Alloy Design Based on Molecular Orbital Method

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A molecular orbital approach to alloy design has recently made great progress. It is based on the electronic structure calculations by the DV-Xα cluster method, and new alloying parameters are obtained for the first time from the calculations. A theory for alloy design relevant to transition-metal based alloys has been developed using alloying parameters. For example, New PHACOMP has been developed in order to predict the formation of harmful and brittle phases (e.g., σ phase) in nickel-based superalloys. A universal relation has also been discovered between electron density minima and atomic (or ionic) radii in various materials from a series of molecular orbital calculations. Furthermore, another electronic approach is explained focusing on the energy expression of the chemical bond between atoms in hydrides and hydrocarbons. All the hydrides and hydrocarbons are located on an atomization energy diagram, despite the significant differences in the nature of the chemical bond among them. One of the applications of this approach is the catalyst design. The catalytic activities of metal oxides (e.g., Nb2O5) are evaluated quantitatively on the dehydrogenation reaction of magnesium hydride (MgH2), MgH2 → Mg + H2.

1. Introduction

Nowadays, a word of alloy design seems platitudinous because of its wide spread and long use in the field of metallurgy. However, it was quite new when the author started the research of alloy design in the beginning of the 1980’s. In view of history, we started using a word of alloy design, since PHACOMP method was developed in 1964 in order to predict the formation of harmful and brittle phases in Ni-based alloys.1,2) However, in those days alloy design was still too difficult to be practical, and most of alloys were developed relying on many trial-and-error experiments. On the contrary, these days the importance of materials informatics3) is well recognized in every field of materials. As the author recalls those days, it seems as if we were in another world.

In those days the author was engaged in the investigations to examine the local ionic arrangements in VOx and stabilized zirconia by measuring X-ray diffuse scattering.4–7) Also, the electronic structure of zirconia was calculated using the DV-Xα molecular orbital method.8) In these circumstances, by putting up a signboard of “alloy design based on molecular orbital method”, the author set foot in the unknown research field.

In this paper, theory for alloy design will be explained first. A universal relation found in the electron density distribution will also be described briefly. Then, recent approach will be explained focusing on the energy expression of the chemical bond between atoms in hydrides and oxides using the atomization energy concept. Finally, two recent topics will be discussed. One is a trial toward the design of metal compounds in view of non-metal elements, and the other is a problem of the local lattice strains formed around substitutional alloying elements in Mg metal.

2. Theory for Alloy Design

2.1 Alloying parameters

It is well known that physical and chemical properties of metals and alloys are related closely to the electronic state in them. Most of practically used alloys consist of multiple components. For these complex alloy systems, it is very difficult to calculate the electronic state accurately, and even if the calculation could be performed in some ways, it might be meaningless for alloy design, because the number of combinations of alloying species and compositions are infinitely large in the multiple-components alloys.

For alloy design, it is more practical to use alloying parameters which exhibit explicitly the character of each element in a mother metal. However, despite a long history of metallurgy or metal science, we do not have any alloying parameters, so most of alloying properties have been evaluated by using the parameters assigned to pure metals (e.g., the electrons-per-atom-ratio (e/a), atomic radius, electronegativity).9,10) The same value of the parameter is always used for the same element even if the alloy system is varied, resulting in very poor prediction of alloying properties along this approach. To solve this problem, it is first necessary to determine alloying parameters theoretically using molecular orbital methods.

To this end, the DV-Xα cluster method is used. This is the first-principle calculation method that is more appropriate to the simulation of the local electronic structure around alloying element as compared with the conventional band calculation method. The detailed explanation of the DV-Xα cluster method is given elsewhere.11,12)

The transition-metal based alloys such as Fe alloys and Ti alloys are so common in our daily life. The chemical bond is characterized by d electrons in the transition metals. Needless to say, depending on the use of alloys, we have to select most suitable alloying parameters. In case of the structural use, two alloying parameters are very useful for the design of transition-metal based alloys.13–15)

One alloying parameter is the bond order (hereafter referred to Bo). As shown in Fig. 1(a), Bo is a parameter to

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show the overlapping of the electron clouds between alloying element (M) and mother metal (X). So, this is a measure of
the strength of the covalent bond between M and X atoms. In case when both M and X are transition metals, the $d$-$d$
covalent bond is most important between them. As the $Bo$
value increases, the stronger chemical bond is operating
between M and X atoms.

Another alloying parameter is the $d$ orbital energy level
(hereafter referred to $Md$). As shown in Fig. 1(b), when M
atom makes a molecule with X atom, the bonding level at the
lower energy and the anti-bonding level at the higher energy
are formed by hybridizing the $d$ orbitals of isolated M and X
atoms. As shown in the figure, if the $d$ level of an isolated M
atom is higher than that of an isolated X atom, the electrons
move from M to X so as to reduce the energy. As the result of
such a charge transfer, the effective charge becomes positive
for M, and negative for X. Thus, the energy level controls the
direction for charge transfer, and hence it is related to the
electronnegativity. Higher electronnegativity element has the
lower $d$ orbital energy level ($Md$).

Also, $Md$ correlates with the atomic radius. Any atom with
the larger atomic radius has the larger average radius of the
$d$ orbital. In such a case, the average distance between $d$
electrons and the nucleus at a center increases, which
weakens the attractive Coulomb force operating between
them. As the result, the $d$ orbital level ($Md$) becomes high as
the atomic radius increases.

It is stressed here that both $Md$ and $Bo$ are new alloying
parameters obtained for the first time from the molecular
orbital calculation. These two electronic parameters change
following the order of elements in the periodic table. As most
of physical and chemical properties change following the
periodic table, these are indeed suitable parameters for
treating alloying properties. Furthermore, these two
parameters represent the characteristic of the two-dimensional
periodic table. The use of only one parameter (for example,
Mendeleev number) never expresses any changes following
the periodic table.

### 2.2 Molecular orbital calculation of nickel alloys

The Ni-based superalloy is one of important high-temperature
alloys used for jet engines and gas turbines. This alloy
is strengthened by the precipitation of Ni$_3$Al(γ') phase in the
Ni(γ) matrix phase.

As shown in Fig. 2(a), Ni$_3$Al has a L1$_2$ type structure. In
pure Ni$_3$Al a central Al atom is surrounded by twelve Ni
atoms in the first-nearest-neighbors and by six Al atoms in the
second-nearest-neighbors, as shown in Fig. 2(b). This
cluster model of (MNi$_2$Al$_6$) is used for the calculation, where M
is an alloying element substituted for a central Al atom,
and the 3$d$, 4$d$ and 5$d$ transition metals are chosen as M in the
calculation. As M is surrounded by twelve Ni atoms, M is
placed in a circumstance as in fcc Ni. The interatomic
distance is set from the experimental value of the lattice
parameter. The density of states of electrons in pure Ni$_3$Al
obtained from the cluster calculation resembles the result of
the band calculation despite the use of a relatively small
cluster in the calculation.

The results of the level structure are shown in Fig. 3 for
Ni$_3$Al alloyed with various 3$d$ alloying elements. In this
figure, the energy of the Fermi level ($Ef$) of Ni$_3$Al is set to be
zero and used as a reference. In case of pure Ni$_3$Al cluster
(i.e., M = Al) the levels of 13a$_{1g}$ to 15e$_g$ originate mainly
from the Ni 3$d$ orbital, and form the Ni 3$d$ band where the
Fermi energy level lies as is indicated by an arrow. In case of
alloyed cluster, new energy levels due mainly to the $d$
orbital of the alloying transition metal, appear above the Fermi
energy level. For instance, the 16e$_g$ and 14e$_{2g}$ levels (drawn as
broken lines) correspond to these new levels. Their energy
height changes systematically with the order of elements in
the periodic table. The $Md$ level is defined by taking the
average of these two levels. Also, the bond order, $Bo$,
between Ni-$d$ and M-$d$ electrons is calculated for every M
atom, following the Mulliken population analysis.

The $Md$ and $Bo$ values are listed in Table 1 for various
alloying elements, M. Here, the $Md$ value is expressed
using the eV unit, where 1 eV = $1.60 \times 10^{-19}$ J. The bond
order, $Bo$, shows a maximum at the 6A group elements such
as Cr, Mo and W. The high $Bo$ elements such as Cr, Mo, Ta,
W and Re are principal alloying elements in the Ni-based
superalloys.

For an alloy, the average values of $Md$ and $Bo$ are defined
simply by taking the compositional average, and $Md$ and $Bo$
are defined as,

$$\overline{Md} = \frac{1}{n} \sum_{i=1}^{n} X_i \cdot (Md)_i,$$

$$\overline{Bo} = \frac{1}{n} \sum_{i=1}^{n} X_i \cdot (Bo)_i.$$  

Here, $X_i$ is the atomic fraction of component $i$ in the alloy,
$$(Md)_i$$
and $(Bo)_i$, are the respective values for component $i$
which are listed in Table 1. The summation extends over the
components, $i = 1, 2, \ldots, n$. The $Md$ is the average value of the $d$
level of each alloying element, so it represents a center of
gravity in the $d$-band of the alloy. The values of $Md$ and $Bo$
are calculated simply from the alloy composition using
eqs. (1) and (2).
2.3 New PHPCOMP and d electrons alloy design

2.3.1 New PHACOMP

A solid solubility problem of alloy is one of the important problems in metallurgy. According to the classical approach by Hume-Rothery and Darken-Gurry,9,10 this problem has been treated by using the atomic radius and electronegativity. However, there are some difficulties in this approach when both solute and solvent atoms are transition metals.

In 1964, PHACOMP (PHase COMPutation) method1,2 was developed in USA to predict the solid solubility limit of elements in the Ni matrix (γ) so as to suppress the precipitation of harmful and brittle phases (e.g., the σ phase) in the γ matrix. The electron vacancy number, N_v, is used for the prediction in this method. Here, N_v is the number of electron vacancies or holes existing above the Fermi energy level in the d band, and expressed approximately as

\[ N_v = 10.66 - \frac{e}{a} \]

where e/a is the electrons-per-atom ratio. For example, for the 6A group elements (i.e., e/a = 6) such as Cr, Mo and W, the N_v value is 4.66. However, the atomic radius is smaller in Cr than in Mo or W. Thus, the atomic size concept is missing in the N_v parameter. In this sense, this method is very different from the classical approach by Hume-Rothery and Darken-Gurry,9,10 and inevitably the prediction is poor along this N_v method. Nevertheless, PHACOMP has been employed widely for the design and the quality control of nickel-based superalloys.

The author proposed New PHACOMP in 1984.14 This is the method for predicting the solid solubility limit by using the Md parameter. As explained earlier, the Md parameter is concerned with the electronegativity and the atomic radius of elements. It is important to note here that this parameter is determined using the alloy cluster which has the same chemical circumstance as in the Ni alloy. Therefore, the Md parameter has a great possibility of dealing with the present solubility problem of alloys, both solute and solvent being transition metals.

Two typical phase diagrams of Ni-Co-Cr and Ni-Cr-Mo are shown in Fig. 4(a) and (b). In each phase diagram, the \( \gamma \)/\( \gamma + \sigma \) phase boundary is traced using the iso-Md line of 0.925. For simplicity, the unit of Md (eV) is omitted in the
figure. For comparison, the iso-$N_v$ line and iso-$R$ line are also shown in each phase diagram. Here, $N_v$ and $R$ are the compositional averages of $N_v$ and atomic radius, $R$, of elements, respectively. The iso-$N_v$ line of $N_v = 2.49$, that is often used for the prediction of the $\gamma/\gamma + \sigma$ phase boundary, is far away from the boundary. On the other hand, the iso-$R$ line traces well the boundary shown in (a), but it is far away from the boundary shown in (b). Compared to these, the iso-$Md$ line is close to the boundary in both (a) and (b). The validity of this $Md$ method has been confirmed through the examination of more than 30 ternary phase diagrams.\textsuperscript{21-24}

The temperature dependence of the $Md$ values for the $\gamma/\gamma + \sigma$ phase boundary, are expressed approximately as,

$$Md = 6.25 \times 10^{-5} T + 0.834$$ \hspace{1cm} (3)

Here, $T$ is the absolute temperature (K). The temperature coefficient above eq. (3) is close to the coefficient of the thermal energy, $k_B T = 8.62 \times 10^{-5} T$ (eV), where $k_B$ is the Boltzmann constant.

Besides the $\gamma/\gamma + \sigma$ phase boundary, the $\gamma/\gamma + \mu$ phase boundary is traced using the iso-$Md$ line. For example, the $Md$ value is 0.900 eV for the $\gamma/\gamma + \mu$ phase boundary in the Ni-Co-Mo alloy at 1473 K.\textsuperscript{21} This $Md$ value for the $\mu$ phase is smaller than the value of 0.925 eV for the $\sigma$ phase shown in Fig. 4. Such a $Md$ value is an indicator for the stability of the $\sigma$ or $\mu$ phase relative to the $\gamma$ phase.\textsuperscript{21} For example, it is known that the $\mu$ phase precipitates even in the $\sigma$-free alloy\textsuperscript{21} because of its lower $Md$ value.

New PHACOMP is applicable to not only ternary phase diagrams, but also practically used alloys with multiple components in order to predict the formation of brittle phases in them.\textsuperscript{14,21,25}

There is a certain correlation of the $Md$ and $Bo$ parameters with thermodynamic data of the Ni alloys. For binary Ni-10 mol% M alloys, the experimental values of enthalpy of mixing for liquid alloys, $\Delta H^L$, and the enthalpy of formation for solid solutions, $\Delta H^S$, are taken from Ref. 26. The values of $\Delta H^L$ and $\Delta H^S$ for various M are plotted in Fig. 5 against (a) $Md$ and (b) $Bo$. For each element M, $\Delta H^L$ is very similar to $\Delta H^S$, although experimental temperatures are different between them. For example, in case of $M = Mn$, $\Delta H^L$ is $-4.7$ kJ/mol which is measured at 1743 K, and $\Delta H^S$ is $-5.0$ kJ/mol which is measured at 1050 K. So, as shown in Fig. 5, the $\Delta H^L$ data indicated by $\bullet$ symbol, are overlapped with the $\Delta H^S$ data indicated by $\circ$ symbol for various elements, $M (= Cu, Co, Fe, Mn and Pd)$.\textsuperscript{26}
As shown in Fig. 5(a), $\Delta H^L$ and $\Delta H^S$ change linearly with the $Md$, and $\Delta H^L$ is expressed approximately as, $\Delta H^L = 6.91 - 9.89Md$, with the correlation coefficient of 0.99. So, the iso-$Md$ line shown in Fig. 4 may be a line to express a constant enthalpy of formation for solid solutions of the alloys, as $\Delta H^S$ is nearly equal to $\Delta H^L$. On the other hand, as shown in Fig. 5(b), $\Delta H^L$ and $\Delta H^S$ become more negative with increasing Bo, since the chemical bond between M and Ni atoms becomes stronger with the Bo as described before.

2.3.2 d electrons alloy design

For nineteen conventional cast superalloys, $Md$ and Bo are calculated from the alloy composition, and the results are plotted in the $Bo-Md$ diagram as shown in Fig. 6.27,28) The contour lines showing the 0.2% yield strength at 1255 K are also indicated by dotted lines. The 0.2% yield strength shows the maximum at a small shadowed region in the diagram. Not only the 0.2% yield strength but also the creep strength at high temperature is very large for the alloys in this small region. Single crystal superalloys are also positioned in this region. So, this is a target region for alloy design. In any alloy located in this target region, a large amount of alloying elements are added so far as no brittle phases precipitate in the $\gamma$ matrix. The volume fraction of the strengthening $\gamma'$ phase in the alloy is also as high as about 60%,28) resulting in the high strength of the alloy. Thus, a target region for alloy design is specified concretely on the $Bo-Md$ diagram.

In addition, alloying vectors are shown in Fig. 6. The vector starts from the position of pure Ni and ends at the position of Ni-10 mol%M binary alloy in the $Bo-Md$ diagram, where M is an alloying element in Ni. As the M composition increases, the alloy position moves on the line toward the vector direction of M. The directions and the magnitudes of these vectors vary with alloying elements. It is noticed that the vector directions are similar among the same group elements in the periodic table, for example, among Ti, Zr, Hf (4A group elements), V, Nb, Ta (5A elements) and Cr, Mo, W (6A elements). This reflects the fact that both the Bo and the Md parameters change following the order of elements in the periodic table, as mentioned earlier.

Recent single-crystal Ni-based superalloys contain about 6 mass% Re.25) As Re is only one element to increase both the strength and corrosion resistance, its content keeps increasing. In order to keep the target alloy position on the $Bo-Md$ diagram nearly unchanged with the Re content, alloy compositions may be adjusted among those elements which have a similar vector direction. For example, the Re addition may require to reduce the Cr content in the alloy, since their vectors point to the similar direction. Such a compositional change is actually seen in the history of the advance in single-crystal Ni-based superalloys, for example, alloy modification from PWA 1480 (the first generation superalloy) to PWA 1484 (the second generation superalloy). Further decrease in the Cr content and attendant increase in the Re content is seen in René N6 (the third generation superalloy). Recently, Ru of a relatively low $Md$ value (Table 1) is added preferably into the advanced superalloy in order to suppress the lowering of phase stability of the Ni ($\gamma$) matrix due to the further increase of Re content in the alloy.25)

2.4 Examples of alloy design

2.4.1 Ni based superalloys

Following the method described above, several superalloys have been developed for use of gas turbine in power plants.27-33) For example, a blade of single-crystal superalloy (height: about 170 mm) is shown in Fig. 7(a). This is a third generation superalloy containing about 5 mass% Re. It possesses about 20 K higher temperature capability than the 2nd generation superalloy, CMSX-4, and also exhibits the better hot-corrosion resistance and oxidation resistance than CMSX-4.33)

2.4.2 Heat resisting high Cr ferritic steels

The DV-Xα cluster calculation is performed using a bcc Fe alloy cluster, and the $Md$ and Bo parameters are determined for alloying elements in iron.24) The alloying vectors are shown in Fig. 8. The alloying vectors for all the ferrite forming elements (e.g., Cr, Mo, W) start at the pure Fe position and point to the right and up direction. On the other hand, the alloying vectors for the austenite forming elements (e.g., Co, Ni, Cu, Mn) point to the left and down direction.
except for Mn. The vector of Mn is small and exists near pure Fe.

It is desirable to suppress the formation of the δ ferrite in ferritic steels because of the detrimental effect on the creep resistance and the fracture toughness of the steels. The measured volume fraction of the δ ferrite existing in the steels normalized at 1323 K, are plotted against the $Md$ parameter as shown in Fig. 9. For Ni-free and Co-free steels the δ ferrite starts forming as the $Md$ value exceeds 0.852 (eV), and its volume fraction increases with increasing $Md$ value. However, the presence of Ni and Co in the steel increases the critical $Md$ value for the δ ferrite formation. For example, the critical $Md$ value is about 0857 (eV) in the 1 mass% Ni containing steel. This is also the case of another austenite forming element, Cu. So, the addition of Ni, Co or Cu into the steel gives a room to increase the amount of ferrite forming elements such as Mo and W without forming the δ ferrite, resulting in the increase in creep properties at high temperature.

Following this result, heat resisting high Cr ferritic steels are developed by adding about 3 mass% Co into the steel. A photograph shown in Fig. 7(b), is a 10 ton steam turbine rotor (diameter: 640 mm, length: 2270 mm). The creep rupture life is about 4,000 hours (14.4 Ms) under the creep condition of the temperature, 923 K and the applied stress, 157 MPa, which is about several times longer than the currently used rotor steel.

Also, for high Cr ferritic steels, the long-term creep strength at 923 K shows a maximum at 8.5~9.0 mass% Cr. In addition, the creep strength increases significantly when 0.2~0.5 mass% Re is added into the steel. Furthermore, in case of the ferritic steels for boiler, sulfur (S) remaining by about 50 ppm in the steel improves the steam oxidation resistance remarkably.

### 2.4.3 Titanium alloys

The $Bo$ and $Md$ values are calculated using both bcc Ti cluster and hcp Ti cluster. Their values are not so sensitive to the crystal structure. The $Bo$ and $Md$ values for alloying elements in bcc Ti are listed in Table 2.

#### Table 2 List of $Bo$ and $Md$ values for alloying elements in bcc Ti.

<table>
<thead>
<tr>
<th>Element</th>
<th>$Bo$ (eV)</th>
<th>$Md$ (eV)</th>
<th>Element</th>
<th>$Bo$ (eV)</th>
<th>$Md$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>2.790</td>
<td>2.447</td>
<td>Zr</td>
<td>3.086</td>
<td>2.934</td>
</tr>
<tr>
<td>V</td>
<td>2.805</td>
<td>1.872</td>
<td>Nb</td>
<td>3.099</td>
<td>2.424</td>
</tr>
<tr>
<td>Cr</td>
<td>2.779</td>
<td>1.478</td>
<td>Mo</td>
<td>3.063</td>
<td>1.961</td>
</tr>
<tr>
<td>Mn</td>
<td>2.723</td>
<td>1.194</td>
<td>W</td>
<td>3.125</td>
<td>2.072</td>
</tr>
<tr>
<td>Fe</td>
<td>2.651</td>
<td>0.969</td>
<td>Ru</td>
<td>2.704</td>
<td>0.859</td>
</tr>
<tr>
<td>Co</td>
<td>2.529</td>
<td>0.807</td>
<td>Nb</td>
<td>2.736</td>
<td>0.561</td>
</tr>
<tr>
<td>Ni</td>
<td>2.412</td>
<td>0.724</td>
<td>Pd</td>
<td>2.208</td>
<td>0.347</td>
</tr>
<tr>
<td>Cu</td>
<td>2.114</td>
<td>0.567</td>
<td>Ag</td>
<td>2.094</td>
<td>0.196</td>
</tr>
</tbody>
</table>

Fig. 8 Allowing vectors for elements in bcc Fe.

Fig. 7 (a) Ni-based single crystal superalloy for use of blade in power plant, and (b) ten tons steam turbine rotor made of heat-resisting high Cr ferritic steel.

Fig. 9 Prediction of δ ferrite formation by $Md$ parameter.
example, a typical Ti alloy, Ti-6Al-4V alloy (No. 9) is located in the $\alpha + \beta$-type field. Even if the alloy-type is unknown, we can predict it readily by calculating the Bo and Md values from the alloy composition and locating the alloy position in Fig. 10. Further information is not included on this diagram to avoid the complexity, but for example, the region where the martensite phase appears, or the region where either slip or twin deformation takes place, is specified concretely on this diagram.\textsuperscript{44,45} This Bo-Md diagram is now used widely over the world as a road map for alloy development.

Following this method, high temperature $\alpha$-type alloy,\textsuperscript{44} high strength $\alpha$-type alloy,\textsuperscript{45} and high corrosion resistant alloys\textsuperscript{46-48} have been developed. Also, $\beta$-type Ti alloy for bio-implant applications\textsuperscript{49} has been successfully developed. This method is now used for developing low elastic-modulus alloys.\textsuperscript{50} In addition, gum metal\textsuperscript{51} appears only when $\text{Bo}=2.87$ and $\text{Md}=2.46$ (eV). The shape memory effect is also discussed with the aid of this method.\textsuperscript{52}

2.4.4 Other alloys

Using the molecular orbital calculations, the following alloys have been investigated.\textsuperscript{53,54}

(i) Intermetallic compounds (improved ductility of TiAl,\textsuperscript{55} and construction of crystal structure maps for intermetallic compounds\textsuperscript{56,57}).

(ii) Transition-metal alloys (alloy design of Zr alloys,\textsuperscript{58} Nb alloys\textsuperscript{59} and Mo alloys\textsuperscript{59,60} for nuclear applications, and improvement of the brittleness of Cr alloys\textsuperscript{61}).

(iii) Simple-metal alloys (evaluation of mechanical properties of Al alloys,\textsuperscript{62,63} Mg alloys,\textsuperscript{64,65} Zn alloys,\textsuperscript{66} and application to alloy design).

3. A Universal Relation of Electron Density Distribution in Material

Through these investigations, electronic structures for a variety of materials have been calculated using the DV-Xα molecular orbital method. It has been discovered that there is a universal relation between electron density minima and atomic (or ionic) radius.\textsuperscript{67} As shown in an inset in Fig. 11, natural logarithm of the electron density, $\log(\rho(r))$, is illustrated along the line linking the first-nearest-neighbor atoms in MgO or Al$_2$O$_3$. Here, let’s define the minimum electron density, $\rho_{\text{min}}$, and the atomic or ionic radius, $r_{\text{min}}$, where $\rho_{\text{min}}$ is observed. For example, in case of MgO, $r_{\text{min}}(O)$ for O atom is about 1.02 nm and $r_{\text{min}}(Mg)$ for Mg atom is about 0.9 nm. The $\rho_{\text{min}}$ and $r_{\text{min}}$ are calculated for gasses, water and solids, and the results are summarized in Fig. 11. In this figure the vertical axis is $Z(n/r)_{\text{min}}$ and the horizontal axis is $2(Z(n/r)_{\text{min}}/Z^2)$ and $Z(n/r)_{\text{min}}$ where Z is the atomic number and n is the principal quantum number. These coordinates are chosen, because for the radial distribution functions of hydrogen-like atom, $\rho(r)/Z^2$ is a function of only one variable, $2(Z(n/r)r)$. It is surprising that every matter falls on one curve, irrespective of gasses, water and solids, despite the large differences in the nature of the chemical bond between atoms...
among them. For example, some of matters shown in Fig. 11 are gasses (H₂, O₂), water (H₂O), diamond (C), metals (Fe, Al), semi-conductors (Si, Ge), oxides (MgO, Al₂O₃, SiO₂, BaTiO₃), alkali halide crystals (NaCl, KCl), and metal compounds (TiC, ZrN). Thus, this curve is indeed a universal curve that is common to every matter. By setting \( y = \log(\beta_{\text{min}}/Z) \) and \( x = 2(Z/n)_{\text{min}} \), it is expressed in a simple formula as,

\[
y = -5.29\log(1.01 + 0.285x).
\]  

4. Materials Design Based on the Atomization Energy

Recently, another approach has been investigated to express the chemical bond between atoms in materials in an energy scale.\(^{68}\) Namely, using energy density analysis\(^{69,70}\) total energy is partitioned into the atomic energy densities of constituent elements in materials. The atomization energy of each element is then evaluated by subtracting the atomic energy density from the energy of the isolated neutral atom, as explained below. The atomization energy is the energy gained or lost by arranging each atom in a crystalline solid, as compared with the gas state. As the character of individual atom in materials reflects the value of the atomization energy, this approach provides us useful information for materials design. It is first applied to hydrogen storage materials.\(^{71,72}\)

4.1 Definition of atomization energy

For example, in case of binary hydride, MH, when the energy of the isolated neutral atom, \( E_{\text{atom}}^{\text{M}} \) for metal M or \( E_{\text{H}}^{\text{atom}} \) for hydrogen H, is taken as a reference, the atomization energies, \( \Delta E_M \) and \( \Delta E_H \), are defined as,\(^{73}\)

\[
\Delta E_M = E_{\text{atom}}^{\text{M}} - E_{\text{M}}^{\text{hydride}},
\]

\[
\Delta E_H = E_{\text{atom}}^{\text{H}} - E_{\text{H}}^{\text{hydride}},
\]

where \( E_{\text{M}}^{\text{hydride}} \) and \( E_{\text{H}}^{\text{hydride}} \) are the atomic energy densities for M and H in MH, respectively. The total energy calculated by the Gaussian03 is first divided into \( E_{\text{M}}^{\text{hydride}} \) and \( E_{\text{H}}^{\text{hydride}} \), using the energy density analysis,\(^{69,70}\) and then \( \Delta E_M \) and \( \Delta E_H \) are obtained from eqs. (5) and (6).

In case of ternary hydrides, (M1M2)H\(_n\), \( \Delta E_M \) is defined as \((\Delta E_{M1} + \Delta E_{M2})/n\), that is the average atomization energy of M1 and M2 to be counted per hydrogen atom. Even in the other type of ternary hydrides, \( \Delta E_M \) is defined in a similar way.

Then, the cohesive energy, \( E_{\text{coh}} \), of the hydride per hydrogen atom is defined as,

\[
\Delta E_M + \Delta E_H = E_{\text{coh}}.
\]

Thus, \( \Delta E_M \) and \( \Delta E_H \) are the components of \( E_{\text{coh}} \). The advantage of using the atomization energy is to know the contribution of each constituent element to the hydride formation. Such a quantity is never able to be obtained from the total energy calculation alone.

By setting that \( y = \Delta E_H \) and \( x = \Delta E_M \), we obtain a relation, \( y = -x + E_{\text{coh}} \). So, \( E_{\text{coh}} \) is expressed as a point of intersection of this line and \( y \)-axis at \( x = 0 \).

For hydrocarbons expressed as a chemical formula, C\(_n\)H\(_n\), \( \Delta E_H \) and \( \Delta E_C \) are defined as,
hydrocarbons and metal hydrides will be explained in more detail as follows.

### 4.2.1 Hydrocarbons (C\(_m\)H\(_n\))

In Fig. 13 the calculated results are summarized for various hydrocarbons.\(^{73}\) In this figure, the atomization energies of \(\Delta E_C\) and \(\Delta E_H\) are given in the vertical axis, and the compositional ratio of C to H, \(m/n\), is given in the horizontal axis.

The atomization energy of C, \(\Delta E_C\), increases linearly with \(m/n\), and \(\Delta E_C\) is expressed as,

\[
\Delta E_C \text{ (eV)} = 7.46 \times (m/n) - 4.46. \tag{10}
\]

According to eq. (8), the slope is \((E_C^{\text{atom}} - E_C^{\text{hydrocarbon}})\), and it is nearly constant, 7.46 eV, regardless of the type of hydrocarbons. On the other hand, the atomization energy for hydrogen, \(\Delta E_H\) is a nearly constant, 6.76 eV, irrespective of the types of hydrocarbons. So, the cohesive energy per one hydrogen atom in hydrocarbons \(E_{\text{coh}}\) is expressed as,

\[
E_{\text{coh}} \text{ (eV)} = 7.46 \times (m/n) + 2.30. \tag{11}
\]

This beautiful relation is satisfied in the hydrocarbons, and the chemical stability of \(C_mH_n\) is dependent only on the \(m/n\) ratio.

### 4.2.2 Metal hydrides

The \(\Delta E_M\) vs. \(\Delta E_H\) diagram for metal hydrides is shown in Fig. 14.\(^{73}\) When the hydrides have a resemblance in the chemical bonding state, their locations are close to each other on the diagram. For example, binary hydrides of transition elements (e.g., NiH and PdH, both shown by solid square (■) in Fig. 14) appear in the higher \(\Delta E_H\) region than those of typical elements (e.g., NaH and MgH\(_2\), both shown by open square (□) in Fig. 14). This indicates that transition elements could stabilize the hydrogen state remarkably in the binary hydrides. In other words, hydrogen atom interacts more strongly with transition elements than typical elements.

For ternary metal hydrides, M1M2H\(_4\), where M2 is a transition metal (e.g., TiFeH\(_2\) shown by open circle (○) in Fig. 14), the M2-H interaction is important, since H is located in the neighborhood of M2 (e.g., M2 = Fe) in the crystal lattice. In case of Mg\(_2\)NiH\(_4\) shown by open circle (○) in Fig. 14, hydrogen atom is located in the neighborhood of Ni, and the strong interaction is operating between Ni and H in it. In agreement with this, Mg\(_2\)NiH\(_4\) is located near NiH rather than MgH\(_2\) on the atomization energy diagram shown in Fig. 14. However, the \(\Delta E_H\) value is smaller in Mg\(_2\)NiH\(_4\) than in NiH, indicating that the H state is destabilized by the presence of Mg in Mg\(_2\)NiH\(_4\). On the other hand, TiFeH\(_2\) is located well above TiH\(_2\), so that the \(\Delta E_H\) value is larger in TiFeH\(_2\) than in TiH\(_2\), indicating that H state is further stabilized by the presence of Fe in the neighborhood instead of neighboring Ti. It is very interesting that TiFeH\(_2\) which desorbs hydrogen at room temperature has the largest cohesive energy, 8.3 eV, among the metal hydrides.

Mg\(_2\)NiH\(_4\) and TiFeH\(_2\) are formed by the hydrogenation of intermetallic compounds, Mg\(_2\)Ni and TiFe, respectively. Therefore, the further analyses are carried out with these compounds. To understand the role of metal atoms in the bond formation, the values of \(\Delta E_{M1}\) (M1 = Ti or Mg) and \(\Delta E_{M2}\) (M2 = Fe or Ni) are plotted in Fig. 15 for TiFe and Mg\(_2\)Ni, together with the values for TiFeH\(_2\) and Mg\(_2\)NiH\(_4\). As shown in the figure, \(\Delta E_{Ti}\) for TiFe and \(\Delta E_{Mg}\) for Mg\(_2\)Ni are negative, whereas \(\Delta E_{Ti}\) for TiFe and \(\Delta E_{Ni}\) for Mg\(_2\)Ni are positive. By hydrogenation, the atomization energy decreases in both M1 and M2 atoms. However, the decrement is more remarkable in \(\Delta E_{M2}\) than in \(\Delta E_{M1}\). This is because, hydrogen exists in the neighborhood of M2 and interacts strongly with M2 (M2 = Fe or Ni) in the hydrides. As a result, most of the energy of M2 transfers to the hydrogen and the H state becomes very stable, for example, \(\Delta E_H = 14.4\text{ eV}\) for TiFeH\(_2\) and \(\Delta E_H = 9.0\text{ eV}\) for Mg\(_2\)NiH\(_4\).

It is interesting to note that in either system of TiFe and Mg\(_2\)Ni there is a large difference between \(\Delta E_{M1}\) and \(\Delta E_{M2}\). This means that when these compounds are formed, a significantly large modification occurs in the electron density distribution between M1 and M2 atoms, which leads to the strong chemical bond formation between atoms in both TiFe and Mg\(_2\)Ni intermetallic compounds. This is a reason why the hydrogenation and dehydrogenation reactions take place smoothly without changing alloy compositions in them. Thus, this approach can clarify the role of constituent elements in the formation of metal hydrides.\(^{73}\)

### 4.3 Oxide catalysts for dehydrogenation reaction of MgH\(_2\)

The atomization energy approach is applied to the analysis of the oxide catalysts to promote the dehydrogenation reaction of MgH\(_2\).
reaction of magnesium hydride (MgH₂).\(^{74}\) MgH₂ has been considered as one of the promising candidates for hydrogen storage, because it possesses a high hydrogen capacity of 7.6 mass%. However, the enthalpy of formation of MgH₂, \(\Delta H\), is \(-74\) kJ/mol H₂, indicating that MgH₂ is a relatively stable hydride. As a result, the temperature of the desorption reaction, i.e., MgH₂ \(\rightarrow\) Mg + H₂, is as high as about 573 K. In addition, this desorption reaction proceeds very slowly in the moderate conditions. However, it is found experimentally that some transition metal oxides (e.g., Nb₂O₅) have a large catalytic effect on the hydrogen desorption reaction of MgH₂.\(^{75}\) However, no quantitative method has been proposed for understanding this catalytic problem yet. This problem is treated using the atomization energy concept.\(^{74}\)

### 4.3.1 Atomization energy diagram for binary metal oxides

The atomization energy diagram is first calculated for binary metal oxides for use of catalysts. For metal oxides, \(E_{\text{M}}\) (or \(E_{\text{O}}\)), is taken as a reference, and the atomization energy, \(\Delta E_{\text{M}}\) (or \(\Delta E_{\text{O}}\)), is defined as,

\[
\Delta E_{\text{M}} = (E_{\text{M}}^{\text{atom}} - E_{\text{M}}^{\text{oxide}}) \times (x/y),
\]

\[
\Delta E_{\text{O}} = (E_{\text{O}}^{\text{atom}} - E_{\text{O}}^{\text{oxide}}).
\]

Here, \(E_{\text{M}}^{\text{oxide}}\) and \(E_{\text{O}}^{\text{oxide}}\) are the atomic energy densities for M and O in M₂O₃, respectively. Thus, \(\Delta E_{\text{M}}\) is the average energy of M to be counted per O atom.

The plots of \(\Delta E_{\text{M}}\) vs. \(\Delta E_{\text{O}}\), are shown in Fig. 16 for binary metal oxides, M₂O₃.\(^{76}\) Those oxides which are located in the upper right region in Fig. 16, have large cohesive energies. Also, the contribution of each element in the oxide to the cohesive energy is understood from this figure. For example, the cohesive energy is nearly same between Nb₂O₅ and Al₂O₃ (Nb₂O₅: \(E_{\text{coh}} = 10.1\) eV, Al₂O₃: \(E_{\text{coh}} = 10.7\) eV). However, they are located in the very different positions in Fig. 16. Nb₂O₅ has a large \(\Delta E_{\text{O}}\) value, but a very small \(\Delta E_{\text{M}}\) value, indicating that the O atoms in Nb₂O₅ make a significant contribution to the cohesive energy. On the other hand, in case of Al₂O₃, the value of \(\Delta E_{\text{O}}\) is almost zero. Instead, its \(\Delta E_{\text{M}}\) value is very large. Thus, the metal atoms in Al₂O₃ contribute mainly to the cohesive energy. Thus, an inequality relation, \(\Delta E_{\text{O}} > \Delta E_{\text{M}}\) is satisfied for transition metal oxides like Nb₂O₅, but \(\Delta E_{\text{O}} < \Delta E_{\text{M}}\) is satisfied for Al₂O₃. This difference reflects the catalytic activity of oxides, as explained later.

### 4.3.2 Qualitative analysis of catalytic activity

The catalytic effect is measured at 573 K as a measure of the catalytic activity of each metal oxide.\(^{75}\)Nb₂O₅ is most active among various oxides.

To evaluate the catalytic activity quantitatively, the atomization energies of constituent elements in metal oxides are used. As is evident from eqs. (12) and (13), atomization energies are defined as the values per O atom. However, metal oxides, M₂O₃, are mixed by a mole unit in the experiment. So, the values of the atomization energies are needed to be converted into the values per mole unit. Therefore, each of \(\Delta E_{\text{O}}\) and \(\Delta E_{\text{M}}\) is multiplied by the number of O atoms, \(y\), in M₂O₃, that is expressed as \(y \times \Delta E_{\text{O}} = (E_{\text{O}}^{\text{atom}} - E_{\text{O}}^{\text{oxide}}) \times y\), and \(y \times \Delta E_{\text{M}} = (E_{\text{M}}^{\text{atom}} - E_{\text{M}}^{\text{oxide}}) \times x\).

In Fig. 17, the measured desorption rate is plotted against the atomization energy for O atoms, \(y \times \Delta E_{\text{O}}\).\(^{74}\) It is apparent that metal oxides which have large \(y \times \Delta E_{\text{O}}\) values tend to accelerate the hydrogen desorption rate of MgH₂. But, such a clear correlation is not found between \(y \times \Delta E_{\text{M}}\) values and the hydrogen desorption rate.\(^{74}\)

As mentioned before in section 4.2.2 about the hydrogenation process of TiFe or Mg₂Ni, the element (e.g., Fe or Ni) with the higher atomization energy interacts more strongly with hydrogen atom than the other element (e.g., Ti or Mg) with the lower atomization energy.\(^{73}\) As a result, hydrogen atoms are located near Fe in TiFeH₂, and near Ni in Mg₂NiH₄. This is also the case in metal oxides. The element with the higher atomization energy in the metal oxide must interact more strongly with hydrogen atom in MgH₂.
stronger O-H interaction probably leads to the higher catalytic activities of oxides. On the other hand, in case of Al₂O₃ where the atomization energy of the O atom is low, the catalytic activity is very low as shown in Fig. 17. Thus, in the metal oxides with large \( y \times \Delta E_O \) values, the strong O-H interaction is operating, which works to destabilize MgH₂ and to enhance the catalytic activities. It is stressed here that the catalytically active element in the hydrogen desorption reaction is the O atom, but not the M atom in metal oxides, M₂O₃. The \( \Delta E_O \) value changes with M in M₂O₃, so that the catalytic activity changes with M₂O₃.

The presence of the O-H interaction is confirmed experimentally from the observation of the O-H stretching mode in the FT-IR spectra during the dehydrogenation of the Nb₂O₅-catalyzed MgH₂. Thus, the catalytic activities of oxides are evaluated quantitatively using the atomization energy concept.

In addition, it is known that the decomposition reaction of NaAlH₄ expressed as, NaAlH₄ \( \rightarrow \) 1/3 Na₃AlH₆ + 2/3 Al + H₂, is accelerated by mixing metal chloride catalysts (e.g., TiCl₃). The catalytic activities of chlorides are evaluated quantitatively with the aid of the atomization energy concept.

4.4 Functional design of metal compounds

The present analysis is useful for the functional design of not only hydrides and oxides, but also other metal compounds. Metal compounds (e.g., borides, carbides, nitrides, fluorides, sulfides) are one of interesting material groups, because they exhibit a variety of chemical and physical properties such as superconductivity, ferroelectricity, ferromagnetism, proton conductivity and hydrogen storage. For example, there are superconducting MgB₂ and super-ferromagnetic Nd₂Fe₁₄B in the borides. It is supposed that non-metal elements are one of key factors for the emergence of new functions in the compounds. For example, there are non-metal elements, O and F etc. in the Fe-based superconductor, LaFeAsO₁₋ₓFₙ.

However, to the author’s limited knowledge, the chemical bond has been investigated individually in each compound. It is needed to find out a general trend of the chemical bond in a variety of compounds using the atomization energy concept. The knowledge or information of the characters or roles of whole non-metal elements (B, C, N, O, F, S etc.) in the compound formation will provide us a new insight for materials design in view of non-metal elements rather than metal elements.

The result of the first trial is shown in Fig. 18. This is the atomization energy diagram for 3d transition-metal compounds, M₄X₃n, where, M = Ti, Cr, Fe and X = B, C, N, O, F, S. All the compounds are expressed on this atomization energy diagram. For example, it is known that oxygen atom (O) resembles fluorine atom (F), but the compositional dependence of the atomization energies, \( \Delta E_X \) and \( \Delta E_M \), is completely reverse between oxides and fluorides. It is important to elucidate further the nature of the chemical bond in the compounds following the atomization energy concept, and then to construct a new platform for quantum materials design from a view of non-metal elements.

4.5 Application to alloy problems

Finally, it is stressed here that the atomization energy approach is applicable even to alloy problems. Recently, local lattice strains introduced around substitutional alloying elements, M, in hcp Mg metal, have been calculated with a supercell model of MMg₃₅ using the pseudopotential method.

The lattice parameters of pure Mg metal are optimized to be \( a = 0.32137 \text{ nm}, \ c = 0.51628 \text{ nm} \) and \( c/a = 1.6065 \). The local lattice strains are then calculated by optimizing the positions of twelve first-nearest-neighbor Mg atoms from M at the center. The calculated local strains of the Mg lattice vary significantly with M. In particular, local strains are large when M’s are the transition metals (e.g., Fe and Mn).

For example, the results are shown in Fig. 19(a) for M = Mn and (b) for M = Ca, where only the twelve Mg atoms around M are illustrated. The values of local strains along the a- and c-axes of hcp Mg lattice are presented for six Mg atoms on a central hexagon around M, and for three Mg atoms on the upper or lower triangles. The strain, \( \Delta a_1 \) (nm) and \( \Delta a_1/a (\%) \), along the a-axis for six Mg atoms on the hexagon is negative for Mn, but positive for Ca. The strain \( \Delta c_1 \) along the c-axis is null, \( \Delta c_1 = 0 \). On the other hand, the strain \( \Delta a_2 \) along the a-axis and the strain \( \Delta c_2 \) along the c-axis are introduced to the three Mg atoms on the upper or lower triangles. As indicated by the vectors along the c-axis, the strain direction is opposite between the three Mg atoms.
sitting on the upper and lower triangles. Both the strains, $\Delta a_2$ (nm), $\Delta a_2/a$ (%) and $\Delta c_2$ (nm), $\Delta c_2/c$ (%), are negative for Mn, but positive for Ca. As a whole, these strains cause the local Mg lattice to contract around Mn, but to expand around Ca as shown in Fig. 19(a) and (b). For any alloying element M, its local strain mode is classified by either the Mn-type or the Ca-type without exception.81)

For simplicity, the average strains are defined as, $\Delta a/a = (\Delta a_1/a + \Delta a_2/a)/2$ (%) and $\Delta c/c = 2\Delta c_2/c$ (%), where $\Delta c/c$ is set twice as large as $\Delta c_2/c$, since the opposite strain direction of the upper and lower triangles yields twice the effect on the lattice parameter change $\Delta c$ along the c-axis.

Such local lattice strains are understood using the atomization energies of M, $\Delta E_M$, and the neighboring Mg, $\Delta E_{Mg}$. As shown in Fig. 20, local lattice strains, $\Delta a/a$ and $\Delta c/c$ (%), formed around M vary monotonously with $\Delta E_M$. It is evident from Fig. 20 that there is a general trend that $\Delta E_M$ is negative for those M atoms (e.g., Ca, Sr) which expand the local Mg lattice (i.e., $\Delta a/a > 0$ and $\Delta c/c > 0$), whereas $\Delta E_M$ is positive for those M atoms (e.g., Mn, Fe) which contract the local Mg lattice (i.e., $\Delta a/a < 0$ and $\Delta c/c < 0$). This $\Delta E_M$ change with M is due simply to the charge transfer between Mg and M atoms. When electrons transfer from M to Mg, the electron density decreases around M, and hence the Coulomb attraction energy between the electrons and M nucleus decreases, resulting in the negative $\Delta E_M$. On the contrary, when electrons transfer from Mg to M, the situation is reverse, resulting in the positive $\Delta E_M$.

Nevertheless, the atomization energy, $\Delta E_{Mg}$ of the twelve first-nearest-neighbor Mg atoms from M, keeps nearly unchanged regardless of a charge transfer. For example, $\Delta E_{Mg}$ is 1.07~1.09 eV for M = Ca, that is comparable to 1.06~1.10 eV for M = Fe. Here, Fe is an alloying element to yield the largest negative strains among M as shown in Fig. 20. This indicates that the electron density distribution around the first-nearest-neighbor Mg atoms scarcely changes with M. However, the value is still larger than the $\Delta E_{Mg}$ value of 0.78~0.82 eV for the rest of Mg atoms locating in the region beyond the second-nearest-neighbors from M. This means that the electron density is higher near the first-nearest-neighbor Mg atoms, as compared with the rest of Mg atoms. As a whole, these results are probably interpreted as due to the electron screening that works to adjust the electron density distribution over the Mg lattice so as to moderate the influence of the M atom doped in a nearly free electron-like Mg metal.81)

5. Conclusions

In view of the electron bonding, it is no longer needed to distinguish between iron and steels and non-ferrous alloys, and even the current classification into metals, semiconductors, ceramics and polymers is not necessarily needed. The alloy design theory and the atomization energy method are useful not only for the fundamental understanding of materials, but also for the materials design and development without relying on trial-and-error experiments. Also, there are several calculation methods which are not explained in this paper. For example, the calculation of phase diagrams using the CALPHAD method82) and the analysis of microstructural evolution using the phase field method83) are now progressing steadily. The investigations of multi-scale simulations84) and materials informatics3) are also in progress these days. It is greatly expected that the computational material science makes remarkable progress and most of materials are designed in a rational way.

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