

# A Study About Atomic Interaction at the Interfaces of Transient-metal/ceramics\*

By Kunio TAKAHASHI\*\*, Yasuo TAKAHASHI\*\*\* and Kimiyuki NISHIGUCHI\*\*\*

## Abstract

*Results of valence AES analyses, which have been performed for transient-metal/ceramic interfaces by the authors, are summarized in the present study. Atomic interactions at the interfaces are discussed by using thermo-chemical data. The data do not give a consistent full explanation of all. A simple jellium model is introduced to interpret them. The interactions are systematically discussed considering two extremes of electronic property.*

**Key Words:** *Transition metal, Ceramics, Interface, Reduction, Jellium model, Surface energy, Interface energy, Chemical bonding, Thermodynamics, Metallization*

## 1. Introduction

The electronic states of metals are different from those of ceramics. At the interface of these materials, how is the electronic state? This question is interesting from a scientific point of view. It is also essential for the metallization technology and the design of composites.

Recently, the metal/ceramic interfaces are usually investigated by using the transmission electron microscopy (TEM). Lattice images at the interface can be observed by the method. However, the method is applicable only for special cases, in which the lattice-directions of the materials fortunately coincide with each other. The information on the electronic states can not be obtained by the method.

Pask et al<sup>1,2)</sup> suggested the chemical states at the interface on the basis of thermochemical data. However, the interface is not always in equilibrium thermochemically. When one applies the thermochemical data to the interface, it is essential to assume the local thermal equilibrium. It is also essential to measure the interfacial chemical states for the purpose stated above.

The chemical states include the electronic state. The electronic states have two faces. One is the face approximated by the LCAO (linear combination of atomic orbital). The other is the face approximated by plane waves which is well known from Bloch theorem. The thermochemical data can be represented by the former. The surface and the interface energy<sup>3,4)</sup> can be calculated by the latter for jellium-like metals. Hence, the surface and the interface energy are caused by the electronic penetration at the interface. The penetration may break the assumption of local thermal

equilibrium at the interfaces.

Now, it is important to measure the chemical states at the interface, compare them with the thermochemical data and discuss on the basis of the plane wave approximation. We have already proposed a method for measurement of the chemical state at the interface<sup>5)</sup> by using Auger electron spectroscopy (AES) and performed the measurement for several simple ternary systems<sup>6-9)</sup>. In this paper, we summarize the experimental data and discuss them using the thermochemical data and the plane wave approximation.

## 2. Prior work

### 2.1 Thermochemical data

Figs. 1 (a) and (b) show the thermochemical data on the systems used in the present study. The ordinate is the free energy change per one mole of the ceramic for each reaction and the abscissa is the temperature. This figure predicts the reduction of the ceramics induced by the metal mixture. The ceramics would be reduced for the systems with negative  $\Delta G$ . When the local thermal equilibrium is assumed, the reduction is expected in the systems of Ti/SiO<sub>2</sub>, Ti/AlN and Ti/Si<sub>3</sub>N<sub>4</sub>. It means that the reduction does not take place in the other system (ex. Ti/Al<sub>2</sub>O<sub>3</sub>). The Ti/Al<sub>2</sub>O<sub>3</sub> system has the smallest  $\Delta G$  in Fig. 1. This system is the most likely to be affected by other contributions such as induced from the plain wave characteristics of electron. The formation energy of TiAl may cause the system to reduce the  $\Delta G$ . There are few thermochemical data on intermetallic compounds such as TiAl. The reference<sup>10)</sup> gives the data only for  $T=298$  K. Even if the formation energy of TiAl is taken into account, the reduction is not expected at  $T=298$  K.

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\*\* Department of Mechanical and Intelligent Systems Engineering, Faculty of Engineering, Tokyo Institute of Technology

\*\*\* Department of Welding and Production Engineering, Faculty of Engineering, Osaka university

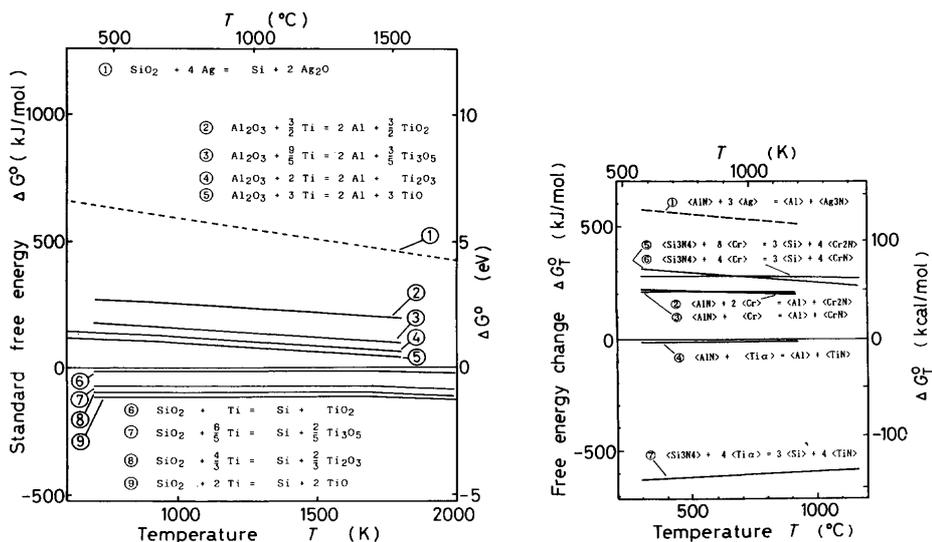


Fig. 1 Thermochemical data for (a) Ti-oxide systems, and (b) Metal-nitride systems.

For the other systems whose  $\Delta G$  is greater than that of Ti/Al<sub>2</sub>O<sub>3</sub> system, the influence of the intermetallic compound is smaller than the Ti/Al<sub>2</sub>O<sub>3</sub> system.

2.2 Model on jellium-like approximation

2.2.1 One electron approximation in step-potential

It is suggested that the thermochemical data is applicable to the homogeneous systems and the interface is not homogeneous<sup>11)</sup>. In order to estimate the contribution of the electronic penetration to the stability of interface, it is not necessary to accomplish exact heavy calculations which are always case-by-base. Even if they were self-consistent, the accuracy and the reliability of the calculation would be affected by the selection of the basic functions. It is also necessary to take in to account the trend of the material by using a simplified model<sup>4)</sup>.

The model as stated above has been already reported in detail<sup>8)</sup>. Here, we represent it easily. As mentioned above, the charge transfer (electronic penetration) is important at the inhomogeneous interface. In order to estimate the order of the contribution, We consider the electronic characteristics approximated by the plane wave. Just as the electrons penetrate into the vacuum at the surface<sup>4)</sup>, it penetrate into the ceramics at the metal/ceramic interface.

Fig. 2 shows a schematic illustration of the model. The metal side (left) is approximated by the jellium and it is assumed that the Fermi electrons penetrate to the conduction band of the ceramics where the potential barrier height is  $V$  (eV). Although more exact calculations suggest existence of interfacial states<sup>11)</sup>, the model is simplified to know the trend of the materials.

To estimate the energy change of the interface, the wave equation become,

$$H\phi = \epsilon\phi \dots\dots\dots(1)$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 + v(x) \dots\dots\dots(2)$$

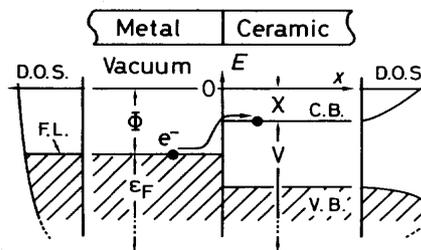


Fig. 2 Schematic illustration of a simple model of Metal/Ceramic interfaces.

where  $v(x)=0$  for  $x<0$  and  $v(x)=V$  for  $x>0$ ,  $\hbar$  is the Plank constant and  $m$  is the mass of the electron. Eq. 1 can be analytically solved. The eigenfunction gives the relative electronic density distribution. Now, we assume that a metal atom provide one Fermi election. The excess energy  $\Delta E$  can be written as

$$\begin{aligned} \Delta E &= \langle k_F | H | k_F \rangle (r=r) - \langle k_F | H | k_F \rangle (r=\infty) \\ &= \frac{V}{\pi r \sqrt{r-1}} \\ &= \frac{\epsilon_F^{3/2}}{\pi \sqrt{\Phi-X}} \dots\dots\dots(3) \end{aligned}$$

where

$$\epsilon_F = \frac{\epsilon^2}{2m} k_F^2 \dots\dots\dots(4)$$

$$V = \epsilon_F + \Phi - X \dots\dots\dots(5)$$

$$r = \frac{V}{\epsilon_F} \dots\dots\dots(6)$$

2.2.2. Calculated results

Fig. 3 shows the relative density distribution of Fermi electrons. The distribution can be given as a function of  $r$ . As shown in Fig. 3, the penetration become maximum at  $r=1$  and decreases with the increase of  $r$ . Since the conduction band is the anti-bonding state of the ceramics, the penetrating electron

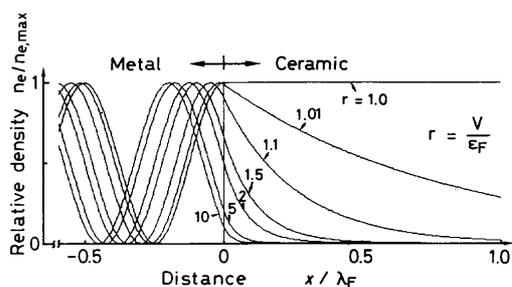


Fig. 3 Relative density of Fermi electron as a function of a parameter  $r$ .

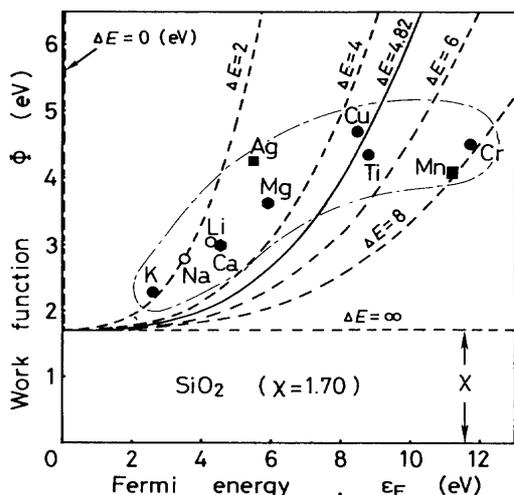


Fig. 4 Contour curves of the excess energy induced by the penetration effect, depending on Fermi energy  $\epsilon_F$  and work function  $\Phi$ .

increases the excess energy of the system and the interface becomes unstable.

If a combination of the metal and the ceramic is selected, the work function and the Fermi energy of metal can be defined and the electronic negativity of the ceramic can be given. In other words, if the combination is selected, the value of Eq. 3 can be calculated. Fig. 4 shows the excess energy as a function of the Fermi energy and the work function. The contour line is given by

$$\Phi = \left( \frac{1}{\pi \Delta E} \right)^2 \epsilon_F^3 + X \dots \dots \dots (7)$$

Fig. 4 shows the case of  $\text{SiO}_2$  whose  $X = 1.70 \text{ eV}^{12)}$  For the case of  $\text{Al}_2\text{O}_3$  ( $X = 0.65 \text{ eV}$ ) or  $\text{AlN}$  ( $X = 0.80 \text{ eV}$ ), the contour is given by shifting Fig. 4.

When  $X = \Phi$ , an infinite number of electrons penetrate the ceramics and break the neutrality of charge, therefore the model is not applicable. It is well known that the jellium approximation is not applicable for the metal which has large electron density<sup>3)</sup>. In the extreme case when the Fermi energy becomes large, this model becomes unavailable. In the same manner, in the case, of  $\epsilon_F = 0$ , it is unavailable.

The Fermi energy and the work function of metals always take values in the region marked with the dash-dotted line in Fig. 4. Fig. 4 shows a trend that the interface between ceramics and large  $\epsilon_F$  metal tends to have a large  $\Delta E$ . Since the model is sim-

plified, it is not quantitative. However, it is helpful to know the trend and understand the interface systematically.

### 3. Procedures of valence Auger analysis

We have made the valence Auger analysis across the interfaces;  $\text{Ti}/\text{SiO}_2$ ,  $\text{Ti}/\text{Al}_2\text{O}_3$ ,  $\text{Cr}/\text{AlN}$ ,  $\text{Ti}/\text{AlN}$ ,  $\text{Ag}/\text{AlN}$ ,  $\text{Cr}/\text{Si}_3\text{N}_4$ ,  $\text{Ti}/\text{Si}_3\text{N}_4$  etc. and suggested that the AES analysis is applicable to the atomic interaction (chemical bonding) measurements at the metal/ceramic interfaces<sup>9)</sup>. The detail will not be repeated here.

These adhered interfaces were prepared by the electron beam deposition. Samples were sputtered from the metal side and the interfaces were exposed in AES chamber. Primary electron beam was focused on the analyze-points across the interface. The beam damages by the Ar ion and the primary electron are important in the valence Auger analysis<sup>5,7)</sup>. In order to equalize the degree of the beam damages at the analyzed points, the beam current and the irradiation periods of the primary electron were kept constant across the interface. Al(Si)-LVV Auger peaks were investigated to detect the reduction at the narrow interfacial region.

### 4. AES results and discussion

#### 4.1 Results of valence Auger analysis

The valence auger results are summarized in Table 1. The table lists the thermochemical predictions and AES results from a view point that the ceramic substrate is reduced or not. The thermochemical predictions show good agreement with the AES results. The applicability of the interfacial valence Auger analysis is supposed.

#### 4.2 Comparison with thermochemical data

A strange result is shown with the  $\text{Ti}/\text{Al}_2\text{O}_3$  system. The thermochemical data does not predict the reduction of the substrate. From AES results, the reduction is observed at the annealed interface while it is not observed at the as-deposited one. The facts are well

Table 1 Summary of thermochemical data and AES results.

Specimens	Thermochemical prediction	AES results
$\text{Ti}/\text{Al}_2\text{O}_3$ as-depo.	×	×
$\text{Ti}/\text{Al}_2\text{O}_3$ annealed	×	○
$\text{Ag}/\text{SiO}_2$ as-depo.	×	×
$\text{Ag}/\text{SiO}_2$ annealed	×	×
$\text{Ti}/\text{SiO}_2$ as-depo.	○	○
$\text{Ti}/\text{SiO}_2$ annealed	○	○
$\text{Cr}/\text{AlN}$ as-depo.	×	×
$\text{Cr}/\text{AlN}$ annealed	×	×
$\text{Ti}/\text{AlN}$ as-depo.	○	○
$\text{Ti}/\text{AlN}$ annealed	○	○
$\text{Ag}/\text{AlN}$ as-depo.	×	×
$\text{Ag}/\text{AlN}$ annealed	×	×
$\text{Cr}/\text{Si}_3\text{N}_4$ as-depo.	×	×
$\text{Cr}/\text{Si}_3\text{N}_4$ annealed	×	×
$\text{Ti}/\text{Si}_3\text{N}_4$ as-depo.	○	○
$\text{Ti}/\text{Si}_3\text{N}_4$ annealed	○	○

○ : Ceramic substrate is reduced at neighbourhood of the interface.  
 × : Ceramic substrate is not reduced at neighbourhood of the interface.

known that the  $\text{Al}_2\text{O}_3$  is not used as the deposition crucible for titanium and that in the brazing of ceramics a metal containing titanium is used<sup>13)</sup>. These facts suggest that the difference between the thermochemical predictions and the AES measurements is significant.

#### 4.3 Discussion with the new model

Although the excess energy  $\Delta E$  calculated by Eq. 3 is not a qualitative one,  $\Delta E$  takes a value of eV order (see Fig. 4). As shown in Fig. 1, the formation energy of  $\text{Al}_2\text{O}_3$  is also in the order of eV, while  $\Delta G$  includes the contribution of the entropy. Taking these facts into consideration, the contribution of the electronic penetration effect may not be negligible.

Davies<sup>14)</sup> investigated the charge transfer from metals to ceramics at finite temperature on the basis of the statistical mechanics. The minimum degree of instability can be estimated by the excess energy  $\Delta E$  calculated by Eq. 3.

When deducing Eq. 3, it has been assumed that a metal atom provides one Fermi electron. The number of the Fermi electrons may change from one-tenth to ten. Therefore,  $\Delta E$  may change from one-tenth to ten. However, the trend of the materials can be suggested by Fig. 4. For example,  $\Delta E$  of Ti or Cr is larger than that of K and Ag, and it may be larger than the formation energy of ceramics shown in Fig. 1. In such case, it is expected that the Al-O bonds in  $\text{Al}_2\text{O}_3$  or Si-O bonds in  $\text{SiO}_2$  can be broken in a frequency, i. e. the reduction can take place.

$\Delta G$  of the Ti/ $\text{Al}_2\text{O}_3$  system (see Fig. 1) is the smallest in the systems investigated in the present study. It is only 1~2 eV per one molecular  $\text{Al}_2\text{O}_3$ . As mentioned in the section of prior work, if the assumption of the local thermal equilibrium is broken at the interface, the system of Ti/ $\text{Al}_2\text{O}_3$  can be the most affected of all. On the other hand, the excess energy calculated by Eq. 3 suggest that the larger  $\epsilon_F$  metal lead to the larger  $\Delta E$ . Ti/ $\text{Al}_2\text{O}_3$  system is one of the systems which show a large  $\Delta E$ .

The experimental results by AES show the break of the local thermal equilibrium assumption for the system of Ti/ $\text{Al}_2\text{O}_3$ . It may be due to the penetration effect of the metal electrons.

We should remember that the model is a very simplified one. It is difficult using the model to estimate the instability of interface quantitatively. The jellium approximation can not be available for large electron density materials; large  $\epsilon_F$  materials. However, it is a fact that the difference between thermochemical data and the AES measurement can be detected for the Ti/ $\text{Al}_2\text{O}_3$  system, for which the interfacial excess energy  $\Delta E$  calculated by Eq. 3 may be comparable to the formation energy  $\Delta G$ . Although many more investigations are needed, it may be due to the penetration effect of the electron at the interface.

## 5. Conclusion

The results of the valence Auger analysis are summarized which have been carried out by authors. They are compared with the thermochemical data. For most of the systems, they are in good agreement with each other. Only for the system of annealed Ti/ $\text{Al}_2\text{O}_3$ , they do not agree with each other. A simple jellium-like model is represented and applied to the metal/ceramics interface. It is suggested the difference between thermochemical data and AES result is due to the penetration effect of the metal electron.

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