ABSTRACT

In order to assure the reliability of advanced gas turbine systems, it is very important to evaluate the damage of high temperature materials such as Ni-base superalloys under creep and fatigue conditions quantitatively. Since the micro texture of the gamma-prime ($\gamma'$) phase was found to vary during the creep damage process, it is possible, therefore, to evaluate the creep damage of this material quantitatively by measuring the change of the micro texture. The mechanism of the directional coarsening of $\gamma'$ phases of Ni-base superalloy under uni-axial strain at high temperatures, which is called rafting, was analyzed by using molecular dynamics (MD) analysis. The stress-induced anisotropic diffusion of Al atoms perpendicular to the finely dispersed $\gamma/\gamma'$ interface in the superalloy was observed clearly in a Ni(001)/Ni3Al(001) interface structure. The stress-induced anisotropic diffusion was validated by experiment using the stacked thin films structures which consisted of the (001) face-centered cubic (FCC) interface. The reduction of the diffusion of Al atoms perpendicular to the interface is thus, effective for improving the creep and fatigue resistance of the alloy. It was also found by MD analysis that the dopant elements in the superalloy also affected the strain-induced diffusion of Al atoms. Both palladium and tantalum were effective elements which restrain Al atoms from moving around the interface under the applied stress, while titanium and tungsten accelerated the strain-induced anisotropic diffusion, and thus, the rafting phenomenon.

INTRODUCTION

Ni-base superalloy has been widely applied to gas turbine blades in combustion power plants and aircraft engines. Directionally solidified Ni-base superalloys are mainly employed for the blade material used at high temperature because they show the superior stress-rupture resistance, higher thermal fatigue resistance, and higher incipient melting temperatures comparing with the polycrystalline Ni-base superalloys. The strength of the Ni-base superalloys at high temperatures is improved by the fine cuboidal $\gamma'$ phase (Ni3Al) orderly-dispersed in a $\gamma$ phase (Ni-rich matrix) because the fine texture in a grain prevents dislocations from moving in the grain easily. However, directional coarsening of the $\gamma'$ phase perpendicular to a principal stress, which is called “RAFTING,” has been found to occur when an uni-axial external stress is applied to the superalloys at high temperatures. The morphological change of the directionally solidified Ni-base superalloy (CM247LC) observed during a creep test at 1173 K [1, 2] is summarized in Fig. 1. The magnitude of the uni-axial stress applied to the specimens was fixed at 216 MPa during the test. Since the direction of the uni-axial load in this figure is up and down, the rafting proceeded along the horizontal direction of this figure, which is perpendicular to the direction of the applied load.

The average size of the initially dispersed $\gamma'$ phase was about a few hundred nm. With increasing the loading time, the $\gamma'$ phase starts to grow perpendicularly to the direction of
γ Phase (Ni-base)

γ' Phase (Ni3Al)
(Precipitated hardening phase)

5 μm

(a) Initial finely dispersed texture of Ni-base superalloy

Crack

5 μm

(a) Damaged layered structure of the alloy (Uni-axial stress was applied up and down in this photograph)

Fig. 1 Change of the micro texture of Ni-base superalloy under uni-axial stress at high temperature

Fig. 2 Example MD models of the interface between γ' and γ phase

Table 1 Analytical condition

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Relaxation Analysis</th>
<th>Main Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time Step</td>
<td>0.5 fs</td>
<td>0.5 fs</td>
</tr>
<tr>
<td>Number of Steps</td>
<td>20,000 steps</td>
<td>200,000 steps</td>
</tr>
<tr>
<td>Applied strain</td>
<td>0%</td>
<td>1%</td>
</tr>
<tr>
<td>Potential Function</td>
<td>GEAM***</td>
<td>GEAM</td>
</tr>
<tr>
<td>Temperature</td>
<td>1173K</td>
<td>1173K</td>
</tr>
</tbody>
</table>

*NTP: Number of atoms, temperature, pressure are fixed.
**NTV: Number of atoms, temperature, volume are fixed.

the applied load, and the initial finely-dispersed texture changed to a large layered texture as shown in Fig. 1. Similar micro texture change was observed in this alloy near crack tips after fatigue loading [3]. Once the layered texture appears, the strength of the alloy at high temperatures decreases drastically and cracks start to propagate rapidly along the layered interface between the γ' and γ phase and thus, creep fracture is accelerated seriously. Therefore, it is very important to clarify the mechanism of the rafting phenomenon for improving the strength of the Ni-base superalloy at high temperatures under the applied load and thus, assuring the reliability of the turbine systems. Though, not a few research activities have been continued actively, the mechanism of the micro texture change has not been clarified fully yet [4-10].

In this study, the strain dependence of the diffusion characteristics of the component elements near the Ni/Al and Ni/Ni3Al interface structures was analyzed quantitatively by using molecular dynamics (MD) simulations in order to make clear the mechanism of the rafting phenomenon. In particular, the anisotropic diffusion of Al atoms around the interface under uni-axial strain, which is presumed to be the dominant process for the rafting evolution, was analyzed. In addition to the atomic scale analyses, the estimated strain-induced anisotropic diffusion of the component elements of the Ni-base superalloy was validated by experiments using the stacked thin film structure.

The change of the diffusion profile before and after the annealing of the stacked structure under tensile strain applied parallel to the stacked interface was measured by Auger electron spectroscopy.

**ANALYTICAL MODEL FOR MOLECULAR DYNAMICS ANALYSIS**

In the last decade, computational chemistry has made remarkable progress in the theories and calculation methods and it has a growing role in the field of materials chemistry. It has also been regarded as an efficient tool for obtaining detailed information on atomic scale for diffusion properties. Actually, we successfully simulated the oxygen ion diffusion in strained solid electrolytes [11, 12] and numerous atomistic simulations based on MD have been employed to analyze the characteristics of the interface between γ' and γ phases [13, 14].

In this study, a simple interface structure between single-crystalline Ni and Al was used as shown in Fig. 2 to analyze the effect of the applied uni-axial strain at the interface with mismatch of lattice constant on the atomic diffusion. Three-dimensional periodic boundary conditions were applied to all the calculations. Since Ni and Al are the most important elements in the Ni-base superalloy, this simple analysis indicates the basic idea of the mechanism of the rafting, i.e. the anisotropic diffusion of Al which determines the morphological change of γ' phase in the alloy. The (001) atomic layer corresponds to the coherent interface of Ni(001) and Al(001) in this model. Since large strain more than a few percent exists at the interface due to the lattice mismatch between Ni and Al crystal, the drastic change of the diffusion constant is expected to occur under high strain filed. In addition to the analysis of the Ni(001)/Al(001) interface, MD
calculations were also carried out for the Ni(001)/Ni$_3$Al(001)
interface to validate the anisotropic diffusion in Ni-base
superalloy at temperature of 1173 K. While the actual γ and γ’
phases include other elements such as Co, Cr, etc., the authors
used a simple model of pure Ni as γ and Ni$_3$Al as γ’ structure in
order to focus the analysis on the anisotropic diffusion of Al in
the matrix. To investigate the role of strain on the diffusion
characteristics of Ni and Al, the self-diffusion coefficient
obtained from the slope of mean square displacements (MSD)
was evaluated quantitatively. The analytical condition used in
this analysis is summarized in Table 1. The interatomic
potential defined by Zhou et. al., [15] was used for all the
calculations. This potential is the generalized embedded atom
method (GEAM) interatomic potential which reproduces the
structural features of Ni, Al, and Ni$_3$Al such as lattice constants,
thermal expansion coefficients and so on. Since there is a large
mismatch between the lattice constant of Ni and Al crystal, the
structural relaxation calculation by changing the volume was
performed at 300 K for 10 ps in order to obtain the equilibrium
lattice parameters of the Ni(100)/Al(100) supercell model.

ANALYTICAL RESULTS AND DISCUSSION

Figure 3 shows example trajectories of Ni and Al atoms in
the Ni/Al interface structure under (a) 0 % strain, (b) 2 % strain
along x-direction (parallel to the interface) and (c) 2 % strain along z-direction (perpendicular to the interface). The
diffusion of Al atoms around the interface under the tensile
strain is increased remarkably comparing with that estimated
around the unstrained interface as shown in Fig. 3. Moreover,
these figures also indicate that the mobility of Al atoms at the
interface under 2 % strain along x-direction is larger than that
under 2 % strain along z-direction. The MSD value of Al atoms
perpendicular to the interface (along z-direction) increases
dramatically near the strained interfaces.

The strain dependence of the atomic diffusion around the
Ni(001)/Al(111) interface structure was also analyzed as shown
in Fig. 4. Slips were found to occur in the both interface
structures under the applied strain. It is obvious that the slip
occurred in the Ni(111)/Al(111) interface under strain because

Fig. 3 Trajectories of Ni and Al atoms in Ni(001)/Al(001)
interface

Fig. 4 Change of the atomic configuration around the
Ni(001)/Al(111) interface caused by tensile strain parallel to the
interface

(111) planes in Al crystal are easy to glide to the slip direction
equivalent for x-direction in the interface model) when tensile
strain was applied parallel to the interface. Since high strain
causd both dislocations and slips in the Ni(111)/Al(111)
interface structure, no stress-induced anisotropic diffusion of
both Al and Ni was observed around the interface. When stress
was applied to the crystal structure, the structure deforms to
relieve the applied stress or the high strain energy. However,
the slip generation was strictly prohibited in the
Ni(001)/Ni$_3$Al(001) interface structure because the resolved shear
stress within the slip system was not large enough to activate
the slip generation. Thus, the anisotropic diffusion
perpendicular to the interface occurred to relieve the strain
energy. The anisotropic diffusion leads to the mixing of Al and
Ni atoms at the interface, resulting in that the lattice mismatch
at the Ni/Al interface becomes small and consequently
reducing the high strain field. Hence, it is concluded that the
stress-induced anisotropic diffusion is expected to occur at the
interface for reducing the strain energy under the elastic
condition, which is significantly dependent of both the
amplitude and direction of the applied load, and the
crystallographic interface structure.

In order to validate the estimated stress-induced
anisotropic diffusion of Al in Ni-base superalloy, MD
calculations were applied to the Ni(001)/Ni$_3$Al(001) interface
under 2% strain parallel to the interface. Since the Ni/Ni$_3$Al
interface has a small strain because of small lattice mismatch
between Ni and Ni$_3$Al crystal, the magnitude of diffusion
constant is smaller than that obtained in the case of the
Ni(001)/Al(001) interface. However, it was found that the
applied strain enhanced the diffusion of Al atoms perpendicular
to the interface (z-direction), which was similar to that
observed in the Ni(001)/Al(001) interface system. The
diffusion constant of Al atoms perpendicular to the interface increased by about 20 times when the uni-axial strain of 2% was applied parallel to the interface. This diffusion characteristic of Al atoms in the Ni₃Al phase corresponds the fact that the γ' phase forms layered rafts perpendicular to the stress direction. Therefore, it is highly possible that the morphological change of rafting occurs predominantly by stress-induced anisotropic diffusion of Al atoms.

Similar stress-induced anisotropic diffusion phenomenon of elements was observed at the Cu(001)/Al(001) interface as shown in Fig. 6. Though the acceleration rate of each element was different from that obtained from the Ni(001)/Al(001) interface, the diffusion constant of both copper and aluminum perpendicular to the interface was accelerated significantly when tensile strain was applied parallel to the interface. Thus, this stress-induced diffusion occurs when face centered cubic metals form (001) crystallographic interface. Effect of the tensile stress applied parallel to the interface which is consisted by metals with various crystallographic structures on the diffusion constant of each element was also analyzed as shown in Fig. 7. No effective acceleration of the diffusion constant was observed around the interfaces such as BCC (body-centered cubic)/BCC, BCC/HCP (close-packed hexagonal lattice), and BCC/FCC.

Since the anisotropic diffusion of Al atoms plays a key role in the rafting phenomenon of γ' phase, the reduction of the mobility of Al atoms perpendicular to the interface between Ni(001) and Ni₃Al(001) should decrease the evolution of the rafting and thus, improve both the creep and fatigue resistance of the Ni-base superalloy. The addition of different alloying elements is, therefore, an effective method for controlling the kinetics of the rafting because it is generally possible to change the lattice constant of γ and γ' phases, and consequently to modify the coherency stress between the two phases. The effect of component elements in the Ni-base superalloy on the strain-induced anisotropic diffusion of Al atoms was, therefore, analyzed by replacing some Ni atoms in the Ni₃Al(001)/Ni(001) interface system by dopant atoms. Tensile strain of about 2% was applied parallel to the interface and the MSD of Al atoms perpendicular to the interface was calculated. Then, the diffusion constant of Al atoms under the strain was calculated by using Einstein’s equation.

Figure 7 summarizes the effect of the dopant element on the MSD of Al atoms under the strain. It was found that Al, Ti, Co, Zr, and W atoms accelerated the strain-induced anisotropic diffusion of Al atoms. On the other hand, Mg, Fe, Cu, Mo, Pd and Ta atoms decreased the diffusion significantly. In particular, Pd is one of the most effective elements which restrain Al atoms from moving around the interface. Both the atomic radius and the binding energy with aluminum of the dopant element are the dominant factors which change the diffusion of Al atoms in the Ni-base superalloy. Dopant elements which have larger lattice constant reduce the diffusion of Al. The elements which binding energy with Ni and Al is larger than Al enhance the diffusion of Al because they break the Ni-Al bonds in γ' (Ni₃Al) phase. Since both Mo and W atoms are already doped in the alloy, these elements may deteriorate the reliability of this alloy at high
temperatures, even though there are clear purposes for doping these elements into the alloy. The material design, i.e., optimization of the component of this alloy should be discussed again in detail from the point of view of the long life at high temperatures.

**EXPERIMENTAL VALIDATION OF THE STRAIN-INDUCED ANISOTROPIC DIFFUSION AROUND FCC(001)/FCC(001) INTERFACES**

In order to validate the estimated strain-induced anisotropic diffusion phenomenon, thin film stacked structures which consisted of FCC metals with (001) crystallographic interfaces were made by using an electron beam deposition method. A heavily rolled copper foil was annealed to form strongly (001) orientated substrate as shown in Fig. 8. This foil was used for the substrate to form stacked thin film structures with FCC(001)/FCC(001) interfaces. 1-μm thick nickel and 0.1-μm thick aluminum was deposited on the substrate continuously without breaking vacuum condition.

Figure 9 shows an example of the measured x-ray diffraction pattern of the stacked structure. It was confirmed that both the deposited nickel and aluminum layers mainly consisted of (001) crystallographic orientation. This stacked structure was annealed at various temperatures for 48 hours under tensile strain applied parallel to the interface. A four-point bending method was used for the loading. After the annealing, the change of the depth profile of the atomic composition of the stacked structure was measured by auger electron spectroscopy. The effect of the applied tensile stress was investigated by measuring the change of the diffusion depth of aluminum in the transition area indicated by dashed lines in the figure.

Figure 10 shows an example of the measured change of the diffusion depth of nickel around the Ni/Cu interface after the four-point loading at 200°C. When tensile strain of 0.2% was applied parallel to the stacked Ni(100)/Cu(100) interface, the diffusion of nickel perpendicular to the interface was enhanced slightly. The diffusion depth of nickel into the copper substrate was increased. The strain-induced anisotropic
accelerated diffusion of nickel was clearly enhanced at 200°C. This result clearly indicates that the strain-induced anisotropic diffusion of component elements occurs significantly when tensile strain is applied parallel to the FCC(001)/FCC(001) interface.

Next, the effect of the dopant elements on the stress-induced anisotropic diffusion was investigated using the thin-film stacked test structure as shown in Fig. 11. The dopant element was deposited in the nickel layer periodically. In this test sample, the stacked layer structure with a 20-nm thick nickel layer and a 2-nm thick titanium layer were deposited three times on the copper substrate by using a multi-element electron beam deposition method. Then, this stacked structure was annealed at 200°C for 192 hours under tensile strain applied parallel to the interface. A four-point bending method was used for the loading again. The dopant elements used in this study were titanium, tungsten, palladium and tantalum.

Figure 12 shows the measured change of the depth profile of nickel around the Ni(001)/Cu(001) interface. It was confirmed that the diffusion of nickel around the interface was accelerated by the doping of titanium in the nickel layer. Similarly, the doping of tungsten enhanced the diffusion of nickel. These results clearly validated the analytical results shown in Fig. 7. Next, the suppression of the diffusion by doping palladium was validated as shown in Fig. 13. The depth profile of nickel around the Ni(001)/Cu(001) interface became sharp clearly.

Based on these validations, it was concluded that the strain-induced anisotropic diffusion of aluminum atoms is one of the dominant factors of the change of the micro texture of the Ni-base superalloy used for gas turbine systems, in other words, the degradation of the strength of the alloy at high temperatures. Since this strain-induced change of the micro texture causes abrupt fracture of the alloy, it is very important to develop the countermeasure which minimizes the strain-induced diffusion of aluminum atoms in order to assure the long life reliability of the alloy in actual operation. In addition, the application of MD analysis to the design of a novel heat resistant material is very effective for improving the efficiency of energy power plants for next generation.

CONCLUSIONS

Molecular dynamics (MD) simulation was applied to explicate the strain-induced anisotropic diffusion of component elements of Ni-base superalloy around the Ni(001)/Al(001) and Ni(001)/Ni3Al(001) interface. It was found the diffusion of aluminum atoms perpendicular to the interface was accelerated by the tensile strain applied parallel to the interface, and thus it should be the main reason for the rafting phenomenon which changes the micro texture of the superalloy from the finely dispersed texture to the coarsened layered texture. The dopant elements in the superalloy also affected the strain-induced diffusion of aluminum atoms. These estimated results were confirmed by experiment by measuring the change of the depth profile of the atomic composition of the stacked thin film structure (Al(001)/Ni(001)) between before and after the annealing under tensile strain applied parallel to the stacked interface. It was also found that cobalt and tungsten atoms which are already doped in the alloy accelerated this phenomenon seriously. On the other hand, palladium, for example, was found to be one of the most effective elements which restrain Al atoms from moving around the interface.

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