

MILAN M. JAKŠIĆ¹
KUNIAKI MURASE²

¹Institute of Chemical
Engineering and High
Temperature Chemical
Processes, FORTH, and
Department of Chemistry,
University of Patras,
Greece

²Department of Materials
Science and Engineering, Kyoto
University, Kyoto 606-8501,
Japan

SCIENTIFIC PAPER

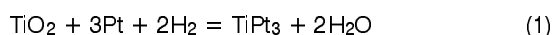
537.12+536.7+66.097

APPENDIX

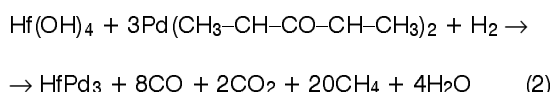
EXTENDED BREWER THERMODYNAMIC BASIS OF FACILITATED THERMAL HYPO-HYPER-*d*-INTERMETALLIC PHASE FORMATION

The point is that hypo-*d*-electronic transition metals are rather oxophilic elements and thereby subject of specific and tedious metallurgical production, while their affinity for intermetallic bonding with hyper-*d*-metals is pronouncedly high and usually results even in extraordinarily stable Laves type intermetallic phases [1-10]. The latter is accompanied by unusually high negative enthalpies of formation and, as a consequence, dramatically increased their intermetallic melting points, and further consequently, by a rather pronounced synergism in electrocatalysis for the HELR [6-12].

The main breakthrough approach of the present method of composite catalysts formation primarily consists in a proper application of the extended Brewer interionic bonding theory [1-4,13,14], to use the hypo-hyper-*d*-interionic *d-d*-bonding effect at molecular level of properly mixed metal ions and/or molecules, for example, their oxides or hydroxides in a consistent stoichiometric ratio, and reduce the overall reaction on the 'neutralization' or water production (steam withdrawal), such as



One of such examples represents interactive decomposition of hyper-*d*-metal acetylacetonates (2,4-pentanedionates, M-acac), along with spontaneous catalytic reduction of hypo-*d*-oxides or hydroxides mixed together at their molecular level by a proper sol-gel procedure, such as,



where at a rather low temperature decomposed Pd-acac affords finely dispersed Pd atoms (or any other hyper-*d*-electronic element in another equivalent reaction, like Eq. (2)), as scattered self-catalytic centers (sites) for further interactive bonding into an extra-stable Laves phase (HfPd₃) under relatively mild conditions.

In other words, while there is no real technological ability to reduce individually titania, hafnia, zirconia, ceria, lanthania, etc., at reasonably and attainably high temperatures to their metallic state (Fig. 1), the extended Brewer *d-d*-interactive method enables to combine them properly and substantiate the entire desirable intermetallic phase formation within the simultaneous reaction with Pt, Pd, Ir, Ni, Co, or their oxides (Eq. (2)) and/or other salts (preferably nitrates, acetates, oxalates and similar combinations, because of their simple thermal decomposition), at only few hundreds degree of centigrade [13,14]. In other words, the extraordinarily high enthalpies of formation of the Brewer type stable Laves phases, as a thermodynamic driving force, succeed in a greater amount to annul (subtract) the prevailing part of heats necessary to reduce hypo-*d*- and/or hypo-*f*-oxides and hydroxides in such a properly composed overall reaction.

The main theoretical impact to establish a novel nanotechnology of broad and specific field of hypo-hyper-*d*-interionic catalysts has been based on the interactive reduction, in which atoms of Pt, Pd, Co, Ni, and/or any other suitable hyper-*d*-electronic transition metal, behave both as the reactant to produce defined intermetallic phase (TiPt₃, HfNi₃, ZrPd₃, CeCo₅, LaNi₅, etc.), and as a self-catalyst to reduce hypo-*d*- or hypo-*f*-oxides, like TiO₂, HfO₂, ZrO₂, CeO₂, LaO₂, in course of their mutual interaction, so that the overall reaction, (Eq. (1)), can be thermodynamically considered to occur as split in two steps, consisting from the straight, catalytically facilitated (Pt) titania reduction,



Author address: M.M. Jakšić, Institute of Chemical Engineering and High Temperature Chemical Processes, FORTH, and Department of Chemistry, University of Patras, Greece
Paper received and accepted: April 27, 2005

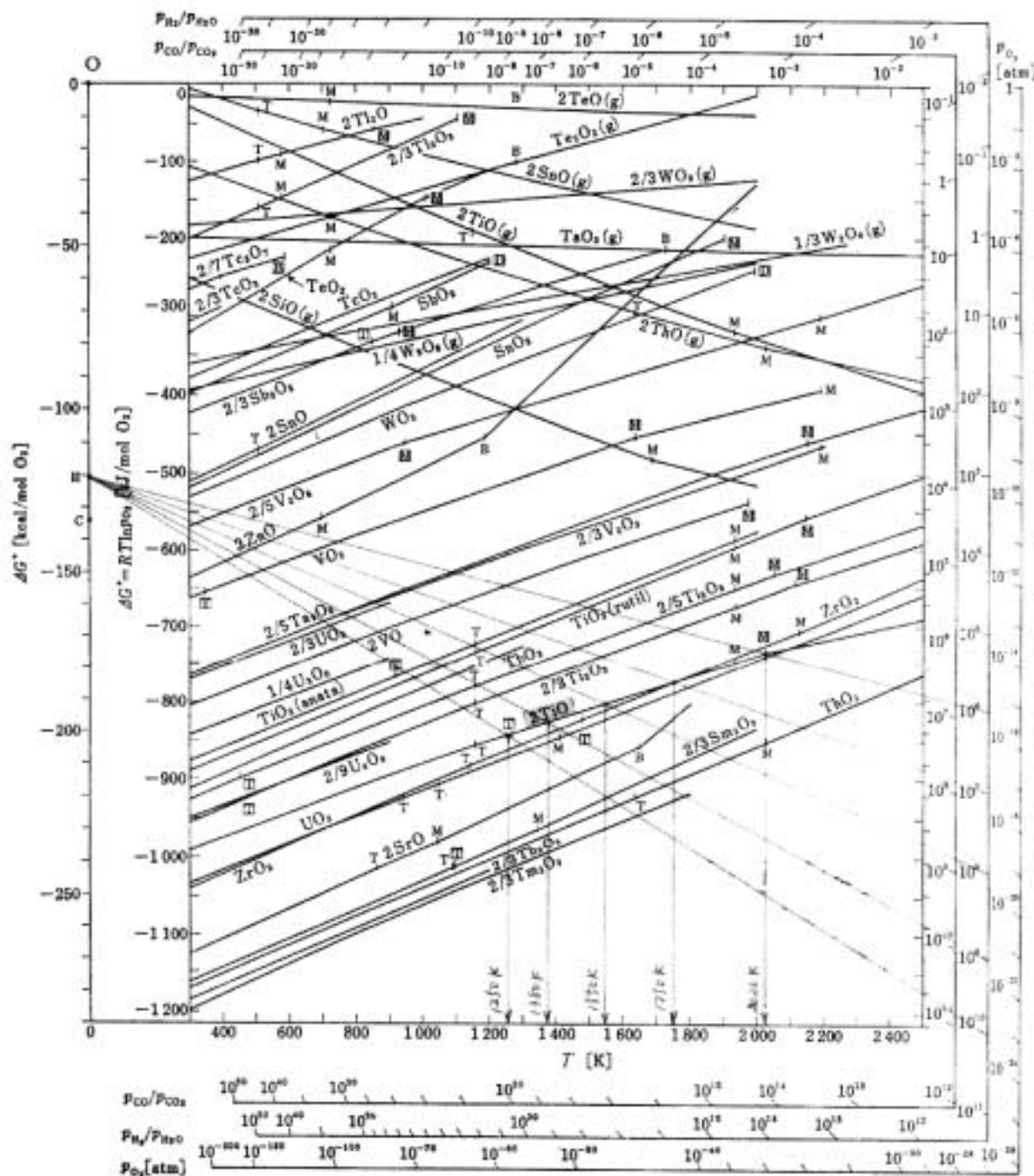


Figure 1. Thermodynamic nomographical assessment of equilibrium temperatures for reduction various oxides to their metallic state as a parametric relation of hydrogen partial pressure relative to the corresponding value for water vapor [17].

and further direct Brewer intermetallic bonding reaction,



The reliable relevant thermodynamic functions for this type of reaction of Pt with Ti, Zr and Hf, we owe to Meschter and Worrell [15,16], while the broad thermodynamic survey of data for oxides afford Kubaschewski et al. [17] (Table 1). Since thermodynamic functions and data are additive within

defined stoichiometry (extended Hess law, Haber-Born cycle), from the existing literature one simply has as follows,

$$\Delta G_1 (TiO_2 \rightarrow TiPt_3) = \Delta G_{1-1} + \Delta G_{1-2} = -RT \ln K_1 = (460,400 - 96.3 T) + (-341,833 + 33.51 T) \quad (3)$$

The point and substance is in a huge free enthalpy of the Brewer type intermetallic hypo-hyper-d-interelectronic phase formation, that succeeds

Table 1. Relevant thermodynamic values for present calculations (after Kubichewski et al. [17]).

Sample	ΔH_{298} (KJmol ⁻¹)	S_{298} (Jmol ⁻¹ K ⁻¹)
TiO ₂ (s) (rutile)	-944.0	50.6
TiO (s) (monocl.)	-542.7	34.7
HfO ₂ (s) (monocl.)	-1117.5	59.4
ZrO ₂ (monocl.)	-1100.8	50.4
H ₂ (g)	0	130.6
Ti (s)	0	30.7
H ₂ O (g)	-241.8	188.7

energetically (or, catalytically) to annul great deal of TiO₂ stability. When one now introduces the equilibria constant in the overall dependence, which practically reflects in the ratio of partial pressures of hydrogen and water vapor, other reactants being at their standard states, there follows a parametric relation,

$$\begin{aligned} \Delta G_1 (\text{TiO}_2 \rightarrow \text{TiPt}_3) &= 118,567 - 62.79 T = \\ &= 38.29 T \log \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right) \end{aligned} \quad (4)$$

When the latter is compared with the individual thermodynamic equation for TiO₂ reduction [17],

$$\begin{aligned} \Delta G (\text{TiO}_2) &= 460,400 - 96.3 T = \\ &= 38.29 T \log \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right) \end{aligned} \quad (5)$$

one becomes able now to compare temperature (T) both of individual titania reduction, along with the overall Brewer effect of mutual interactive reduction, for three such systems TiPt₃, ZrPt₃, HfPt₃, along the partial pressure relation, taken as an axis (Fig. 2). While titania itself thermodynamically requires, for example, minimum of 2180 K to be reduced at simple technical conditions

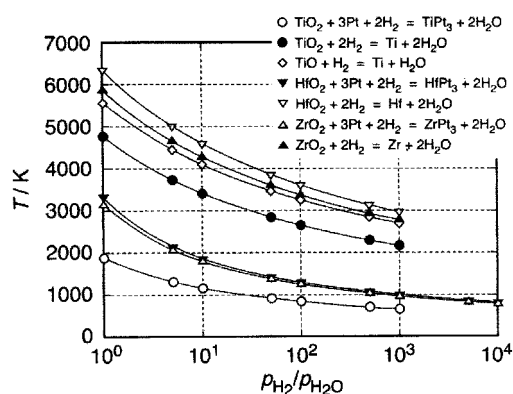


Figure 2. Temperature dependence of various hypo-d-oxides (TiO, TiO₂, ZrO₂, HfO₂) reduction to their individual metallic state, and catalytic formation of their Laves type stable intermetallic phases (TiPt₃, ZrPt₃, HfPt₃), as a function of parametric ratio of hydrogen and water vapor partial pressure.

$\left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right)$ under the same circumstances, there follows

TiPt₃ formation at 667 K. Although one can provide hydrogen supply even with less than 1 ppm of moisture, this graph is restricted at technically accessible real conditions, since in the course of such processes the main accompanying product is deliberated water.

On the electrochemical Volta scale, just for the comparison purposes to assess the Brewer interactive effect contribution, these two reactions would thermodynamically occur in their spontaneous directions at 1.1184 and 0.2587 V, respectively, and such remarkable difference favours the appearance and growth of strongly bonding Laves type of Brewer intermetallic phases. In other words, while rather strong reducing agencies (like NaBH₄) are absolutely unable to reduce individually titania, hafnia, or zirconia, their stoichiometric molecular mixtures with Pt, Pd, Ni salts, resulting in Laves type intermetallic phases, are accordingly, attainable (accessible), at least partially. In such a context it is worthwhile noting that in agreement with the present theory, catalytic literature shows usual (interactive) annealing at about 300–400°C for all intermetallic catalysts, though it is much below their individual melting points.

The same type of corresponding thermodynamic relations for Hf and Zr are as follows, respectively [15–17]:

$$\begin{aligned} \Delta G (\text{HfO}_2 \rightarrow \text{HfPt}_3) &= (633,900 - 100.3 T) + \\ &+ (-475,302 + 52.30 T) = 158,598 - \\ &- 48.0 T \text{ (J mol}^{-1}\text{)} = 38.29 T \log \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right) \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta G (\text{ZrO}_2 \rightarrow \text{ZrPt}_3) &= (617,200 - 104.8 T) + \\ &+ (-452,374 + 52.72 T) = 164,826 - \\ &- 52.08 T \text{ (J mol}^{-1}\text{)} = 38.29 T \log \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right) \end{aligned} \quad (7)$$

This is the substance and basis for a novel nanotechnology of hypo-hyper-d-intermetallic nano-particulate cluster phase formation: the stronger the intermetallic d-d-bonding, the lower is the mutual thermodynamic temperature of intermetallic phase reduction. The bonding effectiveness apparently increases with the exposure of d-orbitals (Fig. 2), from 3d towards 5d level, or from Ti towards Hf, and this way confirms the initial basic statements of the Brewer intermetallic bonding theory [1–4]. The broad common point is that all hypo-hyper-d- and/or hypo-f-hyper-d-intermetallic phases characterizes pronounced strong interionic (or interatomic) bonding effectiveness, and this implies the versatile and broad number of combinations by simple following of the present technology and thermal procedure.

The same thermodynamic calculations based on lower oxide states of TiO, ZrO and HfO, as the starting

reactants, show that in contact with Pt they are absolutely unstable and instantaneously produce stable $TiPt_3$, $ZrPt_3$ and $HfPt_3$ intermetallic phases. Such fact is noteworthy, since supported catalysts (M/TiO_2) immediately undergo a rather facilitated reduction of titania in hydrogen furnace or even by adsorbed H-adatoms ($M-H$) during heterogeneous catalytic process, to a non-stoichiometric state (TiO_x , where $2 > x > 1$), that finally results in either in Magneli phase (Ti_nO_{2n-1}) [18] or in defined intermetallic phases [13,14].

This is the Brewer High Temperature Thermodynamics and there is no remark or reproach. However, kinetics is something else and requires thorough studies. These processes with Ti, Zr, Hf hardly proceed to their completeness, so to be considered fully quantitative. They require other specific catalysts, crystallization agencies and more specific procedure primarily as a time function. Oxides of less oxophilic metals and thereby of lower reduction temperatures, like Mo, W, Cr, V, when combined with Ni, Co, Fe, or their salts, follow the same type of Brewer reactions at much lower temperatures. As thermal gravimetry analysis (TG) shows [13,14], such reactions proceed at dramatically lower temperature relative to individual oxides of oxophilic and refractory metal, and follow the exact stoichiometry.

The aim of the present paper has been to afford thermodynamic bases for the Brewer type intermetallic phase formation out of oxophilic hypo- d -electronic oxides, as the effect of enormous enthalpies accompanying all hypo-hyper- d -interelectronic interactions of transition metals. In other words, the attainable conditions to produce extraordinary stable hypo-hyper- d -interelectronic phases out of hypo- d -oxides result as a direct consequence of the Brewer intermetallic bonding theory [1-5].

The sound proof of such thermodynamic analysis for a direct thermal production of extraordinary stable hypo-hyper- d -intermetallic phases of transition metals, affords the spontaneous growth of a Laves type stoichiometric compound, $TiPt_3$, at the phase boundary of Pt/ TiO_2 (Fig. 3). Namely, H-adatoms from Pt surface, step by step, succeed to produce XPS confirmed $TiPt_3$ intermetallic phase even at lower temperature, about 300°C, than it has been thermodynamically predicted. The point is that thermodynamic calculation implies molecular hydrogen, while one deals here with chemisorbed H-adatoms, which dissociative adsorption upon Pt surface proceeds spontaneously and appear energetically more predestined for the facilitated reduction reaction.

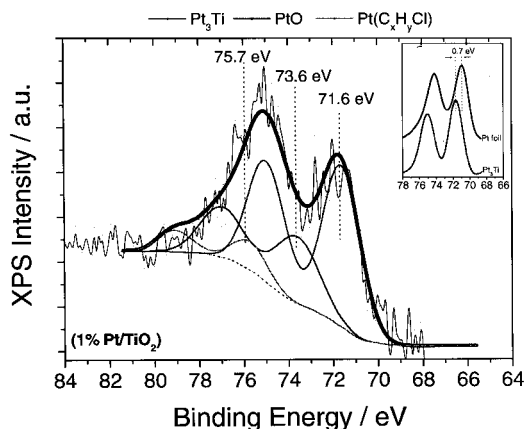


Figure 3. The XPS Pt 4f spectra scanned at the phase boundary of Pt and anatase titania (Pt/TiO_2), indicating the existence of the Brewer predicted intermetallic Laves type $TiPt_3$ phase.

REFERENCES

- [1] L. Brewer, *Science*, **161** (1968) 115.
- [2] L. Brewer, in: P.A. Beck (Ed.), *Electronic Structure and Alloy Chemistry of Transition Elements*, Interscience, New York, 1963, p. 221-235.
- [3] L. Brewer, in: V.F. Zackay (Ed.), *High-Strength Materials*, Wiley, New York, 1965, pp. 12-103; L. Brewer, 'The Cohesive Energies of the Elements', LBL-3720, Berkeley, California, May 4, 1977.
- [4] L. Brewer, in: P. Rudman, J. Stringer, R.I. Haffee, (Eds.), *Phase Stability in Metals and Alloys*, McGraw-Hill, New York, 1967, p. 39-61.
- [5] L. Brewer, P.R. Wengert, *Metal. Trans.* **4** (1973) 83-; P.R. Wengert, *Thermodynamic Stability of Certain Intermetallic Compounds Made from Transition Elements*, Ph.D. thesis, No. UCRL-18727, University of California, Berkeley, California, 1969.
- [6] M.M. Jaksic, *J. Mol. Catal.* **38** (1986) 161-202.
- [7] M.M. Jaksic, *Electrochim. Acta*, **29** (1984) 1539-1550.
- [8] M.M. Jaksic, *High. Temp. Sci.* **30** (1990) 19-50.
- [9] M.M. Jaksic, *Electrochim. Acta* **45** (2000) 4085-4099.
- [10] M.M. Jaksic, *J. New Mat. Electrochem. Systems*, **3** (2000) 153-168.
- [11] M.M. Jaksic, C.M. Lacnjevac, B.N. Grgur and N.V. Krstajic, *J. New Mat. Electrochem. Systems*, **3** (2000) 169-182.
- [12] M.M. Jaksic, *Int. J. Hydrogen Energy*, **26** (2001) 559-578.
- [13] S.G. Neophytides, S. Zafeiratos, M.M. Jaksic, *J. Electrochem. Soc.* **150** (2003) E512-E526.
- [14] S.G. Neophytides, S. Zafeiratos, G.D. Papakonstantinou, J.M. Jaksic, F.E. Paloukis, M.M. Jaksic, *Int. J. Hydrogen Energy*, **30** (2005) 131, 393.
- [15] P.J. Meschter, W.L. Worrell, *Metallurgical Trans. A*, **7** (1977) 299-305.
- [16] P.J. Meschter, W.L. Worrell, *Metallurgical Trans. A*, **8** (1977) 503-509.
- [17] O. Kubaschewski, C.B. Alcock, P.J. Spenser, *Materials Thermochemistry*, 6th ed., Pergamon Press, Oxford, 1993.
- [18] A. Magneli, *Acta Chem. Scand.*, **13** (1959) 5.