

Paper No. 1316

**Development of Aluminum Extruded Alloy for Basket of  
Transport/Storage Casks (1)  
– Strengthening mechanism after long term storage and design of  
chemical composition –**

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## **ABSTRACT**

The new aluminum alloy “A3J04-O” for basket of transport/storage casks was developed on the basis of A3004 (JIS) of Al-Mn-Mg alloy for weight saving and improving thermal conductivity. In this study, the various tests were performed to determine the chemical composition. Regarding Mn content, it was decided from 1.2 mass% to 1.6 mass% in consideration of the strength and impact properties. Moreover, the effect of dispersion hardening by Mn compounds was confirmed not to decrease after the heat treatment which enveloped the heat history for 60 years. As for Mg content, the new evaluation method using diffusion and supersaturation of Mg was developed to evaluate the additive amount for which the solid-solution hardening of Mg hardly changed for 60 years. As a result of the evaluation, the content of Mg was decided from 1.0 mass% to 1.4 mass%. Regarding Si, Cu and Zn, the upper limits of their contents were decided not to generate age hardenability based on the confirmation on the test results.

## **1. INTRODUCTION**

In Japan, the interim storage period of casks is considered up to 60 years and a basket material is used under the condition that the temperature of the material is about 200°C in initial and it is

decreased monotonically to about 100 °C after storage. The basket of transport/storage casks of spent fuels must satisfy the structural strength corresponding to transport/storage conditions such as the criticality prevention function and the heat removal functions. Additionally, the casks should be reduced the weight as much as possible suiting to the design requirement to maximize the storage capacity of fuel assemblies in view of cost and efficiency. Aluminum alloys have the properties of lightweight and high thermal conductivity, which are desirable characteristics for the basket material. On the other hand, the aging degradation of the material must be evaluated properly, because the basket is exposed to the decay heat of spent fuels during the storage period up to 60 years.

The compositional design of the aluminum extruded alloy “A3J04-O” developed this time is based on A3004 alloys. Although some aluminum alloys decrease in their strength after overaging, this potential has been almost eliminated from the new material, which simplifies the evaluation of aging degradation. Strength of the material is increased by dispersion hardening of Mn compounds and solid-solution hardening of Mg. Therefore, these elements have been focused on in terms of the evaluation of aging degradation. Regarding the dispersion hardening of Mn compounds, it was confirmed that the strength property and microstructure did not change by the heat treatment of which condition was evaluated using the diffusion length of Mn in aluminum to envelope the heat history for 60 years. As for Mg, the content with which the effect of solid-solution hardening is maintained for 60 years was determined using the evaluation method that was newly developed using supersaturation and diffusion length<sup>1)</sup>. These two main hardening mechanisms are reflected in the compositional design. In addition to the above two main hardenings, precipitation hardening is also known as strengthen mechanism of metallic materials. Although the strengthen mechanisms is not used for the alloy, it was confirmed that it did not influence on the strength properties from the viewpoint of the evaluation of aging degradation. Generalizing these evaluation results, the chemical composition of the new material was determined.

## **2. FABRICATION PROCESS OF SPECIMENS**

All the specimens used in this study were fabricated in our laboratory-scale facility. Highly purity aluminum, master alloys (Al-20mass%Si, Al-10mass%Fe and Al-10mass%Mn) and industrial pure Mg were used in the air melting process, and billets with various chemical compositions were prepared by direct chill casting. The specific chemical compositions are shown in Table 1. These billets received the homogenized heat treatment at 540°C for 4 hours (hereafter described as “540°C×4 hours”) and the warm extrusion was conducted in the extrusion ratio of approximately 20. The cross-section shape of all these extruded materials was rectangle; width: 100mm and thickness: 10mm. All these materials were annealed at 345 °C×8 hours as the final process.

## **3. CONCEPTS OF THE ALLOY DESIGNING THROUGH STRENGTHEN MECHANISMS**

### **3.1 Dispersion hardening of Mn compounds**

**Table 1 Chemical composition of the specimens. (mass%)**

ID	Si	Fe	Cu	Mn	Mg	Zn	Al
A1	0.05	0.05	0.01	1.05	1.03	0.00	Bal.
A2	0.05	0.05	0.01	1.25	1.03	0.00	Bal.
A3	0.02	0.05	-	1.45	0.94	-	Bal.
A4	0.04	0.21	-	1.58	1.02	-	Bal.
B1	0.16	0.19	0.04	1.52	1.26	-	Bal.
B2	0.25	0.20	-	1.51	0.91	-	Bal.
C1	0.25	0.38	0.10	1.38	1.43	0.10	Bal.
C2	0.26	0.38	0.12	1.64	1.46	0.11	Bal.
C3	0.27	0.42	0.13	1.89	1.44	0.11	Bal.
D1	0.04	0.06	-	1.46	1.04	0.01	Bal.
D2	0.05	0.06	-	1.49	1.94	0.01	Bal.
D3	0.05	0.05	-	1.50	2.97	0.01	Bal.
D4	0.05	0.05	-	1.51	4.00	0.01	Bal.
D5	0.06	0.06	-	1.48	5.09	<0.01	Bal.

\*1)ID: A1-A4 (group A) were prepared changing Mn content with very low content of the additives (Si, Fe, Cu and Zn) to evaluate the strength properties on the safe side.

\*2)ID: B1 and B2 (group B) were prepared assuming the representative chemical composition of the new alloy to evaluate the average properties.

\*3)ID: C1-C3 (group C) were prepared changing Mn content with relatively high Mg (~1.4 mass%) and relatively more content of the additives (Si, Fe, Cu and Zn) than those of other groups to evaluate the impact properties conservatively.

\*4)ID: D1-D4 (group D) were prepared changing Mg content to evaluate the influence on the precipitation kinetics of Mg compounds with very low content of the additives (Si, Fe, Cu and Zn).

It is well known that added Mn in aluminum alloys precipitates as  $Al_6Mn$  or  $Al_{12}Mn_3Si$  during the homogenized heat treatment and these precipitates contribute to dispersion hardening. It is one of the two main hardening mechanisms of the material. Therefore, it is important to investigate the optimum Mn content. Tensile tests at room temperature were conducted using the specimens of group A (A1-A4 shown in Table 1) of which Mn contents were ranged between about 1.1 mass% and 1.6 mass%. The test results are shown in Figure 1. The tensile strength and 0.2% proof strength increased with increasing in Mn content. However, saturation tendencies were shown at about 1.6 mass%. Therefore, it would not be useful to increase Mn contents over 1.6 mass%. To investigate the influence of Mn contents on impact characteristics, Charpy tests at room temperature were conducted using the specimens of group A, B and C (A1-A4, B1 and C1-C3). The test results are shown in Figure 2. The index of the horizontal axis is  $\%Fe+1.07*\%Mn$ . The reason why the index was

adopted is as follows. Yoshikawa and Sakamoto clarified the formation condition of the primary crystals of Al<sub>6</sub>Mn in 3004 aluminum alloys and reported the primary crystallization line was represented by %Fe+1.07\*%Mn=1.815 (at 654 °C)<sup>2</sup>. It is considered that the primary crystals might decrease the impact properties of the alloy because their particle size tends to be much larger than the eutectic crystals. Therefore, the index is considered to be useful to understand the influence of Mn and Fe contents on impact properties. As shown in Figure 2, the absorbed energies clearly decreased over the broken line which shows the primary crystallization line. From this result, the upper limit of Fe contents was determined to be 0.25 mass%. Regarding the Mn content, the additive amount range of content was determined to be from 1.2 mass% to 1.6 mass% considering the results of the tensile tests and Charpy tests in a comprehensive manner.

It is important to evaluate the degradation of the dispersion hardening during the storage period. A long-time heat treatment at 300°C×1,000 hours was conservatively defined as the simulated heat history enveloping 60 years. The diffusion length of Mn atoms expressed by eq(1) shown below was used to evaluate the degree of the heat history.

$$L_{Mn}^* = \sqrt{2D_{Mn}t}, D_{Mn} = D_0 \exp\left(-\frac{Q_d}{RT}\right) \quad (1)$$

$L_{Mn}^*$ : diffusion length of Mn in solid solution,  $D_{Mn}$ : diffusion coefficient of Mn in aluminum,  $t$ : holding time(s),  $D_0$  (Mn): frequency factor (380cm<sup>2</sup>/s)<sup>3</sup>,  $Q_d$ (Mn):activation energy of diffusion (221kJ/mol)<sup>3</sup>,  $R$ : gas constant (8.314J/(K·mol)),  $T$ : temperature(K). Table 2 shows the calculation results. The diffusion length of 300 °C×1,000 hours was about 6 times as large as 200 °C×525,960 hours (60 years) assuming constant temperature during the storage period. The 200 °C was assumed as the condition of the highest temperature of the baskets, which is conservative condition because the actual basket temperature is monotonically decreased to about 100 °C after 60 years storage. Figure 3 shows the results of TEM observation of the specimen B2 before and after the heat treatment. Intermetallic compounds of spherical shape and rod-like shape were observed in both pictures. These intermetallic compounds are considered to be the precipitations of Al<sub>6</sub>Mn or Al<sub>12</sub>Mn<sub>3</sub>Si. There were no significant differences in the TEM images before and after the heat treatment. Figure 4 shows the results of tensile tests of the specimen B2 before and after the heat treatment at 300°C×700 hours and 300 °C×1,000 hours. There were no significant differences about the 0.2% proof strength and tensile strength. Therefore, the effect of the dispersion hardening of Mn compounds is considered to be almost remarkably stable during 60 years. The reason of the stability about the precipitate microstructure and the strength properties was considered that the diffusion coefficient of Mn in aluminum was exceedingly small.

**Table 2 Diffusion length used as the index of the degree of temperature acceleration.**

Heat histories	Diffusion length (μm)
300°C×1,000 hours	4.4×10 <sup>-2</sup>
200 °C×525,960 hours (60years)	7.6×10 <sup>-3</sup>

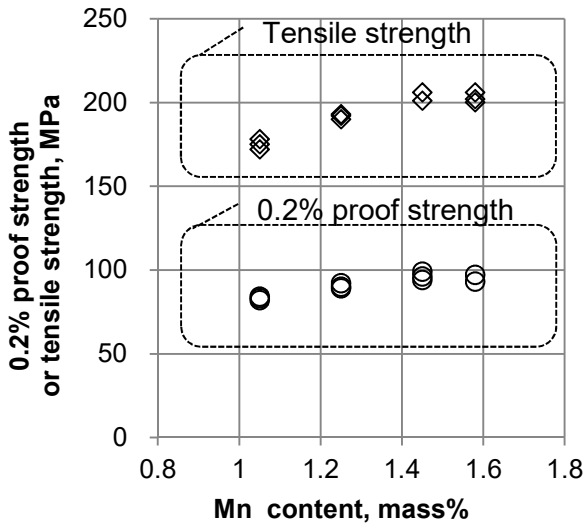


Figure 1 Correlative relationship between Mn contents and strength properties by tensile tests.

\*; The data attached to plots show Mn content.

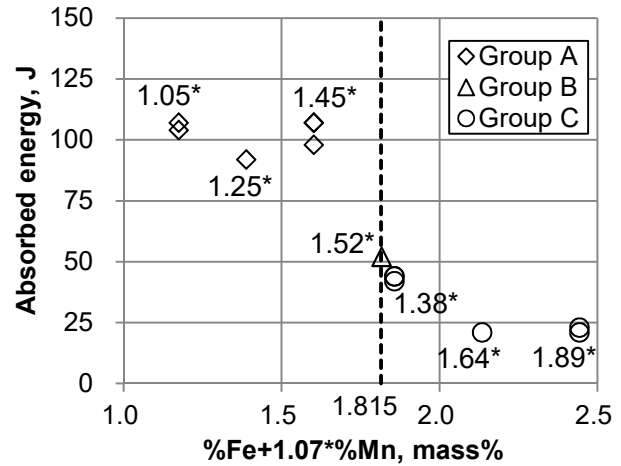
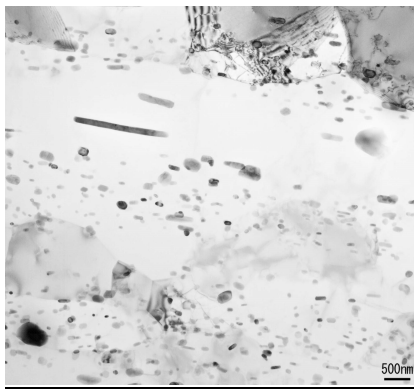
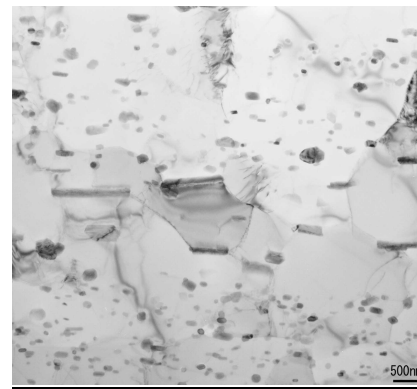


Figure 2 Correlative relationship between the data of %Mn+1.07\*%Fe and absorbed energies by Charpy tests.



(a) As received



(b) After 300°C×1,000h

Figure 3 TEM observation results of the specimen B2

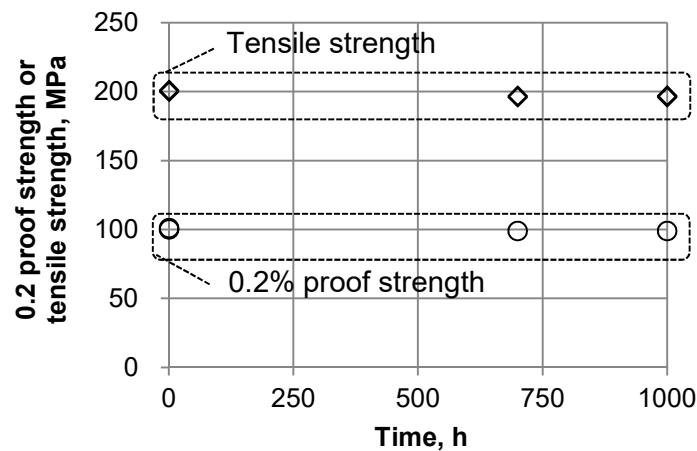


Figure 4 Changing trends of strength properties of the specimen B2 by the heat treatments at 300°C.

### 3.2 Solid-solution hardening of Mg

Solid-solution hardening of Mg is another strengthening mechanism of the alloy. Therefore, the invariability should also be assured for 60 years. In the case where the solid solubility limit of Mg decreases below the Mg content with decreasing temperature of the basket material, Mg compounds might precipitate in the alloy, which is considered not to be able to contribute to the material strength and the effect of solid-solution hardening might degrade. However, it is actually extremely difficult to evaluate it by conventional methods, then the evaluation method was newly developed<sup>1)</sup>. At first, regarding the solubility limit of Mg in aluminum, literature data was scattered especially under 150 °C. Therefore, the optimum Mg content could not be estimated referring the literature data. Moreover, temperature accelerated tests also do not work to access the solid solution amount of Mg after 60 years because the solid solubility limit increased with increasing temperature. The new evaluation method is based on a concept of the double acceleration by temperature and Mg content. Regarding the temperature, the higher conditions than 100°C which is considered to be the temperature at the end stage of storage period were selected. As for Mg content, more than 1.0 mass% that was roughly supposed to be actual Mg content in the alloy for basket use was added in each specimen. In the double acceleration tests, the specimens of group D shown in Table 1 were used. The condition of the aging heat treatment is shown in Table 3. The changing trends of the electric resistibility converted from the electric conductivity of the specimens were analysed by the Johnson-Mehl-Avrami equation which was an empirical equation to explain kinetics of texture variations. In general, electric resistibility is more sensitive than mechanical characteristics to the variation of solid solution. The analysis results of the aging heat treatment were precipitation start times evaluated based on 10% of reaction rate of precipitation, which was defined using Mg content of the specimens, an evaluation formula about solid solubility limit of Mg<sup>4)</sup> and contribution ratios of the solid solution of Mg and the precipitates of Mg compounds on electric resistibility<sup>5)</sup>. The value of 10% was determined so that the influence of the decrement of solid solution of Mg on 0.2% proof strength could be negligible. The precipitation start times evaluated in each aging condition were plotted in a Time-Temperature-Precipitation (TTP) diagram as shown in Figure 5. Regarding the specimens of D1 and D2, their data were not shown in Figure 5 because the electric resistivity didn't change even after 10,000h. The reason was considered to be their very low degree of supersaturation due to relatively low Mg contents. Curve fitting operation on the precipitation start times was performed based on classical nucleation theory and the solid solubility limit of Mg<sup>4)</sup>, and the precipitation start curves brilliantly accorded the data points as shown in Figure 5. In this figure, the precipitation reaction is considered not to generate in the shorter time side of each curve. The reason why the precipitation start curves of the specimens with more Mg content locate in shorter time side is that the degree of supersaturation which is the driving force of precipitation increases with increasing Mg content.

Although the TTP diagram was well evaluated, it is impossible to determine the Mg content of the actual material by this figure because the evaluation time was only 10,000h against 60 years (about

530,000h) and the Mg contents of the evaluated specimens were much more than 1.0 mass% which was roughly supposed to be the actual content.

It is known that the kinetics of precipitation is influenced by the diffusion and the degree of supersaturation of elements in solid solution. Accordingly, a reassessment of TTP diagram was considered using two indexes of the diffusion length and the degree of supersaturation. The equations used in this operation are expressed as follows.

$$S = \frac{C - C_{eq}}{C_{eq}} \quad (2)$$

$$L^{*'} = L^* \times \sqrt[3]{C(at\%)/1.0(at\%)} \quad (3)$$

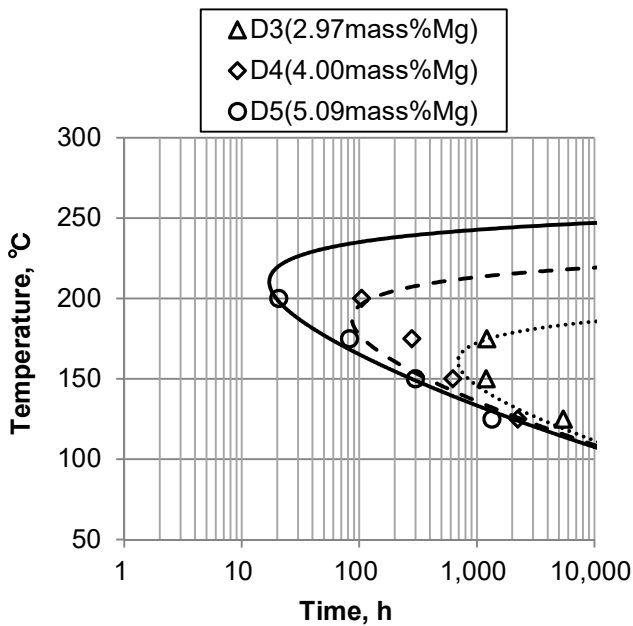
$$L_{Mg}^* = \sqrt{2D_{Mg}t}, \quad D_{Mg} = D_0 \exp\left(-\frac{Q_d}{RT}\right) \quad (4)$$

$S$ : the degree of supersaturation,  $C$ : Mg amount in solid solution (mass%),  $C_{eq}$ : solid solubility limit of Mg<sup>4)</sup> (mass%),  $L_{Mg}^*$ : diffusion length of Mg in solid solution,  $D_{Mg}$ : diffusion coefficient of Mg in aluminum,  $D_0$  (Mg): frequency factor ( $0.1\text{cm}^2/\text{s}$ )<sup>3)</sup>,  $Q_d$ (Mg): activation energy of diffusion ( $121\text{kJ/mol}$ )<sup>3)</sup>. In addition, Mg amount in solid solution was considered to be approximately equal to Mg contents of specimens. Regarding  $L^{*'}$  in eq(3), the normal diffusion length expressed by eq(4) was corrected based on a consideration in which the average distance between nucleation sites and Mg atoms in solid solution decreased in proportion to third roots of Mg amount in solid solution. In other words,  $L^{*'}$  could be considered to be the diffusion length related the precipitation.

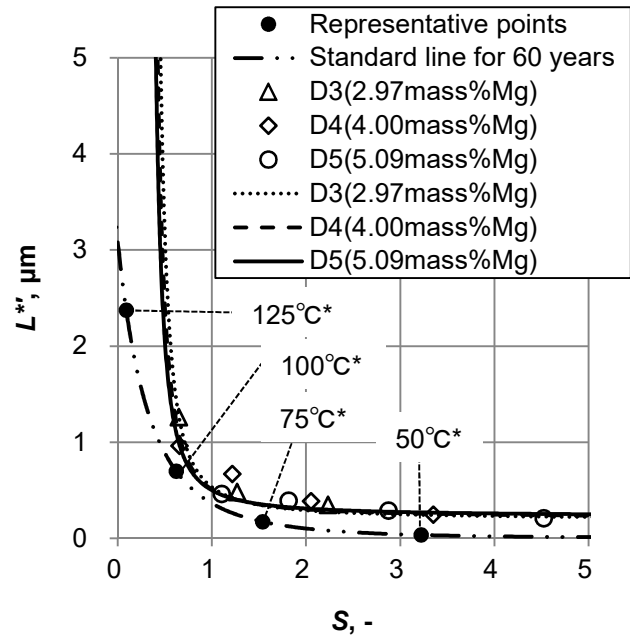
The TTP diagram shown in Figure 5 was re-evaluated as shown in Figure 6. This graph was named as “S-L plane” for  $S$  of the horizontal axis and  $L^{*'}$  of the vertical axis. In this S-L plane, the precipitation start curves of the specimens with different Mg contents lap over brilliantly and the data points evaluated from the experimental results located along the curves. This fact is considered to mean that the precipitation start conditions are defined by  $S$  and  $L^{*'}$ . The area including the origin side of the precipitation start curve is regarded as the safe zone in which the strength degradation due to decreasing of Mg amount in solid solution does not occur, and the opposite side of the origin is regarded as the red zone in which the strength degradation might occur. The two-dot chain line shown in the S-L plane indicates the actual condition of basket in casks, which was calculated for 1.0 mass% of Mg content. This curve was named as “60 years standard curve”. This 60 years standard curve was calculated on the assumption in which the temperature stayed constant for 60 years. This assumption is very safe side considering the temperature dependence of the diffusion because the actual temperature is monotonically decreased for 60 years. As shown in the S-L plane, the standard curve locates in the area of the origin side. Therefore, it is evaluated that the strength degradation does not occur for 60 years at 1.0 mass% of Mg content.

**Table 3 The condition of aging heat treatment.**

Item	Test condition
Specimens	Group D (D1-D5); 1.04-5.09 mass%Mg
Temperature(°C)	125, 150, 175, 200
Time(hours)	0(initial condition), 1, 5, 20, 50, 100, 200, 300, 600, 1000, 2500, 5000, 10000



**Figure 5 Time-Temperature-Precipitation (TTP) diagram evaluated using precipitation start times of each ageing treatment condition<sup>1)</sup>.**



\*) Each point was evaluated at shown temperatures for 60 years.

**Figure 6 The S-L plane diagram transformed from the TTP diagram<sup>1)</sup>.**

### 3.3 Confirmation test of “no” age hardening

The main strengthen mechanisms of the new alloy are dispersion hardening of Mn compounds and solid-solution hardening of Mg as described above. Although age hardening is often used in aluminum alloys, this strengthen mechanism is not adequate for the basket of casks because its effect easily decreases when the materials are exposed to heat histories. Therefore, the new alloy was developed as annealed material and the elements (Si, Cu and Zn) which might contribute to the mechanism were limited to eliminate the age hardenability. Confirmation tests of these approaches to prevent age hardening were performed using the specimen of C2 shown in Table 1. Si, Cu and Zn contents were slightly increased to estimate the potential to generate age hardening in the specimen. Table 4 shows the test conditions. The temperature conditions of the aging treatment were determined in consideration of the detectability of the aging hardening. Figure 7 shows the test

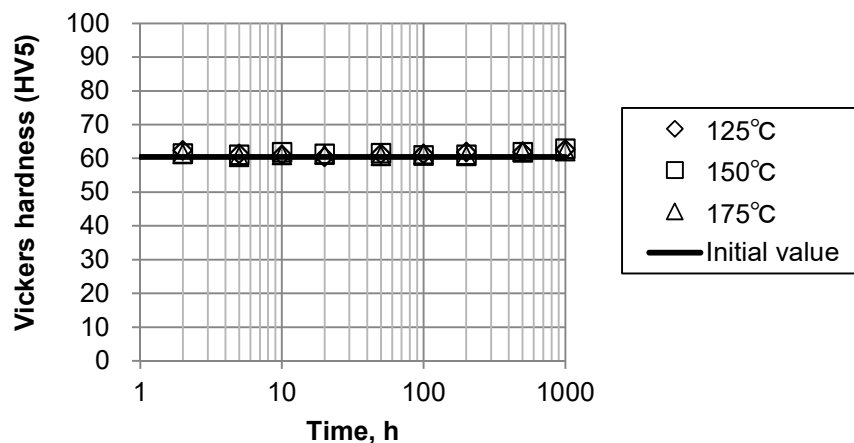


results. The data of Vickers hardness after various aging conditions hardly changed from the initial value for 1,000 hours. According to these test results, it is considered that the age hardening does not occur on the new alloy. This fact is considered to be very important to discuss the material reliability of the new alloy for 60 years.

**Table 4 The condition of the confirmation test of “no” age hardening.**

Item	Test condition
Specimens	C2 (shown in Table1)
Temperature(°C)	125, 150, 175
Time(hours)	0(initial condition), 2, 5, 10, 20, 50, 100, 200, 500, 1000
Evaluation test	Vickers hardness test -Test force: 5kgf -Number of data: 6*

\*The average values of 4 points eliminating maximum and minimum values were calculated.



**Figure 7 Changing trend of Vickers hardness at various aging conditions.**

#### 4. DETERMINATION OF THE CHEMICAL COMPOSITION OF A3J04-O

The chemical composition of A3J04-O was determined as shown in Table 5 in consideration of the test results describe above. Regarding Mg content, 1.0 mass% was determined as the lower limit and the upper limit was determined as 1.4 mass% in consideration of the manufacturability. Mn content was determined as 1.2-1.6 mass% in consideration of the balance between the strength and the impact properties. As for Si, Cu and Zn, the upper limits were determined below their contents of the specimen C2 to assure the elimination of age-hardening. The noteworthy feature of A3J04-O is considered to be the stability of strength properties which hardly change during the storage period of casks. The characteristics make the evaluation of long-term soundness easy to a great extent.

**Table 5 The chemical composition of A3J04-O. (mass%)**

	Si	Fe	Cu	Mn	Mg	Zn	Al
A3J04-O	≤0.25	≤0.25	≤0.05	1.2-1.6	1.0-1.4	≤0.05	Bal.
A3004(JIS) (reference)	≤0.30	≤0.7	≤0.25	1.0-1.5	0.8-1.3	≤0.25	Bal.

## 5. CONCLUSION

The aluminum alloy “A3J04-O” for basket of casks was developed on the chemical composition of A3004 (JIS) in terms of strengthening mechanisms of materials. The Mn content was determined based on the results of tensile tests and Charpy impact tests using the specimens with various Mn content. Moreover, the conservation of the dispersion hardening of Mn compounds was well confirmed by the long-time heat treatment at 300 °C×1,000 hours which enveloped the heat history of 60 years. As for Mg content, the new evaluation method using the diffusion length and the degree of supersaturation was developed and it was evaluated that the effect of solid-solution hardening did not decrease if the Mg content was 1.0 mass%. For the purpose of eliminating the age hardenability, Si, Cu and Zn contents were limited based on Vickers hardness test results after the aging treatment using the specimen with the slightly increased contents of Si, Cu and Zn. As a result of these test results, the chemical composition of A3J04-O was determined.

## ACKNOWLEDGMENTS

The present study was sponsored by Japanese 11 electric companies organized by Tokyo Electric Power Company Holdings from 2016 to 2018.

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