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## Properties of Aluminum Alloys for Transportable Storage Cask Basket After Long Term Storage

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### Abstract

A basket for transportable storage cask for spent nuclear fuel is designed to maintain prescribed geometrical arrangements of spent fuel assemblies under accidents during transport and storage condition, and also designed for effective removal of decay heat from spent fuel assemblies. Various kinds of aluminum alloys are widely used for basket material as structural members of the transportable storage casks, for the high heat-transfer performance and material workability. Considering transportation to a reprocessing facility after long term storage at an interim storage facility, it is important to maintain integrity of basket structure under transport accidents. However, mechanical properties of these alloys are possibly changed by thermal aging during storage since cask service temperature may affect microstructure of aluminum alloys over the long time period. It is therefore essential in cask design qualification to identify degradation of mechanical strength of basket material both for normal storage and transport accident after long term storage. MHI has conducted evaluation of mechanical properties considering thermal aging of the aluminum alloys A6N01 containing boron carbide (B<sub>4</sub>C) and commercial A3004 without boron for the basket, which resulted in construction of a data base for assessing structural integrity of the basket [1–2]. In this paper, effects of thermal aging on mechanical properties of these materials are presented, and the microstructural strengthening mechanisms which play important roles in the evolution of mechanical properties are discussed.

### 1. Introduction

Spent fuel transport/storage casks are one of the components necessary for the nuclear fuel cycle. The casks are required to undergo safety assessment with the assumption that they will be transported from a plant to an interim storage facility, stored for 60 years at the longest, and finally transported to a reprocessing facility or a final disposal site after the storage. The safety functions of the cask are subcriticality, shielding, heat removal and sealing. The cask is required to have a structural strength necessary to achieve these functions. Its basket is a member that is mainly required to have subcriticality and heat removal functions, and have structural strength that ensures them. This paper addresses mechanical properties of two materials for the basket, A6N01 containing B<sub>4</sub>C and A3004. A6N01 containing B<sub>4</sub>C is a material that has all the three functions: subcriticality, heat removal and structure, while A3004 can be used as a material that has two functions: heat removal and structure.

### 2. Conditions for evaluation of basket materials

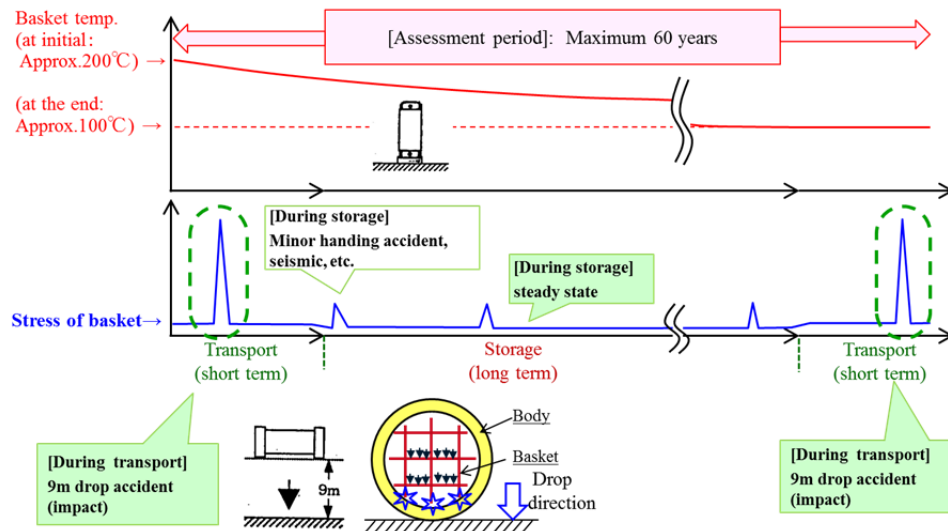
#### 2.1. Thermal and mechanical load on the cask

Casks are used for transport 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 is provided with a required treatment at the storage facility, and again serves for storage for 60 years at the longest. After the storage, it serves for transport 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, and keep it during storage for 60 years at the longest. Fig. 1 shows a schematic diagram of the cask's thermal and mechanical loading in its operating environment. Thermal loading on cask is represented by a gradual temperature decrease from approximately 200°C to approximately 100°C lasting for 60 years in terms of heat.

Mechanical loads causes very low level of stress in the basket under normal operating condition of the casks during storage. In addition, an largest mechanical load is assumed for accident conditions of transport (drop of cask from 9 meters high) during transport and post-storage transport in terms of structure. The basket is required to have mechanical properties enough for keeping structural integrity

against this stress level, even after thermal deterioration due to the long-term exposure at approximately 200°C.

There are also functional requirements such as sub-criticality and heat removal characteristic. This paper focuses on the thermal impact on mechanical properties.



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

## 2.2. Basket materials

The following two materials are used for baskets of MSF-type (MITSUBISHI Spent Fuel) cask.

A6N01 material containing B<sub>4</sub>C: This is a composite material consists of fine particles of B<sub>4</sub>C and matrix base metal of A6N01, an Al-Mg-Si alloy designated in Japan Industrial Standards (JIS). This composite material is produced through powder metallurgy process and finally shaped in tube through hot extrusion process (hereafter called “BC-A6N01”) [1].

A3004: This is a hot extrude commercial Al-Mn alloy designated as JIS standard A3004.

## 3. Thermal deterioration of mechanical properties during storage

### 3.1. Strengthening mechanisms

Metallurgical factors which contribute to mechanical strength of aluminum 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 aluminum 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 aluminum 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 aluminum). In this paper, the change in mechanical properties of basket materials mentioned above is referred as “thermal deterioration”. Therefore, for the reasonable design and safety assessment of casks, it is necessary to assess the material properties taking the thermal deterioration brought by the cask operating environment into account.

Followings are general explanations of each strengthening mechanism together with its specific contribution in the two materials for basket.

#### (1) Solid solution strengthening

The introduction of solute atoms into solvent matrix invariably produces an alloy which has higher mechanical strength than pure metal. This is achieved by strain field around the solute atom from

difference in atomic size between matrix and solute. This reduces mobility of dislocation. Magnitude of the solution strengthening depends on concentration and atomic size of the solute.

Typical aluminum alloy strengthened by this mechanism is Al-Mg alloys. In the case of basket material BC-A6N01, there is solid solution strengthening by solute elements like Mg and Si, but the contribution is very small because contents of these alloying elements are as low as about 1 mass% in total. This is similar for A3004, and solubility of its main alloying element Mn in aluminum matrix is practically zero in the equilibrium state.

(2) Precipitation strengthening

In this mechanism, the dislocation mobility is reduced by fine precipitates or strain field created by the precipitates. In the aluminum alloys, this is achieved by solution heat treatment followed by quenching to generate supersaturated solid solution, and then aging at room temperature to about 200 °C. Through this process, solute atom clusters or fine precipitates appear. With excess temperature or time of aging, the precipitates grows and its number density decreases. This causes loss of precipitation strengthening and called as “over aging”. Al-Cu, Al-Cu-Mg, Al-Mg-Si, Al-Zn-Mg and Al-Li alloys have significant hardenability by precipitation strengthening.

BC-A6N01 has precipitation hardenability from Mg-Si fine precipitates. However, as for the application for MSF-type cask, no intentional heat treatments for the precipitation hardening are applied. Nevertheless, there would be small precipitation strengthening due to slight supersaturation during cooling from hot extrusion. In any cases, the precipitation strengthening cannot be expected as the principal strengthening mechanism at the final stage of storage, because the precipitates grows to lose its contribution to strengthening.

In hot 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 [4]. 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.

(3) Strain hardening

Strain hardening occurs in metallic material by introducing cold working (plastic deformation at relatively low temperature, typically at ambient temperature) in it. Any cold works lead to increment in dislocation density, which causes interaction between dislocations and therefore impede migration of dislocations. Industrially applied cold working is rolling, forging, forming and tensile deformation, but no intentional strain hardening is introduced in the two basket materials. However, small degree of work hardening may be introduced during it manufacturing process. Strain hardening disappears by exposure to elevated temperature, because of migration of dislocation and extinction. Strain hardening is assumed to be far from dominating factor in the mechanical strength of the basket materials, however, it has to be taken into account as a potential factor in the thermal deterioration.

(4) Strengthening from grain boundaries

In this strength mechanism, grain boundaries are barriers to migration of the dislocations. At the temperature level where recovery of dislocation structure occurs, interaction between dislocations creates new grain boundaries or causes grain boundary migration. This comes to decrease of strength from grain boundaries. BC-A6N01 consists of fine crystal grains created through the powder metallurgy process, and its coarsening may decrease mechanical strength. Al-Mn alloys including A3004 have high resistance to grain coarsening since the particles of Al-Mn second phases suppresses grain growth. Hence the two basket materials are considered to have some extent of strength from grain boundaries, and it should be evaluated as one of potential factor in the thermal deterioration.

### **3.2. Material property evaluation for thermal deterioration**

It is necessary to evaluate the properties at the thermally deteriorated state in the light of the cask operating environment described in 2.1 and material characteristics of each materials described in 3.1. The followings are procedures for producing thermally deteriorated material and investigation on it.

### 3.2.1. Test materials

The following two materials were used for a verification test.

BC-A6N01: Hot extrusion product of BC-A6N01 was selected. The extrusion profile is hollow tube with thickness of 5.5mm and outer dimension of 150mm x 150mm for a cross section vertical to extrusion direction.

A3004: Hot extrusion product of A3004 was selected. This is also hollow tube profile, and its thickness is 16mm, outer dimension is 60mm x 200mm for a cross section vertical to extrusion direction.

Chemical composition requirements of BC-A6N01 and A3004 are shown in Table 1. None of the materials have been heat treated after hot extrusion. This state is referred as “As extruded”.

**Table 1 Chemical composition requirements of BC-A6N01 and A3004 (mass%)**

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al	B <sub>4</sub> C
BC-A6N01	0.5-0.9	≤0.35	≤0.35	≤0.50	0.4-0.8	≤0.30	≤0.25	≤0.10	Bal.	6.9-7.1
A3004	≤0.3	≤0.7	≤0.25	1.1-1.5	1.0-1.3	—	≤0.25	—	Bal.	—

### 3.2.2. Heat treatment process for evaluation of thermal deterioration

In this study, two kinds of approach were taken to obtain the terminal state of thermal deterioration which is reasonable as a basis of defining mechanical strength for designing cask. One is long-term over aging heat treatment. This is proposed to reduce strength by long aging with temperature higher than actual basket. The other approach is application of high-temperature annealing defined in the previous report.[5] The aim of this process is complete removal of unequilibrium excess solid solution strengthening and precipitation strengthening. The details of the two heat treatment processes are given here.

#### (1) Long-term over aging treatment

The difficulty in this method is validation of appropriateness of heat treatment conditions. Acceleration of aging by temperature elevation is often used with conditions determined based on extrapolation parameters like Larson-Miller parameter [6] assuming the similar thermal activation processes for thermal aging as those in creep. However, in contrast to the creep, this method is not necessarily widely accepted as a valid method for thermal aging due to lack of fundamental data. Considering this difficulty, the principles for determining over aging conditions were proposed. Temperature and duration of long-term over aging were determined so that following four conditions were satisfied:

- A) Temperature range which causes phase transformation or growth of precipitates expected at temperature of basket
- B) Higher temperature than that of actual basket in order to accelerate kinetics of phase transformation or growth of precipitates.
- C) Temperature not too much high to prevent drastic grain structure by recrystallization that does not occur in conditions of use of basket
- D) Duration long enough to verify that changes in mechanical properties decay

Temperature of 300°C was chosen by investigating metallurgical characteristics of BC-A6N01 and A3004 reported in literatures. The duration has to be determined experimentally by observing effect of aging temperature on mechanical properties so that its change decays.

#### (2) Annealing

This method is proposed for full removal of precipitation strengthening and unequilibrium excess solid solution strengthening by holding material at high temperature, and following cooling with cooling rate small enough to avoid any supersaturated solution. It is important to determine holding temperature, and cooling rate enough to achieve above quasi-static condition. For the two materials addressed in this study, holding temperature was selected as 520°C. In a preliminary study, it was confirmed that this was the highest temperature which did not significantly affect grain size. As for the cooling rate necessary for

removal of unequilibrium excess solid solution strengthening, each material has its own sensitivity to cooling rate depending on the diffusion rate of solute atoms in the matrix, and it should be determined by experimental approach.

The principles of determining annealing conditions is to hold material at temperature high enough to terminate initial precipitation strengthening and strain hardening. It is also necessary to promote recrystallization within an extent that expected during storage. Cooling condition has to be determined carefully not to cause unexpected strengthening from excess supersaturation or precipitation. The conditions of annealing were found by preliminary experiments, surveying effect of temperature and cooling rate on mechanical properties of the two materials. Table 2 shows the heat treatment conditions for the test material. For BC-A6N01, cooling rate was limited to relatively small values such as 2, 1 and 0.5 °C/hr since the material has age hardenability, and high cooling rate causes unexpected supersaturation of solute elements. Cooling rate of 0.3 °C/hr was added to the testing condition for A3004, since the material appeared to have higher sensitivity to cooling rate as described in 4.2.

### 3.2.3. Characterization of materials

The materials treated by long-term over aging or annealing were evaluated to know if the treatments were effective to realize the terminal state appropriate for evaluation of mechanical properties considering long thermal exposure of basket materials. In the case of annealing, electrical conductivity was measured by eddy current method on polished surface of samples. The unit of electrical conductivity %IASC is an expression as a relative value to that of annealed commercial pure copper in percent (%). Electrical conductivity of a metallic material decreases by existence of solute atoms, dislocations or precipitates decrease electrical conductivity. For this reason, electrical conductivity is widely used as an index of solute atom concentration in aluminum alloys. In this study, electrical conductivity was measured at various condition of thermal history of materials to know the degree of solid solution strengthening.

Tensile tests were carried out to evaluate mechanical properties after various heat treatment process using round bar specimen with diameter of 4mm and gauge length of 20mm. Specimens were cut from the materials so that the tensile direction was parallel to extrusion direction.

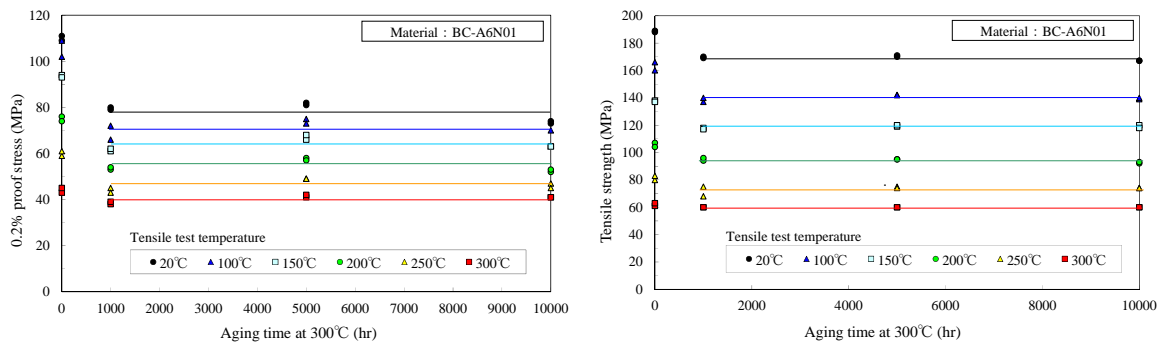
**Table 2 Heat treatment conditions to survey effect of annealing condition on strength**

Material Parameter Number	BC-A6N01			A3004		
	Temperature (°C)	Hold time (hr)	Cooling Rate (°C/hr)	Temperature (°C)	Hold time (hr)	Cooling Rate (°C/hr)
SC1	520	10	>600 (Air cooling)	520	10	>600 (Air cooling)
SC2			10			
SC3			5			
SC4			2			
SC5			1			
SC6			0.5			
SC7			0.3			

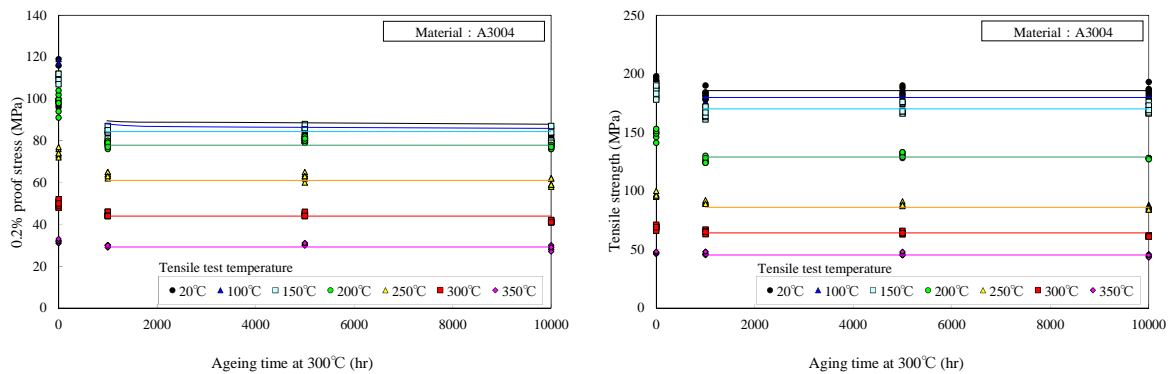
## 4. Result and discussion

### 4.1. Effect of long-term over aging on mechanical strength

Fig.2 presents dependence of 0.2% proof stress and tensile strength of BC-A6N01 on aging time at 300°C. Both 0.2% proof stress and tensile strength decrease soon after aging, but the reduction after 1000hr becomes faint and it is considered almost stable before aging of 10,000hr. This was similar for A3004 aged at 300°C displayed in Fig.3. In both materials, it is considered that initial reduction of strength was attributed to loss of the slight precipitation hardening existed in the state of as extruded. Aging for 10,000hr at 300°C is well assumed to be practically sufficient to stabilize change in strength due to exposure to temperature level of basket.



**Fig 2 Effect of aging time on tensile properties of BC-A6N01**



**Fig 3 Effect of aging time on tensile properties of A3004**

#### 4.2. Effect of annealing conditions on mechanical strength

##### (1) BC-A6N01

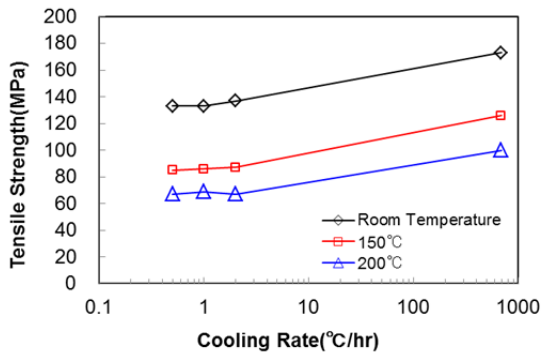
Fig. 4 and Fig. 5 show effect of cooling rate after high temperature annealing on tensile strength and electrical conductivity, respectively. Tensile strength decreases with decreasing cooling rate, but with the cooling rate smaller than  $2^{\circ}\text{C/hr}$ , the tensile strength is stable. Similarly, electrical conductivity does not change if cooling rate is below  $2^{\circ}\text{C/hr}$  (Cases SC4, SC5 and SC6). These facts clearly tell that, after solution treatment at  $520^{\circ}\text{C}$ , the cooling rate below  $2^{\circ}\text{C/hr}$  is quasi-static enough to realize an equilibrium strengthening state without solid solution hardening by excluding solute atoms during cooling, even if there was supersaturated solid solution before the cooling.

##### (2) A3004

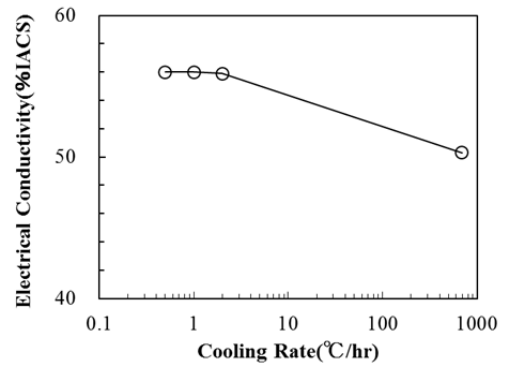
Fig. 6 and Fig. 7 show effect of cooling rate after annealing on tensile properties and electrical conductivity of A3004. With decreasing cooling rate, tensile strength decreases and electrical conductivity increases. However, in contrast to the behavior of BC-A6N01, the changes in tensile strength and electrical conductivity seem to become saturated at cooling rate smaller than  $0.5^{\circ}\text{C/hr}$ . These data show cooling rate as small as  $0.3^{\circ}\text{C/hr}$  (SC7) is necessary to avoid effect of cooling rate.

Considering the fact that in annealed Al-Mn alloy there are neither fine precipitates nor high density of dislocations, both of which are effective to decrease electrical conductivity, the above change in electrical conductivity can be attributed to change in concentration of solute elements in the solid solution. More specifically, it suggests that there exist solid solution which cannot be phase decomposed during cooling after being formed at  $520^{\circ}\text{C}$ . 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 [7]. This unequilibrium excess Mn causes significant solid solution strengthening. Furthermore, it is also reported that once formed, the Mn-supersaturated solid solution does not easily decompose by heat treatments. Although no special heat treatment for Mn-supersaturation is applied to A3004 as a basket material, the slight effect of it cannot be completely denied according to the current result.

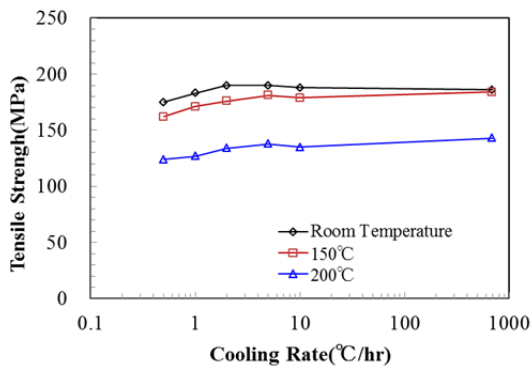
These results suggest that holding at high temperature is not sufficient to obtain fully annealed state. Cooling rate has to be chosen carefully and controlled to have strength low enough to be assumed as its stable state. In addition, different aluminum alloys requires different heat treatment conditions to achieve stable state in terms of mechanical properties after thermal deterioration, since sensitivity of change in each strengthening mechanism to thermal history differs according to its alloying elements. The evaluation of materials for cask requires further studies ranging from microstructural mechanistic consideration to data collection of macroscopic mechanical behaviors.



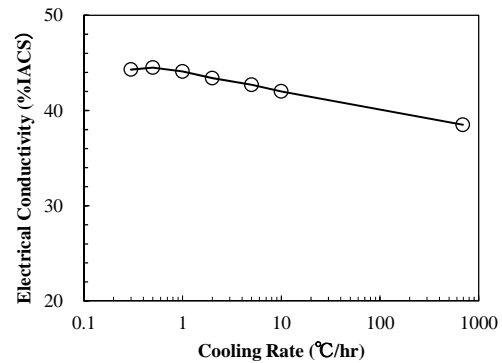
**Fig. 4 Effect of cooling rate after annealing on tensile strength of BC-A6N01 [5]**



**Fig. 5 Effect of cooling rate after annealing on electrical conductivity of BC-A6N01 [5]**



**Fig. 6 Effect of cooling rate after annealing on tensile strength of A3004**



**Fig. 7 Effect of cooling rate after annealing on electrical conductivity of A3004**

Conditions of long-term aging and annealing were examined from the viewpoint of diffusion distance of solute elements. The diffusion coefficient  $D$  ( $m^2/s$ ) at  $T$  (K) is expressed in the following formula:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

$Q$  (kJ/mol) is the activation energy for diffusion,  $R$  (J/(mol · K)) is the gas constant and  $D_0$  ( $m^2/s$ ) is a constant called maximal diffusion coefficient. The mean diffusion distance  $x$  (m) of a certain solute element during time  $t$  (s) is proportional to the square root of the product of diffusion coefficient of the solute element  $D$  and  $t$ .

$$x \propto \sqrt{Dt}$$

Diffusion distance of solute elements in the basket materials were evaluated using  $Q$  and  $D_0$  reported in literature [8]. Table 3 shows calculated ratio of the mean diffusion distance of solute elements calculated for long-term aging and annealing of BC-A6N01 and A3004 against the mean diffusion distance for 60 years

**Table 3 Diffusion distance estimated for long-term aging and annealing**

Solute element	Relative mean diffusion distance (Ratio against 60 years at 200°C)	
	Long-term aging 10,000hr at 300°C	Annealing 10hr at 520°C
Al	3.2	6.3
Si	2.2	2.5
Fe	2.7	4.4
Cu	2.2	2.8
Mg	2.5	3.6
Mn	2.0	2.0

at 200°C, the maximum storage period. The values for solute elements Si, Fe Cu, Mg and Mn for 10,000hr at 300°C, 10hr at 520°C and 10hr at 540°C are larger than unity, which indicates that all of the three kind of heat treatment cause diffusion of these elements more significant than that expected at the end of the storage period.

## 5. Conclusion

Two kinds of approach to assess the basket materials thermally deteriorated during use for 60 years were proposed. The results are summarized as follows:

- (1) In order to obtain mechanical properties suitable for evaluation of thermal deterioration expected to occur during storage, it is necessary to determine the condition of heat treatment according to type of the material with consideration of its own strengthening mechanisms.
- (2) Even if neither BC-A6N01 nor A3004 were intentionally heat treated for precipitation hardening, their 0.2% proof stress and tensile strength decrease when long-term aging or annealing followed by cooling at small cooling rates are applied.
- (3) In both BC-A6N01 and A3004, application of long-term aging at 300°C for 10,000hr makes dependence of tensile properties on aging time stable.
- (4) Tensile properties and electrical conductivity of BC-A6N01 after annealing is free from cooling rate rate from 520°C if it is smaller than 2°C/hr. On the other hand, stabilization of electrical conductivity of A3004 requires cooling rate smaller than 0.5°C/hr.
- (5) Cooling rate after annealing has to be determined carefully from the viewpoint of supersaturation of solute elements, which affects mechanical propeties.

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