CORRECTED NORDHEIM'S LAW FOR ALUMINUM BASE HIGH CONCENTRATION SOLID SOLUTIONS

Shin-ya KOMATSU*, Masahiko IKEDA*, Tomohiro KOHMOTO** and Hideaki YUKIMACHI***
* Faculty of Engineering, Kansai University. (Suita, Osaka, 564-8680 JAPAN)
** Graduate School, Kansai University. (Suita, Osaka, 564-8680 JAPAN) [Present address; Tomakomai factory, Nippon Light Metal Co. (Tomakomai, Hokkaido, 053-0833 JAPAN]
*** Graduate School, Kansai University. (Suita, Osaka, 564-8680 JAPAN)

ABSTRACT

Corrected Nordheim's law has been applied to Al-Mg, Al-Cu and Al-Zn solid solution avoiding the effect of G.P. zone or cluster by appropriate reversion treatment. Obtained resistivity increase per unit concentration of each solute $\Delta\rho$ has been employed to correct the effect of deviation from Matthiessen's rule (DMR) on previously proposed relation between resistance ratio and resistivity. Scattering of previously reported $\Delta\rho$ values is discussed on the view point of effects of the second order term of concentration according to Nordheim's law and of the DMR as dependence of the $\Delta\rho$ on temperature.

keywords: *Al solid solution, resistivity, concentration effect, temperature effect, resistance ratio.*

1. BACKGROUND, MOTIVATION AND AIMS

J.O.Linde corrected the well-known Nordheim's law to fit high concentration solid solutions consisted of noble metal-multivalent metal, for example Cu-Zn, Ag-Al, etc. [1], as:

$$\rho^{SS}_{T1} = \rho^{PURE}_{T1} + \Delta\rho^{X}_{T1} X (1 - \nu X) \qquad (1),$$

where ρ^{PURE}_{T1} is the resistivity of ideally pure solvent metal at T_1, $\Delta\rho^X$ is contribution to resistivity per unit atomic fraction X of a solute and ν is a non-dimensional constant. Later, Komatsu et al independently found that the correction can be applied to Mg-0 to 9at. (9.7mass)%Al solid solutions [2].

The eq. (1) can be approximated in dilute solid solutions as

$$\rho^{SS}_{T1} = \rho^{PURE}_{T1} + \Delta\rho^{X}_{T1} X,$$

or $$\rho^{SS}_{T1} = \rho^{PURE}_{T1} + \Delta\rho_{T1} (C/\text{at.\% or mass\%}) \qquad (2).$$

It has been proposed by Komatsu et al. [3, 4] that the relation between resistivity at 77K, ρ^{SS}_{77}, and resistivity ratio, $R = \rho_{300}/\rho_{77}$ can be written as:

$$\rho^{SS}_{77} = (\rho^{PURE}_{300} - \eta\, \rho^{PURE}_{77})/(R - \eta) \qquad (3),$$

where η is ratio of $\Delta\rho$ at 300K and 77K, $\Delta\rho_{300}/\Delta\rho_{77}$, which deviates from unity when deviation from Matthiessen's Rule (DMR) exists. Komatsu et al. [3, 4] have determined empirically the eq. (3) for many dilute solid solutions and utilized to detect or to average the error in size factor measurement, for example in Al-Mn system having the most negative DMR [5]. However, in solid solutions containing more than 1 at% solute (or $X>0.01$), eq.(1) means that the $\Delta\rho_{T1}$ decreases with increasing solute concentration. Therefore, determination of the $\Delta\rho^X$ is necessary, especially in the case of high concentration solid solution, to correct the effect of DMR on the relation between ρ_{77} and R.

In aluminum based solid solution, the order of solute showing large maximum solubility will be Zn (X=0.665), Mg (0.189), Cu (0.025), Si (0.0159) and Mn (0.0047) [6]. However, perhaps because of small $\Delta\rho$, a little difference of Mg contents in specimens for chemical analysis and for resistivity measurement and effect of impurities in dilute alloys, in Al-Mg solutions below 4at%Mg, the negative curvature of X-ρ curve could not be clearly detected [7].

In this report, the eq. (1) is applied to Al-Mg, Al-Cu and Al-Zn concentrated solid solution alloys to determine the $\Delta\rho^X$ at 300K and 77K avoiding the effect of G.P. zone and to examine validity of the eq.(3).

2. EXPERIMENTAL PROCEDURE

0.5mm^t×3mm^w×180mm^L specimens were sheared from finally 92% cold rolled plates of Al-0(0), -0.47(0.52), -0.93(1.03), -1.45(1.61), -1.89(2.09), -2.87 (3.18), -3.79(4.19), -5.05(5.58), -6.00(6.62), -7.15(7.88), and Al-8.10(8.91)mass(at)%Mg alloys. Solute contents of Al-Cu and Al-Zn plates are shown in **Table 1**. Fe, Si and Cu in the Al-Mg alloys were below 0.001, 0.005 and 0.001 mass%, respectively. Fe and Si in all of Al-Cu and Al-Zn alloys were below 0.001mass%. Table 1 also shows G.P. zone solvus ($T_{G.P.}$) [8, 9] and temperature of reversion (T_{REV}) for Al-Cu and Al-Zn alloys. It has been reported by Osamura and Ogura [10] that an Al-5.1at%Mg alloy quenched from 723K shows resistivity increase after 60ks aging at 293K. All of present Al-Mg alloys were annealed at 623K for 3.6ks. Therefore, concentration of equilibrium and quenched-in vacancy and also the rate of G.P. zone formation which will elevate the resistivity should be lower than the case of ref. [10]. In Al-Mg alloys, resistivity was measured within 1.8 ks or at least 3.6ks after water quenching from 623K and no reversion treatment was carried out.

Each specimen was mounted loosely on a frame made of silica glass rod by spot-welding to 0.5mm$^\phi$ wires of four nine aluminum wound on the frame and all heat treatments and measurements were carried out with this specimen assembly.

Resistivity, ρ_D, was measured at 77K and 300K by direct current four contact method and size factor obtained by density-mass method. **Fig. 1** shows relation between concentration and density for Al-Cu and Al-Zn alloys measured on 3mm^t×30mm^w×180mm^L plates. Because previously reported $\Delta\rho^X$ values are rather small especially in Al-Zn alloys and then errors in density measurement effect severely on the measured ρ_D values, the density obtained by regression of measured values shown in the Fig. 1 was employed to determine the ρ_D.

Table 1. Solute contents, G.P. zone solvus temperature $T_{G.P.}$/K, reversion temperature T_{REV}/K, solvus temperature T_{SOL}/K [6] and temperature of solution treatment T_{ST}/K of Al-Cu and Al-Zn alloys.

solute	mass%	at%	$T_{G.P.}$	T_{REV}	T_{SOL}	T_{ST}
Cu	0.46	0.196	358	363	593	623
	1.01	0.431	403	393	647	673
	1.52	0.651	440	433	680	723
	1.92	0.837	461	453	701	723
	3.02	1.31	473	473	742	773
	4.04	1.76	482	483	772	813
Zn	0.80	0.332	226	----	300	623
	1.63	0.679	253	----	340	623
	2.42	1.01	271	----	360	623
	3.19	1.34	285	323	380	623
	4.47	1.89	306	323	400	623
	5.95	2.54	322	353	420	623

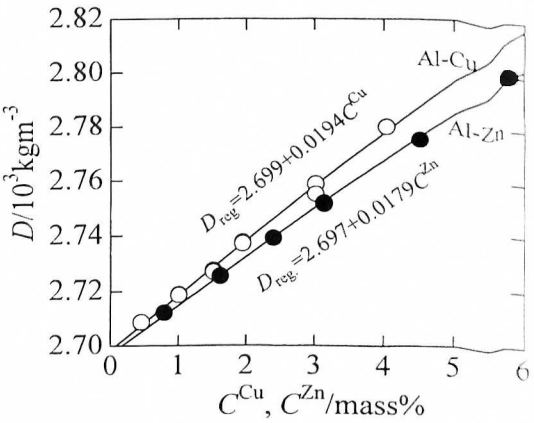

Fig. 1 Relation between solute concentration and density measured by Archimedes method.

3. RESULTS

3.1 Al-Mg SYSTEM

Fig. 2 (a) compares relations between ρ_{D300} or ρ_{D77} and atomic fraction X of Mg or $X(1-\nu X)$. The ν was varied and chosen to give correlation factor r closest to unity. The largest r is obtained when ν=1.72. The difference of measured resistivity, ρ_D, from regressed value is plotted in **Fig. 2(b)** and **(c)**. The negative curvature of X-ρ curves is clarified by expanding the concentration range to 8.91at%Mg, as shown in Fig. 2(b) and (c). The $\Delta\rho^X_{300}$ and $\Delta\rho^X_{77}$ are obtained as 550.6 and

527.5nΩm. η in the eq. (3) is 1.043. **Fig. 3(a)** compares the relation of eq. (3) for η=1.043 and 1. The technique similar to Fig. 2(b) and (c) is applied and the difference between measured and regressed values are shown in **Fig. 3(b)**. The systematic deviation from linear relation in the curve for η=1 is clearly decreased to ±0.4nΩm by using η=1.043 and is changed to a random scattering. It has been already pointed out that the solid solution having positive DMR shows a positive curvature in the relation between $1/(R\text{-}1)$ and ρ_{77} [3].

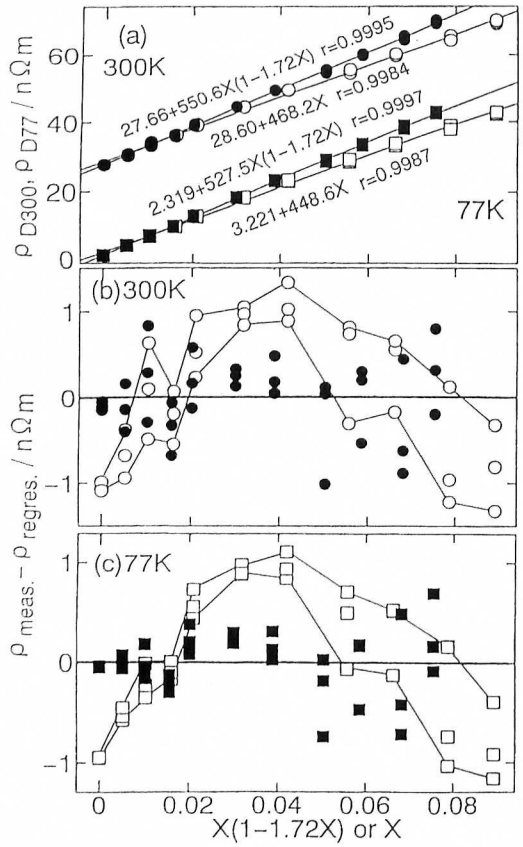

Fig. 2 Relations between atomic fraction X of Mg or $X(1\text{-}\nu X)$ and measured resistivity at 300K and 77K (a), difference between measured and regressed values at 300K (b) and at 77K (c), for 623K-3.6ks annealed Al-Mg solid solution.

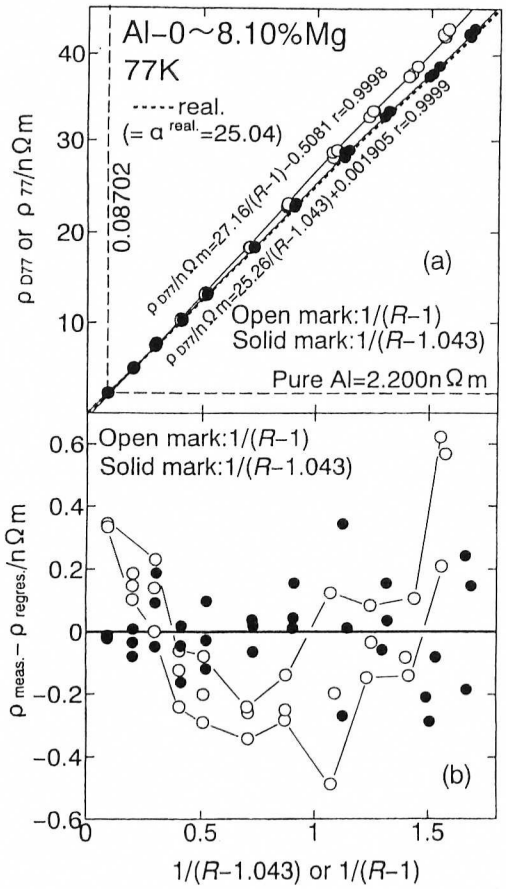

Fig. 3 Relation between $R=\rho_{300}/\rho_{77}$ and measured ρ_{D77} for Al-Mg solid solution employing η=1 and 1.043 (a), difference between measured and regressed values compared for η=1 and 1.043 (b).

3.2 Al-Cu SYSTEM

Fig. 4 shows change in ρ_{D77} of Al-4.04%Cu with room temperature (RT) aging and reversion. Unrelated to RT aging time, all specimens show an almost same value after 0.3 to 0.6ks reversion at 483K. Because all other Al-Cu alloys and Al-Zn alloys containing more than 3.19%Zn show a same behavior, the corrected Nordheim's law is investigated using the ρ_D after reversion.

Fig. 5 shows simillar relations to the Fig. 2 for Al-Cu solid solutions. In Al-Cu system below 1.76at%, the negative curvature due to X^2 term in the eq. (1) appears. The best fit ν is 5.64. The $\Delta\rho^X_{300}$ and $\Delta\rho^X_{77}$ are 772.1 and 798.6nΩm and the η is 0.967, showing a negative DMR. The relation between $1/(R\text{-}\eta)$ and ρ_{D77} is compared in **Fig. 6** for η=1 and 0.967.

Because the η of solute Cu is close to unity, difference between η=1 and 0.967 is hard to recognize in Fig. 6(a). Differences between measured and regressed value are plotted in **Fig. 6(b)**. The negative curvature characteristic to solution systems of negative DMR [3] is corrected by employing η= 0.967 and the systematic deviation in case of employing η=1 is changed by η=0967 to a random scattering ranging ±0.02nΩm.

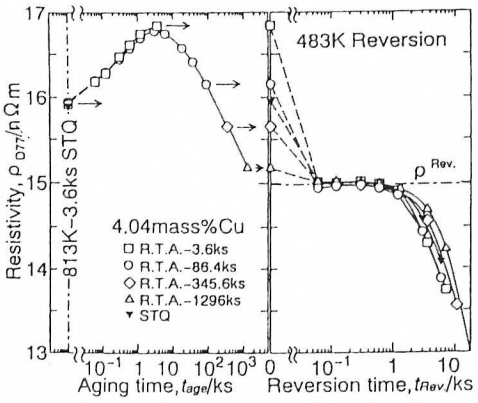

Fig. 4 Changes in ρ_{D77} of Al-4.04%Cu alloy by room temperature aging and reversion.

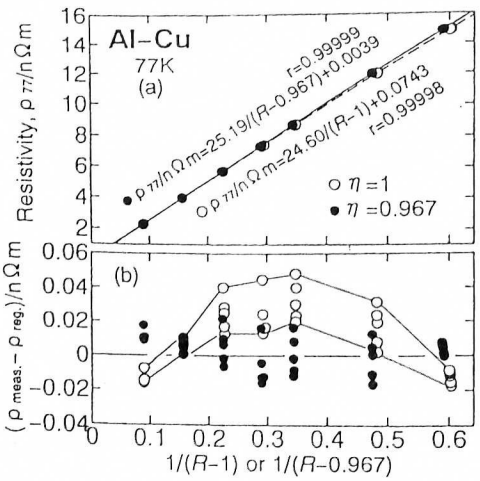

Fig. 6 Comparison of relation between $1/(R\text{-}1)$ or $1/(R\text{-}0.967)$ and measured ρ_{D77} for Al-Cu solid solution (a), difference between measured and regressed values (b).

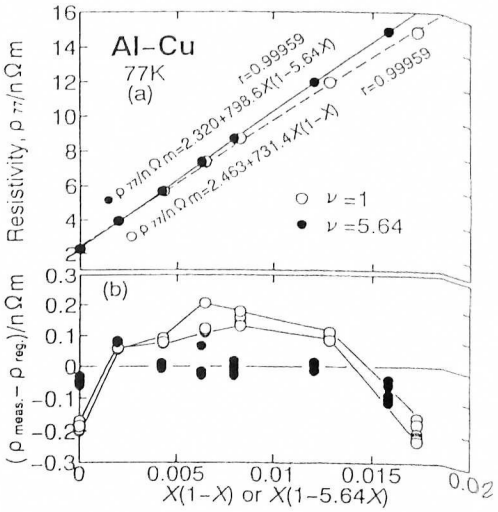

Fig. 5 Relations between atomic fraction X of Cu or $X(1\text{-}\nu X)$ and measured resistivity at 77K (a), difference between measured and regressed values at 77K (b), for Al-Cu solid solution after reversion.

3.3 Al-Zn SYSTEM

The measured values in Al-Zn solid solutions are handled similarly to above, as shown in **Fig. 7**. By employing ν=3.21, the systematic deviation is annihilated and random scattering after the correction is shrunk to $\pm$0.02nΩm. $\Delta\rho^{X}_{300}$ and $\Delta\rho^{X}_{77}$ of solute Zn are 240.1 and 244.2nΩm and the η is 0.983. The value of η for solute Zn in Al is more closer to unity than that of solute Cu. The effect of correction of the relation between $1/(R\text{-}1)$ and ρ_{D77} is the smallest in solid solutions of present work, as shown in **Fig. 8**.

4. DISCUSSION

Table 2 compiles experimentally obtained constants in the eq.(1). The temperature dependence of $\Delta\rho^{X}$ is rather small. However, when the η deviates more than 0.04 from unity, the measured resistivity ρ_{D77} shows the innegligible systematic deviation from straight line of regression just as predicted previously [3]. This can be seen in the case of Mg and Cu, Figs. 3 and 5.

As Linde [1] has already noted, the $\Delta\rho^{X}$ in eq. (1) corresponds to the $\Delta\rho$ in eq. (2) extrapolated to infinitely dilute binary solid solution. Therefore, the scattering of previously reported $\Delta\rho$ values will come from neglecting the effect of X^2 term in eq. (1) and rather small but innegligible DMR.

Fig. 9 is comparing previously reported $\Delta\rho$ values of Cu and Zn in nΩm•at%$^{-1}$ with present work as function of the temperature at which the resistivity was measured. It should be very interesting to study on causes of these wide spread values. Larger $\Delta\rho$ values will come from the effect of G.P. zones or impurites in case of very dilute alloy and smaller values will be due to using concentrated alloys and neglecting the corrected Nordheim's law.

Table 3 shows constants in the DMR corrected empirical equations (DMRCEE), which are the eq. (3) written as $\rho_{77}/n\Omega m = \alpha/(R\text{-}\eta)+\beta$. According to the eq. (3), the α equals to $\rho^{PURE}_{300}\text{-}\eta\ \rho^{PURE}$...

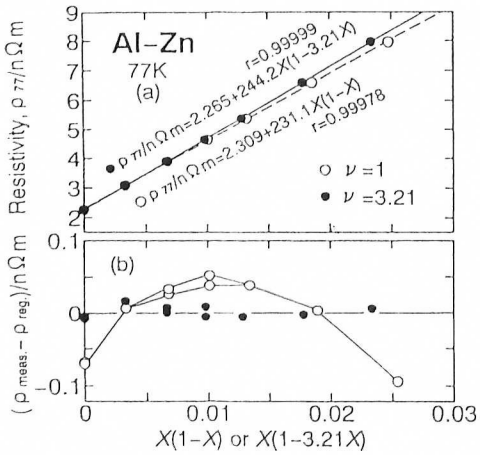

Fig. 7 Relations between atomic fraction X of Zn or $X(1-\nu X)$ and measured resistivity at 77K (a), difference between measured and regressed values at 77K (b), for Al-Zn solid solution after annealing at 623K or reversion.

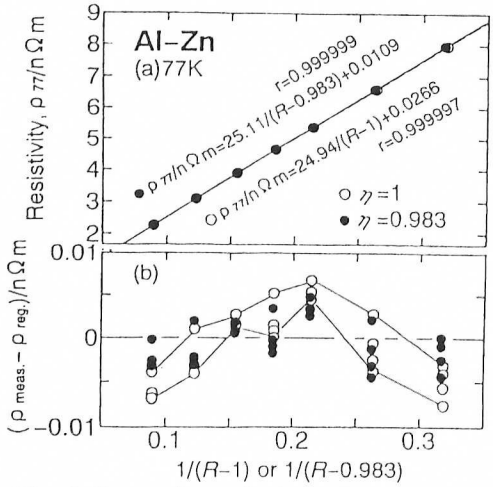

Fig. 8 Comparison of relation between $1/(R-1)$ or $1/(R-0.967)$ and measured ρ_{D77} for Al-Zn solid solution (a), difference between measured and regressed values (b).

Table 2 ν, ρ^{PURE}/nΩm and $\Delta\rho^{X}$/nΩm in the eq.(1).

solute	conc. range (at%)	ν	ρ^{PURE}/nΩm		$\Delta\rho^{X}$/nΩm	
			300K	77K	300K	77K
Mg	0-8.9	1.72	27.66	2.319	550.8	527.5
Cu	0-1.76	5.64	27.47	2.320	772.1	798.6
Zn	0-2.05	3.21	27.42	2.265	240.1	244.2

Using ρ^{PURE} values in Table 2, this relation gives α values for Mg, Cu and Zn as 25.24, 25.22 and 25.19, respectively. These values are in fairly good coincidence with the empirical α in Table 3. It is necessary to remember that these DMRCEE are only applicable to binary and random solid solutions. A large volume fraction, to say more than 1 vol.% in concentrated alloys, of precipitates increases the measured resistivity ρ_{D77} deviating from these DMRCEE. However, one can estimate quantitatively the volume fraction of precipitates from the deviation of ρ_{D77}.

Writing $\rho^{PURE\,A}{}_{300}-\eta^{B}\rho^{PURE\,A}{}_{77}=\alpha^{B}$ for an A-B-C-D--- N elements solid solution consisted of solvent A, solute B, C, D ----, the eq. (3) was rewritten (4) as

$$\rho^{SS}{}_{77}=[\ \alpha^{B}+\sum_{i=C}^{N} C^{i}\bullet\Delta\rho^{i}{}_{77}\bullet(\eta^{i}-\eta^{B})]/(R-\eta^{B}) \qquad (4)$$

where C^{i}, $\Delta\rho^{i}{}_{77}$ and η^{i} are solute concentration $\Delta\rho$ at 77K and η of "i"th element, respectively and η^{B} is the η of second element or first solute. When C and other constants of C to N element are knew, the ideal relation between R and $\rho^{SS}{}_{77}$ can be predicted. The deviation from eq. (4) suggests the existence of trump elements or precipitates.

5. SUMMARY

The contribution of most important alloying elements in aluminum, Mg, Cu and Zn, to resistivity has been clarified. This is the starting point to many investigations evaluating quantitatively the total amount of precipitates, change in dislocation and grain boundary density and so on. The relation between microstructure and macroscopic properties will be made clearer by these investigations.

Table 3 Empirically obtained constants in the eq. (3) written as
$\rho_{77}/n\Omega m=\alpha/(R-\eta)+\beta$

solute	range of $\rho_{77}/n\Omega m$	η	α	β
Mg	2.3-42.7	1.043	25.26	0.0019
Cu	2.3-14.8	0.967	25.19	0.0039
Zn	2.3-8.0	0.983	25.11	0.0109

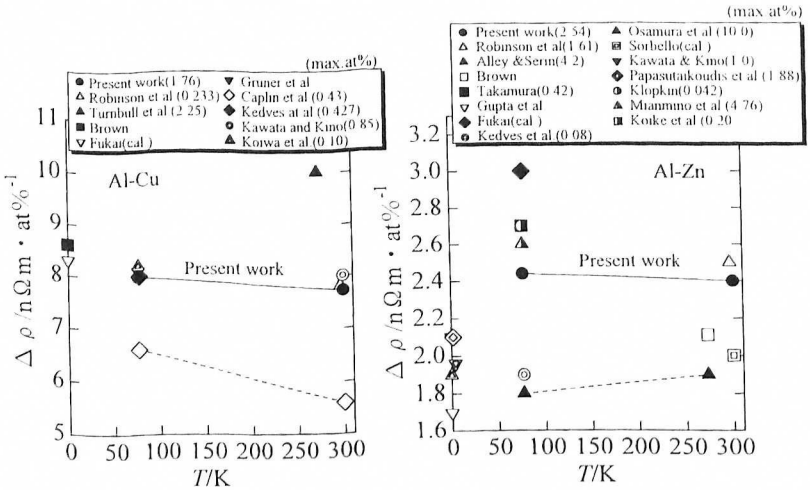

Fig. 9 Comparison of previously reported $\Delta\rho$ values in Al-Cu and Al-Zn solid solutions.

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