

**NOBLE METAL REACTION WITH SOLID OXIDES OR A MELT COMPONENTS: A NEW REPRESENTATION OF BINARY PHASE DIAGRAMS.** A. Borisov, SN2, Planetary Science Branch, NASA JSC, Houston, TX 77058, USA (e-mail: aborisov@ems.jsc.nasa.gov).

**Abstract.** I suggest here a new representation of binary phase diagrams, which is actually a combination of “ $t^\circ$ -composition” and “ $t^\circ$ - $fO_2$ ” diagrams. Such diagrams may be useful for consideration of very reducing conditions, where interaction of noble metals with solid oxides or melt components ( $SiO_2$ ,  $FeO$ , etc.) becomes important and may result in melting of initially solid noble metals.

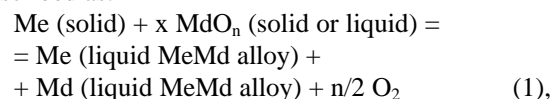
**Introduction.** Precious metals are not really noble at high temperatures and easily react with certain substances. In any serious catalog on noble metal labware one can find recommendations to avoid working with sulfur, selenium and tellurium, phosphorus, arsenic, antimony and borax, molten lead, zinc, tin, bismuth, etc. Such reactions can be so unexpected, that they have been given their own name in material science literature (for example, “bismuth reaction”). It was found during developments of high-performance ceramic multilayer capacitors, that  $Bi_2O_3$  flux reacts with Pd-containing electrodes at temperatures even lower than  $900^\circ C$  [1].

At low oxygen fugacity noble metals can react not only with such “exotic” substances, but even with silica, the main component of silicate melts. For example, Borisov with coworkers, during experimentation with a loop technique to determine Pd and Au solubilities in silicate melts [2, 3] revealed that slightly below IW buffer conditions all experiments failed because of the destruction of the Pd- and PdAu loops. The reason was found to be Pd alloying with silica of the melt [2]. Chen and Presnall [4] showed, that the main reason why platinum capsules melt far below the melting point of pure platinum is also an interaction with silica of the charge. The PGE-Si systems have very low, from an experimental petrologist’s point of view, eutectic temperatures. In Pd-Si binary, for example, it is only  $760^\circ C$  and the eutectic composition is about 16 at.% Si. It is obvious, that at “normal working” temperatures ( $1300^\circ C$  or higher) a much smaller fraction of silicon would be enough to destroy a capsule or a loop.

**Thermodynamics.** In the following discussion I will designate a noble metal as *metal* (Me) and the alloying partner, that is usually stable as oxide at redox conditions at which the noble metal is stable in metallic state, as *metalloid* (Md). The latter could be Si, Ge, As, Bi and other nonmetals, but also Fe, Co, Ni or other metals. Again, by definition, the Me/Me oxide equilibrium line in the  $t^\circ$ - $fO_2$  field lies in a

much more oxidizing region, than Md/Md oxide one.

The reaction of Me with Md oxide (for example, Pd with pure  $SiO_2$  or silica of the melt) can be described as:



with the reaction constant:

$$K_1 = (fO_2)^{n/2} \times a_{\text{Me}}^{\text{alloy}} \times a_{\text{Md}}^{\text{alloy}} / a_{\text{MdO}_n} \times a_{\text{Me}} \quad (2),$$

where  $a_i$  is the activity of a component  $i$ . For pure Me the equation (2) can be rewritten as:

$$\begin{aligned} \log fO_2 = 2/n \log(K_1 \times a_{\text{MdO}_n}) + \\ + 2/n \log(a_{\text{Me}}^{\text{alloy}} \times a_{\text{Md}}^{\text{alloy}}) \end{aligned} \quad (3).$$

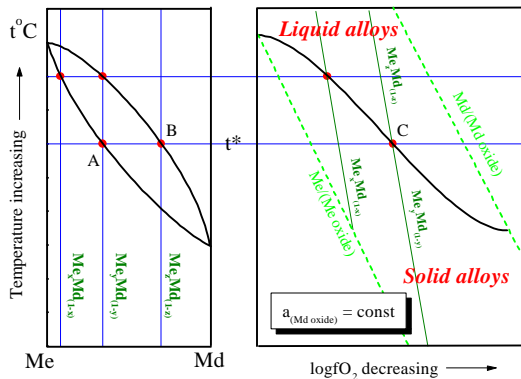
At constant activity of Md oxide, the oxygen fugacity, at which solid Me converts in liquid MeMd alloy is a strong function of temperature. Indeed, even assuming temperature independent  $K_1$ , the atomic fractions (and activities) of Me and Md in liquid MeMd alloy will change with temperature along the liquidus, affecting  $fO_2$  according to equation (3).

Now, let me discuss a few simple types of binary diagrams.

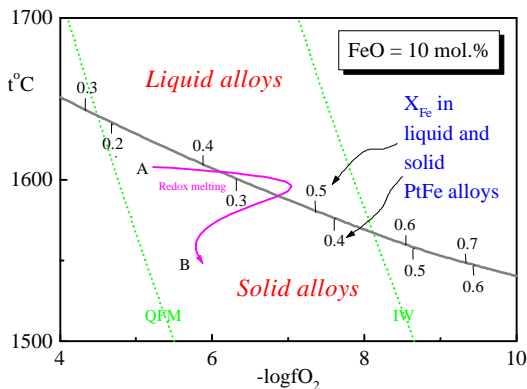
**A binary system with complete solid solution between Me and Md** will transfer into a  $t^\circ$ - $fO_2$  diagram as is shown in Fig. 1. It represents, for example, a common case of a PGE solid metal saturation (and consequent melting) with iron or other iron group metal from a silicate melt with constant activity (or, in first approximation, constant concentration) of  $MdO_n$ . What would happen, if we slowly decrease  $fO_2$  at  $t^* = \text{const}$ ? Initially pure solid Me will slowly consume Md from  $MdO_n$ , with fraction of Md in Me-Md alloy increasing as  $fO_2$  decreases. At some  $fO_2$  the system will reach invariant point C (see right graph) and  $fO_2$  will not decrease before all solid  $Me_yMd_{(1-y)}$  converts into liquid  $Me_zMd_{(1-z)}$ . Further decreasing  $fO_2$  will result in further consumption of Md from  $MdO_n$  and evolution of liquid alloy composition.

On Fig. 2 I showed the calculated melting diagram of Pt-Fe alloy in silicate melt with constant concentration (10 mol. %) of  $FeO$  (thermodynamic data from [5-7]). Trend A-B clearly demonstrates that even at decreasing temperature one could emerge the situation with melting of an initially solid alloy. It could be a spike of very reducing  $H_2$ -containing deep fluid, or quick decompression of carbon-containing melts or any other process with temporal sharp

decrease of  $fO_2$ . I would suggest a term “*redox melting*” to emphasize the process, when it is not temperature but oxygen fugacity, which is responsible for solid phase melting. If these Pt-Fe alloy droplets are small enough, they will easily reequilibrate after  $fO_2$  “normalization” to have a composition relevant to  $t$ - $fO_2$  conditions in point B (see Fig. 2). An attempt to reconstruct the maximum temperature for such alloy composition by simple using solidus of Pt-Fe binary will thus result in ironically high overestimation.



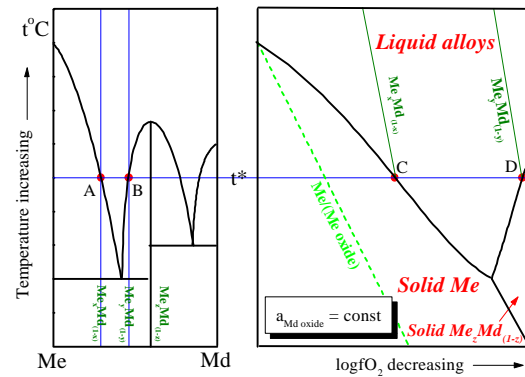
**Fig. 1.** A binary system with complete solid solution between metal and metalloid.



**Fig. 2.** A melting diagram of Pt-Fe binary alloys in equilibrium with basaltic melt containing 10 % mol. FeO.

**A binary eutectic system with congruently melted compound**  $Me_zMd_{(1-z)}$  will transfer into a  $t^*$ - $fO_2$  diagram as is shown in Fig. 3. It represents, for example, a common and very simplified case of a PGE solid metal interaction with solid  $SiO_2$  or silica of a melt. What would happen this time, if we slowly decrease  $fO_2$  at  $t^* = \text{const}$ ? The solid Me will not consume Md from  $MdO_x$  and will stay practically pure

with  $fO_2$  decreasing down to some specific  $fO_2$  (invariant point C on right graph of Fig. 3). At this point  $fO_2$  will not decrease before all solid pure Me converts into liquid  $Me_xMd_{(1-x)}$ . Further  $fO_2$  decrease will result in consumption of Md from  $MdO_n$  and evolution of liquid alloy composition from  $Me_xMd_{(1-x)}$  to  $Me_yMd_{(1-y)}$ . At much lower  $fO_2$ , however, the system will reach another invariant point D and  $fO_2$  will not decrease before all liquid  $Me_yMd_{(1-y)}$  converts into solid  $Me_zMd_{(1-z)}$ .



**Fig. 3.** A binary eutectic system with congruently melted compound.

Most of the binary Me-Md phase diagrams are more complicated than those shown above. Their quantitative representation would require great effort and thermodynamic data on Me-Md solutions. Alternatively, such melting diagrams may be constructed experimentally. But, being done, these diagrams could be useful instruments in cosmochemistry, geochemistry and technology at consideration of very reducing conditions.

*This work was performed while the author held a National Research Council - JSC/NASA Research Associateship.*

**References:** [1] Wang S.F. and Huebner W. (1992) *J. Amer. Ceram. Society* **75**, 2339; [2] Borisov A. et al. (1994) *Geochim. Cosmochim. Acta* **58**, 705; [3] Borisov A and Palme H. (1996) *Mineralogy and Petrology* **56**, 297; [4] Chen C.-H. and Presnall D.C. (1975) *Am. Mineralogist* **60**, 398; [5] Moffatt W.G. (1986) *The handbook of binary phase diagram*; [6] Heald E.F. (1967) *Trans. Met. Soc. AIME* **239**, 1337; [7] Grove T.L. (1981) *Cont. Min. Petr.* **78**, 298.