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STUDY FOR EVALUATE METHOD OF DESIGN STRENGTH OF ALUMINIUM ALLOY FOR BASKET MATERIALS

T. Maeguchi
Research & Innovation Center, Mitsubishi Heavy Industries, LTD., Takasago, Japan

Y. Kawahara
Construction & Maintenance Engineering Department, Nuclear Energy Systems Division Power Systems, Mitsubishi Heavy Industries, LTD., Kobe, Japan

R. Yamamoto
Research & Innovation Center, Mitsubishi Heavy Industries, LTD., Takasago, Japan

T. Hase
Nuclear Plant Component Designing Department, Nuclear Energy Systems Division Power Systems**,** Mitsubishi Heavy Industries, LTD., Kobe, Japan

ABSTRACT

To set a design strength of basket aluminium alloys for keeping structural integrity, it is necessary to evaluate the effect of thermal history during service period on mechanical strength of the material. A thermal ageing evaluation method for strength evaluation of aluminum basket was proposed. In this method, mechanical strength of a basket material is evaluated by mechanical properties of the materials experienced the heat treatments on the specially designed to promote the evolution of microstructure that occurs during the service period of the basket. The guidelines to determination of the heat treatmens were proposed, and applied to an Al-Mn alloy basket material. It was concluded that mechanistic study on microstructure evolution including coarsening of precipitates and grains, change in alloying element in the matrix and dislocations are crucially important to determine the temperature levels and cooling rate.

1. INTRODUCTION

Aluminium alloys are widely recognized as suitable materials for basket of a cask because of high thermal conductivity and low density. A basket of a dry transportable storage cask (dual-purpose cask) is expected to keep mechanical strength enough to maintain sub-criticality during its whole service period, *i.e*. transportation to a reprocessing plant, and long-term storage at an interim storage site or a power station. The temperature of basket is approximately 200^{o}C at the beginning of its use and gradually decreases due to decrease of decay heat from spent fuel assemblies. Since mechanical strength of aluminium alloys are affected by exposure at such temperature levels, application of aluminium alloys to basket requires enough consideration of effects of thermal histories. In order to set design strengths taking account for the change of mechanical properties during storage period, mechanical test data for the materials subjected to relevant thermal history should be obtained. However, it is not realistic to carry out heat treatment for many decades. Instead of exposing the materials to an elevated temperature for such a long period, shorter heat treatment with accelerated change in mechanical strength and relevant from the viewpoint of microstructural evolution should be implemented. In this paper, several guidelines for determining conditions for the heat treatment are proposed, and an example of application to one of basket materials is presented in detail. At this moment, regulations and guidelines for the evaluation of long-term reliability of aluminium alloys for basket materials held at elevated temperatures are not available or under development in most countries.

2. PROBLEM IN USE OF ALUMINIUM ALLOY AS BASKET

2.1. THERMAL AND MECHANICAL LOAD ON CASK

A cask used for transportation of spent fuels to a storage facility inside or outside the site of a nuclear power plant after being loaded with them at the plant. After the spent fuel transportation, the cask serves for storage for 60 years at the longest. After the storage, it serves for transportation of the fuels to a spent fuel reprocessing facility or a final disposal site. The cask is required to have a safety function as a Type B package for such a long period. **Figure 1** shows a schematic diagram of the thermal and mechanical loading on a cask during its service [1]. Thermal loading on a cask is represented by a gradual temperature decrease from approximately 200°C at the beginning to approximately 100°C at the end of 60 years of storage.

Under normal storage conditions, only limited level of stress is generated in basket. However, it is necessary to design a cask with enough structural strength against mechanical load assumed in the case of accident, more specifically, the drop from a height of 9 meters required by IAEA. The basket strength used to satisfy this requirements should be determined taking account for the effect of long-term exposure to temperature of approximately 200°C.

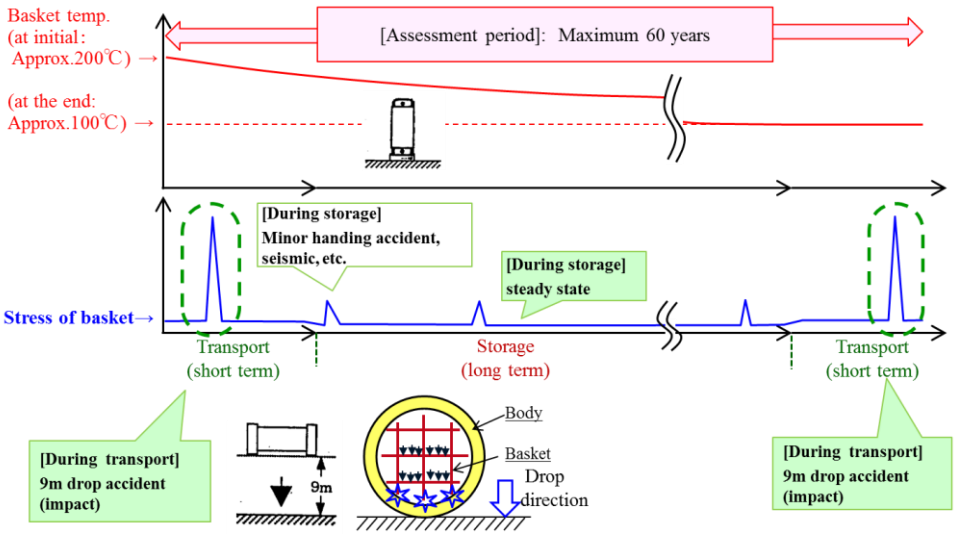


Figure 1. Schematic illustration for history of thermal and mechanical load on cask

1.2. MECHANICAL PROPERTIES OF BASKET MATERIAL DURING SERVICE

Metallurgical factors which contribute to mechanical strength of aluminium alloys are: (1) solid solution strengthening, (2) precipitation strengthening, (3) strain hardening and (4) strengthening from grain boundaries. All of these strengthening mechanisms are effective through decreasing mobility of dislocations in a crystal in its each way, which leads to enhance necessary stress to cause yielding and slip of crystals. These mechanisms are basically the same for all metallic materials including ferrous materials. However, some special considerations is required for those in aluminium alloys for basket, because time-dependent changes in the strengthening mechanisms have to be taken into account even at operation temperature explained in Section 2, while it is negligible for ferrous materials at this temperature level. This difference between aluminium alloys and ferrous materials essentially comes from the difference in thermal stability of the matrices, for example, as seen in difference in their melting points (1811K for iron, 933K for aluminium).

3. METHODS FOR STRENGTH EVALUATION

3.1. CONVENTIONAL METHOD

The first approach to assess the design strength of materials that are used at temperature T_0 is to anneal it at temperature level far higher than T_0. With this treatment, strengthening factors lose most of their effects on strength. For example, precipitates get coarser, dislocation disappears, and crystal grains become larger, each of which reduces strength of the material. The strength level obtained through this way is considered to be "inherent strength". The strength does not decrease below inherent strength.

On the other hand, it can also be acceptable to get strength level using mechanical test data obtained through "an acceleration test". In acceleration test, a material is subjected to slightly higher temperature than that of actual use so that the temperature dependent change of properties is accelerated. Arrhenius's law is assumed to estimate a testing duration equivalent to temperature of components. This acceleration method based on Arrhenius's law is widely used for assessment of thermally activated process like creep or stress corrosion cracking.

To define a limitation of this acceleration test, assume a material strengthened by a single strengthening factor Z, and the time dependent change of Z is diffusion controlled. From these assumptions, temperature dependency of rate of change of Z is expressed by Arrhenius type formula.

$$\dot{Z} = AD_0 \exp(-\frac{Q}{RT})$$

Changing this formula with $\ln(AD_0) = C$

$$\frac{Q}{R} = T(C - \ln \dot{Z})$$

The left term is constant. Therefore, if Z is effective for strengthening at both temperature T_1 and T_2, u_1, u_2, rate of change of Z at T_1, and T_2 are connected by next relationship.

$$T_1(C - \ln \dot{Z}_1) = T_2(C - \ln \dot{Z}_2)$$

This relationship tells that, if the time and the rate of change are parameterized as $T(C - \ln \dot{Z})$, it is possible to estimate the rate of change of Z at one temperature level from the data at different temperature level. This is called Larson-Miller parameter (LMP) method.

As hypothesized previously, following three are the preconditions for LMP application:

(a) Single strengthening factor is dominant in time-dependent strength change
(b) No change in the nature of the strengthening factor between T_1 and T_2
(c) Temperature elevation leads to an acceleration

The condition (b) can be satisfied by choosing temperature levels for acceleration test by considering metallurgical state of the material. However, there is no warrant that the condition (a) is always satisfied, because a metallic material is generally strengthened by multiple factors like precipitates, grains, solute elements and dislocation. The condition (c) is also not always satisfied as mentioned later.

Figure 2 (a) is 0.2% proof stress of aluminium alloy A6061-T6 tested at room temperature after holding at elevated temperature ranging from 100 to 370°C for various durations [2]. The 0.2% proof stress rapidly decreases when exposed to these temperature levels, because A6061-T6 is precipitation hardening material usually heat treated at temperature level between 100 to 180°C. Over this temperature, the precipitates become coarser and lose strengthening effect. **Figure 2** (b) is 0.2% proof stress plotted against LMP for all of data points in **Figure 2** (a). All of the data from different holding temperature levels forms single curve. Hence it is probable that LMP is applicable to this alloy.

Figure 3 (a) is similar data for different aluminium alloy A5083-O [2], which is strengthened mainly by solution strengthening of an alloying element Mg. In this case, unlike the case of A6061-T, 0.2% proof stress does not change at 370°C, while it changes at lower temperature levels. The reason of this behavior

is solubility of Mg into aluminium matrix is larger at higher temperature. The higher the holding temperature, the more Mg is solutioned into the aluminium matrix, which cause more solution strengthening. Above 230°C, all Mg is solutioned into the matrix, therefore, holding does not cause reduction in strength. As shown in **Figure 3** (b), the data does not constitute single curve against LMP. In such case, the condition (c) is not satisfied.

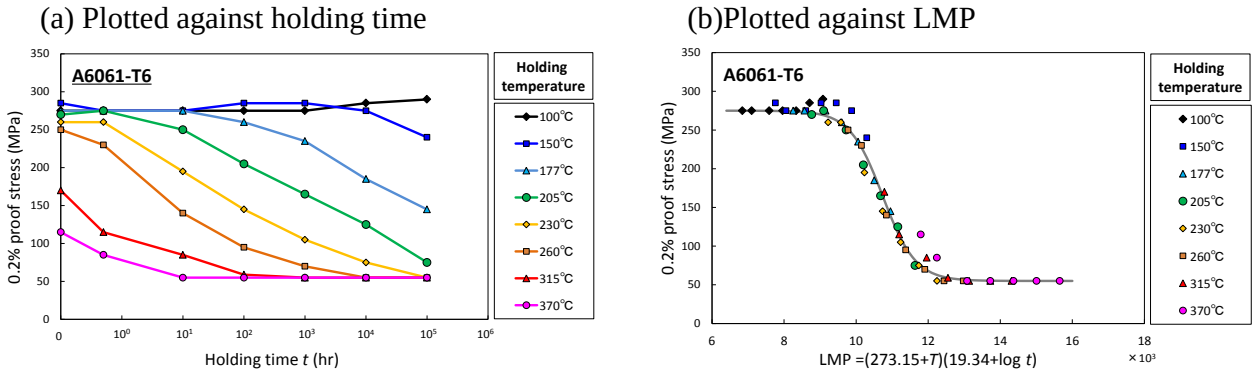


Figure 2. Room temperature 0.2% proof stress of A6061-T6 after holding at various temperature levels from 100 to 370°C

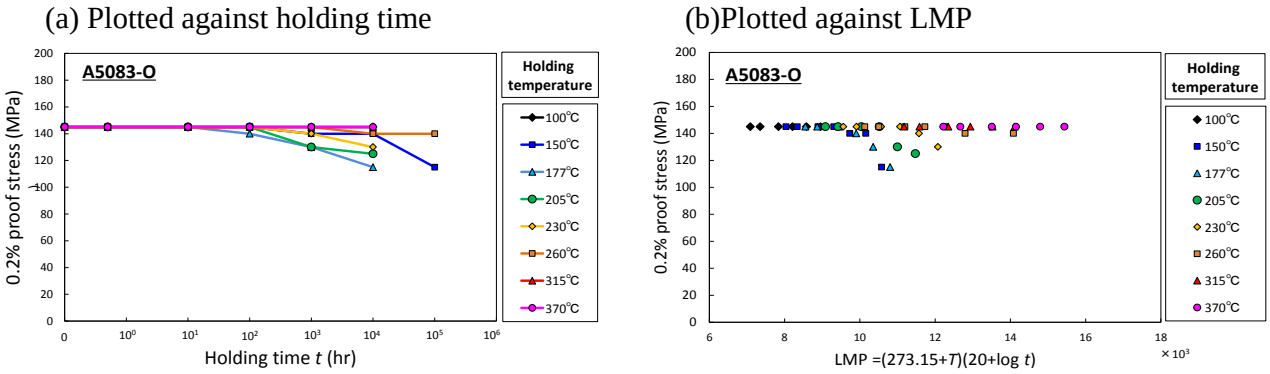


Figure 3. Room temperature 0.2% proof stress of A5083-O after holding at various temperature levels from 100 to 370°C

2.2 PROPOSED METHOD

(1) LONG-TERM OVER AGEING TREATMENT

In the case of the conventional method in 2.1, ageing conditions are determined by the extrapolation parameters like Larson-Miller parameter, assuming the thermal activation processes for ageing similar as those in creep. However, in contrast to creep, this method is not necessarily widely accepted as a valid method for ageing due to lack of fundamental data.

The basic concept of the method proposed here, "long-term over ageing treatment" [1], is the same as that in the conventional method. The only difference is that the appropriateness of heat treatment conditions are confirmed both theoretically and experimentally in the proposed method. Considering the limit of the conventional method described in 2.1, the temperature and duration of long-term over ageing should be determined so that following three conditions are satisfied:

A) Temperature range which causes phase transformation or microstructural evolution expected at temperature of basket

B) Temperature higher than that of actual basket in order to accelerate kinetics of phase transformation or growth of precipitates, but does not cause drastic recrystallization which does not occur in conditions of use of basket

C) Duration long enough to show that changes in mechanical properties decay

(2) ANNEALING

Annealing is to hold the material at elevated temperature much higher than that for long-term over ageing treatment. It is possible by annealing to remove most of the excessive strengthening factors, existing in as-manufactured condition. Here, "excessive" means that the strengthening factors that are not thermodynamically stable at a service temperature and susceptible to change during use at such temperature level. The annealing should be followed by a cooling with cooling rate small enough to avoid any supersaturated solution. If cooling rate is not small enough, supersaturated solution makes strength after the annealing higher just as the example of A5083-O shown in 2.1.

It is essential to select right holding temperature, time and cooling rate to obtain the design strength of structural materials for the casks in view of services for several decades. Following D) and E) are the proposed guidelines to achieve this.

D) Temperature high enough to remove excessive precipitation strengthening, strain hardening initially existing in as-manufacturing state, and to promote recrystallization within an extent that expected during storage.

E) Cooling rate small enough to avoid any supersaturated solution that leads excessive solution strengthening

Figure 4 presents schematic diagrams for the thermal histories for long-term over ageing and annealing. In both methods, it is important to determine temprature, holding time and cooling rate based on detailed metallurgical understanding on the material fo interest.

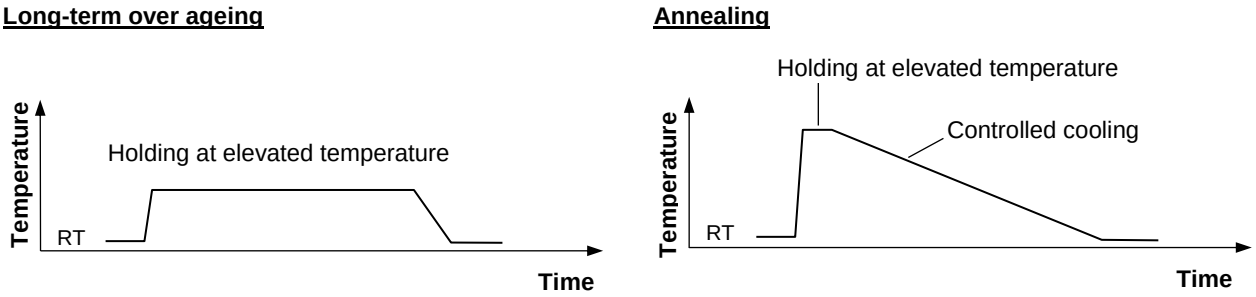


Figure 4. Schematic diagrams for the thermal histories for long-term over ageing and annealing.

4. EXAMPLE OF APPLICATION

In this section, an example of application of the proposed method to a basket material is shown focusing on how to determine the heat treatment conditions satisfying the guidelines mentioned above.

4.1 MATERIAL

A3004-H112 is a hot extrude commercial Al-Mn alloy designated in Japan Industrial Standards (JIS). It has been employed as basket material of Mitsubishi MSF-type casks. The chemical compositions of the sample material are shown in **Table 1**. This sample is a basked shaped extrusion profile produced through the same manufacturing process as that of actual basket material.

In an as-extruded A3004, there are particles of Al-Mn second phases dispersed in the matrix. But these second phases are not considered as strengthening factors because of its large size and low number density [3]. Although there are some reports of precipitation hardening of A3004 caused by Al-Cu-Mg precipitates [4], A3004 generally does not have significant precipitation hardenability.

In the other hand, Mn in aluminum matrix is practically zero in the equilibrium state. It is known that Mn is relatively easily supersaturated into aluminum matrix depending its thermal history, for example, rapid cooling from molten metal [5]. This unequilibrium excess Mn can cause solid solution strengthening.

Table 1. Chemical compositions in mass% of sample

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
JIS H 4000 A3004-H112	0.3 max	0.7 max	0.25 max	1-1.5	0.8-1.3	—	0.25 max	—	Bal.
Sample (Mark C)	0.20	0.5	0.19	1.1	1.0	0.01	0.05	0.02	Rem.

4.2 LONG-TERM OVER AGENG TREATMENT

Temperature of 250°C and 300°C were chosen by investigating metallurgical characteristics of A3004-H112 was well as with the help of computational phase diagram. **Figure 5** is the phase diagram of the sample C calculated by Thermo-Calc. According to this result, Al_6Mn phase is stable at the service temperature range of basket material (200°C or lower). At the temperature higher than 310°C, ratio of α-Al(Mn,Fe)Si becomes significant. This means that, in order to simulate microstructural evolution during the service, holding temperature should not exceed 310°C during long-term over ageing. Not to mention, the holding temperature should be higher than actual basket. For this reason, 250°C and 300°C were selected. Through such discussion, temperature has been fixed satisfying the guidelines A) and B). The maximum holding time was 10^4h, which was determined looking the time-dependent trend of mechanical properties. Therefore, the guidelines C) cannot be determined before the start of a long-term over ageing treatment.

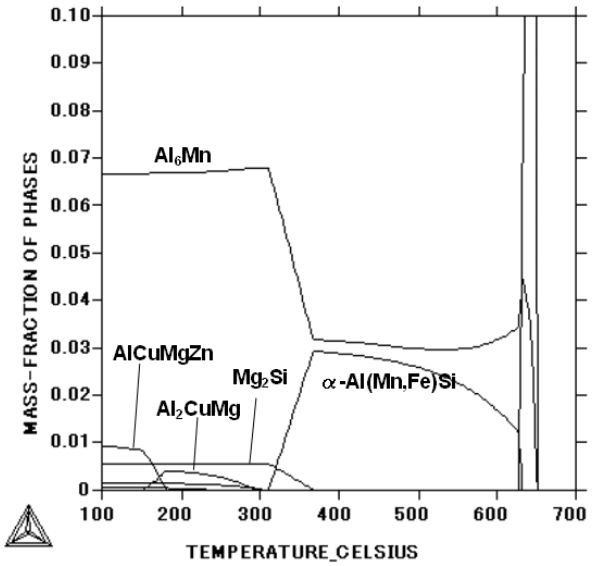


Figure 5. Mass-fraction of stable phases calculated for the chemical composition of the A3004-H112 sample.

Figure 6 shows the tensile test results of the sample held for 1.0×10^3, 5.0×10^3 and 1.0×10^4h at 250 or 300°C. The horizontal axis is holding time. The different symbols indicate temperature levels for tensile test. The 0.2% proof stress decrease soon after the beginning of ageing, but the reduction after 1.0×10^3 h becomes faint and almost stable before ageing for 1.0×10^4 h. This trend was same for 250 and 300°C. It is considered that initial reduction of strength was attributed to loss of the slight precipitation hardening existed in the state of as extruded. From these observation, ageing for 1.0×10^4 h is practically sufficient to stabilize change in strength due to exposure to temperature level of basket.

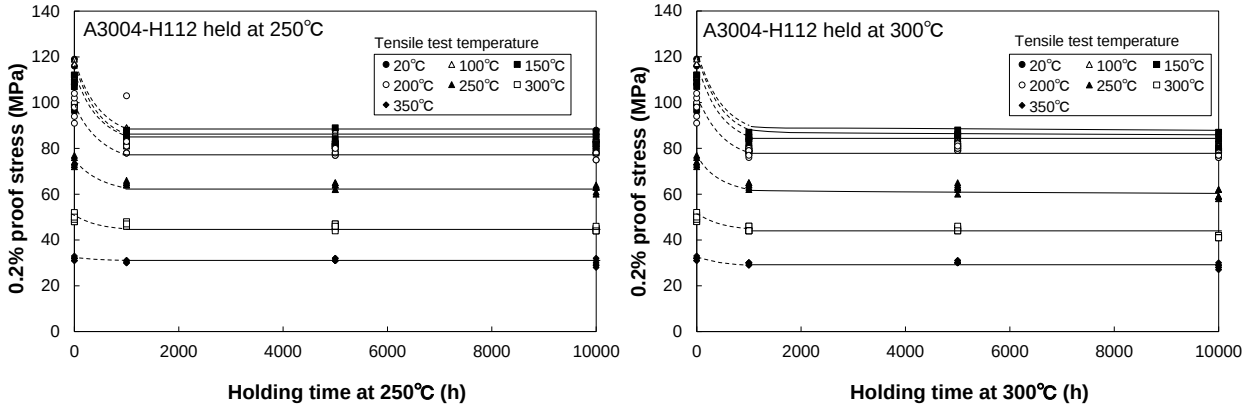


Figure 6. Effect of ageing at 250°C and 300°C on 0.2% proof stress of the A3004-H112 specimen. (0h corresponds to as-extrusion state)

4.3 ANNEALING

The temperature for the annealing treatment was determined through preliminary tests. Block specimens were held at 350, 400, 450, 500, 520, 530, 540, 560 and 580℃ for 10h and then air cooled. Here, the holding temperature levels higher than 345°C, which is required for O-temper in JIS H 0001, were chosen for this test. The tensile test results for these heat treated specimens are shown in **Figure 7**. Significant strength reduction was observed in the case of the temperature of 560°C or over. Microstructure observation result confirmed that this was caused by grain coarsening. Based on the results obtained by further investigation by electrical conductivity measurement and microstructure observation [6], it was concluded that a temperature range from 450°C to 520°C meets the requirement E) mentioned in 3.2 (2). The highest of this range, 520°C was chosen as holding temperature for this work.

In order to a choose cooling rate that satisfied the requirement F), effect of cooling rate on 0.2% proof stress was investigated by tensile test, microstructure observation, electrical conductivity. As presented in **Figure 8**, 0.2% proof stress decreases with decreasing cooling rate. Cooling rate should be 0.5°C/h or smaller to obtain 0.2% proof stress in its bottom. **Figure 9** is the effect of cooling rate on electrical conductivity of the A3004-H112 specimen held at 520°C for 10h. With decreasing cooling rate, electrical conductivity increases. The change in electrical conductivity seems to be saturated at cooling rate smaller than 0.5°C/h. These facts suggest that during cooling, excessive Mn concentration in the matrix takes relatively long time to become equilibrium concentration at lower temperature.

To confirm such behavior of Mn content in the matrix, a direct measurement of concentration of Mn solutioned in the aluminium matrix was performed by phoenol filtrate method [6]. In this method, the samples were machined into chips and soluted in hot phoenol. Then, in order to eliminate second-phase particle, the solution was filtrated using a filter with pores 100nm in diameter. Finally the Mn concentration of aluminium matrix was quantified by analyzing the filtrated solution using ICP spectroscopy. **Figure 10** shows the effect of cooling rate on Mn concentration in the aluminium matrix. The matrix Mn concentration was 0.33mass% at the as-extrusion, 0.0613mass% in the sample cooled with rate of 1°C/h.

From these results, annealing conditions which satisfy the requirements E) and F) should be 10h at 520°C followed by controlled cooling with rate of 0.5°C/h or smaller.

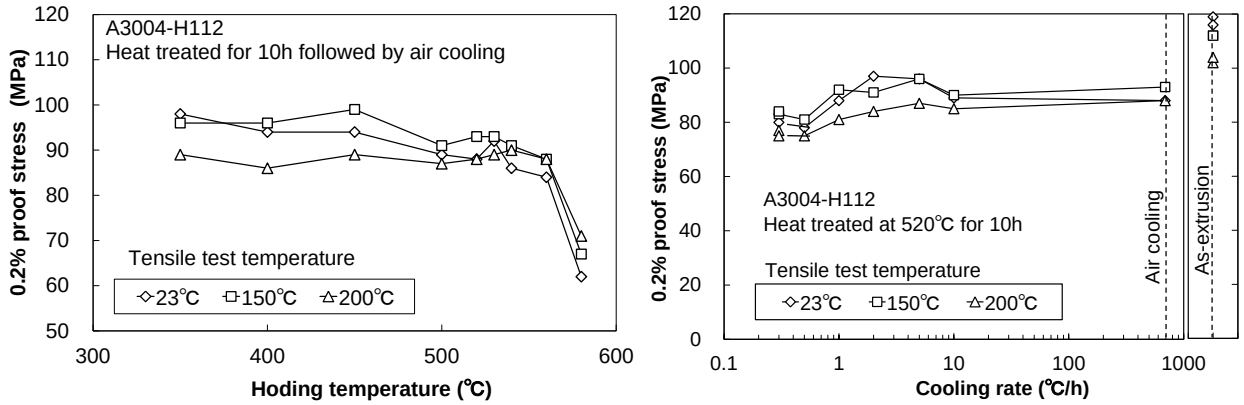
4.4 COMPARISON OF LONG-TERM OVER AGEING AND ANNEALING

Table 2 shows grain structure and Mn containing dispersoids in as-extruded, long-term aged (1.0×10^4h at 250°C) and annealed conditon (10h at 520°C, controlled cooling with 0.5°C/h). The grain size and shape does not differ significantly among the three condition. The average particle diameter of the dispersoids calculated from the TEM micrographs is almost same for the three states, 114, 119 and 107nm,

respectively. It was confirmed that the loss of strength from coarsening of the dispersoids does not occur in these treatments.

As explained in **Table 3**, similar level of 0.2% proof stress was obtained by long-term over ageing and annealing. The slight difference between the two method is Mn content in the matrix. In the case of the long-term over ageing at 250°C, Mn content reaches equilibrium solubility limtit at 250 °C, while smaller Mn content is obtained in the annealing followed by small cooling rate. This is natural considering the dependency of solubility limit of Mn into aluminium matrix. However, the the difference in solution strengthening caused by such level of Mn concentration is small, and the its impact on the 0.2% proof stress is small. Because grain structure and dispersoid did not significantly change, the 0.2% strength reduction is explained by solution strengthening and strain hardening introduced in the manufacturing process.

As described in this paper, in order to set the right conditions of the heat treatment, it is important to carry out mechanistic study on microstructure evolution including coarsening of precipitates and grains, change in alloying element in the matrix and dislocations.



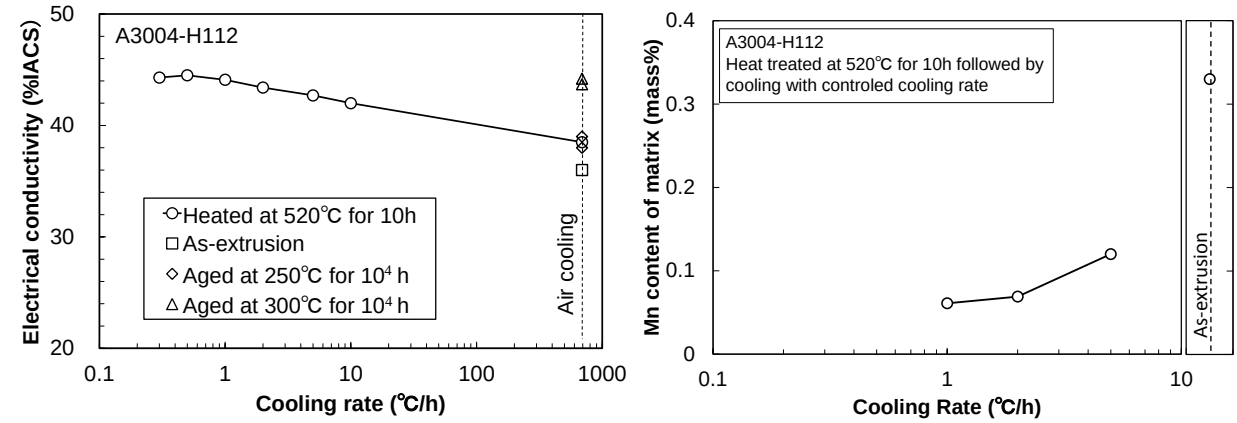


Figure 9. Effect of cooling rate on electrical conductivity of the A3004-H112 specimens

Figure 10. Effect of cooling rate on Mn content in matrix of the A3004-H112 specimens

Table 2. Microstructures of A3004-H112 observed by optical micrographs and TEM

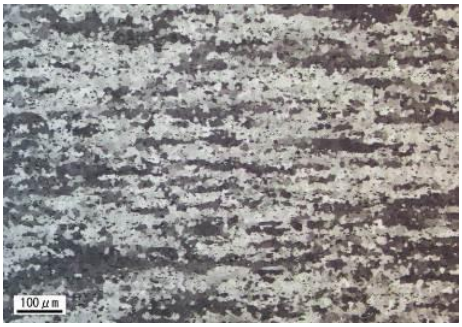
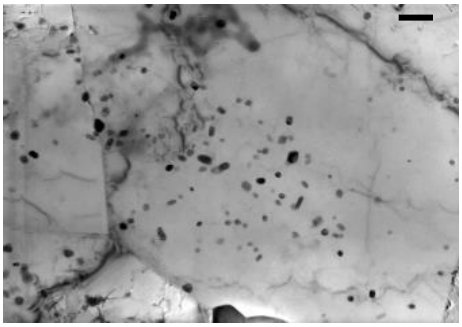
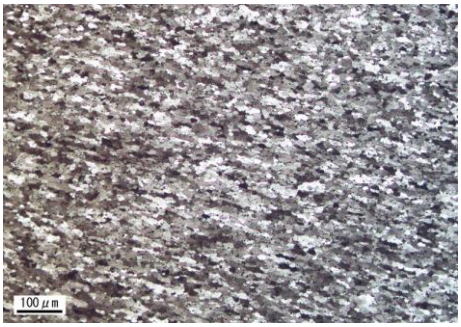
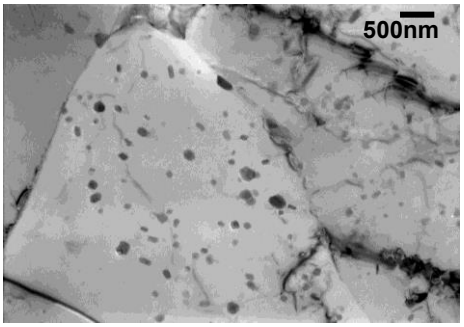
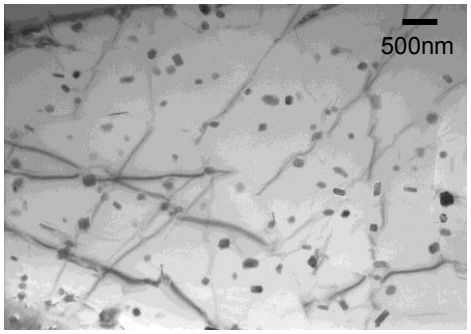
Observation / Conditions	Crystal grains (Optical microscope)	Dispersion particles (Transmission electron microscope)
As-extrusion		
10^4h at 250°C		
10h at 520°C, controlled cooling with 0.5°C/h		

Table 3. Balance sheet for the change in strengthening factors caused by heat treatments

Items / Applied heat treatment	Long-term over ageing ($1.0x10^4$h at 250°C)	Annealing (10h at 520°C, control cooling with 0.5°C/h or smaller)
0.2% proof stress at RT (MPa) before heat treatment	117	117
0.2% proof stress at RT (MPa) after heat treatment	83	80
Change in 0.2% proof stress at RT, $\Delta\sigma_{0.2}$ (MPa)	-34	-37
Change in matrix Mn (mass%)	-0.08 [1)]	-0.30 [1)] -0.27 [2)]
Estimated loss in solution strengthening, $\Delta\sigma_{sol}$ (MPa) [3)]	-1.7	-6
Estimated loss in strain hardening, $\Delta\sigma_{st}$ (MPa) [4)]	-32	-31

1) Estimation by electrical resistivity method
2) Direct measurement by phoenol filtration method
3) Estimation from the literature data, 21MPa/mass%Mn [7]
4) Since grain structure was not significantly affected, $\Delta\sigma_{st} = \Delta\sigma_{0.2} - \Delta\sigma_{sol}$

5. CONCLUSION

(1) A method to evaluate the strength of an aluminium basket material after use at elevetated temperature for several decades has been proposed. In this method, mechanical strength of a basket material is evaluated after the heat treatments specially designed to promote the evolution of microstructure that occurs during the service period of the basket. For this purpose, either long-term over ageing or annealing is applied to an as-manufactured basket material.

(2) The generalized guidelines to determine the heat treatment conditions for materials have been proposed based on the thermal stability of strengthening factors.

Long-term over aging conditions should satisify following A) to C):

A) Temperature range which causes phase transformation or microstructural evolution expected at temperature of basket

B) Temperature higher than that of actual basket in order to accelerate kinetics of phase transformation or growth of precipitates, but does not cause drastic recrystallization which does not occur in conditions of use of basket

C) Duration long enough to show that changes in mechanical properties decay

Annealing conditions should satisify following E) and F):

D) Temperature high enough to remove excessive precipitation strengthening, strain hardening initially existing in as-manufacturing state, and to promote recrystallization within an extent that expected during storage.

E) Cooling rate small enough to avoid any supersaturated solution that leads excessive solution strengthening

(3) This method was applied to aluminium alloy A3004-H112, one of the basket materials for Mitsubishi MSF cask.

References

[1] D.Ishiko, J.Kishimoto, Y.Kawahara, T.Maeguchi, R.Yamamoto, Proceedings of the 18th International Symposium on the Packageing and Transportation of Radioactive Materials PATRAM 2016, September 18-23, 2016, Kobe, Japan

[2] J. Gilbert Kaufman, Properties of Aluminium Alloys, ASM, (1999)

[3] T.Kajiyama and K.Fukuda, “Aluminium-Manganese and Aluminium-Manganese-Magnesium alloys”, Journal of the Japan Institute of Light Metals, Vol. 38, No. 6, pp.362-368, 1988

[4] T.Inaba, E.Usui and N.Shimano, “Age-hardening behavior of Al-1% Mn-1% Mg alloy”, Journal of the Japan Institute of Light Metals, Vol. 39, No. 1, pp.3-7, 1989

[5] Y.Murakami and K.Mori, “Highly supersaturated Al-Mn solid solution alloys and their decomposition by heat-treatment” , Journal of the Japan Institute of Light Metals, Vol. 18, No. 6, pp.339-345, 1989

[6] T. Maeguchi, Y. Kawahara, R. Yamamoto, K. Sakima and H. Tamaki, Journal of The Japan Institute of Light Metals, Vol. 68, No. 12, 2018

[7] A.K.Vasudevan, R.D.Doherty, Aluminum Alloys – Contemporary Research and Applications, 1989