ELSEVIER

Journal of Alloys and Compounds 218 (1995) 216–220

Journal of ALLOYS AND COMPOUNDS

Influence of annealing on hydrogenation characteristics and microstructure of $LaNi_{4.55}Al_{0.45}$ alloy

H. Nakamura, Y. Nakamura, S. Fujitani, I. Yonezu

SANYO Electric Co., Ltd., New Materials Research Center, 1-18-13 Hashiridani, Hirakata City, Osaka 573, Japan

Received 15 April 1994; in final form 18 August 1994

Abstract

The influence of annealing time and temperature on the plateau slope and microstructure of a hydrogen-absorbing $LaNi_{4.55}Al_{0.45}$ alloy was investigated. The homogenizing behaviour during annealing was also analysed to clarify the effects of annealing quantitatively.

Electron probe microanalysis and X-ray powder diffraction analysis indicated that the plateau slope is caused mainly by the fluctuation of Al concentration in the dominant phase. The dependence of the homogenizing behaviour on the annealing conditions is reasonably explained with a non-steady-state Al diffusion model where Al is distributed periodically.

Keywords: Annealing; Hydrogenation; Diffusion; Pressure–composition isotherms

1. Introduction

Heat pumps utilizing the large reaction heat of hydrogen-absorbing alloys with hydrogen gas [1–4], such as in a refrigeration system, have been attracting much attention from the environmental standpoint because they are free from chlorofluorocarbons (CFCs). In these systems the plateau flatness of pressure–composition (P–C) isotherms of the alloys is important for the system performance because it is a direct determinant of the effective hydrogen gas transfer [5].

Annealing of the alloy is an effective method for flattening the plateau region [6–8] and is therefore widely applied in alloy manufacturing. However, annealing conditions such as annealing time and temperature have been determined empirically and there have been few discussions on the relationship between the annealing conditions, the plateau flatness and the microstructure of the alloy.

In this work we investigated the influence of annealing time and temperature on the plateau flatness and microstructure of an $LaNi_{4.55}Al_{0.45}$ alloy developed as an F-class refrigeration system material [1]. The homogenizing behaviour during annealing was also analysed with a non-steady-state Al diffusion model where Al is distributed periodically in the dominant phase with the $CaCu_5$ structure.

2. Experimental procedures

A base ingot of the $LaNi_{4.55}Al_{0.45}$ alloy was prepared by induction melting a mixture of 99.9% pure Ni and Al metals and 99% pure La metal in an atmosphere of high purity argon. Some samples from the base ingot were vacuum annealed in an electric furnace for times $t = 0–259.2$ ks at a temperature $T = 1323$ K to examine the annealing time dependence. Other samples from the base ingot were pre-annealed for 28.8 ks at 1323 K and annealed for 57.6 ks at 1073–1373 K to examine the annealing temperature dependence.

The samples were crushed and ground into powder with diameters of about 100 μm for measurement of P–C isotherms and about 50 μm for X-ray powder diffraction (XRD) measurement.

The phase structures were determined by analysis of the XRD profiles measured using an X-ray diffractometer with Cu Kα radiation. The powder samples for the XRD measurement were coated with epoxy resin to prevent the samples from oxidation during the measurement process. Distributions of La, Ni and Al in the alloy samples were examined with electron probe microanalysis (EPMA).

P–C isotherms of each sample at 353 K were measured with a Sieverts apparatus and analysed with a model we reported previously [9], where the plateau region is expressed in terms of a gaussian distribution

SSDI 0925-8388(94)01407-8

function for the logarithmic equilibrium hydrogen pressure $\ln(P/P_0)$. This model is based on the idea that the plateau slope is caused by a statistical distribution of hydrogen chemical potential in the alloy at a given temperature and that the distribution is due to heterogeneity of the lattice such as grain boundaries and lattice defects and/or compositional fluctuation such as segregation. The plateau slope is evaluated with the standard deviation σ of the gaussian distribution function for $\ln(P/P_0)$: a larger σ indicates a steeper plateau slope and a more heterogeneous structure of the alloy. This model permits quantative characterization of the plateau slope with the parameter σ and, furthermore, assists the physical interpretation of sloping P–C isotherms with parameters including the interstitial site free energy as proposed by Kirchhein et al. [10] and Griessen [11].

3. Results and discussion

Desorption P–C isotherms at 353 K of the as-cast $LaNi_{4.55}Al_{0.45}$ alloy and the alloy annealed for 259.2 ks are shown in Fig. 1. Annealing flattened the plateau slope without reduction of the maximum hydrogen content, while the plateau slope parameter σ correspondingly decreased from 0.566 to 0.095.

Fig. 2 shows XRD patterns of these two alloys. All peaks except one at $2\theta = 43.8°$ were assigned to the hexagonal $CaCu_5$ structure. The peak at $2\theta = 43.8°$ was assigned to the (111) plane of $AlNi_3$. The peak width of the dominant phase, evaluated from the average full width at half-maximum (FWHM) of Cu $K\alpha_1$ peaks between 60° and 80°, decreased from 0.41 to 0.17 after annealing, which means that lattice strain, defects, etc. introduced into the alloy during casting have been removed [12,13] and/or that growth of microcrystals has lessened the particle size broadening. Compositional homogenization of the dominant phase by annealing is also considered to narrow the peak width.

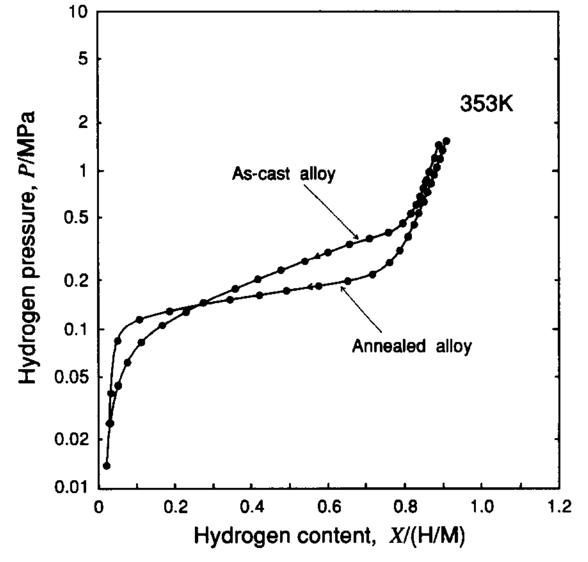

Fig. 1. Desorption P–C isotherms of the as-cast $LaNi_{4.55}Al_{0.45}$ alloy and the alloy annealed for 259.2 ks at 1323 K.

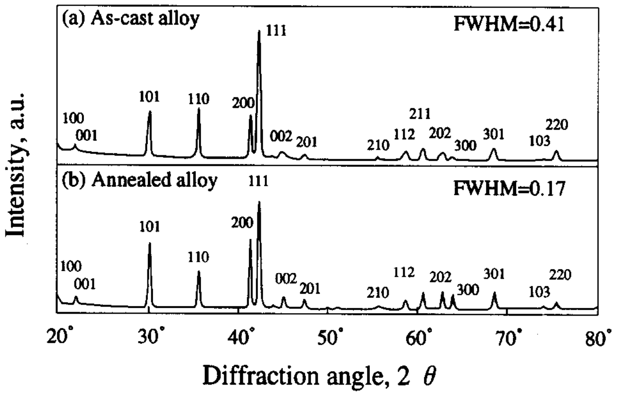

Fig. 2. X-ray powder diffraction patterns of the as-cast $LaNi_{4.55}Al_{0.45}$ alloy and the alloy annealed for 259.2 ks at 1323 K.

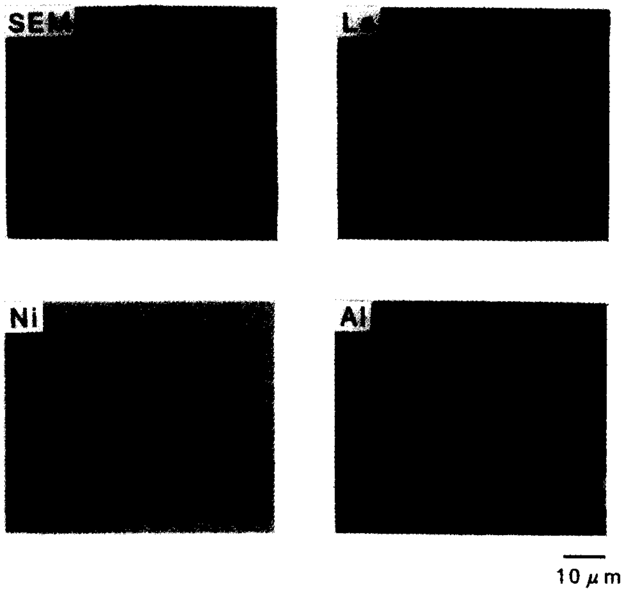

Fig. 3. SEM image and X-ray images of the as-cast $LaNi_{4.55}Al_{0.45}$ alloy.

Fig. 3 shows a scanning electron microscopy (SEM) image and X-ray images of the as-cast alloy. An Al-rich and La-poor precipitated phase surrounded by an Al segregation area was observed. On the other hand, the Al distribution in the dominant phase of the annealed alloy was uniform but the Al-rich phase remained precipitated as shown in Fig. 4. These results suggest that the plateau slope is caused by fluctuation of the Al concentration in the dominant phase and that Al diffusion through annealing gives a homogeneous composition to the dominant phase and flattens the plateau slope.

The effect of defect annealing on the flattening of the plateau slope is considered to be small, because a rapidly quenched $LaNi_{4.55}Al_{0.45}$ alloy which is compositionally homogeneous exhibits a very flat (but nar-

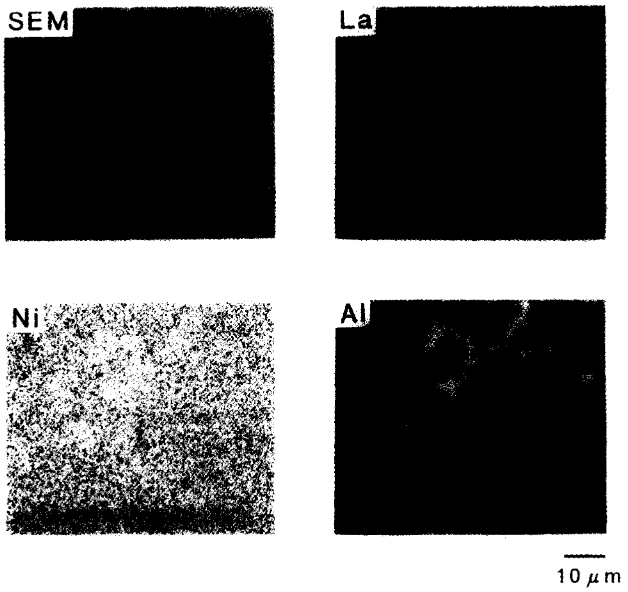

Fig. 4. SEM image and X-ray images of the $LaNi_{4.55}Al_{0.45}$ alloy annealed for 259.2 ks at 1323 K.

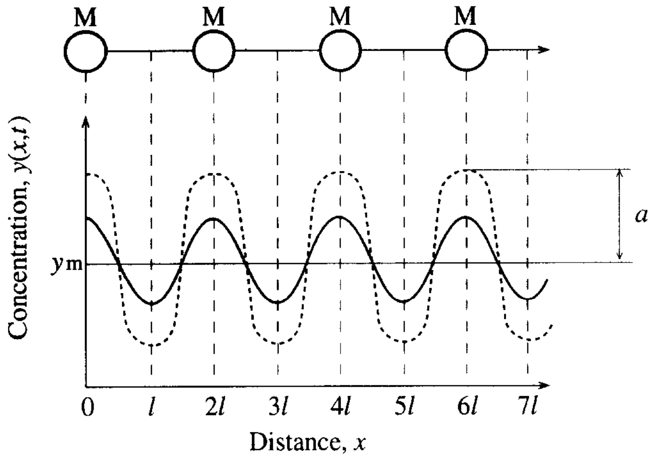

Fig. 5. One-dimensional Al diffusion model for an $LaNi_{5-y}Al_y$ alloy with precipitated Al-rich phases (denoted by M).

row) plateau region, though its XRD pattern shows broad peaks caused by lattice defects [14].

To clarify the influence of the annealing conditions on the plateau characteristics quantitatively, we consider here a one-dimensional Al diffusion model as shown in Fig. 5. In this model the Al concentration y in the dominant phase with composition $LaNi_{5-y}Al_y$ has a periodic profile at intervals of $2l$ along the x axis, which is determined by the precipitated Al-rich phases (denoted by M). The precipitated phases are assumed to be stable and not to affect the homogenizing behaviour throughout the annealing process, as suggested from Figs. 3 and 4. In this one-dimensional system Al diffuses according to

$$\frac{\partial y(t,x)}{\partial t}=D\frac{\partial^2 y(t,x)}{\partial x^2} \tag{1}$$

where

$y(0,x)=f(x)$ initial condition

$\frac{\partial y(t,0)}{\partial t}=\frac{\partial y(t,l)}{\partial x}$ boundary condition

The general solution of Eq. (1) is given by

$$y=\sum_{n=0}^{\infty}\exp\left[-\left(\frac{n\pi}{l}\right)^2 Dt\right]A_n\cos\left(\frac{n\pi x}{l}\right) \tag{2}$$

where

$$A_n=\frac{2}{l}\int_0^l f(x)\cos\left(\frac{n\pi x}{l}\right)\,dx$$

Assuming that the initial Al profile has a trigonometric function

$$f(x)=y_m+a\cos\left(\frac{\pi x}{l}\right) \tag{3}$$

then the diffusion equation is solved analytically as

$$y(x,t)=y_m+a\exp\left[-\left(\frac{\pi}{l}\right)^2 Dt\right]\cos\left(\frac{\pi x}{l}\right) \tag{4}$$

For the $LaNi_{5-y}Al_y$ alloy system the next relation between the logarithmic equilibrium hydrogen pressure $\ln(P/P_0)$ in the plateau region and the Al concentration y is known [15,16]:

$$\ln\left(\frac{P}{P_0}\right)=\ln\left(\frac{P_{LaNi_5}}{P_0}\right)-ky(x,t) \tag{5}$$

where P_0 is the standard hydrogen pressure (0.1 MPa), P_{LaNi_5} is the equilibrium hydrogen pressure of $LaNi_5$ and k is a constant coefficient. By substituting Eq. (4) into Eq. (5) and differentiating both sides of Eq. (5), the following equation is obtained:

$$\ln\sigma(t)=\ln\sigma(0)-\left(\frac{\pi}{l}\right)^2 Dt \tag{6}$$

where $\sigma(0)=(1/\sqrt{2})ka$. Assigning an Arrhenius-type dependence on the annealing temperature T to the diffusion coefficient D, the following equation relating the plateau slope parameter to the annealing condition is obtained:

$$\ln\sigma(t)=\ln\sigma_0-\left(\frac{\pi}{l}\right)^2 D_0 t\exp\left(-\frac{Q}{RT}\right) \tag{7}$$

where σ_0 is the initial value at $t=0$ and Q is the activation energy of Al diffusion.

This model suggests four important points.

(1) The parameter $\ln\sigma$ decreases linearly with annealing time t.

(2) The parameter $\ln(\ln\sigma_0-\ln\sigma)$ decreases linearly with reciprocal temperature $1/T$.

(3) The plateau pressure P_m at the midpoint of the plateau region corresponding to y_m does not change through annealing and only the plateau slope becomes flatter.

(4) A smaller precipitation interval $2l$ gives a faster σ decrease.

Fig. 6 shows the influence of the annealing time t on the plateau slope parameter σ. The parameter ln σ decreased rapidly from $t=0$ to 11.0 ks (region I) and then decreased linearly from $t=11$ to 259.2 ks (region II). The relations between ln σ and annealing time t in regions I and II are given by

$$\ln \sigma = -0.55 - 7.9\times10^{-5}\,t \quad \text{(region I)} \tag{8}$$

$$\ln \sigma = -1.47 - 3.7\times10^{-6}t \quad \text{(region II)} \tag{9}$$

These linear decreases corresponding to Eq. (6) of the Al diffusion model described above suggest that the apparent interval of the precipitated Al-rich phases changed around $t=11$ ks. If the diffusion coefficient D has a value around 10^{-14} m^2 s^{-1}, which is of the order of the Ni–Al interdiffusion coefficient in the Ni-rich part of the Ni–Al system at 1323 K [17], the Al-rich precipitation intervals in regions I and II are estimated as 7×10^{-5} and 3×10^{-4} m respectively. The large-scale SEM image of the as-cast alloy in Fig. 7 shows that the Al-rich ($AlNi_3$) phases are distributed at intervals of (1–3) $\times 10^{-4}$ m, which is in good agreement with the values estimated from Eq. (6). These results indicate that the effect of annealing on the flattening of the plateau slope is rationally evaluated with the parameter D/l^2.

An Arrhenius plot of ln(ln σ_0 − ln σ) for $T=1073$–1423 K is shown in Fig. 8. The value ln(ln σ_0 − ln σ) shows a linear decrease with $1/T$ according to

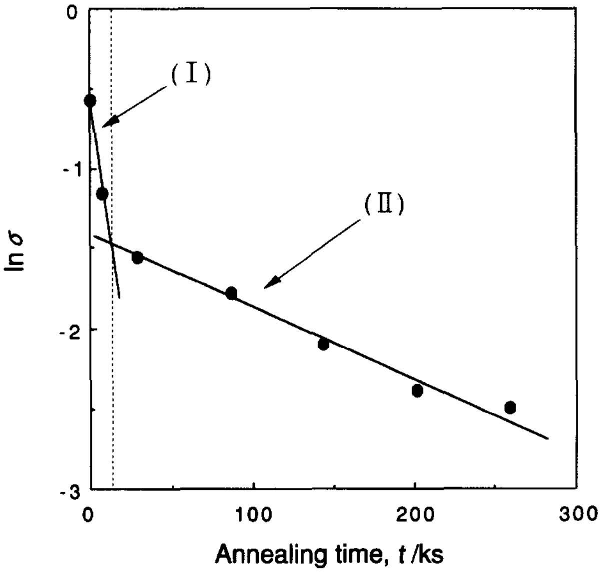

Fig. 6. Influence of the annealing time t on the plateau slope parameter σ.

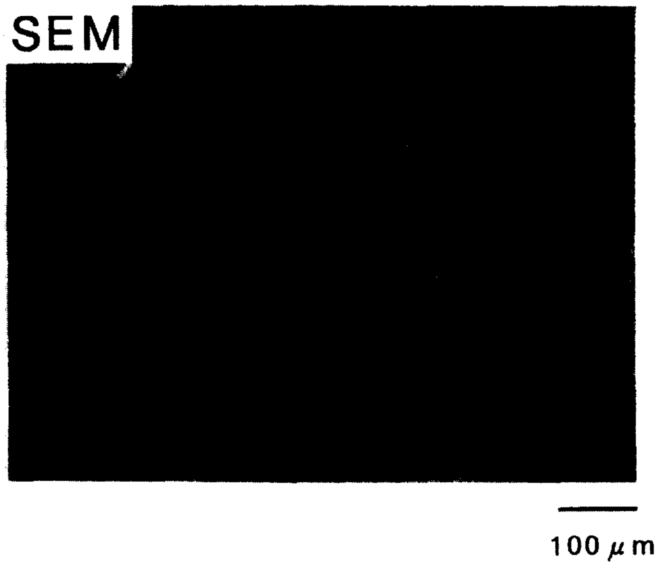

Fig. 7. Large-scale SEM image of the as-cast $LaNi_{4.55}Al_{0.45}$ alloy.

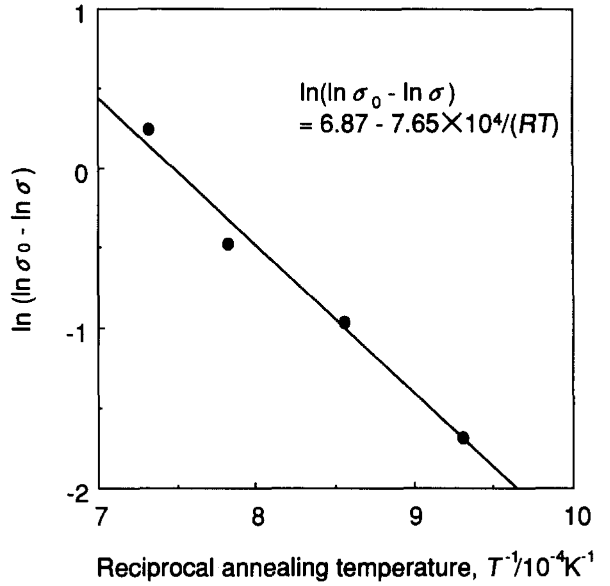

Fig. 8. Arrhenius plot of the parameter ln(ln σ_0 − ln σ) for $T=1073$–1423 K.

$$\ln(\ln \sigma_0 - \ln \sigma) = 6.87 - \frac{7.65\times10^4}{RT} \tag{10}$$

From Eq. (8) the activation energy of Al diffusion in $LaNi_{4.55}Al_{0.45}$ alloy is 7.65×10^4 J mol^{-1}, which is of the order of that of Ni–Al interdiffusion obtained from inert marker observation [17].

Fig. 9 shows the influence of the annealing time t and temperature T on the plateau pressure P_m. The plateau pressure was independent of t and T as indicated in the diffusion model proposed here. The initial decrease in the plateau pressure caused by a few kiloseconds of annealing suggests that the average concentration of Al in the dominant phase became slightly higher owing to the Al diffusion from the Al-rich area

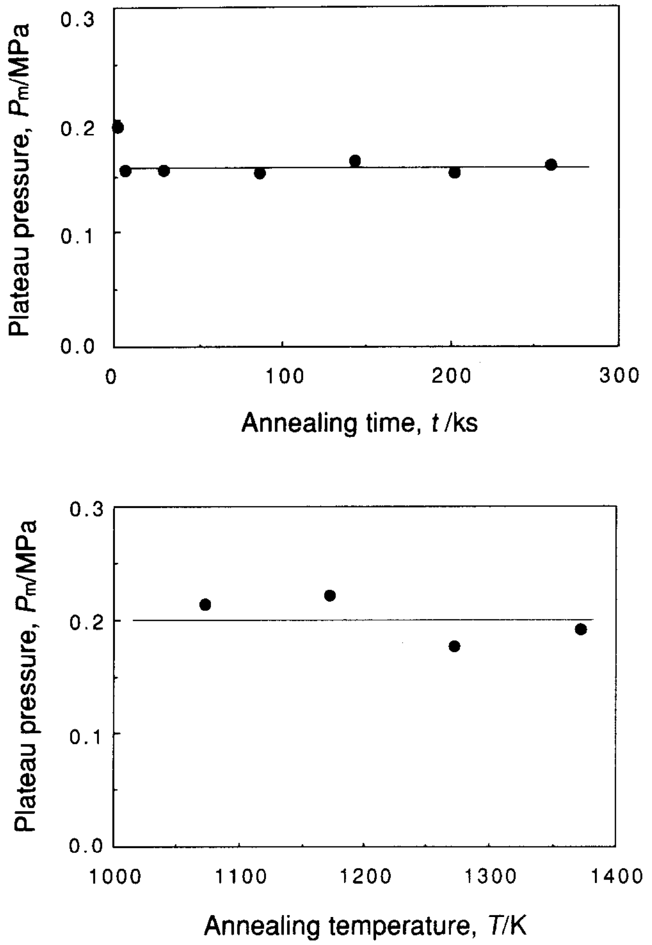

Fig. 9. Influence of the annealing time t and temperature T on the plateau pressure P_m.

around the precipitated phase of $AlNi_3$ to the dominant phase.

Regarding the enhancement of the annealing effect on the flattening of the plateau slope, we reported that rapid quenching of $LaNi_{4.55}Al_{0.45}$ alloy with a melt-spinning method homogenizes its microstructure and gives a very flat plateau region even without annealing [14]. This indicates that rapid solidification processes such as the melt-spinning method will give an effective microstructure for annealing by reducing the precipitation interval l in pseudobinary alloys.

4. Conclusions

The influence of annealing on the plateau flatness of P–C isotherms of $LaNi_{4.55}Al_{0.45}$ alloy and its microstructure was investigated for annealing times t between 0 and 259.2 ks and annealing temperatures T between 1073 and 1473 K. The homogenizing behaviour during annealing was also analysed with a non-steady-state Al diffusion model. The conclusions are as follows.

(1) The plateau slope is caused mainly by fluctuation of the Al concentration in the dominant phase.

(2) The logarithmic plateau slope parameter $\ln \sigma$ decreases linearly with annealing time t.

(3) The Arrhenius plot of $\ln(\ln \sigma_0 - \ln \sigma)$ shows a linear decrease with reciprocal temperature $1/T$.

(4) The dependence of the homogenizing behaviour on the annealing conditions is reasonably explained with a one-dimensional Al diffusion model.

The Al diffusion model we proposed here provides a rational evaluation of the effects of annealing and can be used to determine the annealing conditions in alloy manufacturing.

References

[1] K. Nasako, T. Yonesaki, K. Satoh, T. Imoto, S. Fujitani, H. Hiro, T. Hirose, T. Saitoh and I. Yonezu, *Z. Phys. Chem., 183* (1994) 1271.

[2] I. Sheft, D.M. Gruen, G.J. Lamich, L.W. Carlson, A.E. Knox and J.M. Mendelsohn, *Proc. Int. Symp. on Hydrides for Energy Storage, Geilo, August 1977*, Pergamon, Oxford, 1978, p. 551.

[3] D.M. Gruen, M. Mendelsohn, I. Sheft and G. Lamich, *Proc. 2nd World Hydrogen Energy Conf., Zurich, August 1978*, Pergamon, Oxford, 1978, p. 1931.

[4] M. Nagel, Y. Komazaki, M. Uchida, S. Suda and Y. Matsubara, *J. Less-Common Met., 104* (1984) 307.

[5] T. Nishizaki, K. Miyamoto and K. Yoshida, *J. Less-Common Met., 89* (1983) 559.

[6] G.D. Sandrock, *Proc. 12th Intersociety Energy Conversion Engineering Conf.*, Vol. 1, 1977, p. 951.

[7] M.N. Mungle, K.N. Rai, R. Balasubramaniam and K.P. Singh, *Int. J. Hydrogen Energy, 17* (1992) 603.

[8] M.N. Mungle, K.N. Rai, R. Balasubramaniam and K.P. Singh, *Int. J. Hydrogen Energy, 17* (1992) 607.

[9] S. Fujitani, H. Nakamura, A. Furukawa, K. Nasako, K. Satoh, T. Imoto, T. Saitoh and I. Yonezu, *Z. Phys. Chem., 179* (1993) 29.

[10] R. Kirchheim, F. Sommer and G. Schluckebier, *Acta Metall., 30* (1982) 1059.

[11] R. Griessen, *Phys. Rev. B, 27* (1983) 7575.

[12] K. Nomura, H. Uruno, S. Ono, H. Shinozuka and S. Suda, *J. Less-Common Met., 107* (1985) 221.

[13] E.H. Kisi, C.E. Buckley and E.M. Gray, *J. Alloys Comp., 185* (1992) 369.

[14] Y. Nakamura, H. Nakamura, S. Fujitani and I. Yonezu, *J. Alloys Comp., 212* (1994) 299.

[15] M.H. Mendelshon, D.M. Gruen and A.E. Dwight, *Nature, 269* (1977) 45.

[16] M.H. Mendelshon, D.M. Gruen and A.E. Dwight, *J. Less-Common Met., 63* (1977) 193.

[17] M.M.P. Janssen, *Metall. Trans., 4* (6) (1973) 1623.