JOURNAL OF MATERIALS SCIENCE **37** (2002) 1915–1920

The effect of long range order on the activation energy for atomic migration in NiAl alloys; resistivity study

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The influence of the degree of long range order (S) on the migration energy in NiAl was investigated by electrical resistivity and X-ray diffraction. Iron (12at.%) was over-alloyed to the stoichiometric NiAl in order to decrease the order-disorder transition temperature.(NiAl12Fe) The degree of LRO in NiAl12Fe decreased gradually as temperature increased. The activation energies for migration of iron in NiAl12Fe ($Q_A^{Fe^*}$) that were measured from the temperature dependence of jumping frequency ($1/\tau_{Fe^*}$) were 1.42 ± 0.19 eV, 1.35 ± 0.18 eV, 1.16 ± 0.06 eV for the alloys quenched from 1073 K, 1273 K, and 1473 K respectively. The activation energies for migration of excess vacancy ($Q_A^{V^*}$) in NiAl single crystal, were 1.55 ± 0.02 eV for the specimen quenched from 1473 K and 1.40 ± 0.11 eV for one quenched from 1673 K. The degree of LRO (S) in single crystalline NiAl calculated from the result of Hughes Lautensclager, Cohen and Brittain, *J. Appl. Phys.* **42** (1971) 3705 seems to be consistent with this decreasing tendency in the activation energy. The reduction of the degree of LRO (S) can explain these variations in the migration energy as the Girifalco's model. © *2002 Kluwer Academic Publishers*

1. Introduction

NiAl is a well known Hume-Rothery electron compound with B2 structure [1]. This ordered phase has been considered over several decades as a potential high temperature structural material that could substitute the Ni based superalloys due to its high melting point, low density, and excellent phase stability at high temperature, etc. [2, 3].

NiAl was reported to conserve the ordered structure up to its melting temperature and the order-disorder transition was regarded to take place at over the melting temperature [4]. According to the report of Liu *et al.*, even electron irradiation could not induce complete disorder in the alloy [5]. These behavior was interpreted to be caused by it's large heat of formation of NiAl phase (-72 ± 2 kJ/molK) and the degree of long range order (S) was assumed to remain perfect ($S = 1$) over all temperature range [6–8]. This means that the degree of ordering in NiAl has been out of consideration in a case of solid state diffusion.

The degree of long range order may affect theoretically the activation energy for migration of an atom or point defect in the ordered phases [9, 10]. There were recently a few reports about the correlation of long range order and diffusion behavior in order-disorder alloy, where disordering in an ordered alloy takes place before melting [11–14]. Girifalco suggested that the activation energy for atomic migration in an ordered alloy depends on the degree of LRO (S) as follows [9];

$$Q_A^O = Q_A^D(1 + \alpha S^2) \quad (1)$$

where, Q_A^O is activation energy for migration in the ordered phase and Q_A^D is one in the disordered phase. α is a constant.

If the transition point of order-disorder is lowered in NiAl alloy, it will be easier to observe a change in the degree of LRO (S) and the related variation in atomic scale. In an experiment of Cahn *et al.*, Fe addition decreased the order-disorder transition temperature of Ni_3Al [15]. In order to reduce the disordering temperature of NiAl phase, iron was alloyed over its solubility limit (NiAl12Fe) in the present investigation. If a

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phenomenon that happened in NiAl12Fe alloy by lowered degree of LRO takes place in NiAl, it could be said that the phenomenon was also due to the low degree of long range order in NiAl. Thus the observation of iron precipitating in the NiAl12Fe was compared with an annealing-out procedure of the vacancy quenched in NiAl single crystal of stoichiometric composition.

X-ray diffraction was used to measure the degree of long range order in the alloys and electrical resistivity measurement was carried out to investigate the atomic migration in NiAl.

Isothermal variation of the resistivity with aging time in intermetallic compounds can be described as a parallel process of two first order kinetics (fast, slow stage) as follows [16];

$$\frac{\rho(t)-\rho(\infty)}{\rho(o)-\rho(\infty)} = A_{\mathrm{f}}\exp\left(-\frac{t}{\tau_{\mathrm{f}}}\right) + A_{\mathrm{s}}\exp\left(-\frac{t}{\tau_{\mathrm{s}}}\right) \qquad (2)$$

where, $\rho(t)$ is the resistivity at a time, t, $\rho(0)$ is one at the beginning ($t = 0$), and at an infinite time is $\rho(\infty)$. A_{f} and A_{s} are constants for the fast and the slow kinetics stage, respectively, which should meet a condition that $A_{\mathrm{f}} + A_{\mathrm{s}} = 1$. $1/\tau_{\mathrm{f}}$ and $1/\tau_{\mathrm{s}}$ are jumping frequencies of atoms corresponding to each kinetics. The fast kinetic stage starts right after the beginning of isothermal annealing, which was proposed due to excess point defects. The slow kinetics was known to operate when vacancy concentration was less than 10^{-5}. Thus the effect of slow kinetics on the fast kinetic stage is relatively negligible. The change related with the degree of LRO would appear at the fast kinetics stage because the degree of LRO is dependent on the concentration of point defects in NiAl [17]. Thus, the present study was focused on the fast kinetics stage. By neglecting the second term of Equation 2,

$$\ln\frac{\rho(t)-\rho(\infty)}{\rho(0)-\rho(\infty)} = -\frac{1}{\tau}\cdot t + C \qquad (3)$$

where, C is constant.

The activation energy for migration, Q_{A}, can be calculated from the temperature dependence of τ from the following relation;

$$\tau = \tau_{\mathrm{o}}\exp\frac{Q_{\mathrm{A}}}{kT} \qquad (4)$$

The purpose of the present study is to measure the degree of LRO and the activation energy for the atomic migration, and to investigate whether Girifalco's model is effective in NiAl.

2. Experimental procedures

Elemental pellets of Ni (99.5 wt% purity), Fe (99.95 wt% purity) and Al (99.99 wt% purity) were used to produce a casting of NiAl12Fe alloy in a copper chill mold by vacuum induction melting. The NiAl12FE ingot was homogenized at 1473 K under purified Ar flow for 24 h. Single crystalline NiAl with a composition of stoichiometry was prepared by the Brigdemann Method. A homogenization treatment was carried out on the NiAl at 1673 K for 24 h in the Ar atmosphere. All the samples were wrapped with Ta foil to prevent oxidation and no evidence of the existence of oxides was found after the annealing.

Measurement of the degree of long range order in NiAl12Fe was made with X-ray diffraction (XRD). The XRD samples of NiAl12Fe alloys were cut into a sheet of 17 × 16 × 1 mm^3 by EDM (electro-discharge machining). The specimens were heat-treated at a series of five temperatures for 2 h by a step of 100 K from 1073 K to 1473 K respectively, and then quenched in iced water. Any evidence of oxidation on the surfaces was not found from a weight change and an observation with an optical microscopy. The XRD measurement was made using Cu K_α radiation with a scanning step of 0.004°.

The specimens for the electrical resistivity measurement were cut into a dimension of 28.0 mm(L) × 3.8 mm(W) × 0.9 mm(t). NiAl12Fe alloys and NiAl single crystals were isothermally heat-treated for 2 h, followed by water quenching. The temperature at which the NiAl12Fe and NiAl were annealed before quenching was, in the present work, designated as a quenching temperature, T_{q}. The quenching temperatures of NiAl12Fe were 1073 K, 1173 K, 1273 K, 1373 K and 1473 K. The single crystalline NiAl samples were quenched from 1273 K, 1373 K, 1473 K, 1573 K, and 1673 K.

In situ change of the electrical resistivity was measured under isochronal and under isothermal conditions. Four-point probe method was used applying a constant current of 2 A. Fully annealed pure Cu wires were spot-welded on the samples. The heating rate was 2.5 K/min for isochronal annealing.

3. Results and discussions

Fig. 1 is the spectra of X-ray diffraction of NiAl12Fe alloys as a function of quenching temperature. The intensities of superlattice peaks like (100), (111), (210) increased as the quenching temperature (T_{q}) lowered. One exception was that the (100) peak intensity for 1473 K was not reduced, probably due to an increased atomic mobility at higher temperatures.

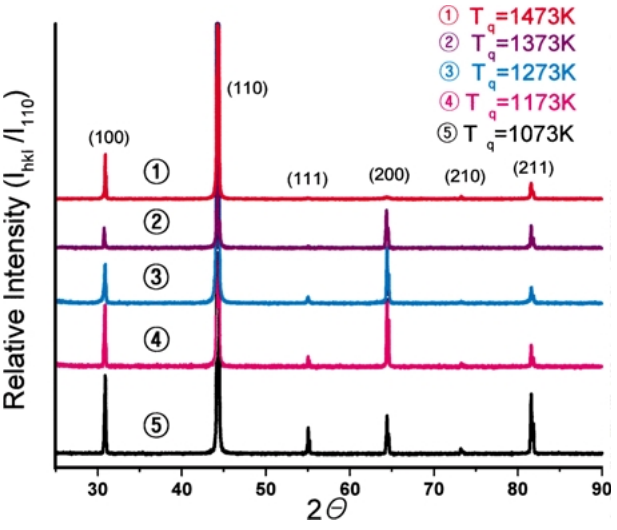


Figure 1 X-ray diffraction spectra of NiAl12Fe alloys as a function of temperature.

Fig. 2 shows the variation of the degree of LRO (S) as a function of temperature in NiAl12Fe measured using the XRD peak intensities in Fig. 1. The degree of long range order (S) was calculated from the following relationship;

$$\frac{S}{S_o} = \sqrt{\frac{(I_s/I_f)_S}{(I_s/I_f)_{S_o}}} \tag{5}$$

where, S is the degree of long range order measured by X-ray peak intensity and S_O is one when perfectly ordered(unity). I_s and I_f represent the intensities of superlattice peak and fundamental peak, respectively. The degree of LRO (S) at each temperature was normalized assuming that the degree of order was unity at room temperature. It was shown in Fig. 2 that the degree of long range order (S) in NiAl12Fe alloys decreased with temperature above $0.6T_m$.

Fig. 3 shows the *in situ* resistivity change under continuous heating condition in NiAl12Fe alloy that was quenched from 1473 K. As-quenched resistivity of NiAl12Fe was 70 at 300 K. The resistivity rose slowly to about 77 with temperature up to 650 K followed by an abrupt drop to 58 at 820 K, then a rapid rise to 87 at about 1000 K. Upon cooling, a steep decrease from 82 to 60 appeared in a temperature range between 930 K and 730 K. The resistivity reduced to 49 at 300 K.

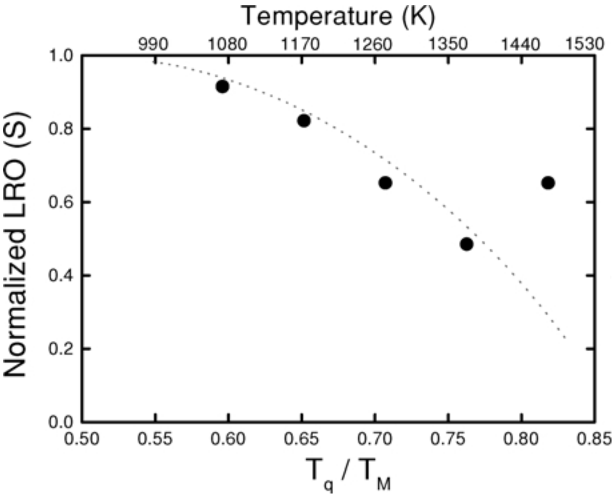


Figure 2 Variation of the degree of long range order (S) with temperature.

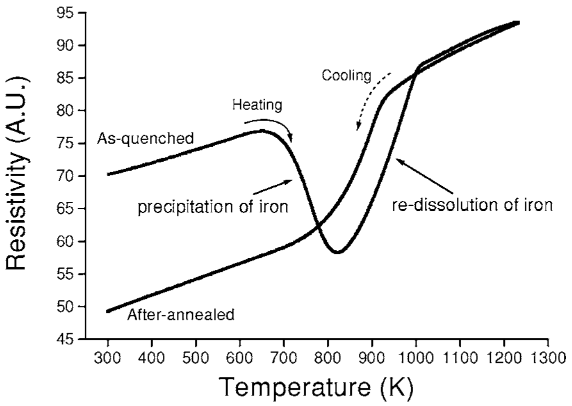


Figure 3 Variation of electrical resistivity in NiAl12Fe alloys under isochronal annealing; the alloy was quenched from 1473 K.

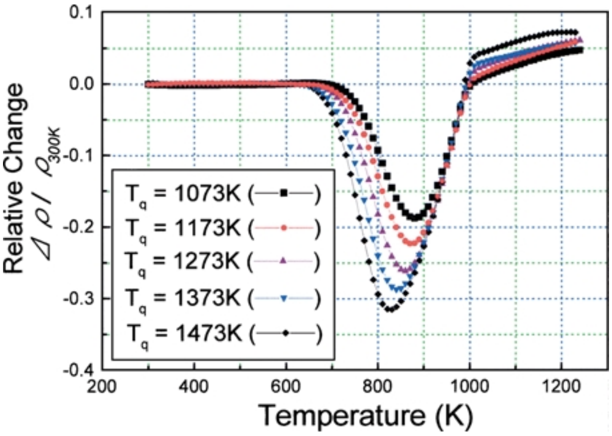


Figure 4 Variation of relative change of the resistivity in NiAl12Fe alloys as a function of quenching temperature.

The increase up to 40% of the as-quenched value of resistivity compared to the after-annealed was considered mainly due to the excess iron atom over its solubility in the matrix. The reduction in resistivity at a temperature range between 650 K and 820 K resulted from the precipitation of iron that was over-alloyed in NiAl, while the increase in the range of 820 K–1000 K was caused by the re-dissolution of iron into the matrix. The 820 K, at which the drop in resistivity was observed, was regarded as a transition temperature where the mechanism of resisitivity changed from precipitation to re-dissolution of iron. This result is in accordance with the work of Ko *et al.* [18], where the change in the magnetization was shown to be caused by the precipitation of ferromagnetic iron particle in NiAl.

Fig. 4 is a plot of the relative change of resistivity in NiAl12Fe alloys with a constant heating rate with respect to quenching temperature (T_q).

The increase in the relative change over a range of 630 K–880 K showed a tendency that it shifted to lower temperature as the quenching temperature was higher. It means that the iron precipitation in NiAl matrix probably began at lower temperature as the alloy was quenched from higher temperature. The precipitation of iron supersaturated in NiAl should be via migration of iron atom in the matrix, i.e., the diffusion of Fe in the matrix. Thus, it can be said that the migration of iron was initiated at lower temperature in the alloys quenched from higher temperature.

The peaks at around 820 K–880 K, which appears to be a transition point of the resistivity change mechanism from the precipitation to the re-dissolution of iron in NiAl, showed a shift to lower temperature as the alloys was quenched from higher temperature.

These changes in the peak temperature can be explained as phenomena caused by a decrease of the degree of long range order (S) based on Girifalco's model. It was suggested in the model that activation energy of atom migration in an ordered alloy be lowered as the ordering level (S) decreases. With the lowered activation energy the reaction can be occurred at the lower temperature if there is ni change in activation process. It was shown in Figs 1 and 2 that the degree of order (S) of NiAl12Fe decreased along with the quenching temperature. Thus, the lowered degree of LRO (S) can have the relation with the decrease of the peak temperature in Fig. 4.

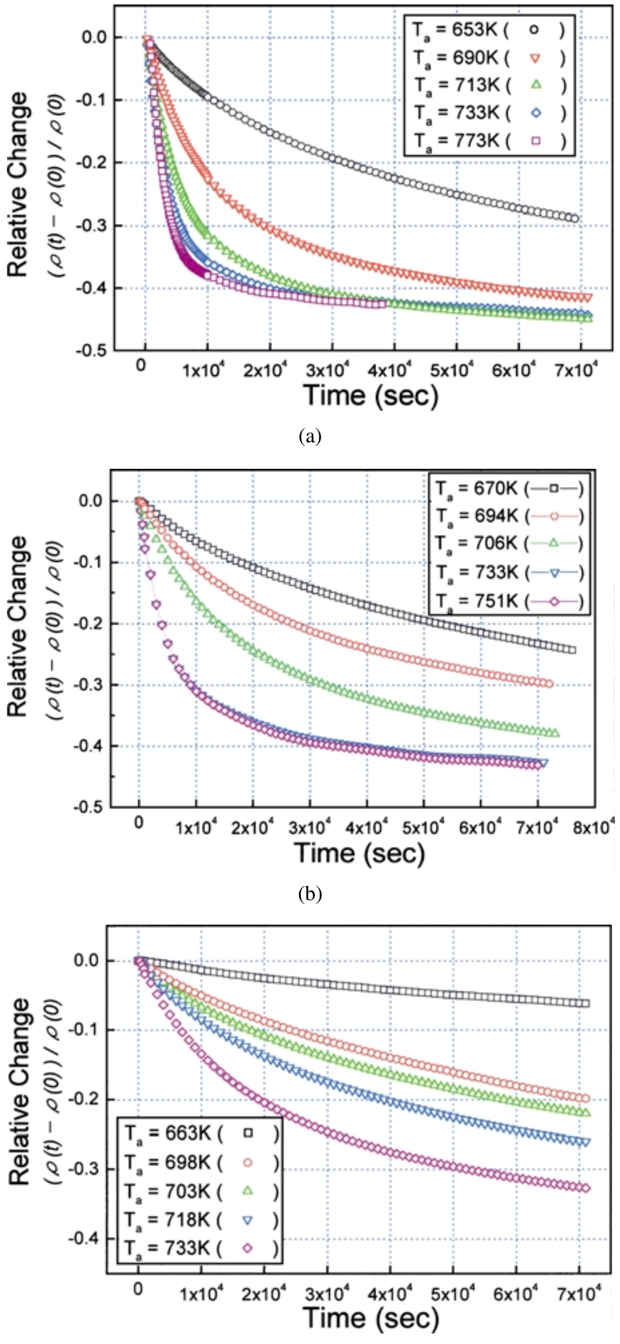
The activation energy of iron precipitation in the NiAl12Fe alloy was measured as a function of quenching temperature in order to prove that the activation energy was really lowered with the degree of LRO. From the growth rate measurement of Fe precipitates in NiAl [19], the precipitation of iron was regarded to be controlled by migration of supersaturated Fe in the NiAl matrix. Thus, the activation energy of the precipitation was considered as the activation energy for migration of the supersaturated Fe ($Q_A^{Fe^*}$) in the alloy.

Fig. 5a–c are the isothermal change of the relative resistivity of NiAl12Fe alloys quenched from 1473 K, 1273 K, and 1073 K respectively. $\rho(t)$ and $\rho(0)$ are the resistivities measured at a time, t, and at $t = 0$. T_a is the isothermal annealing temperature.

There was a rapid decrease of resistivity at the beginning of annealing, then slow in rate afterward in all the conditions. Thus, the precipitation process via migration of iron under isothermal condition can be described as a parallel process of two first order kinetics in Equation 2.

The activation energies ($Q_A^{Fe^*}$) were obtained from the temperature dependence of the jumping frequency of the iron atom ($1/\tau_{Fe^*}$) using Equation 4.

In Fig. 6a–c, the activation energy for migration of supersaturated Fe in NiAl ($Q_A^{Fe^*}$) was measured as a function of the quenching temperature.

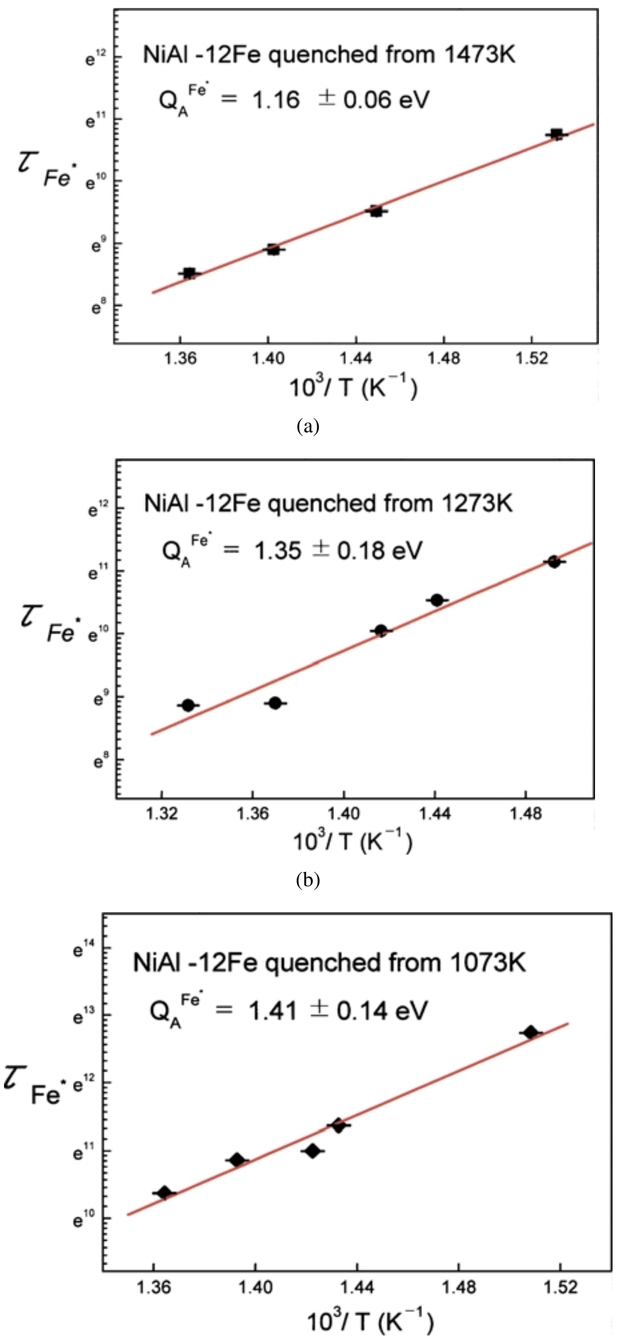


(a)

(b)

(c)

Figure 5 Isothermal variation of relative change of the resistivity in NiAl12Fe alloys with aging time; the decrease of resistivity was caused by the precipitation of iron in the alloy. (a) is when the quenching temperature was 1473 K, (b) is when the quenching temperature was 1273 K, and (c) is when the quenching temperature was 1073 K.



(a)

(b)

(c)

Figure 6 The measured activation energies for migration of supersaturated iron in NiAl12Fe alloys ($Q_A^{Fe^*}$) as a function of quenching temperature; (a) $T_q = 1473$ K, (b) $T_q = 1273$ K, and (c) $T_q = 1073$ K.

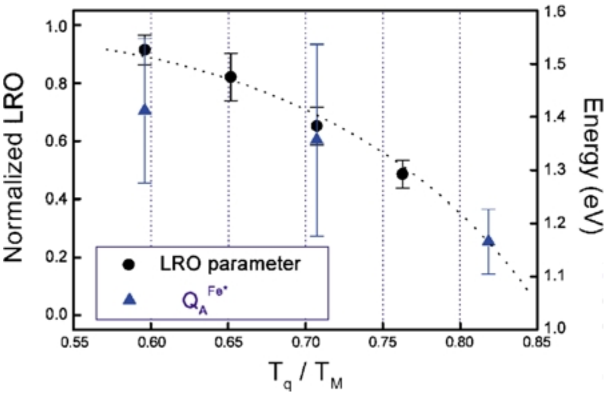


Figure 7 Variation of the migration energy of supersaturated iron ($Q_A^{Fe^*}$) and the degree of long range order (S) as a function of temperature.

The measured activation energies were 1.16 ± 0.06 eV, 1.35 ± 0.18 eV, and 1.42 ± 0.19 eV for the alloys quenched from 1473 K, 1273 K, and 1073 K, respectively. The activation energy for migration of supersaturated iron ($Q_A^{Fe^*}$) was lowered by about 18% from 1.42 eV in (c) to 1.16 eV in (a).

The activation energy for migration of iron ($Q_A^{Fe^*}$) in NiAl12Fe surveyed in the present work was plotted with the degree of LRO (S) as a function of temperature in Fig. 7. It was seen that the variation of the activation energy was consistent with the degree of order (S) in the alloy. When the normalized degree of LRO (S) was 0.9 at 1073 K, the activation energy was 1.42 ± 0.19 eV. The energy was 1.35 ± 0.18 eV at 1273 K with the degree of order (S) being 0.65. The activation energy was 1.16 ± 0.06 eV at 1473 K when normalized degree of LRO (S) would be in between 0.3 and 0.4.

The observation of lowered activation energy for migration of the iron supersaturated in NiAl means that the atomic moving in NiAl intermetallic matrix was easier as suggested in Girifalco's model when the degree of LRO (S) was lower.

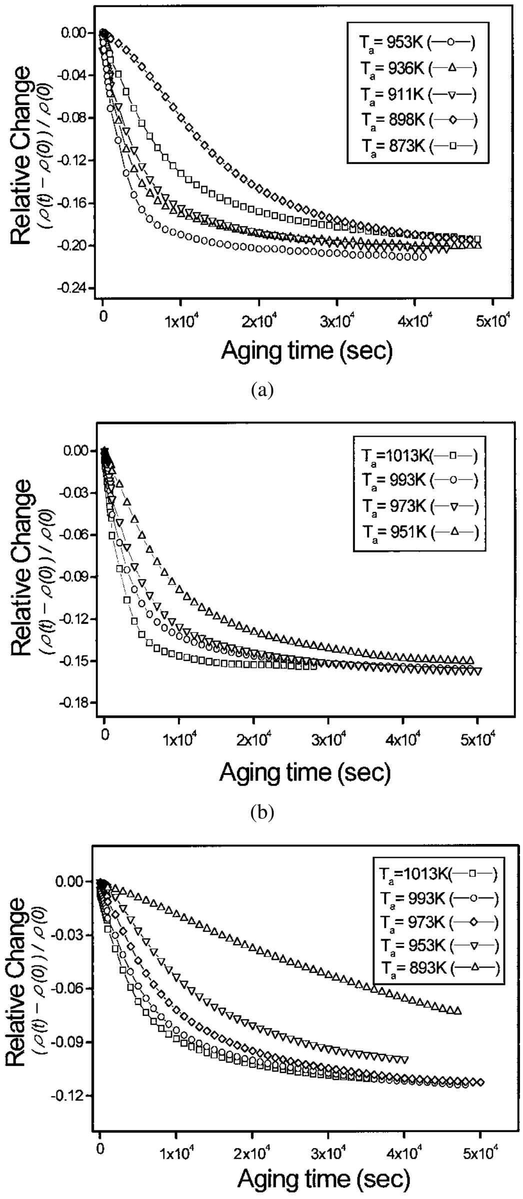
In Fig. 8, it was shown the relative resistivity change in pure NiAl single crystal with aging time as a function of quenching temperature under isothermal condition.

In a case of single crystalline NiAl with a composition of stoichiometry, the lowering of resistivity is through the annealing-out of thermal vacancy that was quenched in. Thus, the measured activation energy ($Q_A^{V^*}$) is the energy required for excess thermal vacancy to move to annihilate.

Fig. 9a–c are the measured activation energies for migration of the excess thermal vacancy ($Q_A^{V^*}$) that was trapped in equiatomic NiAl at 1673 K, 1573 K, and 1473 K, respectively. The activation energy was calculated from the jumping frequency ($1/\tau_{V^*}$) of excess thermal vacancy using Equation 2–4.

The activation energies for excess vacancy migration ($Q_A^{V^*}$) were 1.40 ± 0.11 eV, 1.55 ± 0.09 eV, and 1.55 ± 0.02 eV.

The activation energies for vacancy miagration are a bit lower than the reported migration energies in NiAl [8, 20]. The origin of these low values seems to come from the fact that the measurement of the activation energy was carried out on the initial fast kinetic stage, where the migration of atoms took place under non equilibrium.



(a)

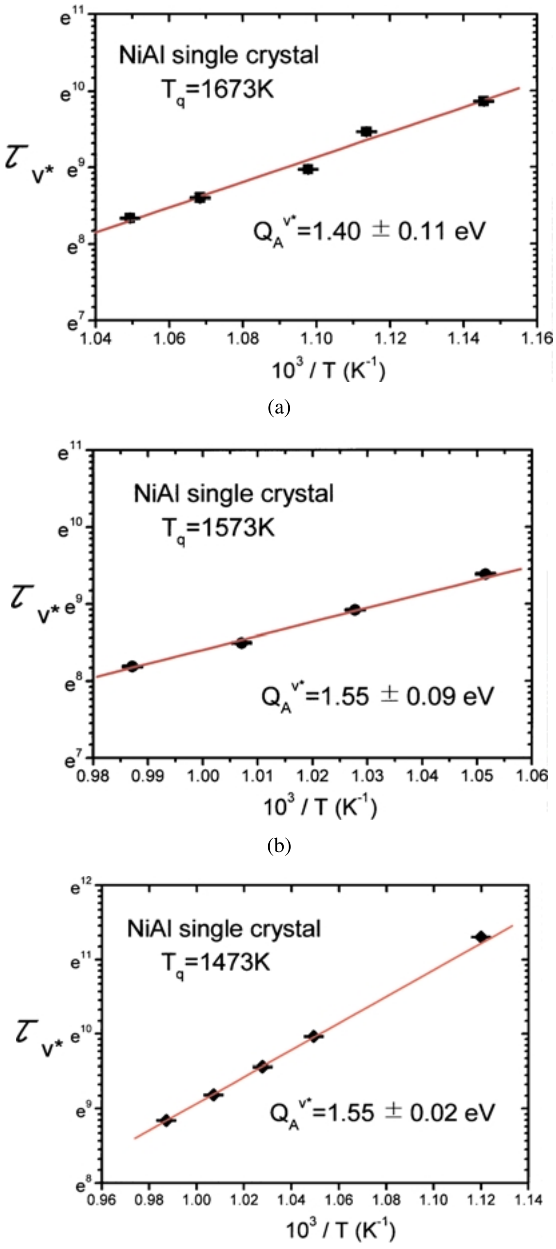
(b)

(c)

Figure 8 Isothermal variation of relative change of the resistivity in stoichiometric NiAl single crystal with aging time; the decrease was caused by an annealing out of thermal vacancy quenched in the matrix. (a) is when the quenching temperature was 1673 K, (b) is when the quenching temperature was 1573 K, and (c) is when the quenching temperature was 1473 K.

The observed activation energy of vacancy migration ($Q_A^{V^*}$) was reduced from 1.55 eV to 1.40 eV by about 10%. According to Hughes *et al.*, the degree of LRO (S) of β'-NiAl alloy decreased at over 1273 K from a measurement of (100) peak intensity by X-ray diffraction study, while the degree of LRO remained nearly maximum ($S = 1$) up to a temperature of 1273 K [4]. If Girifalco's model is effective in NiAl, the activation energy will decrease in relatively small value in accordance with the small decrease in the degree of long range order.

In Fig. 10, the migration energy of the excess vacancy in NiAl measured in the present study was compiled with the degree of long range order (S) calculated from the result of Hughes *et al.* as a function of temperature. The degree of LRO (S) was normalized to the intensity below 1273 K assuming that the degree of LRO (S) remains maximum (unity) as Hughes *et al.* suggested [4].



(a)

(b)

(c)

Figure 9 The measured activation energies of supersaturated vacancy in NiAl ($Q_A^{v^*}$) as a function of the quenching temperature; (a) when $T_q = 1673$ K, (b) when $T_q = 1573$ K, and (c) when $T_q = 1473$ K.

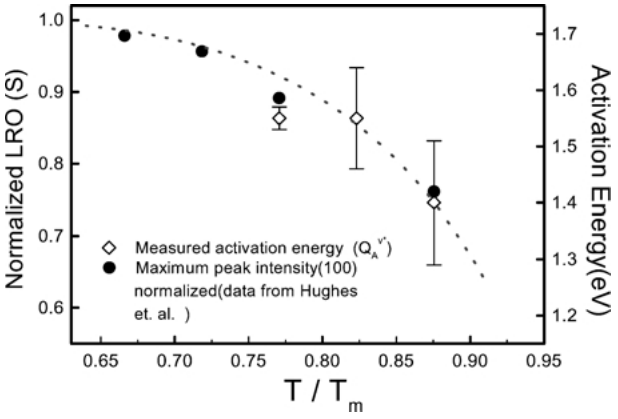


Figure 10 Variation of the migration energy of quenched-in vacancy ($Q_m^{Fe^*}$) and the LRO (S) as a function of temperature; the degree of LRO (S) was obtained from the work by Hughes *et al.* [4].

When the degree of order (S) was about 0.9, the activation energy was 1.55 ± 0.02 eV. The activation energy was 1.40 ± 0.11 eV when the degree of LRO (S) was about 0.8. The activation energy was lowered as the degree of LRO (S) decreased as in Girifalco's model [9].

4. Conclusions

The influence of the degree of long range order (S) on the activation energy for atomic migration in NiAl was investigated by electrical resistivity and X-ray diffraction. Iron was over-alloyed to NiAl in order to decrease the order-disorder transition temperature.(NiAl12Fe) The degree of LRO in NiAl12Fe decreased gradually as temperature increased. The migration energies of iron supersaturated in NiAl12Fe ($Q_A^{Fe^*}$) were measured from the temperature dependence of jumping frequency ($1/\tau_{Fe^*}$) as 1.42 ± 0.19 eV, 1.35 ± 0.18 eV, 1.16 ± 0.06 eV for the alloys quenched from 1073 K, 1273 K, and 1473 K, respectively. The activation energies for migration of excess vacancy ($Q_A^{v^*}$), which was quenched in NiAl single crystal, were 1.55 ± 0.02 eV for the specimen quenched from 1473 K and 1.40 ± 0.11 eV for one quenched from 1673 K. The reduction of the degree of LRO can explain these variations in the migration energy as the Girifalco's model suggested.

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Received 13 June 2000
and accepted 2 November 2001