Electronic States Calculation of Cobalt by Using the DV-Xα Cluster Method

Dong-Su Bae\textsuperscript{1}, Seung-Ju Jang\textsuperscript{2}, Hiroshi Yukawa\textsuperscript{3}, Yoshinori Murata\textsuperscript{3} and Masahiko Morinaga\textsuperscript{3}

\textsuperscript{1}Department of Advanced Materials Engineering, Dong-Eui University, Pusan 614-714, Korea
\textsuperscript{2}Department of Computer Engineering, Dong-Eui University, Pusan 614-714, Korea
\textsuperscript{3}Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-01, Japan.

Using the DV-Xα cluster method, two alloying parameters were calculated in fcc Co. One was the bond order (Bo) which is a measure of the covalent bond strength between atoms and the other was the d-orbital energy level (Md) of alloying transition elements. These two alloying parameters were found to change monotonically with the atomic number of alloying 3d transition metals, M. The changes in the Bo with alloying elements could be understood in terms of the difference electron density maps. Also, the Co-M binary phase diagrams could be classified well using Bo-Md map. In addition, local spin moments at the alloying 3d transition metals were obtained. These results will provide us some guide for the design of cobalt-based alloys.

(Received November 7, 2000; Accepted April 19, 2001)

\textbf{Keywords}: discrete-variational (DV)-Xα cluster method, cobalt-based alloys, alloy design, electronic structure, transition metals, bond order, local spin moments

1. Introduction

Cobalt-based alloys are expected to continue in a strong secondary position to nickel alloys for turbine applications, because they possess advantages in the hot-corrosion resistance, even tough their oxidation resistance is not nominally as good as nickel-base alloys. They exhibit slightly higher thermal conductivity and slightly lower thermal expansion properties. They are thus suitable for the use of large structural parts, with long life and good thermal-fatigue resistance.\textsuperscript{1}\)

Most of the alloys developed previously, however, have been carried out relying on many trial-and-error experiments. In the super-computer age, it is needless to say that computer-aided alloy design is more preferable in order to save cost and time necessary for alloy development.

Thus, it is very important for computer-aided alloy design to elucidate alloying effects of various elements on the electronic state of Co-based alloys by computer calculations. Most of previous publications, however, have been concerned with the electronic states and phase stability of Fe-based and Ni-based alloys,\textsuperscript{2-6} and only a few investigators have referred to the electronic states of cobalt\textsuperscript{7} and also to the magnetic properties of iron-cobalt alloy.\textsuperscript{8}

In response to the needs of the times, an electronic approach to the design of Co-based superalloy was proposed in this study. This approach was constructed on the basis of the DV(Discrete-Variational)-Xα cluster method,\textsuperscript{9,10} and several new alloying parameters relevant to Co, were calculated theoretically. The purpose of this study is to investigate the alloying effects of the 3d transition metals on the electronic states of Co in order to obtain useful information for alloy design.

2. DV-Xα Cluster Method and Cluster Model

The DV-Xα cluster is a molecular orbital method in which a local exchange-correlation potential is given by the Slater’s Xα potential:\textsuperscript{9}

\[ V_{xc} = -3\alpha[3\rho(r)/8\pi]^{1/3} \]

where, \( \rho(r) \) is the density of electrons at position \( r \), the parameter \( \alpha \) is fixed at 0.7 and the self-consistent change approximation is used in this calculation. The matrix elements of the Hamiltonian and the overlap integrals are calculated by a random sampling method. The molecular orbitals are constructed by a linear combination of numerically generated atomic orbitals. The atomic orbitals used in this study were 1s-4p for Co and alloying 3d transition metals, M.

The cluster model, MCo\textsubscript{18}, used in the calculation is shown in Fig. 1. It consisted of a central alloying element, M, and the surrounding twelve first- and six second-nearest-neighbor cobalt atoms. The alloying elements, M, chosen for this calculation were Ti, V, Cr, Mn, Fe, Ni and Cu (3d transition metals). When M=Co, the cluster corresponds to that for pure Co. The lattice constant used was 0.3544 nm for Co, the same value as in the bulk. Spin-polarized calculations were performed in this study.

For characterization of the electronic states, the electron densities of states were calculated from the energy level structure using the overlapping Gaussian functions which have a width of 0.25 eV and their centers located at each cluster energy level.\textsuperscript{15} Also, local spin moments were calculated at each alloying transition metal in Co.

Furthermore, two alloying parameters were obtained. One is the bond order (hereafter referred to as Bo), which is the overlap population of electrons between atoms, and it is calculated following the Mulliken population analysis.\textsuperscript{11-14} The Bo parameter describes the covalent bond strength between atoms and correlates with several physical properties of alloys. In particular, Bo is related in some ways to the strength of alloys and the high Bo elements are known to be the principal alloying elements in most structural alloys.

Another parameter is the d-orbital energy level for alloying transition element (hereafter referred to as Md). The Md for each alloying element was obtained from the energy level
structure of the cluster. The height of this energy level is related to the charge transfer, and hence to the electronegativity of elements. This level was also found to be associated with atomic radius. Both the electronegativity and atomic radius are classical parameters which have been used in describing the nature of the chemical bond between atoms in solids. Also, the solid solubility problem of alloys has been treated by these classical parameters. Instead of the classical parameters, the alloying behavior was examined with the aid of newly calculated alloying parameters.

3. Results

3.1 Electron density of states

The electron densities of states for pure fcc Co are shown in Fig. 2(a) for the DV-Xa cluster calculation, and for comparison, in Fig. 2(b) for the band calculation.16 Although there still exists a little difference between them, the trend of the calculated results was in good agreement with each other. For example, in either case, there was a large valley in the energy band near the Fermi energy level, $E_F$. Therefore it may be said that the electronic state of crystal could be described well with the small cluster model consisting of only 19 atoms as shown in Fig. 1.17

3.2 Energy level and d-orbital energy level (Md)

The 3d component of a central alloying transition element appeared in the $t_{2g}$ and the $e_g$ levels because of the Oh symmetry of the cluster used in this molecular orbital calculation. Since the d-d covalent interaction is most significant in transition metals, both the $t_{2g}$ and the $e_g$ levels are considered to be the levels characteristic of alloying elements.18 Each representative energy level was calculated for pure Co and for the Co containing 3d transition metals, Ti, V, Cr, Mn, Fe, Ni and Cu. For example, in case of Ti as shown in Table 1, among the $t_{2g}$ and the $e_g$ orbitals, the $17t_{2g}$ and the $19e_g$ orbitals of having the largest fractions were selected as a basis for the calculation of the $Md$ parameter.

<table>
<thead>
<tr>
<th>Orbitals</th>
<th>up (%)</th>
<th>down (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$17e_g$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$18e_g$</td>
<td>2.4</td>
<td>0.0</td>
</tr>
<tr>
<td>$19e_g$</td>
<td>54.9</td>
<td>52.9</td>
</tr>
<tr>
<td>$20e_g$</td>
<td>14.4</td>
<td>6.9</td>
</tr>
<tr>
<td>$21e_g$</td>
<td>14.4</td>
<td>6.0</td>
</tr>
<tr>
<td>$15t_{2g}$</td>
<td>5.4</td>
<td>0.5</td>
</tr>
<tr>
<td>$16t_{2g}$</td>
<td>2.6</td>
<td>0.2</td>
</tr>
<tr>
<td>$17t_{2g}$</td>
<td>52.0</td>
<td>46.2</td>
</tr>
<tr>
<td>$18t_{2g}$</td>
<td>16.8</td>
<td>12.7</td>
</tr>
<tr>
<td>$19t_{2g}$</td>
<td>0.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

As the $e_g$ shows double degeneracy and the $t_{2g}$ shows triple degeneracy,18 the average of the $t_{2g}$ and the $e_g$ and/or the average of $A$ and $B$ could be represented as eq. (4).

$$(2A + 3B)/(2 + 3) = C$$ (4)

The $Md$ value is then obtained by deducting the Fermi energy level of Co from $C$.

$$Md = C - E_F$$ (5)

where, the $E_F$ value of Co in this calculation has $E_F = -0.51761$ (eV).

By simplifying the eqs. from (2) to (5); $Md$ could be obtained as follows;

$$Md = \frac{[2(e_g(up) + e_g(down)) + 3(t_{2g}(up) + t_{2g}(down))]}{10 - E_F}$$ (6)
As shown in Figs. 3(a) and (b), Md tends to increase with increasing atomic radius of 3d transition alloying element, M. This is simply due to the weaker interaction operating between electrons and the nucleus with increasing distance between them, resulting in the appearance of a higher Md level in the level structure. In addition, as shown in Figs. 3(a) and (b), Md increased with decreasing electronegativity values of elements except for Cu. In fact, it is known that the eigenvalue obtained by the Xα calculation reflects the electronegativity itself.11)

### 3.3 Bond order (Bo)

The changes in the bond order with alloying 3d transition elements, M, are shown in Fig. 4, and their respective values are given in Table 3 together with the Md values. As the d-d covalency is a major part of the total cohesive energy of transition metals and alloys, the bond order was calculated from the overlap populations of the d electrons between atoms in the cluster. In Fig. 4, Co–Co indicates the bond order between the first-nearest-neighbor Co(1) atoms and the second-nearest-neighbor Co(2) atoms form a central M atoms in the cluster. M–Co indicates the bond order between the alloying element M and its first- and second-nearest-neighbor Co atoms. Also, the curve labeled 'Total' denotes their sum.

The Co–Co bond order scarcely varied with alloying elements. On the other hand, the M–Co bond orders changed largely with the alloying elements. Accordingly, the total bond order was considerably dependent on the alloying elements, M.

### 3.4 Ionicity

Ionicity represents the charge transfer between two atoms and hence it is a parameter for the strength of ionic bond.19–21) The change of ionicity with the alloying elements was ob-
Electronic States Calculation of Cobalt by Using the DV-Xα Cluster Method

Fig. 3  (a) Atomic radius and electronegativity of alloying 3d transition elements, and (b) changes in the d-orbital energy level (Md) in Co with alloying elements.

Fig. 4  Changes in the bond order with alloying 3d transition elements.

Fig. 5  Changes in the ionicity with alloying 3d transition elements.

Table 3  List of the Md and Bo values elements in fcc Co.

<table>
<thead>
<tr>
<th>Element</th>
<th>Md (eV)</th>
<th>Bo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>2.1742</td>
<td>1.575</td>
</tr>
<tr>
<td>V</td>
<td>1.4487</td>
<td>1.532</td>
</tr>
<tr>
<td>Cr</td>
<td>1.0327</td>
<td>1.411</td>
</tr>
<tr>
<td>Mn</td>
<td>0.9001</td>
<td>1.154</td>
</tr>
<tr>
<td>Fe</td>
<td>0.4810</td>
<td>1.099</td>
</tr>
<tr>
<td>Co</td>
<td>0.1352</td>
<td>1.062</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0444</td>
<td>0.968</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0319</td>
<td>0.811</td>
</tr>
</tbody>
</table>

tained from the Mulliken population analysis. Figure 5 shows the change of ionicity with the alloying element in this cluster model. Co(1) and Co(2) indicate the ionicity for the first-nearest-neighbor Co(1) atoms and the second-nearest-neighbor Co(2) atoms from the central M atom in the cluster, respectively. The ionicities of Co(2) were always positive and almost constant, independent of alloying elements, M. But the ionicities of Co(1) were always negative and changed slightly with the alloying elements, M.

On the other hand, the ionicities of central alloying elements, M, changed largely from positive values to negative values as the atomic number of alloying elements, M, increased. This change followed the electronegativity of M, since the most electropositive Ti atom had a large positive ionicity, whereas the most electronegative group of Ni and Cu atom had a large negative ionicity.

4. Discussion

4.1 Slater-Pauling curve

Figure 6 shows the relation between alloying element and local spin moment obtained from the present calculation, and compared with the Slater-Pauling curve. The calculated local spin moments were a little different from those of Slater-Pauling curve, but the tendency was in good agreement between them. The local spin moment has a maximum value at
the Fe substitution, whereas a minimum value at the Cr substitution for Co in fcc Co. The calculated local spin moment of the central Co in pure Co cluster was 1.9 \( \mu_B \) which was slightly higher than the value of pure Co, 1.7 \( \mu_B \). The calculated local spin moments of the 1st neighbor and the 2nd neighbor Co atoms were 1.8 and 1.9 \( \mu_B \) respectively and their values were less sensitive to the alloying elements. By contraries, the local spin moments of central alloying elements, M, changed greatly with M. For example, it is 3.0 \( \mu_B \) for Fe, and 1.1 \( \mu_B \) for Ni. The value shown in the Slater-Pauling curve is 2.2 \( \mu_B \) for pure Fe and 0.6 \( \mu_B \) for pure Ni, so there was a difference between them. However, the trend of local spin moment changes with M was still similar between the present result and the Slater-Pauling curve as shown in the figure. In addition, Collins and Forsyth have reported that the local spin moment of Fe in the Co-rich Co–Fe alloys is about 3.0 \( \mu_B \), in good agreement with the present calculation. It is also noted that the anti-ferromagnetic spin coupling is seen in Ti, V and Cr. In particular the alloying of Co into Co yields a local spin moment of about –2.2 \( \mu_B \).

### 4.2 Difference electron density map

The difference electron density, \( \Delta \rho \), was calculated for alloyed Co. Here, \( \Delta \rho \) was defined as

\[
\Delta \rho = \rho(\text{MCo}_{18}) - \rho(\text{CoCo}_{18})
\]

where, \( \rho(\text{MCo}_{18}) \) and \( \rho(\text{CoCo}_{18}) \) are the electron densities of the corresponding cluster donated in parentheses. Therefore, this \( \Delta \rho \) means the change in the spatial electron density distribution in the cluster with alloying.

The calculated difference electron density maps on the (110) atomic plane are shown in Fig. 7(a) for the Ti substitution and in Fig. 7(b) for the Ni substitution. In this figure, the region where \( \Delta \rho > 0 \) is indicated by full curves and the region where \( \Delta \rho < 0 \) is indicated by broken curves. Therefore, there are excess electrons in the region where \( \Delta \rho > 0 \), whereas deficient electrons in the region where \( \Delta \rho < 0 \). The appearance of a large positive or negative peak at the substitutional site is simply due to the difference in the total electron number between M and Co atoms.

The changes in the bond orders with alloying elements shown in Fig. 4 could be understood from these difference electron density maps. For example, the differences in the electron density between the first- and second-nearest neighbor Co atoms were almost zero regardless of alloying elements as is indicated by the two letters A and B in Fig. 7(a) and (b), which was in agreement with a little change in the Co–Co bond order with alloying elements shown in Fig. 4. A positive region in the difference electron density considerably increased between a central Ti and the first-nearest-neighbor Co atoms as indicated by the letter C and a little increase between a central Ti and the second-nearest-neighbor Co atoms as indicated by the letter D in Fig. 7(a). These mean that the Ti substitution for Co atoms increased the chemical bond strength in pure Co. Thus, Co–Ti bond order and consequently the total bond order considerably increased with the Ti addition, as shown in Fig. 4.

On the other hand, the presence of a negative \( \Delta \rho \) region indicated by the letters, E and F in Fig. 7(b) means that the Ni substitution for Co atoms weakened the chemical bond strength in pure Co. As the atomic number increases, the peak electron density decreased between a central M and the first-nearest-neighbor Co atoms, and then almost annihilated in the case of Ni. This also agreed with the result that the Ni–Co bond order shown in Fig. 4 was smaller than the Co–Co bond order in pure Co.

### 4.3 Bond order and energy distribution of the overlap populations

As shown in Fig. 4, the total bond order is different among the alloying elements. The total bond order, which represents whole interactions between atoms in the cluster, decreased in the order, Ti > Cr > Co > Ni. In Fig. 8, the energy distributions of the overlap populations between d-electrons are shown for Ti, Cr, Co and Ni. In each figure, the Fermi energy level, \( E_F \), was set to be zero. If the overlap population is positive (+), bonding-type interaction is operating between atoms whereas, if it is negative (–), anti-bonding-type interaction is dominant between atoms. The Fermi energy level of Ti was located in the bonding energy region where there
was positive d-d bonding operating between atoms. The energy region where the anti-bonding-type interaction is operating was enlarged gradually as the atomic number of alloying elements increased in the order, Ti, Cr, Co and Ni. As the \( E_f \) for Ni existed in the anti-bonding region, the d-d bonding was weakest among the alloying elements. As a result, the magnitude of the bond order changed following the order, \( Ti > Cr > Co > Ni \), as shown in Fig. 4.

4.4 Binary phase diagrams of Co–M systems

Bo and Md parameters are associated with the nature of the chemical bond between atoms in solids, through the covalency, electronegativity and atomic radius as explained before. As shown in Fig. 9(a), Co–M binary phase diagrams\(^2\) can be separated into two categories. One is the all proportional solid solution system but with a limited solid solubility at low temperatures (this called type A system), and the other is the peritectic system (this called type B system). The location of alloying elements on the Bo-Md map is shown in Fig. 9(b).

All the elements which form type A system (Cu, Ni, Fe, Mn) are located near the position of Co on this map. And the elements which form type B system (Cr, V, Ti) are located apart from the position of Co. Also, the solubility limit of alloying elements which is indicated by a number in the figure decreased with increasing the distance from the position of Co. From this, it can be said that both the bond order, Bo, and the d-orbital energy level, Md, are convenient parameters for describing the phase constitution in Co-based alloys.

5. Conclusions

The electronic states for Co containing various 3d transition elements were calculated systematically by the DV-Xα cluster method and the results are summarized as follows.

1. Two alloying parameters, the bond order (Bo) and d-
Fig. 9 (a) Classification of Co-M binary phase diagrams, and (b) location of alloying elements on the Bo-Md map.

orbital energy levels (Md) are determined, both of which decreased monotonously with increasing atomic number of 3d transition metals in the periodic table.

2) The Ti substitution for Co atoms increased the chemical bond strength, whereas the Ni substitution weakened the chemical bond strength in pure Co.

3) Local spin moments of 3d alloying elements in Co were dependant largely on the alloying elements.

4) The Co binary phase diagrams could be classified using a Bo-Md map.

REFERENCES