Asian Journal of Chemistry; Vol. 28, No. 5 (2016), 993-995

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19559

Compound Formation Between Transition Metals Using Orbital Electronegativities

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Received: 11 August 2015; *Accepted*: 26 October 2015; *Published online*: 30 January 2016; AJC-17731

Compound formation between transition metals is predicted by three sorts of bonding parameters based on simplified bond orbital model and orbital electronegativities. These bonding parameters are constructed for *sp*, *sd* and *sd*(α_s) bonding modes. Overlapping effect of *s*-orbital on *d*-orbital is considered in construction of *sd*(α_s) bonding parameter. In the present study, *sd* and *sd*(α_s) bonding are assumed for 3*d*/3*d* combination and for remnant ones, respectively and *sp* bonding effect is also considered in Sc, Y and La compounds. Using these bonding parameters, formation of binary transition metal compound with a fixed melting point can be judged using these bonding parameters at the agreement of about 84 % with phase diagram results. Subsequently, heat of formation for AB compound is calculated from a proposed energy function and the calculated values show good agreement with experimental ones. Further, the agreement is comparable with the results by Miedema's empirical rule.

Keywords: Compound formation, Transition metal, Electronegativity, Bonding parameter, Energy function.

INTRODUCTION

Prediction of compound formation and structural classification is a subject of interest of many investigators [1,2]. Quantum mechanical calculations and empirical approaches have clarified the formation and classification of compounds with various complex structures. Among various compounds, bonding characteristics of transition metal compounds are generally more complicated than those in *sp*-bonded compounds and these compounds occupy the important situation from the standpoint of alloy design. Therefore, much interest has been paid in compound chemistry and physics of transition metals [3-5].

Quantum mechanical approaches are, in most cases, difficult to apply to technological problems, therefore, various simple parameters have been proposed for understandings of compound properties and applications to technological problems such as alloy design. Among simple parameters, the empirical rule by Miedema [6] is one of successes to predict the compound formation by heat of formation. On the other hand, various parameters such as redefined electronegativities have also been proposed on the basis of quantum mechanical calculation many successes have been obtained to explain structural mapping and compound properties. However, versatility of these parameters seems to be insufficient for technological applications.

In the present study, we try to propose a versatile and simple parameter for predicting transition metal compound. We construct bonding parameters for transition metals on the basis of simplified bond orbital model and orbital electronegativities which redefined using Zunger's orbital radii. For simplicity, as shown later, bonding parameters for transition metals are constructed by assuming predominance of *s*-*d* hybridization. Subsequently, compound formation is examined by the bonding parameters based on three sorts of bond modes which are *sp*, *sd* and *sd*(α_s) bondings. Further, we propose an energy function based on the bonding parameters and examine the correlation between heat of formation of AB compound and the value of the energy function. Finally, the correlation is compared with Miedema's empirical rule.

EXPERIMENTAL

Construction of bonding parameters for transition metals: In the present study, we assume for simplicity that *s*-*d* hybridization is predominantly formed in the compounds between transition metals because the difference between s- and *p*-orbital electronegativities is smaller than those between *s*- (or p-) and *d*-orbital electronegativities. When the assumption is permitted, the following formula on bonding parameter for *s*-*d* hybridization is easily expected from the analogy of *s*-*p* bonding;

$$\Psi(sd) = (\alpha_s/n_{av})^{1/2} + (\alpha_d/n_{av})^{1/2} - [(S_{sd}^{A} + S_{sd}^{B})/n_{av}]^{1/2} \quad (1)$$

where α_s, α_d and S_{sd}^{i} (i = A and B) are similarly defined as in the previous work [7]. On account of limited space, we list up only orbital electronegativities of 3*d* transition elements in Table-1.

TABLE-1
ORBITAL ELECTRONEGATIVITIES OF 3*d* TRANSITION ELEMENTS

	$(Z/r_s)^{1/2}$	$(Z/r_p)^{1/2}$	$(Z/r_d)^{1/2}$
Sc	1.57	1.40	3.11
Ti	1.87	1.67	3.78
V	2.14	1.93	4.39
Cr	2.37	2.09	4.90
Mn	2.66	2.39	5.52
Fe	2.90	2.63	6.03
Co	3.13	2.86	6.55
Ni	3.23	2.86	7.16

When the energy difference between *s*- and *d*-electrons is not so larger than that between *s*- and *p*-electrons, sp^3 hybridization will fairly contribute on the bonding between transition metals. Higher predominance of *sp* bonding is easily expected with decreasing the number of *d*-electron in constituent atom. Accordingly, we can easily imagine the highest predominance of sp bonding in the Sc, Y and La compounds. However, we can not easily estimate the degree of the predominance, so that we assume tentatively that the contribution of *sp* bonding is 50 % only for Sc. Y and La compounds.

Subsequently, we examine the compound formation between transition metals using the above-described *sd*/*sp* bonding modes, resulting in no good agreement to phase diagram results in 3*d*/4*d* and 3*d*/5*d* combinations. We expected that the disagreement may be caused by the overlapping effect of 5*s* or 6*s* orbital to respective *d*-orbital. Therefore, taking into account the over-lapping effect, we modifies the bonding parameter for sd hybridization [$\Psi(sd)$] to following form {write it as $\Psi[sd(\alpha_s)]$};

$$\Psi(sd(\alpha_s)) = [\alpha_d(\alpha_s)/n_{av}]^{1/2} + (\alpha_s/n_{av})^{1/2} - [(S_{sd}^{A} + S_{sd}^{B})/n_{av}]^{1/2} \quad (2)$$

where $\alpha_d(\alpha_s) = |(Z/r_d)_A^{1/2} + (Z/r_s)_A^{1/2} - (Z/r_d)_B^{1/2} - (Z/r_s)_B^{1/2}|$.

Thus, we construct the bonding parameters for combinations including 4*d* and 5*d* transition metals using $\Psi[sd(\alpha_s)]$ instead of $\Psi(sd)$.

Construction of energy function for AB compounds: It is easily recognized that the existence of many intermetallic compounds with no melting point gives rise to unclear critical point for compound formation. Therefore, we need another support for adequacy of the constructed bonding parameters to judge compound formation between transition metals. Among the properties of compound, heat of formation is one of the suitable parameters because the energy itself shows the possibility of compound formation and we can obtain a lot of data on heat of formation for compound formation. Further, we can compare these values with the results derived from Miedema's empirical rule.

In the present study, we select $\Delta N\Psi^2R$ as an energy function for compound formation between transition metals, where Ψ is $\Psi(sd)$ for 3*d*/3*d* and $\Psi[sd(\alpha_s)]$ for remnant combinations and R is $(\Sigma r_s + \Sigma r_d)/2$, respectively. In the compound of Sc, Y and La, $[\Psi(sd) + \Psi(sp)]/2$ and $(\Sigma r_s + \Sigma r_p)/2$ are used for Ψ and R, respectively. Further, the difference of electron number between two transition atoms is used as the value of ΔN. When both *s*- and *d*-orbital electronegativities of A (or B) atom is larger than those of B atom(or A) in A-B bonding, we take the number of valence electron of A(or B) atom as ΔN. The physical meanings of the energy function and correspondence of the present result to Miedema's one will be discussed later.

RESULTS AND DISCUSSION

It is easily recognized that there are two sorts of transition metal compounds, that is, one has a fixed melting point and another is decomposed before melting. Chemical state in compound decomposed before melting must be substantially distinguished from that in the compound which shows a fixed melting point. Comparing the value of bonding parameter with results on phase diagrams, no compound formation can be predicted by the value of Ψ less than zero. However, $\Psi = 0$ is not the critical condition for the formation of some compound with fixed melting point.

Bonding parameter seems to relate to ionic energy in A-B bonding because the parameter basically constructed on electronegativities. Therefore, it is expected that covalent energy is also related to compound formation. In other words, competitive phenomenon between covalent and ionic energies will control the compound formation between transition metals. Accordingly, we consider that whether or not a compound shows a fixed melting point is the boundary for compound formation.

Before comparing ionic energy with covalent one, we must obtain the ionic energy for A-B bonding itself. As described in previous section (construction of energy function for AB compounds), we take the ionic energy as the function of $\Delta N\Psi^2R$. Therefore, we examine correlation between $\Delta N\Psi^2R$ and heat of formation [ΔH(obs.)] of AB compound [8]. Good correlation of ΔH(obs.) to ΔH(pred.) calculated from a function of $\Delta N\Psi^2R$ [$\Delta H = 26(\Delta N\Psi^2R) + 16$] is clearly shown in Fig. 1.

Subsequently, it is assumed that the covalent energy of AB compound by $RT_m(av)$, where R is the gas constant and $T_m(av)$ is the average of melting points of constituent metals. Then, we compare $RT_m(av)$ with ΔH(pred.) which is determined by

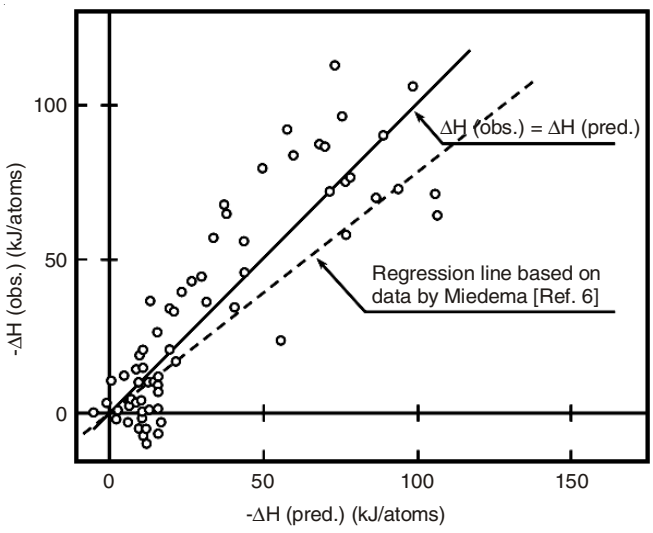

Fig. 1. Relation between ΔH(obs.) and ΔH(pred.) in AB compounds

TABLE-2
TYPICAL RESULT ON COMPOUND FORMATION BETWEEN TRANSITION METALS AND COMPARISON OF MELTING (OR DECOMPOSITION) TEMPERATURE WITH THE ASSUMED SOLIDUS TEMPERATURE [T_m(av)] (BOLD LINE SHOWS THE PREDICTED BOUNDARY OF COMPOUND FORMATION)

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	No $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$	Mn_2Y: 1380K $T_\delta > T_c$	$Fe_{17}Y_2$: 1623 K $T_s > T_c$	CoY: ?	Ni_6Y: 1763 $T_\delta > T_c$
Zr	No $T_\delta > T_c$	No $T_\delta > T_c$	V_2Zr:1573 K $T_\delta > T_c$	Cr_2Zr:1946 K $T_\delta > T_c$	Mn_2Zr:1613 K $T_\delta > T_c$	Fe_2Zr: 1948 K $T_\delta > T_c$	ε: ~1823K $T_\delta > T_c$	Ni_7Zr_2: 1713K $T_\delta > T_c$
Nb	No $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$	CrNb:2043 K $T_\delta > T_c$	Mn_2Nb:1773 K $T_\delta > T_c$	μ: ~1900 K $T_\delta > T_c$	γ: 1753K $T_\delta > T_c$	Ni_3Nb:1650 K $T_\delta > T_c$
Mo	No $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$	Mo_4Mn6:1723 K $T_\delta > T_c$	σ: 1884 K $T_\delta > T_c$	σ: 1892 K $T_\delta > T_c$	NiMo:1635 K $T_\delta > T_c$
Tc	No data	TiTc:~250 K $T_\delta > T_c$	No data	σ: ~2123K $T_\delta > T_c$	No data	σ: 1800 K $T_\delta > T_c$	No data	No $T_\delta > T_c$
Ru	ScRu:2473 K $T_\delta > T_c$	TiRu:2403 K $T_\delta > T_c$	RuV: ?	Cr_2Ru:1853 K $T_\delta > T_c$	No data	No $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$
Rh	No data	TiRh:2213 K $T_\delta > T_c$	r': 2013 K $T_\delta > T_c$	ε: 1973 K $T_\delta > T_c$	MnRh(β): ?	No $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$
Pd	No data	$TiPd_3$:1800 K $T_\delta > T_c$	Pd_2V:1178 K $T_\delta > T_c$	CrPd: 843 K $T_\delta > T_c$	β: 1788 K $T_\delta > T_c$	$FePd_3$: 1093 K $T_\delta > T_c$	No $T_\delta > T_c$	No $T_\delta > T_c$

the equation; $\Delta H(obs.) = 26(\Delta N\Psi^2 R) + 16$. From such comparison, it is indicated that the formation of compound with a fixed melting point can be predicted when the condition of $H(pred.) \geq RT_m(av)$ is satisfied. Thus, it is concluded that the compound with a fixed melting point can be formed when ionic energy exceeds covalent energy. Summarizing the result on all combinations between transition metals, we obtain the agreement of about 84 % with experimental results. Further, it is indicated that the agreement of about 84 % is comparable to the result by Miedema's rule. In this study, only the result for 3*d*/4*d* combination is shown in Table-2 on account of limited space.

There exist several points to discuss in the process to obtain the above results. The first one is the assumption in constructing the ionic energy of AB compound. The square form of Ψ is basically reasonable for expressing ΔH(pred.) because Ψ corresponds to electronegativity difference and square form has been proposed in Pauling's formula [9]. However, it will be more reasonable to interpret that Ψ^2 is a sort of average potential for bonding electrons and Ψ^2R corresponds to ionic energy for one electron.

The use of ΔN, instead of $(\Delta N)^2$, is also somewhat arguable because heat of formation can be expressed by the function of $(\Delta N)^2$ from the standpoint of electron theory [10]. If the assumption for Ψ^2R is permitted, however, it will be easily accepted that total ionic energy for A-B bonding should be proportional to ΔN.

Subsequently, construction of bonding parameters should be further reconsidered for improving the agreement with ΔH(obs.), if we choose ΔH(obs.) as a suitable property for examining bonding energy between transition metals. Especially, precise ratio of *sp* bonding to *sd* bonding are required to reproduce the experimental data. Dependence of ΔH(pred.) on concentration will be reported in near future.

Conclusion

Bonding parameters are constructed for predicting the formation of compound between transition metals on the basis of simplified bond orbital model and orbital electronegativities. Assuming the predominance of *s*-*d* hybridization, three sorts of bonding parameters for *sp*, *sd* and $sd(\alpha_s)$ bonding modes are constructed and the overlapping effect of *s*-orbital is taken into account in the construction of $sd(\alpha_s)$. In the present study, *sd* and $sd(\alpha_s)$ bondings are assumed for 3*d*/3*d* combination and for remnant ones, respectively. Further, *sp* bonding effect is also considered in the Sc, Y and La compounds. It is found that these bonding parameters can predict the formation of compound with a fixed melting point at the agreement of about 84 % with the results on phase diagrams. Further, it is indicated that heat of formation of AB compound can be calculated on the basis of proposed function and the agreement is comparable with the results by Miedema's empirical rule.

ACKNOWLEDGEMENTS

This research was supported by the Ministry of Trade, Industry and energy (MOTIE), KOREA, through the Education Support program for Creative and Industrial Convergence.

REFERENCES

1. A. I. Frolov and M.G. Kiselev, *J. Phys. Chem. B*, **118**, 11769 (2014).
2. S.P. Sun, D.Q. Yi, Y. Jiang, B. Zang, C.H. Xu and Y. Li, *Chem. Phys. Lett.*, **513**, 149 (2011).
3. T.N. Gribanova, R.M. Minyaev and V.I. Minkin, *Phys. Chem. Chem. Phys.*, **14**, 14803 (2012).
4. H. Dagistanli and R.H. Mutlu, *Radiat. Phys. Chem.*, **81**, 240 (2012).
5. K. Richter, A. Birkner and A.V. Mudring, *Phys. Chem. Chem. Phys.*, **13**, 7136 (2011).
6. A.R. Miedema, *Physica B*, **182**, 1 (1992).
7. D. Errandonea, *J. Phys. Chem. Solids*, **67**, 2017 (2006).
8. I.I. Oleinik and D.G. Pettifor, *Phys. Rev. B*, **59**, 8500 (1999).
9. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithica, Ch. 3 (1960).
10. D.G. Pettifor, *Phys. Rev. Lett.*, **42**, 846 (1979).