Resistivity increment by solute vanadium in aluminum

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The contribution per unit concentration of solute vanadium to electrical resistivity of solid aluminum, $\Delta\rho^V$, and its temperature dependence were measured using high purity Al–V binary alloys. $\Delta\rho^V$ at 77 K and 300 K are 37.6 and 37.0 $\text{n}\Omega\cdot\text{mass}\%^{-1}$, respectively, showing a small negative DMR (deviation from the Matthiessen's rule). After a prolonged heat treatment at 923 K, the decrease in the actual size factor due to oxidation of the specimen surface was observed. In the heat treatment temperature-resistivity (T_H – ρ) diagram, the resistivity of Al–V binary alloy calculated from reported equilibrium solubility values locates between those of Al–Ti and Al–Zr alloys. Since the large $\Delta\rho$ and very small diffusivity in aluminum, the vanadium content should be especially restricted in manufacturing or recycling processes of aluminum conductor alloys.

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1. Introduction

Vanadium and titanium content in aluminum conductor alloys are restricted in the industrial standard JIS to be less than 0.005 mass% in their total¹⁾, because they remarkably reduce the conductivity of aluminum alloys. The authors have recently reported the contribution per unit concentration of solutes to electrical resistivity of solid aluminum, $\Delta\rho$, of titanium and zirconium and their temperature dependence²⁾. Titanium³⁾ and zirconium⁴⁾ are typical trace additives to refine the cast structure or grain size and to elevate the softening temperature of various aluminum alloys including conductor alloys. Some values for $\Delta\rho$ of vanadium, $\Delta\rho^V$, in aluminum based solid solution have been reported^{5)~16)}. However, these values have considerable variations and are unreliable perhaps because of difficulties to obtain a complete solid solution. Vanadium in solid aluminum shows very low diffusion constant of, e.g. $1.19\times 10^{-18}\text{ m}^2\text{s}^{-1}$ at 873 K¹⁷⁾, which is less than those of titanium and zirconium¹⁷⁾. Vanadium in aluminum is considered to be originated principally from a carbon electrode used during the electrolytic refining process of the Hall-Heroult method. Vanadium is also frequently found in heavy fuel oil¹⁸⁾. Therefore, the effect of solute vanadium upon the resistivity of aluminum must be quantified exactly in views of quality control and recycling of high purity aluminum conductor alloys. In this study, dependence of the resistivity on the solute concentration at two temperatures of resistivity measurement is investigated, using high purity Al–V binary solid solutions.

2. Experimental procedure

2.1 Specimens

An Al–2.0 mass%V master alloy was prepared by high frequency induction melting in Ar atmosphere, using 5 nine-purity aluminum and sponge vanadium of 99.8 mass%. The master alloy and 5 nine-purity aluminum were arc-melted and solidified in Ar atmosphere to button shaped ingots within a water-cooled copper hearth. The buttons were turned upside down 3 times and melted 4 times to avoid segregation or heterogeneity. Finally, after cutting the button shaped ingots in half, four half-circle pieces were melted to bar shaped ingots. These ingots were cold rolled at a room temperature to 0.5 mm thickness, about 95% reduction. Alloy marks, chemically analyzed vanadium contents and densities measured by the Archimedes method at a room temperature are shown in Table 1. The density of the Al–V alloys increased with the vanadium content.

2.2 Resistivity measurement and heat treatment

The cold rolled plates were cut and finished by polishing into dimensions of 0.5 mm $\times$ 3 mm $\times$ 180 mm. After measurement of the total length and mass, specimens were spot welded to 0.5 mm wires in diameter of 4 nine or higher purity aluminum, loosely wound to a silica glass frame. The distance between 2 potential contacts was then measured. Electrical resistance was measured by the direct current four contacts method in liquid nitrogen at 77 K and in a kerosene bath controlled within 300 ± 0.1 K for the same sample respectively, using a precise potentiometer and a standard resistance. Size factors by the density-mass method DF¹⁹⁾ for determining the resistivity values were calculated using the total length of the specimen and dis-

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Table 1 Chemically analyzed vanadium contents and densities of the alloys

Alloy mark	V (mass%)	density ($10^3 \text{ kg} \cdot \text{m}^{-3}$)
0 V	<0.001	2.6981
5 V	0.054	2.6989
10 V	0.109	2.6998
15 V	0.158	2.7007
20 V	0.209	2.7022

tance between the two potential contacts by a measuring microscope, the mass and densities shown in Table 1. The measured resistivities at 77 K and 300 K were represented as ρ_{D77} and ρ_{D300} to be distinguished from the calculated resistivities ρ_{77}^{cal} and ρ_{300}^{cal} .

The specimens were isothermally heat treated at 923 K, just below the melting point, up to 720 ks in the air or in a silica glass capsule evacuated below 1.3 mPa (10^{-5} torr).

2.3 Application of resistivity ratio

Resistivity of a dilute and multi-component solid solution measured at a temperature T , ρ_T^s , is generally expressed as;

$$\rho_T^s = \rho_T^{\text{PURE}} + \sum C^i \cdot \Delta \rho_T^i \quad (1)$$

where ρ_T^{PURE} is the resistivity of an ideally pure solvent metal at a temperature T , C^i is the concentration of the "i"th solute, $\Delta \rho_T^i$ is $\Delta \rho$ of the "i"th solute at a temperature T and Σ means a summation from B to n in an "n" component solution of solvent A and solute B, C, . . . n. When deviation from the Matthiessen's rule (DMR) is not negligible, $\Delta \rho^i$ shows temperature dependence²⁰. From eq. (1), the relation between the resistivity ratio $R = \rho_{300}/\rho_{77}$ and resistivity at 77 K ρ_{77} has been induced for a binary solid solution as;

$$\rho_{77} = (\rho_{300}^{\text{PURE}} - \eta \rho_{77}^{\text{PURE}}) / (R - \eta) \quad (2)$$

where η is the ratio of $\Delta \rho_{300}/\Delta \rho_{77}$ providing correction about DMR for the relation between R and ρ_{77} ²¹. When the Matthiessen's rule is obeyed, the η is unity. For negative or positive DMR, η is smaller or larger than 1, respectively. Because the numerator of eq. (2) does not include the solute concentration C , the above expression is very useful for a binary solid solution with remarkable DMR, e.g. Al-Mn, Al-Fe and Al-Zr alloys². Komatsu et al.²⁰ called eq. (2) as the DMR corrected equation and a plot of ρ_{77} versus $1/(R - \eta)$ as the DMR corrected plot. However, when a solution contains a large enough amount of third element or lattice defects, e.g. dislocations, those concentrations reappear to the numerator and eq. (2) is rewritten as;

$$\rho_{77} = \{\alpha^B + \sum C^i \cdot \Delta \rho_{77}^i (\eta^i - \eta^B)\} / (R - \eta^B) \quad (3)$$

where B is the first solute or second component in a A-B binary solution and α^B is $\rho_{300}^{\text{PURE}} - \eta^B \rho_{77}^{\text{PURE}}$ or the numerator of eq. (2). In some cases, the DMR of dislocation in aluminum seems to be negative, i.e. $\eta^{\text{DISL}} < 1$ ²². Therefore, high density dislocation in a heavily cold rolled specimen tends to lower the numerator of eq. (3), which is the gradient of straight lines connecting each plot and the origin of the ρ_{D77} versus $1/(R - \eta^B)$ diagram. This

Fig. 1 Change in resistivity ρ_{D300} and ρ_{D77} with isothermal treatment at 923 K.

tendency also lowers the gradient of the regression line for the plots on the diagram. Multiplying both sides of eqs. (2) and (3) by R , the relation between $R/(R - \eta)$ and ρ_{300} can be obtained with the same numerator as eqs. (2) and (3). In a practical experiment, possibly some unanalyzed impurities and errors exist in measurements of the size factor and resistance. Therefore, regression of the DMR corrected plots using measured values of R and ρ_{D77} is expressed as;

$$\rho_{D77} = \alpha / (R - \eta^B) + \beta \quad (4)$$

where α is a gradient and β is an intercept of the regression line². The β should be zero in eqs. (2) and (3). However, after annealing for a long enough period at a high enough temperature, the effects of dislocation or grain boundaries should become negligible. Thus, the use of eq. (2) must be valid. When a plot deviates from the regression line on the DMR corrected plot, the most probable cause of the deviation can be supposed as errors in the size factor measurement or an actual changes in the size factor caused by other effects, e.g. an oxidation of specimens, as discussed later.

3. Experimental Results

Changes in the resistivity with the isothermal treatment at 923 K up to 720 ks are shown in Fig. 1. ρ_{D77} and ρ_{D300} of the each sample attained almost constant values after the treatment for 200 ks, and apparently increased again after 600 ks in almost all samples, suggesting the change in the size factors. Change in ρ_{D77} and ρ_{D300} with concentration of solute vanadium is shown in Fig. 2 with their DMR corrected relation according to eq. (2). The plotted resistivity values are those before the unusual increase as discussed later in 4.1, indicated by the arrows in Fig. 1. ρ_{D77} and ρ_{D300} increase linearly with vanadium contents showing high correlation coefficients. These good linear relations suggest that the major part of added vanadium should be fully in solid solution and that, if any amount of vanadium is still out of the solution, the amount is too small to give rise to detectable decrease in the resistivity.

The gradient of ρ vs. C^V line in Fig. 2(a), i.e. contributions per unit solute vanadium concentration to electrical resistivity of

Table 2 Present $\Delta\rho^V$ compared with the previous values

Investigator	Range of content (mass%)	$\Delta\rho^V$		Measuring temperature (K)
		$\text{n}\Omega\text{m}\cdot\text{mass}\%^{-1}$	$\text{n}\Omega\text{m}\cdot\text{at}\%^{-1}$	
Present Data	0~0.209	37.6	(70.4)	77
	0~0.209	37.0	(69.2)	300
G. G. Gauthier ⁵⁾	0.012~0.067	36	(67)	293
F. Pawlek ⁶⁾	—	(43)	80*	—
L. A. Willey ⁷⁾	—	35.8	(70.0)	293 or 298
F. R. Fickett ⁸⁾	—	(36)	68	—
F. J. Kedves ⁹⁾	(0.02~0.1)	(38~43)	76 $\pm$ 4	78
C. Papastaikoudis ¹⁰⁾	(0.002~0.004)	(44~60)	83~113	4.2
E. Babic ¹¹⁾	(0.009~1.6)	(41)	76	—
A. D. Caplin ¹²⁾	(0.072, 0.72)	(36)	67	—
V. Zlatic ¹³⁾	—	(40)	75**	—
D. Altenpohl ¹⁴⁾	—	43*	81*	—
C. Panseri ¹⁵⁾	0~0.61	43	(80)	293
C. R. Vassel ¹⁶⁾	—	(>28)	>53	—

(): converted *quoted value **Calculated value

Fig. 2 Vanadium content dependence of resistivity ρ_{D300} and ρ_{D77} (a), and their DMR corrected plots (b).

aluminum at 77 K and 300 K, $\Delta\rho^V_{77}$, $\Delta\rho^V_{300}$, are shown in Table 2 together with previously reported values^{5)~16)}. The present value of $\Delta\rho^V_{300}$ is close to Gauthier's value⁵⁾ and $\Delta\rho^V_{77}$ nearly coincides with the lower limit of Kedves's value⁹⁾. The present value of $\eta = \Delta\rho^V_{300} / \Delta\rho^V_{77}$ is 0.985, showing a small negative DMR in accordance with the results of measurement at low temperature below 100 K by Caplin¹²⁾.

Equation (2) suggests that the gradient of the regression line in Fig. 2(b) should be $\rho^{PURE}_{300} - \eta\rho^{PURE}_{77}$. Using $\rho^{Al}_{300} = 27.33 \text{ n}\Omega\text{m}$ and $\rho^{Al}_{77} = 2.200 \text{ n}\Omega\text{m}$ recommended by Desai et al.²³⁾ and the present $\eta = 0.985$, the numerator in eq. (2) becomes 25.16, which shows fairly good agreement with the value of 25.26, the gradient of the regression line in Fig. 2(b). When intercepts of the regression lines in Fig. 2(a) at 300 K and 77 K, 27.52 and 2.296 nΩm, are used, the calculated value according to eq. (2)

Fig. 3 DMR corrected plots of data in Fig. 1.

agrees well with the value in Fig. 2(b). This tendency was also observed in an Al-Mg solid solution²⁴⁾. The small difference of these gradients could be due to the effects of survived lattice defects, e.g. grain boundaries, or trace impurities in the raw materials of the present alloys.

4. Discussion

4.1 Change in actual size factor

The DMR corrected plots for the resistivity change in Fig. 1 with vanadium content and the isothermal treatment at 923 K are shown in Fig. 3 together with the constants α and β in eq. (4) obtained from the regression for each alloy. The resistivity

Fig. 4 Change in the ratio of Matthiessen's size factor MF and size factor DF measured by density-mass method, MF/DF, with isothermal treatment at 923 K.

of the each sample after heat treatment longer than 200~400 ks obviously deviated upward from the regression line for all data, suggesting that the actual DF becomes smaller than the initially determined one. The cause of the decrease in DF can be considered as the decrease in current carrying cross sectional area by high temperature oxidation of specimen due to prolonged heat treatment. Because the initially determined DF for each sample was used to obtain the resistivity values even after the prolonged treatments, the oxidation causes apparent increase in the resistivity in Fig. 1.

Substituting the constants α , β and η for each alloy shown in Fig. 3 to eq. (4), resistivity at 77 K, described as ρ_{M77} to distinguish from ρ_{D77} , can be calculated from R. Using ρ_{M77} , the size factor MF can be inversely calculated as;

$$MF = \rho_{M77} / \Omega_{77} \quad (5)$$

where Ω_{77} is the resistance measured at 77 K¹⁹⁾.

The ratio of MF/DF can be also written as ρ_{M77} / ρ_{D77} . Changes in the MF/DF values with the isothermal treatment are shown in Fig. 4. MF/DF values of almost all alloys decreased to be less than 1.0 after heat treatment for about 200 ks. It is considered that the actual current-carrying cross section decreased by oxidation of the specimen surface by prolonged heat treatment. It was reported that the ratio of size factors, MF/DF may be less than 1.0 due to presence of precipitates or dispersoids in Al-Si²⁵⁾, Al-Fe²⁶⁾ and Al-Mg²⁷⁾ alloys, which also decreases the effective cross section of specimens. From these results, the initial DF are considered to become an over-estimation after the prolonged treatment. Therefore, the resistivity values just before the decrease in MF/DF for each alloy, indicated with arrows in Fig. 1, were employed for determination of $\Delta\rho^V$ to avoid the effect of surface oxidation.

4.2 T_H - ρ diagram

Using eq. (1), resistivity of a dilute Al-X binary solid solution at a temperature T , ρ^{cal}_T , can be calculated as;

$$\rho^{cal}_T = \rho^{PURE}_T + C^X \cdot \Delta\rho^X_T \quad (6)$$

where C^X is the concentration and $\Delta\rho^X_T$ is the contribution per unit concentration of solute X. Equation (6) means a linear rela-

Fig. 5 T_H - ρ plots of Al-V alloy compared with the T_H - ρ diagrams of Al-Ti and Al-Zr alloys.

tion between the solute concentration and calculated resistivity. Substituting the equilibrium solid solubility to C^X as a function of the temperature of heat treatment T_H , T_H - ρ diagram²⁸⁾, that shows the calculated resistivity of binary alloy changing with the equilibrium solute concentration at the each T_H , can be obtained.

Aluminum corner of the equilibrium phase diagram of Al-V alloy has not been defined exactly due to low diffusivity of vanadium, and only two values of equilibrium solubility, 0.2 at% at 933 K and 0.19 at% at 903 K, were reported by Varich²⁹⁾ and Roth³⁰⁾. It is too risky to obtain the equilibrium solubility curve of vanadium from these two data. Therefore, the resistivity values at these two temperatures were calculated using these two solubility data and the present $\Delta\rho^V$, and compared with the T_H - ρ diagrams of Al-Ti and Al-Zr binary alloys²⁾ in Fig. 5. As ρ^{PURE}_{77} and ρ^{PURE}_{300} in eq. (6), the values of Desai et al.²³⁾ were employed respectively. As shown in Table 2, the present $\Delta\rho^V$ is one of the greatest values among $\Delta\rho$ of transition metals common in commercial aluminum alloys³¹⁾. ρ^{cal}_{77} and ρ^{cal}_{300} of vanadium locate between the T_H - ρ diagrams of titanium and zirconium as shown in Fig. 5. Diffusion coefficient of vanadium is quite low, e.g. $10^{-2} \sim 10^{-7}$ times of those of other transition metals at 773 K¹⁷⁾. Therefore, to maintain high enough conductivity, contamination by vanadium should be avoided for aluminum alloys.

5. Conclusion

Dependence of resistivity of an Al-V alloy solid solution on solute concentration and a temperature of measurement were investigated using high purity Al-V binary alloys. The results are summarized as follows.

- (1) Contribution per unit concentration of solute vanadium to the resistivity at 77 K and 300 K, $\Delta\rho^V_{77}$, $\Delta\rho^V_{300}$, are 37.6 and 37.0 nΩm·mass%⁻¹, respectively.
- (2) Vanadium in aluminum shows a small negative DMR.
- (3) Resistivity values of Al-V solid solutions calculated

from equilibrium solubility locate between those of Al-Ti and Al-Zr solid solutions on the T_H - ρ diagram.

(4) Considering the extremely low diffusivity of vanadium in aluminum and the difficulty to make precipitate vanadium, its content should be restricted especially in manufacturing or recycling processes of aluminum conductor alloys.

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