The Combined Effect of Pre-straining and Pre-aging on the Bake-hardening Behavior of Al-Mg-Si Alloy for Automobile Body Panels

Dr. Tetsuya MASUDA[*1], Yasuo TAKAKI[*1], Dr. Takeo SAKURAI[*2], Dr. Shoichi HIROSAWA[*3]

[*1] Aluminum Sheets & Coils Research Dept., Moka Plant, Aluminum & Copper Business
[*2] Technology Control Dept., Moka Plant, Aluminum & Copper Business
[*3] Graduate School of Engineering, YOKOHAMA National University

In order to develop a new Al-Mg-Si alloy for automotive body panels, the effect of pre-straining in combination with pre-aging on the bake-hardening behavior of an Al-0.6mass % Mg-1.0mass % Si alloy was investigated by means of the Vickers hardness test, electrical conductivity measurement, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). The hardness test and DSC analysis revealed that, with a pre-aging at 343K, a pre-strain as small as 3% was found to improve the bake-hardening response during final aging at 443K. The TEM observation confirmed that the improvement of the bake-hardening response is enhanced mainly due to the precipitation of the β'' phase in the matrix. These results are explained by the consideration that dislocations induced by pre-straining reduce the concentration of quenched-in excess vacancies, resulting in both the suppressed clustering of solute atoms during pre-aging and the accelerated precipitation of the β'' phase during final aging.

Introduction

Recently, aluminum alloys are being proactively used for automotive bodies to reduce the weight and to improve the fuel economy. Aluminum sheets for body panels are particularly required to have excellent formability and hemming performance. They are also required to have high strength after the paint-baking heat treatment (e.g., at 443K for 1.2ks). Al-Mg-Si alloys are commonly used for the body panels, because these alloys can have low proof strength in the stamping and hemming processes, exhibit excellent age hardenability during the subsequent paint-baking heat treatment to achieve high strength, and realize excellent surface quality and corrosion resistance simultaneously. The ability to undergo age hardening by a heat treatment at a relatively low temperature for a short time is herein called "bake hardenability". In this alloy system, the precipitation strengthening phase is primarily the β'' phase, and Si rich Al-Mg-Si compositions are known to exhibit excellent bake hardenability[1]-[3].

The pre-aging, applied after the solid solution quenching and prior to the final aging, significantly affects the clustering behavior in the early stage of phase decomposition and the resulting bake hardenability[4]-[6]. Serizawa et al. showed that the clusters (Cluster (1)) formed at temperatures no higher than 343K and including room temperature, have a high thermal stability, decrease the distribution density of β'' precipitates and suppress strengthening in the final aging, causing the negative effect of the two-step aging[7]. They also clarified the fact that the clusters (Cluster (2)) formed at higher temperatures (e.g., 373K) accelerate the formation of β'' phase because of the continuous transformation into the β'' phase, and that these two types of clusters (Cluster (1) and Cluster (2)) are formed competitively in this alloy system. In this paper, the clusters formed under various pre-aging conditions are referred to as either Cluster (1) or Cluster (2), according to the report by Serizawa et al.[7]

The pre-strain, applied after the solution heat treatment and prior to the final aging, largely affects the precipitation kinetics and process. In the case of Al-Mg-Si alloys, pre-straining is reported to decrease the activation energy for the precipitate growth and thus to accelerate the precipitation process[8],[9]. Matsuda et al. reported that the bake hardenability at 473K of an Al-0.37mass%Mg-0.62mass%Si alloy is improved, with increased peak hardness, by applying a pre-strain of 5% after pre-aging at 423K for 60ks[10]. Birol et al. reported that the application of pre-strain shortly after the solid solution treatment suppresses the formation of clusters at room temperature and accelerates the precipitation of β'' phase during the final aging at 453K[11],[12].

These results suggest that a combined process of pre-straining and pre-aging is quite effective in improving the bake hardenability of the Al-Mg-Si alloys for automobile panels. It is considered that the amount of pre-strain and the conditions of pre-aging must be considered for optimization. This paper reports the effect of the process, combining pre-straining (0.5% and 3%) and pre-aging (at 298-343K), on the bake hardenability of Al-0.6mass%Mg-1.0mass%Si alloy for automobile panels.

1. Experimental method

Table 1 shows the chemical composition of the

alloy used for this study. The alloy ingot was homogenized, hot- and cold-rolled into a sheet having a final thickness of 1.0mm. This sheet was solid-solution-treated at 823K for 60s and was quenched into water. The average grain size, measured on the as-quenched material, was approximately 40μm as measured by the cross sectional method. The quenched samples were pre-strained for either 0.5% or 3% using a tensile testing machine. A sample without any pre-straining was also prepared as a reference.

These samples, with and without pre-straining, were aged isothermally at 298K, 313K and 343K (the aging hereinafter referred to as "one-step aging"). The samples were held at room temperature for 300s after quenching, until the start of the aging. The changes in hardness and electrical conductivity during the aging were measured by the Vickers hardness test (load 19.6N, holding time 15s) and eddy current method, respectively. Typical samples were subjected to the differential scanning calorimetry (hereinafter referred to as "DSC analysis") at a temperature rise rate of 0.17K/s. The bake hardenability was studied on the samples pre-aged at 298-343K for 7.2ks and subsequently final-aged at 443K for up to 1.2ks (the aging hereinafter referred to as "two-step aging"). **Fig. 1** shows the flow charts of the heat treatments. The microstructures of the typical samples were measured by transmission electron microscopy (TEM) at an accelerating voltage of 200kV.

Table 1 Chemical composition of the alloy studied

(mass%)

Si	Fe	Mn	Mg	Al
1.02	0.17	0.07	0.57	Bal.

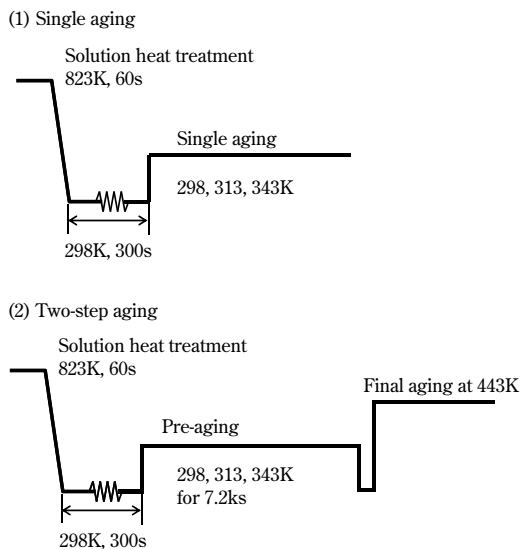(1) Single aging

(2) Two-step aging

Fig. 1 Heat treatment flow charts

2. Experimental results

2.1 The effect of pre-straining on one-step aging behaviors

Fig. 2 shows the changes in hardness and electrical conductivity during one-step aging at 298-343K of the samples pre-strained for 0%, 0.5% and 3%. All the samples aged at 298K and 313K exhibit monotonic increase in their hardness. The hardness change of the samples aged at 313K is greater than that of the samples aged at 298K. Each sample aged at 343K increases in hardness in two stages, with a rapid increase in the second stage occurring at around 10^5s to 10^4s. For all the one-step aging conditions tested this time, the changes in hardness decreased with the increasing amount of pre-strain.

The electrical conductivity of the samples aged at 298K and 313K decreased as the aging time increased, while that of the samples aged at 343K increased slightly at around 3×10^3s and subsequently decreased rapidly. For all the one-step aging conditions tested this time, the electrical conductivity changed less with the increased amount of pre-strain. The change in electrical conductivity represents the change in the state of solid solution and precipitates in a sample. Therefore, the above results clearly indicate that pre-straining delays the age hardening behavior during the one-step aging under the current testing conditions.

Fig. 3 shows the results of DSC analyses conducted to clarify the phase decomposition process during the one-step aging. The endothermic peak (Peak 1) around 480K, the peak indicating the dissolution of Cluster (1)[2)-4)], becomes smaller with the increase in the aging temperature. The area of Peak 1 of the
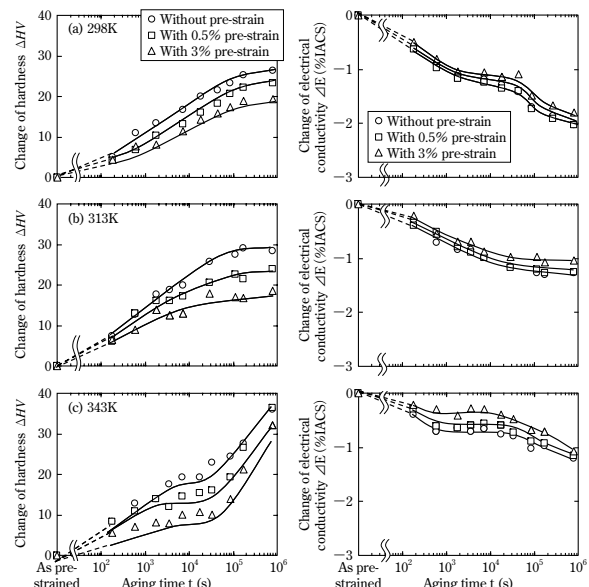

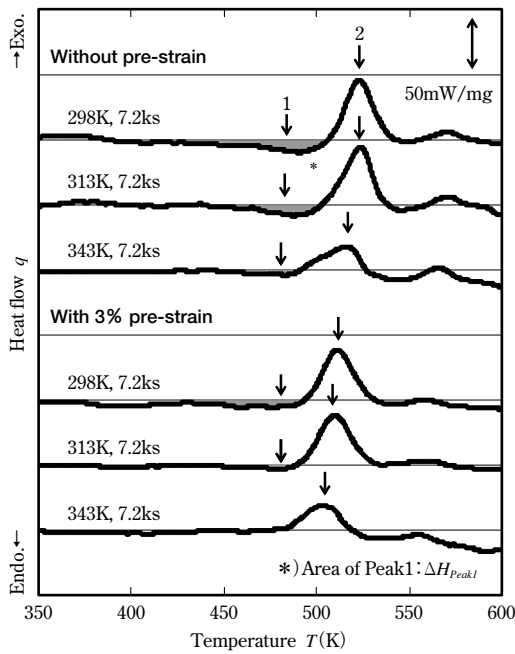**Fig. 2** Changes of hardness and electrical conductivity during one-step aging

Fig. 3 DSC curves

Fig. 4 Changes in hardness and electrical conductivity during final aging at 443K

sample pre-strained for 3% has significantly decreased compared with that for the sample without pre-strain. These experimental results indicate that the area of Peak 1 (i.e., the amount of Cluster (1) formed during the one-step aging at temperatures no higher than 343K) is decreased, not only by the increased pre-aging temperature, but also by the application of the pre-strain. On the other hand, the exothermic peak (Peak 2) around 510K, the peak that indicates the formation of the β'' phase [2)-4), 13), 14)], was shifted towards the low temperature side by the application of 3% pre-strain for all the pre-aging conditions.

2.2 The effect of pre-straining on the final aging behaviors of two-step aged samples

Fig. 4 shows the changes in the hardness and electrical conductivity of the samples pre-strained for 0%, 0.5% and 3%, pre-aged under various conditions and final aged at 443K. All the samples exhibit hardness increase during aging at 443K. The increasing amount of pre-strain significantly improves the bake hardenability and also increases the change in electrical conductivity. The sample pre-strained for 3% and subsequently pre-aged at 343K for 7.2ks exhibits the most excellent bake hardenability (Fig. 4 (c)) with a change in electrical conductivity exceeding that of the sample without pre-aging. These results clearly indicate that an effective combination of pre-straining and pre-aging accelerates the phase decomposition process during the final aging at 443K and improves the bake hardenability.
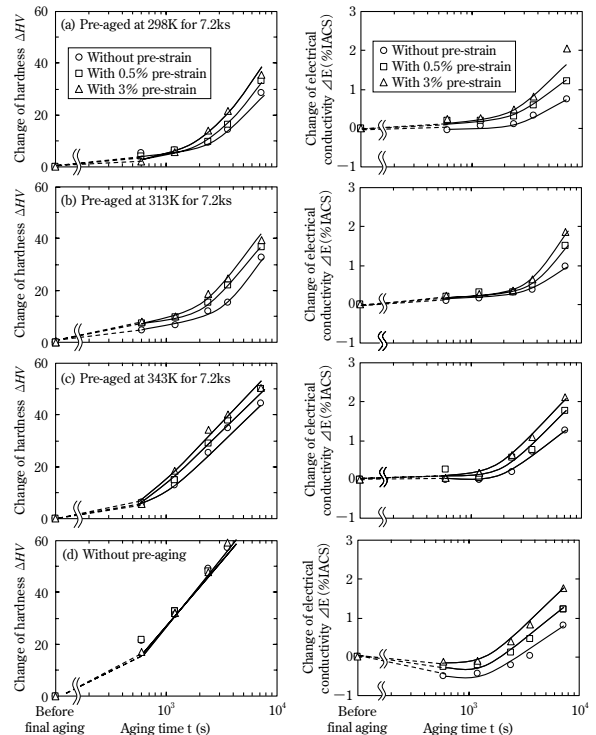
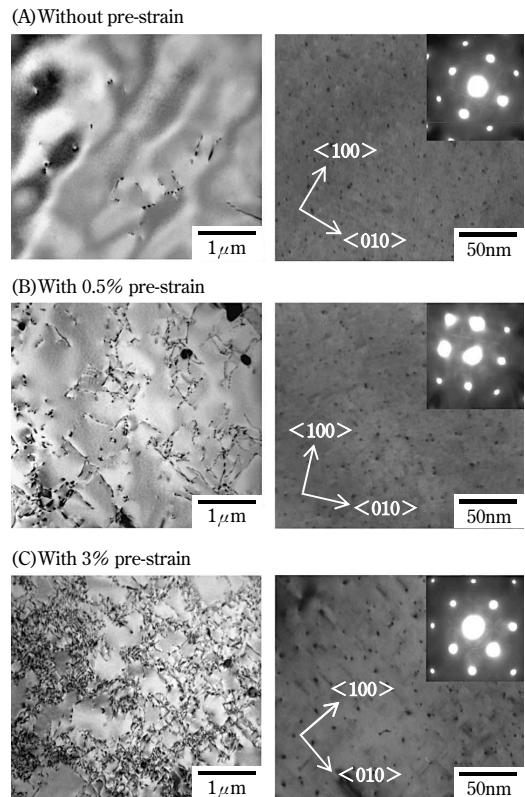**Fig. 5** shows the TEM bright field images and

Fig. 5 TEM bright-field images and selected area diffraction patterns

selected area diffraction patterns of the samples pre-strained for 0%, 0.5%, 3%, pre-aged at 343K for 7.2ks and final-aged at 443K for 3.6ks. It should be noted that the increased changes in hardness of the two-step aged samples that are pre-strained and pre-aged

(Fig. 4 (c)) are attributable to these microstructures. Observations at low magnifications confirmed an increase in dislocation density with the increasing amount of pre-strain. The spherical or needle-like precipitates observed by high-magnification TEM are considered to be β'' phase, judging from the streaks along the $[010]_{Al}$ and $[100]_{Al}$. The samples pre-strained for 0.5% and 3% exhibit stronger strain contrasts, implying the acceleration of the phase decomposition by the pre-straining.

From the above results, the improved bake hardenability achieved by the combined process of pre-straining and pre-aging is considered to be mainly attributable to the accelerated precipitation of β'' phase in the matrix. Although the dark field image shows some precipitates on dislocation lines, the majority of the precipitates are in the matrix because of the small amount of strain applied.

3. Discussion

3.1 The suppression of Cluster (1) formation by pre-straining

Serizawa et al[7]. reported, on the basis of their study using a three dimensional atom probe, that the hardness change during the room-temperature aging of an Al-0.95mass%Mg-0.81mass%Si alloy[6] is attributable to the formation of Cluster (1). A similar kind of cluster is considered to be formed during the one-step aging in the samples studied this time.

As shown in Fig.2, an increased amount of pre-strain decreases the changes in hardness and electrical conductivity during the one-step aging. The result indicates that the pre-straining suppresses the clustering of solute atoms, or the formation of Cluster (1), during the subsequent one-step aging. This is also confirmed by the DSC analysis result (Fig. 3), which shows that the increasing amount of pre-strain decreases Peak 1, which implies the dissolution of the Cluster (1).

The clustering behavior of the solute atoms in the early stage of phase decomposition is considered to be affected by the vacancy concentration in the alloy. On the other hand, the dislocations introduced by pre-straining are considered to act as sink sites for quenched-in excess vacancies[15]. The dislocation density, $N_{annealed}$, in a fully annealed metal is generally reported to be $1 \times 10^{11} - 1 \times 10^{12} \mathrm{m}^{-2}$ [16]. Komatsu et al. reported that the increment of dislocation density, $\triangle N$, caused by a deformation is expressed by the true strain, ε, and the change in electrical resistivity per unit dislocation density, $\triangle \rho$, as the following equation[17]:

$$\triangle N = A \varepsilon^n / \triangle \rho \cdots\cdots\cdots\cdots\cdots\cdots(1),$$

wherein $A = 0.185 \mathrm{n}\Omega\mathrm{m}$, $n = 0.648$ (in the case of Al-0.47mass%Mg alloy) and $\triangle \rho = 3 \times 10 - 25\Omega\mathrm{m}^3$ (99.996% in the case of highly-pure aluminum)[18]. Assuming that these constants are applicable to the alloy system of the present study, the dislocation density, $N_{pre\text{-}strain}$, of the sample pre-strained for 3% ($\varepsilon = 0.0296$) is estimated to be approximately $1 \times 10^{14} \mathrm{m}^{-2}$, since $\triangle N$ is sufficiently larger than $N_{annealed}$. On the other hand, the average distance between dislocations is given by[19]

$$L = 1/N^{1/2} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2),$$

which yields the average distances for the samples with 3% pre-strain and those without pre-strain to be $1 \times 10^{-7}\mathrm{m}$ and $1 \times 10^{-6} - 3 \times 10^{-6}\mathrm{m}$, respectively. From the above, the lifetime, τ, at 298K, of the quenched-in excess vacancies until their annihilation into dislocations is given by the following expression[20].

$$\tau = L^2 / D_v \cdots\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

From the equation (3), the lifetime, τ, is calculated to be 7s and $4 \times 10^2 - 4 \times 10^3$s for the samples with 3% pre-strain and those without pre-strain, respectively. The diffusion coefficient of the vacancies, D_v, is given by the equation (4), wherein $D(T)$ is the self-diffusion coefficient of aluminum at the temperature, T, and $C_v(T)$ is the thermal equilibrium vacancy concentration[21].

$$D_v = D(T) / C_v(T) \cdots\cdots\cdots\cdots\cdots\cdots(4)$$

Here, the term $D(T)$ is expressed by equation (5), using the vibration frequency factor for the self-diffusion of aluminum ($D_0 = 1.37 \times 10^{-5} \mathrm{m}^2 \mathrm{s}^{-1}$), activation energy ($Q = 123 \mathrm{kJmol}^{-1}$) and gas constant ($R = 8.31 \mathrm{Jmol}^{-1}\mathrm{K}^{-1}$).

$$D(T) = D_0 \exp(-Q/RT) \cdots\cdots\cdots\cdots(5)$$

The following equation is used to determine $C_v(T)$[22].

$$C_v(T) = \exp(2.4) \exp(-73.3[\mathrm{kJ}\cdot\mathrm{mol}^{-1}]/RT) \cdots(6)$$

The quenched-in excess vacancies, introduced into the sample by the solution heat treatment, may possibly be annihilated into the defects other than the dislocations (e.g., grain boundaries); however, from the above estimation of the vacancy lifetime, τ, it is considered that the dislocations introduced by the pre-straining mainly, and more effectively, decrease the quenched-in excess vacancy concentration, delaying the diffusion of solute atoms. It is concluded that, as a result of the above, the formation of Cluster (1) during one-step aging is suppressed, which maintains the high supersaturation of solute atoms in the matrix.

3.2 The acceleration of β'' phase formation by pre-straining

As shown in Fig. 4, an effective combination of pre-straining and pre-aging improves bake hardenability during the subsequent aging at 443K,
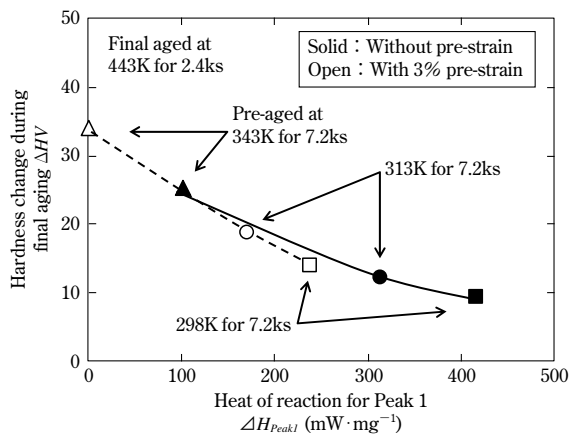
Fig. 6 Relationship between hardness change during final aging at 443K for 2.4ks; ΔHV, and heat of reaction for Peak 1; ΔH_{peak1}

and the effect of pre-straining is particularly enhanced in the sample pre-aged at 343K for 7.2ks. The improvement effect on the bake hardenability brought about by the pre-straining is also confirmed by the result of the DSC analysis (Fig. 3), which shows that Peak 2, an indication of β'' phase formation, shifts towards the low temperature side. These results suggest that a new process that combines pre-straining, as small as $0.5 - 3\%$, with pre-aging is effective in producing automobile panels with high strength without sacrificing their formability.

The acceleration of β'' phase formation by a combined process of pre-straining and pre-aging is explained by the difference in the amount of Cluster (1) formed, an explanation similar to the one that has been applied to the hardness change during the one-step aging (Section 3.1). **Fig. 6** shows the relation between the hardness change during final aging at 443K, ΔHV, and the heat of reaction determined from Peak 1, ΔH_{peak1}. The samples, some with 3% pre-strain and some without, were pre-aged under the various conditions shown in Fig. 4. The heat of the reaction was determined from the area surrounded by the DSC curves and base lines shown in Fig. 3. Referring to Fig. 6, the hardness change, ΔHV, increases with the decrease of ΔH_{peak1} regardless of the pre-straining. This indicates that the bake hardenability at 443K is mainly determined by the amount of Cluster (1) formed during the pre-aging. In other words, the suppressed formation of cluster(1) by pre-straining is attributed to the increased bake-hardening response at 443K due to the accelerated precipitation of the β'' phase from more supersaturated solute atoms.

Conclusions

A study was conducted on the effectiveness of a process that combines pre-straining and pre-aging to improve the bake hardenability of an Al-0.6mass% Mg-1.0mass%Si alloy for automobile panels. Hardness measurements, electrical conductivity measurements, DSC analyses, and TEM observations were used for the study. It has been clarified that an increasing amount of pre-strain decreases the amount of change in hardness and electrical conductivity during the subsequent one-step aging and the heat of reaction for endothermic peak around 480K in DSC traces. These results imply that an increasing amount of pre-strain decreases the amount of Cluster (1) formed during the one-step aging at temperatures no higher than 343K. On the other hand, the TEM observations and DSC analyses have clarified that the pre-straining promotes the precipitation of β'' phase during the final aging at 443K for 7.2ks. The effect of the pre-straining on bake hardenability depends on the subsequent pre-aging conditions, and a pre-straining of 3% has been found to be most effectively combined with a pre-aging at 343K for 7.2ks. These results can be explained by suppressed clustering of solute atoms during pre-aging and accelerated precipitation of the β'' phase from more supersaturated solute atoms during final aging, both of which are attributed to rapid annihilation of quenched-in excess vacancies at dislocations induced by pre-straining.

A part of this article was published in Materials Transactions[23].

References

1) J. Langerweger. *Aluminium Technol*. 1986, Vol.49, p.216-222.
2) W. F. Miao et al. *Scr. Mater*. 1999, Vol.40, p.873-878.
3) A. K. Gupta et al. *Mater. Sci. Eng. A*. 2001, Vol.316, p.11-17.
4) G. A. Edwards et al. *Acta Mater*. 1998, Vol.46, p.3893-3904.
5) M. Murayama et al. *Acta Mater*. 1999, Vol.47, p.1537-1548.
6) S. Hirosawa et al. *Mater. Sci. Forum*. 2005, Vol.475-479, p.357-360.
7) A. Serizawa et al. *Metall. Mater. Trans. A*. 2008, Vol.39A, p.243-251.
8) H-L. Lee et al. *Scr. Metall. Mater*. 1991, Vol.25, p.2165-2170.
9) R. S. Yassar et al. *Metall. Mater. Trans. A*. 2005, Vol.36A, p.2059-2065.
10) K. MATSUDA et al. *Journal of Japan Institute of Light Metals (in Japanese)*. 1995, Vol.45, p.95-100.
11) Y. Birol. *Scr. Mater*. 2005, Vol.52, p.169-173.
12) Y. Birol et al. *Scr. Mater*. 2006, Vol.55, p.625-628.
13) I. Dutta et al. *J. Mater. Sci. Lett*. 1991, Vol.10, p.323-326.
14) N. Maruyama et al. *Scr. Mater*. 1997, Vol.36, p.89-93.
15) M. Murakami et al. *Philos. Mag*. 1970, p.1119-1126.
16) W. D., Jr. Callister. *Materials Science and Engineering, An Introduction. John Wiley & Sons*, 2007, p.166.
17) S. Komatsu et al. *Proceedings of ICAA-6*. 1998, p.991-996.
18) J. G. Rider et al. *Philos. Mag*. 1966, Vol.13, p.289-303.
19) J. Friedel. *Dislocations. Pergamon Press*. 1964, p.239.
20) G. ITO. *NETSU SHORI (in Japanese)*. 1998, Vol.38, p.165-173.
21) R. O. Williams. *Acta Metall*. 1957, Vol.5, p.55-56.
22) R. O. Simmons et al. *Phys. Rev*. 1960, Vol.117, p.52-61.
23) T. Masuda et al. *Mater. Trans*. 2010, Vol.51, p.325-332.