Molecular Dynamics Study on Adhesion of Various Ni/Al Interface for Ni-Plated Aluminum Alloys

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As a fundamental study on the adhesion of Ni-plating on aluminum alloys, various molecular dynamics simulations are performed on Ni/Al infinite laminate structure under tension, by changing mixing concentration of Ni and Al at the interface. The adhesion shows the highest at the perfect (001) Ni/Al interface while it decreases with the rate of random mixing in Ni/Al phases (10%, 30% and 50% substitution in each phase). Especially the 50% substitution in Al phase remarkably decreases the adhesion compare to the same substitution in Ni phase. The (111) interface shows weaker adhesion than (001) for perfect Ni/Al interface, and the substitution doesn’t largely affect to the adhesion reduction as the (001) interface. The (001) interfaces are always ruptured in brittle manner near the interface in Al side, and few Ni atoms are observed on the fracture surface. The (111) interface shows shear-lip breakage by void formation and growth in Al side further away from the interface. We obtained simple conclusion that the Ni/Al interface is inherently strong and the delamination never takes place at the interface, since the surface energy and elastic coefficients of Ni is much larger than Al. The large reduction of adhesion by atom mixing in the (001) interfaces can be explained with the initial misfit at the interface while it doesn’t largely affect to the close-packed (111) interface. Assuming various phenomena in real Ni-plating, we also performed simulations with Ni3Al and NiAl interlayer, (001)-(110) surfaces combination; and all results in the same story above mentioned. Finally, we performed calculations on Ni-P system, and revealed that the surface energy of amorphous Ni-P is close to that of Al. Thus interfacial delamination can be occurred between the amorphous Ni-P plating and aluminum base.

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1. Introduction

Ni-plating is often used to give corrosion and wear resistance on lightweight aluminum alloys. Our slide-ball experiments on Ni-plated A7075 exhibit that there is a best temperature in heat treatment after plating to give the highest wear resistance; however, there is no remarkable change from non-heated virgin plating in the morphology of cross-sectional TEM images, crystalline diameter in XRD, and element analysis by XPS on the peeled Ni plating surface.1) Thus what causes the best wear resistance is unclear so far in the heat treatment.

The interface and crystallographic phenomena between substrate and plating metals are very complicated,2) so that it is impossible to give direct simulation by molecular dynamics (MD); however, fundamental aspects of the adhesion between Ni and Al can be discussed for Ni-plating. Targeting Ni-based superalloys and other related Ni–Al alloys, various potential functions for Ni–Al system are developed3–7) and we also reported some MD and quasi-continuum (QC) studies for dislocations in gamma/gamma-prime microstructure in Ni-based superalloys.8,9) On the MD studies including Ni/Al interface, Henz et al. discussed the kinetic sintering process of Ni and Al nanoparticles.10) Murch’s research group performed MD simulations on Al-coated nanoparticle for alloying reaction.11,12) Wu and Zhao discussed the reaction pathway of Ni/Al clad particles.13) On the other plating materials, Liu et al. proposed a DFT and MD study on sliver electroplating; and reported adsorption behaviors of the agents 5,5-dimethylhydrazotin (DMH) and nicotinic acid (NA) on silver and copper surfaces.14) Nikonov et al. performed tensile and sliding simulations on amorphous like Ni–P coating on crystalline nickel.15) However, there is no study that discusses about the adhesion of Ni/Al interface supposing the local phenomena in the macroscopic Ni-plating.

In the present study, MD simulations are implemented on the adhesion of various Ni/Al interfaces in infinite laminate structure of periodic simulation cell, changing the atomic composition near the interface, crystal orientation, interlayers of order alloys of Ni3Al and NiAl. Furthermore, surface energy calculation of Ni–P system is also performed for the effect of phosphorus in Ni-plating.

2. Simulation of the (001) and (111) Interfaces

All the simulations are performed with LAMMPS16) and different EAM potentials of Ni–Al7) and Ni–P17) are used, respectively. The former was improved its transferability in Ni–Al alloy system, so that it can represent various Ni–Al phases including L12 Ni3Al and B2 NiAl, guaranteeing strict properties of pure Ni and Al. Figure 1 shows the dimensions of the periodic cells for the (001) and (111) semi-coherent interfaces. Considering the lattice difference between Ni(0.352 nm) and Al(0.405 nm), we set the size of the cross section as 20 × 20 lattices for Al and 23 × 23 for Ni, respectively, in order to minimize the misfit strain in perfect Ni/Al multilayer (the cell has two Ni/Al interfaces at the center and top-bottom periodic boundary). Furthermore, supposing the variation near the interface, we randomly substitute the atom type in the adjacent 2 unit lattices of Ni and Al phases, respectively, with the ratio of 10%, 30% and 50%. The initial structure is relaxed with 30000 fs under the stress control of \( \sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0 \). Then the strain is increased by \( \Delta \varepsilon_{zz} = 0.5 \times 10^{-6} \) at every step. During the
tension, the cell lengths in the lateral directions are fixed. The temperature is set to 0.1 K in both relaxation and tension, to eliminate the effect of thermal vibration so far.

Figure 2 shows the stress-strain curves of the (001) interfaces. The stress peak or adhesion shows the highest in the perfect Ni/Al interface, and decreases with the random substitution especially in Al side. Figure 3 summarizes the fracture morphology of the (001) interfaces at $\varepsilon_{zz} = 0.1$. The dark shaded circles indicate Ni atoms while light gray Al ones. The figure zooms-up the side view of the ruptured interface in the upper column, while the top view of the fracture surface are shown in the lower column. The 50% substitution in Ni-phase (Fig. 3(d)) shows simultaneous fracture in the two interfaces so that the gap in the $z$-direction is about half of the others. The fracture always takes place in the Al-phase; there is no Ni atoms on the fracture surface of the perfect and Ni-side substitution, although the base Ni atoms can be seen through the surface Al lattices. For the Al-side substitution, a few Ni atoms are observed on the fracture surface, and they also can be seen in the Al-side fracture surface in the 10% substitution of Fig. 3(e); that is, the fracture occurs near the substituted Ni atoms in the Al-phase, especially in the case of 10% substitution it occurs narrow area between the sparse Ni atoms.

We can deduce that these difference in the Ni- or Al-side substitution could be due to the residual strain by the lattice difference. The substituted Ni atoms could feel high tensile strain in the longer lattice length of Al, while the Al ones do compression in the Ni lattices. Thus we evaluate the atomic mean stress $\sigma_{nn}$ after the initial relaxation, and average them.
Fig. 3  Fracture after the stress strain peak of (001) interface models. Dark shaded circles are Ni while light gray ones Al atoms.

Fig. 4  Mean stress averaged at each layer distance of $d_z = 0.005L_z$ ($L_z = 38$ nm) and snapshots with gray scale color of atomic mean stress $\sigma_{m}$ (magnified side view of upper interface and 3D cut view of the misfit dislocation network) in the perfect (001) Ni/Al interface.
in each layer distance in z-direction, \(d_z = L_z/200\) (\(L_z\) is cell length, the cell has 200 atomic layers). Figure 4 shows the stress distribution in the z-direction (0.25\(L_z\) shifted to avoid the discontinuity at the periodic boundary interface), zoom-up snapshots and 3D view of its cutting plane of the perfect (001) interface. The atoms are colored with gray scale by \(\sigma_{zz}\); white is positive or tension and black is negative or compression. Although we set the lattice number with no length difference, misfit dislocations are formed on the interface. It is remarkable that Al shows light color and Ni black at the dislocation core; however, the layer average shows the large compression at the interface. The Al layer faced to the interface shows the highest compression of \(-4.5\) GPa, and the Ni layer does second of \(-1.3\) GPa. It is natural that these initial negative stress works as buffer against tensile loading.

Figure 5 shows the averaged mean stress distribution of each substituted (001) interface. In accord with our prediction above mentioned, tensile stress emerges in the substituted Al-side while the distribution of compressive stress are widen in the Ni-side substitution. Here readers may wonder why the large initial compression in Ni-side substitution doesn’t work as buffer; actually the compression shifts to Ni-side and the highest compression in Al phase reduced to \(-0.6\) GPa in the 50\% substitution from the \(-4.5\) GPa of the perfect interface.

Figures 6 and 7 indicate the stress-strain curves and magnified snapshots near the fractured interface at \(\varepsilon_{zz} = 0.1\) in the (111) simulations. The perfect interface shows the highest adhesion but lower than the (001) perfect interface. All models show shear-lip like fracture surface by void formation and growth in Al phase far away from the interface while large substitution leads amorphization and the void initiates from the interface between the amorphous interlayer and Al-matrix. Besides the 30\% substitution in Ni side shows slip deformation from the interface toward Al phase at \(\varepsilon_{zz} = 0.06\sim0.08\). Figure 8 shows magnified side views of the (111) interfaces and 50\% substituted (001) interface before tension. The substitution is controlled with the 2 unit lattices in each crystal orientation, so that the substitution is in 6 layers in the (111) while that in 4 layers in the (001). The 50\% substitution in the (001) remains crystal structure both in the Ni and Al phases while the substituted area is largely disordered in the 30\% and 50\% substitution in Al phase and 50\% in Ni of the (111) interface. Moreover, the difference in the adhesion of these three models is relatively small. The 30\% substitution in Ni side keeps the crystal structure and the
substituted Al atoms in Ni phase are happen to align in the
same slip plane across the interface at many points, as shown
with thick broken line in Fig. 8(b). This may activate the slip
deformation from the interface.

Figure 9 illustrates the distribution of the mean stress
averaged in each layer distance, $d_z = L_z/180$ (the (111) cell
has 180 layer). The residual stress is relatively small in the
perfect (111) interface, however, we can see tension in the Al
side. In accord with the previous discussion, the substitution
in Al side causes tension around substituted Ni atoms while
that in Ni side does compression around Al ones. Despite of
the large difference in this stress distribution around the
interface, the amorphized 30% and 50% in Al and 50% Ni
substitutions show same adhesion. Thus we can conclude that
the anisotropy and discontinuity between Al lattices and
amorphous layer play important role for adhesion in these
models rather than the initial misfit.

3. Discussions on Surface Energy and Elastic Constants

All the fractures always occur in Al phase and a few Ni
atoms are observed on the fracture surface. The reason can be
explained with the difference in the surface energy and elastic
constants of Ni and Al. Table 1 shows the surface energies
and elastic constants evaluated by this EAM potential. For
the later section the properties of the L1$_2$ Ni$_3$Al and B$_2$ NiAl
are also listed. Both the surface energies and elastic constants
of Al are about half of those of Ni and Ni$_3$Al alloys. Thus the
pure Al-phase is subjected to large elastic elongation under
the force equilibrium between Ni and Al phase, and breaks
first in pure Al phase since the surface contains Ni atoms
needs larger energy. We can conclude that the Ni/Al interface
is inherently strong and delamination at the interface never
takes place between Ni and Al lattices.

4. Simulation for Ni$_3$Al and NiAl Interlayer

We set the interlayers of the ordered Ni$_3$Al and NiAl in the
previous (001) and (111) systems as shown in Fig. 10. Here
the Ni$_3$Al is made by regular 25% or 75% substitution in Ni
and Al sides, respectively, for the (001) interface. Thus we
can easily imagine that large tension emerges in Ni$_3$Al in Al
side substitution. For the (111) system, we can apply regular
75% substitution only in Al side for Ni$_3$Al interlayer, since Ni
lattices are odd number of 23 × 23. On the NiAl, we can set
the bcc lattice orientation to [100], [010] and [100] for the
(001) system; however, due to the lattice misfit the B2 lattice
is stretched by 2.2%. For the (111) system, we also set the
$z$-axis of the NiAl interlayer to its close-packed slip plane so
that the crystal orientations are set to [00\bar{1}], [110] and [1\bar{1}0] for \(x, y\) and \(z\), respectively, with the lattice stretch of 0.6\% in \(x\) and 3.2\% in \(y\) directions.

Figures 11 and 12 summarize the results of the alloy interlayer models. On the results of (001) models, the Ni\(_3\)Al interlayer in Ni-side shows almost same adhesion with the perfect (001) interface, since there is little difference in the lattice length between Ni and Ni\(_3\)Al. On the other hand, the Ni\(_3\)Al in the Al side and NiAl interlayer show same weak adhesion. It is revealed that they have same initial mean stress of 4\textendash}5 GPa tension in the Al lattices next to the interlayer. The (111) model with Ni\(_3\)Al interlayer also shows same weak adhesion as shown in Fig. 11(b), and it has also same initial tensile stress in the Al phase. On the other hand, NiAl interlayer in the (111) model activates slip from the interface due to the same reason of the broken line in Fig. 8(b). In this model, the fracture initiates from the cross slip point in Al phase further away from the interface (Fig. 12(e)).

The equilibrium lattice parameters of Ni\(_3\)Al and NiAl are 0.353 nm and 0.283 nm, respectively, in the adopted EAM potential. They are slightly smaller than experimental values.

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Table 1 Surface energies in unit mJ/m\(^2\) and elastic constants in GPa at 0.1 K.

|       | (001) | (111) | (110) | C11  | C12  | C44  |
|-------|-------|-------|-------|------|------|------|
| Al    | 945.8 | 871.8 | 994.5 | 113.8| 61.5 | 31.6 |
| Ni    | 1937.7| 1759.1| 2079.2| 241.3| 150.8| 127.3|
| Ni\(_3\)Al | 2050.0| 1969.8| 2172.1| 238.2| 166.4| 130.2|
| NiAl  | 2033.0| 2011.4| 1388.0| 190.9| 142.9| 121.5|
so that the magnitude relations of the stress-strain curves could be slightly changed; however, the main mechanisms revealed in Sec. 3, i.e. difference of surface energies and elastic constants, are not affected since the deformation and fracture always take place in Al phase.

5. Simulation for (001) and (110) Interface Combination

Finally we consider the grain boundary like combination of the interfaces of Ni and Al phases. For the 45 degree rotated crystal orientation we can set the periodic length in the \( x \) and \( y \) without misfit as shown in Fig. 13(a). The Al (001) planes are largely disordered on the Ni (110) phase and this causes large reduction in the adhesion as same story as the amorphization in the (111) interface in Sec. 2. In the Al (110) model, single slip occurs from the interface throughout the Al phase, showing small peak at the smaller strain of \( \varepsilon_{zz} = 0.05 \). Then many slips take place and finally void nucleates from the cross point of the interface and multiple cross slip.
6. Discussion on Effect of P in Ni-Plating

Generally Ni-plating involves P atoms, so that we perform simulations of Ni-P system to evaluate the change in the structure and surface energy. Ni atoms in a $10 \times 10 \times 10$ fcc bulk cell are randomly substituted to P atom with different ratio of 10%, 20% and 30%, then the cell is relaxed under NPT ensemble of 100 ps of $T = 0.1$ K and 0 pressure to evaluate the bulk Ni-P energy. The surface energy is evaluated with additional 100 ps NVT calculation making surfaces by tripling the cell size in the $x$-direction. Table 2 summarizes the results: Ni-P amorphous have low surface energy as same order of fcc Al. That is, the interface delamination can occur in the amorphous Ni-P/Al base. Unfortunately there is no potential function applicable for Ni-Al-P system, so that the direct simulation on the effect of the P atoms to the Ni-Al interface is a future work.

7. Conclusion

Seeking fundamental aspects of the adhesion of Ni-plating on Al alloys, various molecular dynamics simulations are performed on Ni/Al interfaces and Ni-P system. It is concluded that the Ni/Al interfaces are inherently strong and the fracture necessarily occurs in Al side, since the Al phase is subjected to large elastic strain due to the smaller elastic coefficients than Ni and the high surface energy of Ni and Ni–Al alloys forces the breakage in Al phase. On the other hand, high P concentration leads amorphous Ni–P of which surface energy is same order of fcc Al. Thus interface delamination can be occurred between amorphous Ni–P plating and Al base. In the present work, the temperature effect is intentionally eliminated so that we can’t give direct answer to the question about the experimental heat treatment first mentioned in Introduction; however, there is a possible story that the heat treatment reduces the residual stress which plays important role in the adhesion, as shown in this paper.

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Table 2 Structure and surface energy of Ni–P at 0.1K.

| P concentration | Structure under bulk | Surface energy |
|------------------|----------------------|----------------|
| 10%              | FCC                  | 1896.2 mJ/m²   |
| 20%              | Amorphous            | 982.3 mJ/m²    |
| 30%              | Amorphous            | 876.6 mJ/m²    |

Fig. 13 Simulation models, stress-strain curves, and fracture morphology of the (001)-(110) interfaces of Ni and Al perfect lattices.