AN ELECTRONIC APPROACH TO THE TWIN DEFORMATION PROCESS IN TIAL

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ABSTRACT

The evolution of the electronic states of TiAl compound during the twin deformation was investigated using a discrete variational (DV) Xα cluster method. It was shown that resistance to the twin deformation was attributable mainly to the electronic interactions around the Al site rather than the Ti site. This site dependence may cause the non-stoichiometric effect that the twin deformation is more active in the Ti-rich TiAl than in the Al-rich TiAl. Also, it was found from the bond order analysis that the twin deformation will be enhanced by substituting transition metals (for example, Mn, Cr, V) for Al atoms. This agrees with the recent experimental results.

INTRODUCTION

Recently there have been great demands for the development of new heat-resisting materials in advanced aerospace industry. An intermetallic compound TiAl is one of the most promising materials for such high temperature structural applications[1,2]. This is because, TiAl possesses attractive properties of high melting temperature, low density and high elastic modulus[3]. However, at the moment the poor ductility at room temperatures yields a large barrier to the practical use of this material[4]. In order to solve this problem extensive investigations have been carried out recently and several clues to the problem have been obtained. For example, the addition of third elements into TiAl could improve the ductility to some extent[5,6,7]. The scavenging of impurities by the addition of rare-earth elements into TiAl may be another effective approach to this problem[8,9].

Recently electron theories have also been utilized in understanding the low ductility of TiAl. For example, Greenberg et al[10] have suggested that Ti-Ti directional bonds make this compound brittle at room temperature. Morinaga et al[11] have reported that the addition of those elements which weaken Al p - Ti d interactions but enhance Ti d - Ti d interactions, is most effective in improving the ductility of TiAl. The existence of the directional p-d bond is probably one of the reasons for the brittleness of this compound. In fact, Fu et al[12] have calculated the spatial electron density distribution map and shown clearly the presence of such a directional p-d bond in TiAl. However, as yet there have been no simulations on the electronic structures in the actual deformation process. The dynamical nature of bond changes during deformation will determine the deformability of materials. Therefore, such an electronic approach is really needed in order to understand the mechanical properties of TiAl in a fundamental manner. In TiAl both the slip and the twin mechanisms are operating, but it seems that the twin mechanism works more dominantly than the slip mechanism. In this study, the evolution of the electronic states of TiAl in the twin deformation process was simulated for the first time using a molecular orbital method (the DV-Xα cluster method). The possibility of improving the ductility of TiAl will be discussed with the aid of calculated electronic structures.

CALCULATION METHOD

DV-Xα cluster method

This is a kind of molecular orbital calculating method, assuming a

Slater's Xα exchange-correlation potential[13]. The parameter α was fixed at 0.7, an empirically appropriate value[14], and the self-consistent change approximation was used in the calculation[14]. The matrix elements of the Hamiltonian and the overlap integrals were calculated by the random sampling method. The molecular orbitals were constructed by a linear combination of numerically generated atomic orbitals of Ti 1s-4p and Al 1s-3d. Compared to the MS-Xα method, no muffin-tin potential was used and hence this method was more convenient in treating electronic states in deformed crystals with non-symmetrical potential. A more detailed explanation is given elsewhere [15,16].

The electron density of states were calculated in the deformation process. In addition, using a Mulliken population analysis, the bond order, which is a measure of the strength of the covalent bond between atoms, was calculated in order to realize the chemical bond change with deformation. The higher bond order is, the stronger chemical bond exists between atoms.

Cluster models

TiAl has the $L1_0$ type structure as shown in Fig.1, in which the Ti and Al atomic layers are stacked alternately in the [001] direction. The twin deformation of TiAl takes place along the $[11\bar{2}]$ direction on the (111) atomic plane[17,18]. Following this deformation mechanism, two cluster models were constructed. One is the Al central cluster model shown in Fig.2(a) and the other is the Ti central cluster model shown in Fig.2(b). Both cluster models consisted of the three successive (111) layers, ① , ② and ③ . For stoichiometric TiAl the central atom (No.15) is an aluminium atom in the former cluster model (a), but a titanium atom in the latter cluster model (b). Needless to say, as there are two kinds of atom sites in TiAl, the use of these two cluster models is needed for the calculation. The arrangements of aluminium atoms and titanium atoms are completely reverse in these cluster models.

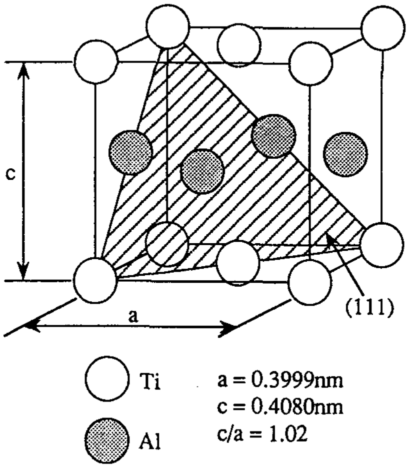

Fig.1 Crystal structure of TiAl with $L1_0$ type structure.

Each cluster model was devised so that the central atom (No.15) had always first-nearest neighbour atoms during the deformation. In the present calculation both the ① and the ② atomic layers were fixed, and only the ③ atomic layer was slid gradually along the $[11\bar{2}]$ direction. For example, the Al central cluster models are shown concretely in Fig.3(a) and (b) for the two extreme cases of before and after twin deformation, respectively. It is seen from Fig.3(b) that the ③ atomic layer is symmetrical to the ① atomic layer with respect to the ② mid atomic layer, as might be expected from the twin relationship between them. The stacking of atomic layers after twin deformation resembles partially that of the superlattice intrinsic stacking fault (SISF). Also, the twin deformation is supposed to be identical to the slip deformation in the case when a $1/6[11\bar{2}]$ partial dislocation runs in TiAl.

In the present calculation the ③ atomic layer was slid gradually in three steps, and attendant changes in the electronic states were simulated accurately in each step. In order to examine the alloying effect on the twin deformation, the central No.15 atom was replaced by Ti, V, Cr and Mn atoms for the Al central cluster model. Similarly, it was replaced by Al, V, Cr, Zr, Nb and Mo atoms for the Ti central cluster model.

The lattice parameter used was a=0.3999nm and c=0.4080nm, which are the values determined experimentally for stoichiometric TiAl. Any lattice relaxation during deformation was not counted because of the difficulties in estimating the magnitude of relaxation. Also, no dislocation was involved in this calculation, since as yet the twin mechanism has not been fully understood using dislocation reactions. Therefore, the present calculation treated a sort of ideal twin deformation. However, the cluster model is so small that the electronic state of the local region in a crystal deformed by the twin mechanism may be simulated approximately in this way.

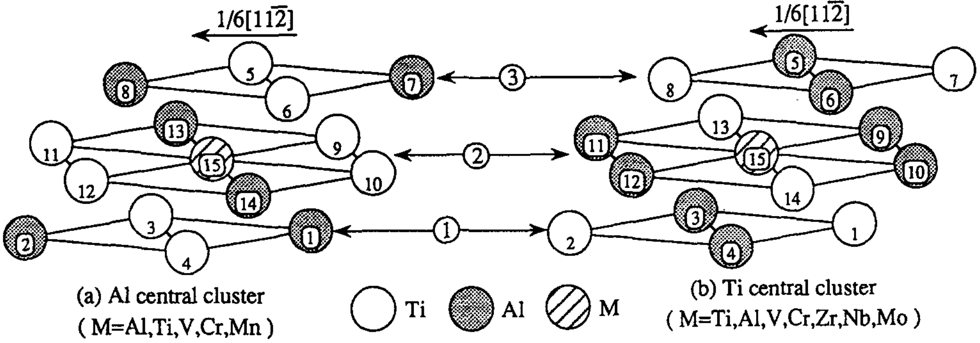

Fig.2 Cluster models employed in the calculation, (a) Al central cluster and (b) Ti central cluster.

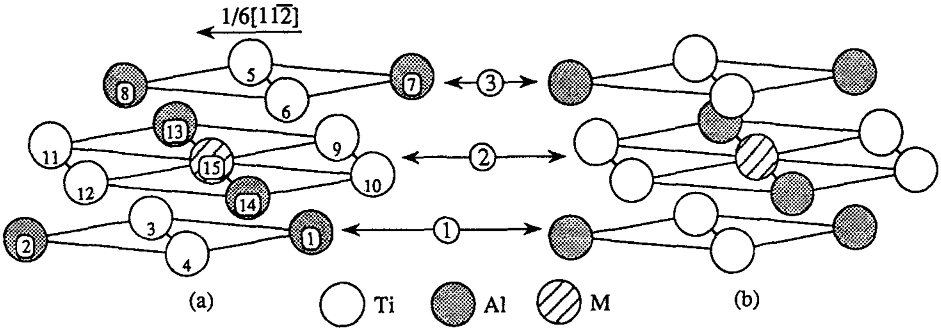

Fig.3 Appearance of the cluster model before deformation (a) and after deformation by the magnitude of 1/6[11$\bar{2}$] (b).

RESULTS

Electron density of states

The electron densities of states of stoichiometric TiAl during the twin deformation were calculated using the Al central cluster model and the results are shown in Fig.4. These were obtained using the Gaussian function with the width of 0.2eV[19]. The position of the Fermi energy level, E_f, is indicated by an arrow in each figure. The results shown in (a) and (c) correspond to the density of states before and after twin deformation respectively, and the result shown in (b) corresponds to the density of states in the middle of the deformation. In figure (a), the Fermi energy level was located in a valley of the energy band, and the Ti 3d component distributed mainly near the Fermi energy level. The components of the Al 3s and 3p conduction electrons which is shown by a broken line extended to a wide energy range.

It is evident from these figures that the density of states changed gradually with twin deformation. In particular, there was a clear change in the Ti 3d component with deformation. Such a change in the density of states was also seen in the slip deformation process[19].

For comparison, the electron densities of states for the Ti central cluster model are also shown in Fig.5 for stoichiometric TiAl. When compared Fig.5(a) with Fig.4(a), it is apparent that the density of states before deformation varied depending on the cluster model of either the Al center or the Ti center. This is also true in the middle of deformation (b) and after deformation (c). Thus, a clear site dependence of the electronic states was observed in TiAl. In addition, it is evident that the twin deformation modified the density of states, irrespective of the cluster models employed in the calculation. However, these modifications due to the twin formation were not so remarkable as those due to the formation of anti-phase domain boundary (APB) or complex stacking faults (CSF) in TiAl[19].

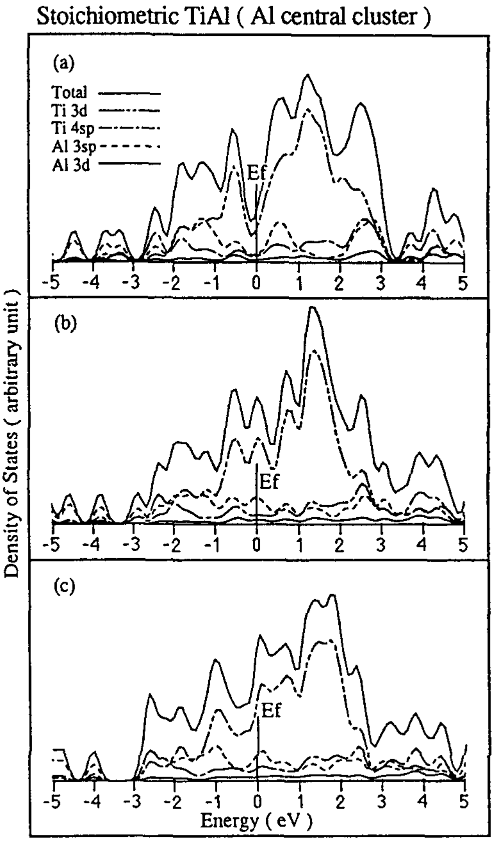

Fig.4 Change in the electron density of states during the twin deformation of stoichiometric TiAl (the Al central cluster model).

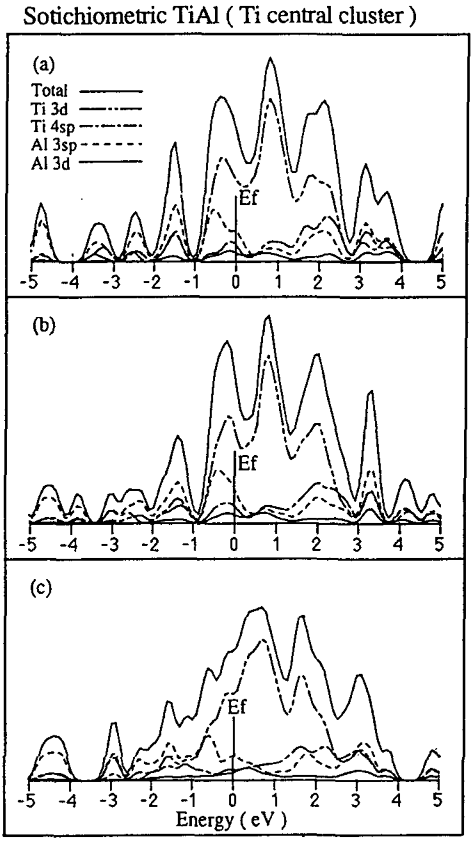

Fig.5 Change in the electron density of states during the twin deformation of stoichiometric TiAl (the Ti central cluster model).

Bond Order

The chemical bond strength between atoms is probably very important in understanding the twin deformation mechanism, since there are strong covalent bonds between atoms in TiAl. In order to investigate the change of the chemical bond strength during twin deformation, the bond order was calculated in each step of deformation. As stated before, the bond order is a parameter to show the covalent bond strength between atoms.

Al central cluster model

The change of the bond order with deformation is shown in Fig.6 for the Al central cluster model. The contributions from all the s,p,d electrons were included in this calculation. In each figure, P_1 and P_3 denote the state before and after deformation respectively, and P_2 is the intermediate state between them. The opened circle (○) and the closed circle (●) in the figure indicated the bond order between the central No.15 atom (M) and the surrounding Ti atoms (the M-Ti bond order) and between the central No.15 atom (M) and the surrounding Al atoms (the M-Al bond order), respectively. The triangle (△) denotes the sum of them.

Fig.6(a) is the result for stoichiometric TiAl, because the central M atom is an Al atom in the Al central cluster model. It is seen from this result that the M-Ti bond order was higher than the M-Al bond order. This is because, an M atom in the Al central cluster model has eight Ti atoms and four Al atoms as the first-nearest neighbour atoms, and hence the number of M-Ti bond pairs is larger than that of M-Al bond pairs in this cluster model. It is evident from Fig.6 that there were almost no changes in the M-Ti and the M-Al bond orders during the twin deformation in stoichiometric TiAl and also in alloyed TiAl.

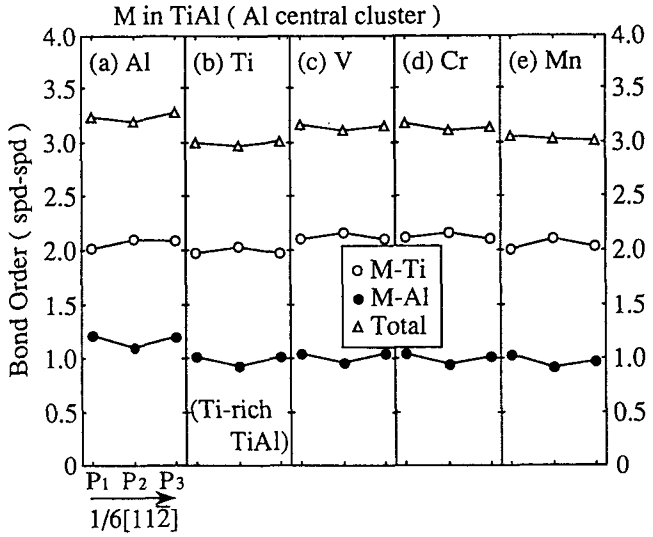

Fig.6 Change in the bond orders with twin deformation for the Al central cluster model. All the s,p,d electrons are included in this calculation.

The components of the bond orders were examined in detail in Fig.7. For stoichiometric TiAl the p-d bond order between the Al (No.15) 3p and the surrounding Ti 3d electrons is shown in Fig.7(a), because this is an important interaction in TiAl[18~20]. This bond order scarcely changed as twin deformation proceeds in stoichiometric TiAl, indicating that the electronic instability scarcely occurs in the course of twin deformation. Therefore, it can be said that the twin deformation is the relatively easy deformation mechanism in TiAl.

The p-d and d-d bond orders are shown in Fig.7(b)~(e) for the alloyed TiAl. The p-d interaction is operating between the alloying element M 3d and the surrounding Al 3p electrons. Also, the d-d interaction is operating between the M 3d and the surrounding Ti 3d electrons. In other words, the d-d bonding becomes dominant together with the p-d bonding when the transition metal is substituted for the central Al atom. From the present calculation the d-d interaction was shown to be larger than the p-d bond order in the alloyed TiAl. Also, there was a peak in the d-d bond order in the middle of deformation. Interestingly, for TiAl alloyed with Ti and V the d-d bond order was reduced, but the p-d bond order was enhanced after twin deformation. By contraries, for TiAl alloyed with Mn the d-d bond order was enhanced but the p-d bond order was reduced after twin deformation. For TiAl alloyed with Cr both the p-d and the d-d bond orders were reduced after twin deformation. From these results, it was found that there was a clear difference in the alloying effect of elements on the atomic bonding, and also the twinning modified the local bond nature to some extent in the alloyed TiAl.

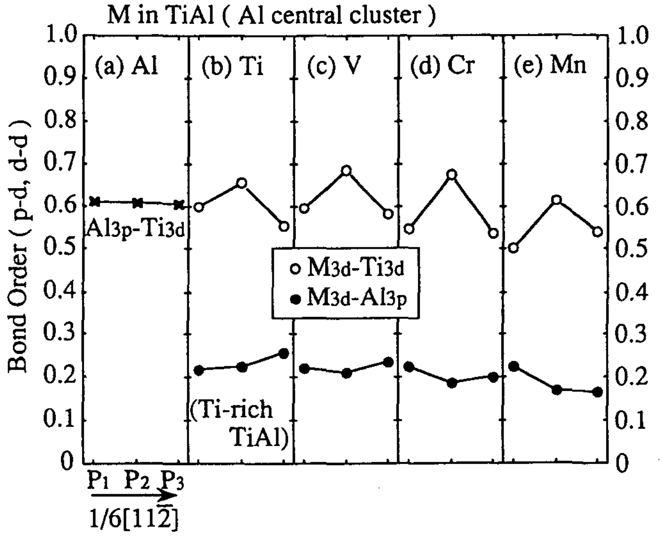

Fig.7 Change in the bond orders with twin deformation for the Al central cluster model. Only the p-d and the d-d interactions are shown in this figure.

<u>Ti central cluster model</u>

The change of the bond order is shown in Fig.8 for the Ti central cluster model. Similarly to Fig.6 for the Al central cluster model, the contributions from all the s,p,d electrons were included in this calculation. The M-Al bond order (●) was much larger than the M-Ti bond order (○). This is because, the central M atom is surrounded by eight Al atoms and four Ti atoms as the first-nearest neighbours. This is completely the reverse of the case for the Al central cluster model. As shown in Fig.8(a), for stoichiometric TiAl there were only slight changes in the respective bond orders with twin deformation. On the other hand, the alloying yielded some changes in the bond order. This was, in particular, remarkable in the case of the substitution of the 4d transition elements (Zr, Nb, Mo).

The change in the p-d and the d-d bond orders during twin deformation are also shown in Fig.9. For example, Fig.9(b) is the result for the Al-rich TiAl since an Al atom is substituted for the central Ti atom in the cluster. In this case, the p-d interaction became dominant between the substituted Al 3p and the surrounding Ti 3d electrons. The Al 3d - Ti 3d interaction was nearly nil, so this was omitted drawing in the figure. When compared (a) with (c) and (d), it is apparent that the d-d and the p-d interactions were nearly unchanged by the V and the Cr substitution. However, the bond order increased largely by the substitution of 4d transition metals. This is in contrast with the bond order change shown in Fig.8, in which the bond order became smaller by alloying. At the moment, it is still unknown why such a large change was introduced to the bond order by adding 4d transition metals into TiAl. However, it is likely that the addition of these 4d transition metals affects strongly the occurrence of the twin deformation in TiAl, if they are possibly substituted for Ti atoms.

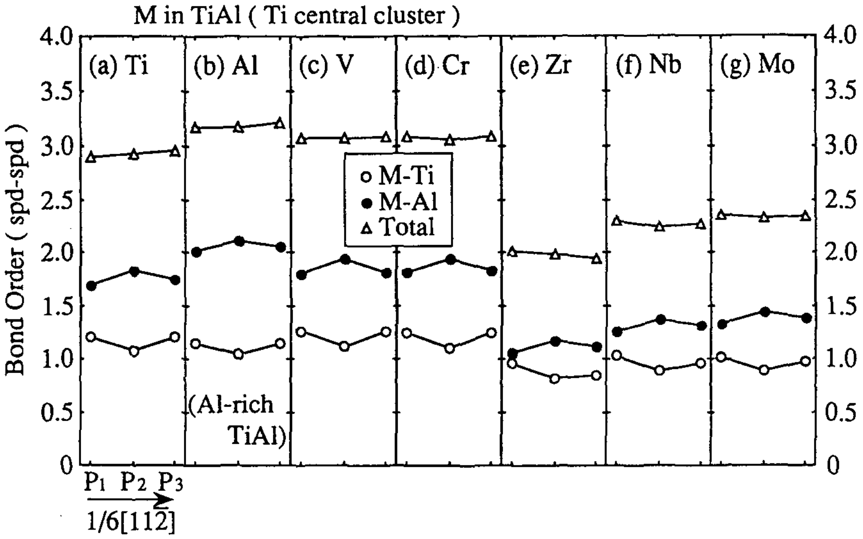

Fig.8 Change in the bond orders with twin deformation for the Ti central cluster model. All the s,p,d electrons are included in this calculation.

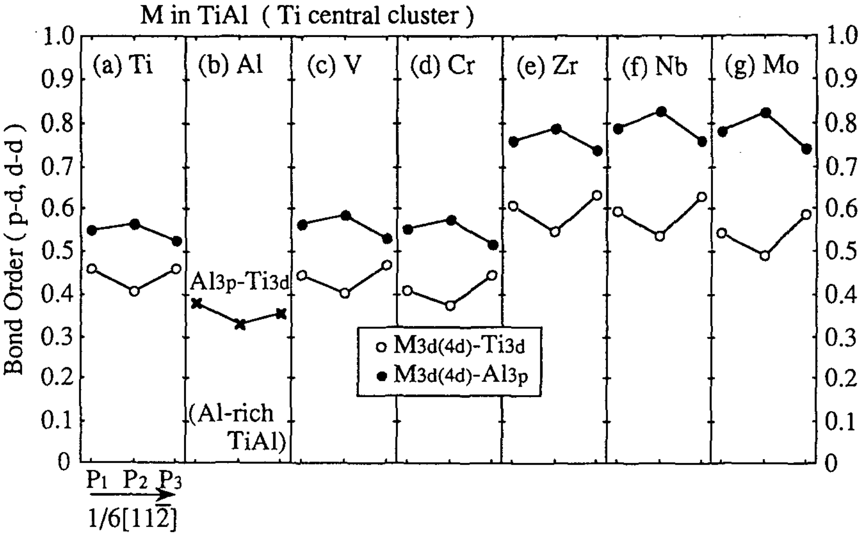

Fig.9 Change in the bond orders with twin deformation for the Ti central cluster model. Only the p-d and the d-d interactions are shown in this figure.

DISCUSSION

Non-stoichiometry and alloying effects on twin deformation

The nature of the chemical bond between atoms is modified with non-stoichiometry. For example as shown in Fig.7(a) and (b), the Al 3p - Ti 3d interaction is most dominant in stoichiometric TiAl, but the M (=Ti) 3d - Ti 3d interaction is rather dominant than the M (=Ti) 3d - Al 3p interaction in the Ti-rich TiAl. Also, there is a large peak in the M (=Ti) 3d - Ti 3d interaction in the middle of twin deformation. Such an increase in the d-d bonding probably provides a favorable circumstance for the twin deformation, because of the increase of the electronic stability in the intermediate state of P_2. Therefore, twin deformation will be active in the Ti-rich TiAl than in stoichiometric TiAl.

For the Al-rich TiAl, the situation is completely the reverse of that for the Ti-rich TiAl. This is because, as the result of the Al substitution for the central Ti atom in the cluster, the Ti 3d - Ti 3d interaction disappears and instead the substituted Al 3p - Ti 3d interaction appears in the Al-rich TiAl, as was shown in Fig.9(a) and (b). For stoichiometric TiAl, the change in the M (=Ti) 3d - Ti 3d interaction during twin deformation is complementary to the attendant change in the M (=Ti) 3d - Al 3p interaction. On the other hand, for the Al-rich TiAl the Al 3p - Ti 3d interaction exhibited a small minimum at P_2, indicating that the electronic state is less stable at P_2 than P_1, and hence this probably causes the resistance to the twin deformation. Thus, the twin deformation is supposed to be less active in the Al-rich TiAl than in stoichiometric TiAl. Experimentally, twin deformation is observed, irrespective of the composition of TiAl[3,6,22,23]. However, more twins are observed in the Ti-rich TiAl than in the Al-rich TiAl[24,25], in agreement with the present calculation.

According to our previous study[11], it was suggested that the existence of the stronger d-d interaction but of the weaker p-d interaction makes TiAl more deformable. This criterion is satisfied in the Ti-rich TiAl as shown in Fig.7(b). By contraries, it is not satisfied in the Al-rich TiAl, since the d-d interaction is nearly nil as is shown in Fig.9(b). This also supports the higher deformability of the Ti-rich TiAl than the Al-rich TiAl. Furthermore, there is the site dependence even in stoichiometric TiAl. The principal interaction is attributable to the p-d interaction on the Al site (see Fig.7(a)), and to the p-d and d-d interactions on the Ti site (see Fig.9(a)). It is supposed that the Al site is more responsible to the resistance to deformation compared to the Ti site in TiAl, because of the lack of the d-d interaction on the Al site.

In addition, as shown in Fig.7(c)~(e) the atomic interactions in the TiAl alloyed with V, Cr and Mn quite resemble those in the Ti-rich TiAl (Fig.7(b)). Therefore, twin deformation is expected to be enhanced with alloying of these elements. In fact, it is experimentally found that twin deformation is enhanced by the substitution of V, Cr and Mn atoms for Al atoms in TiAl[27,28]. In particular, the Mn substitution is known to be effective in promoting twin deformation[5,22]. These experimental results agree with the present estimate from the calculations. Also, compared to Fig.9(c),(d) with (a), it is evident that the bond order scarcely changes with the V and Cr substitution for Ti atoms. This suggests that such a substitution will not enhance the twin deformation. This is also supported by the recent experiment[27].

Comparison of slip deformation with twin deformation

For slip deformation of stoichiometric TiAl, similar calculations have been carried out using an Al central cluster model[19]. Some results of the bond order during slip deformation are shown in Fig.10(a)~(c). In this calculation, three slip directions were selected according to the Burgers vector of dislocations in TiAl. Fig.10(a), (b) and (c) are the respective results for the slip directions along the 1/2[110] ordinary dislocation, the 1/2[101] super-dislocation and the 1/6[211] (or $1/6[12\bar{1}]$) partial dislocation. The anti-phase domain boundary (APB) and the complex stacking fault (CSF) are formed in these slip deformation processes as indicated in the figure. Both the M (=Al) - Ti bond order (○) and the M (=Al) - Al bond order (●) changed with slip deformation. In particular, it was remarkable when the APB and the CSF are formed. Recalling that the very small change in these bond orders during the twin deformation (see Fig.7), we know that compared to the formation of twin faults, the formation of the APB and the CSF introduced a large modification to the nature of the chemical bond in TiAl.

However, the change in the M (=Al) - Ti and the M (=Al) - Al bond orders along the 1/2[110] direction of the ordinary dislocation, was as small as that of the twin deformation shown in Fig.6. Experimentally, the 1/2[110] ordinary dislocation and the deformation twins are observed in stoichiometric TiAl[9,21]. But, any super-dislocations and partial dislocations are not observed. It is likely that the observed deformation mode is associated with the electronic states during deformation. In other words, the deformation mode probably becomes active when the M-Ti, and the M-Al bond orders are less-changed during deformation.

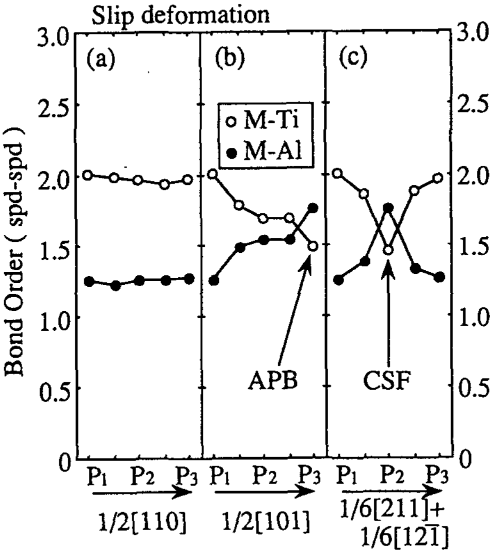

Fig.10 Change in the bond orders with slip deformation of stoichiometric TiAl (Al central cluster model).

CONCLUSION

The evolution of electronic structure of TiAl was simulated in the twin deformation process by using a DV-Xα cluster method.

The electron density of states varied as twin deformation proceeds. However, the change due to the twinning was not so remarkable as the change due to the formation of the anti-phase domain boundary and the complex stacking fault. For stoichiometric TiAl, it was shown that the Al site acts as the principal resistance to the twin deformation rather than the Ti site. The site dependence is probably one of the characteristics of the deformation for intermetallic compounds with several sublattice sites. Therefore, for TiAl the substitution of alloying elements for Al atoms will promote twin deformation. This is the case for the enhanced twin deformation due to the V, Cr and Mn substitution. In addition, it was shown from the calculation that the twin deformation is more active in the Ti-rich TiAl than in the Al-rich TiAl.

Compared to slip deformation, the bond order change during the twin deformation was small and comparable to the case of the slip deformation along the 1/2[110] direction of the ordinary dislocation. In accordance with the calculation, both twins and 1/2[110] ordinary dislocations are observed experimentally in TiAl. It is likely that plastic deformation takes place readily if the electronic states are not modified strongly in the deformation process, irrespective of twin or slip deformation.

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