent valency level of lead (Fig. 2) is two; the corresponding lead(II) oxide PbO undergoes a solid phase transition at $371\,°C$. Due to the low $t_{fus} = 886\,°C$ PbO is a suitable solvent for crystal growth from high tem-perature (melt) solutions; $PbWO_4$ is known as scintillator crystal [5]. It is interesting, that PbO is not stable in air ($p_{O_2} = 0.21$ bar) at room tempera-ture. Obviously, the transformation rates $Pb^{II} \longrightarrow Pb^{III} \rightarrow Pb^{IV}$ are too low to be observed. Pb(III) oxide is only stable at elevated t.

Ga_2O and Ga_2O_3 are the two stable Ga oxides. Gallium(III) oxide is compo-nent of some interesting compounds as the substrate crystals $LiGaO_2$ (for GaN epitaxy) [6] and $SrPrGaO_4$ (for high T_c superconductor epitaxy) [7]. Ga_2O_3 is stable over an extended $t - p_{O_2}$ range; but unfortunately at $t \gtrsim 1200\,°C$ re-duction to the volatile Ga_2O may occur. In highly reducing atmosphere with $p_{O_2} < 10^{-11}$ bar the reduction can proceed even to Ga metal. The liquid Ga is known to alloy quickly with Pt and other noble metals – leading to serious
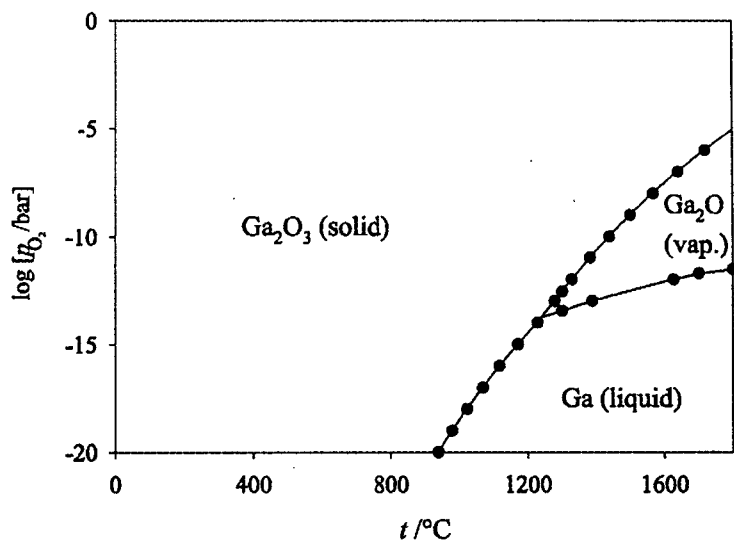
Fig. 3. Predominance diagram for Ga and its oxides Ga_2O and Ga_2O_3 in the $t - p_{O_2}$ plane

damage of crucibles and other parts. Due to the volatility of Ga_2O the reduction $Ga^I \rightarrow Ga$ can occur even at metallic parts that are not in direct contact to the melt.
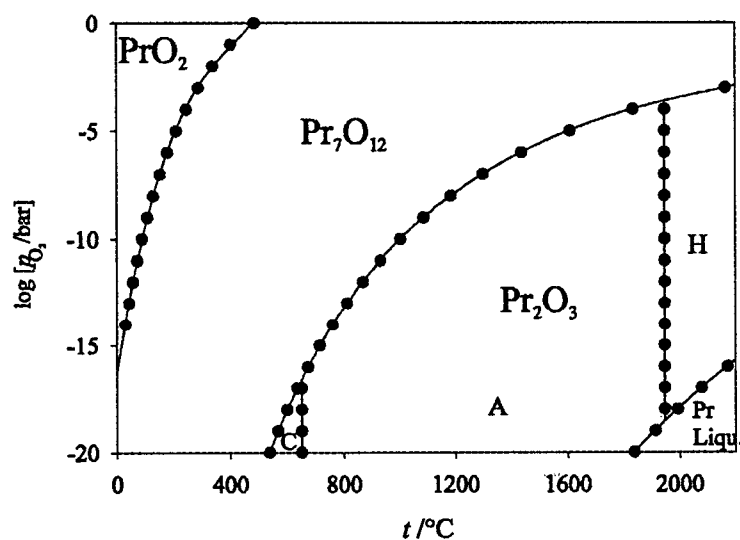
Fig. 4. Predominance diagram for Pr and its oxides Pr_2O_3, Pr_7O_{12} and PrO_2 in the $t - p_{O_2}$ plane

Praseodymium is chosen as the last example for elements that are interesting as starting material for oxide crystal growth. Pr^{III} and Pr^{IV} are stable. No stability region was found for the commercially available Pr_6O_{11}, instead the mixed-valency praseodymium(III,IV) oxide Pr_7O_{12} was found. Pr_7O_{12} and Pr_2O_3 show extended predominance regions; the latter undergoes a range of solid state phase transitions. Reduction to metallic Pr has not to be expected under usual crystal growth conditions. The Pr^{3+} ion gives oxide crystals a green color; whereas Pr^{4+} colours red or brown. $SrPrGaO_4$ crystals that are

grown under conditions close to the phase boundary Pr_7O_{12}/Pr_2O_3 (Fig. 4) did show a green color with red stripes – thus indicating the valency transition $Pr^{III} \rightleftharpoons Pr^{IV}$ [7].
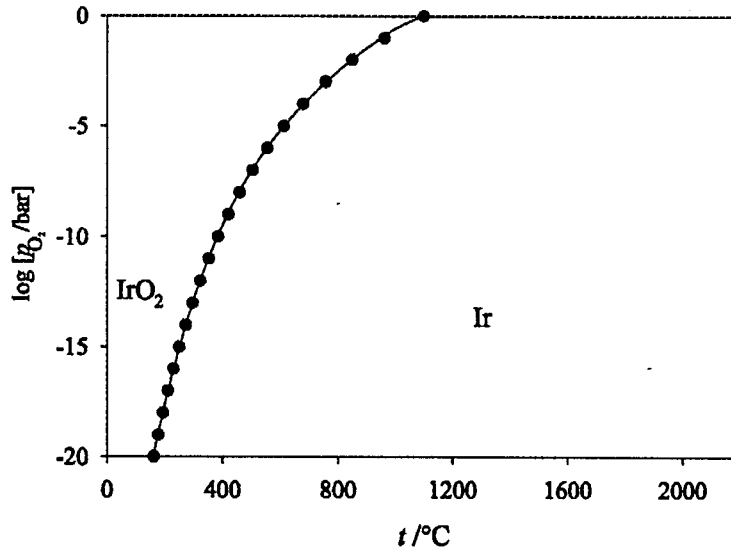
3.2 Construction materials

Fig. 5. Predominance diagram for Ir and IrO_2 in the $t - p_{O_2}$ plane

Iridium crucibles are often used for high t oxide crystal growth as Ir shows high mechanical strength even at $t \approx 2000\,°C$. Some technological important oxides as garnets (YAG, GGG) and perovskites have t_{fus} in this very high t range. It is well known, that Ir crucibles cannot be heated within air, as the metal would be oxidized to IrO_2. From the predominance diagram (Fig. 5) it follows, that IrO_2 is under ambient air indeed stable for $t \lesssim 1100\,°C$. If higher temperatures are applied, no oxidation of Ir parts can occur.

Carbon (graphite, vitreous carbon) is a construction material which shows high chemical and mechanical stability even at highest t. Unfortunately, p_{O_2} does not exceed 10^{-15} bar even at equilibrium temperatures of $2000\,°C$ (Fig. 6). Accordingly, C can only be used under extremely reducing conditions, e.g. within noble gases.

3.3 Atmosphere

The atmosphere within the growth chamber has to be fulfill the following two conditions:

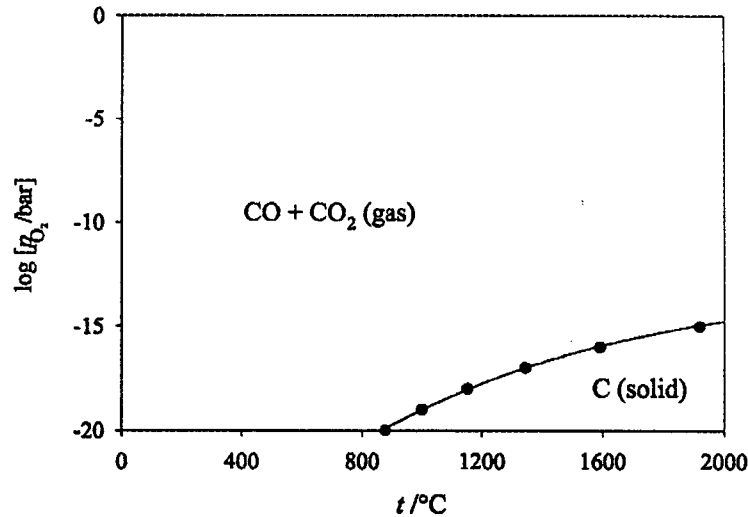(1) The oxygen partial pressure must be in that range where the favored

Fig. 6. Predominance diagram (= stability range) for C in the $t - p_{O_2}$ plane

valency of the metal is stable. Often this condition is fulfilled if $p_{O_2} > p_{O_2}^{min}$ with $p_{O_2}^{min}$ – the partial pressure where reduction of the oxide to the metal takes place for the given growth temperature.

(2) The oxygen partial pressure must be low enough to avoid oxidation of construction parts (crucible, seed holder) being in contact with the melt. This second condition is fulfilled if $p_{O_2} < p_{O_2}^{max}$ with $p_{O_2}^{max}$ – the partial pressure where the construction material is in equilibrium with its oxide in the lowest valency state.

Both conditions are fulfilled, if $p_{O_2}^{min} < p_{O_2} < p_{O_2}^{max}$. In some special cases the melt itself demands the adjustment of p_{O_2} within a lower and an upper limit to keep the favored oxidation states stable. $SrPrGaO_4$ is such an example. At the growth temperature $t \lesssim 1500\,°C$ one has to keep $p_{O_2} > 10^{-9}$ bar to avoid reduction of Ga_2O_3 and $p_{O_2} < 10^{-6}$ bar to avoid oxidation of Pr_2O_3.

Defined p_{O_2} within the growth chamber can be maintained by rinsing it with different pure gases or with mixtures of them. Fig. 7 shows $p_{O_2}(t)$ for air, CO_2, CO, and for wet CH_4. (p_{O_2} within pure CH_4 is always zero!) Consider, that the scale of the ordinate extends down to -30 in contrast to the other diagrams were this axis extends only down to -20.

4   Summary

Upon the growth of oxide crystals from hot melts or melt solutions the oxygen partial pressure within the growth chamber has to kept high enough to keep the oxide at the given temperature stable with respect to decomposition into oxides with lower valency or into the corresponding metal. On the other side,
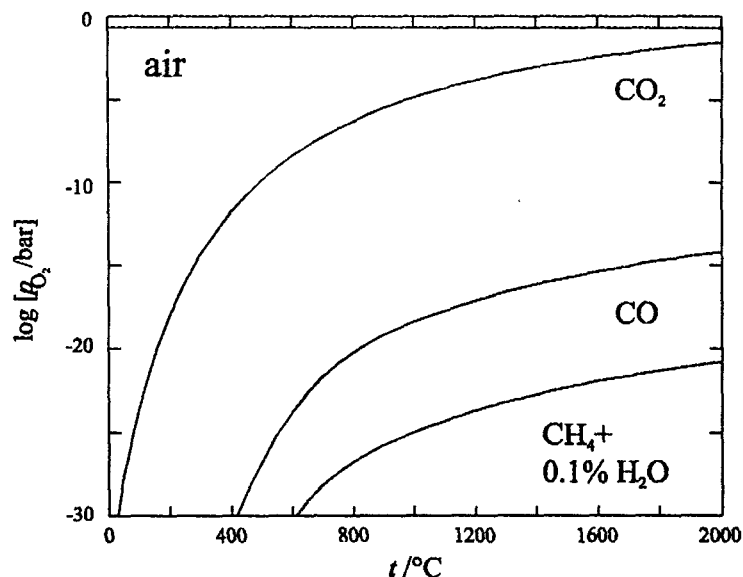
Fig. 7. Temperature dependence of p_{O_2} within different gases and gas mixtures (logarithmic plot)

p_{O_2} may not exceed the equilibrium partial pressure between the constructive parts and their oxides during the whole growth process including the heating and cooling phases.

Graphite parts usually cannot be used for high t oxide crystal growth, as p_{O_2} in equilibrium with C is very low. Other high melting materials as tungsten or molybdenum were not discussed here in detail – but these metals are restricted to the few oxide systems with low oxygen decomposition pressure $p_{O_2} \lesssim 10^{-5}$ bar at 2000 °C. Iridium proves to be superior for many oxide systems – but for $t \lesssim 1100$ °C the atmosphere has to be kept slightly reducing. Above this temperature Ir is stable even at ambient air.

Gas mixtures in the order O_2 – air – CO_2 – CO – CH_4 allow the adjustment of p_{O_2} over > 20 orders of magnitude.

Acknowledgement

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$CO + CO_2$ (gas)

C (solid)

$\log (P_{O_2}/\text{atm})$

$T / °C$

0

-5

-10

-15

-20

0   400   800   1200   1600   2000